The chemistry of
organic selenium and tellurium compounds
Volume 1

THE CHEMISTRY OF FUNCTIONAL GROUPS

A series of advanced treatises under the general editorship of
Professor Saul Patai

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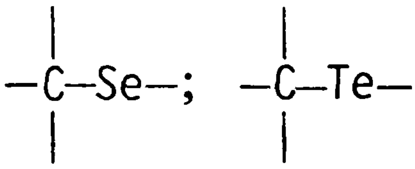

$$-\overset{|}{\underset{|}{C}}-Se-;\quad -\overset{|}{\underset{|}{C}}-Te-$$

The chemistry of
organic selenium and tellurium compounds
Volume 1

Edited by

SAUL PATAI
and
ZVI RAPPOPORT
The Hebrew University, Jerusalem

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Foreword

The present volume in 'The Chemistry of Functional Groups' series deals with organic compounds containing selenium or tellurium atoms. This material falls outside the scope of the set of four volumes in the same series, entitled 'The Chemistry of the Metal–Carbon Bond' now in the process of publication.

The authors have been requested, whenever possible, to make comparisons between analogous compounds containing the three chalcogen atoms sulphur, selenium and tellurium.

Originally we intended to publish all chapters of the present volume simultaneously. However, various technical problems forced us to change this plan and to publish eighteen chapters separately and with separate author and subject indices for this volume. The literature coverage of most chapters is up to the end of 1983, with occasional references from 1984.

A second volume (edited by one of us, S.P.) is now already under active preparation and will hopefully be published towards the end of 1986. The chapters it contains include: PES, Mossbauer, UV, visible and Raman spectroscopy; synthetic methods; preparative uses; seleno and telluro carbonyl derivatives; photochemistry; electrochemistry; H-bonding, acidity and complex formation; biochemistry and pharmacology; insertion and extrusion reactions; organo Se/Te halides; Se—N and Te—N bonds; Se—P, Se—As, Te—P and Te—As bonds; semiconductors, metals and superconductors; Se/Te analogues of ethers; SeCN and TeCN derivatives and Se/Te free radicals. Thus we hope that these two volumes will cover all important aspects of the organic chemistry of the derivatives of selenium and tellurium.

We will be very grateful to readers who would communicate to us mistakes, omissions and proposals relating to this volume as well as to other volumes in the Functional Groups series.

Jerusalem
July 1985

SAUL PATAI
ZVI RAPPOPORT

The Chemistry of Functional Groups
Preface to the Series

The series 'The Chemistry of Functional Groups' is planned to cover in each volume all aspects of the chemistry of one of the important functional groups in organic chemistry. The emphasis is laid on the functional group treated and on the effects which it exerts on the chemical and physical properties, primarily in the immediate vicinity of the group in question, and secondarily on the behaviour of the whole molecule. For instance, the volume *The Chemistry of the Ether Linkage* deals with reactions in which the C—O—C group is involved, as well as with the effects of the C—O—C group on the reactions of alkyl or aryl groups connected to the ether oxygen. It is the purpose of the volume to give a complete coverage of all properties and reactions of ethers in as far as these depend on the presence of the ether group but the primary subject matter is not the whole molecule, but the C—O—C functional group.

A further restriction in the treatment of the various functional groups in these volumes is that material included in easily and generally available secondary or tertiary sources, such as Chemical Reviews, Quarterly Reviews, Organic Reactions, various 'Advances' and 'Progress' series as well as textbooks (i.e. in books which are usually found in the chemical libraries of universities and research institutes) should not, as a rule, be repeated in detail, unless it is necessary for the balanced treatment of the subject. Therefore each of the authors is asked *not* to give an encyclopaedic coverage of his subject, but to concentrate on the most important recent developments and mainly on material that has not been adequately covered by reviews or other secondary sources by the time of writing of the chapter, and to address himself to a reader who is assumed to be at a fairly advanced post-graduate level.

With these restrictions, it is realized that no plan can be devised for a volume that would give a *complete* coverage of the subject with *no* overlap between chapters, while at the same time preserving the readability of the text. The Editor set himself the goal of attaining *reasonable* coverage with *moderate* overlap, with a minimum of cross-references between the chapters of each volume. In this manner, sufficient freedom is given to each author to produce readable quasi-monographic chapters.

The general plan of each volume includes the following main sections:

(a) An introductory chapter dealing with the general and theoretical aspects of the group.

(b) One or more chapters dealing with the formation of the functional group in question, either from groups present in the molecule, or by introducing the new group directly or indirectly.

(c) Chapters describing the characterization and characteristics of the functional groups, i.e. a chapter dealing with qualitative and quantitative methods of determination including chemical and physical methods, ultraviolet, infrared, nuclear magnetic resonance and mass spectra: a chapter dealing with activating and directive effects exerted by the group and/or a chapter on the basicity, acidity or complex-forming ability of the group (if applicable).

(d) Chapters on the reactions, transformations and rearrangements which the functional group can undergo, either alone or in conjunction with other reagents.

(e) Special topics which do not fit any of the above sections, such as photochemistry, radiation chemistry, biochemical formations and reactions. Depending on the nature of each functional group treated, these special topics may include short monographs on related functional groups on which no separate volume is planned (e.g. a chapter on 'Thioketones' is included in the volume *The Chemistry of the Carbonyl Group*, and a chapter on 'Ketenes' is included in the volume *The Chemistry of Alkenes*). In other cases certain compounds, though containing only the functional group of the title, may have special features so as to be best treated in a separate chapter, as e.g. 'Polyethers' in *The Chemistry of the Ether Linkage*, or 'Tetraaminoethylenes' in *The Chemistry of the Amino Group*.

This plan entails that the breadth, depth and thought-provoking nature of each chapter will differ with the views and inclinations of the author and the presentation will necessarily be somewhat uneven. Moreover, a serious problem is caused by authors who deliver their manuscript late or not at all. In order to overcome this problem at least to some extent, it was decided to publish certain volumes in several parts, without giving consideration to the originally planned logical order of the chapters. If after the appearance of the originally planned parts of a volume it is found that either owing to non-delivery of chapters, or to new developments in the subject, sufficient material has accumulated for publication of a supplementary volume, containing material on related functional groups, this will be done as soon as possible.

The overall plan of the volumes in the series 'The Chemistry of Functional Groups' includes the titles listed below:

The Chemistry of Alkenes (two volumes)
The Chemistry of the Carbonyl Group (two volumes)
The Chemistry of the Ether Linkage
The Chemistry of the Amino Group
The Chemistry of the Nitro and Nitroso Groups (two parts)
The Chemistry of Carboxylic Acids and Esters
The Chemistry of the Carbon–Nitrogen Double Bond
The Chemistry of the Cyano Group
The Chemistry of Amides
The Chemistry of the Hydroxyl Group (two parts)
The Chemistry of the Azido Group
The Chemistry of Acyl Halides
The Chemistry of the Carbon– Halogen Bond (two parts)
The Chemistry of the Quinonoid Compounds (two parts)
The Chemistry of the Thiol Group (two parts)
The Chemistry of Amidines and Imidates
The Chemistry of the Hydrazo, Azo and Azoxy Groups (two parts)
The Chemistry of Cyanates and their Thio Derivatives (two parts)
The Chemistry of Diazonium and Diazo Groups (two parts)
The Chemistry of the Carbon–Carbon Triple Bond (two parts)

Supplement A. The Chemistry of Double-bonded Functional Groups (*two parts*)
The Chemistry of Ketenes, Allenes and Related Compounds (*two parts*)
Supplement B: The Chemistry of Acid Derivatives (*two parts*)
Supplement C: The Chemistry of Triple-Bonded Functional Groups (*two parts*)
Supplement D: The Chemistry of Halides, Pseudo-halides and Azides (*two parts*)
Supplement E: The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and their Sulphur Analogues (*two parts*)
The Chemistry of the Sulphonium Group (*two parts*)
Supplement F: The Chemistry of Amino, Nitroso and Nitro Groups and their Derivatives (*two parts*)
The Chemistry of the Metal–Carbon Bond (*three volumes*)
The Chemistry of Peroxides
The Chemistry of Organic Se and Te Compounds Vol. 1

Titles in press:

The Chemistry of Cyclopropanes
The Chemistry of Organic Se and Te Compounds Vol. 2

Advice or criticism regarding the plan and execution of this series will be welcomed by the Editor.

The publication of this series would never have started, let alone continued, without the support of many persons. First and foremost among these is Dr Arnold Weissberger, whose reassurance and trust encouraged me to tackle this task. The efficient and patient cooperation of several staff-members of the Publisher also rendered me invaluable aid (but unfortunately their code of ethics does not allow me to thank them by name). Many of my friends and colleagues in Israel and overseas helped me in the solution of various major and minor matters, and my thanks are due to all of them, especially to Professor Z. Rappoport. Carrying out such a long-range project would be quite impossible without the non-professional but none the less essential participation and partnership of my wife.

The Hebrew University
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SAUL PATAI

Contents

The Chemistry of Organic
Selenium and Tellurium
Compounds Volume 1
Edited by S. Patai and Z. Rappoport

CHAPTER 1

Organic derivatives of sulphur, selenium and tellurium—an overview

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I. INTRODUCTION

The chalcogens, constituting Group VI in the Periodic Table, exhibit differences in their chemical properties that run parallel to those observed in other non-metals within Groups IV–VII (Table 1). Thus, O, like other second period members of the family, has unique characteristics rooted in its high electronegativity and lack of d orbitals whereas S and Se share with pairs of third and fourth period elements from other Groups a striking similarity in their chemical properties. By passing on to the fifth period, i.e. Te within Group VI, we note another jump in properties. This overall pattern reflects the increase in atomic radii, and hence in coordination numbers, as clearly brought out by considering the oxo anions derived from the various elements in their highest oxidation states (Table 2): S and Se are comparable, but distinctly different from Te. In their divalent states, however, the Group VI elements exhibit a more gradual change, moving towards lower electronegativity with increase in atomic weight. Consequently, hydride stability decreases. On substitution of H with organic radicals more stable molecules are formed so that R_4Pb, R_3Bi and R_2Po are still species of reasonable stability.

In the present context our attention will be limited to *organic* derivatives of the chalcogens. Based on common knowledge, set out in Tables 1 and 2, we shall enquire into the degree of similarity existing within the organic chemistry of S, Se and Te. By necessity, such a venture must be selective and inevitably biased by the personal interests of the authors. We shall draw on numerous sources including established monographic treatises on organoselenium[1,2] and organotellurium[3] chemistry, assorted reviews on more restricted topics, original articles, and the useful, current awareness publication, *Organic Compounds of Sulphur, Selenium and Tellurium*, issued within the Specialist Periodical Report series by The Royal Society of Chemistry and thus far covering the literature published until March 1980. With a view to ordering the discussion we shall briefly dwell on both historical aspects and nomenclature rules before proceeding to discuss various classes of compound according to functionality, as well as certain aspects of interest to synthetic chemistry. No attention will be given in the present 'overview' to biological aspects which will be discussed in a different chapter of this volume.

TABLE 1. Periodic Table of Group IV–VII elements

	Group			
Period	IV	V	VI	VII
2	C	N	O	F
3	Si	P	S	Cl
4	Ge	As	Se	Br
5	Sn	Sb	Te	I
6	Pb	Bi	Po	At

TABLE 2. Oxo-anions of Group IV–VII elements in their highest oxidation state

Coordination number	Group IV	 V	 VI	 VII
3	CO_3^{2-}	NO_3^-		
4	SiO_4^{4-}	PO_4^{3-}	SO_4^{2-}	ClO_4^-
4	GeO_4^{4-}	AsO_4^{3-}	SeO_4^{2-}	BrO_4^-
6	$Sn(OH)_6^{2-}$	$Sb(OH)_6^-$	TeO_6^{6-}	IO_6^{5-}
6	$Pb(OH)_6^{2-}$			

The present chapter has as its chief objective to introduce the general subject of this volume, to place it in a broader context, but above all to whet the appetite for additional and more detailed information.

II. NOMENCLATURE

Since organoselenium compounds were as a rule discovered later than the corresponding sulphur compounds they have frequently been named by adding the prefix seleno- to the name of the corresponding sulphur compound, e.g. selenocystine, selenoglutathione, selenouracil, selenoxanthate, selenomercaptan. Similarly, a Te analogue of methionine has been called telluromethionine. In the rules formulated by the Commission on Nomenclature of Organic Chemistry of the International Union of Pure and Applied Chemistry (IUPAC)[4] this practice is not accepted. Nevertheless, it is being widely followed in the literature when the sulphur compound is a natural product with an accepted trivial name, as for example selenocysteine. In other cases systematic names should be used. According to the IUPAC rules a 'selenoxanthate' is an *O*-alkyl diselenocarbonate, and a 'selenomercaptan' is a selenol. The use of the seleno- prefix to indicate replacement of S by Se in new compounds is to be strongly discouraged, *inter alia* because the *Chemical Abstracts* indexes enter systematically correct terms without cross-references to new trivial names.

The prefix seleno- has, however, traditionally also been used to indicate replacement of O by Se. The IUPAC Commissions of both organic[4] and inorganic[5] chemistry have adopted this rule if the corresponding oxygen compound has an accepted functional class ending or if an oxygen-containing radical has an accepted prefix. Consequently, selenocyanate, selenourea, selenosemicarbazide, selenoketones, selenobenzamide, etc., and the prefixes selenocyanato- and selenocarbonyl-, are all recommended IUPAC names.

In analogy with the suffix name-thione for $>C{=}S$, the name -selenone has repeatedly been used in the literature to designate $>Se{=}O$. This is, however, confusing since -selenone is the suffix also for an isologue of a sulphone, R_2SeO_2. In sulphur chemistry we have at our disposal the prefixes sulph- and thio-, derived from Latin and Greek, to distinguish, for example, between disulphane, H_2S_2, and the heterocyclic compound dithiane. An analogous opportunity to use Latin luna and tellus along with Greek selene and gea was neglected long ago and is now unrealistic. The IUPAC nomenclature commissions therefore decided to introduce the prefixes sel- and tell- to be used along with selen- and tellur-. In this way, diselane, H_2Se_2, and ditellane, H_2Te_2, can be distinguished from the heterocyclic species diselenane and ditellurane, and the suffix for $>C{=}Se$ becomes -selone (cyclohexaneselone, 4-thiazoline-2-selone, etc.), and for $>C{=}Te$, -tellone.

The last edition of *Nomenclature of Organic Chemistry*[4] contains detailed rules for

TABLE 3. Suffixes and prefixes for selected groups of Se- and Te-containing species

Suffix or functional class name			Prefix
—SH thiol	—SeH selenol	—TeH tellurol	Mercapto, hydroseleno, hydrotelluro
—S—	—Se—	—Te—	Thia, selena, tellura sulfa[a], sela[a], tella[a]
—SR sulfide	—SeR selenide	—TeR telluride	R-thio, R-seleno, R-telluro[b], or R-sulfenyl, R-selenyl, R-tellurenyl
$>C{=}S$ thione	$>C{=}Se$ selone	$>C{=}Te$ tellone	Thiooxo, selenoxo, telluroxo
—CSSH carbodithioic acid	—CSSeH carboselenothioic acid	—CSTeH carbotellurothioic acid	Dithiocarboxy, selenothiocarboxy, tellurothiocarboxy
$>SO$ sulfoxide	$>SeO$ selenoxide	$>TeO$ telluroxide	Sulfinyl, seleninyl, tellurinyl
$>SO_2$ sulfone	$>SeO_2$ selenone	$>TeO_2$ tellurone	Sulfonyl, selenonyl, telluronyl
—SO_3H sulfonic acid	—SeO_3H selenonic acid	—[c]	Sulfo, selenono
—SO_2H sulfinic acid	—SeO_2H seleninic acid	—[c]	Sulfino, selenino
—SOH	—SeOH	—[c]	Sulfeno, seleneno
R_3S^+ sulfonium	R_3Se^+ selenonium	R_3Te^+ telluronium	Sulfonio, selenonio, telluronio

[a] In homogeneous chains (cf. Ref. 4, Rule D–4).

[b] R-tellurio in organometallic compounds

[c] Extension of the system to cover the Te analogues should be carefully considered since such compounds may be polymers.

naming characteristic groups containing Se or Te (Rules C–10.1, C–10.42, C–22.1, C–82.1, C–701, C–833, C–974, C–985 and D–1.54) and guidelines for naming heterocyclic rings with Se or Te (Rules B–1, B–3, B–4 and Appendix, Table IV). A comprehensive discussion of the nomenclature of organoselenium compounds is also available[6].

In Table 3 a list is presented of suffixes and prefixes recommended by IUPAC. A few comments are made as footnotes to the table.

Throughout the present chapter the following abbreviations have been used: X = halogen, Y = chalcogen, R = organyl radical.

III. HISTORY

The organic chemistry of sulphur dates from the discovery by W. C. Zeise of the xanthates in 1822 and 'mercaptan' (ethanethiol) in 1831. His work initiated extensive studies in organic sulphur chemistry with the result that most of the characteristic sulphur-containing organic groups were known by about 1865[7].

Without much delay organic compounds of Se and Te also became known. Berzelius, the discoverer of Se (1818), found that alkali metal selenides and tellurides resemble sulphides, and in 1840 F. Wöhler[8] prepared the first organic Te compound, diethyl telluride, in a similar way to the sulphide. Löwig[9] had already prepared diethyl selenide, mixed with the diselenide, in 1836, but the pure compounds were not isolated until 1869[10]. Several other organic Se and Te compounds were synthesized about the same time, most of them in Wöhler's laboratory[11]: ethaneselenol (1847), diethyl telluroxide (1851), dimethyl telluride, dimethyl diselenide (1856), and others. Selenonium and telluronium salts[12] were discovered in 1865, but selenoxides[13] not until 1893. From SeO_2, inorganic selenocyanate, selenourea (discovered[14] in 1884), and some heterocyclic compounds, containing N and Se in the same ring, were prepared in 1889–90[15–17]. 2,5-Dimethylselenophene[18] was synthesized in 1885, selenophene itself not until 1927, and tellurophene only in 1972.

After the pioneering period organic Se and Te chemistry developed only slowly. The investigations were hampered by the compounds often being evil-smelling, toxic and sensitive to air and light. Many of the compounds prepared were of low purity and several reports on the isolation of new compounds were unwarranted.

Since about 1950, modern methods and equipment have made it possible to prepare organic Se and Te compounds in higher yields and purity and to isolate compounds of low stability. The development has been catalysed by technical and biological interest in Se and Te compounds, and the study of their chemical reactions has resulted in important new methods in organic synthesis.

IV. ANALOGUES OF ALCOHOLS AND ETHERS

A. Alcohol Analogues

Thiols (**1**), selenols (**2**) and tellurols (**3**) are synthetically accessible from salts of hydrogen sulphide (**4**), hydrogen selenide (**5**) and hydrogen telluride (**6**). The acidity of the hydrides increases dramatically from **4** to **6**, the respective pK_{a1} values being 7.0, 3.8 and 2.6.

RYH	H_2Y	R^1YR^2
(**1**) $Y = S$	(**4**) $Y = S$	(**7**) $Y = S$
(**2**) $Y = Se$	(**5**) $Y = Se$	(**8**) $Y = Se$
(**3**) $Y = Te$	(**6**) $Y = Te$	(**9**) $Y = Te$

In analogy with alcohols normally being weaker acids than water, **1**, **2** and **3** may be expected to be weaker acids than **4**, **5** and **6**, respectively, with acidity constants increasing in the order **1**, **2**, **3**. Consequently, the corresponding bases, RS^-, RSe^- and RTe^-, must be weaker bases than RO^-, with the basicity decreasing in the order given. Mainly due to their high polarizability, however, the anions of **2** and **3** are better nucleophiles than the anion derived from **1**, and much better than the RO^- ion.

Selenols (**2**) undergo oxidation to diselenides even more easily than do thiols (**1**) to disulphides. Tellurols (**3**) are so sensitive to oxidation, leading to elemental Te and other products, that ditellurides have not been isolated from this process. Tellurols as such are poorly known; older reports on the characterization of simple alkanetellurols appear highly dubious. Lately, however, arenetellurolates have become available in solution by subjecting diaryl ditellurides to reduction (with $NaBH_4$, or Na in liq. NH_3), or by base-induced disproportionation, yielding tellurinates as the oxidized products[19]. Insertion of metallic Te into the carbon–metal bond of various organolithium compounds, notably of the heteroaromatic series, provides a convenient route to lithium arenetellurolates[20].

Weaker hydrogen bonding accounts for the lower boiling points of the lower members of the classes **1**, **2** and **3** when compared with the analogous alcohols.

Chemically, **1**, **2** and **3** possess reducing properties increasing in that order; thus, arenetellurolates have lately proven useful in the reduction of *vic*-dibromides to alkenes[21], and of α-halocarbonyl compounds to the reduced halogen-free counterparts[22]. Similarly, sodium hydrogen telluride serves as an efficient, selective reagent for reducing α,β-unsaturated carbonyl compounds (aldehydes, ketones and esters) to the saturated analogues[23].

B. Ether Analogues

Organic sulphides (**7**), selenides (**8**) and tellurides (**9**) are generally more stable than the corresponding hydrides, (**1**), (**2**) and (**3**). Numerous diorganyl chalcogenides are known, varying widely in the nature of the radicals R^1 and R^2; thus, besides the more common alkyl and aryl radicals, R^1 and R^2 may also represent, for example, metalorganic radicals (R_3Sn, R_3Ge, etc.). Several selena compounds, in which one or more methylene groups have been substituted by Se, have been synthesized, notably in connection with biological studies.

Generally, selenides (**8**) are light-sensitive, colourless compounds with an obnoxious odour, prepared by methods analogous to those used for making sulphides (**7**). The selenides exhibit great stability towards alkali and reducing reagents but can be oxidized to the synthetically important selenoxides (cf. Section VII of this chapter). Other features of interest in the present context are the ability to undergo alkylation to selenonium salts, and to lose an α-proton to give Se-stabilized carbanions. The C—Se bond is readily cleaved with alkyllithium reagents or by lithium dissolved in amines. These features provide the background for a rapidly expanding synthetic chemistry utilizing Se-containing intermediates[24].

Contrary to the generally inaccessible tellurols, the diorganyl tellurides (**9**) have been the subject of rather detailed studies involving crystal structure determination, spectroscopical characterization, dipole moment measurements, etc. Tellurides share with selenides the ability to form diorganyl chalcogen dihalides on treatment with halogens, and chalcogenonium salts on alkylation, but differ from the selenides in undergoing C—Te fission on oxidation. The yellow or red diorganyl tellurides are stable compounds when aromatic, but far less so in the aliphatic series. Sulphide reduction of organyltellurium trihalides provides an easy entrance into the series of organic ditellurides. In all of the Groups IV–VI, the heaviest element forms a weak bond to carbon. Thus, extensive studies within the class of tetraalkylleads, containing different radicals, have revealed that redistribution reactions easily occur[25]. This seems also to be the case with diorganyl tellurides[26]. Hence, reported syntheses of homogeneous, non-symmetrical diorganyl tellurides must be regarded with scepticism.

Only a few triselenides, and no tritellurides, are known, though unstable species have been recognized containing arrangements such as —SeSSe—, —STeS—, etc. All of these are, as expected, highly sensitive to nucleophilic reagents such as hydroxide ions. Tertiary phosphines have been used to abstract Se or Te from diorganyl dichalcogenides.

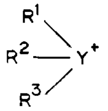
All compounds of the types RYH, R_2Y and R_2Y_2 (Y = S,Se,Te) have a pronounced ability to combine with transition metals thus producing a large number of coordination compounds[27].

In summary, the overall chemistry of selenides and tellurides is strongly reminiscent of that of sulphides, with the proviso that the Se, and more notably the Te, analogues are of lower stability and often of greater complexity in their chemical behaviour.

V. ONIUM SALTS AND YLIDES

A. Onium Salts

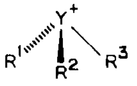
Triorganylsulphonium ions (**10**) and the isologous selenonium (**11**) and telluronium (**12**) ions were discovered in 1865[12]. Since then a considerable number of their salts have been prepared, either by the classical method (dialkyl chalcogenide and alkyl halide) or by various other methods which have made it possible to prepare also onium salts with different radicals, aromatic radicals, etc. Salts with anions other than those derived from halogens can be prepared by anion exchange or by precipitation with complex anions which often form sparingly soluble salts.



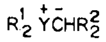
(**10**) Y = S

(**11**) Y = Se

(**12**) Y = Te



(**13**)



$R^1_2\overset{+}{Y}\overset{-}{C}HR^2_2$

(**14**) Y = S

(**15**) Y = Se

(**16**) Y = Te

Little is known about the Se and Te analogues of the many heterosulphonium salts (**10**) in which one or more of the radicals R^1, R^2 and R^3 represent O, N, S or halogen. Protonated selenols, $RSeH_2^+$, and tellurides, R_2TeH^+, have been observed by NMR spectroscopy in superacid solutions of selenols and tellurides but not been isolated[28].

The chalcogenium ions **10**–**12** form salts which are solid, salt-like compounds, usually insoluble in non-polar solvents but soluble in water. Their aqueous solutions exhibit electrolytic conductivity and give the qualitative reactions of the anions. With silver oxide in water the halides form strongly alkaline solutions. The hydroxides thus formed cannot usually be isolated but their aqueous solutions can be neutralized with HX to form new salts. On heating, the onium salts decompose, usually into R_2Y and RX. Their thermal stability increases from S to Te and generally with the size of the anion.

Sulphonium and selenonium ions adopt the geometry of stable trigonal pyramids (**13**) as evident from their chirality, documented through resolution into enantiomers (for $R^1 \neq R^2 \neq R^3$) which was achieved for **10** in 1900[29,30] and for **11** in 1902[31]. The reported resolution of a telluronium salt[32] could not be confirmed[33].

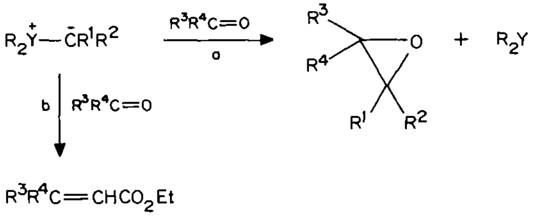
According to their properties the onium salts would be expected to be strong electrolytes. Recent investigations indicate, however, that this is an oversimplification. In the solid state onium salts of 'hard', complex anions have the expected ionic structure with non-coordinating anions. This has been proved by an X-ray structure analysis of the telluronium salt [Me_3Te] [BPh_4]. Onium salts of the 'soft' halide and pseudohalide anions tend to possess a more complicated structure, the tendency increasing from S to Te, and from Cl to I. Therefore, deviations from a purely ionic structure are especially prominent among telluronium halides[34]. Distances are here often less than the sum of the respective van der Waals' radii, which may be characterized as secondary bonding. The intermolecular interactions appear to be the result of directed forces rather than of electrostatic or van der Waals' forces. As a consequence the crystal units may be described as oligomeric, resulting in a distorted octahedral geometry.

Te also forms compounds of the type R_4Te. The most stable representatives contain two 2,2'-biphenyldiyl radicals. An analogous but very unstable Se compound has also been obtained[35]. Attempts to prepare analogous S compounds of the type R_4S were unsuccessful. These compounds are possibly oligomeric in the solid state but no structure determinations have been reported.

B. Ylides

Onium ions may be deprotonated to form ylides, i.e. zwitterions or chalcogen-stabilized carbanions. Stable ylides, **14**, **15** and **16**, e.g. cyclopentadienides, have been prepared from both sulphonium, selenonium and telluronium ions.

More attention has lately been accorded to moderately stable and unstable ylides[36] which undergo reaction with non-enolizable carbonyl compounds to give oxirans in both the Se[37] and the Te[38] series (path a, equation 1).



(1)

If $R^1 = CO_2Et, R^2 = H$ and $Y = Te$, however, the reaction proceeds differently, the stabilized tellurium ylide giving an α,β-unsaturated ester[39] (path b, equation 1) in a reaction unprecedented in the sulphur and selenium ylide series. It provides another illustration of qualitatively different reaction paths operating with S/Se compounds on the one hand, and Te compounds on the other.

VI. INSERTION COMPOUNDS

In a characteristic reaction the chalcogens, both as elemental substances (S_8, Se_x, Te_x) and as reactive derivatives, can be inserted into chains, rings and clusters of other atoms, even under mild conditions. A few examples shall serve to illustrate that S, Se and Te behave similarly in such reactions.

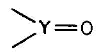
S and Se have been found to insert into the Si—Si bond of decamethylcyclopentasilane with the formation of the six-membered ring selenapentasilacyclohexane[40]. Similarly, Te inserts into the Si—P bond of the phosphine $Me_3SiPBu^t_2$ rather than producing a phosphine telluride (cf. Section XI), to give a product containing the — SiTeP group[41]. Other examples comprise insertion of selenium dioxide into stannoxanes, $R_3SnOSnR_3$, to give distannyl selenites, $R_3SnOSe(O)OSnR_3$[42] and of sulphur dioxide, selenium dioxide or tellurium dioxide into the Mo—C bond of the cycloheptatrienylmolybdenum compounds η-$C_7H_7Mo(CO)_2CH_3$, to give products of the type η-$C_7H_7Mo(CO)_2Y(O_2)CH_3$[43]. Often, however, reduction takes place at the same time. Thus, SeO_2reacts with ditellurides to form tellurenyl tellurinyl selenides, RTeSeTe(O)R[44].

Insertion reactions are quite common with organometallic cyclopentadienyl and carbonyl compounds. As an example, elemental S, Se or Te insert into the Co—Co bond of $(\eta$-$C_5H_5)_2(Me_2P)_2Co_2$ to give products containing a CoYCo structure[45]. Often, however, reactions with carbonyl compounds are complicated by replacement of CO and reduction.

More related to organic chemistry is the reaction of carbon diselenide with tetraalkylmethylenediamines, $R_2NCH_2NR_2$, to give diselenocarbamate esters, $R_2NCH_2SeC(Se)NR_2$[46].

VII. ANALOGUES OF SULPHOXIDES, SULPHONES AND RELATED COMPOUNDS

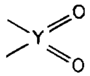
The pyramidal sulphoxides (**17**) and the tetrahedral sulphones (**20**) have their counterparts in the selenoxides (**18**) or telluroxides (**19**) and the selenones (**21**) or tellurones (**22**). Double bonds are used throughout the present discussion subject to the proviso that varying degrees of polarization and d orbital participation may be involved, as evident from dipole moment measurements and spectroscopic data[47].



(**17**) Y = S

(**18**) Y = Se

(**19**) Y = Te



(**20**) Y = S

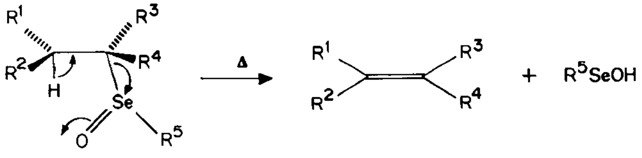
(**21**) Y = Se

(**22**) Y = Te

A. Selenoxides and Telluroxides

Although stable, optically active sulphoxides have been known for more than 50 years, the first report on the synthesis of structurally simple, monochiral, optically active selenoxides (**18**) reached the literature only quite recently[48]. Enantiomerically enriched telluroxides (**19**) are unknown[33]. The basic properties of the diorganyl chalcogen oxides increase from **17** to **19** as does the ability to form tetravalent, symmetrical hydrates. With acids, both **18** and **19** form salts of the type $R_2Y(OH)Z$ (Z = halogen, carboxylate, nitrate, etc.), and selenoxides (**18**) form coordination compounds with many metal salts.

Selenoxides (**18**) are reasonably stable species provided that they do not contain β-positioned hydrogen atoms. If so, they undergo a remarkably facile, stereospecific *E* elimination, often at temperatures well below 20 °C (equation 2).



(2)

This reaction, discovered less than a decade ago, has rapidly been put to good use in modern organic synthesis[24]. Selenoxides (**18**) are generally prepared by oxidation of selenides, or by hydrolysis of the mostly easily accessible selenide dihalides.

Telluroxides (**19**), accessible through the same routes[49,50] are more basic compounds exhibiting distinctive alkaline reaction in aqueous solution. They share with the selenoxides (**18**) the ability to undergo thermal elimination to olefins though more drastic conditions are occasionally required[51]. In recent years aromatic telluroxides have attracted interest as mild oxidizing reagents[52].

B. Selenones and Tellurones

Selenones (**21**), like sulphones (**20**), are stable compounds of moderate reactivity, accessible through appropriate oxidation of selenides or selenoxides. An interesting variant of the 1,4-Grob-type elimination, induced by base treatment of vinylic phenylselenones, utilizes the $PhSeO_2$ group as an efficient nucleofuge[53]. The properties and chemistry of selenones deserve further exploration.

The first, fully characterized tellurone, **23**, was described only in 1982[54]. It was prepared by oxidation of the corresponding telluroxide. Previously reported representatives of **22** were obviously assigned erroneous structures. The aromatic tellurone **23** has mildly oxidizing properties of potential synthetic interest[54].

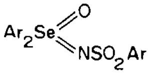
$(4\text{-}MeOC_6H_4)_2TeO_2$

(23)

$Ar_2Y{=}NSO_2R$

(24) Y = Se

(25) Y = Te

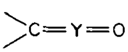


$Ar_2Se(=O)=NSO_2Ar$

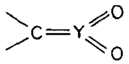
(26)

The tri- and tetra-coordinate isologues of *N*-sulphonylated sulphimides and sulphoximides, **24**, **25** and **26**, are known compounds, readily prepared by methods well known from the chemistry of sulphur (cf. Section XI).

Se and Te analogues of the sulphines and sulphenes, **27** and **28**, have yet to be produced and characterized.



(27) Y = S, Se, Te

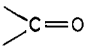


(28) Y = S, Se, Te

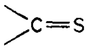
In general, the chemistry of selenoxides and telluroxides is similar to that of the sulphoxides, though with minor, but synthetically useful, differences. On closer inspection, however, we note once again a greater similarity in chemistry between members of the S and Se series on one hand, and the Te isologues on the other, the latter standing apart notably by their marked ability to attain higher coordination numbers as evident from X-ray structure analyses of compounds such as Ph_2TeO and $Ph_2Te(OH)NO_3$[55].

VIII. ANALOGUES OF CARBONYL COMPOUNDS

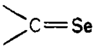
Within the series **29**–**32** of carbonyl compounds and their analogues, a diminishing stability is to be expected in the order given, mainly because of the decreasing electronegativity of the chalcogen element (the electronegativity of Te is almost the same as that of C).



(29)



(30)



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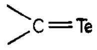


(32)

A. Analogues of Aldehydes and Ketones

A great variety of thials and thiones can be found in the literature[56], many of them stabilized by charge dislocation or tautomerism. Until recently, simpler aliphatic thials, thiones and their Se analogues were known only as polymers. When it was recognized some years ago that the polymers dissociate by pyrolysis, it became feasible to study the microwave spectra of the monomers in a flow system at low temperature. Thus, monomeric thioformaldehyde[57], thioacetaldehyde[58], thioacetone[59], thioketene[59] and selenoacetaldehyde[60] were identified but none of these species had half-lives long enough to permit their isolation. Since 1976, however, it has become evident that bulky substituents or hindered structures may provide enough protection against polymerization to allow the preparation of monomeric species of much higher stability. Moreover, the recognition that the instability of the Se and Te compounds is due both to their high electrophilic reactivity and susceptibility to catalytic influence has made it possible to design methods and equipment suitable for the isolation of these sensitive compounds. A selection of compound types, all formally containing doubly bonded chalcogen atoms, shall serve to illustrate these trends.

The counterparts of the perfectly stable carbonyl sulphide (**33**) and carbon disulphide (**35**), viz. carbonyl selenide (**34**), thiocarbonyl selenide (**36**) and carbon diselenide (**38**), are known compounds, though less stable and more cumbersome to prepare than **33** and **35**. Their general reactivity does not differ significantly from that of the S isologues. As for the Te analogues, thiocarbonyl telluride (**37**) decomposes at temperatures above its melting point, – 54 °C, and carbon ditelluride (**39**) is as yet unknown. A similar trend is noted in the halogen-substituted series: thiocarbonyl chloride (**40**) is a perfectly stable red liquid and selenocarbonyl chloride (**41**) a blue compound only recently prepared by pyrolysis of 2,2,4,4-tetrachloro-1,3-diselenetane (**42**) and decomposing at temperatures above – 130 °C[61].

$O{=}C{=}Y$

(**33**) Y = S

(**34**) Y = Se

$S{=}C{=}Y$

(**35**) Y = S

(**36**) Y = Se

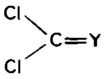
(**37**) Y = Te

$Se{=}C{=}Se$

(**38**)

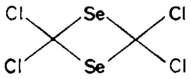
$Te{=}C{=}Te$

(**39**)



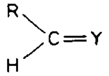
(**40**) Y = S

(**41**) Y = Se

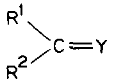


(**42**)

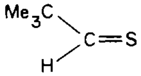
Thials (**43**) and thiones (**46**) no longer constitute chemical curiosities. The recent synthesis of 2,2-dimethylpropanethial (**48**) as a distillable pink monomeric compound[62] raises doubt as to the validity of regarding the non-stabilized thials as species of only transient existence. Monomeric selenals (**44**) and tellurals (**45**), on the other hand, have so far eluded isolation.



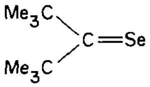
(43) Y = S
(44) Y = Se
(45) Y = Te



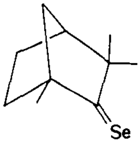
(46) Y = S
(47) Y = Se



(48)



(49)



(50)

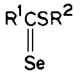
Aromatic thiones have been known for more than 60 years whereas stable monomeric aliphatic species are of more recent date and notably encountered within the class of polycyclic structures (cf. Ref. 56). Dipole moment measurements reveal a much smaller, perhaps even reversed, polarity when compared with the ketones. Until recently, monomeric authentic selones (**47**) had eluded isolation, but the preparation a few years ago of the blue selones **49** and **50** altered the situation, although the method employed for their synthesis is not of general utility[63]. Convincing evidence for the existence of non-stabilized tellones seems to be lacking.

Stable thioketenes (**51**), known since 1966, became available after 1975, including the parent compound **51** ($R^1 = R^2 = H$), through the remarkably general and efficient flash thermolysis of 1,2,3-thiadiazoles[64]. An analogous approach resulted in the synthesis and characterization of the first selenoketenes (**52**), including the parent compound **52** ($R^1 = R^2 = H$)[65]. In both series, the nature of the substituents, R^1 and R^2, defines the stability. With bulky radicals, selenoketenes can be isolated and stored in the cold[66]. Telluroketenes have not yet been prepared.

$R^1R^2C{=}C{=}S$ (**51**) $R^1R^2C{=}C{=}Se$ (**52**)

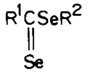
B. Carboxylic and Carbonic Acid Analogues

Whereas selenocarboxylic and selenocarbonic acids are very unstable species, several esters derived from them are known compounds. Those containing doubly bonded Se, i.e. **53** and **54**, are intensely coloured species, very sensitive to O_2 and light. Se shares with Te the ability to form derivatives of dithioic and diselenoic acids with a central Se or Te atom bound in a planar arrangement to four S or Se atoms, e.g. **55**[67].



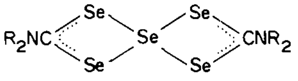
$R^1\underset{\underset{Se}{\|}}{C}SR^2$

(53)



$R^1\underset{\underset{Se}{\|}}{C}SeR^2$

(54)



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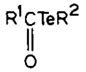
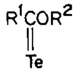


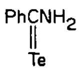
$R^1\underset{\underset{O}{\|}}{C}TeR^2$

(56)



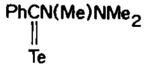
$R^1\underset{\underset{Te}{\|}}{C}OR^2$

(57)



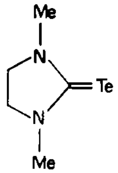
$Ph\underset{\underset{Te}{\|}}{C}NH_2$

(58)



$PhC(=Te)N(Me)NMe_2$

(59)



(60)

RTeCN

(61)

Derivatives of tellurocarboxylic acids are of a more recent data. Tellurol esters (**56**) have been prepared by acylation of tellurols[68], and the first species with double-bonded Te (**57**) were prepared from steroid alcohols, *t*-butyl(chloromethylene)dimethylammonium chloride and sodium hydrogen telluride[69].

Selenoamides, selenosemicarbazides and selenoureas, as well as several heterocyclic derivatives of these (selenouracil etc.) are fairly stable compounds. Recently, also telluroamides (**58**)[70,71], tellurohydrazides (**59**)[70] and a derivative of tellurourea (**60**)[72] have become synthetically available.

Attempts to prepare organic tellurocyanates (**61**) only became successful when it was recognized that the tellurocyanate ion is decomposed instantaneously by water[73]. In solvents like dimethylformamide or acetonitrile, however, Te readily reacts with onium cyanates to form onium tellurocyanates, unsuited for alkylation. Organic tellurocyanates have been prepared, however, by alkylation of potassium tellurocyanate, formed *in situ* in dimethyl sulphoxide. The crystal structure of the very stable 4-nitrobenzyl tellurocyanate has recently been determined[74]. The lability of the tellurocyanate ion is attributable to the weak C═Te bond. Association of the nitrogen end of the ion with protic solvents or hard Lewis acids results in further bond weakening. Together, the above observations call for a judicious choice of solvents and cations in the synthesis of tellurocyanates.

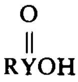
The combined experience from the syntheses of tellurocyanates, telluroamides and telluro esters reveals no fundamental difference between selenocarbonyl and tellurocarbonyl derivatives; with due precautions in synthetic methodology the preparation of many additional tellurocarbonyl compounds seems feasible and hence to be expected.

IX. OXO ACIDS OF SULPHUR, SELENIUM AND TELLURIUM

Oxygen-containing isologous acids, with the chalcogens in the valency states 2,4 and 6 (**62**, **63** and **64**), are known for Y = S, Se, Te, yet not without exceptions. Dramatic changes are encountered, however, within the formally analogous series, both with regard to properties and stability. We shall elaborate on this in the following.

RYOH

(62)



$RY(=O)OH$

(63)

$RY(=O)_2OH$

(64)

A. Valency State Six

In the highest valency state, sulphuric and selenic acid, $H_2YO_4 (Y = S, Se)$, are very similar strong acids whereas telluric acid, $Te(OH)_6$, is a very weak acid forming salts either with the formal composition M_2TeO_4, or, in the case of certain cations, M_6TeO_6 (e.g. Ag_6TeO_6). However, the $TeO_4{}^{2-}$ ion is a polymer, containing hexacoordinate Te with oxygen bridges. The only known organic derivative of telluric acid appears to be the ester $Te(OMe)_6$. No derivative of the hypothetical telluronic acid (**64**; Y = Te) is known and probably never will be, because any potential candidate most likely would prove to be an amphoteric polymer and not a true analogue of the well-authenticated sulphonic and selenonic acids (**64**; Y = S, Se); these resemble sulphuric acid in being strong acids. As selenic acid, the selenonic acids possess oxidizing properties, to the extent of becoming explosive (like, for example, organic nitrates). Care must be exercised, however, in accepting structures previously reported or assigned to new selenonic acids; thus, early reports of the preparation of benzeneselenonic acid by selenation of benzene was later revised, the reaction product being a salt formed between protonated benzeneseleninic acid and the benzeneselenonate anion. A few authentic areneselenonic acids are known whereas only salts of the aliphatic counterparts seem stable.

B. Valency State Four

In the tetravalent series, selenious acid differs from sulphurous acid in being weaker but also in exhibiting predominantly oxidizing properties. Selenium dioxide, the anhydride of selenious acid, is a well-established, specific oxidation reagent in synthetic organic chemistry. Again, seleninic acids (**63**; Y = Se) are weaker not only than selenonic acids (**64**; Y = Se) but also than sulphinic acids (**63**; Y = S); they may, in fact, behave as bases forming cations of the type $RSe(OH)_2{}^+$. Unlike sulphinic acids, selininic acids are moderately oxidizing species existing in aqueous solution as hydrates with the structure $RSe(OH)_3$. A great variety of seleninic acid derivatives is known including chlorides, amides, esters and anhydrides. Benzeneseleninic acid anhydride has lately drawn interest as a mild and remarkably specific reagent in organic chemistry[75–78]. Organic derivatives of tetravalent Te behave rather differently. Although TeO_2, like SeO_2, is an oxidizing amphoteric compound, its basic properties are more pronounced; thus, it readily affords Te(IV) salts with strong acids. Organyltellurium trihalides, $RTeX_3$, are hydrolysed to what formally are tellurinic acids. However, the insolubility in water and organic solvents of the latter, as well as their very high and often ill-defined melting points, strongly suggest that one is here dealing with polymers containing oxygen bridges, derived from $RTe(OH)_3$. Apart from a few halogenated derivatives, such as $RTeX_3$ and RTe(O)X, no authentic tellurinic acid seems to have been prepared.

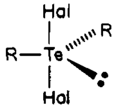
C. Valency State Two

Divalent S and Se compounds containing the radicals RY— are numerous and several of them important. They encompass halides, pseudohalides, acetates, amides, etc. For systematic reasons, the hydroxides, RYOH, are named sulphenic acids, selenenic acids and tellurenic acids. They are amphoteric in nature and only a few are known as stable compounds because they easily disproportionate into compounds of lower and higher oxidation states. Characteristic for several derivatives of **62**, the chalcogen atom behaves as the electrophile towards nucleophilic attack, with displacement of X^-. Thus, species such as RSeSR, RSeCN, RSeSCN and RSeSeCN can be efficiently prepared from selenenyl halides, RSeX, and the appropriate nucleophiles. Though far less well explored, the aromatic tellurenyl halides behave similarly. Thus, 2-formylbenzenetellurenyl bromide reacted with AgCN to form the first organic tellurocyanate[79]. The first known tellurenyl compound, 4-methoxybenzenetellurenyl methanesulphonate, reacted with *O*-methyl dithiocarbonate to form the corresponding tellurenyl derivative[80]. In certain respects, however, tellurenyl halides react differently from selenenyl halides (cf. Section X of this chapter). Of considerable interest in a synthetic context is the application of selenenyl halides for α-arylselenenation of enolizable carbonyl compounds and for the stereospecific *trans* addition to alkenes (cf., for example, Ref. 81).

X. HALOGEN COMPOUNDS

From the many types of known organic compounds containing one or more chalcogen–halogen bonds, three major classes are here singled out for a brief discussion, viz. the monohalides (**65**), the dihalides (**66**) and the trihalides (**67**).

RYX (**65**) R_2YX_2 (**66**) RYX_3 (**67**)


(**68**)

A. Monohalides

Within group **65**, sulphenyl (Y = S) and selenenyl (Y = Se) halides are well-known species, generally available on halogenolysis of disulphides or diselenides. Several, notably aromatic derivatives, are rather stable compounds often serving as important reagents in modern synthetic chemistry. In view of the known stability of other types of organic compounds with Te–halogen bonds, it seems surprising that 2-naphthalenetellurenyl iodide until recently remained the sole well-characterized tellurenyl halide. Additional, though rather unstable, aromatic analogues were prepared in 1975[82]. They combine with halide ions to ions of the type $RTeBrCl^-$ (isolated as for example, tetraphenylarsonium salts). X-ray studies have revealed a T-shaped geometry, with a nearly linear arrangement of the X—Te—X′ group for such ions[83]. S and Se do not form analogous compounds.

B. Dihalides

As known from the beginning of this century, diorganyl chalcogenides, R_2Y, react with halogens to give compounds of type **66**. The stability of these increases from S to Te, and from I to F; thus, the least stable species, such as R_2SI_2, behave as charge-transfer complexes. In general, the bromides and iodides dissociate into the components on heating or dissolution. Non-aqueous solutions exhibit no signs of dissociation whereas the observed conductivity in aqueous solution is attributable to aqua ions, $RYX(H_2O)^+$, and hydrolysis to $R_2YX(OH)$. Diorganyltellurium dihalides (**66**; Y = Te) are reasonably stable, crystalline compounds possessing, according to X-ray analysis, the geometry of trigonal bipyramids (**68**); they are frequently used as intermediates in preparing pure tellurides. Fluorides (**66**; X = F) have been prepared by metathesis with Ag_2F or Na_2F and by direct fluorination at low temperature[84]. On fluorination, Ph_2S forms Ph_2SF_4; analogous Se and Te compounds have not been encountered.

C. Trihalides

The organyl chalcogen trihalides **67** constitute a large and well-studied class of compounds. They may be prepared by halogenation of diselenides or ditellurides; in the aromatic series by electrophilic substitution in activated nuclei by means of selenium and tellurium tetrachloride. The stability of type **67** compounds is fair to good, highest in the Te series in keeping with the tendency of Te to attain tetravalency. The trihalides (**67**) are widely used in the synthesis of other types of products; thus, **67** (X = S, Se) on hydrolysis affords sulphinic or seleninic acids, whereas the Te analogue (**67**; X = Te) gives a formal tellurinyl chloride, RTe(O)Cl. which, however, behaves more like an inorganic oxide chloride. The structure of $PhTeCl_3$ is polymeric with bridging Cl atoms so that each Te atom is surrounded by four Cl atoms[85]. On the other hand, 8-ethoxy-4-cyclooctenyltellurium trichloride has been established as monomeric[86], undoubtedly because the bulky organic radical shields the $TeCl_3$ group.

Once again, the halogen compounds of S and Se display obvious similarities in their properties and reactivities whereas the more 'metallic' character of Te is reflected in a somewhat deviating behaviour of its organic derivatives.

XI. CHALCOGEN DERIVATIVES OF GROUP V ELEMENTS

A. Nitrogen Compounds

The sulphenamides (**69**; Y = S) constitute a large and well-examined class of compounds, whereas only a limited number of selenenyl amides (selenenamides) (**69**; Y = Se), or other compounds with a Se—N bond, have been prepared thus far, mostly by reaction of selenenyl halides or alkoxides (selenenic esters) with ammonia or amines. They seem to be less stable than the sulphenamides, a conclusion which may well require revision, however, when additional members of the class become known.

$RYNH_2$	$RN{=}Se{=}NR$	R_3PY
(69)	**(70)**	**(71)**

Trifluromethylselenyl bromide reacts with ammonia to form CF_3SeNH_2, $(CF_3Se)_2NH$ and $(CF_3Se)_3N$[87], all distillable liquids resembling ordinary amines in their reactions. Thus, CF_3SeNH_2, on reaction with an isocyanate, yields a CF_3Se-substituted urea.

Tellurenamides (**69**; Y = Te) have apparently not yet been reported.

The selenenyl amides react with nucleophiles in the same way as selenenyl halides. Thus, *N*-phenylselenenylphthalimide, prepared from potassium phthalimide and phenylselenenyl chloride[88,89], is a useful substitute for selenenyl halides in a great variety of reactions (cf. the reactions of similar *N*-sulphenylphthalimides[90]).

Other chalcogen–nitrogen compounds are known, such as *N*-4-methylbenzenesulphonylated selenimides and tellurimides, **24** and **25**, both stable compound types which have recently been subjected to spectroscopy and X-ray diffraction studies[91,92]. The known selenoximides (**26**) are stable analogues of the extensively studied sulphoximides[93].

The easily prepared selenium diimides (**70**; R = *t*-Bu, 4-$MeC_6H_4SO_2$) have been utilized as efficient reagents for allylic amination of alkenes[94].

B. Phosphorus and Arsenic Compounds

Tertiary phosphines react with elemental S or Se to form phosphine sulphides (**71**; Y = S) and phosphine selenides (**71**; Y = Se). Tertiary arsines and stibines form similar compounds. More recently, elemental Te has been found to react similarly to give phosphine tellurides (**71**; Y = Te)[95].

Diphosphanes react with ditellurides to yield telluradiphosphanes, R_2PTePR_2, by insertion of Te abstracted from the ditelluride[41]. The analogous reaction in the Se series takes a different course, giving a substituted 3-membered ring compound, derived from selenadiphosphirane[96].

Phosphorus trichloride and arsenic trichloride react with $(CF_3Se)_2Hg$ to form the substituted phosphines and arsines, $(CF_3Se)_3P$ and $(CF_3Se)_3As$[87].

Numerous derivatives of Se isologues of phosphorus acids are known[97], whereas very few analogous Te compounds have been investigated, probably because of their extreme sensitivity to air. Several decades ago, an alkaline solution of a dialkyl phosphite was shown to react smoothly with S, Se or Te to form a chalcogenophosphate (phosphorochalcogenate)[98]. The Te compound $(EtO)_2P(O)TeNa$ has recently been utilized as an efficient reagent for the deoxygenation of epoxides[99].

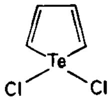
XII. HETEROCYCLIC COMPOUNDS

Thiophene (**72**) represents the classical sulphur analogue of benzene. By the same token, selenophene (**73**) and tellurophene (**74**) assume similar key compound roles in the heterocyclic chalcogen chemistry.

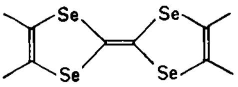
(**72**) Y = S

(**73**) Y = Se

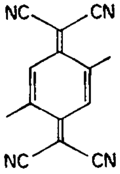
(**74**) Y = Te



(**75**)



(**76**)



(**77**)

Derivatives of selenophene have been known for about 100 years whereas the parent compound (**73**) was only synthesized, from acetylene and Se, in 1927. Detailed studies of its properties and chemistry have all confirmed its striking similarity to thiophene (**72**)[100].

Tellurophenes are less well explored, and tellurophene (**74**) itself remained unknown until 1972 when its rather straightforward synthesis disproved the suspected instability of **74**. In fact, its properties are surprisingly similar to those of **72** and **73** with the notable exception that **74**, contrary to **72** and **73**, produces a stable 1,1-dichloro compound, (**75**), on reaction with Cl_2. Otherwise, the similarity persists into numerous other Te-containing heterocyclic systems[101].

Much interest has recently been accorded to heterocyclic Se compounds, analogous to the S-containing 1,2-dithioles and 1,3-dithioles, as well as the derived systems, trithiapentalene and tetrathiafulvalene, in connection with the studies of organic compounds with metallic conductivity. Thus tetramethyl tetraselenafulvalene (TMTSF) (**76**) forms a charge-transfer complex with 2,5-dimethyl-7,7,8,8-tetracyano-*p*-quinodimethane (**77**) possessing a conductivity that surpasses that of a closely related sulphur-analogue by a factor of ten[102]. More recently, several salts of the type $TMTSF_2X$, where X represents various inorganic anions, have been found to exhibit superconductivity[103]. Only recently has the synthesis of an analogous Te compound been reported[104].

Saturated Te heterocycles such as 1,4-oxatellurane, 1,4-selenatellurane, tellurolane and others, seem to be very similar to their Se analogues. Many Se-containing nitrogen heterocycles are known, e.g. selenazoles, selenadiazoles, and condensed ring systems derived from these. Surprisingly, analogous Te compounds are rare. Benzo[*d*]-1,2-tellurazole exhibits abnormal physical properties, attributed to very short intermolecular Te—N bonds[105]. To what extent the shortage of such compounds is caused by their properties or rather by the lack of appropriate synthetic methods remains to be established.

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CHAPTER 2

General and theoretical aspects of organic compounds containing selenium or tellurium

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I. INTRODUCTION

Even before Mendeleev introduced the concept of periodicity of the chemical elements, certain atoms and their compounds were studied in relation to one another. One of these

TABLE 1. A comparison of experimental first ionization potentials (eV) of Group VI elements and their dihydrides

Species	X = O	S	Se	Te
X^1	13.614	10.357	9.750	9.01
H_2X^{2-7}	12.61	10.47	9.881	9.138

families of elements was O, S and Se, which is now augmented by the inclusion of Te. It is now well known that the basis for the chemical similarities of a family is electronic, that is, the valence electron shells of these elements (O to Te) are all of ns^2np^4 configuration, where n is the principal quantum number. Therefore the four atoms O to Te all have ^3P atomic ground electronic states. The trends one finds for the physical and chemical properties of these elements and their compounds truly justify the original notion that they indeed represent a family and therefore may be studied comparatively. For example, the first ionization potentials (*IP*) of the atoms (X),

$$X(ns^2np^4) \rightarrow X^+(ns^2np^3) + e^-$$

and the first *IP* of their dihydrides,

$$H_2X \rightarrow H_2X^+ + e^-$$

which is normally associated with the removal of an electron from one of the higher occupied orbitals (lone pair), underline the above notion as seen from Table 1.

However, as well as similarities, the differences that exist between these elements also need to be examined. Considering the theoretical aspects only, a number of theoretical computable components of the total electronic energies of these elements can be compared, such as the Hartree–Fock energy (E_{HF}), the correlation energy (E_{cor}) and the relativistic energies (E_{rel}). Two points should be made concerning the energy values quoted in Table 2. Firstly, the energies are quoted in Hartree atomic units (1 hartree = 2625.5 kJ mol^{-1} = 627.51 kcal mol^{-1} = 27.232 eV particle^{-1}). Secondly, it should be noted that E_{cor} and E_{rel} are increasing rapidly as one goes from O to Te. The consequence or implication of this is that experimental quantities such as *IP* are insignificant with respect to E_{cor} and E_{rel}. The ionization potentials of H_2Se and H_2Te for example, are 0.36 and 0.34 hartree, respectively, which compared to their respective relativistic energies of − 26.92 and − 165.63 hartree[8] are certainly insignificant. However, it should be noted that the relativistic effects will be much more important for the core electrons than for the valence electrons and therefore, the relativistic contribution to the first *IP* is not expected to increase significantly from O to Te. Consequently, certain atomic and molecular

TABLE 2. Total experimental electronic energies of Group VI elements and their theoretical computable components[8,9]

	Energy (hartree)			
Component	O	S	Se	Te
E_{HF}	− 74.8095	− 397.5050	− 2399.8669	− 6611.785
E_{cor}	− 0.2575	− 0.6400	—	—
E_{rel}	− 0.0490	− 1.0335	− 26.9247	− 165.6293
E_{total}	− 75.1160	− 399.1785	—	—

quantities cannot be determined theoretically to any desired level of accuracy with the theoretical methods available at the present time. However, it should be pointed out that for certain non-energy-related properties the correlation and relativistic contributions are very small and that for certain energy related properties (ΔEs), the correlation (ΔE_{cor}) and relativistic (ΔE_{rel}) contributions effectively cancel, that is, $\Delta E_{cor} \simeq 0$ and $\Delta E_{rel} \simeq 0$.

II. THEORETICAL BACKGROUND

In any exact science, experiment and theory play an equally important, but complementary, role. This dynamic interaction is illustrated in Figure 1. From this point of view it is necessary to briefly elaborate on some of the important aspects of theoretical chemistry and its application to the Group VI elements, in particular to Se and Te, as well as to their chemistry. In considering the theoretical background necessary for such applications, we shall focus our attention on two factors, namely the atomic orbitals (basis sets) used in the theory and the theoretical method or level of sophistication adopted for the computations. The interdependence of these two components is illustrated in Figure 2. Therefore, two sections covering these methodological aspects will be given followed by a separate section concerning the applications of these methods to the study of organic compounds containing Se and Te.

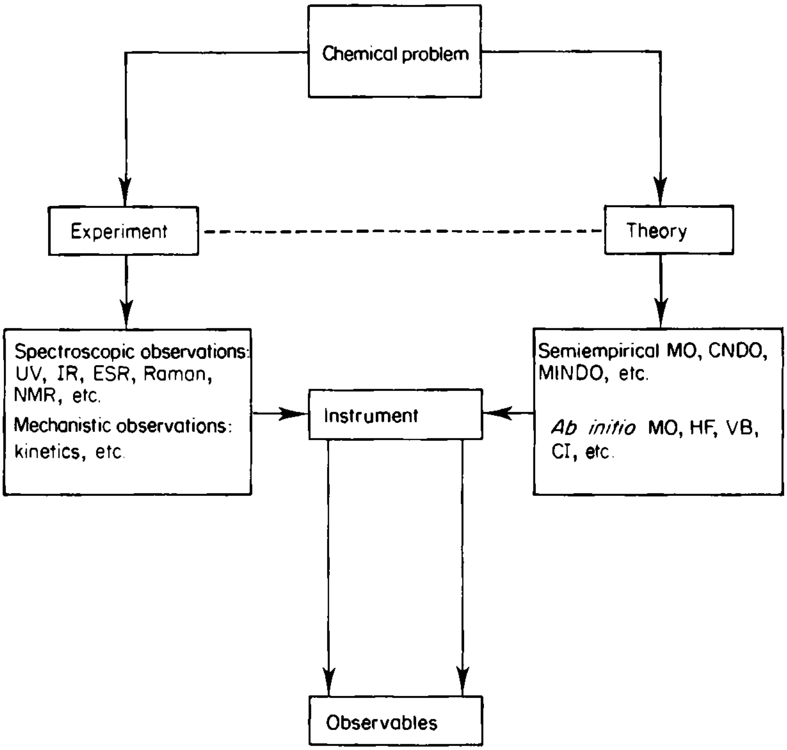

FIGURE 1. An illustration of the dynamic interaction between experiment and theory

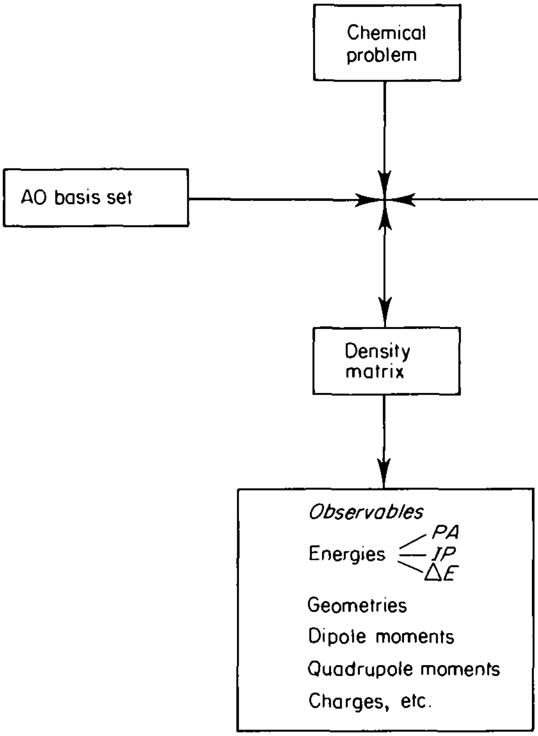

FIGURE 2. An illustration of the factors to be considered for the application of theoretical methods, namely the basis set or atomic orbital (AO) and the *ab initio* method or level of sophistication (e.g. SCF, MC-SCF, CI)

A. Atomic Orbital Basis Sets

In molecular orbital theory[10], molecular orbitals (MO), ϕ, are expressed as a linear combination of a set of functions, η, or atomic orbitals (LCAO),

$$\phi_j = \Sigma_i C_{ij} \eta_i$$

Therefore a fundamental question involved in these types of calculations is choosing the type of functions for η. Two types of functions are widely used, depending on the size of the system: firstly, the exponential-type functions (ETF), frequently called Slater-type orbitals (STO) and which are closely related to the hydrogen orbitals,

$$\text{STO: } \eta(\zeta) = N_\zeta r^{(n-1)} e^{-\zeta r} S_{l,m}(\theta,\phi)$$

and secondly the Gaussian-type orbitals (GTO or GTF),

$$\text{GTO: } \eta(\alpha) = N_\alpha r^{2(n-1)} e^{-\alpha r^2} S_{l,m}(\theta,\phi)$$

where only the lowest angular functions are usually used, that is, 1s, 2p, 3d, 4f,... and no 2s, 3s,... or 3p, 4p,... are used explicitly.

Although nowadays the GTO are more popular for molecular computations, due to the tremendous simplification in the integral evaluations, we cannot, however, ignore Slater-type orbitals altogether for two important reasons. One of the reasons is the conceptual ease in analysing results in terms of STOs, in particular for minimal basis set size (see below). The second reason is due to the fact that in some cases, a linear combination of GTO (contraction) is tailored to fit the shape of STOs (STO-NG basis sets).

In general basis sets can be characterized within one of the categories of these three groups: (*i*) minimal, double-zeta, triple-zeta,... basis sets, (*ii*) split valence (which are minimal in core and can be double-zeta, or triple-zeta... in valence) or (*iii*) general contracted basis sets which do not clearly fall into any of the (*i*) or (*ii*) schemes. These are specified in the following way:

Minimal basis

H	1s
C,N,O,F	1s2s2p
Si,P,S,Cl	1s...3s3p
Ge,As,Se,Br	1s...3d4s4p
Sn,Sb,Te,I	1s...4d5s5p

Double-zeta basis

H	1s1s′
C,N,O,F	1s1s′2s2s′2p2p′
Si,P,S,Cl	1s1s′...3p3p′
Ge,As,Se,Br	1s1s′...3d3d′4s4s′4p4p′
Sn,Sb,Te,I	1s1s′...4d4d′5s5s′5p5p′

Split Valence (double-zeta in valence)

H	1s1s′
C,N,O,F	1s2s2s′2p2p′
Si,P,S,Cl	1s2s2p3s3s′3p3p′
Ge, As, Se, Br	1s...3s3p3d4s4s′4p4p′
Sn, Sb, Te, I	1s...4s4p4d5s5s′5p5p′

where the notation 2p, 3p,... stand collectively for $2p_x$, $2p_y$, $2p_z$ and $3p_x$, $3p_y$, $3p_z$... and 3d... stand collectively, in the case of GTOs, for $3d_{xx}$, $3d_{yy}$, $3d_{zz}$, $3d_{xy}$, $3d_{xz}$, $3d_{yz}$....

Among these basis sets just described, certain basis set exponents are optimized with the constraint that the 2s exponent is equal to the 2p exponent (2s = 2p), and similarly for 3s, 3p and 3d exponents (3s = 3p = 3d) and so on. In these cases the functions are refered to as 2sp and 3spd, respectively.

Finding a set of suitable orbital exponents via careful optimization methods is an elaborate, but now routine, process. In the early days of quantum chemistry, in the absence of such sophisticated methods, theoreticians relied on simple rules to obtain acceptable orbital exponents for an AO basis set. The rules are commonly known as Slater's Rules[11], and were originally proposed by Slater and subsequently have been elaborated on by others[12,13]. Several basis sets, many more for the lighter elements and fewer for the heavier elements, exist for most of the elements of the periodic table[14]. Table 3 summarizes the available STO basis sets (single-zeta and double-zeta) for Se and Te. Whenever possible, the compatible O and S basis sets were included. Table 4 gives the corresponding total energies computed at the RHF level. The Hartree–Fock Limit (HFL) of the atoms are also included for the sake of comparison[8].

In the case of GTO-type basis sets, which have been tabulated elsewhere[14], it must be recognized that there are a great many GTO basis sets for O[20–51], a relatively large number for S[24,31,41,42,45,52–64] and only a few for Se[65–69] and Te[70–72]. However, the GTO basis sets which have been used in the present study for Se and Te are reproduced here in Tables 5 and 6. These basis sets will be discussed further in the results section. Descriptions and atomic energies for the basis sets of Tables 5 and 6, along with those of other available Se and Te basis sets are given in Table 7.

TABLE 3. STO basis sets for elements of Group VI

Orbital	O	S	Se	Te
Single-zeta basis sets				
1s	7.6579	15.5253	33.2068	
2s	2.2458	5.2721	12.3157	
3s		1.5309[a]	4.7764[a]	
4s			1.4041[a]	
5s				
2p	2.2266	5.9719	14.8916	
3p		1.2655[b]	4.4567[b]	
4p			1.1248[b]	
3d			6.1697	
Ref.	12	15	15	
1s	7.6579	15.5409	33.2622	
2s	2.2458	5.3144	12.4442	
3s		2.1223	6.4678	
4s			2.4394	
2p	2.2266	5.9885	15.0326	
3p		1.8273	6.2350	
4p			2.0718	
3d			6.1590	
Ref.	12	12	12	
1s			33.255	
2s			12.448	
3s			6.466	
4s			2.569[c]	
4s			2.589[d]	
2p			15.033	
3p			6.235	
4p			2.280[c]	
4p			2.221[d]	
3d			6.159	
Ref.			16	
Double-zeta basis sets				
1s	9.46635	17.07720	35.03650	53.41410
1s′	6.83768	12.69440	24.36140	36.66320
2s	2.68801	6.72875	16.58670	27.70620
2s′	1.67543	5.24284	13.73710	23.28810
3s		2.66221	7.95809	17.29340
3s′		1.68771	5.66700	11.83340
4s			3.13870	6.98359
4s′			1.88996	5.10844
5s				3.14692
5s′				1.90779
2p	3.69445	9.51251	22.43360	33.70530
2p′	1.65864	5.12050	13.83180	22.38020

TABLE 3. (*Contd.*)

Orbital	O	S	Se	Te
3p		2.33793	7.27814	12.65670
3p′		1.33331	4.68101	11.13750
4p			2.71504	6.95455
4p′			1.51140	4.73195
5p				2.73670
5p′				1.56177
3d			9.29756	18.76030
3d′			4.53759	10.90960
4d				6.33002
4d′				3.68881
Ref.	19	19	19	19
1s	10.1085	17.6913	35.0365	
1s′	7.0623	13.7174	24.3614	
2s	2.6216	5.7486	16.5867	
2s′	1.6271	3.0757	13.7371	
3s		3.1596	7.95809	
3s′		1.8151	5.66700	
4s			3.188	
4s′			1.918	
2p	3.6813	8.9026	22.4336	
2p′	1.6537	4.9073	13.8318	
3p		2.3336	7.27814	
3p′		1.3217	4.68101	
4p			2.699	
4p′			1.503	
3d			12.018	
3d′			6.611	
4d			3.658	
4d′			2.440[e]	
Ref.	17	17	16[e]	
1s	9.55070	17.0249		
1s′	6.87575	12.6622		
2s	2.67094	6.28905		
2s′	1.66028	4.88212		
3s		2.74325		
3s′		1.71063		
2p	3.68560	9.50066		
2p′	1.65546	5.11766		
3p		2.33450		
3p′		1.33110		
Ref.	18	18		

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[a] These are for 2s-type STOs

[b] These are for 2p-type STOs.

[c] Optimized for the C_{3v} structure of SeH_3^+.

[d] Optimized for the D_{3h} structure of SeH_3^+.

[e] Inner core from Ref. 19.

TABLE 4. Total energies for the STO basis sets of Table 3

Basis	O	S	Se	Te
Single-zeta	– 74.5404	– 396.6411	– 2392.4892	—
	– 74.5404	– 396.6276	– 2392.7274	—
Double-zeta	– 74.8043	– 397.5023	– 2399.756	– 6611.762
	– 74.8042	– 397.4990	—	—
	– 74.8043	– 397.5023	—	—
HF[8]	– 74.8095	– 397.5049	– 2399.867	– 6611.785

TABLE 5. GTO basis sets for Se and Te

		Contraction coefficients		
Function	Exponents	s-coeff.	p-coeff.	d-coeff.
Extended [5*s*4*p*2*d*][67]				
S1	1.10166(+ 5)[a]	1.66(– 3)		
	1.6454(+ 4)	1.280(– 2)		
	3.7725(+ 3)	6.176(– 2)		
	1.0960(+ 3)	2.0702(– 1)		
	3.69448(+ 2)	4.2560(– 1)		
	1.35783(+ 2)	3.9446(– 1)		
S2	3.447(+ 1)	4.0930(– 1)		
	1.51604(+ 1)	6.7456(– 1)		
S3	4.40667	4.8930(– 1)		
	1.92114	7.5122(– 1)		
S4	3.8505(– 1)	1.0		
S5	1.5(– 1)	1.0		
P1	7.872(+ 2)		2.310(– 2)	
	1.86702(+ 2)		1.5197(– 1)	
	5.93369(+ 1)		4.4110(– 1)	
	2.13502(+ 1)		4.8726(– 1)	
P2	6.61516		4.5975(– 1)	
	2.31882		6.5091(– 1)	
P3	3.86413(– 1)		1.0	
P4	1.2(– 1)		1.0	
D1	4.9208(+ 1)			7.258(– 2)
	1.37737(+ 1)			3.1279(– 1)
	4.45			5.2895(– 1)
	1.4			3.6502(– 1)
D2	3.3(– 1)			1.0
Minimal [4*s*3*p*1*d*][66]				
S1	5.7153831(+ 3)	6.291(– 2)		
	8.6651303(+ 2)	3.7333(– 1)		
	1.9030059(+ 2)	6.8429(– 1)		

TABLE 5. (*Contd.*)

		Contraction coefficients		
Function	Exponents	s-coeff.	p-coeff.	d-coeff.
S2	2.5523194(+2)	−1.0632(−1)		
	2.411743(+1)	7.1498(−1)		
	9.81016	3.5219(−1)		
S3	2.057072(+1)	−2.3096(−1)		
	3.26003	7.6658(−1)		
	1.34144	3.6426(−1)		
S4	1.99401	−2.1281(−1)		
	3.4561(−1)	6.5746(−1)		
	1.3017(−1)	4.7783(−1)		
P1	3.3471076(+2)		9.028(−2)	
	7.757597(+1)		4.4372(−1)	
	2.261235(+1)		6.184(−1)	
P2	5.864604(+1)		−2.808(−2)	
	6.58902		4.693(−1)	
	2.20366		6.1892(−1)	
P3	4.50393		−4.306(−2)	
	4.1935(−1)		5.1696(−1)	
	1.2751(−1)		5.8734(−1)	
D1	3.033647(+1)			1.5381(−1)
	7.90696			5.1289(−1)
	2.12105			5.7605(−1)
Minimal STO-3G fits				
1s[27]	2.22766	1.54329(−1)		
	4.05771(−1)	5.35328(−1)		
	1.09818(−1)	4.44635(−1)		
2sp[27]	9.94203(−1)	−9.99672(−2)	1.55916(−1)	
	2.31031(−1)	3.99513(−1)	6.07684(−1)	
	7.51386(−2)	7.00115(−1)	3.91957(−1)	
3spd[68]	4.55950(−1)	−2.27764(−1)	4.95151(−3)	2.19768(−1)
	1.39079(−1)	2.17544(−1)	5.77766(−1)	6.55547(−1
	5.36612(−2)	9.16677(−1)	4.84646(−1)	2.86573(−1)
4sp[68]	2.46458(−1)	−3.08844(−1)	−1.21547(−1)	
	9.09586(−2)	1.96064(−2)	5.71523(−1)	
	4.01683(−2)	1.13103	5.49895(−1)	
4spd[71]	2.33486(−1)	−3.30610(−1)	−1.28393(−1)	1.25066(−1)
	9.09182(−2)	5.76110(−2)	5.85205(−1)	6.68679(−1)
	4.00224(−2)	1.11558	5.43944(−1)	3.05247(−1)
5sp[71]	1.34901(−1)	−3.84264(−1)	−3.48169(−1)	
	7.26361(−2)	−1.97257(−1)	6.29032(−1)	
	3.20846(−2)	1.37550	6.66283(−1)	

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[a] This paper contained a printing error: the basis set is listed as [5s4p2d], but the table showed only 4s, the contraction was therefore assumed to be (6, 2, 2, 1, 1/4, 2, 1, 1/4, 1) instead of the (6, 4, 1, 1/4, 2, 1, 1/4, 1).

TABLE 6. Exponents (scale factors) for the Se and Te STO-3G fits of Table 5[68,71]

Orbital	Exponents[a] Se	Te
1s	33.37	51.07
2sp	14.40	22.71
3spd	6.22	12.03
4sp	2.22	—
4spd	—	5.36
5sp	—	2.28

[a] The valence exponents are averages of exponents optimized on a small number of molecules. The atom values are Se: 4sp = 2.19 and Te: 5sp = 2.25.

TABLE 7. Total energies for the Se and Te GTO basis sets

(s/p/d)	[s/p/d]	Contraction scheme	Energy (Ref.)
Se			
(14/11/5)	—	—	−2399.786915(61)[a]
(14/11/5)	—	—	−2399.7717(62)[a]
(13/9/5)	—	—	−2399.703348(61)[a]
(12/8/5)	[5/4/2]	(62211/4211/41)	−2395.9455(63)[b]
(12/9/3)	[4/3/1]	(3333/333/3)	−2390.0932(65)[c]
(12/9/3)	[4/3/1]	(3333/333/3)	−2373.52734(64)[d]
Te			
(18/14/8)	[16/12/8]	(3111.../3111.../111...)	−6611.6648(66)
(15/12/3)	[5/4/2]	(33333/3333/33)	−6547.12236(67)[d]
(15/11/6)	[10/8/4]	52111.../4111.../3111...)	−6611.0593(68)[a,e]

[a] Energy for uncontracted basis set.
[b] First basis set in Table 5.
[c] Second basis set in Table 5.
[d] STO-3G basis set, see Tables 5 and 6.
[e] Other contraction schemes were also considered in Ref. 72.

Although no comparative studies are available on the quality of these Se and Te basis sets (Tables 5–7), earlier studies do exist[47,48,62,73–75] on the quality of basis sets for first-row[47,48,73] and second-row[62,74,75] elements. These studies reveal that care must be taken in choosing a basis set, since poorly balanced basis sets can give drastically different results even when compared with basis sets of similar sizes.

B. *Ab Initio* Computational Methods

All theories of molecular quantum chemistry aim to obtain a solution for the Schrödinger equation, $H\Psi = E\Psi$, of the molecule in question. There are two broad categories, the semiempirical and non-empirical or *ab initio* methods. The semiempirical methods neglect a great many details of the calculations, but try to compensate for this with the use of experimental parameters. In contrast to these, the *ab initio* methods carry out all computations rigorously, without any mathematical neglect. However, even in *ab initio* methods, the explicit form of the wave function Ψ has to be assumed initially[10]. The simplest rigorous wave function that can be used in an *ab initio* calculation is a single Slater determinant (an antisymmetrized spin-orbital product), which will lead to the computation, in a limiting sense, of an energy value normally referred to as the Hartree–Fock Limit (HFL). However, the more general the wave function used in the computation, the more accurate is the resulting energy (E) along with the computed molecular properties which are also expected to improve, but not necessarily monotonically.

The most general wave function that can be used is a linear combination of a very large number of Slater determinants, where the use of such a wave function will lead, in the limiting sense, to an energy value that is normally referred to as the Non-Relativistic Limit (NRL). Traditionally, the molecular Hamiltonian is formulated within the non-relativistic quantum theory. This means that even the most general wave function can only lead to the non-relativistic energy limit. In order to be able to compute the total energy of the atomic

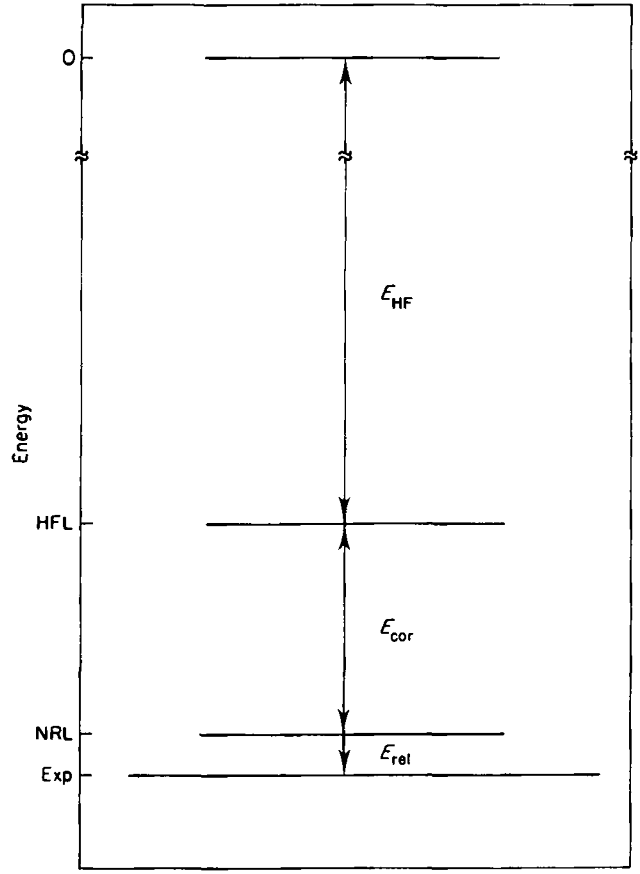

FIGURE 3. The theoretical components of the total experimental energy; E_{HF} at the Hartree–Fock Limit (HFL), $E_{HF} + E_{cor}$ at the Non-Relativistic Limit (NRL) and $E_{exp} = E_{HF} + E_{cor} + E_{rel}$

or molecular system a relativistic Hamiltonian is necessary, so that the relativistic correction can be included in the total non-relativistic energy (Figure 3).

For relatively large chemical systems, and that could mean a medium-size organic molecule containing only H, C, N and O or systems containing one heavy atom with an appropriate number of small ligands (e.g. CH_3), one may hope to use the non-relativistic Hamiltonian with only the simplest possible rigorous wave function. These single determinantal or SCF calculations always yield energies that are above the HFL, sometimes by a substantial amount. Consequently, all the results that are summarized in the next chapter are of this latter level of sophistication. It is perhaps not unreasonable to assume that in the forseeable future, more sophisticated calculations will be performed on organic compounds containing Se and Te. These more sophisticated calculations could include methods such as: Multi Configuration-Self Consistent Field (MC-SCF) theory, Generalized Valence Bond (GVB) theory, Configuration Interaction (CI) theory and the like for which programs exist[76].

In addition to the computation of the total energy with the previous explicitly assumed form of the wave function, that traditionally underline the overall theoretical problem, we also need nowadays the gradients of the energy or forces[77] (i.e. the first partial derivatives of the energy with respect to the geometrical parameters, q_i). For a molecule with N atoms, the energy will be multidimensional function of $3N - 6$ independent internal coordinates:

$$E = (q_1, q_2, q_3, \ldots, q_{3N-6})$$

with $3N - 6$ partial derivatives:

$$\partial E/\partial q = (\partial E/\partial q_1,\ \partial E/\partial q_2, \ldots,\ \partial E/\partial q_{3N-6})$$

These gradients are necessary for the efficient search for geometries of stable molecular structures and for transition states, both of which correspond to critical points on the energy hypersurface, where the gradient of E with respect to each and every internal coordinate is zero:

$$(\partial E/\partial q_1, \partial E/\partial q_2, \ldots, \partial E/\partial q_{3N-6}) = (0, 0, \ldots, 0)$$

Stable molecules (minima) and transition states (first-order saddle-points) are distinguished by their Hessian matrix H:

$$H = \begin{bmatrix} \partial^2 E/\partial q_1^2 & \partial^2 E/\partial q_1 \partial q_2 & \cdots & \partial^2 E/\partial q_1 \partial q_{3N-6} \\ \partial^2 E/\partial q_2 \partial q_1 & \partial^2 E/\partial q_2^2 & \cdots & \partial^2 E/\partial q_2 \partial q_{3N-6} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \partial^2 E/\partial q_{3N-6} \partial q_1 & \cdot & \cdots & \partial^2 E/\partial q_{3N-6}^2 \end{bmatrix}$$

For example, for a minimum, all the eigenvalues of H are positive (0th order) and for a first-order saddle-point, one eigenvalue is negative. Other critical points are also possible, but these are the two types of critical points which are chemically significant. Examples of three efficient gradient optimization methods[78–80] used by the authors are, two variable-metric methods, one developed by Broyden, Fletcher, Goldfarb and Shanno (BFGS)[78] and the other is the Optimally Conditioned method of Davidon (OC)[79]. The third method is a minimization of sum of squares (gradients) technique[80] referred to as VA05AD. The gradient method of optimization has not been used in the results we found in the literature on organic compounds containing Se and Te. However, we do include some of our own calculations in which the OC[79] gradient method of geometry optimization has been used for a selected few compounds.

III. RESULTS

Relatively few organic molecules containing Se or Te have been investigated until now. Even those that have been reported in the literature were studied with basis sets of different quality which would not lend themselves to easy comparison. Furthermore, the majority of the studies involved fixed geometries. Results for compounds of Se and Te that have been studied using *ab initio* methods and GTO-type basis sets are summarized in Table 8. We have recently undertaken the computation of a number of organic compounds containing Se[83]. These provide some energy differences as well as molecular properties other than energies. The basis sets used in these calculations are of two types: minimal and 'split valence'. Two minimal basis sets were used; an STO-3G[27,49,68,71] basis set which is

TABLE 8. Previous calculations on organic Se and Te compounds

Species/Geometry[a]		Energy (hartree)	Basis set	Ref.
H_2Se (C_{2v})				
H—Se	1.454		(12s8p5d)→[5s4p2d]	67
HSeH	93.8		(LWD)	
H—Se	1.52		Pseudopotential	81
HSeH	92.0		calculations	
H—Se	1.42	−2097.403	FSGO	82
HSeH	92.9			
H—Se	1.439	−2374.69243	STO-3G	68
HSeH	92.4			
CH_3SeH (C_s)				
C—Se	1.931	−2413.27744	STO-3G	68
C—H	1.085			
H—Se	1.441			
CSeH	94.9			
HCH	109.0[b]			
Se=C=O ($C_{\infty v}$)				
Se—C	1.662	−2484.79450	STO-3G	68
C—O	1.168			
H_2Te (C_{2v})				
H—Te	1.624	−6548.26782	STO-3G	71
HTeH	92.4			
Te=C=S ($C_{\infty v}$)				
Te—C	1.859	−6977.67673	STO-3G	71
C—S	1.517			
$TeBr_2$(C_{2v})				
Te—Br	2.512	−11636.51567	STO-3G	71
BrTeBr	98.0			

[a] Bond lengths in Å, bond angles in deg.
[b] Average value.

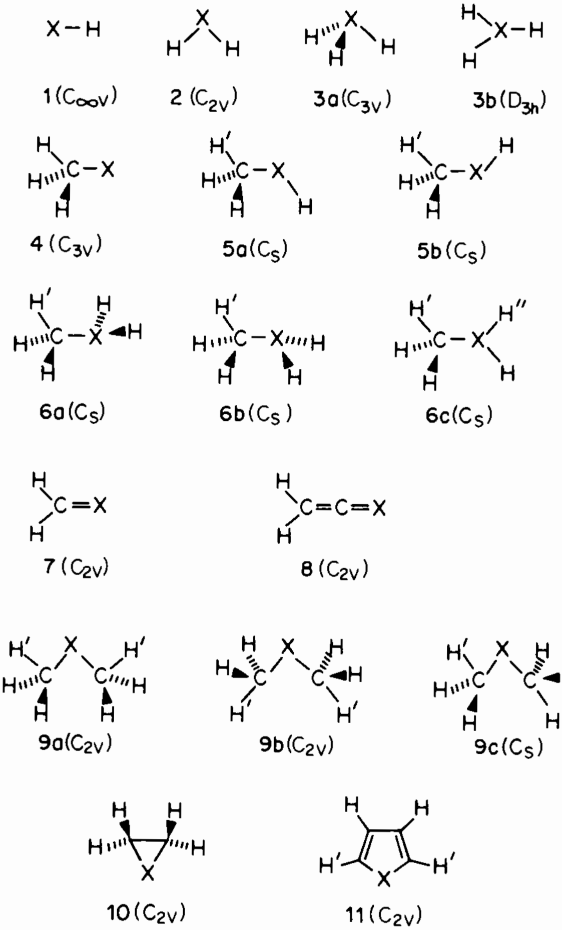

FIGURE 4. The structures which have been studied; X = O, S, Se or Te

available for O, S, Se and Te, and MINI-1[47,61,69] which is available only for O, S and Se. The 'split valence' basis set used for Se is due to Lehn, Wipff and Demuynck (LWD)[67] and a 3-21G[48,49,62] basis set of similar size was used for O and S. The corresponding STO-3G, MINI-1 or 3-21G C and H basis sets were used for the calculations. Therefore the three basis sets which will be referred to here are STO-3G, MINI-1 and 3-21G/LWD basis sets. The total molecular energies for the compounds that have been studied (Figure 4) with the STO-3G, MINI-1 and 3-21G/LWD basis sets are summarized in Tables 9, 10 and 11, respectively. The corresponding geometries for these three basis sets are given in Tables 12, 13 and 14, respectively. Some of the energies given in Tables 9, 10 and 11 (due to the similarities of the basis sets used) can be taken as components in calculating energy differences. The most obvious energy difference is that associated with the protonation and deprotonation process. These differences are in fact the measure of gas-phase basicity and acidity, respectively. One may construct isodesmic (same number of bonds) reactions and with the aid of the total energies summarized in Tables 9, 10 and 11 and of the

TABLE 9. Total STO-3G energies (hartree) of organic Se compounds and their O and S analogues

Molecule	X = O	S	Se
1	− 74.065017	− 393.505782	− 2373.971037
2	− 74.965901	− 394.311630	− 2374.692428
3a	− 75.330440	− 394.666717	− 2375.027599
3b	− 75.328392	− 394.610381	− 2374.976386
4	− 112.706365	− 432.105884	− 2412.558568
5a	− 113.549190	− 432.896073	− 2413.277422
5b	− 113.545983	− 432.893752	− 2413.275780
6a	− 113.929589	− 433.272428	− 2413.635563
6b	− 113.927448	− 433.270066	− 2413.633824
6c	− 113.926562	− 433.220118	− 2413.587693
7	− 112.354347	− 431.671367	− 2412.053568
8	− 149.726105	− 469.047854	− 2449.431475
9a	− 152.133873	− 471.482795	− 2451.863997
9b	− 152.125018	− 471.476644	− 2451.859916
9c	− 152.129285	− 471.479771	− 2451.861986
10	− 150.928501	− 470.276760	− 2450.659590
11	− 225.751253	− 545.092313	− 2525.464839

other molecules involved, calculate the energies of the reactions. The energies of isodesmic reactions may in fact be used as measure of relative stabilities of analogous compounds containing O, S, Se and Te. An example is the energy of hydrogenation, in which the O, S and Se compounds are hydrogenated to methane and their corresponding dihydrides (H_2X).

With the aid of Koopman's theorem[84] we can also estimate the ionization potentials (*IP*) of the closed-shell molecules shown in Figure 4, where the various *IP*s are associated with the removal of an electron from one of the high-lying occupied molecular orbitals and the *IP* is taken as being equal to the negative of the orbital energy. This model has basically two defects in that it does not allow for relaxation of the remaining electrons and does not incorporate correlation effects.

Finally, from these energies conformational and isomeric stabilities of a given compound may be obtained by taking energy differences of different conformations and isomers, respectively. Table 15–19 summarize these four properties based on energy differences for the compounds containing O, S and Se.

Other than the energy-related properties just described, non-energy-related properties can also be calculated; these include geometries and one-electron properties, which are simple expectation values of various one-electron operators. These properties are also of interest and help in making chemical conclusions. One of the key questions is the polarization of the charge distribution that a molecule may have. The most popular way to look at charge distribution is by using Mulliken Population Analysis[85]. However, care

TABLE 10. Total MINI-1 energies (hartree) of organic Se compounds and their O and S analogues

Molecule	X = O	S	Se
1	− 74.700722	− 396.084524	− 2390.654254
2	− 75.495566	− 396.675544	− 2391.220955
3a	—	− 396.897095	− 2391.444659
3b	− 75.796876	− 396.868963	− 2391.400034
4	− 113.520089	− 434.857815	− 2429.425041
5a	− 114.256527	− 435.449603	− 2429.997472
5b	− 114.254128	− 435.448080	− 2429.996165
6a	− 114.573429	− 435.701197	− 2430.249507
6b	—	− 435.699716	− 2430.248149
6c	− 114.573139	− 435.676153	− 2430.210330[a]
7	− 113.058942	− 434.244980	− 2428.794502
8	− 150.638673	− 471.820396	− 2466.371803
9a	− 153.019023	− 474.224778	− 2468.774726
9b	− 153.012318	− 474.220794	− 2468.771489
9c	− 153.015450	− 474.222862	
10	− 151.805715	− 473.024873	− 2467.578289
11	− 227.044415	− 548.229798	—

[a] Energy converged, but the gradient length is 2×10^{-3}.

TABLE 11. Total 3-21G/LWD energies (hartree) of organic Se compounds and their O and S analogues

Molecule	X = O	S	Se
1	− 74.868630	− 396.148616	− 2395.378373
2	− 75.585960	− 396.704666	− 2395.940727
3a	—	− 396.952162	− 2396.218306
3b	− 75.891228	− 396.921097	− 2396.158421
4a	− 113.724796	− 434.958881	− 2434.186645
5a	− 114.398017	− 435.526291	− 2434.761960
5b	− 114.395660	− 435.524560	− 2434.760266
6a	− 114.724919	− 435.802889	− 2435.065389
6b	− 114.713811[a]	− 435.800979	− 2435.063072
6c	− 114.724838	− 435.774001	− 2435.010508
7	− 113.221819	− 434.336245	− 2433.557808
8	− 150.876524	− 471.974929	− 2471.196862
9a	− 153.213209	− 474.348581	− 2472.988686[b]
9b	− 153.206554	− 474.343681	− 2473.579401[b]
9c	− 153.209029	—	− 2473.581864[b]
10	− 152.000703	− 473.157121	− 2471.885849[c]
11	− 227.350082	− 548.473505	− 2547.710125

[a] This structure has a similar conformation to **6a**, except that the OH_2 group is much flatter.

[b] Note that the relative stabilities are reversed.

[c] This structure, although a critical point, is much higher in energy than expected and is perhaps a first-order saddle-point.

TABLE 12. Geometries[a] of organic Se compounds and their O and S analogues calculated with the STO-3G basis set

Molecule/ parameter		X = O	S	Se	Molecule/ parameter		X = O	S	Se
1	H—X	1.0681	1.3457	1.4341	**6a**	C—H	1.0954	1.0888	1.0880
						C—H′	1.0968	1.0889	1.0882
2	H—X	0.9893	1.3288	1.4401		C—X	1.4848	1.8411	1.9787
	HXH	100.02	92.50	92.52		H—X	0.9899	1.3491	1.4674
						XCH	105.85	107.04	106.96
3a	H—X	0.9903	1.3537	1.4737		XCH′	108.82	109.61	108.93
	HXH	113.80	96.60	96.34		CXH	115.46	100.07	99.28
						HCXH′	120.81	120.79	120.68
3b	H—X	0.9831	1.3410	1.4607		HXCH′	65.73	49.01	48.68
4	C—H	1.1324	1.0998	1.0925	**6b**	C—H	1.0951	1.0883	1.0878
	C—X	1.3682	1.7987	1.9278		C—H′	1.0965	1.0886	1.0876
	XCH	117.13	114.89	113.54		C—X	1.4874	1.8487	1.9859
						H—X	0.9879	1.3485	1.4669
5a	C—H	1.0951	1.0867	1.0852		XCH	107.34	108.58	108.02
	C—H′	1.0915	1.0850	1.0838		XCH′	106.49	106.95	107.04
	C—X	1.4330	1.7975	1.9304		CXH	116.97	100.61	99.79
	H—X	0.9911	1.3306	1.4407		HCXH′	119.91	119.53	119.69
	XCH	112.37	110.00	111.42		HXCH′	111.81	131.04	131.35
	XCH′	107.64	108.51	108.44					
	CXH	103.86	95.42	94.90	**6c**	C—H	1.0967	1.0914	1.0907
	HCXH′	118.91	119.00	119.15		C—H′	1.0949	1.0914	1.0911
						C—X	1.4757	1.8459	1.9984
5b	C—H	1.0942	1.0864	1.0847		H″—X	0.9827	1.3359	1.4535
	C—H′	1.0920	1.0843	1.0838		H—X	0.9830	1.3360	1.4535
	C—X	1.4387	1.8039	1.9359		XCH	107.45	107.75	106.97
	H—X	0.9890	1.3293	1.4397		XCH′	106.15	105.33	104.77
	XCH	110.00	111.02	110.69		CXH″	122.25	122.85	123.08
	XCH′	113.11	111.32	110.19		CXH	121.48	123.17	123.26
	CXH	104.69	95.96	95.27		HCXH′	119.58	119.29	119.32
	HCXH	120.70	120.14	119.92					

(Contd.)

TABLE 12. (*Contd.*)

Molecule/ parameter		X = O	S	Se
7	C—H	1.1014	1.0900	1.0897
	C—X	1.2167	1.5741	1.6891
	XCH	122.75	124.00	124.07
8	C—H	1.0750	1.0801	1.0820
	C—C	1.2996	1.2953	1.2924
	C—X	1.1828	1.5370	1.6477
	CCH	120.25	121.48	121.53
9a	C—H	1.0949	1.0870	1.0854
	C—H′	1.0915	1.0852	1.0840
	C—X	1.4334	1.7964	1.9277
	CXC	109.49	98.23	96.79
	XCH	112.05	112.08	111.39
	XCH′	107.43	108.60	108.67
	HCXH′	119.10	119.17	119.28
9b	C—H	1.0945	1.0867	1.0850
	C—H′	1.0913	1.0843	1.0840
	C—X	1.4372	1.8040	1.9344
	CXC	113.56	101.26	99.30
	XCH	109.52	110.78	110.64
	XCH′	113.65	111.89	110.58
	HCXH′	120.91	120.34	120.02
9c	C—H	1.0939	1.0865	1.0848
	C′—H	1.0949	1.0869	1.0854
	C′—H′	1.0918	1.0854	1.0842
	C—H″	1.0913	1.0846	1.0842
	C—X	1.4406	1.0840	1.9342
	C′—X	1.4332	1.7971	1.9285
	C′XC	111.00	99.41	97.78
	XCH	109.54	110.96	110.77
	XC′H	112.25	112.22	111.50
	XC′H′	107.19	108.31	108.42
	XCH″	113.39	111.43	110.19
	HCXH″	120.79	120.16	119.87
	HC′XH′	118.91	118.99	119.17
10	C—H	1.0876	1.0833	1.0832
	C—C	1.4828	1.5067	1.5030
	C—X	1.4325	1.7736	1.9079
	CCH	119.47	117.59	117.39
	CCX	58.83	64.86	66.81
	CXC	62.34	50.27	46.39
	HCCX	105.04	110.00	109.92
11	C—H	1.0774	1.0804	1.0815
	C—H′	1.0819	1.0790	1.0793
	C—C	1.4443	1.4542	1.4615
	C=C	1.3397	1.3344	1.3309
	C—X	1.3755	1.7317	1.8640
	CCH	126.71	123.18	123.87
	XCH′	116.54	120.42	121.37
	C—C=C	106.13	112.06	114.20
	C=C—X	111.15	112.76	112.58
	CXC	105.43	90.35	86.43

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[a] Bond lengths in Å, bond angles in deg.

TABLE 13. Geometries[a] of organic Se compounds and their O and S analogues calculated with the MINI-1 basis set

Molecule/ parameter		X = O	S	Se	Molecule/ parameter		X = O	S	Se
1	H—X	1.0540	1.3895	1.4957	**6a**	C—H	1.1355	1.1304	1.1269
						C—H′	1.1366	1.1293	1.1258
2	H—X	1.0045	1.4123	1.5187		C—X	1.5392	2.0097	2.1010
	HXH	103.36	94.59	93.14		H—X	1.0169	1.4529	1.5587
						XCH	105.78	103.39	104.51
3a	H—X	—	1.4695	1.5733		XCH′	107.85	107.51	108.02
	HXH	—	99.32	96.14		CXH	120.35	102.91	99.58
						HCXH′	120.78	121.10	120.97
3b	H—X	1.0215	1.4548	1.5592		HXCH′	79.07	50.75	48.60
4	C—H	1.1419	1.1133	1.1107	**6b**	C—H	—	1.1305	1.1262
	C—X	1.4647	1.9288	2.0503		C—H′	—	1.1295	1.1269
	XCH	116.42	112.28	111.91		C—X	—	2.0192	2.1097
						H—X	—	1.4522	1.5581
5a	C—H	1.1261	1.1157	1.1137		XCH	—	105.93	106.70
	C—H′	1.1228	1.1156	1.1142		XCH′	—	102.56	103.78
	C—X	1.4773	1.9220	2.0331		CXH	—	103.46	100.11
	H—X	1.0056	1.4108	1.5169		HCXH′	—	119.33	119.39
	XCH	112.30	110.27	110.38		HXCH′	—	129.24	131.45
	XCH′	107.26	106.21	106.68					
	CXH	106.36	97.20	95.58	**6c**	C—H	1.1363	1.1346	1.1339[b]
	HCXH′	118.70	118.80	118.87		C—H′	1.1348	1.1352	1.1348
						C—X	1.5380	2.0313	2.1457
5b	C—H	1.1251	1.1155	1.1136		H″—X	1.0153	1.4363	1.5413
	C—H′	1.1237	1.1150	1.1134		H—X	1.0156	1.4364	1.5412
	C—X	1.4816	1.9280	2.0390		XCH	106.83	103.25	103.14
	H—X	1.0037	1.4099	1.5160		XCH′	105.90	101.61	101.43
	XCH	109.72	108.59	108.97		CXH″	122.00	124.07	124.44
	XCH′	113.02	109.93	109.75		CXH	121.17	124.23	124.44
	CXH	107.06	97.59	95.88		HCXH′	119.48	119.30	119.31
	HCXH′	120.69	120.14	120.05					

(*Contd.*)

TABLE 13. (*Contd.*)

Molecule/ parameter		X = O	S	Se
7	C—H	1.1353	1.1238	1.1215
	C—X	1.2678	1.6970	1.8067
	XCH	122.09	122.22	122.73
8	C—H	1.1084	1.1174	1.1180
	C—C	1.3464	1.3342	1.3333
	C—X	1.2277	1.6722	1.7853
	CCH	119.60	120.67	120.92
9a	C—H	1.1256	1.1151	1.1131
	C—H′	1.1229	1.1155	1.1140
	C—X	1.4753	1.9167	2.0282
	CXC	110.67	98.85	96.84
	XCH	111.69	110.14	110.31
	XCH′	107.26	106.89	107.42
	HCXH′	119.13	119.09	119.13
9b	C—H	1.1257	1.1155	1.1135
	C—H′	1.1225	1.1140	1.1126
	C—X	1.4775	1.9241	2.0353
	CXC	114.65	101.64	99.06
	XCH	109.34	108.80	109.33
	XCH′	112.98	110.00	109.70
	HCXH′	120.78	120.17	119.96
9c	C—H	1.1251	1.1152	—
	C′—H	1.1257	1.1151	—
	C′—H′	1.1233	1.1157	—
	C—H″	1.1225	1.1144	—
	C—X	1.4811	1.9242	—
	C′—X	1.4746	1.9173	—
	C′XC	112.19	99.84	—
	XCH	109.33	108.96	—
	XC′H	111.90	110.22	—
	XC′H′	107.07	106.65	—
	XCH″	112.79	109.57	—
	HCXH″	120.72	120.06	—
	HC′XH′	118.94	118.95	—
10	C—H	1.1187	1.1140	1.1129
	C—C	1.5383	1.5244	1.5179
	C—X	1.5022	1.9521	2.0688
	CCH	119.08	118.30	118.12
	CCX	59.20	67.02	68.48
	CXC	61.60	45.97	43.04
	HCCX	104.49	106.12	106.72
11	C—H	1.1061	1.1102	
	C—H′	1.1140	1.1100	
	C—C	1.4822	1.4945	
	C=C	1.3785	1.3657	
	C—X	1.4152	1.8495	
	CCH	126.64	122.59	
	XCH′	116.80	119.45	
	C—C=C	106.41	113.70	
	C=C—X	110.58	111.80	
	CXC	106.03	88.99	

[a] Bond lengths in Å, bond angles in deg.

[b] Converged to a gradient length of only 2×10^{-3}.

TABLE 14. Geometries[a] of organic Se compounds and their O and S analogues calculated with the 3-21G/LWD basis set

Molecule/	parameter	X = O	S	Se	Molecule/	parameter	X = O	S	Se
1	H—X	1.0289	1.3726	1.4701	**6a**	C—H	1.0744	1.0768	1.0793
						C—H′	1.0740	1.0758	1.0773
2	H—X	0.9666	1.3506	1.4557		C—X	1.5404	1.9439	1.9774
	HXH	107.65	95.82	92.58		H—X	0.9733	1.3500	1.4574
						XCH	104.69	104.50	106.56
3a	H—X	—	1.3516	1.4611		XCH′	106.36	107.91	108.69
	HXH	—	99.55	93.91		CXH	121.45	101.43	97.17
						HCXH′	120.75	121.05	120.88
3b	H—X	0.9788	1.3341	1.4458		HXCH′	85.69	50.47	47.20
4	C—H	1.1340	1.0861	1.0849	**6b**	C—H	1.0744	1.0762	1.0780
	C—X	1.3482	1.9083	1.9981		C—H′	1.0739	1.0751	1.0777
	XCH	117.27	110.62	110.34		C—X	1.5401	1.9588	1.9900
						H—X	0.9732	1.3493	1.4567
5a	C—H	1.0853	1.0774	1.0780		XCH	104.71	106.50	107.76
	C—H′	1.0786	1.0780	1.0801		XCH′	106.36	103.87	106.54
	C—X	1.4403	1.8941	1.9701		CXH	106.59	101.94	97.82
	H—X	0.9658	1.3523	1.4560		HCXH′	120.73	119.62	119.78
	XCH	112.28	109.69	109.69		HXCH′	62.57	129.51	132.90
	XCH′	106.25	105.49	106.59					
	CXH	110.42	97.89	95.33	**6c**	C—H	1.0738	1.0732	1.0746
	HCXH	118.51	118.64	118.80		C—H′	1.0742	1.0762	1.0787
						C—X	1.5398	1.9958	2.0261
5b	C—H	1.0814	1.0766	1.0781		H″—X	0.9727	1.3358	1.4455
	C—H′	1.0848	1.0778	1.0786		H—X	0.9732	1.3358	1.4458
	C—X	1.4450	1.9022	1.9777		XCH	105.58	103.49	105.60
	H—X	0.9637	1.3507	1.4543		XCH′	104.55	101.73	103.12
	XCH	109.29	107.84	108.74		CXH″	121.93	123.72	123.17
	XCH′	112.58	109.46	108.76		CXH	121.30	123.95	123.70
	CXH	111.11	98.34	95.86		HCXH′	119.36	119.15	118.87
	HCXH	120.45	120.14	119.74					

(Contd.)

TABLE 14. (*Contd.*)

Molecule/ parameter		X = O	S	Se
7	C—H	1.0832	1.0734	1.0734
	C—X	1.2068	1.6381	1.7392
	XCH	122.53	121.77	121.73
8	C—H	1.0695	1.0736	1.0740
	C—C	1.2960	1.2853	1.2877
	C—X	1.1620	1.6025	1.6937
	CCH	120.06	120.69	120.85
9a	C—H	1.0863	1.0789	1.0599
	C—H′	1.0793	1.0788	1.0633
	C—X	1.4326	1.8851	2.0480
	CXC	114.00	99.06	99.88
	XCH	111.47	109.59	105.13
	XCH′	106.86	106.48	102.61
	HCXH′	119.28	119.03	118.81
9b	C—H	1.0822	1.0775	1.0788
	C—H′	1.0854	1.0786	1.0796
	C—X	1.4345	1.8975	1.9738
	CXC	118.76	102.45	99.99
	XCH	109.35	108.21	109.02
	XCH′	112.01	109.42	108.98
	HCXH′	120.37	120.01	119.75
9c	C—H	1.0819	1.0776	1.0789
	C′—H	1.0856	1.0785	1.0793
	C′—H′	1.0795	1.0789	1.0808
	C—H″	1.0853	1.0792	1.0802
	C—X	1.4392	1.8960	1.9732
	C′—X	1.4326	1.8872	1.9641
	C′XC	116.01	100.38	97.99
	XCH	109.15	108.40	109.20
	XC′H	111.75	109.65	109.69
	XC′H′	106.58	106.19	107.08
	XCH″	112.15	109.08	108.55
	HCXH″	120.38	119.91	119.61
	HC′XH′	119.00	118.84	118.91
10	C—H	1.0708	1.0697	1.0619
	C—C	1.4742	1.4633	1.5495
	C—X	1.4695	1.9337	2.0603
	CCH	119.24	118.65	116.22
	CCX	59.89	67.77	67.91
	CXC	60.21	44.47	44.18
	HCCX	103.30	104.30	99.79
11	C—H	1.0647	1.0692	1.0702
	C—H′	1.0618	1.0653	1.0671
	C—C	1.4501	1.4481	1.4423
	C=C	1.3397	1.3354	1.3416
	C—X	1.3802	1.7970	1.8763
	CCH	126.59	122.87	122.84
	XCH′	116.51	120.34	121.71
	C—C=C	106.67	113.74	115.09
	C=C—X	109.83	111.67	111.47
	CXC	106.99	89.19	86.87

[a] Bond lengths in Å, bond angles in deg.

TABLE 15. Proton affinities ($kJ\,mol^{-1} \times 10^{-2}$) of organic Se compounds and their O and S analogues calculated with the results given in Tables 8, 9 and 10

	X = O			X = S			X = Se		
Molecule	A[a]	B[a]	C[a]	A	B	C	A	B	C
1	23.7	20.9	18.8	21.2	15.5	14.6	18.9	14.9	14.8
2	9.57	7.91[b]	8.01[b]	9.32	5.82	6.50	8.80	5.87	7.29
4	22.1	19.3	17.7	20.7	15.5	14.9	18.9	15.0	15.1
5a	9.99	8.32	8.58	9.88	6.61	7.26	9.40	6.62	7.97
Deviation[c]	3.1	1.0	—	4.5	0.7	—	2.7	+ 0.7	—

[a] A = STO-3G, B = MINI-1, C = 3-21G/LWD.

[b] Calculated using structure **3b**.

[c] Mean absolute deviation from the 3-21G/LWD basis set.

TABLE 16. Energies of hydrogenation ($kJ\,mol^{-1}$) for a series of isodesmic reactions of organic Se compounds and their O and S analogues

		Energies of hydrogenation[b]		
Reaction[a]	X	A	B	C
$CH_3XH + H_2 \rightarrow CH_4 + H_2X$	O	− 68.4	− 120	− 110
	S	− 65.4	− 85.1	− 84.8
	Se	− 64.0	− 78.7	− 85.8
$H_2C{=}X + 2\,H_2 \rightarrow CH_4 + H_2X$	O	− 271	− 318	− 250
	S	− 347	− 302	− 261
	Se	− 343	− 291	− 299
$CH_3XCH_3 + 2\,H_2 \rightarrow 2CH_4 + H_2X$	O	− 133	− 235	− 212
	S	− 125	− 167	− 168
	Se	− 124	− 155	− 175
$H_2C{=}C{=}X + 4\,H_2 \rightarrow 2CH_4 + H_2X$	O	− 587	− 593	− 450
	S	− 650	− 588	− 503
	Se	− 642	− 572	− 540
$C_2H_4X + 3\,H_2 \rightarrow 2CH_4 + H_2X$	O	− 364	− 475	− 447
	S	− 357	− 372	− 348
	Se	− 352	− 351	—
$C_4H_4X + 7\,H_2 \rightarrow 4CH_4 + H_2X$	O	− 787	− 816	− 742
	S	− 799	− 802	− 730
	Se	− 820	—	− 728
Mean absolute deviation	O	+ 67.8	+ 57.7	—
	S	+ 62.2	+ 37.2	—
	Se	+ 62.2	+ 16.8	—

[a] Energies (hartree) for H_2 and CH_4 are: − 1.117506 and − 39.726864 for STO-3G, − 1.122073 and − 39.928559 for MINI-1 and − 1.122960 and − 39.976878 for 3-21G/LWD, respectively.

[b] A = STO-3G, B = MINI-1, C = 3-21G/LWD.

TABLE 17. First ionization potentials (eV) (Koopman's theorem) for organic Se compounds and their O and S analogues

	X = O			X = S			X = Se		
Molecule	A[a]	B[a]	C[a]	A	B	C	A	B	C
1	—	—	—	—	—	1.76	—	0.31	1.74
2	10.68	12.64	12.99	7.57	10.76	10.68	7.59	10.04	9.84
3a	24.65	—	—	20.37	21.40	20.97	19.06	20.50	20.28
3b	24.21	25.36	25.22	17.88	19.69	19.20	16.85	18.39	17.85
4	—	—	1.16	—	0.25	1.57	—	0.42	1.50
5a	9.78	11.74	11.82	7.08	10.07	9.91	7.07	9.42	9.17
5b	9.70	11.66	11.74	7.06	10.05	9.88	7.05	9.40	9.16
6a	20.82	21.45	21.34	18.66	19.63	19.25	17.66	18.91	18.73
6b	20.66	—	—	18.59	19.57	19.18	17.61	18.86	18.68
6c	20.40	21.37	21.32	16.40	18.04	17.55	15.53	16.88	16.53
7	9.64	11.89	11.78	6.59	9.79	9.65	6.60	9.07	9.03
8	7.56	10.19	9.78	6.10	9.49	9.07	6.29	8.92	8.65
9a	9.24	11.22	11.15	6.70	9.53	9.30	6.64	8.91	7.41
9b	8.93	10.94	10.88	6.60	9.46	9.22	6.57	8.87	8.57
9c	9.07	11.06	10.99	6.65	9.49	9.25	6.60	—	8.59
10	9.99	12.10	12.12	6.94	9.73	9.51	6.79	9.00	7.89
11	7.39	9.64	9.01	7.22	10.07	9.30	7.14	—	8.98

[a] A = STO-3G, B = MINI-1, C = 3-21G/LWD.

TABLE 18. Experimental ionization potentials (eV) and percentage errors of the calculated first ionization potentials

			% Error[a]		
Molecular	X	Exp.[2]	A	B	C
2	O	12.61	−15	+0.2	+3.0
	S	10.47	−28	+2.8	+2.0
	Se	9.881	−23	+1.6	−0.4
5a	O	10.85	−9.9	+8.2	+8.9
	S	9.43	−25	+6.8	+5.1
7	O	10.88	−11	+9.3	+8.3
8	O	9.60	−21	+6.1	+1.9
9a	O	9.96	−7.2	+1.3	+1.2
	S	8.7	−23	+9.5	+6.9
10	O	10.56	−0.5	+1.4	+1.4
11	Se	8.86[b]	−19	—	+1.4
Average			−17	+4.7	+3.6

[a] A = STO-3G, B = MINI-1, C = 3-21G/LWD.

[b] Average of the two reported values in Refs. 86 and 87.

TABLE 19. Conformational stabilities ΔE (kJ mol^{-1}) for organic Se compounds and their O and S analogues

	X = O			X = S			X = Se		
Conformers	A[a]	B[a]	C[a]	A	B	C	A	B	C
3b–**3a**	5.38	—	—	148	73.9	81.6	134	117	157
5b–**5a**	8.42	6.30	6.19	6.09	4.00	4.54	4.31	3.43	4.45
6b–**6a**	5.62	—	29.2	6.20	3.89	5.01	4.57	3.57	6.08
6c–**6a**	7.95	0.76	0.21	137	65.8	75.8	126	103	144
9b–**9a**	23.2	17.6	17.5	16.1	10.4	12.9	10.7	8.50	−1551[b]
9c–**9a**	12.0	9.38	11.0	7.94	5.03	—	5.28	—	−1557[b]

[a] A = STO-3G, B = MINI-1, C = 3-21G/LWD.

[b] This reflects the instability of **9a**.

should be exercised in using this method as the results of Mulliken Population Analysis are somewhat arbitrary and basis-set-dependent to a large degree. Thus only trends may have any significance. A more rigorous measure of the charge distribution, although not so easy to interpret, is the molecular dipole moment. The reason it is rigorous is due to the fact that the dipole moment is a proper observable in the Dirac sense, implying that it is the expectation value of a bonafide quantum-mechanical operator. The reason it is more difficult to interpret a dipole moment is that it is a single vector that is the resultant of the detailed charge distribution. The net charges calculated with the STO-3G, MINI-1 and 3-21G basis sets are given in Tables 20, 21 and 22, respectively. The magnitude of the dipole moments and related results are tabulated in Tables 23 and 24.

IV. DISCUSSION

As far as the applicability of the theory to organic compounds containing Se and Te is concerned, two factors can be considered at this time. First, given the existing comparable basis sets, it is possible to produce as many interesting chemical conclusions as the data will permit. This approach is chemically the most pleasing but has the shortcoming that the reliability of the chemical conclusions cannot be ascertained. Therefore, the second factor addresses itself to this question of basis set reliability. Ultimately it would be desirable to attach a yardstick to each basis set as far as its numerical reliability is concerned in calculation of a given molecular property.

Each property calculated for the selected organoselenium compounds will be discussed in the following sections with special attention being paid to the point concerning basis set reliability.

A. Energy-related Properties

1. Proton affinities

Proton affinities (*PA*) have been calculated for HX^-, H_2X, CH_3X^- and CH_3XH for X = O, S and Se and are tabulated in Table 15. A plot of *PA* as a function of atomic number is shown in Figure 5. The STO-3G basis set consistently gives results of *PA*s greater than the MINI-1 and 3-21G basis set values. The MINI-1 basis set predicts *PA*s which are generally in good agreement with the 3-21G results. Therefore the STO-3G gives the larger mean absolute deviation from the 3-21G basis set, 3.1, 4.5 and 2.7 for O, S and Se respectively, whereas the MINI-1 mean absolute deviations are 1.0, 0.7 and 0.7 for O, S and

TABLE 20. Net charges (from Mulliken populations) of organic Se compounds and their O and S analogues calculated with the STO-3G basis set

Molecule		X = O	S	Se
1	X	−0.742	−0.741	−0.823
	H	−0.258	−0.259	−0.177
2	X	−0.331	+0.072	+0.028
	H	+0.165	−0.036	−0.014
3a	X	−0.256	+0.524	+0.565
	H	+0.419	+0.159	+0.145
3b	X	−0.287	+0.331	+0.357
	H	+0.429	+0.223	+0.214
4	X	−0.640	−0.610	−0.708
	C	−0.046	−0.265	−0.255
	H	−0.105	−0.042	−0.012
5a	X	−0.280	+0.118	+0.061
	C	−0.071	−0.272	−0.264
	H(X)	+0.174	−0.042	−0.025
	H(C)	+0.054	+0.063	+0.074
	H′(C)	+0.070	+0.070	+0.080
5b	X	−0.284	+0.114	+0.058
	C	−0.073	−0.272	−0.264
	H(X)	+0.178	−0.041	−0.023
	H(C)	+0.062	+0.066	+0.077
	H′(C)	+0.056	+0.067	+0.075
6a	X	−0.218	+0.517	+0.537
	C	−0.021	−0.226	−0.221
	H(X)	+0.386	+0.130	+0.118
	H(C)	+0.160	+0.153	+0.153
	H′(C)	+0.147	+0.143	+0.143
6c	X	−0.248	+0.321	+0.311
	C	−0.008	−0.159	−0.143
	H(X)	+0.395	+0.179	+0.172
	H″(X)	+0.397	+0.180	+0.173
	H(C)	+0.154	+0.159	+0.163
	H′(C)	+0.155	+0.159	+0.161
7	X	−0.188	+0.119	+0.058
	C	+0.075	−0.236	−0.215
	H	+0.056	+0.058	+0.078
8	X	−0.186	+0.147	+0.088
	C(X)	+0.260	−0.088	−0.076
	C	−0.246	−0.216	−0.198
	H	+0.087	+0.079	+0.093
9a	X	−0.236	+0.165	+0.101
	C	−0.065	−0.275	−0.269
	H	+0.056	+0.062	+0.070
	H′	+0.071	+0.069	+0.077
9b	X	−0.246	+0.155	+0.090
	C	−0.064	−0.273	−0.266
	H	+0.063	+0.065	+0.075
	H′	+0.060	+0.066	+0.072
9c	X	−0.240	+0.160	+0.096
	C	−0.069	−0.276	−0.269
	C′	−0.062	−0.273	−0.267
	H(C)	+0.063	+0.064	+0.074
	H(C′)	+0.056	+0.062	+0.071
	H′	+0.071	+0.069	+0.078
	H″	+0.061	+0.067	+0.073

6b	X	−0.226	+0.513	+0.533	**10**	X	−0.208	+0.127	+0.041
	C	−0.018	−0.224	−0.219		C	−0.045	−0.205	−0.187
	H(X)	+0.388	+0.130	+0.118		H	+0.074	+0.071	+0.083
	H(C)	+0.152	+0.147	+0.147					
	H′(C)	+0.163	+0.156	+0.156	**11**	X	−0.201	+0.254	+0.197
						C	−0.101	−0.084	−0.075
						C(X)	+0.047	−0.178	−0.168
						H	+0.072	+0.063	+0.067
						H′	+0.082	+0.071	+0.077

TABLE 21. Net charges (from Mulliken populations) of organic Se compounds and their O and S analogues calculated with the MINI-1 basis set

Molecule		X=O	S	Se	Molecule		X=O	S	Se
1	X	−0.855	−0.949	−0.940	**5a**	X	−0.421	−0.156	−0.053
	H	−0.145	−0.051	−0.060		C	−0.253	−0.454	−0.502
						H(X)	+0.267	+0.124	+0.078
2	X	−0.507	−0.277	−0.186		H(C)	+0.129	+0.167	+0.157
	H	+0.253	+0.138	+0.093		H′(C)	+0.148	+0.159	+0.162
3a	X	—	+0.033	+0.243	**5b**	X	−0.424	−0.159	−0.055
	H	—	+0.322	+0.252		C	−0.254	−0.453	−0.501
						H(X)	+0.270	+0.125	+0.078
3b	X	−0.497	−0.172	−0.025		H(C)	+0.140	+0.165	+0.161
	H	+0.499	+0.391	+0.342		H′(C)	+0.128	+0.158	+0.157
4	X	−0.675	−0.727	−0.714	**6a**	X	−0.431	+0.071	+0.293
	C	−0.284	−0.478	−0.514		C	−0.190	−0.356	−0.423
	H	−0.014	+0.068	+0.076		H(X)	+0.463	+0.282	+0.217

(*Contd.*)

TABLE 21. (*Contd.*)

Molecule		X = O	S	Se
	H(C)	+ 0.234	+ 0.244	+ 0.235
	H′(C)	+ 0.227	+ 0.233	+ 0.226
6b	X	—	+ 0.066	+ 0.288
	C	—	− 0.351	− 0.419
	H(X)	—	+ 0.281	+ 0.217
	H(C)	—	+ 0.236	+ 0.299
	H′(C)	—	+ 0.250	+ 0.239
6c	X	− 0.436	− 0.139	− 0.006
	C	− 0.188	− 0.277	− 0.310
	H(X)	+ 0.464	+ 0.325	+ 0.276
	H″(X)	+ 0.466	+ 0.326	+ 0.277
	H(C)	+ 0.231	+ 0.256	+ 0.256
	H′(C)	+ 0.231	+ 0.253	+ 0.252
7	X	− 0.264	− 0.055	+ 0.013
	C	− 0.024	− 0.301	− 0.360
	H	+ 0.144	+ 0.178	+ 0.173
8	X	− 0.266	− 0.037	+ 0.026
	C(X)	+ 0.329	+ 0.001	− 0.062
	C	− 0.422	− 0.356	− 0.353
	H	+ 0.180	+ 0.196	+ 0.194
9a	X	− 0.344	− 0.023	+ 0.097
	C	− 0.240	− 0.458	− 0.508
	H	+ 0.132	+ 0.154	+ 0.152
	H′	+ 0.148	+ 0.162	+ 0.156
9b	X	− 0.352	− 0.034	+ 0.087
	C	− 0.237	− 0.455	− 0.505
	H	+ 0.141	+ 0.160	+ 0.156
	H′	+ 0.132	+ 0.152	+ 0.150
9c	X	− 0.347	− 0.029	—
	C	− 0.243	− 0.458	—
	C′	− 0.237	− 0.457	—
	H(C)	+ 0.141	+ 0.159	—
	H(C′)	+ 0.132	+ 0.154	—
	H′	+ 0.148	+ 0.162	—
	H″	+ 0.133	+ 0.154	—
10	X	− 0.297	− 0.089	− 0.020
	C	− 0.170	− 0.313	− 0.345
	H	+ 0.159	+ 0.179	+ 0.177
11	X	− 0.312	+ 0.076	—
	C	− 0.202	− 0.172	—
	C(X)	+ 0.018	− 0.213	—
	H	+ 0.164	+ 0.167	—
	H′	+ 0.176	+ 0.180	—

TABLE 22. Net charges (from Mulliken populations) of organic Se compounds and their O and S analogues calculated with the 3-21G basis set

Molecule		X = O	S	Se
1	X	−1.025	−0.911	−1.042
	H	+0.025	−0.089	+0.042
2	X	−0.733	−0.170	−0.373
	H	+0.366	+0.085	+0.187
3a	X	—	+0.202	+0.037
	H	—	+0.266	+0.321
3b	X	−0.714	+0.038	−0.107
	H	+0.571	+0.321	+0.369
4	X	−0.866	−0.666	−0.809
	C	−0.038	−0.758	−0.629
	H	−0.032	+0.141	+0.146
5a	X	−0.677	+0.017	−0.194
	C	−0.270	−0.834	−0.681
	H(X)	+0.373	+0.069	+0.166
	H(C)	+0.177	+0.246	+0.236
	H′(C)	+0.220	+0.256	+0.235
5b	X	−0.683	+0.011	−0.195
	C	−0.267	−0.835	−0.686
	H(X)	+0.377	+0.070	+0.167
	H(C)	+0.201	+0.254	+0.239
	H′(C)	+0.172	+0.245	+0.236
6a	X	−0.708	+0.293	+0.166
	C	−0.322	−0.790	−0.709
	H(X)	+0.538	+0.240	+0.296
	H(C)	+0.319	+0.343	+0.319
	H′(C)	+0.317	+0.330	+0.315
6b	X	−0.642	+0.289	+0.167
	C	−0.389	−0.784	−0.714
	H(X)	+0.528	+0.238	+0.294
	H(C)	+0.335	+0.334	+0.318
	H′(C)	+0.306	+0.350	+0.323
6c	X	−0.710	+0.044	−0.024
	C	−0.321	−0.635	−0.646
	H(X)	+0.539	+0.275	+0.331
	H″(X)	+0.537	+0.276	+0.333
	H(C)	+0.320	+0.349	+0.338
	H′(C)	+0.315	+0.341	+0.330
7	X	−0.482	+0.168	−0.134
	C	+0.131	−0.703	−0.374
	H	+0.175	+0.267	+0.254
8	C	−0.548	+0.334	−0.148
	C(X)	+0.544	−0.288	+0.129
	C	−0.555	−0.611	−0.543
	H	+0.280	+0.283	+0.281

(*Contd.*)

TABLE 22. (*Contd.*)

Molecule		X=O	S	Se	Molecule		X=O	S	Se
9a	X	−0.643	+0.236	−0.088		H(C′)	+0.176	+0.236	+0.226
	C	−0.250	−0.837	−1.649		H′	+0.217	+0.248	+0.231
	H	+0.177	+0.236	+0.563		H″	+0.173	+0.238	+0.227
	H′	+0.217	+0.248	+0.566					
					10	X	−0.552	+0.086	−0.237
9b	X	−0.662	+0.219	+0.003		C	−0.191	−0.604	−1.033
	C	−0.237	−0.837	−0.693		H	+0.234	+0.280	+0.576
	H	+0.198	+0.247	+0.234					
	H′	+0.171	+0.234	+0.224	**11**	X	−0.645	+0.541	+0.127
						C	−0.340	−0.202	−0.257
9c	X	−0.650	+0.229	+0.003		C(X)	+0.141	−0.598	−0.315
	C	−0.248	−0.845	−0.696		H	+0.250	+0.254	+0.249
	C′	−0.246	−0.837	−0.685		H′	+0.271	+0.276	+0.260
	H(C)	+0.201	+0.247	+0.233					

TABLE 23. Dipole moments (D)[a] for organic Se compounds and their O and S analogues calculated with the STO-3G, MINI-1 and 3-21G/LWD basis sets

	X = O			X = S			X = Se		
Molecule	A[b]	B[b]	C[b]	A	B	C	A	B	C
2	1.71	2.04	2.39	1.03	2.00	1.83	1.47	1.66	1.19
5a	1.51	1.81	2.12	0.96	2.14	2.12	1.53	1.89	1.81
5b	1.58	1.87	2.23	1.04	2.20	2.19	1.60	1.94	1.86
7	1.54	2.06	2.66	0.82	2.49	2.42	1.69	2.27	2.13
8	0.84	1.48	1.82	0.30	2.47	2.46	1.44	2.28	1.97
9a	1.33	1.64	1.85	0.87	2.11	2.07	1.49	1.88	3.82
9b	1.43	1.70	1.97	1.05	2.20	2.21	1.64	1.98	2.04
9c	1.39	1.69	1.93	0.97	2.17	2.16	1.57	—	2.00
10	1.46	1.83	2.78	0.75	2.54	2.81	1.67	2.39	4.66
11	0.53	0.73	1.10	0.11	1.48	1.35	0.57	—	0.96

[a] 1 Hartree/angstrom^2 = 2.5417655 D.
[b] A = STO-3G, B = MINI-1, C = 3-21G/LWD.

TABLE 24. Experimental dipole moments (D) and percentage errors of the calculated dipole moments

				% Error[a]		
Molecule	X	Exp.	Ref.	A	B	C
2	O	1.85	88	− 7.6	+ 10	+ 29
	S	0.97	88	+ 6.2	+ 106	+ 89
	Se	0.62	89	+ 137	+ 168	+ 92
5a	O	1.70	88	− 11.2	+ 6.5	+ 25
	S	1.52	88	− 37	+ 41	+ 39
7	O	2.33	88	− 34	− 12	+ 14
8	O	1.414	90	− 41	+ 4.7	+ 29
9a	O	1.30	91	+ 2.3	+ 26	+ 42
11	O	0.67	94a	− 21	+ 9.0	+ 64
	S	0.55	94a	− 80	+ 169	+ 145
	Se	0.398	94a	+ 43	—	+ 141
MAD[b]	O	—	—	0.31	0.17	0.45
	S	—	—	0.35	0.86	0.75
	Se	—	—	0.51	1.04	0.57

[a] A = STO-3G, B = MINI-1, C = 3-21G/LWD.
[b] MAD = Mean absolute deviation.

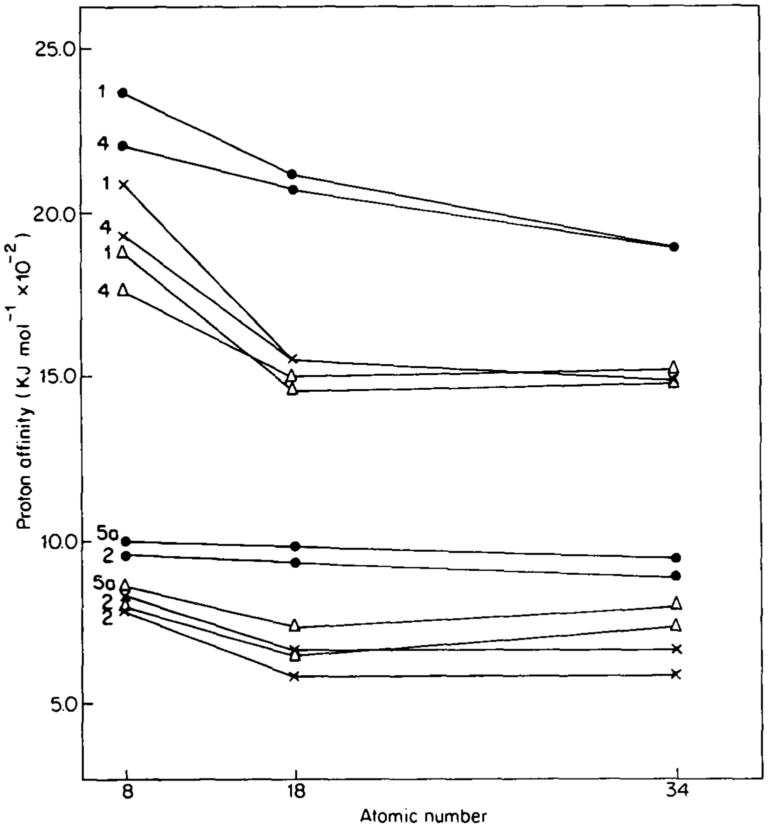

FIGURE 5. Proton affinities (kJ mol^{-1} × 10^{-2}) as a function of atomic number; ● : STO-3G values, × : MINI-1 values and △: 3-21G/LWD values

Se, respectively. Where the STO-3G basis set has the largest deviation for the S compounds, the MINI-1 basis set has the largest deviation for the O compounds.

The trend on going from O to Se varies slightly with basis set. However, the overall trend is that the *PA*s decrease on going from O to Se compounds with *PA*(O) < PA(S) < PA(Se) and the *PA*s of S and Se are similar. The 3-21G actually consistently predicts an increase in *PA* on going from S to Se.

2. Energies of hydrogenation

Energies of hydrogenation for isodesmic reactions of the type in which the compounds are hydrogenated to CH_4 and H_2X have been calculated (Table 16). The energies of hydrogenations have also been plotted against the atomic number in Figure 6. Mean absolute deviations from the 3-21G energies of hydrogenation are given at the bottom of Table 16 for the STO-3G and MINI-1 basis sets. The MINI-1 results are in better agreement with the 3-21G results than are the STO-3G results. Both the STO-3G and MINI-1 basis sets do progressively better overall in going from O compounds to Se compounds. Generally the STO-3G basis set is known to do poorly at predicting energies

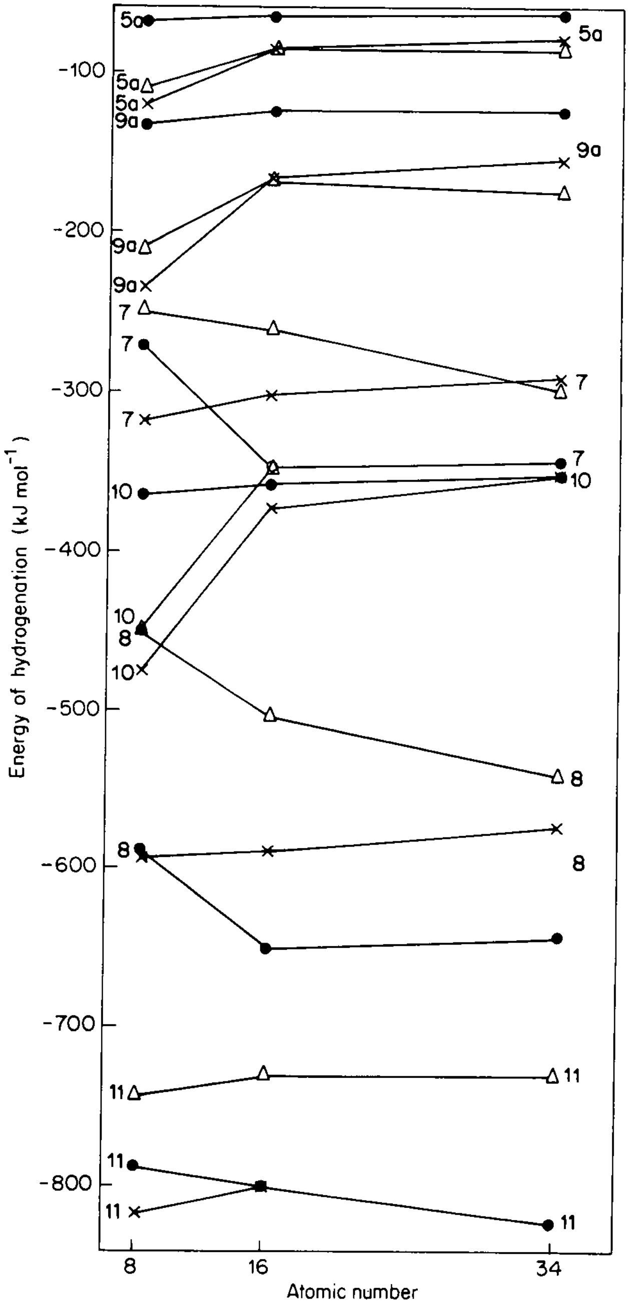

FIGURE 6. Energies of hydrogenation (kJ mol^{-1}) as a function of atomic number; ● : STO-3G values, × : MINI-1 values and △: 3-21G/LWD values

of hydrogenation, giving a mean absolute deviation of 93 kJ mol^{-1} for first-row compounds[48]. The 3-21G basis sets are known to be better at predicting energies of hydrogenation, giving a mean absolute deviation of 41 kJ mol^{-1} for the same set of 18 comparisons[48]. Therefore the results of Table 16 should in general be in similar agreement with the experimental energies of hydrogenation.

3. Ionization potentials

First ionization potentials (*IP*s) have been obtained using Koopman's theorem for most of the compounds and are tabulated in Table 17. These can be compared directly with the available experimental values[2,86,87]. Ionization potentials are available for the series of O, S, Se and Te dihydrides (H_2X), for which experimental values are given in Table 1. These are also included in Table 18 along with other available experimental *IP*s and with percentage errors of the *IP* predicted by each basis set. The 3-21G and MINI-1 basis sets are both in excellent agreement with the experimental values, with the 3-21G basis set giving slightly better results overall. The larger difference between STO-3G and the other two basis sets is not that surprising. Both MINI-1 and the 3-21G basis set have been carefully optimized. The 3-21G basis set was optimized for good valence-shell description[48,62], while the minimal MINI-1 basis set was optimized for good orbital energies[47,61,69], thus explaining the excellent values predicted for the *IP*s. In general the

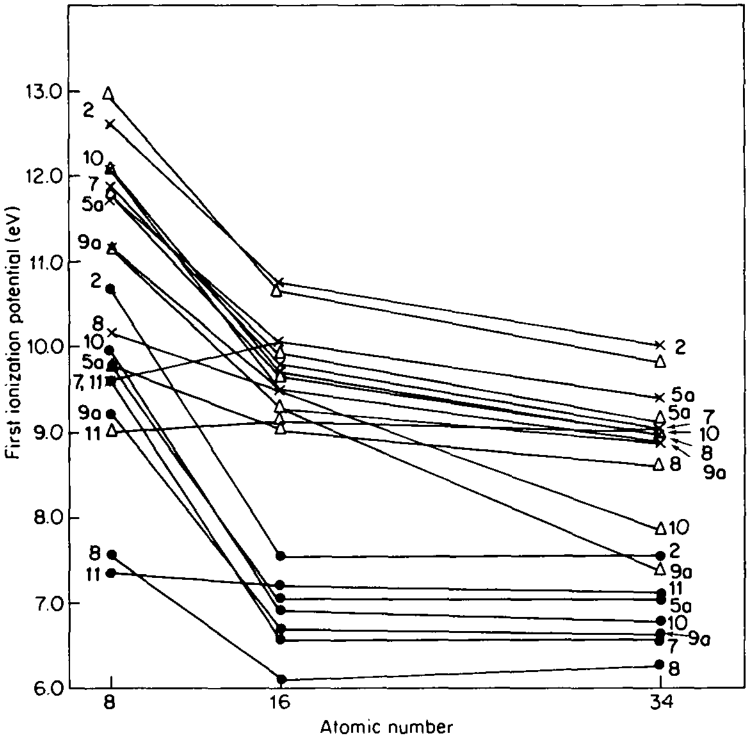

FIGURE 7. First ionization potentials (eV) as a function of atomic number; ● : STO-3G values. × : MINI-1 values and △: 3-21 G/LWD values

calculated values using the 3-21G and MINI-1 basis sets are larger than the experimental values by about 4%, whereas the STO-3G results are lower by about 17%. A modified STO-NG basis set[92] gave a better *IP* for H_2Se, 9.12 eV compared to 7.59 eV with the current standard STO-3G basis set. Normally good-quality orbital energies predict *IP*s which are too high compared to the true values. A systematic study using the DZ basis set gives values which are 8% too high[93].

The *IP*s for the lowest energy conformations of the neutral molecules are plotted as a function of atomic number in Figure 7. The trends of the *IP*s from O to Se are generally consistent for all three basis sets. However, three problems show up in Figure 7. The change in *IP* in going from O to S for both the STO-3G and MINI-1 and from S to Se for the 3-21G basis set do not follow the trends.

4. *Relative stabilities of conformers*

For structures **3**, **5**, **6** and **9**, a number of conformations were calculated. The relative stabilities of these conformations are given in Table 19.

The first energy difference in Table 19 (**3b**–**3a**) represents the inversion barriers for the protonated dihydrides. These inversion barriers are predicted to generally increase in going from O to Se, indicating a preference for pyramidality in going from O to Se. Only the STO-3G basis set predicts a non-planar C_{3v} structure for H_3O^+, where the other two basis sets predict only the planar D_{3h} structures.

The stability of conformer **5b** relative to **5a** increases in going from O to Se at all three basis set levels. This is expected since the H–H repulsion in **5b** should decrease due to the increase in C—X distance in going from O to Se.

The relative stabilities of **6a** and **6b** would also be expected to decrease in going from O to Se due to the decreased repulsion between the hydrogen atoms on the C and X atoms. However, the predicted trends are not consistent with this expectation. In the case of **6c**–**6a**, this is again a measure of the increased preference for pyramidality in going from O to Se, whereas the stability of **6c** increases with respect to **6a** in going from O to Se.

For structure **9**, the results indicated a general increase in stability of **9b** and **9c** relative to **9a**. However, the 3-21G basis set predicts **9b** and **9c** to be much more stable than **9a** for the Se compound, indicating that structure **9a** for Se is probably not a minimum (perhaps a saddle-point).

In general the results indicate the large changes in preferred conformation for the O, S and Se compounds. The results are also very sensitive to the basis set.

B. Non-energy-related Properties

1. *Charge distribution*

Net charges calculated using Mulliken Population Analysis are tabulated in Tables 20, 21 and 22 for the STO-3G, MINI-1 and 3-21G/LWD basis sets, respectively. The dipole moments are tabulated in Table 23. Net charges at O, S and Se are plotted as a function of atomic number in Figure 8 and dipole moment are plotted as a function of atomic number in Figure 9.

As can be seen from Figure 8, the net charge at S and Se is in general more positive than at O and the net charge at Se is predicted to be in some cases more positive and in other cases more negative (in some cases substantially so) than at S (e.g. + 0.09 for S and – 0.24 for Se in structure **10**).

For the dipole moments it is evident that the trends predicted by STO-3G and the other two basis sets are different. The major difference appears to be for the sulphur compounds. From some of the available experimental values the trend, as is expected, is that the

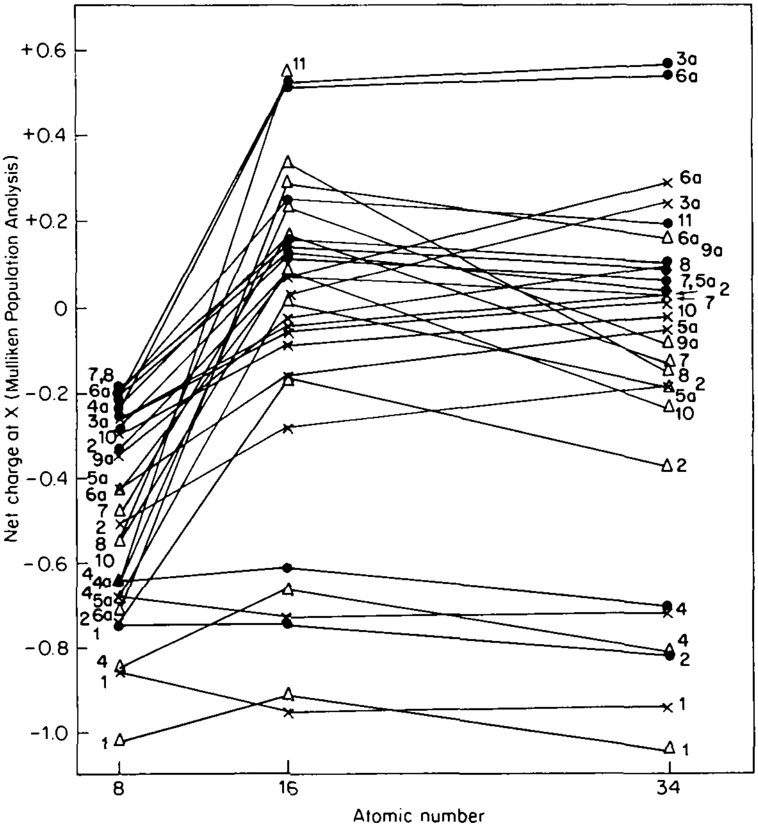

FIGURE 8. Net charges at X(X = O, S and Se) calculated from Mulliken Population Analysis as a function of atomic number; ● : STO-3G values, × : MINI-1 values and △: 3-21G/LWD values

magnitude of the dipole moment decreases from O to Se, e.g., H_2O ($\mu = 1.85$), H_2S ($\mu = 0.97$) and H_2Se ($\mu = 0.62$) and similarly for CH_3XH and C_4H_4X (Table 24). The calculated trends as seen from Figure 9 do not follow the expected or experimentally observed trends. The problems appear to be mainly in going from O to S for the MINI-1 and 3-21G basis sets and from S to Se for the STO-3G basis set. This may be due to the lack of d-polarization functions on S. Table 24 contains the percentage errors for the three basis sets compared to experimental values. Normally, predicted dipole moments are too large except for STO-3G which frequently underestimates the magnitude[48,68]. This is consistent with the calculated errors in Table 24. The MINI-1 minimal basis set, unlike the STO-3G basis set, gives values which are generally too large and are more similar to the 3-21G basis set. Mean absolute deviations are also included in Table 24 for the O, S and Se compounds. These indicate that the STO-3G results are better than the MINI-1 and 3-21G results overall and that MINI-1 does poorly for the S and Se compounds.

2. *Geometries*

The gradient optimized geometries are given in Tables 12, 13 and 14 for the STO-3G, MINI-1 and 3-21G/LWD basis sets, respectively. Some of the available experimental

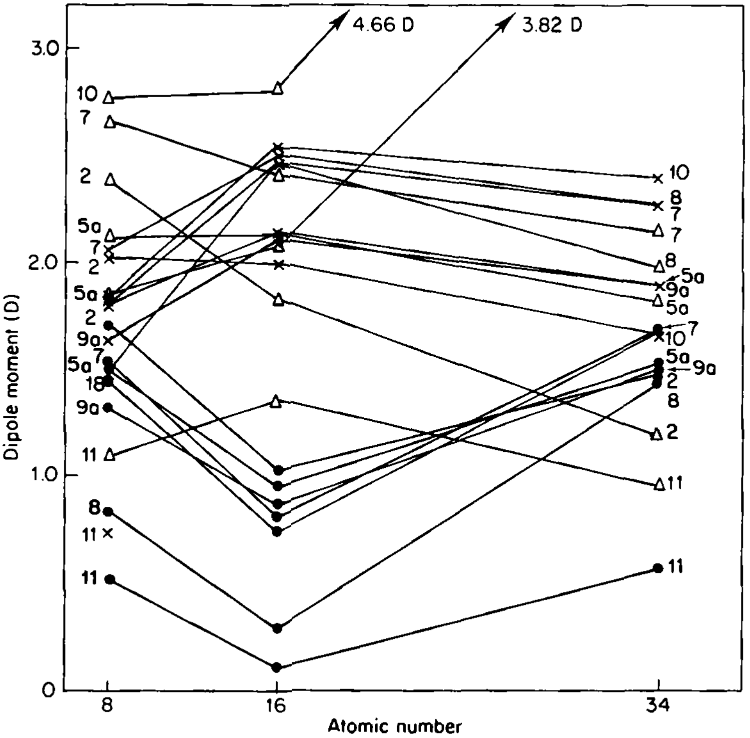

FIGURE 9. Dipole moments (D) as a function of atomic number; ● : STO-3G values, × : MINI-1 values and △: 3-21G/LWD values

geometries[94] are given in Table 25. The deviations from experiment of some of these geometrical parameters and mean absolute deviations for bond lengths and bond angles are given in Table 26. Overall, there is no clear preference. MINI-1 does poorly on bond lengths for the S compounds but very well on the bond angles of compounds containing O, The largest error being for the C—S bonds, which are predicted to be too long by about 1 Å. Previous studies[48] give a mean absolute deviation from experiment for AB bond lengths of 0.028 Å and 0.01 Å (45 comparisons) and mean absolute deviations from experiment for AH bond lengths of 0.035 Å and 0.016 Å (6 comparisons) for the STO-3G and 3-21G basis sets, respectively.

V. CONCLUSIONS

Ab initio MO computations on Se compounds are well within the realms of possibility, but similar computations on Te compounds are more difficult to come by at this time.

The comparison of the available results tend to suggest that there is a general trend on going through a series of analogous compounds containing O, S, Se and Te. The trends indicate a gradual quantitative change rather than a quantum jump that could manifest itself in qualitative differences as one compares S with Se or, in the few cases available, Se with Te. The fundamental cause for the observed trends is most likely related to the change in size of these elements. Since the trends in some cases are rather subtle, this increases the difficulty of predicting these trends reliably at these low-level calculations.

TABLE 25. Experimental geometries[a] of organic Se and Te compounds and their O and S analogues[94]

Molecule/ parameter		X = O	S	Se	Te
2	H—X	0.959	1.336	1.460	1.653
	HXH	*103.9*	*92.1*	*91*	*90.2*
5a	C—H	1.093	1.091	—	—
	C—H′	1.093	1.091	—	—
	C—X	1.421	1.819	—	—
	H—X	0.963	1.336	—	—
	XCH	129.8	—	—	—
	XCH′	107.0	—	—	—
	CXH	108.0	96.5	—	—
	HCH	108.5	109.8	—	—
7	C—H	1.101	1.093	—	—
	C—X	1.203	1.611	—	—
	XCH	127.0	126.2	—	—
8	C—H	1.071	—	—	—
	C—C	1.329	—	—	—
	C—X	1.150	—	—	—
	CCH	118.35	—	—	—
9a	C—H	1.096	1.091	1.096	—
	C—H′	1.096	1.091	1.088	—
	C—X	1.410	1.802	1.945	—
	CXC	111.7	98.9	96.3	—
	XCH	—	—	110.3	—
	XCH′	—	—	105.0	—
	HCH	109.5	109.6	109.9	—
10	C—H	1.082	—	—	—
	C—C	1.472	—	—	—
	C—X	1.436	—	—	—
	CCH	—	—	—	—
	CCX	—	—	—	—
	CXC	61.4	—	—	—
	HCH	116.7	—	—	—
11	C—H	1.077	1.081	1.081	—
	C—H′	1.075	1.078	1.078	—
	C—C	1.431	1.423	1.423	—
	C=C	1.361	1.370	1.370	—
	C—X	1.362	1.714	1.863	—
	CCH	127.94	124.27	122.54	—
	XCH′	115.92	119.85	124.39	—
	C—C=C	106.06	112.45	114.92	—
	C=C—X	110.68	112.47	111.22	—
	CXC	106.55	92.17	87.72	—

[a] Bond lengths in Å, bond angles in deg.

TABLE 26. Deviation from experiment of some calculated geometrical parameters[a]

Molecule/ parameter	X	A	B	C
Bond lengths				
2 H—X	O	+0.030	+0.046	+0.008
	S	+0.018	+0.076	+0.015
	Se	+0.014	+0.059	−0.004
	Te	−0.029	—	—
5a H—X	O	+0.028	+0.043	+0.003
	S	−0.005	+0.075	+0.016
C—X	O	+0.012	+0.056	+0.019
	S	−0.022	+0.103	+0.075
7 C—X	O	+0.014	+0.065	+0.004
	S	−0.037	+0.086	+0.027
8 C—X	O	+0.033	+0.078	+0.012
9a C—X	O	+0.023	+0.065	+0.023
	S	−0.006	+0.115	+0.083
	Se	−0.017	+0.083	+0.103
10 C—X	O	−0.004	+0.066	+0.034
11 C—X	O	+0.014	+0.053	+0.018
	S	+0.018	+0.136	+0.083
	Se	+0.001	—	+0.013
MAD[b]	O	0.02	0.06	0.02
	S	0.02	0.10	0.05
	Se	0.01	0.07	0.04
Bond angles				
2 HXH	O	−3.9	−0.5	+3.8
	S	+0.4	+2.5	+3.7
	Se	+1.5	+2.1	+1.6
	Te	+2.2	—	—
5a CXH	O	−4.1	−1.6	+2.4
	S	−1.1	+0.7	+1.4
9a CXC	O	−2.2	−1.0	+2.3
	S	−0.7	−0.1	+0.2
	Se	+0.5	+0.5	+3.6
10 CXC	O	+0.9	+0.2	−1.2
11 CXC	O	−1.1	−0.5	+0.4
	S	−1.8	−3.2	−3.0
	Se	−1.3	—	−0.9
MAD	O	2.4	0.8	2.0
	S	1.0	1.6	2.1
	Se	1.1	1.3	2.0

[a] A = STO-3G, B = MINI-1, C = 3-21G/LWD.

[b] MAD = Mean absolute deviation.

Of the three basis sets studied, the split valence 3-21G/LWD basis set is the most reasonable basis set for studying Se compounds. The minimal MINI-1 basis set, however, gives results which are comparable to the 3-21G/LWD basis set. For this reason, the other MINI-N ($N = 2$–4) or MIDI-N ($N = 1$–4) basis sets[69] are expected to give results which are better than the basis sets compared in the present study. However, comparable studies on Te compounds must wait for the development of such basis sets. At present the only economical basis set available for Te is the STO-3G.

VI. ACKNOWLEDGEMENTS

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The Chemistry of Organic
Selenium and Tellurium
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CHAPTER 3

Structural chemistry of organic compounds containing selenium or tellurium

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I. INTRODUCTION

The structural chemistry of selenium and tellurium is somewhat in the shadow of the structural chemistry of sulphur. With the development of the chemistry of these elements, progress in their structural chemistry is inevitable. This progress is expected primarily in experimental studies where their position in the periodic system is not a disadvantage, whereas for theoretical calculations it may be.

The present review is concerned with the metrical aspects of the structural chemistry of Se and Te. Although a comprehensive literature search preceded writing, completeness is not aimed at, except perhaps for gas-phase studies which are not numerous anyway but usually deal with the most fundamental molecules.

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The criterion for a structure to be included in this review is that at least one of the Se or Te bonds is to carbon. As earlier periods have been at least partially covered in other works (e.g. References 1 and 2) our attention has focused on the past decade.

A convenient guiding principle in systematizing the structure is the coordination number of Se or Te. Further subdivision is applied only to the two-coordinated selenides and tellurides.

Although gas-phase and crystal-phase structures are discussed together, the available material does not as yet allow a meaningful discussion of gas/crystal structural differences.

Attempts have been made to systematize the collected structural information and to search for regularities in the structural variations. Substituent effects and characteristic differences as compared with sulphur have been looked for. For possible interpretation of such observations only qualitative considerations have been employed. Electron-pair repulsions and non-bonded interactions are useful in discussing sulphur stereochemistry[3]. Of these two the relative importance of the non-bonded interactions diminishes for Se and Te as compared with S due to the longer bonds of the former two elements.

Very little attention is devoted in our review to the consequences of molecular vibrations and librations. The well-defined physical meaning of the parameters is important especially in discussing subtle structural effects and those structural variations which are on the borderline of the observed differences. Furthermore, in the case of large-amplitude vibrations, the determined structures may differ considerably from what they would be in the equilibrium structure (cf. Reference 4). As neither subtle structural differences nor large-amplitude motion have special importance in the accumulated structural chemical information for Se or Te *for the time being*, a detailed discussion of the physical meaning of the determined parameters has been avoided. The different representations of the molecular geometry and the meaning of the parameters r_e, r_0, r_s, r_a, r_g, r_α, r_z etc. are summarized and references are given in the review[4] cited above.

The experimental errors and uncertainties have been cited as communicated in the original reports; in some cases, though, they have been rounded to one digit. Generally they correspond to the usual requirements of the respective techniques used at the time of the particular studies. Throughout this review, the uncertainties are given in parentheses following the parameter value and they refer to the last digit of the parameter. The most common experimental techniques are denoted as follows: MW, microwave spectroscopy; ED, gas electron diffraction; XD, X-ray diffraction crystallography.

II. ONE-COORDINATED SELENIUM AND TELLURIUM

The only structure belonging here and involving tellurium is S=C=Te. It was determined three decades ago by means of microwave spectroscopy (MW)[5]. The length of the C=Te bond is 1.904 Å. The carbon atom is formally in sp hybridization. Our discussion will first deal with C=Se bonds with sp carbon, and then with C=Se bonds with sp^2 carbon. All the available geometrical data for the C(sp)=Se bond refer to the vapour phase and mostly originate from MW.

Table 1 presents the bond distances in the analogues of CO_2 and CO. The selenium–

TABLE 1. C—X bond distances (Å)[a] with X = O, S or Se

X	OCX	SCX	SeCX	CX
O	1.1598[6]	1.1543(3)[7]	1.1535(1)[8]	1.12834(1)[9]
S	1.5628(4)[7]	1.5526[10]	1.553(2)[11]	1.53496(3)[9]
Se	1.7098(1)[8]	1.695(2)[11]	1.6917(15)[12]	1.67620(7)[9]

[a] All distances are r_e except those for SCSe.

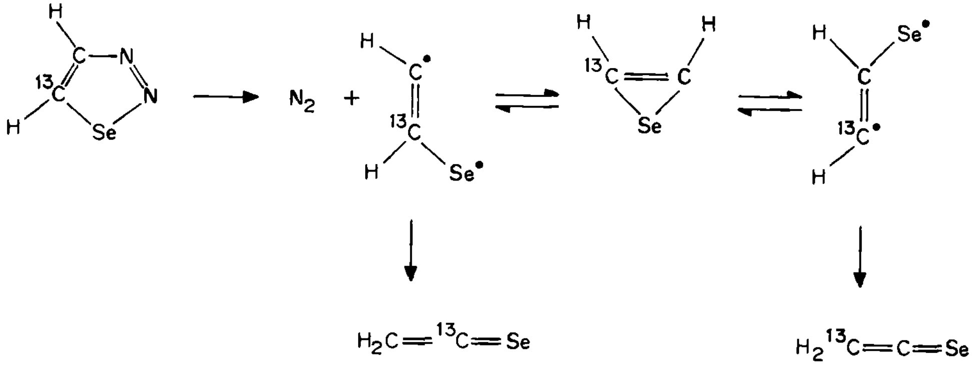
TABLE 2. Bond lengths and bond angles of isocyanic acid, isothiocyanic acid and isoselenocyanic acids, $HN{=}C{=}X$, from MW

X =	O[16]	S[17]	Se[15]
H—N (Å)	0.986	0.989	0.99 (assumed)
∠ H—N=C(deg.)	128.0	135.0	143
N =C(Å)	1.209	1.216	1.195
C=X(Å)	1.166	1.560	1.717

carbon bond distance is 1.73(1) Å in crystalline (1-6-η-methylbenzoate)dicarbonylselenocarbonylchromium[13], $[Cr(PhCOOMe)(CO)_2(CSe)]$. The Cr—C(Se) bond is 1.786(11) Å, shorter than the Cr—C(O) bonds, 1.862 Å (average). This is in accord with the observation, based on spectroscopic, structural and theoretical evidence, that the strength of the linkages to CSe, CS and CO groups decreases in this order[13,14].

A new molecular species, isoselenocyanic acid, $HN{=}C{=}Se$, was detected in the microwave spectrum[15] as HBr gas was passed through dry AgNCSe. The molecular parameters are given in Table 2 together with those of isocyanic acid[16] and isothiocyanic acid[17].

Selenoketene, $H_2C{=}C{=}Se$, was obtained by pyrolysis of 1,2,3-selenadiazole[18,19]. Bak and coworkers[19] suggested the reaction path shown in Scheme 1. MW allowed the elucidation of a complete substitution geometry (r_s)[19]. It is presented in Table 3 together with the structural parameters of ketene[20] and thioketene[21].



SCHEME 1

TABLE 3. The molecular geometries of ketene, thioketene and selenoketene, $H_2C{=}C{=}X$, from MW[a]

X =	O[20]	S[21]	Se[19]
C =X(Å)	1.1614 (r_s)	1.554 (r_s)	1.698 (r_s)
C =C(Å)	1.3142 (r_s)	1.314 (r_s)	1.311 (r_s)
C—H (Å)	1.0768 (r_0)	1.090 (r_s)	1.090 (r_s)
∠ H—C—H (deg.)	122.24 (r_0)	120.3 (r_s)	119.7 (r_s)

[a] r_0 is an effective parameter derived directly from ground-state rotational constants; r_s is the substitution parameter obtained from an appropriate set of isotopically substituted species.

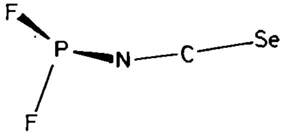


FIGURE 1. The molecular model* of difluoro(isoselenocyanato)phosphine (after Reference 22)

The molecular structure of difluoro(isoselenocyanato)phosphine, F_2PNCSe, has been determined by electron diffraction (ED)[22] (Figure 1). The effects of perpendicular vibrations on the molecular configurations of isothiocyanates and analogues have been discussed in detail[4]. Due to the low-frequency bending modes, the effective bond angle P—N=C as determined from ED (r_a parameter) may be considerably smaller than that which would correspond to the average structure (r_α). The average structure may be obtained from the effective parameters by applying harmonic corrections based on the vibrational spectra and normal coordinate analysis. In the ED investigation of F_2PNCSe the correction procedure was part of the structure refinement and both r_a *and* r_α parameters have been directly obtained from the analysis. The results are shown in Table 4 together with those for F_2PNCS and F_2PNCO. Noteworthy is the gradual increase in the P—N=C bond angles from O to Se.

The consequences of the low-frequency, large-amplitude bending vibrations are particularly striking for the bond angles Si—N=C of isoselenocyanatosilane[24], $H_3SiNCSe$, and isothiocyanatosilane[25], H_3SiNCS. Unfortunately the strong correlation among the parameters prevented the determination of an unambiguous structure for the selenium derivative from the ED data[24a]. Two somewhat differing parameter sets have been obtained and their mean values are presented for orientation in Table 5 together with the parameters of H_3SiNCS.

The selenium–carbon bond in selenocarbonyl difluoride, $F_2C{=}Se$, involves an sp^2 carbon atom. The structure of this molecule has been determined by ED in the vapour phase[26]. The geometrical parameters are presented in Table 6 together with those of

TABLE 4. Bond lengths and bond angles of F_2PNCX from ED

	X = O[23]	S[23]	Se[22]
r_a(P—N) (Å)	1.683(6)	1.686(6)	1.670(12)
r_a(P—F) (Å)	1.563(3)	1.566(3)	1.547(4)
r_a(N=C) (Å)	1.256(6)	1.221(6)	1.220(8)
r_a(C=X) (Å)	1.165(6)	1.553	1.700(10)
∠ P—N=C(r_α)(deg.)	134.8(8)	144.0(7)	149.0(15)
∠ P—N=C(r_a)(deg.)	130.6(8)	140.5(7)	143.9(13)

TABLE 5. Bond lengths and bond angles of H_3SiNCX, isothiocyanatosilane and isoselenocyanatosilane, from ED

X =	S[25]	Se[24]
r_a(Si—N) (Å)	1.704(6)	1.716
r_a(N=C) (Å)	1.197(7)	1.183
r_a(C=X) (Å)	1.563(6)	1.754
∠ Si—N=C(r_α)(deg.)	180	180
∠ Si—N=C(r_a)(deg.)	163.8(26)	159.5

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*This figure and many others are simplified projections of three-dimensional structures. Bonds that make an angle with the plane of the drawing are shown as wedges, in order to illustrate them in an exaggerated perspective. The broader end of the wedge is considered nearer to the observer.

TABLE 6. The molecular geometries of $F_2C{=}X$

X =	O[a]	S[b]	Se[c]
C=X (Å)	1.170(3)	1.589(2)	1.743(3)
C—F (Å)	1.317(2)	1.316(2)	1.314(2)
∠ F—C—F (deg.)	107.6(2)	107.1(2)	107.5(4)

[a] MW[27], r_z parameters.
[b] ED + MW[26], r_{av} parameters.
[c] ED[26], r_α^0 parameters.

thiocarbonyl difluoride[26] and carbonyl difluoride[27]. A characteristic feature of these structures is that the F—C—F bond angle is smaller than 120°, and accordingly, the F—C=X angles are invariably larger than 120°. This is in complete agreement with the valence-shell electron-pair repulsion (VSEPR) model[28] according to which multiple bonds exercise greater repulsions towards the neighbouring electron pairs than do single bonds.

The molecular structure of selenoacetaldehyde, $CH_3CH{=}Se$, has been determined by microwave spectroscopy[29]. The geometry of the CH_3CH fragment was assumed to be the same as in thioacetaldehyde[30], $CH_3CH{=}S$. The parameters for the thio and seleno derivatives are as follows:

$CH_3CH{=}S$		$CH_3CH{=}Se$	
C=S	1.610(9) Å	C=Se	1.758(10) Å
∠ C—C=S	125.3(11)°	∠ C—C=Se	125.7(3)°

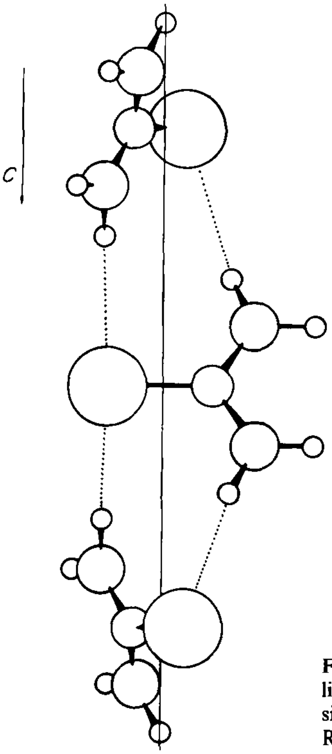
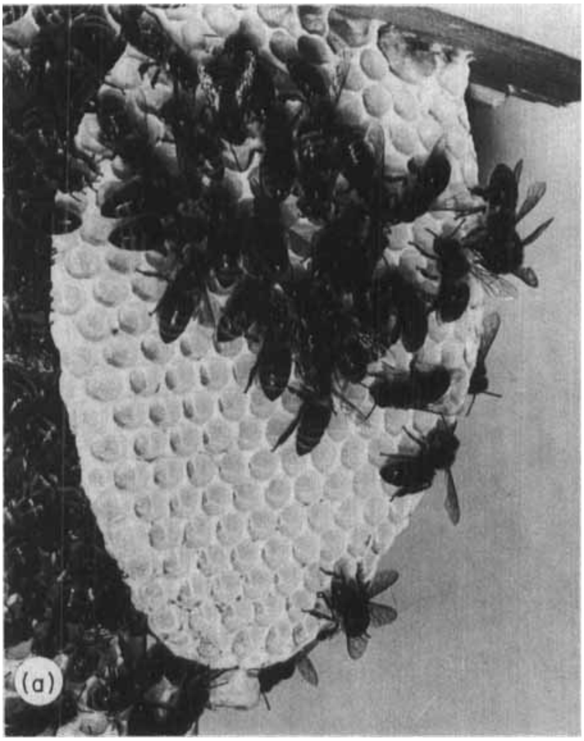


FIGURE 2. A chain of selenourea molecules in the crystal, linked by N—H···Se hydrogen bonds. Reproduced by permission of the Akademische Verlagsgesellschaft, Wiesbaden from Reference 33

These bond angles, as well as the comparison of $F_2C{=}S$ and $F_2C{=}Se$ geometries, clearly indicate that, in accord with the above assumption, the S/Se substitution has no appreciable effect on the structure of the rest of the molecule.

On the other hand, Anthoni and coworkers[31], based on CNDO/2 calculations, have recently suggested that 'selenation' may involve considerable changes in the electronic structure. The term selenation[32] is used to compare the spectra of compounds containing a thioamide group with the corresponding selenium analogues. It has been stated that the method works 'almost like an isotopic substitution'[31]. Anthoni and coworkers[31] have examined in detail the foundation and limitations of this method.

The crystal and molecular structure of selenourea, $(H_2N)_2C{=}Se$ (1), and several of its derivatives has been determined by X-ray diffraction (XD). The crystal structure of selenourea[33] contains N—H···Se hydrogen bonds similar to the N—H···O and N—H···S hydrogen bonds of urea and thiourea, respectively. There are hydrogen bonds forming chains of molecules (Figure 2), which are then also connected to each other by N—H···Se hydrogen bonds. Rutherford and Calvo[33] found the crystal structure of selenourea to be very similar to that of urea and thiourea when they form inclusion compounds with certain hydrocarbons, rather than to the crystal structure of urea and thiourea themselves. In the inclusion compounds the urea or thiourea molecules form a honeycomb structure and the hydrocarbon molecules form the honey. Analogues of the inclusion compounds have not been observed for selenourea in which both the honeycomb frame and the honey in it consist of selenourea molecules (Figure 3). The unit cell contains 27 molecules, of which 18 molecules are involved in building the frame and the remaining 9 are distributed in the channels, three to each. The 27 molecules of the unit



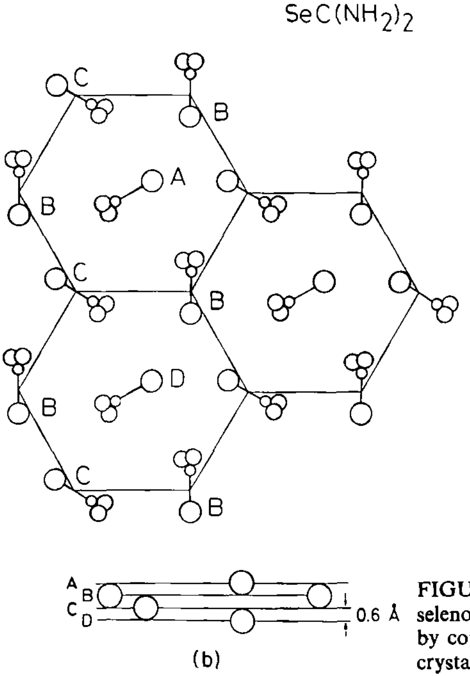
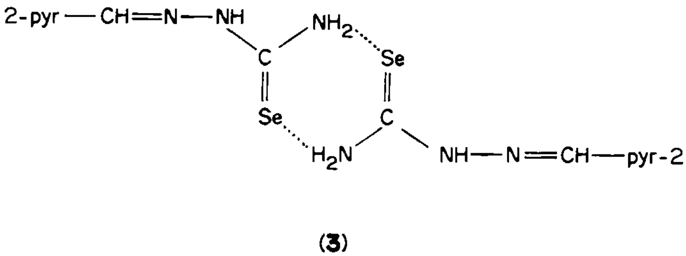


FIGURE 3.(a) Part of a honeycomb to illustrate the selenourea crystal structure. Photograph reproduced by courtesy of Professor Pál Zoltán Örösi. (b) The crystal structure of selenourea projected onto the *x*,*y* plane. Displacements of molecules along the *z* axis are indicated below. Reproduced by permission of the Akademische Verlagsgesellschaft, Wiesbaden from Reference 33

cell indeed form nine spiral chains one of which is represented by Figure 2. The dimensions of the selenourea molecule are reported from a low-temperature study (– 100 °C). The weighted averages of the bond lengths referring to nine molecules per asymmetric unit are $r(C{=}Se) = 1.86(3)$ Å and $r(C{-}N) = 1.37(2)$ Å. The C=Se bond is much longer than in selenoacetaldehyde[29]. The average Se=C—N bond angle is barely larger than 120°, viz. 120.5°. In fact it was reported to be 120°. One would expect the Se=C—N bond angle to be larger than the N—C—N bond angle. However, the Se=C—N bond angles in other derivatives have also been seen to only slightly exceed 120°. In tris(acetylacetonato)cobalt(III)-selenourea(1/2)[34], $Co(acac)_3 \cdot 2\,SeC(NH_2)_2$, for example, the Se=N—C angle is 120.8(4)°. The other molecular parameters for the selenourea moiety are: C=Se = 1.853(5) Å, C—N = 1.320(12) Å and $\angle$N—C—N = 118.3(4)°. The



(3)

selenourea moieties are brought into chains by N—H···Se intermolecular hydrogen bonds of 3.49 Å length. The selenourea moiety of the selenourea solvate of tris(selenourea)sulphate–selenourea–water(1/1/2)[35], $[SeC(NH_2)_2]_3SO_4{\cdot}SeC(NH_2)_2{\cdot}2H_2O$ (**2**) has the following geometrical parameters: C═Se = 1.867(4) Å, C—N = 1.316(5) Å, ∠Se═C—N = 120.6(3)° and ∠N—C—N = 118.8(4)°. The bonding arrangement in the N_2CSe part of 2-formylpyridine selenosemicarbazone[36] (**3**) is somewhat asymmetric, with two different Se═C—N bond angles, 122.9(24) and 119.8(23)°, whose difference is not however significant. The C═Se and C—N bonds are 1.83(2) and 1.37(2) Å long, respectively, and the N—C—N angle is 117.2(28)°. There are weak N—H···Se intermolecular hydrogen bonds forming dimer-like molecules, which in turn, are linked into a three-dimensional network by strong intermolecular N—H···N hydrogen bonds. Other selenosemicarbazones have also been investigated.

III. TWO-COORDINATED SELENIUM AND TELLURIUM

A. Acyclic Selenides and Tellurides

The carbon–selenium bond lengths and the selenium bond angles of *free* organoselenide molecules are listed in Table 7 for quick reference.

The molecular geometry of dimethyl selenide, Me_2Se, (Figure 4) was determined by MW[37,38]. Both Me groups are staggered with respect to the other Se—C bond. The rotational axes (axes of quasi-C_{3v} symmetry) of the Me groups do not coincide with the Se—C bonds but are tilted by 2.6° toward the lone electron pairs of the Se atom. The substitution structure shows a slight asymmetry in the structure of the Me group characterized by the parameters given in Figure 4. The structure is similar to that of Me_2S[50,51]. The C—Se—C skeleton is highly bent (cf. Table 7). A suggestion that it is

TABLE 7. C—Se bond lengths and Se bond angles in acyclic organoselenides from MW and ED

Molecule	C—Se (Å)		∠C—Se—X (deg.)	Reference
Me_2Se	r_s 1.945(0.4)		96.3(1)	37
	r_s 1.943(1)		96.2(2)	38
$(CF_3)_2Se$	r_a 1.980(9)[a]		94.1(20)[a]	39
	r_a 1.975(9)[b]		97.0(20)[b]	
MeSeH	r_0 1.959(10)		95.45(174)	40
EtSeH, *anti*	r_s 1.962(2)		93.5(6)	41
gauche	r_s 1.957(4)		93.1(3)	
anti	r_0 1.958(5)		93.3(10)	42
gauche	1.958[c]		93.9(10)	
MeSeCN	r_s 1.956[d]	r_0 1.837[e]	96.1	43
	r_0 1.950(25)[d]	1.851[e]	95.6	44
F_3CSeCN	r_a 1.984(20)[a,d]	1.854(16)[a,e]	92.2(20)[a]	45
	r_a 1.984(20)[b,d]	1.851(20)[b,e]	103.0(25)[b]	
PhSeMe	r_a 1.957(19)[d]	1.912(13)[f]	99.6(25)	46
PhSeBr		r_a 1.899(6)[f]	99.8(12)	47
$(F_3CSe)_3N$	r_g 1.973(5)		104.3(9)	48
$(MeSe)_3B$	r_a 1.954(4)		102.5(5)	49

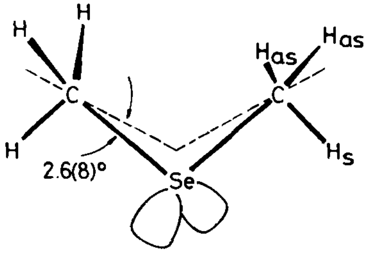
[a,b] Two possible solutions: model A and B (see text).

[c] Assumed parameter.

[d] $C(sp^3)$—Se bond.

[e] C(sp)—Se bond.

[f] $C(sp^2)$—Se bond.



		C-Hs	1.088(13) Å
		C-Has	1.096(4) Å
Se-C-Hs	105.0(7)°	Has-C-Has	109.9(5)°
Se-C-Has	110.3(3)°	Has-C-Hs	110.6(5)°

FIGURE 4. The molecular model of dimethyl selenide and the geometrical parameters (r_s) of the Me group[37]

linear[52] has been strongly criticized[53] on the basis of extended spectroscopic evidence in addition to the unambiguous MW structure determination. Spectroscopically calculated mean amplitudes of vibration of Me_2Se have been reported[54] together with those of Me_2S and Me_2O.

Two solutions (A and B forms in Figure 5) have been reported as to the conformational properties of bis(trifluoromethyl) selenide, $(CF_3)_2Se$ from an ED investigation[39]. Both forms have C_2 symmetry although form A has essentially C_{2v} symmetry. On the basis of ED data it was not decided whether both forms were present in the vapour or whether one was merely a mathematically possible solution. This uncertainty did not hinder the determination of the geometry of the $SeCF_3$ part of the molecule. However, the result for the bond angle C—Se—C was sensitive to the choice of the conformational model: 94.1(20)° and 97.0(20)° were determined for models A and B, respectively. It is in fact this sensitivity that may facilitate our preferring one of the two conformational models on the basis of observed geometrical variations in analogous molecules. The C—S—C bond angle decreases from 98.9(2)° in Me_2S[50] to 97.3(8)° in $(CF_3)_2S$[55]. This change is in complete agreement with the valence-shell electron-pair repulsion (VSEPR) model[28]. According to this model, increasing ligand electronegativity results in increasing electron-withdrawing

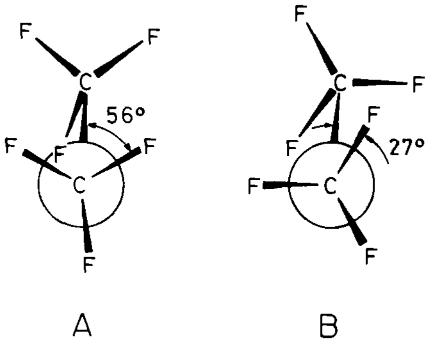


FIGURE 5. The two models of bis(trifluoromethyl) selenide[39] viewed along the C—Se bond

TABLE 8. Bond angles and non-bonded distances in X_2S and X_2Se

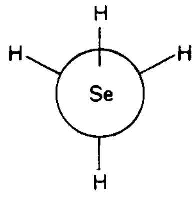
X_2Y	X_2S			X_2Se		
	∠X—S—X (deg.)	X···X (Å)	Ref.	∠X—Se—X (deg.)	X···X (Å)	Ref.
H_2Y	92.12	1.923[a]	56	90.57	2.075[a]	59
Me_2Y	99.05	2.746[a]	51	96.3	2.898[a]	37
$(CF_3)_2Y$	97.3	2.731[a]	55	94.1	2.90	39
$(SiH_3)_2Y$	97.4	3.210	57	96.6	3.396	60
$(GeH_3)_2Y$	98.9	3.358	58	94.6	3.445	61

[a] Calculated from the bond distance and bond angle given in the reference.

ability, which in turn lessens the electron-pair repulsion in the vicinity of the central atom. Thus the respective bond angles may close somewhat. Atom–atom non-bonded interactions might be expected to cause an opening of the C—S—C bond angle upon CH_3/CF_3 substitution. That the reverse occurs is witness to the prevailing importance of the electron-pair repulsions in these structures. The relative importance of the atom–atom interactions is certainly smaller in the Se analogues as compared with the S derivatives. Accordingly, the C—Se—C bond angle in $(CF_3)_2Se$ is predicted to be smaller than that in Me_2Se. This favours model A for $(CF_3)_2Se$. Marsden and Sheldrick noted[39] that model B may be fortuitous as it involves a very short F···F distance (2.51 Å) between the two different trifluoromethyl groups.

Comparison of the analogous X_2S and X_2Se molecules shows increasing non-bonded distances and slightly decreasing bond angles from S to Se (Table 8). All the cited non-bonded distances are greater than twice the postulated 1,3 non-bonded radii, viz. $r_{1,3}$ (H) = 0.92, $r_{1,3}$(C) = 1.25, $r_{1,3}$(Si) = 1.55 and $r_{1,3}$(Ge) = 1.58 Å[62,63]. H_2S and H_2Se are included in Table 8 for comparison. The angle H—Te—H is 90.25° in H_2Te[64] with a 2.350 Å H···H distance. A recent ED investigation of dimethyl telluride, Me_2Te yielded Te—C = 2.142(5) Å, C···C = 3.14 Å, ∠C—Te—C = 94(2)°[65]. The analogous O bond angles are considerably greater with smaller non-bonded distances: Me_2O 111.7°, 2.334 Å[66]; $(SiH_3)_2O$ 144.1°, 3.107 Å[67]; and $(GeH_3)_2O$ 126.5°, 3.154 Å[58].

The diminishing bond angles in the series of analogous O, S and Se derivatives have been noted also by Thomas[40]. He pointed out the importance of this geometrical variation in relation to the changes in the methyl rotational barrier. This barrier is 4.2(2) kJ mol^{-1} in methaneselenol, MeSeH, as determined by MW[40]. The conformation (viewed along the Se—C bond in 4) is staggered and the Me group is tilted by 1.5(10)° towards the lone electron pairs of the Se atom. The Me tilt in the Se derivatives occurs in the same direction and is similar in magnitude to those in the analogous S compounds, viz. Me_2S 2.8°[50] and MeSH 2.2°[68].



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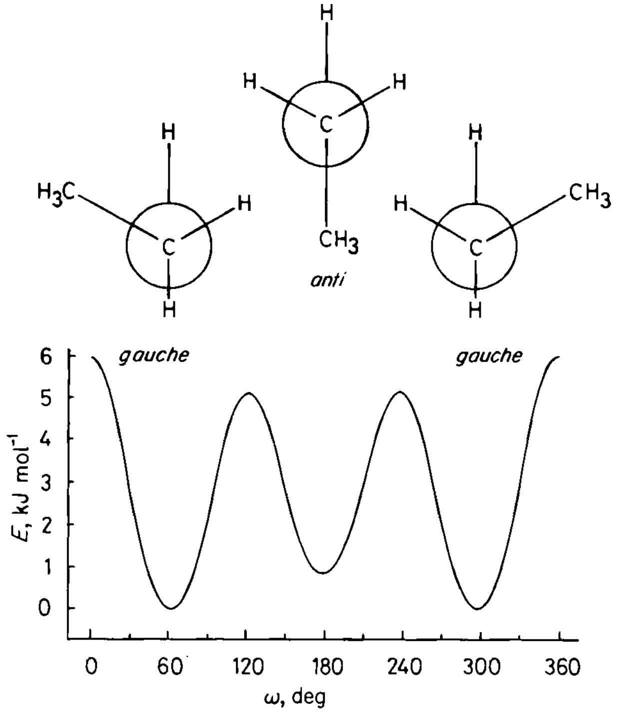


FIGURE 6. The potential energy (E) of ethaneselenol as a function of the dihedral angle ω(CCSeH), the angle of rotation about the C—Se bond. Above: projections of the *gauche* and *anti* forms along the C—Se bond. Drawn after Reference 42

Both *gauche* and *anti* conformers, with respect to rotation about the C—Se bond, were found in the vapour of ethaneselenol, EtSeH, by MW[41,42]. The potential energy curve describing internal rotation about the C—Se bond is shown in Figure 6 after Durig and Bucy[42]. The Et group is assumed to have a staggered conformation. The complete structures of both forms have been determined from the rotational spectra[41]. The dihedral angle CCSeH of the *gauche* form is 61.6(8)°[41]. Notable differences between the two conformers occur in the bond angles of the methylene carbon. This was attributed to a tilt δ of the axis of internal rotation from the C—Se bond (Figure 7). The bond angles around the methylene carbon were then used in both studies[41,42] to calculate the tilt angle and the angle β between the rotation axis and the C—C bond. Values obtained for ethaneselenol, $\beta = 111.9°$ and $\delta = 3.2°$[41], are very similar to those for ethanethiol[41,69].

The MW of methyl selenocyanate, MeSeCN, has been analysed[43,44]. The available data allowed an unambiguous determination of the Se—CH_3 bond length. A tentative refinement based on several assumed parameters yielded r(Se—CN) and the bond angle C—Se—C (Table 7). The observed difference between the two types of selenium–carbon bond length is 0.12 Å (0.14 Å is given in the original paper[43]), nearly the same as found between the analogous sulphur-carbon bond lengths in MeSCN[70]. The barrier to internal rotation of the Me group was determined from MW to be 5.2(2) kJ mol^{-1} in methyl selenocyanate[43,44] and 6.6 kJ mol^{-1} in methyl thiocyanate[71]. The rotational barrier and the Me tilt in MeSeCN are similar to those in MeSeH.

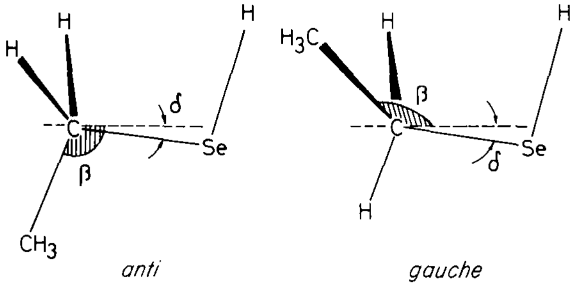


FIGURE 7. Tilt (δ) of the rotational axis (dashed line) from the C—Se bond in ethaneselenol. It is assumed that the axis of rotation lies in the C—Se—H plane. β is the angle of the axis with the C—C bond

Trifluoromethyl selenocyanate, F_3CSeCN, has been studied by ED[45]. Again two conformational models approximated well to the experimental data (Figure 8). Model A may be considered as an effective structure arising from a staggered equilibrium conformation performing torsional vibrations about the F_3C—Se bond. The bond angle ∠ C—Se—CN = 92.2(20)° seems to be more plausible than the much larger one obtained for model B (103°). Fortunately, the other geometrical parameters are unaffected by the choice of the conformational model (cf. Table 7).

Vibrational spectroscopic studies indicated the variability of conformational properties of organic selenide molecules. Two or more conformers may be present in the liquid state and solutions of $CH_2{=}CHSePh$ and $CH_2{=}CHSeC_6H_4NO_2$-*p* according to their infrared spectra[72]. For diisopropyl selenide the solid state spectra were interpreted by a single conformer (C_2 symmetry), while three forms were detected in the liquid state (presumably C_2, C_s and C_1) with the C_2 form being the most stable[73].

The presence of a single conformation was assumed in the ED structure analysis of selenoanisole, PhSeMe[46]. The Se—CH_3 bond is rotated from the plane of the benzene ring by about 40°. A similar conformation has been reported for thioanisole[74] (Figure 9).

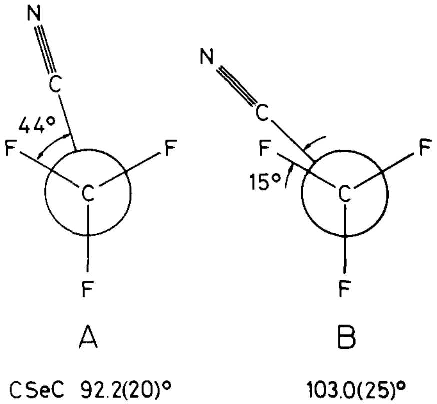


FIGURE 8. The two models of trifluoromethyl selenocyanate[45] projected along the F_3C—Se bond

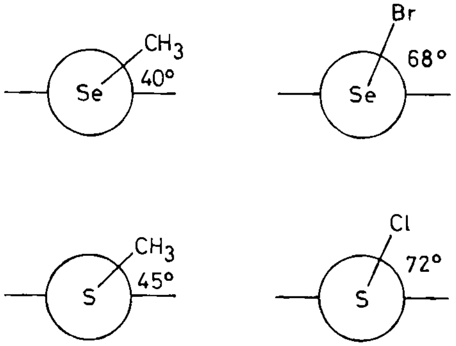
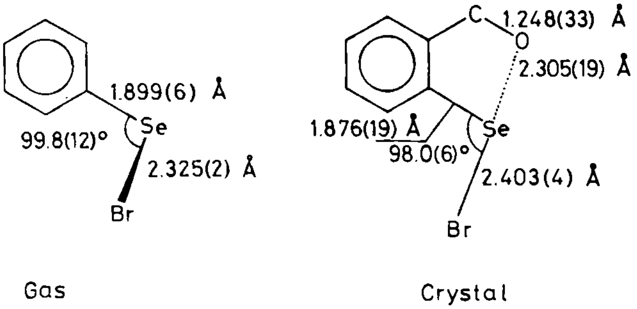


FIGURE 9. Conformation of selenoanisole[46], thioanisole[74], benzeneselenenyl bromide[47] and benzenesulphenyl chloride[75]. Projections along the Se—C(phenyl) or S—C(phenyl) bond. The horizontal line represents the plane of the Ph ring

The structure of benzeneselenenyl bromide, PhSeBr, has also been determined by ED[47]. It has a greater deviation from planarity than selenoanisole. A similar change is observed in benzenesulphenyl chloride[75] as compared with thioanisole (cf. Figure 9).

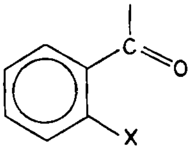
It is especially interesting to compare the gas-phase structure of benzeneselenenyl bromide with the crystal XD molecular structure of 2-formylbenzeneselenenyl bromide[76] (Figure 10). The crystals are orthorhombic, Pc2$_1$n. The molecule has a planar *syn* conformation (**5**) similar to the analogous Te derivative[77]; the Br—Se···O and Br—Te···O chains are roughly linear. The planarity of the crystal molecular conformation is strikingly different from the non-planar structure of free benzeneselenenyl bromide. The coplanarity may be a consequence of the presence of the aldehyde group in the *ortho* position and/or the intermolecular forces in the crystal. Generally speaking, the most common of the possible gas/crystal structural differences are the conformational changes. Thus it is tempting to ascribe this change to crystal field effects. On the other hand, similarly drastic conformational change is observed in the free molecules of benzenesulphenyl chloride[75] and 2-nitrobenzenesulphenyl chloride[78a], both studied by ED. The flattening here may be a consequence of interaction between the substituents in the *ortho* positions (Figure 11). The S—Cl bond lengths are the same in the two molecules and much larger than in free sulphur dichloride itself viz. 2.015 Å[79]. The considerable lengthening of



Gas

Crystal

FIGURE 10. Geometrical parameters of benzeneselenenyl bromide[47] and 2-formylbenzeneselenenyl bromide[76]



(5)

syn

the S—Cl bond thus appears to be a consequence of Ph/Cl substitution, and no appreciable change is observed that could be ascribed to the presence of the nitro group in the *ortho* position. This is in contrast with the situation of the Se—Br bond as seen in Figure 10. Unfortunately, there is no reliable information on the structure of selenium dibromide (cf. References 3 and 80). If, however, the presence of the *ortho* aldehyde group were assumed to produce no change in the Se—Br bond length, the considerable lengthening of the Se—Br bond in 2-formylbenzeneselenenyl bromide as compared with benzeneselenenyl bromide should be ascribed to the crystal field effect. This situation could be clarified by information on structural changes induced by aldehyde versus nitro groups in the *ortho* position, and from gas/crystal structure determinations of the same molecules. According to a recent ED study of 2-nitrobenzeneselenenyl bromide, this molecule is practically planar, and the Se bond configuration is characterized by C—Se 1.917(11) Se—Br 2.354(3) Å, ∠ C—Se—Br 98.5(7)° and Se···O 2.36 Å[78b].

The most interesting structural feature of the *ortho*-substituted benzeneselenenyl and benzenesulphenyl halides is undoubtedly the interaction between the O and the Se (or S) atom. The relatively short Se···O distance indicates partial bonding. A similar situation was observed in 2-formylbenzenetellurenyl bromide by XD[77]. The Se···O and Te···O interaction has been discussed by Baiwir and coworkers[76] in relation to C=O bond lengths and vibrational frequencies and proton magnetic resonance data in analogous molecules. Table 9 contains further available structural data on such bonding situations. The Se···O and Te···O distances invariably fall between the sums of the covalent radii and 1,3 intramolecular non-bonded radii[62,86] (Table 10).

Zaripov and coworkers[46] discussed the conformational properties of the anisole analogues PhXMe with X = O, S, Se and Te. Of the many effects influencing internal rotation two were singled out for closer examination, viz. the p, π conjugation tending to

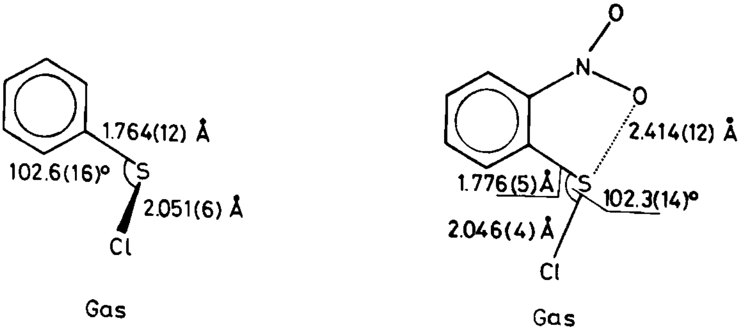
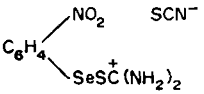
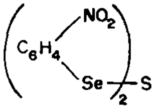
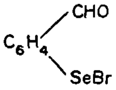
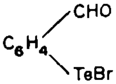
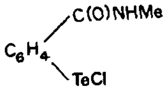
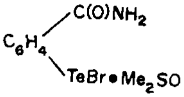
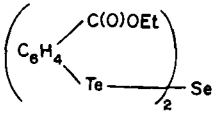
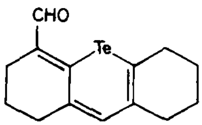


FIGURE 11. Geometrical parameters of benzenesulphenyl chloride[75] and 2-nitrobenzenesulphenyl chloride[78a]

TABLE 9. Se and Te bond configurations in *ortho*-substituted benzeneselenenyl and benzenetellurenyl derivatives from XD

Molecule	Bond lengths (Å)		Angle (deg.)	Distance (Å)	Reference
	C—Se 1.939(8)	Se—S 2.189(3)	C—Se—S 98.9(3)	Se···O 2.505(8)	81
	C—Se 1.918(8)	Se—S 2.202(2)	C—Se—S 102.0(3)	Se···O 2.574(8)	82
	C—Se 1.876(9)	Se—Br 2.403(4)	C—Se—Br 98.0(6)	Se···O 2.305(19)	76
	C—Te 2.081(21)	Te—Br 2.618(3)	C—Te—Br 94.2(6)	Te···O 2.31	77
	C—Te 2.133(10)	Te—Cl 2.516(3)	C—Te—Cl 92.7(3)	Te···O 2.250(7)	83
	C—Te 2.105(9)	Te—Br 2.646(1)	C—Te—Br 95.1(2)	Te···O 2.237(8)	83
	C—Te 2.123(8)	Te—Se 2.536(1)	C—Te—Se 97.9(2)	Te···O 2.658(6)	84
	C—Te 2.076[a]	Te—C 2.055[a]	C—Te—C 94.2[a]	Te···O 2.575[a]	85

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[a] Average from two crystallographically independent molecules.

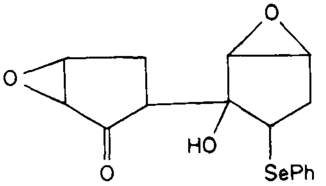
TABLE 10. Atomic radii (Å) and calculated internuclear distances (Å): covalent, non-bonded 1,3 and van der Waals'

	r_{cov}^{87}	$r_{1,3}^{62,86}$	$r_{vdW}^{88,89}$
C	0.767	1.25	1.70
O	0.745	1.12	1.40
S	1.020	1.45	1.85
Se	1.163	1.60	2.00
Te	1.356	1.75	2.20
	Σr_{cov}	$\Sigma r_{1,3}$	Σr_{vdW}
SC	1.787	2.70	3.55
SeC	1.930	2.85	3.70
TeC	2.123	3.00	3.90
SO	1.765	2.57	3.25
SeO	1.908	2.72	3.40
TeO	2.101	2.87	3.60

stabilize the planar form, and the Me/Ph hydrogen–hydrogen interaction tending to displace the system from coplanarity. Tschmutowa and Bock[90] concluded from photoelectron spectra that the p, π conjugation diminishes in the order of $O \gg S > Se > Te$ and accordingly the probability of planar conformation should also decrease in the same order. The non-planarity of the structures may be the consequence of d, π or σ, π interaction as well as that of steric hindrance[46]. All this refers to the intramolecular interactions governing the conformational choice of the free molecules. In the crystalline phase, effects from intermolecular interaction have to be considered in addition.

Some results of X-ray crystallographic studies will be cited here for comparison with the gas-phase data of Table 7.

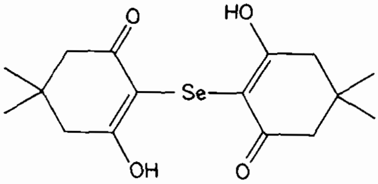
The C—Se—C bond angle in crystalline acetylselenocholine iodide, $MeC(O)SeCH_2CH_2\overset{+}{N}Me_3{\cdot}I^-$ (**6**), is 97(1)°[91], the same as in Me_2Se (Table 7). In analogous molecules of biological interest the $\overset{+}{N}$—C—C—O chain prefers the *gauche* conformation while $\overset{+}{N}$—C—C—S and $\overset{+}{N}$—C—C—Se adopt the *anti* conformation[91,92]. The *anti* form has been found in **6** and in (2-(dimethylamino)ethyl) selenobenzoate hydrochloride, $PhC(O)SeCH_2CH_2\overset{+}{N}HMe_2{\cdot}Cl^-$ (**7**)[92]. The C—Se—C angle in **7** is 96.4(2)°, and both C—Se bond lengths have been determined as 1.945(5) Å[92]. In the Se analogue of a tetrapeptide derivative, *S*-benzyl—L-Cys—L-Pro—L-Leu—Gly—amide, the Se—C bonds are 1.92(4)–1.99(2) Å long and the C—Se—C angles are 100(1) and 102(1)° in two crystallographically independent molecules[93]. In the crystal of **8**,



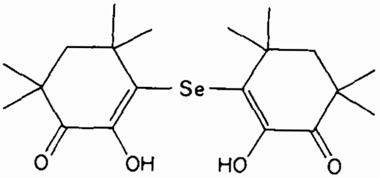
(8)

disorder in the position of the Ph ring hinders the accurate determination of the parameters, viz. Se—C(sp^3) = 1.97(1) Å, and for the two positions of the Ph ring, Se—C(sp^2) = 1.97(2) and 1.83(2) Å, and ∠ C—Se—C = 97.0(7) and 99.7(7)°[94].

The structures of crystalline bis(6-hydroxy-4,4-dimethyl-2-oxo-6-cyclohexenyl) selenide (**9**)[95] and bis(2-hydroxy-4,4,6,6-tetramethyl-3-oxo-1-cyclohexenyl) selenide (**10**)[96] are different in that **9** is intramolecularly hydrogen-bonded while **10** is intermolecularly hydrogen-bonded. The molecular packing of **10** is illustrated in Figure 12 after Kivekäs and Laitalainen[95]. The Se—C bonds are of the same length (1.916 Å) in the two molecules whereas the Se bond angle opens somewhat in **10** as compared with **9**, viz. 103.9(2) vs. 100.9(4)°. The Se bond configurations show no unusual features. The conjugated bond



(**9**)



(**10**)

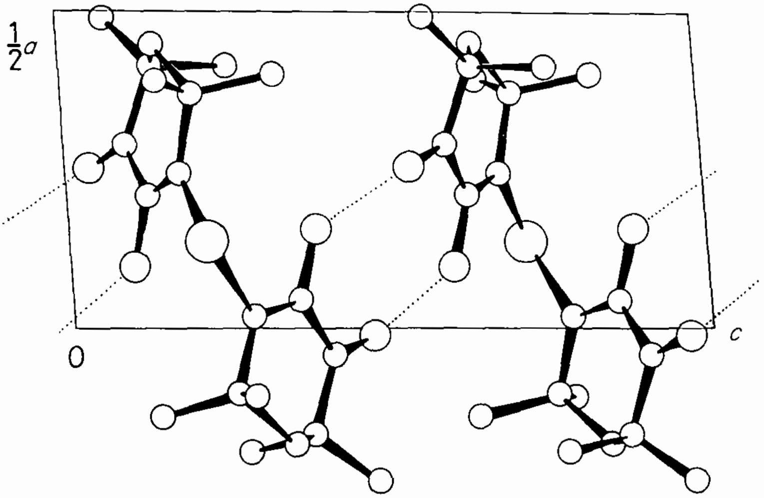


FIGURE 12. Molecular packing in the crystal of **10**. Reproduced (simplified) by permission of Acta Chemica Scandinavica from Reference 95

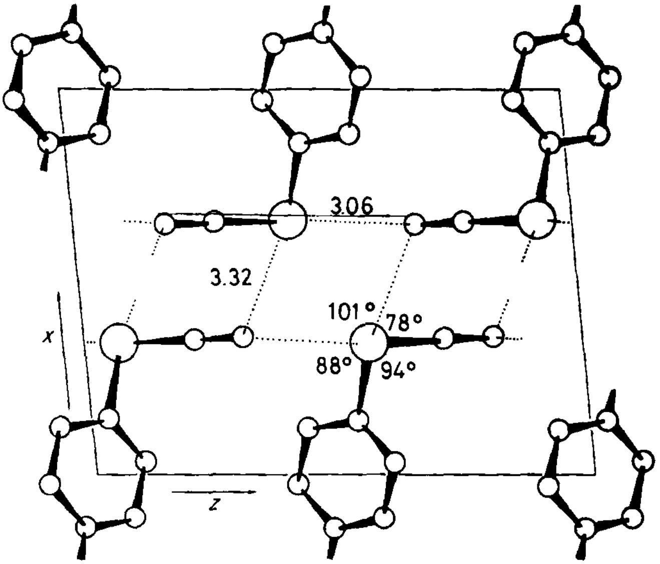


FIGURE 13. Molecular packing in the crystal of *p*-diselenocyanatobenzene (**11**): projection along the *b* axis. Reproduced by permission of the Royal Society of Chemistry from Reference 97

system in **10** is coplanar and the rings are in half-chair conformation. The rings of **9** take a half-boat form.

The crystal structure of *p*-diselenocyanatobenzene, *p*-$NCSeC_6H_4SeCN$ (**11**), has been determined by XD[97]. The two types of selenium–carbon bonds, Se—CN = 1.837(23) Å and Se—C_6H_4 = 1.916(19) Å, are similar in length to the corresponding single bonds to sp- and sp^2-hybridized carbon in free molecules of methyl selenocyanate and selenoanisole (see Table 7). The C—Se—C angle in **11** is 94°, and the selenium obviously has intermolecular contacts as seen in Figure 13.

The last two molecules listed in Table 7 possess practically planar Se_3X skeletons. Both structures have been elucidated by ED. The overall structure of tris(trifluoromethylseleno)amine, $(F_3CSe)_3N$, is shown in Figure 14. The C—Se—N planes are nearly perpendicular to the Se_3N plane[48]; the deviations have been reported to be 10–14°. The CF_3 groups are staggered with respect to the adjacent Se—N bonds. The

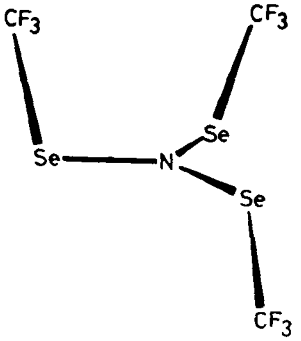


FIGURE 14. The molecular model of tris(trifluoromethylseleno)amine

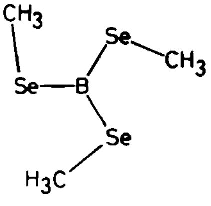


FIGURE 15. The planar skeleton of tris(methylseleno)borane with C_3 symmetry

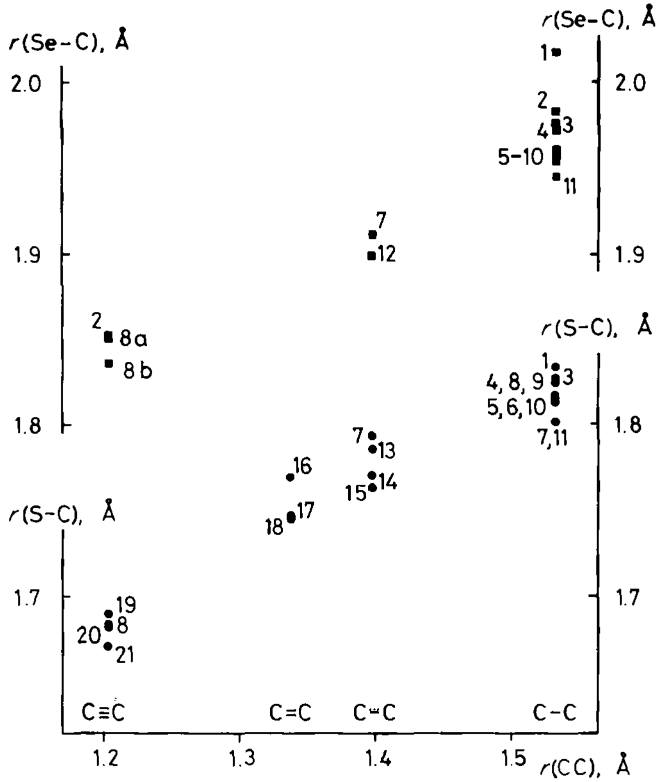


FIGURE 16. The lengths of Se—C and S—C single bonds with sp, sp^2 (non-aromatic and aromatic) and sp^3 carbon atoms. The abscissa represents the carbon–carbon bond distance in acetylene, ethylene, benzene and ethane. *Se compounds.* 1: $(CF_3)_2Se_2$, 2: F_3CSeCN, 3: $(CF_3)_2Se$ (mean of two models[39]), 4: $(F_3CSe)_3N$, 5: MeSeH, 6: EtSeH (mean of *anti* and *gauche* forms[41]), 7: PhSeMe, 8: MeSeCN (a: Reference 44, b: Reference 43), 9: $(MeSe)_3B$, 10: Me_2Se_2, 11: Me_2Se, 12: PhSeBr. See Tables 7 and 11 for references. *S compounds.* 1, 3–11: see the Se analogues, 13: Pyr_2S, 14: Ph_2S, 15: PhSCl, 16: HC(O)SH, 17: $CH_2{=}CH{-}SMe$, 18: $CH_2{=}C{=}CH{-}SMe$. 19: EtS—CN. 20: $HC{\equiv}C{-}SMe$, 21: $MeS{-}C{\equiv}C{-}SMe$. See References 3, 20 and 100

most interesting feature of this structure is that two of the CF_3 groups are situated above the Se_3N plane and the third CF_3 group below this plane. Thus there is a striking absence of threefold symmetry. The structure is very much the same as that of the corresponding S compound, tris(trifluoromethylthio)amine, $(F_3CS)_3N$, as also determined from ED[98]. The barrier to internal rotation about the S—N bond was estimated from NMR data to be 25(4) kJ mol^{-1} [98], which is probably greater than the as yet unestimated barrier about the longer Se—N bond.

An essentially planar heavy-atom skeleton characterizes the geometry of tris(methylseleno)borane, $(MeSe)_3B$[49] (Figure 15). Tris(methylthio)borane has a similar structure[99].

In concluding this section it is of interest to examine the variation in lengths of Se—C single bonds in different environments. A characteristic sample from the available data is presented in Figure 16. There is an appreciable change in the Se—C bond lengths upon changing carbon hybridization. The variation nicely parallels the tendency observed for the S—C bond lengths in sulphides[3,100], which are also presented in Figure 16 for comparison.

B. Acyclic Diselenides and Ditellurides

The structure and conformation of dimethyl diselenide, Me_2Se_2[101] and bis(trifluoromethyl) diselenide, $(CF_3)_2Se_2$[102] have been determined by ED. The experimental data are consistent with C_2 overall symmetry, which has been assumed in both studies. The spatial geometry is illustrated in Figure 17 while the conformational properties are depicted in Figure 18 for both molecules. The geometrical data of the CSeSeC skeleton are given in Table 11, and are compared with those of the analogous S compounds. The angle of rotation about the C—Se bonds (Figure 18) is primarily deduced from the scattering contribution of atomic pairs involving the ligands of carbon and the other Se atom. This angle is better determined in the F than in the H derivative. The deviation from the ideal staggered form is not surprising in view of the asymmetric environment of the $SeCX_3$ moiety. Thus this deviation is believed not to be entirely an apparent one as a consequence of averaging over intramolecular torsional vibrations about the C—Se bonds. On the other hand, these vibrations certainly influence the

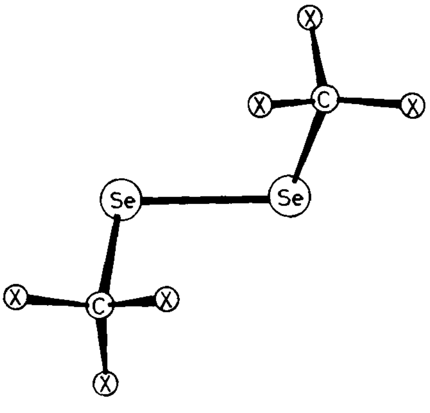


FIGURE 17. The molecular model of dimethyl diselenide (X = H) and bis(trifluoromethyl) diselenide (X = F) (after Reference 101 b)

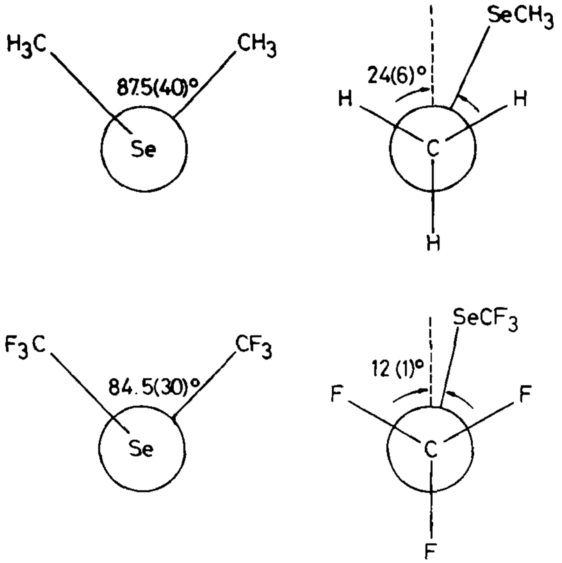


FIGURE 18. Conformation of dimethyl diselenide[101] (above) and bis(trifluoromethyl) diselenide[102] (below): projections along the Se—Se (left) and the C—Se (right) bonds

effective angle of rotation as determined from ED. This may be of importance, especially for the methyl derivative, as relatively large-amplitude, low-barrier torsional vibrations are anticipated.

For a series of XSSX disulphanes it has been observed that the central bond considerably shortens with increasing ligand electronegativity[3]. The Se—Se bond shortening in the diselenides upon CH_3/CF_3 substitution is consistent with this

TABLE 11. Parameters of Me_2S_2, Me_2Se_2 and perfluoro derivatives from gas electron diffraction

	Me_2Y_2	
	Me_2S_2[103]	Me_2Se_2[101]
Y—Y (Å)	2.029(3)	2.326(4)
Y—C (Å)	1.816(3)	1.954(5)
∠Y—Y—C (deg.)	103.2(2)	98.9(2)
ω (CYYC) (deg.)	85.3(37)	87.5(40)
	$(CF_3)_2Y_2$	
	$(CF_3)_2S_2$[104]	$(CF_3)_2Se_2$[102]
Y—Y (Å)	2.030(5)	2.292(10)
Y—C (Å)	1.835(5)	2.018(20)
∠Y—Y—C (deg.)	101.6(6)	98.0(5)
ω(CYYC) (deg.)	104.4(40)	84.5(30)

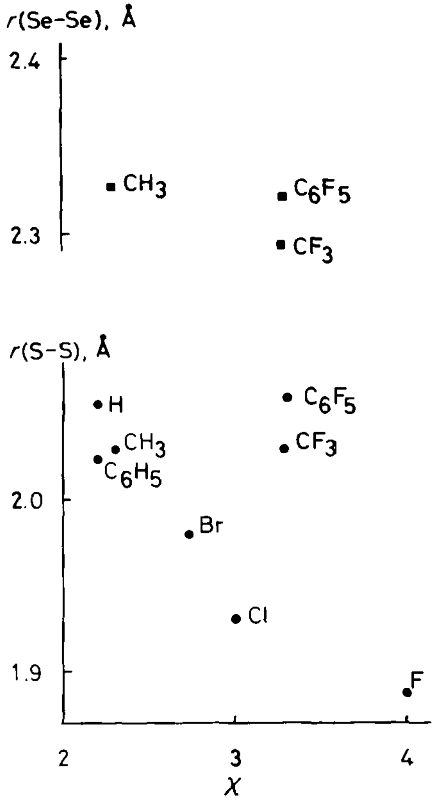


FIGURE 19. Variation of the S—S and Se—Se bond lengths in disulphanes XSSX and diselenides XSeSeX with the electronegativity (χ) of the substituent X. Data from Reference 3

observation as can be seen in Figure 19. From this point of view the structure of $(CF_3)_2S_2$ seems somewhat anomalous as it has a longer S—S bond, 2.030(5) Å [104], than would be expected according to the above mentioned trend. Noteworthy is the greater CSSC dihedral angle (104 ± 4°) determined for this molecule as compared with the rest of the disulphane series—except for $Me_2BSSBMe_2$—or the diselenide molecules, for that matter[3].

Two examples from among crystalline organic diselenides are cited here. Cyclic molecules with a Se—Se fragment will be discussed in Section III.C.

The structure of α,α'-diselenobis(formamidinium) dichloride, $[SeC(NH_2)_2]_2Cl_2$, has been determined by XD[105]. The planes of the two selenourea groups in the bis(selenourea) cation, $[SeC(NH_2)_2]_2^{2+}$ (**12**), are nearly perpendicular to the Se—Se bond. The heavy-atom skeleton is shown in Figure 20. On the other hand, the orientation of the thiourea groups in two salts of the S analogue of **12** has been found to be essentially parallel to the S—S bond[106] (Figure 20). It has been argued[105] that the conformational differences are due to intramolecular spatial interactions rather than packing requirements. Some of the parameters of the S and Se derivatives are listed in Table 12. The Se—Se bond is longer

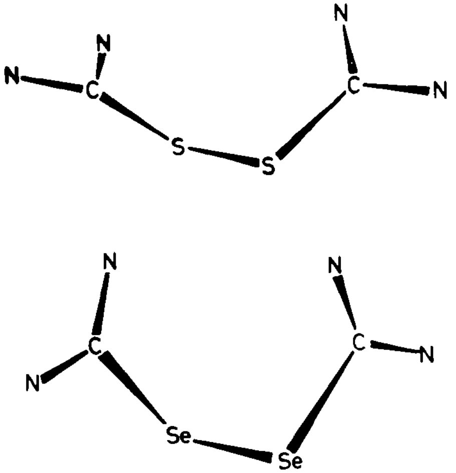


FIGURE 20. Conformation of the $[SC(NH_2)_2]_2^{2+}$ and $[SeCNH_2)_2]_2^{2+}$ cation after Reference 105)

than in Me_2Se_2 (Table 11). The Se—C bond of **12** in its diiodide salt has been determined as 1.943(4) Å [108].

The other example is bis(pentafluorophenyl) diselenide, $(C_6F_5)_2Se_2$ and its S analogue[107], which are isostructural in the crystal, orthorhombic $P2_12_12_1$. Their main parameters are also given in Table 12. An unexpected finding was[107] that the crystal

TABLE 12. Parameters of diselenides and analogous disulphides from X-ray crystallographic studies

	$[YC(NH_2)_2]_2X_2$		
	$[SC(NH_2)_2]_2X_2\cdot H_2O$[106]		
	X = Br	X = I	$[SeC(NH_2)_2]_2Cl_2$[105]
Y—Y (Å)	2.044(10)	2.044(20)	2.380(6)
Y—C (Å)	1.78(3)	1.75(4)	1.94(1)
∠ Y—Y—C (deg.)	104.0	98.9	95.5(6)
ω(CYYC) (deg.)	89.2	104.8	89.5

	$(C_6F_5)_2Y_2$	
	$(C_6F_5)_2S_2$[107]	$(C_6F_5)_2Se_2$[107]
Y—Y (Å)	2.059(4)	2.319(4)
Y—C (Å)	1.770(7)	1.910[a]
Y—Y—C (deg.)	101.2[a]	98.8[a]
ω(CYYC) (deg.)	76.5	75.3
ϕ[b] (deg.)	39.3	34.0

[a] Mean value.

[b] ϕ is the dihedral angle between the planes of the rings.

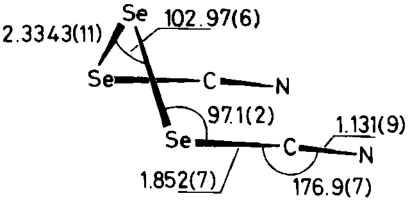


FIGURE 21. The molecular model, bond lengths (Å) and bond angles (deg.) of selenium diselenocyanate[121]. Drawn from the atomic coordinates given in Reference 121

packing and conformation of these molecules proved to be different from those of the corresponding unsubstituted Ph derivatives. Also the chalcogen bond angles seem to be significantly larger in the latter, viz. about 106°, both in Ph_2S_2[109] and Ph_2Se_2[110].

The Se—Se bond lengths in these molecules (Tables 11 and 12) can be compared with those in dimorpholino-di-, -tri- and -tetra-selane and dipiperidinotetraselane[111], where they lie in the range 2.327(2)–2.356(2) Å, and in the cyclic Se_8 molecule of γ-selenium (monoclinic), 2.326(3)–2.344(3) Å [112].

The Te—Te bond length is 2.712(2) Å in crystalline diphenyl ditelluride, Ph_2Te_2, from XD[113]. The mean of the observed Te—C bond lengths is 2.115 Å. In a subsequent study the crystal and molecular structure of *p,p'*-ditolyl ditelluride has also been determined[114]: Te—Te = 2.697(3) Å and Te—C = 2.13(1) Å. The authors[114] noted a great dissimilarity between the molecular conformation in the crystals of Ph_2Te_2[113], $(p\text{-MeC}_6H_4)_2Te_2$[114] and $(p\text{-ClC}_6H_4)_2Te_2$[115]. It has been suggested that these differences are due to steric hindrances arising from packing peculiarities[114].

Conformational properties and dynamic behaviour of organic dichalcogenide molecules and, among them, diaryl dichalcogenides, have been studied by experimental and theoretical methods (see, for example, References 116–120 and references therein). Apart from intermolecular interactions, the adopted conformation of diaryl dichalcogenides is a result of steric effects on the one hand, and interaction of chalcogen lone pairs with the π electrons of the aromatic rings on the other[116]. The steric effects predominate in the case of ditellurides[116].

The crystal and molecular structures of selenium diselenocyanate, $Se(SeCN)_2$, and also of the isomorphous selenium dithiocyanate, $Se(SCN)_2$, have been redetermined[121], based on XD data, since they were discussed in another volume of this series[4]. Bond lengths and angles of $Se(SeCN)_2$ (Figure 21) are in agreement with the data in Tables 7, 11 and 12 and the parameters of *p*-diselenocyanatobenzene (**11**)[97]. Notable deviations from the results of the earlier investigations have been found in the geometry of the —SeCN group. The molecule lies on a crystallographic symmetry plane and has a *syn* conformation. The SeSeSeC torsional angle is 93.2° (cf. the data on diselenides in Tables 11 and 12). The coordination around each Se atom is completed by N atoms of neighbouring molecules to a roughly square planar arrangement, which, at the same time, gives rise to a network of nearly linear N···Se(C)–Se···N and C–Se···N sequences with intermolecular contacts of 3.253(6), 3.142(6) and 3.085(6) Å, respectively[121] (cf. the stereoscopic view of crystal packing in Reference 4).

C. Heterocycles

Structural data on free non-aromatic ring molecules with Se are scarce. Selenetane, $(CH_2)_3Se$, has been studied by microwave spectroscopy[122]. The geometry has not been determined except for the ring puckering. It is found to be essentially the same as

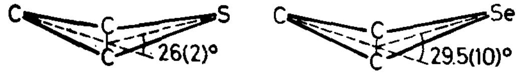


FIGURE 22. Ring puckering in thietane[123] and selenetane[122]

TABLE 13. Puckering angles and inversion barriers of four-membered rings $(CH_2)_3X$

X	Puckering angle CXC/CCC (deg.)	Barrier (kJ mol^{-1})	Technique	Reference
CH_2	35	6.02(2)	ED	124
	26(3)		ED	125
NH	33.1(24)	5.27	ED	126
O	0	0.1856(6)	MW	127
SiH_2	33.6(21)	5.26	ED	128
S	26(2)	3.28(2)	ED	123
Se	29.5(10)	4.58(4)	MW	122

that in thietane shown in Figure 22. The puckering angle and barrier to inversion of some simple four-membered rings are collected in Table 13.

The four-membered ring of tetrafluoro-1,3-diselenetane, $(F_2CSe)_2$, is planar with D_{2h} symmetry[129] (Figure 23) similar to that of tetrafluoro-1,3-dithietane, $(F_2CS)_2$[130,131]. Both structures have been determined by ED. Ring planarity in $(F_2CSe)_2$ has been confirmed by CNDO/2 calculations, which indicated some degree of bonding interaction between the two Se atoms[129]. As two parallel ED studies of $(F_2CS)_2$[130,131] showed some discrepancy, the information on the Se derivative proved to be helpful in resolving the controversy. The two sets of ED results on $(F_2CS)_2$ were in agreement concerning the shape of the molecule. The discrepancy occurred as regards its size. The final arguments in deciding between the two parameter sets were based on the geminal F ··· F distances. This distance was reported to be 2.15(1) Å in $(F_2CSe)_2$[129]. Further, the mean value of F ··· F distances calculated from C—F bond lengths and F—C—F bond angles of 40(!) molecules containing the CF_3 group is 2.162 Å with a standard deviation of 0.008 Å! The F ··· F distance was never found to be smaller than 2.14 Å in those 40 molecules[3,132]. The striking stability of the F ··· F distances points to the importance of the non-bonded interactions between F ligands separated by one bond angle. The mean F ··· F distance is in excellent agreement with the 1,3 non-bonded radius of F, viz. 1.08 Å postulated a long time ago[62]. On this basis one of the two sets of results[130] for $(F_2CS)_2$ could be preferred[3,132]. The most important feature of $(F_2CSe)_2$ and $(F_2CS)_2$ is the planar four-membered ring. In this they are markedly different from selenetane and thietane, or from cyclobutane itself. A matrix isolation

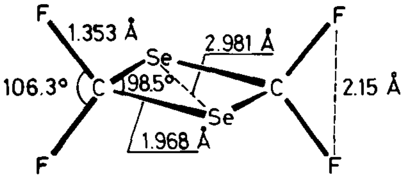
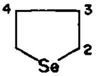


FIGURE 23. Model and geometrical parameters of tetrafluoro-1,3-diselenetane[129]

TABLE 14. The ring geometry of tetrahydroselenophene (C_2 symmetry) from ED[134] and MW[135] studies



	ED (r_a)	MW (r_s)
Bond lengths (Å)		
Se—C	1.975(3)	1.963(2)
C(2)—C(3)	1.538(4)[a]	1.549(3)
C(3)—C(4)		1.527(2)
Bond angles (deg.)		
C—Se—C	89.1(5)	90.73(12)
Se—C—C	105.8(3)	104.97(17)
C—C—C	106.0(7)	106.87(20)
Dihedral angles (deg.)		
CSeCC	15.4(5)	
SeCCC	−42.7(14)[b]	
CCCC	56.9(17)	
θ[c]		29.73(23)

[a] Mean C—C bond distance.

[b] Relative sign of the dihedral angle according to the convention by Klyne and Prelog[136].

[c] θ is the angle between the projections of the bonds Se—C and C(3)—C(4) on a plane perpendicular to the C_2 symmetry axis.

vibrational spectroscopic investigation of 1,3-dithietane[133] concluded C_{2v} symmetry for this molecule with a considerably puckered ring. On the other hand, this molecule was found to have D_{2h} symmetry in the solid state[133]. 1,3-Dithietane may in fact have a quasi-planar ring with low-frequency, large-amplitude deformation motion governed by a double-minimum potential.

Table 14 presents the geometrical parameters of tetrahydroselenophene from both ED[134] and MW[135]. The rotational spectroscopic information permitted distinction between the two different carbon–carbon bond lengths. Tetrahydroselenophene has a well-defined conformation, viz. the one with C_2 symmetry as shown in Figure 24, in accord with spectroscopic results[137,138]. The experimental findings were in complete agreement with the results of molecular mechanics calculations[134]. Tetrahydrothiophene has the same well-defined C_2 conformation as determined by ED[139] and molecular mechanics

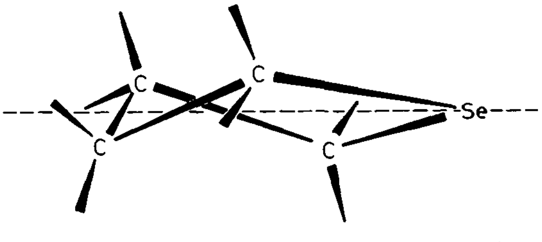
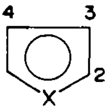


FIGURE 24. The twisted C_2 ring of tetrahydroselenophene with C—H bonds indicated

TABLE 15. Geometries of the planar rings of furan[146], thiophene[147], selenophene[143] and tellurophene[145] from MW

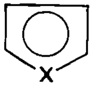


	X = O[a]	S[a]	Se[a]	Te
Bond lengths (Å)				
X—C	1.3621(10)	1.7140(14)	1.8547(9)	2.055
C(2)—C(3)	1.3609(10)	1.3696(17)	1.3695(12)	1.375
C(3)—C(4)	1.4309(20)	1.4232(23)	1.4332(30)	1.423[b]
Bond angles (deg.)				
C—X—C	106.55(7)	92.17(10)	87.77(7)	82.53
X—C—C	110.68(7)	112.47(23)	111.57(13)	110.81
C—C—C	106.05(7)	112.45(18)	114.55(10)	117.93

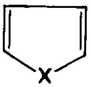
[a] Substitution structure (r_s).
[b] Assumed parameters.

calculations[139]. On the other hand, the structures of cyclopentane[140] and tetrahydrofuran[141,142] are characterized by pseudorotation. An interesting feature of tetrahydroselenophene is that its Se—C bond is longer than that of open-chain Me_2Se (cf. Table 7).

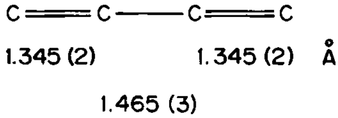
The complete molecular geometry of selenophene has been derived[143] from MW studies[143,144]. In a study of tellurophene[145] some parameters had to be assumed from related molecules. Ring bond lengths and bond angles are shown in Table 15. The most important structural feature of these molecules and their O and S analogues is their planarity. Their aromatic character has been studied and discussed widely. In the chemist's shorthand they are depicted in essentially two forms:



or



representing either the delocalized system of six π electrons or the two double bonds. The nice geometric and electronic symmetry of benzene is of course disturbed when a heteroatom with lone electron pairs replaces the —CH=CH— grouping. The middle carbon–carbon bond in selenophene is longer than the others and they are very similar in length to the corresponding bonds in furan[146] and thiophene[147]—a justification for the assumption made in the study of tellurophene. This bond pattern resembles the conjugated system in 1,3-butadiene[20]:

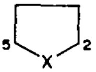
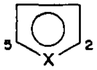


$$\underset{1.345\,(2)}{C=C}\underset{1.465\,(3)}{—}\underset{1.345\,(2)\ \text{Å}}{C=C}$$

The bond length in benzene[148], 1.399(1) Å, lies just between these values.

The bond angle of the heteroatom decreases from furan to tellurophene (Table 16). However, due to the bond lengthening, the C(2)···C(5) distance increases in this order. The ring accommodates itself to this change first of all by opening the angles at C(3) and C(4) (see Table 15). The bond angles of O, S, Se and Te in the ring are smaller and their

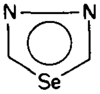
TABLE 16. Parameters of dimethyl chalcogenides and non-aromatic and aromatic five-membered heterocycles

	X = O	S	Se	Te
Me$_2$X				
C—X (Å)	1.410	1.805	1.945	2.142
C···C^a (Å)	2.334	2.746	2.898	3.14
C—X—C (deg.)	111.7	99.05	96.3	94
Reference	66	51	37	65
				
C—X (Å)	1.428	1.839	1.975	
C(2)···C(5)^a (Å)	2.3^b	2.677	2.771	
C—X—C (deg.)	106–111^b	93.4	89.1	
Reference	142	139	134	
				
C—X (Å)	1.362	1.714	1.855	2.055
C(2)···C(5)^a (Å)	2.184	2.470	2.572	2.710
C—X—C (deg.)	106.6	92.2	87.8	82.5
Reference	146	147	143	145
Δ^c (deg.)	5.1	6.8	8.5	12

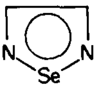
[a] Calculated from the other parameters.
[b] The ring cannot be characterized by constant values because of pseudorotation.
[c] The difference between angle C—X—C in Me$_2$X and C_4H_4X.

bonds are shorter than in the corresponding dimethyl chalcogenides, and the difference in bond angles (Δ) increases from O to Te (Table 16). The angles C—S—C and C—Se—C in thiophene and selenophene are even smaller than in the corresponding saturated heterocycles.

Microwave studies of 1,3,4-selenadiazole (**13**)[149] and 1,2,5-selenadiazole (**14**)[150] confirmed the planarity and C_{2v} symmetry of these molecules and with many assumptions yielded C—Se = 1.868 Å and the surprisingly small C—Se—C = 81.8° for **13** and N—Se = 1.80 Å and N—Se—N = 94.3° for **14**.



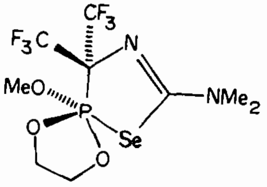
(13)



(14)

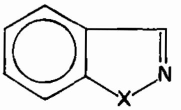
The crystal and molecular structures of diphenyl-substituted[151] and ring-fused derivatives[152] of **14** have been determined by XD and are discussed in relation to the structures of their O and S analogues.

In a $\Delta^4 - 1,4,2\lambda^5$-selenazaphospholine derivative (**15**) the two rings occupy axial–equatorial positions at the distorted trigonal bipyramidal phosphorus atom[153]. The selenazaphospholine ring is nearly planar with single bonds P—Se = 2.273(2) Å, Se—C = 1.972 Å and angle P—Se—C = 89.9°.



(15)

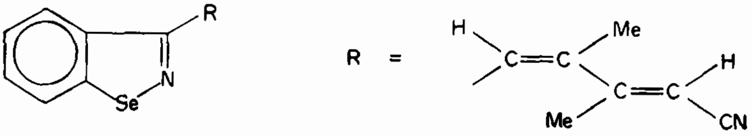
The different crystal structures of 1,2-benzisoselenazole (**16**) and 1,2-benzisotellurazole (**17**) explain why the latter compound has an unexpectedly high melting point and low solubility[154]. There are only van der Waals' intermolecular contacts in the crystals of **16**, whereas short (2.5 Å) Te···N interactions link the molecules of **17** into chains. Mean bond lengths and angles from crystallographically different molecules are C—Se = 1.86 Å, Se—N = 1.86 Å, C—Se—N = 88°, C—Te = 2.08 Å, Te—N = 2.11 Å and C—Te—N = 80°.



(16) X = Se

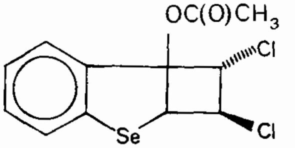
(17) X = Te

In a 3-substituted derivative of **16** (**18**) C—Se = 1.845(11) Å, Se—N = 1.833(7) Å and C—Se—N = 91.0(4)° were determined[155].



(18)

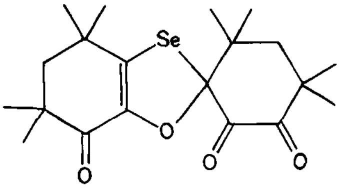
5-Acetoxy-6,7-dichloro-3,4-benzobicyclo[3.2.0]-2-selenaheptene (**19**) is a photo-addition product[156]. The bond angle of the Se atom, 87.4(4)°, is equal to that in selenophene (Table 15). Its bond lengths are the normal values for single bonds, Se—C(sp^3) = 1.949(9) and Se—C(sp^2) = 1.905(9) Å[156].



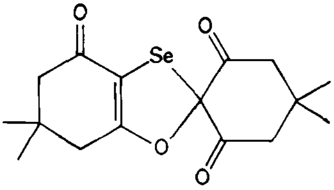
(19)

The molecular structure and conformation of some Se compounds, which are formed in the oxidation of diketones by SeO_2, have been elucidated recently by XD. Two structures, **9** and **10**, have been treated in Section III.A. 5,6-Dihydro-4,4,4′,4′,6,6,6′,6′-

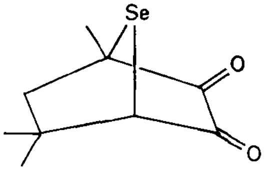
octamethylspiro[1,3-benzoxaselenole-2, 1′-cyclohexane]-2′,3′,7(4*H*)-trione (**20**)[157] and 6,7-dihydro-4′,4′,6,6-tetramethylspiro[1,3-benzoxaselenole-2,1′-cyclohexane]-2′,4,6′(5*H*)-trione (**21**)[158], as well as 1,5,5-trimethyl-7-selenabicyclo[2.2.1]heptane-2,3-dione (**22**)[159], contain the Se atom in five-membered rings. The bond angles of Se are 83.6(2), 82.5 and 78.6(3)° in **20**, **21** and **22**, respectively, and therefore very small in the Se-bridged compound **22**. The selenium–carbon bonds are, in part, longer than in acyclic selenides (cf. Table 7): Se—C(sp^2) = 1.885(5) and 1.903 Å, Se—C(spiro) = 2.012(5) and 2.007 Å in **20** and **21**, respectively (values for **21** are averages from two crystallographically independent molecules), while in **22** the bond to the quaternary carbon is 2.021(7) Å, and to the other bridgehead atom 1.977(7) Å.



(20)

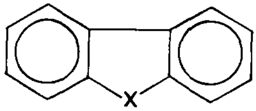


(21)



(22)

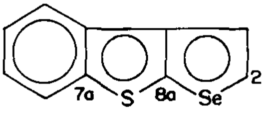
Dibenzoselenophene (**23**)[160] and dibenzotellurophene (**24**)[161] have been studied by XD. The molecules are practically planar, with only small dihedral angles between the best planes of the individual rings. Bond lengths and bond angles within the five-membered rings are given in Table 17, together with those in dibenzofuran (X = O) and dibenzothiophene (X = S). McCullough[161] has discussed the structural changes in this series of molecules and compared chalcogen bond angles with those in dimethyl chalcogenides. The angle pattern is very similar to that found in the respective isolated five-membered rings (Table 15). The bond angle of the heteroatom is somewhat smaller in the fused ring system. Bonds seem to lengthen by ring fusion. Caution is called for, however, in comparing bond distances from MW and XD.



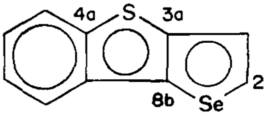
(23) X = Se

(24) X = Te

The bond lengths and bond angles of heteroatoms in selenolo[2,3-*b*] benzothiophene (**25**)[164] are: Se—C(2) = 1.896(17), Se—C(8a) = 1.859(13), S—C(7a) = 1.741(15), S—C(8a) = 1.687(15) Å, ∠C—Se—C = 87.7(7), ∠C—S—C = 91.4(7)°; and in

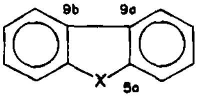


(25) *cis*



(26) *trans*

TABLE 17. Geometries of the planar five-membered rings of dibenzo-furan[162], -thiophene[163], -selenophene[160] and -tellurophene[161] from XD[a]

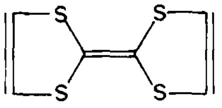


	X = O	S	Se	Te
Bond lengths (Å)				
X—C	1.418(6)	1.740(8)	1.899(5)	2.087(5)
C(5a)—C(9a)	1.382(7)	1.409(11)	1.398(7)	1.394(6)
C(9a)—C(9b)	1.480(6)	1.441(1)	1.453(7)	1.460(7)
Bond angles (deg.)				
C—X—C	104.4(4)	91.5(4)	86.7(2)	81.7(2)
X—C(5a)—C(9a)	112.9(4)	112.3(6)	112.3(4)	112.1(4)
C(5a)—C(9a)—C(9b)	105.6(4)	111.9(7)	114.3(5)	117.1(5)

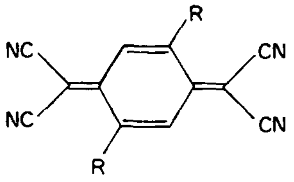
[a] Mean values from chemically equivalent distances and angles as well as their standard deviations are presented after McCullough[161].

selenolo [3,2-*b*] benzothiophene (**26**)[164]: Se—C(2) = 1.861(10), Se—C(8b) = 1.863(9), S—C(3a) = 1.751(8), S—C(4a) = 1.734(8) Å, ∠ C—Se—C = 87.0(4), ∠ C—S—C = 91.0(4)°. The shapes of the heterocyclic rings are similar to the corresponding ones in other molecules.

Tetrathiafulvalene (TTF, $\Delta^{2,2'}$-bis-1,3-dithiole) (**27**) derivatives and Se analogues have been widely studied because of their ability to form charge-transfer salts with electron acceptors like TCNQ (**28**). The structures of a few Se compounds of this type will be touched on here. The pure electron donor 4,4′,5,5′-tetramethyl-$\Delta^{2,2'}$-bis-1,3-diselenole (tetramethyltetraselenafulvalene, TMTSF) (**30**) crystallizes in the triclinic space group P$\bar{1}$ with one molecule in the unit cell[165]. The molecule has thus a centre of symmetry (C_i). The rings are slightly puckered at the Se ··· Se lines, taking envelope forms with 6.1° dihedral angle. The inner Se—C bonds are 1.892(7), the outer ones 1.906(7) Å on the average, while the C—Se—C angles are 93.9°. The molecular packing is determined essentially by van



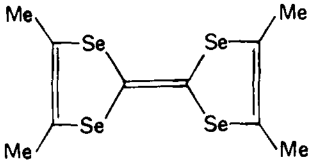
(**27**)



(**28**) R = H

(**29**) R = Me

der Waals' contacts. The crystal of the 1:1 salt of **30** with 2,5-dimethyl-7,7,8,8-tetracyano-*p*-quinodimethane (**29**) consists of separate stacks of the radical anions of **29** and of the radical cations of **30**[166]. The rings of **30** are puckered by only 2.3° and the centrosymmetric molecule has an overall chair conformation. The two kinds of Se—C bonds, 1.879(5) and 1.896(5) Å, are somewhat shorter than in the neutral compound, and the C—Se—C angle is 94.1°.



(30)

The salt of TMTSF with TCNQ has two crystalline forms with interesting properties. One is a highly conducting crystal (black form) built of segregated columns of the donor and acceptor molecules[167]. The other is a semiconducting modification (red form) which consists of mixed stacks of alternating donor and acceptor molecules[168]. The overlap of molecules within a stack is shown in Figure 25. The distance between molecular planes is 3.6 Å in the stack of cations (black form) and 3.5 Å within the mixed stack (red form), about the same as in the TCNQ crystal itself[169]. The stacks of TCNQ anions in the black form of the salt are characterized, on the other hand, by interplanar spacings of 3.26 Å [167]. The Se bond lengths and angles are (in the above order) 1.88(1), 1.90(1) Å and 94.5° in the black form[167,168] and 1.908(4), 1.900(4) Å and 94.3° in the red form[168]. It is noteworthy that S has the same bond angle, 94.4°, in pure crystalline TTF (**27**)[170], and the S—C bonds to the bridgehead carbons and longer than the other S—C bonds, viz. 1.757(2) and 1.730(2) Å. This is in accord with calculated electron populations[170].

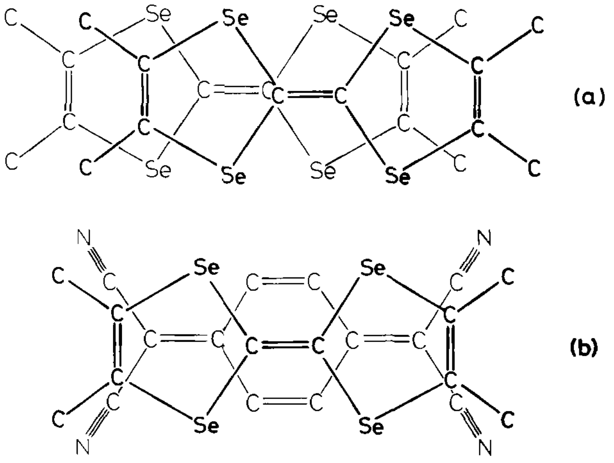
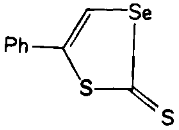
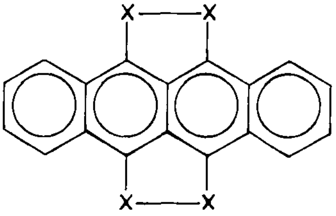


FIGURE 25. Overlap of molecules, as seen along the normal to the mean molecular plane, (a) in the stack of cations in the black form of TMTSF·TCNQ (after Reference 167) and (b) in the mixed stack of cations and anions in the red form of TMTSF·TCNQ (after Reference 168)



(31)

5-Phenyl-1,3-thiaselenole-2-thione (31) is the donor in a charge-transfer complex with TCNQ. 31 is planar in the complex and has bond lengths Se—C(=C) = 1.858 Å, Se—C(=S) = 1.878 Å and angle C—Se—C = 92.0°[171].



(32) X = S

(33) X = Se

(34) X = Te

Chalcogen–chalcogen bonds are present in the planar fused ring system of tetrathiotetracene (TTT) (32) and its derivatives and analogues, which also form charge-transfer salts with different anionic species. The crystal structures of 2:1 complexes of tetraselenotetracene (33) with chloride[172] and thiocyanate[173] ions have been determined. In both crystals the molecules of 33 lie in centres of symmetry and are nearly planar: the atoms of the Se—Se group are on opposite sides of the mean plane of carbons, destroying complete planarity. The molecules form columns along the *c* axis and the anions reside in the canals between these stacks. The stacks, the interstack spaces and the positions of the anions explain why the chloride salt behaves as a metal and has an electric conductivity about a hundred times higher than has the thiocyanate complex[172]. The geometry of the diselenide group in cation 33 is characterized by the following mean parameters:

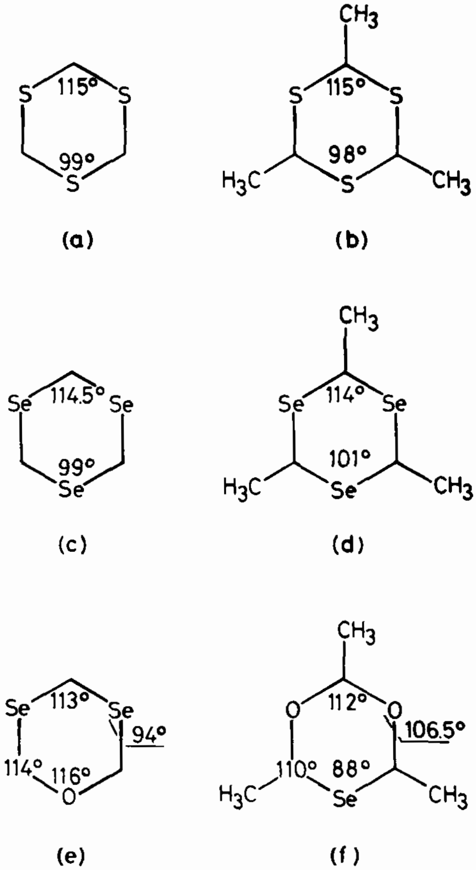
Anion	Se—Se(Å)	Se—C(Å)	C—Se—Se(deg.)
Cl^-	2.323(1)	1.901(6)	91.6
SCN^-	2.320(7)	1.86	90

The molecules form stacks in the crystals of neutral tetratellurotetracene (34)[174] and tetrathiotetracene (32)[175]. The corresponding structural data are:

Molecule	X—X(Å)	X—C(Å)	C—X—X(deg.)
34(X = Te)	2.680(7)	2.135(15)	87.7(8)
32((X = S)	2.100(3)	1.781	95.9

Chalcogen–chalcogen bond distances are comparable with those in acyclic dichalcogenides (Section III.B). Chalcogen–carbon bond lengths are normal for single bonds to an aromatic carbon. Bond angles in these rings are smaller than in acyclic molecules (Tables 7 and 9) and larger than in the rings listed in Table 16. The increasing X—X distance from S to Te gives rise to an opening of carbon bond angles in the five-membered rings of 32–34.

The structures of six-membered rings with alternating carbon and chalcogen atoms have been determined from three-dimensional XD photographic microdensitometer data. (Figure 26). All these rings have the chair conformation in the crystal, and the Me substituents are in equatorial positions. The intraring bond angles of carbon exceed the regular tetrahedral value (see Figure 26 for references). The ring shapes in (a), (b), (c) and (d) of Figure 26 seem to be very similar. The Se and S atoms have practically the same bond angles. The introduction of O atoms in the ring, however, causes appreciable changes. The sum of the bond angles, which is 720° in a planar hexagon and may be a measure for the non-planarity of the ring, is 641–645° in the trithiane and triselenane rings of (a), (b), (c) and (d), 647° in (e) and 633° in (f) of Figure 26, while it is 660° in free 1,3,5-trioxane, with angle C—O—C 108.9(8)°, from an ED study[182]. The average Se—C bond distances in (c), (d), (e) and (f), 1.94–1.95 Å, agree with single-bond lengths in non-cyclic compounds (Table 7).



(a) (b) (c) (d) (e) (f)

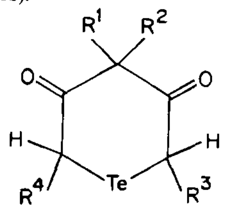
FIGURE 26. Mean endocyclic bond angles in chair-form six-membered rings: (a) 1,3,5-trithiane[176], (b) *cis*-2,4,6-trimethyl-1,3,5-trithiane[177], (c) 1,3,5-triselenane[178], (d) *cis*-2,4,6-trimethyl-1,3,5-triselenane[179], (e) 1,3,5-oxadiselenane[180], (f) *cis*-2,4,6-trimethyl-1,3,5-dioxaselenane[181]

TABLE 18. Structural data of 1-telluracyclohexane-3,5-dione derivatives from XD

Molecule	Te—C (Å)	C—Te—C (deg.)	Reference
35	2.15(1), 2.18(1)[a]	89.5(4)	186
	2.17(1), 2.15(1)[a]	90.8(4)	183
36	2.202(8)[b], 2.157(8)[c]	88.4(3)	184
37	2.184(6), 2.206(7)[a]	89.7(3)	187
38	2.168(5)	86.4(2)	185
39	2.18(1), 2.18(1)[a]	89.3(6)	188

[a] The two Te—C bonds are crystallographically different.
[b] The Te—C(Me) bond.
[c] The Te—CH_2 bond.

Cyclic complexes of Se(II) or Te(II) are formed in the reaction of selenium or tellurium tetrachloride with 1,3-diketones. Acetylacetone or its derivatives function in these complexes as bivalent bidentate ligands, bonded to the chalcogen atom through the carbon atoms next to the carbonyl group. This type of bonding is completely different from the bonding of acetylacetone with other central atoms (see References 183–185 for references). The crystal and molecular structures of some 1-telluracyclohexane-3,5-dione derivatives **35**–**39** (Table 18) were determined in the 1970s. In some of these studies by Dewan and Silver, some museum pieces of crystals obtained about fifty years before were used (see Table 18 for references).



(**35**) $R^1 = R^2 = R^3 = R^4 = H$
(**36**) $R^1 = R^4 = H$; $R^2 = R^3 = Me$
(**37**) $R^1 = R^2 = H$; $R^3 = R^4 = Me$
(**38**) $R^1 = R^2 = Me$; $R^3 = R^4 = H$
(**39**) $R^1 = H$; $R^2 = R^3 = R^4 = Me$

The telluracyclohexane rings have a chair form and the Me groups occupy equatorial positions—except in 4,4-dimethyl-1-telluracyclohexane-3,5-dione (**38**) where this is not possible. The parent compound, 1-telluracyclohexane-3, 5-dione (**35**) itself has been the subject of three XD studies[183,186,189]. The molecules are aligned in piles along axis *a* (Figure 27). Weak association is formed[183] between four of these piles via Te lone pairs at Te···Te distances of 3.95(1), 3.95(1), 3.97(1), 3.97(1) and 4.18(1) Å. Each Te atom has five contacts to two molecules each in neighbouring piles shifted by ± *a*/2 and to one molecule in the diagonally opposite stack[183]. The above listed distances are all shorter than twice the Te van der Waals' distance (Table 10). Crystals of **37** and **39** are isomorphous, monoclinic, $P2_1$; **36** is also monoclinic, $B2_1/c$ (see Table 18 for references). There are zigzag Te···Te···Te chains in these structures along axis *b* with Te···Te distances of 4.068(7) Å (**37**), 4.138(7) Å (**39**) and 4.042(5) Å (**36**). In crystalline **38**, which is orthorhombic, Pmnb, the shortest Te···Te distances are 5.05 Å, much longer than in the other crystals, probably due to the space requirement of the axial methyl group in **38**. The schematic projection of this structure in Figure 28 demonstrates how the lone pairs of tetrahedrally sp^3-hybridized Te(II) atoms are oriented into available space in the structure[185]. Another possible hybridization of Te(II) would be the planar trigonal sp^2 hybrid with the remaining lone pair on a p orbital perpendicular to the plane[183,184]. Some physical properties of these crystals such as Mössbauer spectra[190], colour, crystal growth and variations of the C—Te—C bond angle have been correlated with the existence of one-dimensional chains of molecules in the crystal and with geometric and electronic characteristics of intermolecular Te···Te interactions (see References 183–185, 187, 188 and 190 and references therein). The relatively small angle in **38** has been related[185] to weaker intermolecular Te···Te interactions in this crystal (see above).

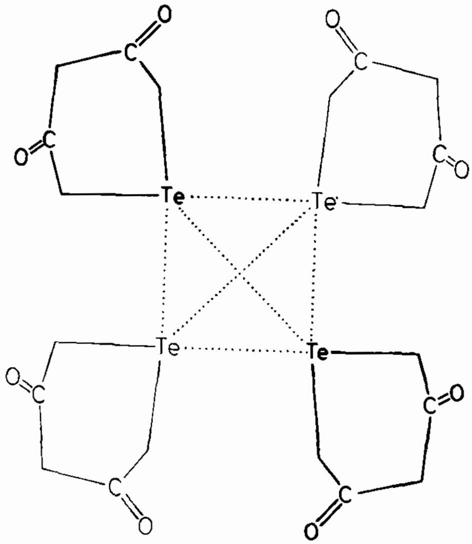


FIGURE 27. Molecular packing in the crystal of 1-telluracyclohexane-3, 5-dione (**35**): projection of four piles of molecules along the *a* axis (after References 183 and 186)

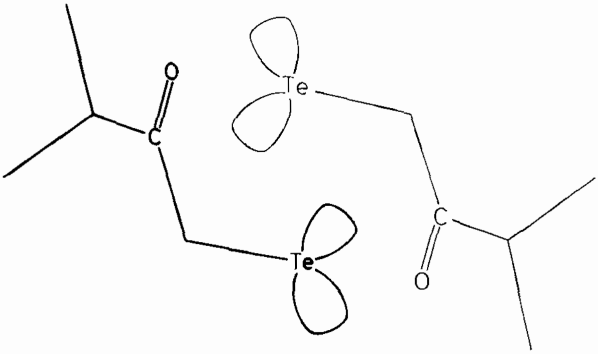
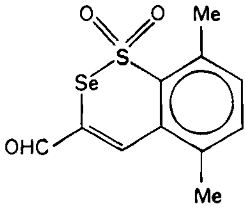


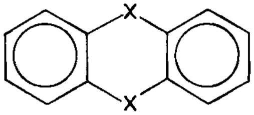
FIGURE 28. Projection of two molecules along the *a* axis in the crystal of 4, 4-dimethyl-1-telluracyclohexane-3, 5-dione (**38**) (after Reference 185)

The non-planar heterocyclic ring of 3-formyl-5,8-dimethyl-1,2-benzothiaselenin-1,1-dioxide (**40**) has bond lengths Se—C = 1.888(7) and S—Se = 2.205(1) Å and bond angle S—Se—C = 92.8(2)°[191].

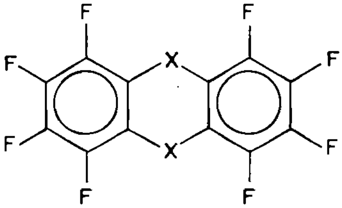


(40)

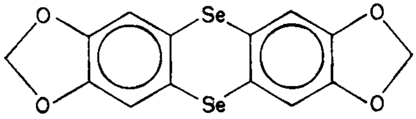
9,10-Dihydroanthracene[192a] and its heterocyclic analogues are folded at atoms 9 and 10, having a boat-form central ring, and are referred to epithetically as 'butterfly' molecules (Figure 29). An exception is dibenzo-*p*-dioxin (**41**), which is, at least in the crystal phase, practically planar[192b]. Geometrical parameters of such molecules containing Se or Te atoms are listed in Table 19, together with those of O and S analogues for comparison,



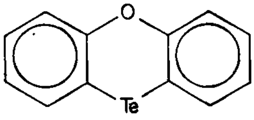
(41) X = O
(42) X = S
(43) X = Te



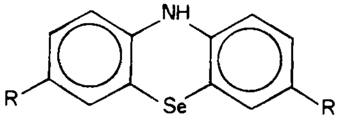
(44) X = O
(45) X = S
(46) X = Se
(47) X = Te



(48)



(49)



(50) R = H
(51) R = Cl

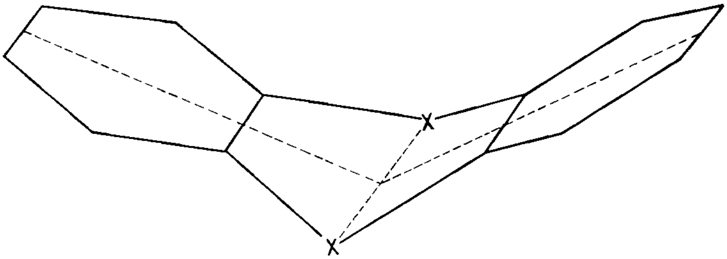
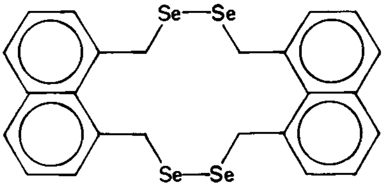


FIGURE 29. The shape of a 'butterfly' molecule

mainly from XD investigations. Thianthrene (**42**) has been studied in the gas phase by ED[194]. Chalcogen–carbon bond distances are normal for single bonds to sp^2-hybridized carbon (cf. Table 7 and diphenyl ditellurides in Section III.B). Bond angles show the usual trend down the chalcogen group. The bond lengths in the perfluoro derivatives **44**–**47** are practically the same as in the other molecules; chalcogen bond angles in **44**,**45** and **47** are smaller than in the corresponding non-fluorinated molecules **41**,**42** and **43** (Table 19). It is instructive to follow the changes[201] in the dihedral angle θ_1 of the two phenylene planes and the fold angle θ_2 of the central ring in the perfluoro compounds (Figure 30). Both angles diminish as the size of the chalcogen atom increases and thus the repulsion of the tetrafluorophenylene rings gets smaller. This is seen for example, from the 1,3 C···C distances in the central rings of the four molecules **44**–**47**: 2.31, 2.69, 2.85 and 3.06 Å. At the same time, the usual chalcogen bond angles are approached only by stronger folding of the central ring, without substantially distorting the carbon bond angles from 120°. The latter angles in the central ring are, nevertheless, systematically larger[195] than 120°, viz. O—C—C 122.8(2), S—C—C 121.3(2), Se—C—C 121.7(9) and Te—C—C 122.5(3)°. Another interesting observation[201] is that, except for perfluorotelluranthrene (**47**), $\theta_1 \geq \theta_2$ is valid in these and similar molecules. This is demonstrated by the data in Figure 30 as well as by θ_1, θ_2 124.0, 120.1° in telluranthrene (**43**), and 145, 138° in phenoxatellurin (**49**), while $\theta_1 = \theta_2$ was found to be 131.4° in thianthrene (**42**), 150° in phenoselenazine (**50**) and 146° in 3,7-dichlorophenoselenazine (**51**) (see Table 19 for references). Repulsion and attraction between the phenylene 'wings' may give an explanation for this phenomenon[201].

The eight-membered ring of 1,3,5,7-tetraselenocane, $(CH_2Se)_4$, has an asymmetric twist-chair conformation in the crystal (Figure 31) with Se—C bond distances of 1.91–1.98 Å and C—Se—C angles of 98.0–101.5° [203]. The relatively large Se—C—Se angles between 114 and 119°, accompanied by Se···Se distances of 3.26–3.38 Å, may be a consequence of the size of the Se atoms[203].

The crystal molecular structure of a dimer (**52**) of 1*H*,4*H*-naphtho[1,8-*d*,*e*] [1,2]-diselenepin has been determined[204]. The molecule possesses C_2 symmetry; the angle between the two naphthalene planes is 87.6°. The CSeSeC dihedral angle is 88.1°, similar to this angle in acyclic diselenides. The Se—Se bond is 2.315(2) Å long and the mean Se—C distance and Se—Se—C bond angle are 1.991(11) Å and 101.8°.



(52)

TABLE 19. Chalcogen bond lengths and bond angles in 9,10-diheteroanthracene molecules **41**–**51**

Molecule	Bond length (Å)	Bond angle (deg.)	Reference
	O—C	C—O—C	
41	1.383(8)	116.4(5)	192b
44	1.374(2)	114.3(2)	193
	S—C	C—S—C	
42	1.770(3)	104.1(1)	194
45	1.765(2)	99.3(1)	195
	Se—C	C—Se—C	
46	1.910(8)	96.5(10)	196
48	1.920(8)	98.2(4)	197
50	1.89(2)	97(1)	198
51	1.921(5)	95.4(2)	199
	Te—C	C—Te—C	
43	2.112(4)	95.6(3)	200
47	2.114	92.9(1)	201
49	2.098	89.4(3)	202

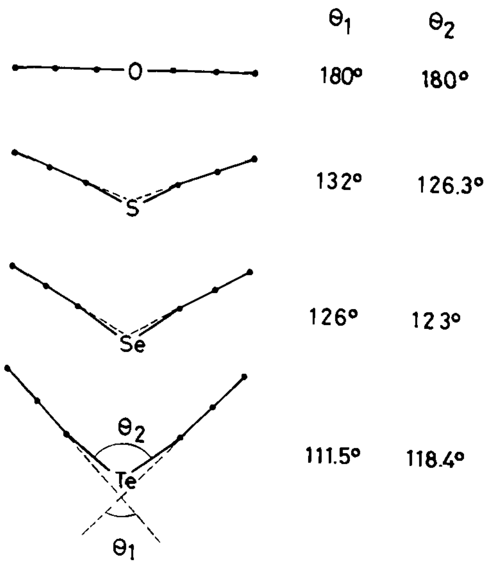


FIGURE 30. Schematic projections of the ring planes, along the chalcogen···chalcogen line, in perfluoro-dibenzo-*p*-dioxin (**44**) -thianthrene (**45**), -selenanthrene (**46**) and -telluranthrene (**47**). Deviations are slightly exaggerated in the drawing. θ_1 is the dihedral angle between the mean planes of the phenylene rings, θ_2 is the fold angle of the central ring. See Table 19 for references

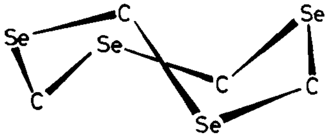


FIGURE 31. The ring conformation in crystalline 1,3,5,7-tetraselenocane. Drawn from the atomic coordinates given in Reference 203

TABLE 20. Bond configuration of Se and Te in organometallic complexes

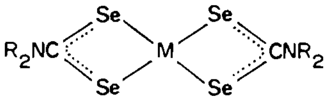
Molecule	M	Se—C (Å)	M—Se (Å)	M—Se—C (deg.)	Reference
53	Cu	1.86	2.43	84	205
59	Cu	1.82	2.50	81.2	206
54	Zn	1.88	2.48	77–95	205
60	Hg	1.89(3)	2.477(3)	104.4(8)	207
57	Se	1.902	2.462	89.1	208
		1.839	2.816	80.1	
58	Se	1.896	2.450	89.5	209
		1.849	2.867	78.5	
61	Te	1.897(7)	2.7229(16)	101.1(2)	210
		1.893(7)	2.8895(17)	99.8(2)	
62	Te	1.884	2.812	91.7(7)	211
				98.0(8)	
63	Mo	1.86(1)	2.492(2)	105.1(4)	212
64	Co	1.952(3)	2.378(1)	92.1(1)	213
65	Co	1.949(10)	2.355(1)	92.7(3)	214
55	Ni	1.88	2.317	85.2	205
56	Ni	1.86	2.31	85.2	215
66	Ni	1.906(10)	2.280(3)	102.8(3)	216
67	Ni	1.86(1)	2.387(1)	87.3[a]	217
68	Ni	1.78(3)	2.391(5)	85[a]	218
69	Rh	1.926(7)	2.527	106.3	219
70	Pt	1.89(2)	2.462(4)	[b]	220
		1.86(3)	2.491(3)	[b]	
		Te—C (Å)	M—Te (Å)	M—Te—C (deg.)	
71	Cr	2.12(2)	2.765(4)	96.1(15)	221
72	Hg	2.10(1.2)	2.697(10)	99.9(16)	222

[a] Calculated from the atomic coordinates given in the original paper; mean value.
[b] Not given.

D. Organometallic Complexes

Bond lengths and bond angles of Se and Te in some organometallic complexes with a two-coordinated chalcogen atom directly bonded to a carbon and a metal atom (**53**–**72**) are summarized in Table 20. Included are some compounds where the central atom is also Se or Te. Complexes with pseudohalide ligands have not been considered. The selenocyanate ligand may be coordinated to metals through the Se or N atom or both, it may form a bridge between two metal atoms, and the choice of binding mode depends rather on steric than on electronic factors[223].

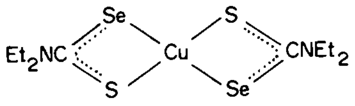
The diselenocarbamate complexes of Cu(II), Zn(II) and Ni(II) (**53**–**56**) are isomorphous with the corresponding dithiocarbamate compounds. Average differences of Se—C and S—C (0.152 Å) and Se–metal and S–metal bond lengths (0.113 Å), compared with the difference (0.14 Å) of Se and S covalent radii (Table 10) may indicate that Se–metal bonds are of higher order than S–metal bonds[205]. The diselenocarbamate complexes (**53**–**58**, **68**, **70**) all contain practically planar Se_2CNC_2 skeletons in their ligands but the environment of the Se atoms and the coordination of the central atom is different in their crystals. The Ni atom has a distorted square planar coordination and monomeric molecules are present in the crystals of **55**[205] and **56**[215] while a pair of centrosymmetrically related molecules is linked by a pair of Se–metal bonds in **53** and **54**[205]. In **53** and **54** the Cu and Zn atoms obtain five close neighbours in different ways (Figure 32) so that the geometry is a distorted tetragonal pyramid around Cu and something between this and a trigonal bipyramid around Zn[205]. Two diselenocarbamate ligands are coordinated to a Se atom in bis(*N*, *N*-diethyldiselenocarbamato)selenium(II) (**57**)[208] and selenium bis(1-pyrrolidinecarbodiselenoate) (**58**)[209], forming two approximately linear three-centre four-electron (3c–4e) bonding systems in a nearly planar trapezoid $SeSe_4$ structure. There are two shorter Se—Se bonds and, in *trans* positions to them, two longer ones (Table 20) and they are all longer than the Se—Se bond in acyclic or cyclic diselenides (Sections III.B and III.C). The adjacent Se—C bonds are, in the same order, longer and shorter and the corresponding Se—Se—C bond angles are also systematically different (see Table 20).



(**53**) M = Cu, R = Et
(**54**) M = Zn, R = Et
(**55**) M = Ni, R = Et
(**56**) M = Ni, R = *n*-Bu
(**57**) M = Se, R = Et
(**58**) M = Se, $—NR_2 = —N(CH_2)_4$

The selenium–carbon bond lengths in the selenocarbamate (**53**–**59**, **68**, **70**) and selenourea (**60**–**62**) complexes are intermediate between the expected length of a single (1.94 Å) and a double bond (1.73 Å)[209] (see also data in Sections II and III.A for comparison), and are comparable with the bond length in crystalline selenourea and related systems (see Section II). The Se—C bonds are remarkably short in the cation of **68**, which is an octahedrally coordinated Ni(IV) complex. The Se bond angles in the bidentate ligands are influenced by strain in the four-membered ring.

The central metal atom is octahedrally coordinated in **63**–**65**, **67**–**69** and **71**. In the cobalt complexes (**64**, **65**) a lengthening of the Co—N bond *trans* to the Se atom has been observed[213,214] and compared to the '*trans* effect' in analogous ethanethiolamine complexes. The Se bond configuration in the selenol complexes (**64**–**66**, **69**) is similar to that found in acyclic selenides (cf. Table 7).

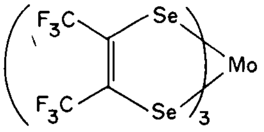


(59)

$[MeHgSeC(NH_2)_2]^+ NO_3^-$
(60)

$PhTe[SeC(NH_2)_2]_2{}^+ Cl^-$
(61)

$Te[SeC(NH_2)_2]_4{}^{2+} 2 Cl^-$
(62)



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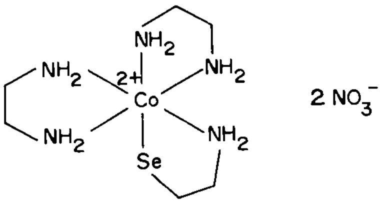

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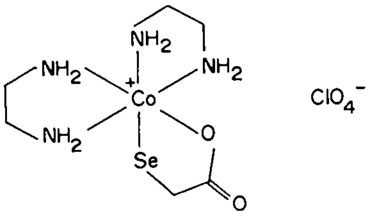

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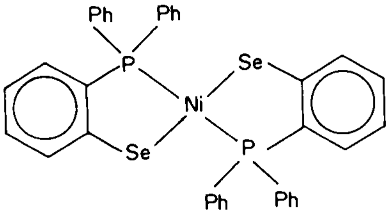

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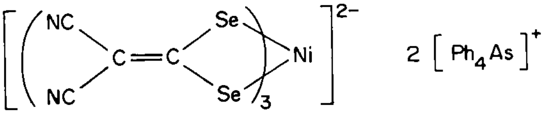

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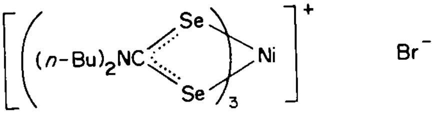

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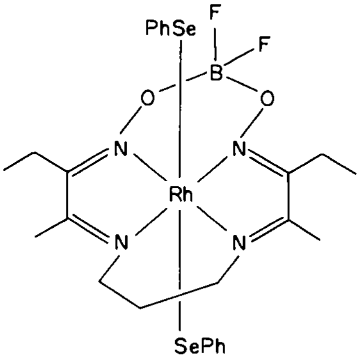

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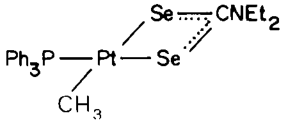

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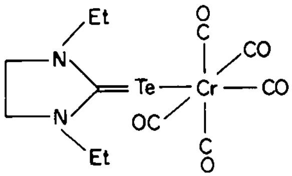
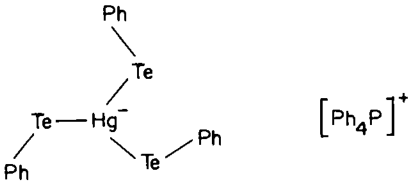


(71)



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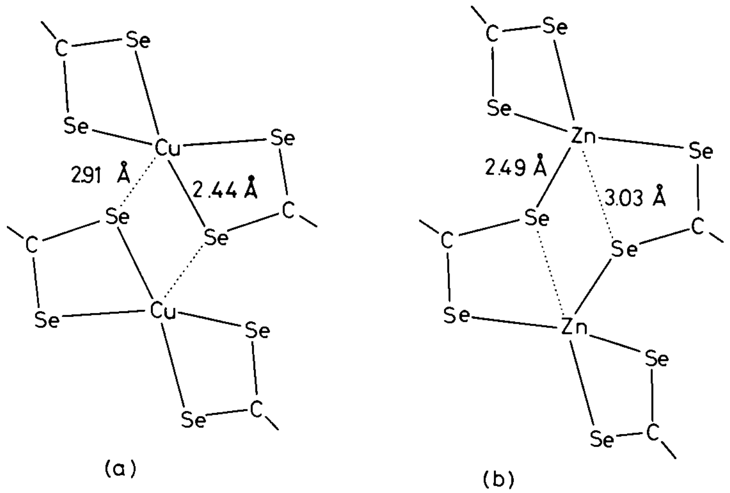
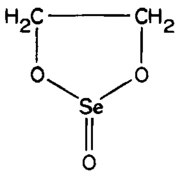


FIGURE 32. Schematic projection of the dimeric molecule in the crystal of (a) bis(*N*,*N*-diethyldiselenocarbamato)copper(II) (**53**) and (b) bis(*N*,*N*-diethyldiselenocarbamato)zinc(II) (**54**) (after Reference 205). The diethylamino groups are not shown

The molecule of the tellurourea complex (71) lies on a crystallographic mirror plane, which bisects the five-membered ring[221]. The tris(tellurophenolato)mercurate(II) anion (72) has a distorted planar trigonal $HgTe_3$ core, which holds the propeller-like arrangement of the phenyl rings[222]. The Hg atom lies 0.09 Å from the plane of the Te atoms, and the distances of *ipso* carbon atoms of the rings from the same plane are −0.59, −0.21 and 0.12 Å. The Ph rings form dihedral angles of 34.6, 71.2 and 11.3° with that plane[222]. The Te—C bond lengths in both compounds (71, 72) are comparable with the sum of the covalent radii (Table 10).

IV. THREE-COORDINATED SELENIUM AND TELLURIUM

Molecular geometry data are relatively scarce for organic Se and Te compounds in which the chalcogen atom is three-coordinate. The structure of no such organic Se or Te compound has been determined in the vapour phase. There are though a few inorganic compounds whose vapour-phase molecular geometry has been elucidated by ED: $SeOF_2$[224], $SeOCl_2$[225], ethylene selenite (73)[226] and trimethylene selenite (74)[227].



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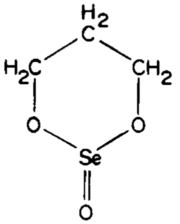


(74)

XD has been used to elucidate the molecular structure of several organic Se and Te compounds in the crystalline phase. The Ph group often occurs as ligand both for Se and Te. Especially noteworthy is the interest in structures in which the organic Se moiety is linked to a transition metal. The fluxional behaviour of some of these structures has also attracted interest.

Crystalline triphenylselenonium isothiocyanate, $Ph_3Se(NCS)$, consists of discrete Ph_3Se^+ and NCS^- ion pairs separated from other ion pairs by van der Waals' distances[228]. Within the ion pairs (Figure 33), the Se···N contact of 3.197(4) Å and the Se···C(NCS) contact of 3.260(5) Å are considerably shorter than the respective van der Waals' distances. The Se bond configuration has a trigonal pyramidal shape with the Se atom lying 0.87 Å out of the plane of the three adjacent carbon atoms. This configuration

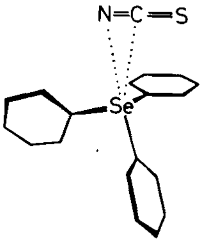


FIGURE 33. An ion pair in the crystal of triphenylselenonium isothiocyanate (after Reference 228)

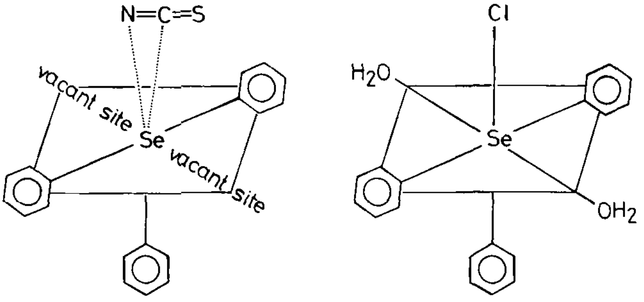


FIGURE 34. Schematic Se coordination in $Ph_3Se(NCS)$ and $Ph_3SeCl\cdot 2H_2O$

may also be considered to be distorted tetrahedral with a lone pair of electrons occupying the fourth position.

The Se bond configurations are the same in $Ph_3Se(NCS)$ and in $Ph_3SeCl\cdot 2H_2O$[229]. The mean values of the Se—C bond lengths and C—Se—C bond angles are as follows:

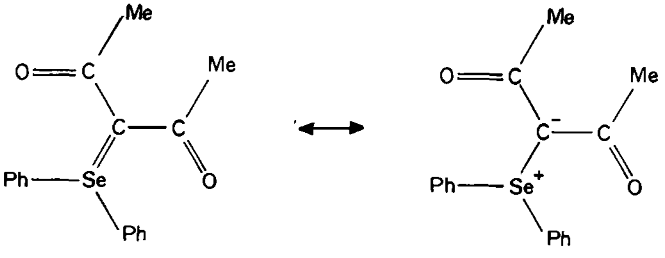
	r(Se—C)(Å)	C—Se—C(deg.)
$Ph_3Se(NCS)$	1.923(8)	100.9(3)
$Ph_3SeCl\cdot 2H_2O$	1.93(1)	100(1)

The Se bond angles are slightly larger than the corresponding mean Te bond angles in the Ph_3Te^+ ion, viz. 95.7(8)° in $Ph_3Te(NCO)\cdot \frac{1}{2}CHCl_3$ [230] and 97.3(6)° in $Ph_3Te(NCS)$[231]. The mean Te—C bond distance in both crystals is 2.13(2) Å [230,231]. The mean C—Te—C bond angle and Te—C bond length in triphenyltelluronium chloride, Ph_3TeCl, is 95.6° and 2.130(4) Å [232].

In the two above-mentioned Se compounds the coordination of the Se atoms is different in spite of the structural similarity of the two cations. The Se is actually four-coordinated in $Ph_3Se(NCS)$ and six-coordinated in $Ph_3SeCl\cdot 2H_2O$. Considering the magnitude of the Se bond angles, viz. N···Se—C and C—Se—C, the Se coordination even in $Ph_3Se(NCS)$ can be visualized as octahedral with three bonds, one coordination linkage and two vacant sites[228]. In $Ph_3SeCl\cdot 2H_2O$ the octahedral coordination of Se comprises three bonds and three coordination linkages. The two different Se coordinations are depicted schematically in Figure 34. The differences between the structures of $Ph_3Se(NCS)$ and its Te analogue are more marked according to Ash and coworkers[228]. They are neither isomorphous, nor isostructural[231,233]. Dimers and polycyclic tetramers coexist in the unit cell of $Ph_3Te(NCS)$[231]. There are tetramers in $Ph_3Te(NCO)\cdot \frac{1}{2}CHCl_3$ [230]. The thiocyanate and cyanate anions occur both in end-to-end and terminally bridging positions in these structures. Te is present in both crystals as five- and six-coordinated atoms in distorted square-pyramidal and octahedral environments, respectively. Ph_3TeCl is dimeric in the crystal, with five-coordinated Te atoms[232].

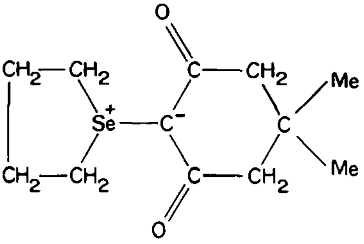
It is of interest to examine the effect of Se substitution on the benzene ring deformation. In $Ph_3Se(NCS)$ the mean value of the *ipso* endocyclic C—C—C bond angles from the three independently determined Ph geometries is 121.4° (see Table 22). This indicates an appreciable amount of ring deformation in the direction usually characteristic for markedly electronegative substituents.

The ylide resonance structures (75) of diacetylmethylenediphenylselenurane gained support from the XD determination of its molecular structure in the crystal[234]. The Se bond configuration is pyramidal with the Se atom lying 0.78 Å out of the plane of the three



(**75a**) (**75b**)

adjacent carbon atoms. The mean value of the three C—Se—C bond angles is 104.4°, but the three angles are considerably different. The smallest is the Ph—Se—Ph angle, viz. 100.8(3)°, not far from the C—Se—C bond angle in Me_2S (cf. Table 7). Noteworthy is the Se—C(alkyl) bond length, 1.906(8) Å, which is the same as the mean of the two Se—C(phenyl) bond lengths (1.912 Å). This is indeed the main indication that there is a large contribution from the ylide resonance structure **75b**. Similarly, and even more so, in **76** the Se—C bonds are longer and the Se atom lies further out of the adjacent CCC plane (by 0.91 Å). This structure was determined by X-ray crystallography by Saatsazov and coworkers[235]. Incidentally, the five-membered ring is non-planar and its geometrical parameters are consistent with those of the free tetrahydroselenophene molecule determined by ED (see Table 14).



(**76**)

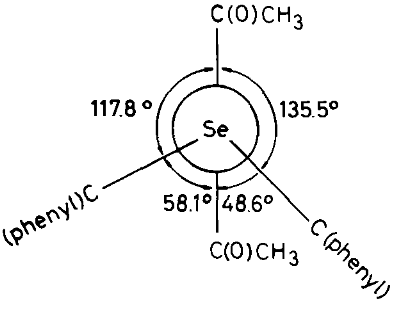


FIGURE 35. Conformation of molecule **75**, viewed along the Se—$C(C(O)CH_3)_2$ bond (after Reference 234)

The molecule **75** does not have exact C_s symmetry in the crystal[234]. The orientation of the two Ph groups is markedly different with respect to what would be the symmetry plane containing the Se atom and the acetyl acetonate moiety. Even the rotational form of the C_2Se—CC_2 skeleton about the Se—C bond is asymmetrical (Figure 35).

The two independently determined Ph geometries differ appreciably. One of them shows an elongation of the ring usually characteristic of substitution with an electropositive ligand. Possible Se and Te substituent effects upon the benzene ring deformation are discussed in the conclusion of this section.

There are two modifications of tetrakis (diphenylseleno) dimercury(I) diperchlorate $(Ph_2Se)_2HgHg(SePh_2)_2(ClO_4)_2$ (**77**), yellow and red. Both have been studied by X-ray crystallography[236,237]. The structural differences of the two modifications are pro-

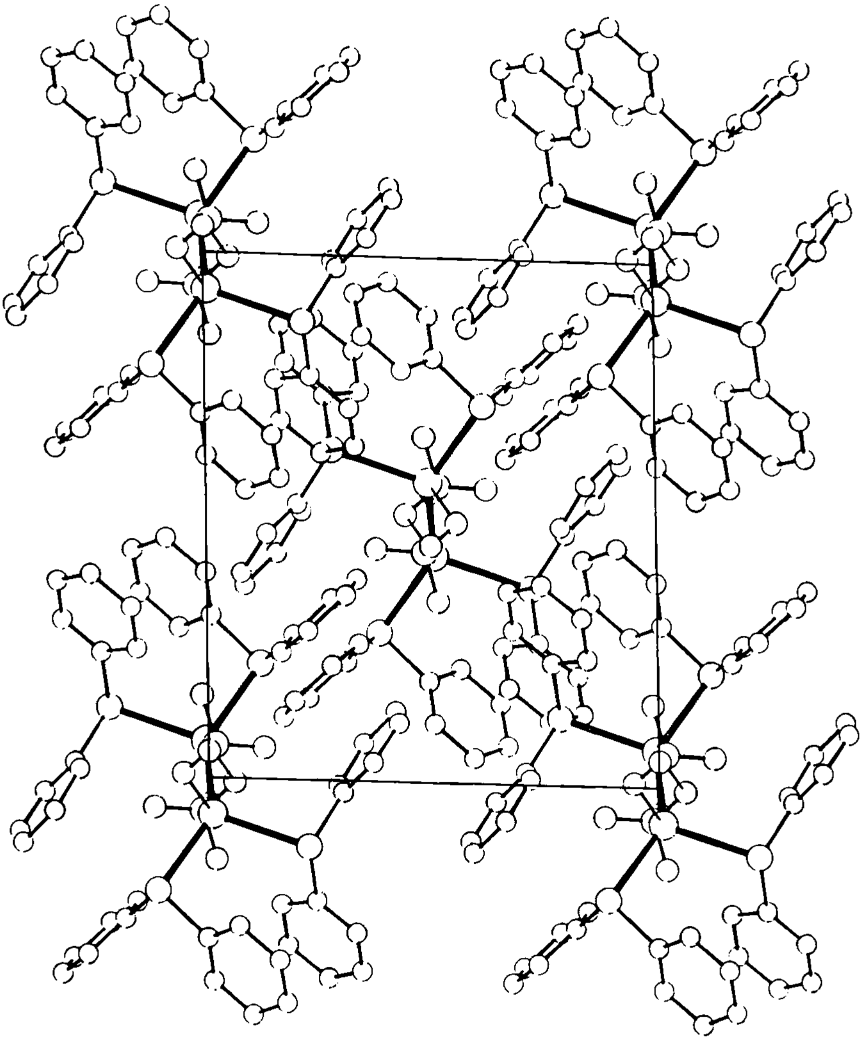


FIGURE 36(a)

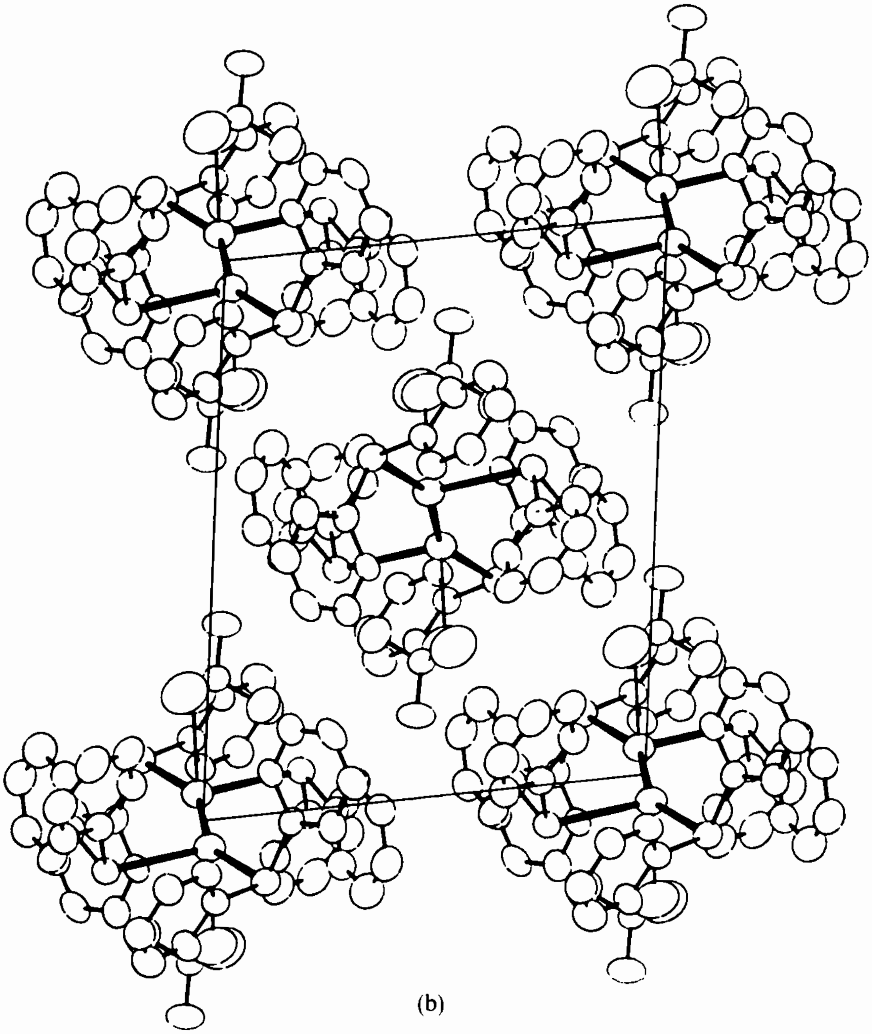


FIGURE 36. Packing of molecules in the crystals of **77**, viewed along direction (010): (a) yellow modification, (b) red modification. Reproduced by permission of the Verlag der Zeitschrift für Naturforschung from Reference 237

nounced in the Hg bond configuration. Although the $Se_2HgHgSe_2$ skeleton is coplanar in both, the Hg bond angles and the Hg—Se bond lengths change considerably. The Se bond configurations may also be somewhat different in the two modifications but large deviations of crystallographically non-equivalent bonds and angles prevent a meaningful discussion of the differences. The configurations are peaked pyramidal, the mean Se bond angles being about 101° in both structures.

The two modifications of **77** have markedly different molecular packing (Figure 36). The 'red' modification has nearly spherical molecular units, while the Ph groups are *sticking out* in the packing of the 'yellow' modification. Thus the most striking differences might be expected in the structures of the Ph groups. The ring sizes appear to be appreciably

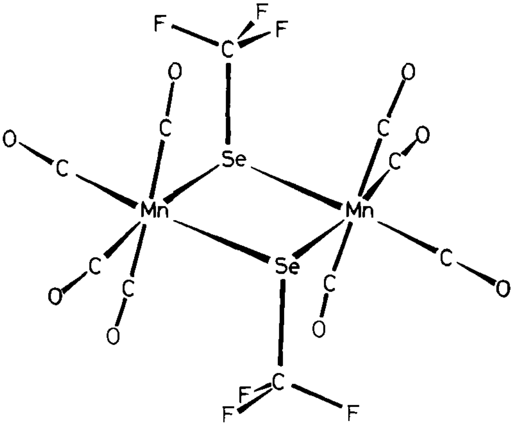


FIGURE 37. The molecular model of **78** (after Reference 238)

different, although the experimental errors are rather large. There are four independent pairs of Ph groups in each molecule, and the four mean C—C ring bond lengths have been reported for both modifications. The mean values of the respective four mean bond lengths are 1.403 Å (yellow) and 1.375 Å (red). Although the angular parameters for the benzene rings were not communicated, it is expected on this basis that considerable differences in the angular deformation also occur in the two modifications.

The structure of the $SeCF_3$ moiety of bis{μ[(trifluoromethyl)seleno]-manganesetetracarbonyl}, $[(CF_3Se)Mn(CO)_4]_2$ (**78**), (Figure 37) is of interest for our discussion. This molecular structure has been determined by XD[238]. The Se—C bond is 1.97 Å long. Noteworthy is the mean of the F···F dis-

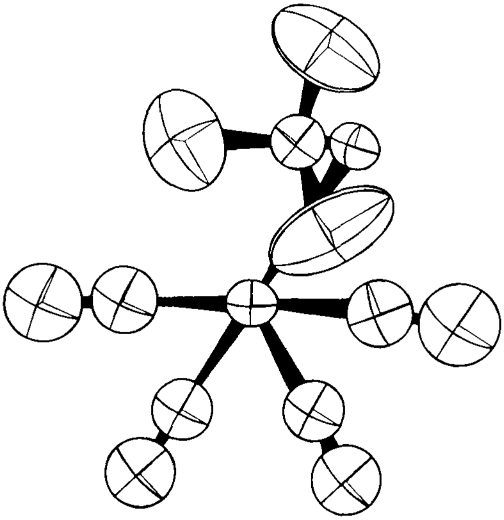


FIGURE 38. Thermal ellipsoids (50% probability level) of the atoms in the asymmetric unit of **78**. Reproduced by permission of Elsevier Sequoia S.A. from Reference 238

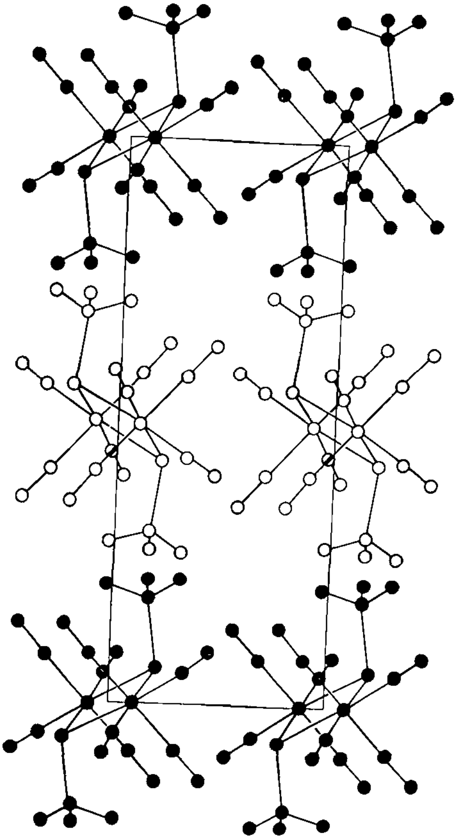
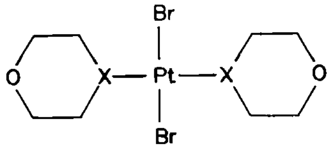


FIGURE 39. Crystal structure of 78 projected along the z axis. Reproduced by permission of Elsevier Sequoia S.A. from Reference 238

tances, referring to fluorines separated by one bond angle, is only 2.10 Å. They are markedly shorter than the mean value of 2.162 ± 0.008 Å found from a large series of free molecules containing CF_3 groups as was discussed in Section III.C. It is not obvious what may be the origin of this discrepancy. An apparent shortening of the C—F bonds may be a consequence of the librational motion. Figure 38 illustrates the thermal motion of the atoms in the asymmetric unit after Marsden and Sheldrick[238]. Packing considerations may also be of importance. The molecule possesses a crystallographic centre of symmetry, the asymmetric unit consisting of one half of one molecule. The molecules are arranged in layers. As for intramolecular interactions, the conformation adopted by the CF_3 groups appears to minimize the repulsion from the two CO groups on the same side of the $(MnSe)_2$ plane, cf. Figure 37. A fluorine may be almost equidistant from two carbons and two oxygens, thus non-bonded interactions seem to be of importance. There may also be non-bonded interactions between molecules. The shortest intermolecular contacts occur between oxygens and fluorines, viz. 2.84 Å within a layer and 3.03 Å between layers. The shortest intermolecular F ··· F non-bonded distances are 3.14 Å between layers. Figure 39 shows the crystal structure in projection down the z axis after Marsden and Sheldrick[238].

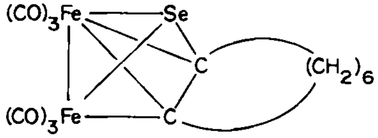


(79) X = S
(80) X = Se

The molecular structure of *trans*-dibromobis(1,4-oxaselenane) platinum(II) (**80**) has been determined by XD[239] along with that of *trans*-dibromobis(1,4-oxathiane) platinum (II)(**79**). In addition to the bond length changes, the largest angular change occurs in the C—Se—C versus C—S—C endocyclic bond angles. Some of the geometrical parameters in the two analogous molecules are:

	79		**80**
S—C	1.81(1) Å	Se—C	1.96(2) Å
	1.82(2) Å		1.86(4) Å
C—S—Pt	113.2(5)°	C—Se—Pt	110.5(7)°
	104.0(4)°		107.2(10)°
C—S—C	96.4(7)°	C—Se—C	90.8(13)°

The C—S—C bond angle in the thio derivative agrees well with the analogous angle in *free* 1,4-oxathiane, viz. 97.1(20)° as determined by ED[240]. 1,4-oxaselenane itself has not been investigated. The most interesting difference between the structures of **79** and **80** occurs in their conformations. Whereas the Pt—S bond is equatorial to the ring, the Pt—Se bond adopts an axial position (Figure 40). According to Barnes and coworkers[239] the difference cannot be explained by intermolecular packing considerations. It was also noted[239] that similar conformational differences have been observed.



(81)

The hexacarbonyl [μ-[1,2-η:2-η)-1-cyclooctene-1-selenolato(2–)-*Se*:*Se*]]diiron(*Fe–Fe*) molecule (**81**)[241] is interesting in that it contains iron–selenium bonds. The selenoketocarbene moiety establishes asymmetric bonding to the diironhexacarbonyl group. The Se

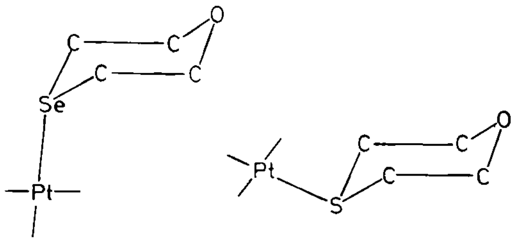


FIGURE 40. Axial and equatorial coordination of 1,4-oxaselenane and 1,4-oxathiane to Pt in complexes **80** and **79**, respectively

bond configuration is characterized by the following parameters:

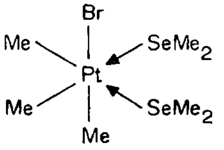
$$r(\mathrm{Se—C}) \quad 1.917(3)\,\text{Å} \quad \angle\,\mathrm{Fe—Se—Fe} \quad 64.1(0)^\circ,$$
$$\angle\,\mathrm{Fe—Se—C} \quad 77.1(1) \text{ and } 57.4(1)^\circ$$

The lengths of the iron–selenium bonds were determined to be 2.398(1) and 2.364(1) Å. Similarly, unequal iron–selenium bonds were found in another compound containing a selenaferrole ring[242].

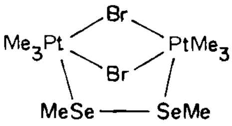
The trimethyltellurium ion, Me_3Te^+, is a discrete entity in the trimethyltelluronium tetraphenylborate, Me_3TeBPh_4(**82**), structure as has been determined by X-ray crystallography[243]. The Me_3Te^+ ion has a trigonal pyramidal geometry with approximate C_{3v} symmetry. It was presumed that the fourth tetrahedral site is occupied by the Te lone pair of electrons, similarly to Me_3TeCl, in which the electron density distribution has also been determined[244]. The geometry of the TeC_3 skeleton in **82** is characterized by the following mean parameters:

$$r(\mathrm{Te—C}) \quad 2.14(2)\,\text{Å} \quad \text{and} \quad \angle\,\mathrm{C—Te—C} \quad 92(1)^\circ$$

As there are no appreciable coordination linkages the lone pair of electrons may be expected to exercise its full stereochemical activity. The absence of secondary interactions has been ascribed to the non-coordinating character of the BPh_4^- ion. The mean value of the crystallographically independent Te—C bond lengths corresponds to the calculated single bond, and agrees well with Te—C bond lengths determined in other substances as well (for references see Reference 243). The C—Te—C bond angles appear slightly smaller than generally observed. This may be a consequence of the repulsion effect of the stereochemically fully active lone pair of electrons of Te. The lone pair may have somewhat diminished activity in other molecules due to secondary coordination.



(83)



(84)

Interesting structures, **83** and **84**, are produced when tetrameric bromotrimethylplatinum reacts with Me_2Se or Me_2Se_2, respectively[245]. **83** is supposed to have an octahedral bond configuration about the central Pt atom. It has been investigated by ^{1}H-NMR spectroscopy. The structure of **84** was determined by XD[245]. The Se—Se bond length is 2.36(1) Å, slightly larger than in open-chain diselenides discussed in Section III.B. The mean of the C—Se—Se and C—Se—Pt bond angles is 99(2)°. The Pt atoms retain an approximate octahedral coordination. The Pt_2Br_2 four-membered ring is puckered, the dihedral angle BrPtBr/BrPtBr is 29°. An ^{1}H-NMR investigation of **84** revealed an atomic inversion process in which the two Se atoms were exchanged. The activation energy was determined to be 64.5(62) kJ mol^{-1} [245].

Abel and coworkers[246] have studied the various structural factors governing the energy barriers to inversion of three-coordinated Se and S. In a typical investigation, a complex, $[ReI(CO)_3\{MeSe(CH_2)_2SeMe\}]$ (**85**), was prepared, its crystal and molecular structure (Figure 41) was determined by XD and the energy barrier associated with the pyramidal inversion at the three-coordinated Se atom was calculated by means of total band-shape dynamic NMR spectroscopic methods[246]. The geometrical parameters characterizing the selenium–carbon bonding systems are listed below:

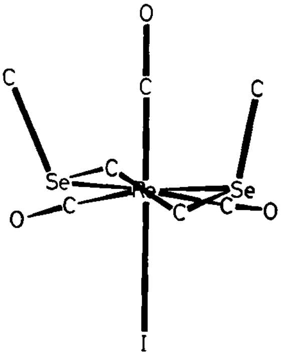


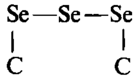
FIGURE 41. The molecular model of **85** (after Reference 246)

Se—CH_3	1.946(11) Å	CH_2—Se—CH_3	96.8(5)°
	1.991(11) Å		97.5(5)°
Se—CH_2	1.970(9) Å	Re—Se—CH_2	102.3(3)°
	1.989(9) Å		100.9(3)°
		Re—Se—CH_3	107.7(4)°
			108.9(4)°

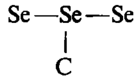
The mean Se—C bond length in the ring is slightly greater than the mean exocyclic Se—C bond length. Concerning the inversion barriers, the following statements can be made[246]: (1) The inversion barriers at Se are higher than those at analogous S. (2) Changing the halogen in the *cis* position to the inverting centre has negligible effect on the overall barrier height. (3) The nature of the metal–Se (S) bond is of great importance for the barrier heights. (4) Substituting the aliphatic backbone of the ligand by an unsaturated backbone lowers the inversion barrier. The lowering is smaller for S inversion than for Se inversion. This change was ascribed to (p–p)π conjugation between the chalcogen lone pair of electrons and the ligand backbone during the inversion. It was suggested that the (3p–2p)π sulphur–carbon conjugation was more effective than the (4p–2p)π selenium–carbon conjugation.

Three-coordinated Se and Te may have a planar T-shaped bond configuration. Such cases will be reviewed next.

Structures of crystals containing the tris(selenourea), $[SeC(NH_2)_2]_3{}^{2+}$, ion have been determined from visually estimated photographic[247] and diffractometer[35] X-ray data. Crystals of $[SeC(NH_2)_2]_3Cl_2 \cdot H_2O$(**86**) and $[SeC(NH_2)_2]_3Br_2 \cdot H_2O$(**87**) are isomorphous, orthorhombic[247], Pbca; the sulphate, $[SeC(NH_2)_2]_3SO_4 \cdot SeC(NH_2)_2 \cdot 2H_2O$ (**88**), is triclinic[35], $P\bar{1}$ and contains a solvate selenourea molecule. The cation geometry is similar in the three salts (Figure 42). All selenourea groups, including the uncomplexed solvate molecule in **88**, are nearly planar. The selenourea planes of the cation are nearly perpendicular to the approximately linear Se—Se—Se sequence, and are thus nearly parallel to each other: the central plane makes dihedral angles of 5–18° with the terminal planes. The two terminal Se—C bonds are nearly coplanar, and the dihedral angle between the least-squares planes of the atoms


$$\begin{array}{ccccc}\mathrm{Se} & — & \mathrm{Se} & — & \mathrm{Se}\\ | & & & & |\\ \mathrm{C} & & & & \mathrm{C}\end{array}$$

and


$$\begin{array}{ccccc}\mathrm{Se} & — & \mathrm{Se} & — & \mathrm{Se}\\ & & | & & \\ & & \mathrm{C} & & \end{array}$$

respectively, is about 75°. This conformation of the tris(selenourea) cation (Figure 42)

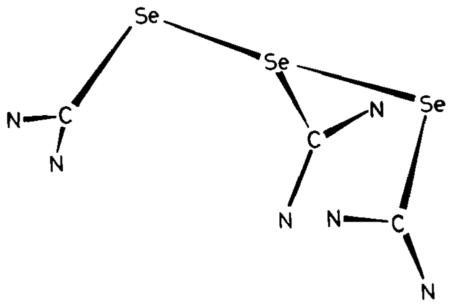


FIGURE 42. The 'easel' shape of the tris(selenourea) cation. Drawn from the atomic coordinates given in Reference 35

resembles the 'easel' shape of the triselenocyanate, $(SeCN)_3^-$ anion, whose dihedral angle is smaller, viz. 44, 57 and 65° in the crystals of the Cs[248], K[249] and Rb salts[250] (see also Reference 4). As to the Se—Se—Se moiety, it is only slightly bent in the triselenocyanate ions with angles of 176–178° while it is more bent in the tris(selenourea) ions, which have Se—Se—Se angles of 173.8° in the dichloride (**86**)[247] and dibromide (**87**)[247] and 168.3° in the sulphate (**88**)[35]. The latter differs from **86** and **87** also in the direction of bending.

The average bond angles (deg.) at the Se atoms of the tris(selenourea) group are as follows:

	86[247]	**87**[247]	**88**[35]
Se—Se—C(terminal)	96.4	96.4	98.0
Se—Se—C(central)	89.1	89.2	86.2

They are similar to those found in the triselenocyanate ion[4,248–250]. The crystallographically different Se—Se bond lengths (Å) are the following:

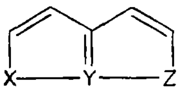
	86	**87**	**88**
Se—Se	2.597(2)	2.624(2)	2.6336(15)
Se—Se	2.717(2)	2.712(2)	2.6639(15)

and the lengths (Å) of the Se—C bonds in the same order:

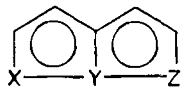
Se—C(terminal)	1.921(8)	1.921(12)	1.903(5)
Se—C(central)	1.940(8)	1.947(12)	1.925(4)
Se—C(terminal)	1.905(8)	1.906(12)	1.903(5)

The central Se—C bond in the tris(selenourea) ion is longer than the terminal Se—C bonds. A similar observation was made for the chalcogen–carbon bonds in trithiapentalenes and analogues[251] (see below). A comparison with triselenocyanates is not feasible because of large estimated errors in the parameters of the latter. There is asymmetry in the Se—Se and terminal Se—C bonds of the tris(selenourea) ion. The longer Se—C bond belongs to the shorter Se—Se bond, although differences in terminal Se—C lengths are hardly significant. Selenium–carbon bonds seem to have a certain amount of double-bond character (cf. Table 7) and are longer than this bond, 1.867(4) Å, in the solvate selenourea molecule in the crystals of **88**. The selenium–selenium bonds are longer than single bonds (see Tables 11 and 12), similarly to those in triselenocyanates[4,248–250] and triselenapentalenes.

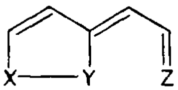
Trithiapentalenes and related systems contain a three-coordinated, formally tetravalent chalcogen atom Y (**89a**), which is involved in a three-centre four-electron bond in the roughly linear chain of atoms X—Y—Z. Form **89b** reflects the delocalized system of ten π



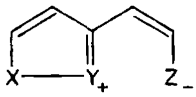
(89a)



(89b)



(89c)

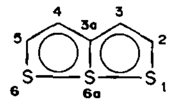
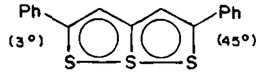
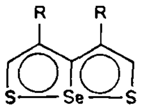
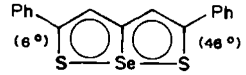
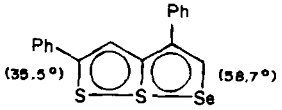


(89d)

electrons in the nearly planar bicyclic molecule, while asymmetric forms like **89c** or **89d** indicate its dynamic properties. Compounds of this type have been extensively studied since their discovery 25 years ago. (See Reference 252 for references to reviews.) Bond length data of Se and Te, as well as O and S atoms in such heteropentalene molecules are compiled in Table 21 from X-ray crystallographic investigations. Some S analogues are also included for comparison. The molecular structures of two compounds have been determined in the gas phase: 1,6,6a-trithiapentalene (**90**) was studied by electron diffraction[266] and 1,6-dioxa-6a-thiapentalene by microwave spectroscopy[267].

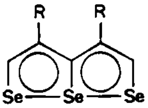
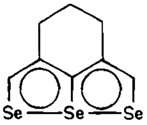
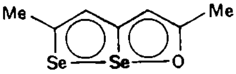
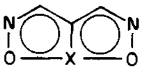
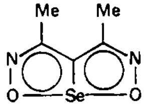
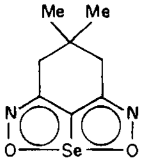
Chalcogen–chalcogen bonds in these systems are longer than normal covalent single bonds, and the relative lengthening diminishes from S to Te[263]. This is in accord with observed ESCA line widths[268,269] and results of CNDO/2 calculations[269]; namely, the total energy of **90** as a function of the displacement of the central S atom (6a) between its fixed neighbours S(1) and S(6) has a rather flat minimum, roughly 0.3 Å wide, about the symmetric position[269,270]. This potential well is much narrower[269] when a Se atom takes

TABLE 21. Bond lengths (Å) of chalcogen atoms in trithiapentalenes and analogues from XD

Molecule		Bond					Reference
		(5)–(6)	(6)–(6a)	(3a)–(6a)	(6a)–(1)	(2)–(1)	
	(90)	1.684(3)	2.363(1)	1.748(3)	2.363(1)	1.684(3)	251, 253
	(91)[a]	1.703(6)	2.304(3)	1.753(6)	2.362(3)	1.712(6)	254
	(92) R = H	1.66(2)	2.446(5)	1.95(2)	2.446(5)	1.66(2)	255
	(93) R = Me	1.691(3)	2.414(1)	1.917(3)	2.414(1)	1.69.1(3)	256
	(94)[a]	1.72(1)	2.419(3)	1.87(1)	2.433(3)	1.71(1)	257
	(95)[a]	1.69(1)	2.492(3)	1.71(1)	2.333(3)	1.82(1)	258

(*Contd.*)

TABLE 21. (*Contd.*)

Molecule		Bond					Reference
		(5)–(6)	(6)–(6a)	(3a)–(6a)	(6a)–(1)	(2)–(1)	
	**(96)** R = H	1.86(3)	2.586(3)	1.90(2)	2.579(3)	1.81(3)	259
	(97) R = Me		2.542(6)				260
	**(98)**	1.78(2)	2.568(3)	1.91(2)	2.554(3)	1.82(2)	261
	**(99)**	1.848(15)	2.384(3)	1.881(15)	2.336	1.22	262
	**(100)** X = S	1.353(5)	1.853(3)	1.683(4)	1.850(3)	1.347(5)	263
	(101) X = Se	1.32(1)	1.987(7)	1.827(8)	1.997(6)	1.34(1)	263
	(102) X = Te	1.36	2.094	1.980	2.080	1.39	263
	**(103)**		1.942(6)				264
	**(104)**	1.337(14)	2.017(9)	1.802(11)	2.030(9)	1.346(14)	265

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[a] Dihedral angles of the Ph rings with the heterocyclic plane are given.

the role of the 'bell-clapper'—as this kind of vibrational motion is called. A double-minimum potential was used, on the other hand, to interpret the electronic spectrum[271], and was also obtained form EHT calculations without using sulphur 3d orbitals[272]. Inclusion of d orbitals yields, however, a broad single-minimum potential[272]. Unfortunately neither XD[273] nor ED could distinguish the two cases of (1) a flat potential well with a single minimum (symmetric equilibrium structure) and (2) a potential with a small hump in the middle (asymmetric equilibrium structure). The MW study of 1,6-dioxa-6a-thiapentalene unambiguously gave a symmetric model[267].

These weak bonds are of course sensitive to changes in their intra- and inter-molecular environment. CNDO/2 calculations have shown that a Me substituent on C(2) causes a lengthening of the distance S(1)—S(6a) but a shortening arises from a 3-Me substitution[270,274]. The influence of a Ph group depends also on its dihedral angle with the plane of the heterocyclic rings[270]. These results are in agreement with structural data on trithiapentalenes[270] and with bond lengths given in Table 21. The scarcity of data and diversity of heteroatoms in Se- or Te-containing pentalenes (Table 21) make it difficult, however, to observe clear trends in the geometrical changes in these molecules. It seems from a comparison of pairs **90** and **91** versus **92** and **94** that Ph substituents have a smaller effect on S—Se bonds, in accord with the narrower potential well, than on S—S bonds. Similar statements cannot be made about other substituents or other sequences of heteroatoms.

The central carbon–sulphur bonds are longer than the terminal ones in a number of trithiapentalenes[251], and this is the case in **90**,**91**,**96** and **98** (Table 21). Bond angles of chalcogen atoms do not seem to be very characteristic and seem to be determined mainly by the geometry of the rest of the ring, e.g. by the carbon–chalcogen bond distances. Just a few bond angles at terminal and central chalcogen atoms should be listed here for rough orientation (mean values when there is asymmetry):

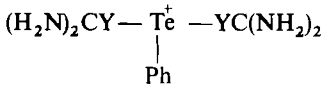
	terminal (deg.)		central (deg.)	
90	C—S—S	92.0(1)	C—S—S	89.1(1)
96	C—Se—Se	88.5	C—Se—Se	88.0
100	N—O—S	113.3	C—S—O	85.9
101	N—O—Se	113.2	C—Se—O	82.2
102	N—O—Te	115	C—Te—O	77.0

It has been noted that the central C—C bonds in trithiapentalenes are longer than the terminal C—C bonds, a feature that resembles the structure of naphthalene, which is also a fused ring system with ten π electrons[251]. A few examples of C—C bond lengths are:

	terminal (Å)	central (Å)
90	1.354(3)	1.409(2)
92	1.35(3)	1.41(3)
96	1.37(mean)	1.41(mean)

In 2,5-dimethyl-1-oxa-6,6a-diselenapentalene (**99**), on the other hand, C—C bond lengths alternate as in a conjugated system, viz. 1.36(3), 1.42(3), 1.34(3) and 1.43(3) Å, continued with the C—O bond of 1.22 Å length[262].

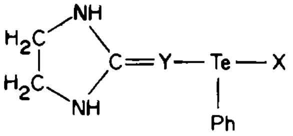
The molecular structures of a series of phenyltellurium derivatives with three-coordinated Te have been determined by Vikane and associates[277–280] using XD, following earlier work by Foss and coworkers[275]. In both phenylbis(thiourea)tellurium (**105**) chloride[210] and phenylbis(selenourea)tellurium (**106**) chloride[210] (cf. **61**) the Te is three-coordinated being bonded to a Ph group and two chalcogen atoms. The S(Se)—Te—S(Se) bonding system is essentially linear and the Te—Ph bond nearly bisects this three-centre arrangement[276]. There is an important difference in the Te coordination in the two structures[210]. In the Se derivative the Te is strictly three-coordinated as the chloride ion is removed into a position that may be considered independent from it. On the other hand, in the thio derivative the chloride approaches the fourth coordination site in what may be considered as a square planar arrangement about Te.



$$(H_2N)_2CY-\underset{\displaystyle Ph}{\overset{+}{Te}}-YC(NH_2)_2$$

(**105**) Y = S
(**106**) Y = Se

In ethylenethiourea(iodo)phenyltellurium (**107**)[277] and ethyleneselenourea(iodo)-phenyltellurium (**108**)[277] each Te atom is strictly three-coordinated with nearly planar bond configuration.



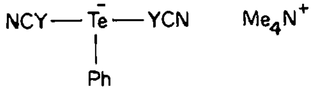
(**107**)	Y = S,	X = I
(**108**)	Y = Se,	X = I
(**109**)	Y = S,	X = Br
(**110**)	Y = Se,	X = Br
(**111**)	Y = S,	X = Cl

Crystals with two different space groups may occur when the 1:1 complex of benzenetellurenyl bromide and ethylenethiourea crystallizes yielding bromo(ethylenethiourea)phenyltellurium (**109**). The crystal and molecular structures of both modifications have been determined and a series of interesting differences in packing and conformation have been noted[278] (Figures 43 and 44). Most of the bond lengths and bond angles in the two modifications cannot be considered to be significantly different with the striking exception of the Te—Br bond being 2.8348(10) and 2.9694(10) Å in the two crystals, respectively.

Bromo(ethyleneselenourea)phenyltellurium (**110**) has only one (known) crystal modification[279] being isomorphous with one ($P2_1/c$) of the two above mentioned forms of its thio analogue. Incidentally, the Te—Br bond in this compound is considerably longer, viz. 3.0537(16) Å, than in either of the two modifications of **109**. While this bond shows great sensitivity, the Te—C(phenyl) bond appears to be remarkably constant (see below). The structure of **110** is characterized by three-coordinated Te, with the Te—C bond nearly perpendicular to the Br—Te—Se chain.

The structure of chloro(ethylenethiourea)phenyltellurium (**111**)[279] is analogous in all essential respects to that of **110**.

The crystal molecular structures of tetramethylammonium phenyl(dithiocyanato)tellurate (**112**) and phenyl(diselenocyanato)tellurate (**113**) have been determined by Hauge and Vikane[280]. The crystals are isomorphous, monoclinic (space group C2/c). The Te bond configuration is regarded as square-planar with one position, *trans* to the Ph ligand, vacant. The Te—C(phenyl) is perpendicular to the S(Se)—Te—S(Se) chain. The latter itself is nearly linear. This description quite generally characterizes the above-described three-coordinated complexes of divalent Te.



$$NCY-\underset{\displaystyle Ph}{\overset{-}{Te}}-YCN \qquad Me_4N^+$$

(**112**) Y = S
(**113**) Y = Se

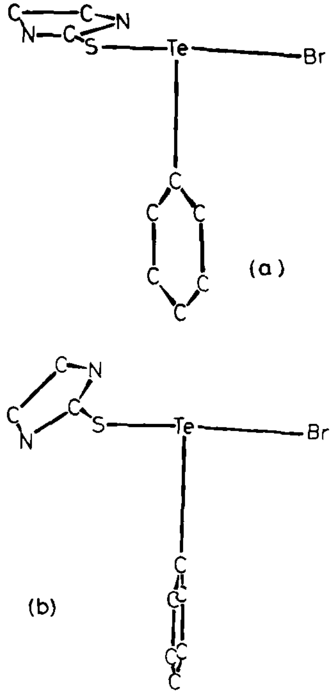
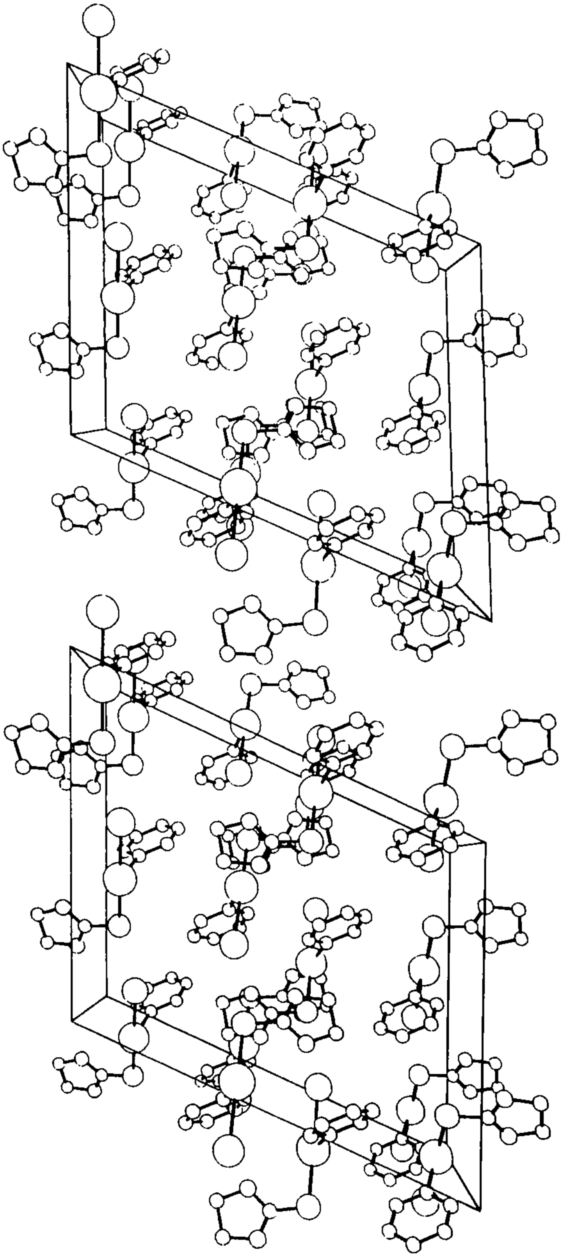


FIGURE 43. Molecular models of **109** in the two crystallographic modifications (a) space group C2/c, (b) space group $P2_1/c$ (drawn after Reference 278)

Among the structures discussed in this section, three Se derivatives and several Te derivatives contain bonding to a Ph group. The lengths of the Se—Ph and Te—Ph bonds are collected in Tables 22 and 23, respectively. Parameters characterizing the deformation of the benzene rings are also given, viz. the *ipso* endocyclic C—C—C angle (α), the mean value of the ring C—C bond distances, and the difference of bond lengths, C(2)—C(3) minus C(1)—C(2), where C(1) is the Ph carbon adjacent to the substituent (Se or Te). Using the covalent radii of two-coordinated Se and Te given in Table 10, the estimated single bond lengths are r(Se—C) = 1.93 Å and r(Te—C) = 2.12 Å, without using electronegativity corrections. According to Tables 22 and 23 the experimentally determined Se—C and Te—C bond lengths are remarkably stable from compound to compound and stay around the values estimated for the single bonds. Where there are crystallographically independent Ph groups in the same structure, and this notably occurs in the Se derivatives, considerable variations are observed. Here again, though, the mean values fall very much in line, viz. 1.923, 1.927 and 1.912 Å for the three Se compounds listed in Table 22. As there is a relatively large series of Te derivatives, it seems worth mentioning that the mean Te—C bond length for the nine compounds listed in Table 23 is 2.114 Å with a standard deviation of 0.010 Å.

Considering all the crystallographically independent Ph groups in the Se derivatives, there seems to be some indication for a possible correlation between the bond length of the substituent to the Ph group and the *ipso* endocyclic C—C—C angles which is known to be the most characteristic of all the parameters related to the benzene ring deformation[281]. Figure 45 shows that with increasing Se—C(phenyl) bond length there may be an increase in the *ipso* endocyclic C—C—C bond angle of the Ph group. The sample is too small to



(a)

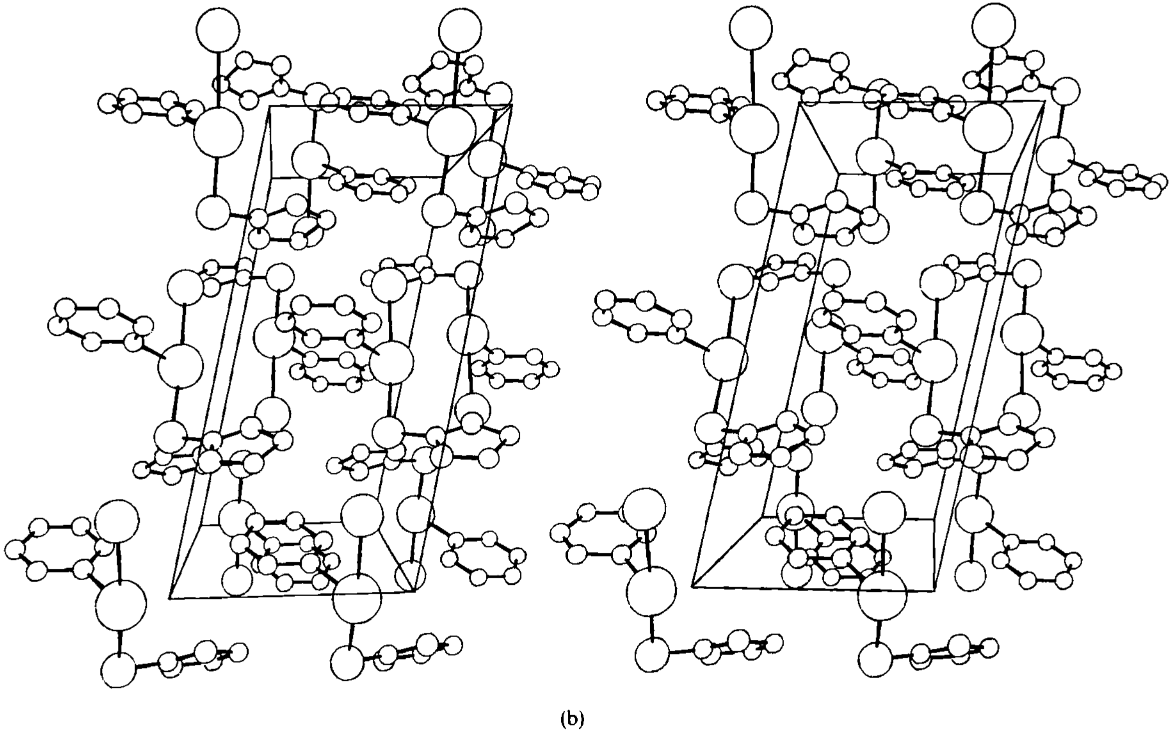


FIGURE 44. Stereoscopic view of crystal packing, seen along the *b* axis, in the two modifications of **109**: (a) space group C2/c, (b) space group $P2_1/c$. Reproduced by permission of Acta Chemica Scandinavica from Reference 278.

TABLE 22. Se—C(phenyl) bond lengths and the characterization of the benzene ring deformation in three-coordinated complexes of divalent Se from XD

Compound	Se—C(Ph) (Å)	α[a] (deg.)	⟨CC⟩[b] (Å)	ΔCC[c] (Å)	Reference
$Ph_3Se(NCS)$	1.936(4)	122.5(4)	1.370	0.020	228
	1.904(5)	119.8(5)	1.369	−0.005	
	1.928(4)	121.8(4)	1.377	0.002	
$Ph_3SeCl \cdot 2H_2O$	1.911(10)	121.6(9)	1.386	0.019	229
	1.936(12)	121.6(11)	1.378	0.038	
	1.934(11)	121.3(10)	1.378	0.000	
75	1.898(9)	118.5(8)	1.382	−0.002	234
	1.926(9)	120.7(8)	1.378	0.002	

[a] Endocyclic C—C—C bond angle adjacent to the substituent.

[b] Mean value of the C—C bond lengths in the Ph group.

[c] Mean value of the differences of bond lengths C(2)—C(3) minus C(1)—C(2) and C(5)—C(6) minus C(6)—C(1), where C(1) is the Ph carbon atom adjacent to the substituent.

TABLE 23. Te—C(phenyl) bond lengths and the characterization of the benzene ring deformation in three-coordinated complexes of divalent Te from XD

Compound	Te—C(Ph) (Å)	α[a] (deg.)	⟨CC⟩[b] (Å)	ΔCC[c] (Å)	Reference
105	2.102(7)	120.2(8)	1.400	0.022	210
106	2.129(6)	122.0(6)	1.397	0.020	210
107	2.124(6)	122.4(5)	1.398	0.017	277
108	2.112(7)	120.1(6)	1.408	−0.020	277
109[d]	2.116(3)	119.6(3)	1.384	0.000	278
	2.123(4)	120.0(4)	1.379	0.011	278
110	2.118(7)	119.2(7)	1.382	0.018	279
111	2.120(2)	118.6(2)	1.373	−0.001	279
112	2.104(5)	119.0(5)	1.378	−0.020	280
113	2.100(6)	120.2(6)	1.381	0.033	280

[a,b,c] See footnotes to Table 22.

[d] Crystallizes in two different space groups.

give much credibility to this correlation, although in a formal sense it is consistent with expectation: If we have a C_6H_5—XY_n system, a lengthening of the C—X bond may be associated with the electron-withdrawing character of the XY_n ligand. At the same time, the presence of a more electronegative ligand is expected to increase the *ipso* endocyclic C—C—C angle. The available data may not be adequate for examining such subtle effects as the case is here. On the other hand, due to various circumstances some important systematic errors may cancel in this series of parameters. The changes depicted in Figure 45 cannot originate from electronic effects, but rather from steric ones as various C_6H_5Se moieties occur in different environments. Even if the correlation is not spurious, in any case this is as far as we can stretch our desire to find substituent effects upon benzene ring deformation in these compound series, relying upon the available data. Even that much indication for correlation cannot be established for the larger sample of the Te derivatives. This in itself is not surprising as the changes in the Te ligands in the series examined are expected to influence appreciably the nature of the Te as a benzene substituent.

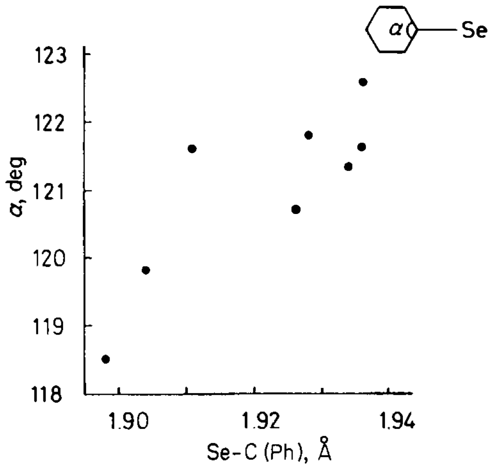


FIGURE 45. Variation of the Se—C(phenyl) bond length and the *ipso* endocyclic C—C—C angle (α) of the benzene ring. See Table 22 for data and references

V. FOUR-COORDINATED SELENIUM AND TELLURIUM

With four-coordinated Se or Te only crystal-phase molecular structures have been determined. The typical bond configuration of the metal is trigonal bipyramidal, made up from four bonds to various ligands and one lone pair of electrons. The systems are of the AX_4E type where A is the central atom, Se or Te, X are ligands and E is a lone pair of electrons. The lone pair invariably occupies one of the equatorial sites (Figure 46). This configuration is in complete agreement with the VSEPR model[28]. It will be of interest to examine structural variations from the point of view of the applicability of the VSEPR model. It has been demonstrated recently[282] that while testing the applicability of the

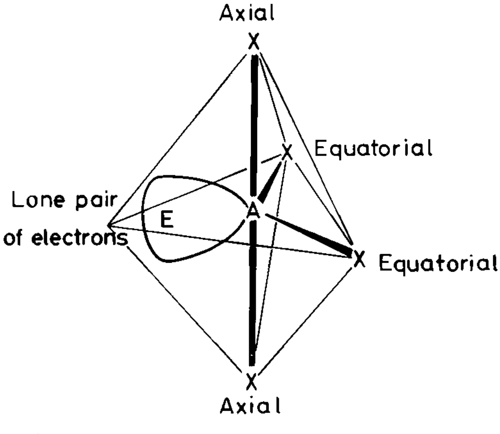


FIGURE 46. The trigonal bipyramidal configuration of an AX_4E-type molecule

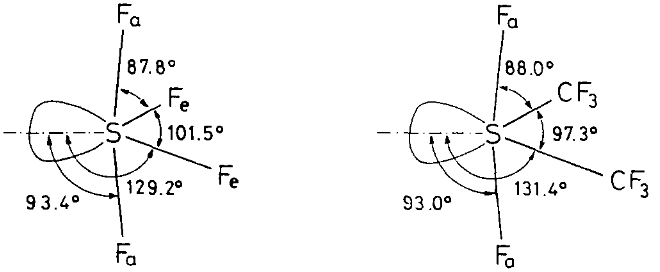


FIGURE 47. Bond angles of the central S atom in SF_4[283] and $(CF_3)_2SF_2$[284]

VSEPR model, all angles of all electron pairs about the central atom have to be examined rather than the bond angles only. Thus, for example in the equatorial plane of the AX_4E bond configuration, there are two E—A—X angles and one bond angle X—A—X. Obviously the two E—A/A—X lone-pair/bond interactions are more important than the single A—X/A—X bond/bond interaction. Fortunately, in this system the angles made by the lone pair can easily be calculated from the bond angles by virtue of symmetry. Comparison of the SF_4 and $(CF_3)_2SF_2$ structures demonstrates the utility of the approach suggested above (Figure 47). As the fluorines in the equatorial positions are substituted by the less electronegative CF_3 groups, the change in the bond angles in themselves would indicate incompatibility with the VSEPR model. The decisive factor, however, is the lone-pair/bonding-pair interactions in the equatorial plane in complete agreement with the VSEPR model.

It has been suggested[285] that the quadruple average angle of the lone pair, α_4^E, be considered as a measure of its generalized space requirement. This angle is the mean of the four angles made by the lone pair in the AX_4E configuration. It has been observed to be fairly constant in such structures in spite of the sometimes considerably varying bond angles. An example is shown by the series of SF_4, OSF_4 and $H_2C{=}SF_4$ molecules in Figure 48. The quadruple average angle will be especially useful in our discussion as in many structures the non-equality of the equatorial ligands will prevent the calculation of the individual E—A—X angles.

In an ideal trigonal bipyramidal structure the two axial bonds are colinear and the equatorial bond angles are 120°. Due to the relatively large space requirement of the lone

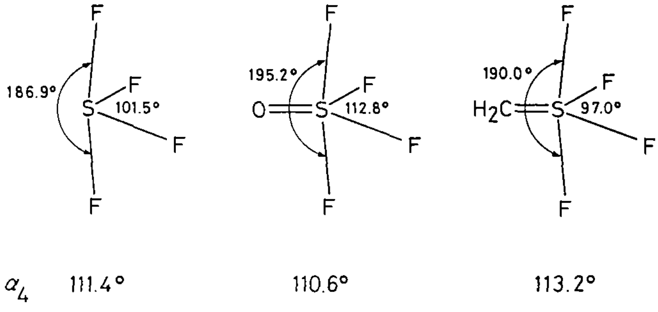
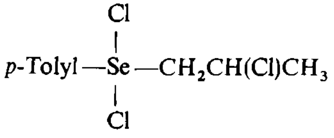


FIGURE 48. Bond angles and the quadruple average angle[285] (α_4) of the lone pair, the O=S and C=S bonds in SF_4[283], OSF_4[286] and $H_2C{=}SF_4$[287], respectively

pair of electrons the angle between the two axial bonds is usually smaller than 180° and the equatorial bond angle is smaller than 120°. For the ideal arrangement the quadruple average angle of an equatorial bond would be 105°. The lone pair of electrons has usually considerably larger quadruple average angles.

Relatively low accuracy was achieved in the X-ray diffraction investigation[288] of dichloro(2-chloropropyl)-*p*-tolylselenium(IV) (**114**). The equatorial

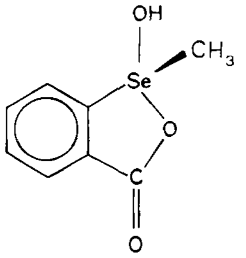


$$p\text{-Tolyl}-\overset{\text{Cl}}{\underset{\text{Cl}}{\text{Se}}}-CH_2CH(Cl)CH_3$$

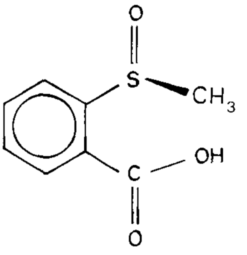
(**114**)

C—Se—C angle was found to be 102° while the two axial Se—Cl bonds were reported to be colinear. This does not agree with general experience. The quadruple average angle of the Se lone pair, α_4^E(Se) is 109.5° according to the reported bond angles, which is much too low as compared with similar structures where a typical value would be about 112°. This may indicate that as much as even 10° deviation from linearity might be expected for the Cl—Se—Cl skeleton.

The crystalline molecular structure of *o*-carboxyphenyl methyl selenoxide (**115**) was studied together with its S analogue (**116**)[289]. The two compounds show very similar atomic positions, but there are important differences in their structures as is already apparent in the structural formulae below. There is a ring closure in the Se derivative (see



(**115**)



(**116**)

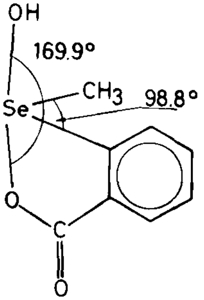
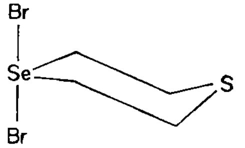


FIGURE 49. The Se bond angles in 115[289]

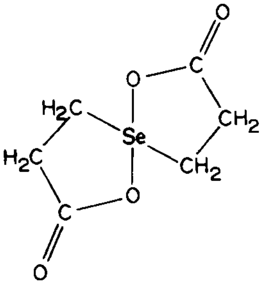
Figure 49) with an Se—O linkage of 2.378 Å length. The selenium–carbon(Me) bond, 1.941(6) Å, is only slightly longer than the selenium–carbon(Ph) bond, 1.928(3) Å. For the S analogue the difference in the two analogous bonds is of the opposite sign, but considering the experimental errors they cannot really be distinguished. The bond configuration about S in **116** is very much the same as in dimethyl sulphoxide[290]. The selenium–oxygen bond, 1.774(3) Å, is nearer to a single bond than to a double bond. The calculated single Se—O bond would be 1.82 Å whereas the Se═O bond in $SeOCl_2$ is 1.614(5) Å[225]. The quadruple average angle of the Se lone pair, $\alpha_4^E(Se)$, is 112.8°.

The quadruple average angle, $\alpha_4^E(Se)$, is 110.0°, somewhat small, for 1-thia-4-selenacyclohexane 4,4-dibromide (**117**)[291] with Br—Se—Br 175.1(1)° and C—Se—C 105(1)°.

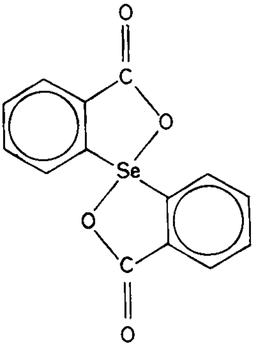


(**117**)

The Se bond configurations are essentially the same in 4,4′-spirobi(4-selena-4-butanolide)(**118**)[292] and 3,3′-spirobi(3-selenaphthalide)(**119**)[293]. In both compounds the two halves of the molecules are related by a two-fold axis. The angles about the Se atom in **118** and **119** are shown in Table 24. The Se–methylene bond in **118** is somewhat longer than the Se–phenylene bond in **119**: Se—C(methylene) = 1.959(3) Å, Se—C(phenylene) = 1.930(1) Å, whereas the Se—O bonds are the same, viz. 1.974(3) Å in **118** and 1.968(7) Å in **119**.



(**118**)



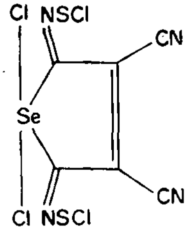
(**119**)

In 1,1-dichloro-2,5-bis[*N*-(chlorothio)imino]-3,4-dicyano-1,1,2,5-tetrahydroselenophene (**120**)[294] the relatively small endocyclic Se bond angle C—Se—C, 86.4(2)°, is the origin of the relatively large E—Se—C angle and consequently of the large quadruple average angle $\alpha_4^E(Se)$, 115.0°. In free selenophene[20,143] the C—Se—C angle is slightly larger, 87.8(2)°, as determined by MW. The Se—C bond of the four-coordinated arrangement is much longer, viz. 1.970(3) Å, than in selenophene itself, 1.855(2) Å. Wudl and Zellers[294] noted some unusual features of the molecular packing in the crystal. Whereas the related **121** forms head-to-tail sheets[295] (Figure 50a) the head-to-head ordering (Figure 50b) of **120** results in rather short intermolecular Cl···Cl contacts.

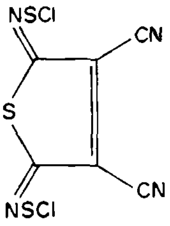
TABLE 24. Angles (deg.) about the Se atom in spiro compounds **118** and **119** from XD[a]

Angle	$\mathbf{118}^{292}$	$\mathbf{119}^{293}$
E—Se—O	93.8	93.8
E—Se—C	129.2	129.2
O—Se—O	172.4	172.4
C—Se—C	101.5	101.0
α_4^E(Se)	111.5	111.6

[a] Angles involving the lone pair of electrons (E) have been calculated from bond angles by virtue of symmetry. The estimated standard deviations for the bond angles are 0.3°.



(120)



(121)

There is a relative abundance of data on four-coordinated organic Te derivatives. The Te bonds again show the typical features of the trigonal bipyramidal configuration, taking also the Te lone pair of electrons into consideration.

Dimethyltellurium tetraiodide, Me_2TeI_4 (**122**), is in fact dimethyltellurium diiodide-diiodine(1/1), an adduct of Me_2TeI_2 with I_2, linked by I···I bonds[296]. One of the I atoms of a Me_2TeI_2 molecule participates in this bonding and it is connected to two I_2 molecules (Figure 51). An I_2 molecule, on the other hand, forms a linear I···I—I···I bridge between two Me_2TeI_2 molecules as part of a zig-zag chain of I atoms. There are also two weak intermolecular Te···I contacts and, accordingly, the Te coordination may also be described as distorted octahedral. Figure 52 gives the bond angles about Te and the angles made by the lone pair of electrons. The distortion from the ideal trigonal bipyramidal arrangement is very well interpreted by the VSEPR model[28,282,296]. An alternative description of the bonding of Te has also been advanced by Pritzkow[296] by considering only s and p orbitals. Huheey[297] has recently shown the consistency of the VSEPR model and Bent's rule involving the p and s character in bonding for simple trigonal bipyramidal systems, even taking the directional effects[298] into consideration. Incidentally, the quadruple average angle of the Te lone pair of electrons, α_4^E(Te), is 112.1°, which seems to be in the region of typical values for well determined structures. The two axial Te—I bonds have strikingly different lengths in **122**. The bond to I that has intermolecular contacts with other I_2 molecules (cf. Figure 51) is much longer, 3.082(2) Å, than the other bond, 2.809(2) Å. Even this latter is considerably longer than what would correspond to the sum of the covalent radii (2.70 Å).

A similar bond configuration was found in an adduct (**123**) of tellurium tetrachloride and propylene by Kobelt and Paulus[299] (Figure 53). The Te—Cl bonds are again longer,

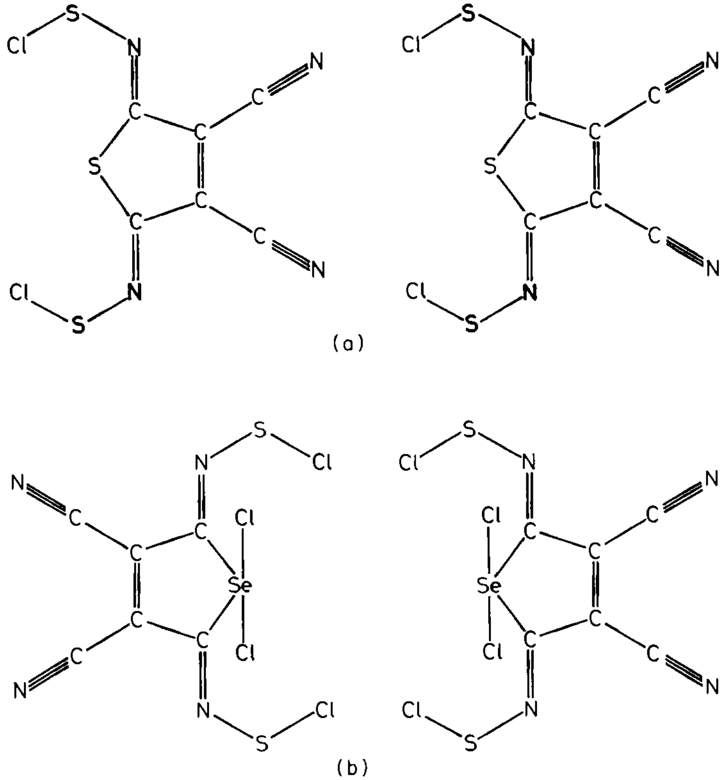


FIGURE 50. Schematic drawings of (a) the head-to-tail ordering of molecules in the crystal of **121** (after Reference 295) and (b) the head-to-head ordering in **120** (after Reference 294)

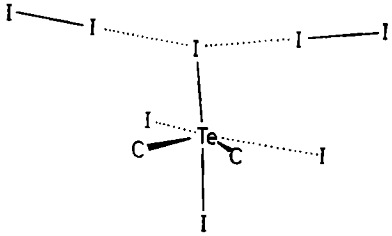


FIGURE 51. The molecular geometry and intermolecular I···I and Te···I contacts in crystalline dimethyltellurium tetraiodide (**122**) (after Reference 296)

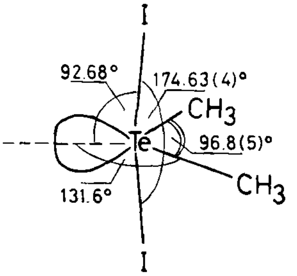


FIGURE 52. Angles around the Te atom in **122**[296]

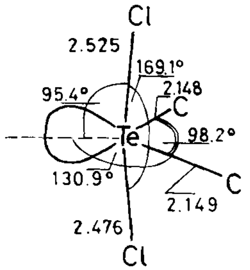
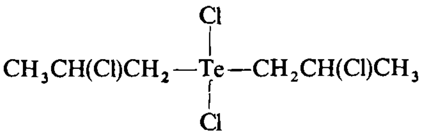


FIGURE 53. Angles around and bond lengths of the Te atom in **123**[299]

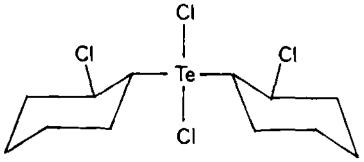


$$CH_3CH(Cl)CH_2{-}\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{Te}}{-}CH_2CH(Cl)CH_3$$

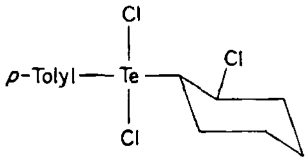
(123)

2.525(15) and 2.476(15) Å than what would correspond to the sum of the covalent radii (2.35 Å), but they are not significantly different.

In dichlorobis(2-chlorocyclohexyl)tellurium(IV) (**124**)[300] the quadruple angle, α_4^E(Te), is markedly small, 109.5°. It would be tempting to ascribe this effect to the bulkiness of the 2-chlorocyclohexyl groups. However, even this would not explain why even the E—Te—Cl angles are smaller (Figure 54) than those in **123**. In both cyclohexyl rings the Te—C and the adjacent C—Cl bonds are equatorial.



(124)



(125)

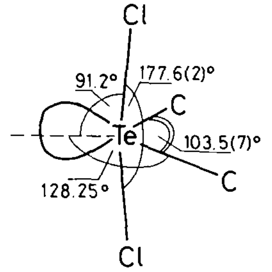
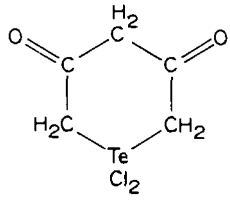


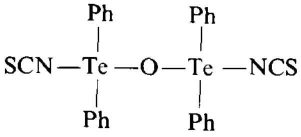
FIGURE 54. Angles around the Te atom in **124**[300]

The molecular geometry of dichloro(2-chlorocyclohexyl)-*p*-tolyltellurium(IV)(**125**)[301] is similar to that of **124**. The Cl—Te—Cl and C—Te—C bond angles are 176.4(3) and 101.0(6)°, respectively, and α_4^E(Te) is 110.6°. The Te—Cl bond lengths are also similar to those in **124**.

Another trigonal bipyramidal Te configuration appears in the crystal of 1,1-dichloro-1-telluracyclohexane-3,5-dione (**126**)[186]. The Cl ligands are in axial positions with Te—Cl 2.49 Å and Cl—Te—Cl 171.8°. The endocyclic C—Te—C angle is somewhat larger, viz. 95.5°, than this angle in 1-telluracyclohexane-3,5-dione (**35**) itself[183,186] (cf. Table 18).



(**126**)



$$\begin{array}{ccccc} & Ph & & Ph & \\ & | & & | & \\ SCN— & Te & —O— & Te & —NCS \\ & | & & | & \\ & Ph & & Ph & \end{array}$$

(**127**)

The molecular configuration of bis(isothiocyanatodiphenyltellurium(IV)) oxide (**127**)[302] is shown in Figure 55. The angular arrangement about the Te atom shows no unusual features, N—Te—O 172.2(3)° and C—Te—C 97.2(4)° with α_4^E(Te) 112.6°. There are relatively short intermolecular Te···S contacts, viz. 3.416(3) Å, serving to link the **127** molecules into molecular chains as shown in Figure 56. Mancinelli and coworkers[302] suggested that the Te bond configuration may be considered to be square pyramidal. Notwithstanding this, the angular parameters of the Te bond configuration also indicate very typical trigonal bipyramidal arrangement.

Smith and coworkers[303] recently determined the crystal and molecular structure of tetraphenyltellurium-benzene(8/1), $Ph_4Te\cdot\frac{1}{8}C_6H_6$ (**128**). There are four independent molecules in the unit cell containing altogether eight molecules. The space group is $P\bar{1}$. The bond configuration about Te is essentially the same in the four independent molecules

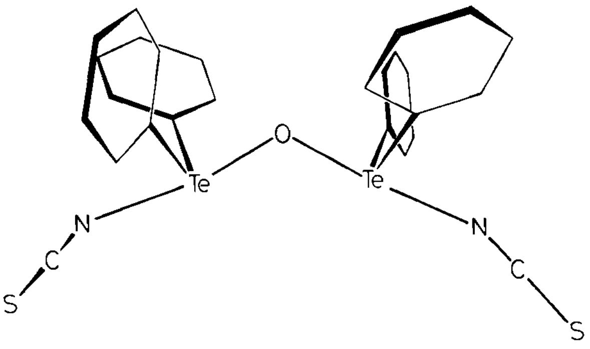


FIGURE 55. The molecular configuration of **127** (after Reference 302)

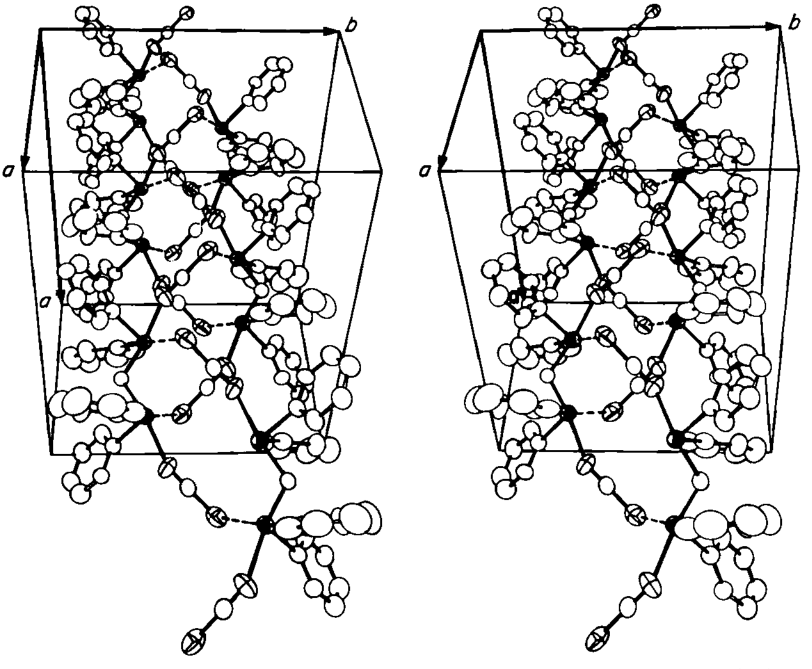


FIGURE 56. Chains of molecules along the *c* axis in the crystal of **127**, a stereoscopic view. Reproduced by permission of Elsevier Sequoia S.A. from Reference 302

which are, however, conformationally different due to differences in the Ph group orientation (Figure 57). The angles about Te are shown in Figure 58. The $\alpha_4^{E}(\mathrm{Te}) = 110.7°$ quadruple average angle suggests that weaker repulsion interactions are in effect between the lone pair and the bonding pairs in **128** than $\alpha_4^{E}(\mathrm{Te}) = 113.2°$ in **123**. The axial bond angles Cl—Te—Cl in **123** and C—Te—C in **128** are the same, 169°. Thus the difference can conveniently be reduced to that in the interactions in the equatorial plane. The difference in the bond angles C—Te—C of **123** and **128** is 10°! Considering the ligand

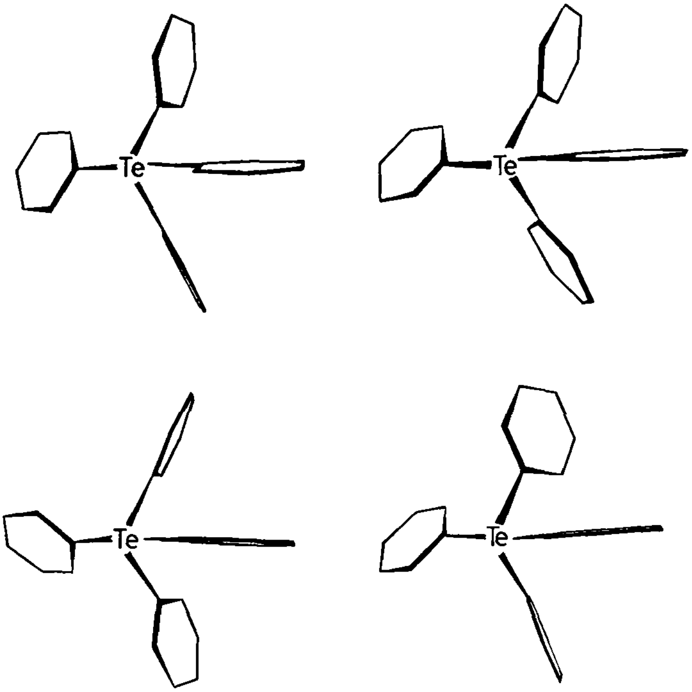


FIGURE 57. Conformations of the four independent molecules of Ph_4Te in crystals of **128** (after Reference 303)

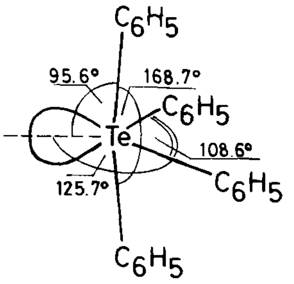


FIGURE 58. Angles around the Te atom in **128**[303]

electronegativities, the Ph group would be expected to draw more electron density from the vicinity of the central atom than would the alkyl group. Thus from a superficial approach in the application of the VSEPR model, but one which is widely used, the C_{eq}—Te—C_{eq} of **128** would be predicted smaller. However, the observed difference in the bond angles is in complete agreement with the VSEPR model if consideration also includes the importance of lone-pair/bonding-pair interactions of which there are two, versus the less important and only *one* bond/bond interaction. Of course, this model may predict the direction of the change but not its magnitude. The amount of the angular opening in the equatorial plane might suggest that steric effects cause at least part of it. On the other hand

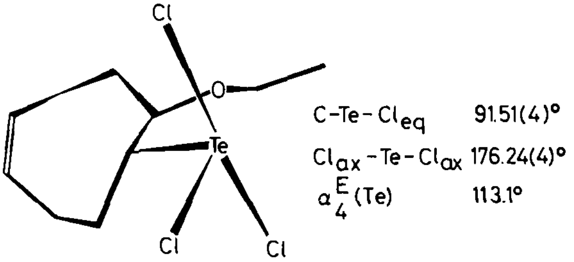
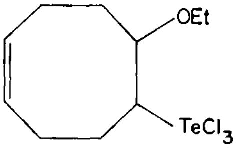


FIGURE 59. The molecular model of **129** (after Reference 304)

the C(phenyl)—Te—C(phenyl) bond angle involving an axial and an equatorial position may be as small as 85°! Indeed the Ph arrangements in Figure 57 do not indicate strong steric hindrances. The axial and equatorial Te—C bond lengths are markedly different, again in agreement with the VSEPR model.

The molecular structure of 8-ethoxy-4-cyclooctenyltellurium trichloride (**129**)[304] has no unusual features in its Te bond configuration as shown in Figure 59.



(129)

McCullough and Knobler[305–307] have studied some 2-biphenylyltellurium trihalides

o-PhC$_6$H$_4$TeBr$_3$ (**130**)

o-PhC$_6$H$_4$TeI$_3$
(**131**) α-modification
(**132**) β-modification

(**130**–**132**) by XD. For all three structures, again, the trigonal bipyramidal configuration is characteristic with two halogens in axial positions, and the third halogen and a carbon atom plus the lone pair of electrons of Te in the equatorial positions. The parameters are given in Table 25. Important and interesting are the differences in intermolecular contacts in the three structures. In the Br derivative (**130**) relatively long Te···Br interactions (3.713 Å) join pairs of molecules into *dimers* across the symmetry centre (Figure 60). In the α-modification of the I derivative (**131**) two different systems of I···I intermolecular

TABLE 25. Angles (deg.) about the Te atom in 2-biphenylyltellurium trihalides from XD

Compound	X_{ax}—Te—X_{ax}	X_{eq}—Te—C	α_4^E(Te)[a]	Reference
130 (X = Br)	178.46(4)	97.1(3)	111.1	305
131 (X = I)	176.54(4)	100.4(3)	110.8	306
132 (X = I)	176.02(5)	98.1(3)	111.5	307

[a] Calculated from the bond angles.

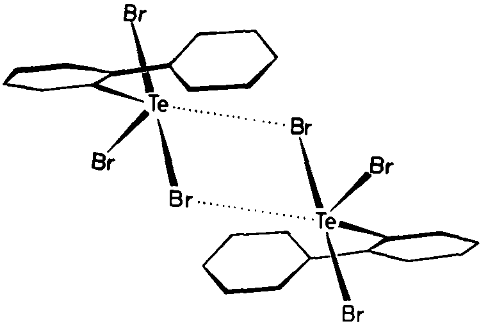


FIGURE 60. A dimer in the crystal of **130** (after Reference 305)

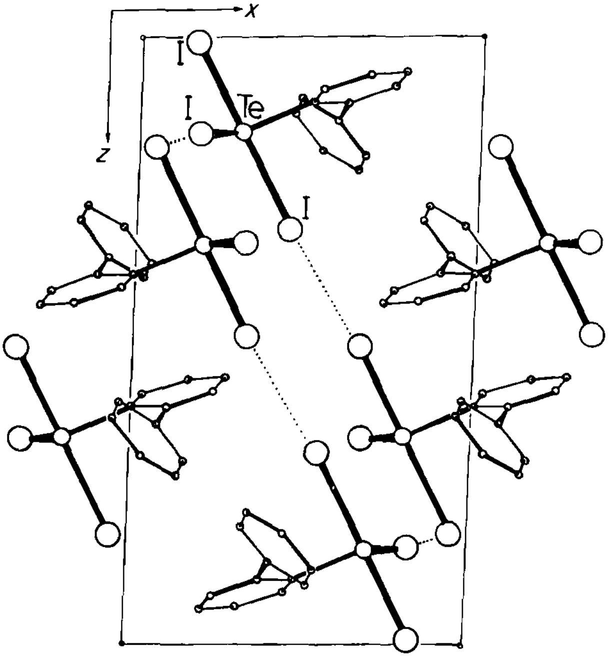


FIGURE 61. Chains of molecules in the crystal of **131** viewed along the *b* axis. Reproduced (simplified) by permission of the American Chemical Society from Reference 306

linkages (of 3.239 and 3.772 Å, respectively) connect the molecules into *chains* (Figure 61). Finally, in the β-modification of the I derivative (**132**), again molecular *chains* are formed by intermolecular contacts. Here, however, they are between Te and I atoms. A selected portion of the structure is shown in Figure 62. McCullough discusses possible correlations between the colour of **131** and **132** and the peculiarities of molecular packing. He notes a relatively short intramolecular Te$\cdots$C distance[307] as shown in Figure 63. As to the benzene ring angular deformations in **130**, **131** and **132**, the mean values of the endocyclic

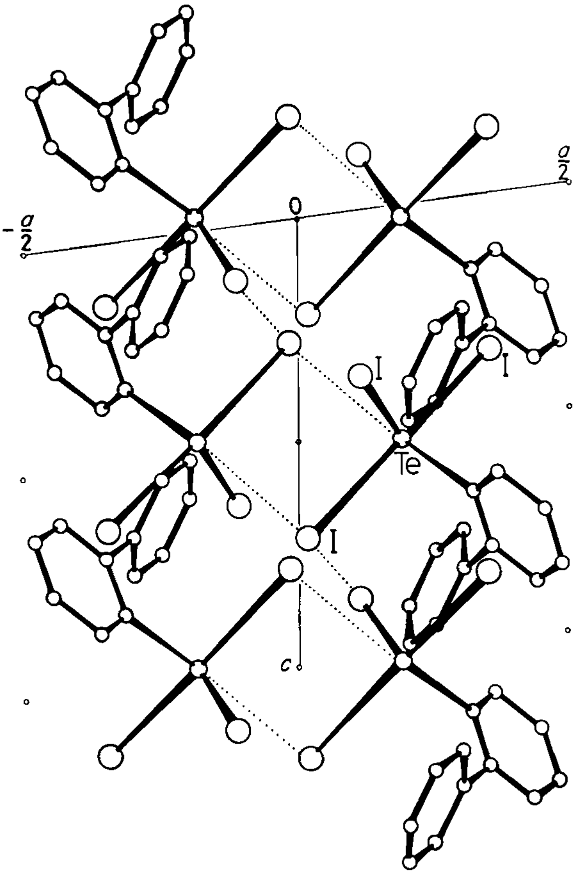


FIGURE 62. Chains of molecules in the crystal of **132** viewed along the *b* axis. Reproduced (simplified) by permission of the American Chemical Society from Reference 307

bond angles are given in Figure 64. The bond angle adjacent to the Te substituent is markedly larger than 120° and the angle adjacent to the second benzene ring is markedly smaller. Then the angular deviations gradually diminish. The mean of the *ipso* angles of the second benzene ring in the three structures is 118.8(7)° in agreement with the deformation observed in biphenyl itself[308].

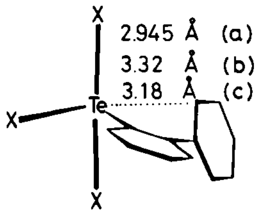


FIGURE 63. Short intramolecular Te···C contacts[307] in the crystals of (a) **130**, (b) **131** and (c) **132**, and the molecular model of **132** (after Reference 307)

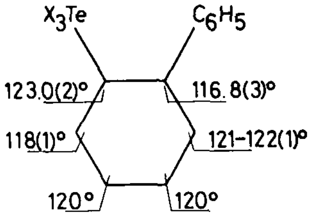
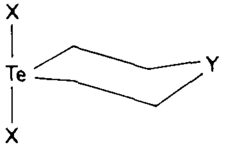


FIGURE 64. Endocyclic bond angles in the phenylene ring of **130**[305], **131**[306] and **132**[307]. Mean values from the three structures with standard deviations

The crystal and molecular structures of 1-thia-4-telluracyclohexane 4,4-dibromide (**133**)[309], 1-oxa-4-telluracyclohexane 4,4-diiodide (**134**)[310] and 1-thia-4-telluracyclohexane 4,4-diiodide (**135**)[311] have been studied by XD. The parameters characterizing the trigonal bipyramidal configuration about Te are collected in Table 26. In the crystal of **133** Te forms coordination linkages with one of the Br atoms of a neighbouring molecule and with the S atom of another neighbouring molecule. An octahedral Te bond configuration is thus formed. The same situation was observed for the Se analogue (**117**)[291]. The bond lengths are compared in Figure 65. It is seen that the analogous intermolecular linkages involving Te and Se are approximately of the same length. As the covalent radius of Te is considerably larger (1.356 Å) than that of Se (1.163 Å), these lengths may indicate that the Te linkages are stronger than the corresponding Se ones.



(**133**) X = Br, Y = S
(**134**) X = I, Y = O
(**135**) X = I, Y = S

The Te atom in **134** may also be considered to have octahedral bond configuration, as coordination linkages are formed to an iodine of a second molecule and to one more iodine of a third molecule, at 2.886(1) and 2.938 Å, respectively. The Te of **135** again establishes intermolecular contacts with I atoms of neighbouring molecules.

The ring puckering in the three structures with *chair* conformation discussed is demonstrated by the average torsional angles in Figure 66. The puckering is the same in the three cases and the molecules seem to be somewhat flatter than free 1,4-dioxane or 1,4-

TABLE 26. Angles (deg.) about the Te atom in dihalides **133**, **134** and **135** from XD

Compound	X—Te—X	C—Te—C	α_4^E(Te)[a]	Reference
133	176.63(6)	99.4(6)	111.0	309
134	177.08(4)	94.1(4)	112.2	310
135[b]	174.9(1)	100(1)	111.3	311
	178.1(1)	100(1)	110.5	

[a] Calculated from the bond angles.

[b] There are two molecules in the asymmetric unit.

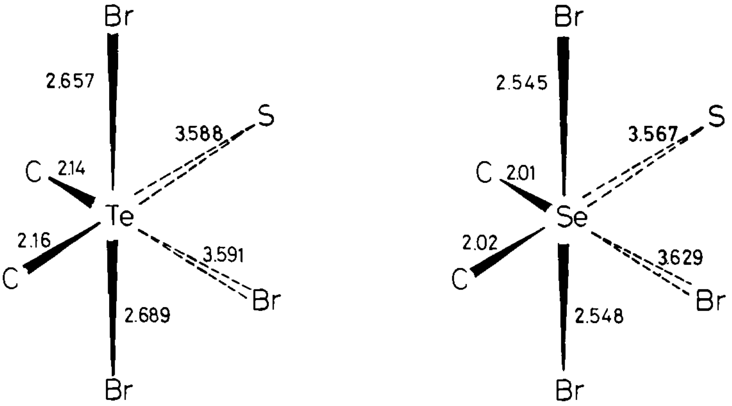


FIGURE 65. Bond lengths and intermolecular contacts (Å) of Te in 133[309] and of Se in 117[291]

oxathiane or especially 1,4-dithiane. For comparison, data on *trans*-2,3-dichlorides of analogous molecules in the crystal are also presented in Figure 66.

A normal coordinate analysis by Hagen and coworkers[315] indicated that the six-membered rings of 1,4-dioxane, 1,4-dithiane, 1,4-diselenane, 1,4-oxaselenane, 1,4-oxatellurane and 1,4-thiaselenane are relatively rigid. The relative rigidity of the rings is

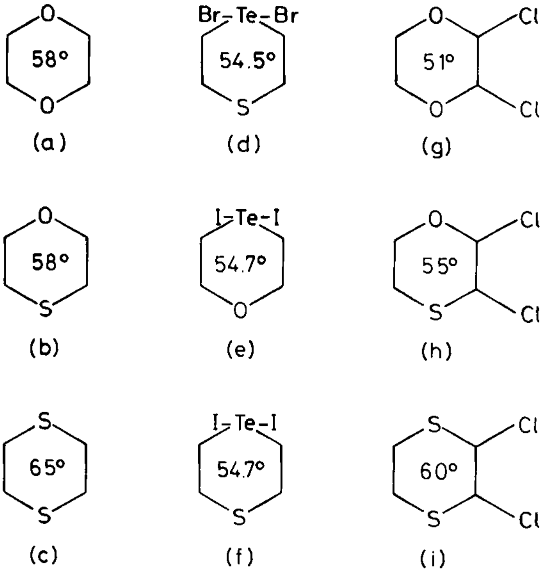


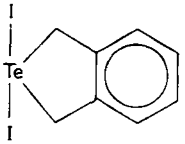
FIGURE 66. 1,4-Diheterocyclohexane derivatives: the mean torsional angles as characterization of ring puckering; (a)[312], (b)[240] and (c)[313], free molecules, (d) 133[309], (e) 134[310], (f) 135[311], (g), (h) and (i)[314], crystals

well characterized by the relatively small mean parallel vibrational amplitudes (l)[316], referring to the 1,4-interactions between the heteroatoms:

$\underline{OCH_2CH_2OCH_2CH_2}$	l(O$\cdots$O)	0.071 Å
$\underline{SCH_2CH_2SCH_2CH_2}$	l(S$\cdots$S)	0.062 Å
$\underline{SeCH_2CH_2SeCH_2CH_2}$	l(Se$\cdots$Se)	0.076 Å
$\underline{OCH_2CH_2SeCH_2CH_2}$	l(O$\cdots$Se)	0.078Å
$\underline{OCH_2CH_2TeCH_2CH_2}$	l(O$\cdots$Te)	0.080 Å
$\underline{SCH_2CH_2SeCH_2CH_2}$	l(S$\cdots$Se)	0.078 Å

The calculated effects of the perpendicular vibrations[316] for the same interactions practically vanish[315].

The crystal and molecular structure of the α-modification of 1,1-diiodo-3,4-benzo-1λ^4-telluracyclopentane (**136**) was determined by XD[317]. The trigonal bipyramidal arrangement about Te is characterized by the axial I—Te—I and equatorial C—Te—C bond angles of 176.53(4) and 86.0(5)°, respectively. The quadruple average angle of the lone pair is relatively large, α_4^E(Te) = 114.4°. The Te$\cdots$I intermolecular contacts, however, create a distorted octahedral Te bond configuration (Figure 67).



(**136**)

Te also forms intermolecular linkages with I atoms in each of the two neighbouring molecules in the crystal of dibenzotellurophene diiodide (**137**)[318]. The intermolecular Te$\cdots$I links which are 3.717 and 3.696 Å long bring the molecules into infinite chains (Figure 68). The intermolecular contacts make the Te bond configuration distorted octahedral. The axial I—Te—I and equatorial C—Te—C bond angles are 178.47(1) and

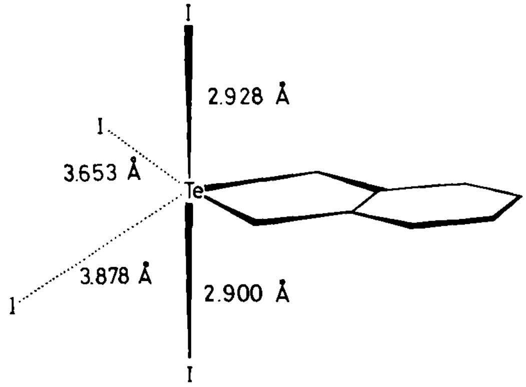


FIGURE 67. The molecular model of 136 with Te—I bond lengths and intermolecular Te$\cdots$I contacts (after Reference 317)

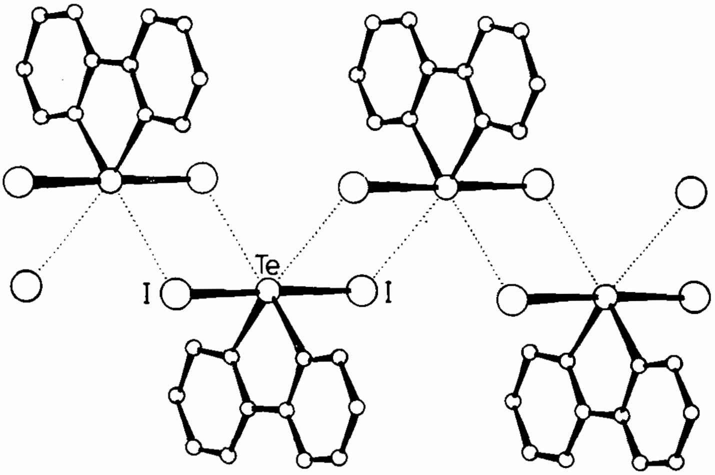
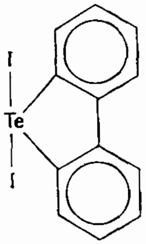


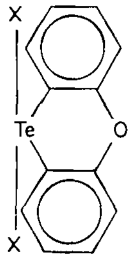
FIGURE 68. Chains of molecules in the crystal of **137**. Reproduced (simplified) by permission of the American Chemical Society from Reference 318

81.8°, respectively. The α_4^E(Te) is 114.9°. This relatively large quadruple average angle of the Te lone pair, i.e. about 115°, seems to be characteristic for the distorted octahedral Te bond configuration; thus it may indicate an increased participation of coordination bonding for the lone pair of electrons.



(137)

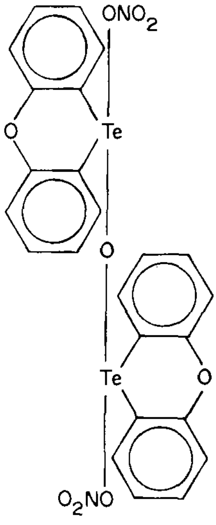
The crystal and molecular structures of several phenoxatellurin derivatives have been determined, i.e. the 10,10-diiodide (**138**)[319], bis(trifluoroacetate) (**139**)[320] and dinitrate (**140**)[321] and 10,10′-oxybis [10,10-dihydro-10-(nitrooxy)phenoxatellurin] (**141**)[322]. One of the characteristic features of the phenoxatellurin structures is the fold angle θ_2 along the Te···O axis where the two planar or nearly planar halves of the molecules meet (Figure 30). These angles are the following: **138** 164°; **139** 152°; **140** 175°; **141** 147°, 163°. The structure of phenoxatellurin (**49**)[202] itself has been discussed in Section III.C dealing with two-coordinated Te. Mangion, Smith and Meyers[321] have interpreted the differences in the fold angles of phenoxatellurin with Te(II) and its derivatives with Te(IV) on the basis of molecular orbital theory. Of the Te(IV) derivatives only the dinitrate (**140**) has a nearly planar ring structure.



(138) X = I

(139) X = $-OC(O)CF_3$

(140) X = ONO_2



(141)

Table 27 presents data on the trigonal bipyramidal configuration about Te. Noteworthy are the relatively large quadruple average angles of the Te lone pair of electrons. In **138** there are again Te ··· I intermolecular contacts with two neighbouring molecules at 3.739 and 3.788 Å. These contacts bring the molecules into infinite chains, similar to those depicted for **137** in Figure 68. For **139** the possible intermolecular contacts have not been discussed. The shortest intermolecular contacts in **140** are O ··· O at 3.14 Å, excluding H atoms. No noteworthy intermolecular contacts have been observed in **141** either.

In conclusion, the various Te—C bond lengths and C—Te—C bond angles for the molecules **122** to **141** are summarized in Table 28. The general tendency for Te—C(alkyl) to be longer than Te—C(phenyl) seems to be present, although the data scatter and overlap. Both types, at least in their mean values, appear to be somewhat longer than what would correspond to the sum of the covalent radii, 2.12 Å. The latter occurs as the mean of the Te—C bond lengths for endocyclic systems involving saturated rings or moieties. The bond angles referring to these systems are obviously smaller than those occurring in open moieties.

TABLE 27. Angles (deg.) about the four-coordinated Te atom in phenoxatellurin derivatives

Compound	ax—Te—ax	C—Te—C	α_4^E(Te)[a]	Reference
138	176.44(6)	91.5(6)	113.0	319
139	167.5(2)	91.5(3)	115.2	320
140	168.0(2)	93.5(2)	114.6	321
141[b]	168.6(1)	90.2(2)	115.3	322
	171.8(2)	91.3(3)	114.2	

[a] Calculated from the bond angles.

[b] The two Te atoms are crystallographically different.

TABLE 28. Te—C bond lengths (Å) and C—Te—C bond angles (deg.) with four-coordinated Te

Compound	Te—C(alkyl)	Te—C(ring)[a]	Te—C(phenyl)	C—Te—C	Reference
122	2.14(1)			96.8(5)	296
123	2.148(5)			98.2	299
124	2.18(1)			103.0(5)	300
125	2.24(2)		2.08(2)	101.0(6)	301
127			2.112(9)	97.2(4)	302
128			2.13(1)eq[b] 2.29(2)ax[b]	109(2)[c]	303
129	2.172(3)				304
130			2.136(8)		305
131			2.152(12)		306
132			2.153(12)		307
126		2.16[d]		95.5[d]	186
133		2.14(1)		99.4(6)	309
134		2.17(1)		94.1(4)	310
135		2.16[d]		100[d]	311
136		2.139(12) 2.145(12)		86.0(5)	317
137		2.111(4)		81.8(2)	318
138		2.10(2)[d]		91.5(6)	319
139		2.066[d]		91.5(3)	320
140		2.068(4)		93.5(2)	321
141		2.091[d]		90.7[d]	322
Mean (σ)	2.18(4)	2.12(4)	2.15(6)	96(6)	
Mean of **122–125**, **127**, **128**				101(4)	
Mean of **126**, **133–141**				92(5)	

[a] Endocyclic Te—C bonds.
[b] Mean of eight values.
[c] Mean of four C(eq)—Te—C(eq) values.
[d] Mean value.

VI. FIVE- AND HIGHER-COORDINATED SELENIUM AND TELLURIUM

Trifluoromethylselenium trichloride, CF_3SeCl_3, is the only Se compound belonging to this section. Its molecular structure was determined in the solid state by Marsden and coworkers[323] using XD. The crystal is orthorhombic, Pbca and built from discrete dimeric molecules (Figure 69). The Se atoms are *five-coordinated* and have a distorted octahedral bond configuration with a Se—C bond and Se lone pair of electrons in the axial positions. The C—Se—Cl bond angles, at least in their mean, do not deviate from 90° significantly and this may suggest relatively weak repulsions from the lone pair of electrons. The reduced stereochemical activity of the lone pair may be related to intermolecular Se···Cl contacts. Although the Se—Cl bond lengths scatter, the bridging bonds are distinctly longer than the terminal ones, viz. 2.51–2.75 vs. 2.13–2.25 Å. The Se—C bonds are 2.01(2) and 2.05(2) Å long. The X-ray scattering by the CF_3 groups was smeared out by the effects of thermal motion, hence assumed C—F bond lengths and F—C—F bond angles were used in the structure refinement. The selected values (1.33 Å and 108.5°) correspond to 2.00 Å F···F non-bonded distances which are much shorter than twice the postulated

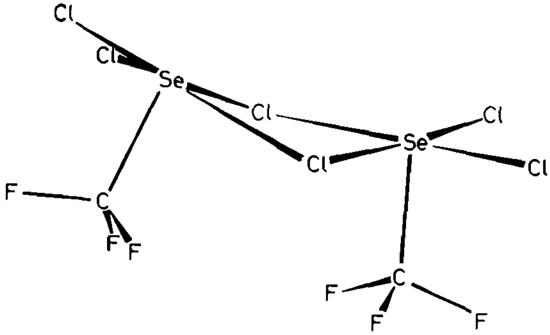


FIGURE 69. The dimeric molecule in the crystal of CF_3SeCl_3. Drawn from the atomic coordinates given in Reference 323

fluorine 1,3 intramolecular non-bonded radius, viz. 1.08 Å (cf. the discussion of the structure of tetrafluoro-1,3-diselenetane in Section III.C). The four-membered ring is puckered and the deviation from planarity may be characterized by the ClSeCl/ClSeCl angle which is about 26°, the same as the analogous feature of the free trimethylene sulphide structure.

The Te bond configuration in di-μ-bromo-μ-1,2-cyclohexylenetetrabromoditellurium, $C_6H_{10}Br_6Te_2$ (**142**), is similar to the Se bond configuration of CF_3SeCl_3. The crystal of **142** is orthorhombic, Pnma or $Pn2_1a$[324]. The Te atoms are somewhat displaced with respect to the plane of the Br atoms and away from the C atom (Figure 70). This indicates that the Te lone pair of electrons may have greater influence in determining the bond configuration here than was the case for Se in CF_3SeCl_3. The Te—C bond lengths are 2.19(4) and 2.26(5) Å. The four-membered ring is considerably puckered and the BrTeBr/BrTeBr angle is 48°. The molecule has a symmetry plane which contains all its six C atoms.

Another octahedral Te bond configuration occurs in phenyltellurium trihalide, $PhTeX_3$, i.e. $PhTeBr_{1.3}Cl_{1.7}$, whose molecular structure was determined by XD[325] (Figure 71 with X being a mixture of Cl and Br). The $PhTeX_3$ units are connected into infinite chains by halogen bridges. The C—Te—X bond angles do not deviate significantly from 90° in their mean. The Te—C bond lengths are 2.122(5) and 2.133(5) Å.

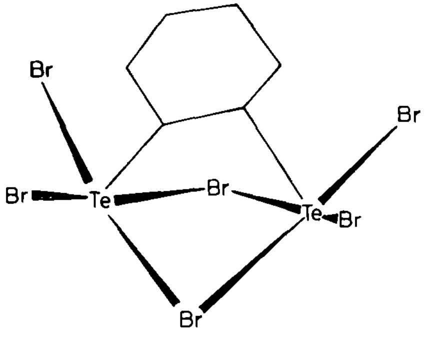


FIGURE 70. The molecular model of **142** (after Reference 324)

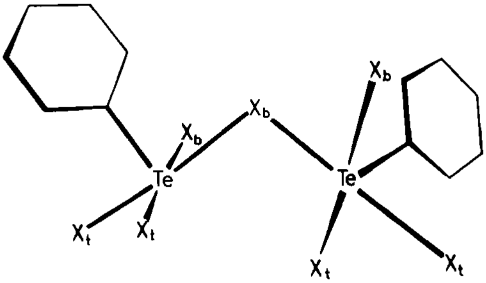
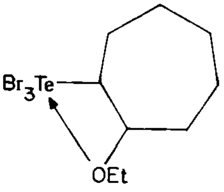


FIGURE 71. A chain molecules in crystalline $PhTeBr_{1.3}Cl_{1.7}$, with bridging (X_b) and terminal (X_t) halogen atoms (after Reference 325)

The ring deformations in the two independent Ph groups show a characteristic pattern. The mean values of the endocyclic bond angles are the following, with α being the *ipso* angle: $\alpha = 122.0$, $\beta = 118.6$, $\gamma = 120.2$ and $\delta = 120.2°$. The error limits of the individual bond angle values are about 0.5–0.6°.

The product of the reaction of $TeBr_2$ with cycloheptene in ethanol was identified by XD as *cis*-2-ethoxycycloheptyltribromotellurium(IV) **(143)**[326]. There are two molecules in the asymmetric unit, the crystal is triclinic, $P\bar{1}$. The bond configuration about Te is distorted octahedral with the Te lone pair of electrons occupying one of the 'equatorial' positions. The 'axial' Te—Br bonds are considerably longer than the 'equatorial' one, viz. 2.66 vs. 2.50 Å (mean values). The Te—C bonds are 2.29(4) and 2.24(4) Å long.



(143)

Infinite polymeric chains are formed by the adduct $TeCl_4 \cdot C_2H_4$ (Figure 72). Its crystal is orthorhombic, Pcma[327]. The Te atom is somewhat displaced with respect to the plane of the Cl atoms and away from the C atoms. The Te—C bond length is 2.164(13) Å.

Another new organotellurium(IV) compound is [2-(6-acetyl-2-pyridinyl)-2-oxoethyl]trichlorotellurium, whose molecular structure was determined by XD[328] (Figure 73). The Te atom is *six-coordinated* and its bond configuration is distorted pentagonal bipyramidal with the Te lone pair of electrons occupying one of the equatorial positions. The Te—C bond length is 2.129(3) Å. This is a normal bond whereas the other Te linkages are appreciably longer than the corresponding sums of the covalent radii.

Esperås and Husebye[329] determined the crystal molecular structure of tris-(diethyldithiocarbamato)phenyltellurium(IV), $(Et_2NCS_2)_3TePh$ **(144)**, by XD. The crystal is monoclinic, $P2_1/c$. The Te atom is *seven-coordinated* with six linkages to S atoms and the seventh to a Ph group. The bond configuration is distorted pentagonal bipyramidal with the Te—C bond in an axial position. The structure is depicted in the simplified model of

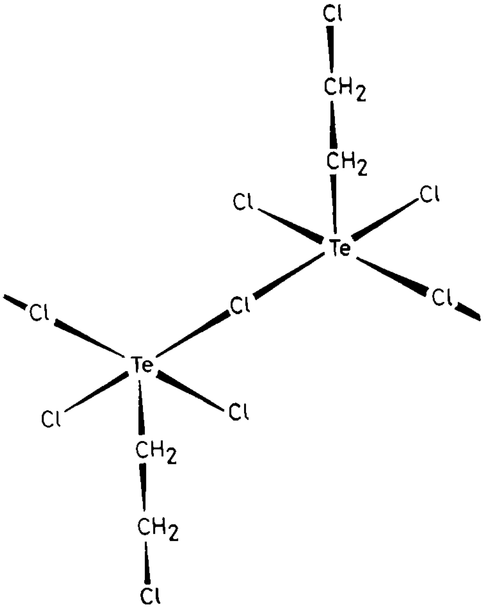


FIGURE 72. A chain of molecules in the crystal of $TeCl_4 \cdot C_2H_4$ (after Reference 327)

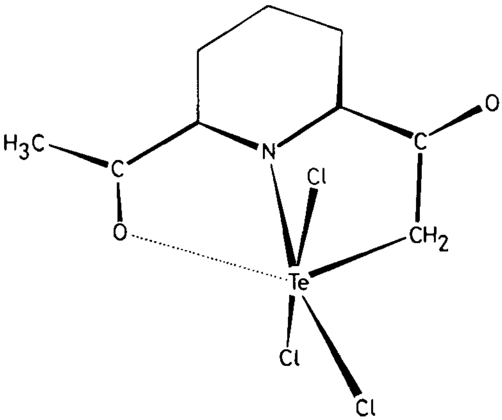


FIGURE 73. The molecular model of [2-(6-acetyl-2-pyridinyl)-2-oxoethyl]trichlorotellurium (after Reference 328). H atoms on the pyridine ring and double bonds are not shown. Wedges indicate a perspective view. The dotted line is a long Te···O linkage

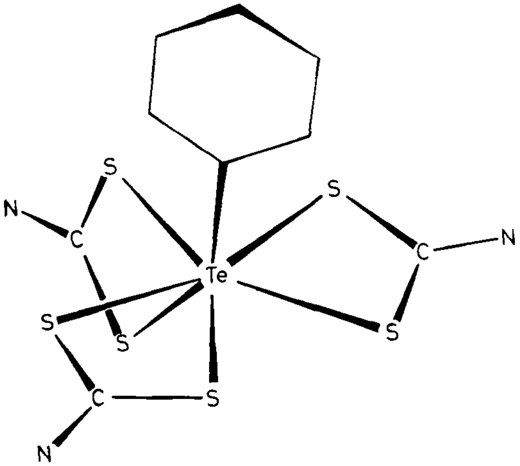


FIGURE 74. The molecular model of **144**. Drawn from the atomic coordinates given in Reference 329

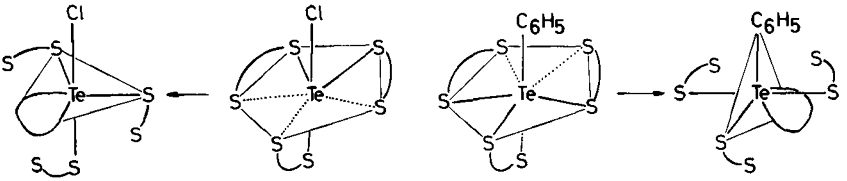


FIGURE 75. The effect of the Te lone pair on a distorted pentagonal bipyramidal arrangement with a Cl ligand (**145**) or with a Ph ligand (**144**) (after Reference 330)

Figure 74. The molecular structure of its Cl analogue $(Et_2NCS_2)_3TeCl{\cdot}C_4H_8O_2$ (**145**), was recently determined by XD[330]. The Te—S bonds are not all equivalent. In both compounds there are three shorter and three longer ones. The Te—C bond is a normal single bond in the Ph derivative, viz. 2.124(11) Å, but the Te—Cl bond is strikingly long in the Cl analogue, viz. 2.686(4) Å. The relative orientation of the Te—S bonds is also different in the two compounds. Von Deuten and coworkers[330] descriptively characterized this difference invoking the VSEPR model. Assuming the limiting case in which only the shorter Te—S linkages are considered to be bonds, both structures may be described by a trigonal bipyramidal configuration with the Te lone pair of electrons in an equatorial position. The more electronegative ligand (Cl) will be in an axial position and the Ph group will take an equational one[330] (Figure 75).

There are no organic eight- or higher-coordinated Se or Te derivatives containing Se—C or Te—C bonds whose structure has been elucidated. Several Te derivatives with purely inorganic Te environment have been investigated by XD[331–333]. It is anticipated that research will expand to include compounds in which one and possibly more organic ligands will find their way into the Te bonding sphere.

VII. ACKNOWLEDGEMENTS

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CHAPTER 4

Thermochemistry of selenium and tellurium compounds

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I. INTRODUCTION

In addition to three comprehensive reviews on thermochemistry[1-3], *Organometallic Chemistry Reviews* and *Advances in Organometallic Chemistry* were consulted. Also the following periodicals from 1970 were searched: *Journal of Organometallic Compounds, Thermochimica Acta, Journal of Chemical Thermodynamics* and *Journal of Inorganic and Nuclear Chemistry.* This search revealed very little information on the thermochemistry of organic selenium compounds and no information whatsoever on organic tellurium compounds. Accordingly this review is confined to selenium compounds and the production of group properties for the prediction of the heats of formation of other compounds. Some indications are made for further desirable studies.

II. ORGANIC SELENIUM COMPOUNDS

A. Heats of Formation

All of the heats of formation of organoselenium compounds have been determined via their heats of combustion. In one sense this is quite a straightforward procedure because the combustion of selenium and its compounds produce only one metallic oxide, selenium dioxide, SeO_2. Since SeO_2 is soluble in water, it is essential to use rotating bomb methods to ensure complete dissolution of the oxide[4]. Early determinations using static bomb methods are therefore suspect for this reason[5].

Although not strictly relevant to this chapter, it is first important to establish the heat of formation of crystalline SeO_2 for the reasons outlined above. Barnes and Mortimer[6]

TABLE 1. Values for ΔH_f^0 $(SeO_2)(c)$

Bomb calorimetry Method	$\Delta H_f^0(SeO_2, c)$ (kcal mol^{-1})	Ref.
Static	− 53.86	7, 8
Static	− 53.35	9
Static	− 53.95	10
Rotating	− 53.9 ± 0.5	6

determined the heat of combustion of Se in the presence of benzoic acid as a combustion acid using a rotating bomb calorimeter. The combustion process refers to reaction (1):

$$Se(c) + O_2(g) + 401\ H_2O(l) \rightarrow SeO_2.401\ H_2O(l) \qquad (1)$$

By making use of the enthalpy of solution ΔH^0 (solution) $= 0.92 \pm 0.02$ kcal mol^{-1}, the heat of formation of the pure crystalline form was found to be -53.90 ± 0.47 kcal mol^{-1}. Table 1 compares this value with previous static bomb determinations. In fact the agreement is very good which suggests that the static bomb experiments *may* not be seriously in error. However Skinner[4] quotes a value of -56.5 ± 1 kcal mol^{-1}.

Merten and Schlüter[5] determined the heat of combustion of diethyl selenide/paraffin oil/benzoic acid mixtures in a static bomb calorimeter. Using $\Delta H_f^0(SeO_2, c) = -53.9 \pm 0.5$ kcal mol^{-1}, this gives $\Delta H_f^0(Et_2Se, l) = -21.7 \pm 0.9$ kcal mol^{-1}. Skinner's[4] value for the latent heat of vaporization of $+9.3$ kcal mol^{-1} gives $\Delta H_f^0(Et_2Se, g) = -12.4$ kcal mol^{-1}.

Barnes and Mortimer[6] determined the heat of combustion of diphenyl selenide using a rotating bomb calorimeter. This yielded a value for $\Delta H_f^0(Ph_2Se, l) = 54.1 \pm 1.4$ kcal mol^{-1}. They calculated a value for the latent heat of vaporization of 15.2 ± 0.6 kcal mol^{-1} from the boiling points at 4, 42 and 760 Torr, which gives $\Delta H_f^0(Ph_2Se, g) = 69.3 \pm 1.5$ kcal mol^{-1}.

Merten and Schlüter[5] determined the heat of combustion of dibenzyl selenide using a static bomb calorimeter. The already cited value for $\Delta H_f^0(SeO_2, c)$ leads to $\Delta H_f^0((PhCH_2)_2Se, c) = 0.5 \pm 5.0$ kcal mol^{-1} as previously calculated by Cox and Pilcher[2]. No information is available on the heat of sublimation.

Mortimer and Waterhouse[11] determined the heat of combustion of diphenyl diselenide using a rotating bomb calorimeter. This leads to $\Delta H_f^0(Ph_2Se_2, c) = (28.8 \pm 0.5)$ kcal mol^{-1}. A Knudsen-effusion technique was used to determine the enthalpy of sublimation $\Delta H_{subl} = (27.9 \pm 0.6)$ kcal mol^{-1} and thus $\Delta H_f^0(Ph_2Se_2, g) = 56.7 \pm 0.8$ kcal mol^{-1}.

Arshadi and Shabang[12] determined the heat of combustion of dibenzyl diselenide using an adiabatic static bomb calorimeter. They found that ΔH_f^0 $((PhCH_2)_2Se_2, c) = 40.8 \pm 0.8$ kcal mol^{-1}. They used a transpiration method to determine the heat of sublimation $\Delta H_s^0 = 31.2 \pm 0.2$ kcal mol^{-1} and thus $\Delta H_f^0(Ph_2Se_2, g) = 72.0 \pm 0.8$ kcal mol^{-1}.

Arshadi and Shabang[12] also determined the heat of combustion of 4-phenyl-1,2,3-selenadiazole using the same technique. They found that $\Delta H_f^0(C_8H_7N_2Se, c) = 85.6 \pm 2$ kcal mol^{-1}, $\Delta H_s^0 = 22.5 \pm 0.2$ kcal mol^{-1} and thus $\Delta H_f^0(C_8H_7N_2Se, g) = 108.1 \pm 2$ kcal mol^{-1}.

The results for these organoselenium compounds are summarized in Table 2.

B. Bond Dissociation Energies

The R—X bond dissociation energy is defined as the energy required to break the R—X bond. No information of this type is available for organoselenium compounds. However,

TABLE 2. Heats of formation for organoselenium compounds

Compound	Bomb calorimetry method	ΔH_f^0 (g) (kcal mol^{-1})	Ref.
Et_2Se	Static	-12.4 ± 0.9	6
Ph_2Se	Rotating	69.3 ± 1.5	7
$(PhCH_2)_2Se$	Static	0.5 ± 5.0[a]	6
$C_8H_7N_2Se$[b]	Static	108.1 ± 2	13
Ph_2Se_2	Rotating	56.7 ± 0.8	12
$(PhCH_2)_2Se_2$	Static	72.0 ± 0.8	13

[a] ΔH_f^0(c) only.
[b] 4-Phenyl-1,2,3-selenadiazole.

mean bond dissociation energies may be determined. This is based upon the heats of formation of the compounds in the gaseous state together with that for the radicals formed and ΔH_f^0(Se, g) = 54.3 kcal mol^{-1} [7]. For diethyl selenide the mean Se—C bond energy is defined as $\Delta H_2^0/2$:

$$\mathrm{Et_2Se} \rightarrow 2\ \dot{\mathrm{E}}\mathrm{t} + \mathrm{Se} \tag{2}$$

Using a value of $\Delta H_f^0(\dot{\mathrm{E}}\mathrm{t}) = 26.5 \pm 1$ kcal mol^{-1} [13], $\bar{D}$(Se—C) = 59.9 ± 1.7 kcal mol^{-1} [15]. Similarly for diphenyl selenide, with $\Delta H_f^0(\dot{\mathrm{P}}\mathrm{h}) = 78.5 \pm 1$ kcal mol^{-1} [13], $\bar{D}$(Se—C) = 71 kcal mol^{-1}. It appears that the effect of the benzene ring is to strengthen the Se—C bond by some 11 kcal mol^{-1}. Unfortunately a similar calculation cannot be made for dibenzyl selenide.

Assuming that $\bar{D}$(Se—Ph) is the same in diphenyl selenide, a consideration of the process:

$$\mathrm{Ph{-}Se{-}Se{-}Ph} \rightarrow 2\ \dot{\mathrm{P}}\mathrm{h} + 2\ \mathrm{Se} \tag{3}$$

would conclude that $\Delta H_3^0 = 2\ \bar{D}(\mathrm{Se{-}Ph}) + D(\mathrm{Se{-}Se}) = 66.9 \pm 2.9$ kcal mol^{-1} close to Gaydon's[14] value for D(Se—Se) of 64.6 kcal mol^{-1}. For comparison D(Te—Se) = 57.6 kcal mol^{-1} and D(Te—Te) = 52 ± 2 kcal mol^{-1} [15]. A similar calculation for dibenzyl diselenide, assuming that $\bar{D}$($PhCH_2$—Se) here is equal to $\bar{D}$(Et—Se) gives D(Se—Se) = 63.3 kcal mol^{-1}. This leads to an average value for D(Se—Se) = 64.9 kcal mol^{-1} with a spread of $\pm$ 1.2 kcal mol^{-1}.

Returning to the monoselenide compounds the mean bond dissociation energies may be compared with those for similar compounds involving other elements in Group VI of the Periodic Table as shown in Table 3. In the two sets of examples, $\bar{D}$(X—R) decreases with the downward movement in Group VI suggesting that D(R—Te) < $\bar{D}$(R—Se).

In the manner of Benson and coworkers[3], Cox and Pilcher[2] derived group additivity values for ΔH_f^0. Using their assignment for Se(C_2) = 0 makes C(H_2)(C)(Se) =

TABLE 3. Mean bond dissociation energies for derivatives of Group VI elements

Compound	$\bar{D}$(X—R) (kcal mol^{-1})	Ref.
Et_2O	86.5	2
Et_2S	69.7	2
Et_2Se	59.9	6
Ph_2O	102.4	2
Ph_2S	84.2	2
Ph_2Se	71	7

3.9 kcal mol^{-1}. This allows heats of formation for other aliphatic monoselenides to be generated. It is emphasized that the group values depend upon only one experimental datum and therefore the results should be treated with caution. No other group values may be derived at this time.

III. CONCLUSIONS

It is obvious that far more data are required to make a comprehensive review of the thermochemistry of Se and Te compounds in terms of both combustion studies and bond dissociation energy determinations. For the latter data only mean bond energy information is available. Probably the best technique here is the VLPP method (very low pressure pyrolysis)[16]. It would be foolish to come to any conclusion other than that Te—R bonds are weaker than the Se—R bonds for the corresponding Se compounds.

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The Chemistry of Organic
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CHAPTER 5

Detection and determination of organic selenium and tellurium compounds

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I. INTRODUCTION

The need to ascertain the composition of organic Se/Te compounds, to qualitatively prove the presence of these chalcogens and to quantitatively determine their percentages has existed since the first organic Se/Te compounds were prepared approximately 150 years ago. During the past one and a half centuries many organic Se compounds and not quite as many organic Te compounds were prepared. The pertinent literature is well summarized in several books[1,2], chapters[3-5] and review articles[6]. Analytical techniques and physicochemical methods were used as they became available for the characterization of organic Se/Te compounds. However, the necessity of determining specific organic Se/Te derivatives in mixtures of such compounds or other matrices did not arise frequently until the effects of Se and its compounds on living organisms became the concern of environmental scientists and the medical profession. Se is now known to be—depending on concentrations—an essential and a toxic element[7-11]. Of special interest is its anticarcinogenic effect against experimentally induced cancer in several animals. Se, chemically related to S, replaces S in many biologically important molecules and is subject to metabolic transformations[8]. There can be no doubt that beneficial and inimical effects of Se are attributable in most cases not to elemental Se but to specific compounds of Se. The identification and determination of organic Se compounds in environmental samples is, therefore, of great importance.

Most of the efforts in the area of analytical Se chemistry were directed toward accurate and precise determinations of Se in inorganic, organic and biological matrices. Few methods were developed which allowed the determination of Se compounds. The sections on analytical chemistry in the books devoted to the biochemistry[8-11] and the medical and biological effects of Se[7] provide little if any information on the methods for the determination of Se compounds, although techniques exist for the gas chromatographic determination of volatile Se compounds[12] and for the element-specific detection of Se compounds in eluents from high-pressure liquid[13] and ion chromatographs[14]. The technique of element-specific detection[15] using graphite furnace atomic absorption spectrometers[14] or plasma emission spectrometers[13] does not seem to have been applied to organic Se compounds.

Future work in analytical Se/Te chemistry will have to concentrate on speciation to provide the techniques required for routine application in research efforts to eludicate the biochemical, medical and biogeochemical roles of these chalcogens.

This chapter discusses the determination of Se/Te in organic compounds and presents the analytically useful methods for the identification and determination of organic Se/Te compounds. The potentially very useful polarographic and other electrochemical techniques have not yet been used for the determination of these compounds. Most of the work in this area, which is summarized in the last section of this chapter, explored the mechanisms of the electrochemical reduction of organic Se compounds.

Infrared spectroscopy, UV–visible spectroscopy, and Mössbauer spectroscopy, which are frequently used to characterize Se/Te compounds, were reviewed recently[1,2,6]. The few photoelectron spectra reported for organic Se/Te compounds are at present not very useful for the characterization of these compounds. Dipole moments, although available for many Se/Te compounds, are often influenced more by functional groups other than Se/Te[1,6], and are, therefore, of rather limited use for the characterization of organic Se/Te compounds. The determination of the conformations of organic Se/Te compounds in solution by means of dipole moment measurements is more in the domain of physical chemistry than analytical chemistry. For these reasons, UV–visible, infrared, Mössbauer and photoelectron spectroscopic techniques, and dipole moment measurements are not covered in this chapter. Other physicochemical techniques such as nuclear magnetic resonance and mass spectrometry are the topics of separate chapters in this book.

II. DETERMINATION OF Se/Te IN ORGANIC COMPOUNDS

The qualitative detection and quantitative determination of Se/Te are the first steps in the characterization of organic compounds of these elements. Although some, rather unstable, Se/Te compounds deposit red Se or black Te on standing and thus reveal that they contain these chalcogen atoms, the decomposition of the organic compounds with concomitant conversion of Se/Te to inorganic chalcogen derivatives is in most cases necessary for the detection and determination of Se/Te.

A. Qualitative Tests for Se/Te

Sensitive, reliable, quick and convenient tests for checking whether organic compounds contain Se or Te are very helpful in synthetic and analytical work.

A spot test for the detection of Se in organic compounds was developed by Feigl[16]. A small quantity of the sample and one drop of 70% perchloric acid are gradually heated in a glycerol bath to 205 °C. After three minutes at 205 °C the reaction mixture is cooled and then treated with one drop of a saturated solution of hydrazine sulphate. Upon warming this mixture on a boiling water bath, a pink colouration or a red precipitation appears indicating the presence of Se. Another method[17] decomposes the sample with potassium chlorate and precipitates selenate with barium ion in the presence of potassium permanganate. The formation of violet crystals is the sign for the presence of Se.

No qualitative tests seem to have been developed specifically for the detection of Te in organic compounds. However, mineralization to an inorganic Te compound and its reduction with sulphur dioxide or hydrazine to black elemental Te, in a procedure similar to the one used for Se, should be applicable.

S, Se and Te may be present together in an organic molecule[1,6]. After mineralization and conversion of selenate to selenite in boiling HCl, hydroxylamine hydrochloride in strongly acidic solution reduces only selenite. Te can then be precipitated by hydroxylamine in ammoniacal solution[18]. S should not interfere with these tests.

Many other reactions potentially useful for the detection of Se/Te in organic compounds[4,18,19] and in biological samples[20,21] are the subject of reviews, which give references to the pertinent literature.

B. Determination of Se/Te in Organic Compounds

Many methods are available for the determination of Se in organic compounds and in biological matrices. The biological samples contain in many cases unidentified organic Se compounds at low concentrations. Te, an element much less abundant than Se, does not have an organic chemistry as extensive as that of Se, and does not have its environmental importance. Therefore, much less attention has been given to the development of methods for the determination of Te.

Unless a non-destructive method is used, the first step in the determination of Se/Te in organic compounds and biological matrices is the mineralization of the organic matter and the conversion of the chalcogen to an inorganic compound. The methods for the mineralization, the subsequent determination of Se[18–28] and Te[6,18,19,26,27,29,30] and the separation of Se and Te[31] have been summarized and evaluated in several reviews. Therefore, only a brief survey of these methods is presented to provide information about the available options.

1. Determination of selenium

Non-destructive methods for the analysis of Se are X-ray fluorescence[19,21,23–25,32,33], neutron activation[19–25,32] and proton-induced X-ray[34,35] or γ-ray[35] emission. These methods have been used almost exclusively to determine Se in biological matrices or to detect its presence in chromatographic fractions, although the chalcogen content of organic Se/Te compounds were claimed to have been obtained within ±0.1% by X-ray fluorescence of KCl or borax disks[36]. An X-ray fluorescence procedure for the determination of Se in solid and liquid samples in the range of 2–40 ± 1 mg/kg or mg/L Se was developed using a seleno steroid and diphenyl selenide as the standards[37]. These results suggest that non-destructive techniques are useful for the determination of Se/Te in organic compounds.

Destructive methods for the analysis of Se mineralize the organic compounds by wet digestion, dry ashing or by combustion in an oxygen atmosphere. The inorganic Se compounds can then be determined by gravimetric, titrimetric, spectrophotometric, fluorometric, electrochemical, gas-chromatographic, mass spectrometric or neutron activation methods.

Wet ashing procedures employ mixtures of acids (sulphuric/nitric, sulphuric/perchloric, sulphuric/nitric/perchloric), mixtures of acids and salts (sulphuric acid/potassium permanaganate, nitric/perchloric acid/ammonium vanadate or sodium molybdate) or a mixture of nitric/perchloric acid and hydrogen peroxide. Several of these wet digestion methods for the determination of Se have been critically reviewed[38]. Dry ashing involves heating the organic compound with magnesium nitrate or with sodium peroxide in a Parr bomb. Combustion methods oxidize the organic compounds in an oxygen-filled flask, in a combustion tube with oxygen flowing over the sample[39] or at low temperature in an oxygen plasma[40].

The solutions obtained after mineralization may contain selenite, selenate or a mixture of these two compounds. Boiling HCl will reduce all selenate to selenite. Se can then be determined gravimetrically by reduction of selenite to selenium with sulphur dioxide or hydrazine sulphate, or titrimetrically through titration of selenite with thiosulphate or of iodine liberated in the reaction between potassium iodide and selenite. Potassium permanganate oxidizes selenite to selenate and excess permanganate can be back-titrated. Selenite can also be determined by titration with silver nitrate or lead nitrate[18,19,27] using a lead-sensitive electrode[41]. A method for the microdetermination of Se in organic compounds employs oxygen flask combustion or digestion with sulphuric/nitric acid and argentometric titration of selenite. Halides can often be determined simultaneously[42]. The simultaneous microdetermination of Se and S in organic compounds uses oxygen-flask combustion, titration of S with barium perchlorate and iodometric determination of Se[43].

Selenite reacts with aromatic *ortho*-diamines to form yellow- to red-coloured piazselenols, which have absorption maxima in the range 270–500 nm and molar extinction coefficients of approximately 20,000. The piazselenols can be determined spectrophotometrically in aqueous solution or after extraction into an organic solvent such as toluene[19,24]. The spectrophotometric determination of Se can be similarly carried out using dithizone, 2-mercaptobenzoic acid, phenyl thiosemicarbazide or similar S-containing reagents[19,24].

Piazselenols extracted into hydrocarbon solvents fluoresce at 580 nm after excitation at 450 nm. This fluorescence allows the very sensitive determination of Se[19,24].

Piazselenols after extraction into toluene can be quantitated by gas chromatography using electron-capture detection[24,44]. This method has the advantage of removing Se from interfering ions.

Electrochemical techniques for the determination of selenite include polarography, anodic and cathodic stripping voltammetry, and amperometric, coulometric or potentiometric titration[19,24]. A coulometric method for the simultaneous determination of C, H, Se and C, Se, S in organic compounds after combustion in an oxygen current has been described[45].

Flame atomic absorption[46,47] or emission[47] spectrometry and the much more sensitive flameless atomic absorption methods[47–49] can be used to determine Se in the aqueous digests or in organic extracts[50–53]. The absolute sensitivities may reach 1 pg Se[19,24]. An inductively coupled plasma emission spectrometer was used to determine Se in organic compounds after their digestion with HNO_3[54].

2. *Determination of tellurium*

The choice of methods for the determination of Te is rather limited. In principle, many of the methods proven to be applicable to the determination of Se should be useful for Te also. However, tellurite does not appear to react with aromatic *ortho*-diamines to form piaztellurols.

Organic Te compounds were mineralized with fuming nitric acid, with mixtures of nitric/perchloric acid or nitric/sulphuric acid, with sodium peroxide/potassium chlorate in a Parr bomb, by the oxygen flask method[42,55] and in a stream of oxygen[56,57]. The tellurium dioxide or tellurite formed during mineralization is then determined gravimetrically[56], by titration with potassium permanganate[58], potassium dichromate[59] or silver nitrate[44], or iodometrically with amperometric indication of the end-point[56]. A method for the simultaneous microdeterminations of C, H and Te employs the coulometric titration of tellurite with sodium thiosulphate[57]. Te in aqueous solution was quantitated by flame atomic absorption spectrometry in an air/acetylene flame at 214.2 nm[55,60]. The general analytical chemistry of Te is summarized in several reviews[18,19,30]. General aspects of the flame atomic absorption spectroscopy of Te[61], the thermal stabilization of inorganic and organically bound Te[62] and interferences by cations in the determination of Te[63] using electrothermal atomic absorption spectrometry are discussed in recent reports.

The formation of complexes of Te with S-containing ligands and the extraction of these complexes has been summarized[64]. The spectrophotometry of these complexes is a sensitive method for the determination of Te, which has not yet been applied to the estimation of Te in organic compounds.

III. IDENTIFICATION AND DETERMINATION OF Se/Te COMPOUNDS

The techniques most often used for the identification and determination of organic Se/Te compounds are paper chromatography, thin-layer chromatography, gas chromatography with electron capture, flame ionization, flame photometric or thermal conductivity detection, ion exchange chromatography, high-pressure liquid chromatography and iodometry. The identification and determination of organic Se/Te compounds becomes easier when element-specific detectors are coupled to chromatographs. Atomic absorption spectrometers with silica tube[65–69] or graphite furnaces[70,71] and microwave-excited emission spectrometers were used as Se-specific detectors[72,73] for gas chromatographs. High-pressure liquid chromatographs were interfaced with a graphite furnace atomic absorption spectrometer[74] and an inductively coupled argon plasma emission spectrometer[13] to determine organic and inorganic Se compounds, respectively. Neutron activation analysis was also suggested as a method for Se-specific detection[75]. The combination of chromatography with element-specific detection systems provides analytical capabilities especially useful when Se/Te compounds need to be determined in complex matrices.

A. Selenols and Tellurols, RYH

Benzeneselenol, PhSeH, was separated from several diorganyl sulphides, diorganyl selenides and benzenethiol by gas chromatography on 20% squalene–80/100-mesh Celite-545 using an argon ionization detector[76]. The selenols corresponding to pantheteine, 4'-phosphopantheteine, dephosphocoenzyme A and coenzyme A were separated from the thiols, disulphides and diselenides of these compounds (see Table 6, items 47–49, 51). The spots were visualized by spraying with an aqueous solution of starch/sodium hydrogen carbonate/0.1 N iodine. The blue background turned brown on drying. Spots caused by selenols, diselenides and selenides returned to the blue background colour upon spraying with dilute phosphoric acid. Spots caused by S compounds remained white. The Se compounds on inorganic thin-layer materials can be determined through oxidation with starch/iodine on the TLC support, extraction of Se compounds from the TLC support into an aqueous solution followed by acidification and colorimetric measurement of the starch–iodine complex. Reproducible results were obtained at concentrations as low as 10^{-8} mole/mL[77].

B. Selenenyl Compounds, RSeX

Benzeneselenenyl bromide was determined by addition of aqueous 0.1 M KI and 6 M H_2SO_4 solution to the solution of the Se compound in CCl_4. The mixture was titrated with sodium thiosulphate solution using starch for the end-point determination[78].

2-Nitrobenzene- and 2,4-dinitrobenzene-selenenyl compounds, RSeX (X = Br, SCN, OMe, OEt, NH_2) reacted in a mixed solvent consisting of ethyl acetate, ethanol and glacial acetic acid with 0.01 N sodium thiosulphate to form $RSeS_2O_3^-$. The excess thiosulphate was back-titrated with an iodine solution[79].

Ethyl selenocyanate, EtSeCN, was separated by gas chromatography from dialkyl selenides and diselenides[80] (see Table 1, item 5).

C. Aryl-selenium and -tellurium Trihalides, RYX_3

Phenylselenium tribromide reacted with KI in H_2SO_4 medium. The mixture was titrated with sodium thiosulphate solution to the starch end-point[78].

Phenyltellurium trichloride was separated by TLC on alumina from tellurium tetrachloride, triphenyltelluronium chloride, diphenyltellurium dichloride and diphenyl telluride[81] (see Table 3, item 6).

D. Seleninic and Selenonic Acids, $RSeO_2H$ and $RSeO_3H$

Benzeneseleninic acids in CCl_4 shaken with an aqueous H_2SO_4 solution of KI were converted to diselenides with liberation of iodine. Iodine was titrated with sodium thiosulphate[78]. The iodometric equivalent masses of *para*-substituted benzeneseleninic acids ($4\text{-}RC_6H_4SeO_2H$, R = H, Me, Cl, Br) are one third of the molecular masses. These iodometric titrations were also carried out in aqueous NaOH solutions with a visual or biamperometric end-point determination[82]. The equivalent masses of the seleninic acids were also determined by titration with NaOH[82].

Benzeneseleninic acid was separated from benzeneselenonic acid by descending chromatography on glass-fibre paper using amyl alcohol/pyridine/ammonium hydroxide (6:14:20). The R_f values were 0.47 ($RSeO_2H$) and 0.21 ($RSeO_3H$)[83].

2-Aminoethaneseleninic acid was separated from 3-aminopropaneseleninic acid and the corresponding selenonic, sulphinic and sulphonic acids on Whatman No. 1 paper with water-saturated 2,4,6-trimethylpyridine/2,6-dimethylpyridine (1:1)[83]. Ion-exchange chromatography with Aminex A-6 and A-5 resins using an amino acid analyser separated the four Se compounds and the sulphinic acids. The selenonic and sulphonic acids eluted together[84].

E. Diorganyl Diselenides, R_2Se_2

Diselenides were detected with the iodine–azide reaction. Heating a diselenide in ethanolic HCl with Raney alloy generated a selenol which liberated nitrogen from a solution containing sodium azide and iodine. Other compounds which gave this test are disulphides, thiols, selenols, thio ketones, thio acids and their derivatives, and mustard oils. In the absence of these substances one microgram of dibenzyl diselenide was detectable[85]. Aromatic diselenides, $(RC_6H_4)_2Se_2$ (R = H, 4-Me, 2-Ph), were titrated iodometrically. The diselenide was added to a solution of iodine monochloride in 12 M HCl. After shaking, the mixture was titrated with standard potassium iodate solution. The diselenide was converted during the titration to arylselenium trichloride[78].

Several dialkyl diselenides were successfully separated from each other, from dialkyl selenides and ethyl selenocyanate by gas chromatography using flame ionization and electron capture detectors. The hydrogen flame ionization detector was much more sensitive to the selenides than the diselenides and ethyl selenocyanate, whereas the electron capture detector had higher sensitivity for the diselenides and ethyl selenocyanate[80].

Dimethyl diselenide and dimethyl selenide are formed by plants and animals from inorganic Se compounds. Several methods were developed to separate these two compounds. The air samples were passed through a column (Alusil[86], silicone oil DC-550[68]) or traps at low temperature[65] to concentrate the Se compounds. After desorption, dimethyl diselenide was separated from dimethyl selenide[65–68,86], dimethyl and diethyl selenide[71] and unidentified Se compounds[68] by gas chromatography using atomic absorption spectrometers as Se-specific detectors[65–68,71].

The methods for the identification, separation and determination of diorganyl diselenides are summarized in Table 1. Diselenides derived from amino acids, and diselenides corresponding to oxytocin, panthetine and coenzyme A are discussed in Section III.I (Table 6).

F. Diorganyl Selenides and Tellurides, R_2Y

Diphenyl chalcogenides, R_2Y, were chromatographed on alumina thin layers. The spots corresponding to Se/Te compounds were visualized with iodine vapour[87].

Attempts were made to separate diphenyl selenide, diphenyl sulphide, diphenyl telluride, diphenyl chalcogen dichlorides, R_2YCl_2 (Y = S, Se, Te) and triphenylselenonium and -telluronium tetrafluoroborates on Silufol UV-254 thin layers. Seven of these compounds were successfully separated. A 0.02% solution of bromocresol green was used for visualization[88].

The separation of dimethyl selenide from dimethyl diselenide and the determination of dimethyl selenide was achieved by gas chromatography using flame ionization or Se-specific atomic absorption spectrometric detectors[65–68,71,80,86]. Several other dialkyl selenides, phenyl alkyl selenides and diphenyl selenide were determined by gas chromatography in mixtures containing selenides, diselenides[80], sulphides, disulphides[76], heterocyclic Se compounds[89] or trimethylarsine[76,90], trimethylstibine[90] and tetramethyltin[70,80].

Dibenzyl selenide and 1,1-dimethylselenourea were separated by high-pressure liquid chromatography on Partisil-PXS-ODS with methanol/water (2:1) as the mobile phase. A graphite furnace atomic absorption spectrometer served as Se-specific detector. Nickel nitrate was added as coanalyte to reduce the volatility of Se in the furnace and enhance the intensity of the Se signal[74]. More details about this and the other separation procedures are given in Table 2.

The applicability of microwave emission systems for the detection of Se in gas chromatographic effluents was checked with dimethyl selenide[72] and diethyl selenide[73]. Absolute detection limits of 12 pg[72] and 62 pg[73] were obtained. The atomic absorption system had a detection limit of 7 ng[70].

The flame photometric detector can distinguish between S and Se compounds. Doping the gas stream with carbon disulphide generated negative Se peaks[92]. Doping with methane reduced the S signal much more than the Se signal[89,92]. The flame photometric detector had an exponential response to Se and Te. The response was made linear by

TABLE 1. Separation, identification and determination of diorganyl diselenides by thin-layer and gas chromatography[a]

Item No.	Diselenide	Separated from	Method	Remarks	Ref.
1	Me_2Se_2	Me_2Se	GC-FID, TP, 15% Si-polymer Se-30 or 10% Apiezon on 80/100 Gas-Chrom-P	Analysis of air exhaled by rats injected with Na_2SeO_3; elution sequence: Me_2Se, Me_2Se_2	86
2	Me_2Se_2	Me_2Se	GC-AA (quartz furnace), TP, 196 nm, 3% OV1 on 80/100 Chromosorb W, DL 0.1 ng Se	Determination of Me_2Se_n in air after preconcentration on GC column at −80°C	65 66 67
3	Me_2Se_2 (17)[b]	Me_2Se (3), unknown Se compounds	GC-AA (quartz furnace), TP 196 nm, 20% PMPE on 60/80 Chromosorb W	Analysis of transpiration gases of *Astragalus racemosus*	68
4	Me_2Se_2 (1)	Me_2Se (3.2), Et_2Se (2)	GC-AA (graphite furnace), 196 nm, 10% PMPE on 80/100 Chromosorb W, DL 0.1 ng Se	Determination of Se compounds in air after preconcentration	71
5	Me_2Se_2 (5.2)	Et_2Se_2 (12.6), Pr_2Se_2 (35.5), Me_2Se (0.6), Et_2Se (1.8), Pr_2Se (4.3), EtSeCN (7.0), MeSeSeEt (4.0), EtSeSePr (8.5)	GC-FID or ECD, TP 20% PMPE on 60/80 Chromosorb W coated with hexamethyldisilazane	Retention times for column temperature of 125°C and injector temperature of 180°C	80
6	Et_2Se_2	See item 5			80
7	Pr_2Se_2	See item 5			80
8	MeSeSeEt	See item 5			80
9	EtSeSePr	See item 5			80
10	Diselenides of amino acids, oxytocin, panthetine, coenzyme A		TLC	See Table 6, items 47–52	77

[a] AA: Atomic Absorption Spectrometry; DL: Detection Limit; ECD: Electron Capture Detector; FID: Flame Ionization Detector; GC: Gas Chromatography; PMPE: PolyMetaPhenyl Ether; TP: Temperature Programmed. [b] Numbers in parentheses represent retention times in minutes.

TABLE 2. Separation, identification and determination of diorganyl selenides by thin-layer and gas chromatography[a]

Item no.	Selenide	Separated from	Method	Remarks	Ref.
1	Me_2Se	Me_2Se_2	GC-FID, GC-AA	See Table 1, items 1 – 5	65 – 68, 71, 80, 86
2	Me_2Se	Et_2Se, Pr_2Se, Bu_2Se, PhSeH, PhSeMe, PhSeEt, corresponding S compounds	GC-Sr-90 ID, 90°C, 20% squalene on 80/100 Celite 545	Pr_2Se not sepd. from PhSH Me_2Se not sepd. from Me_2S	76
3	Me_2Se (1.5)[b]	Me_3As (1.5), Me_4Sn (1.8)	GC-AA (graphite furnace) 196 nm, 5% methylsilicone SP-2100, 3% fluoropropylsilicon SP-2401 on 80/100 Supelcon AWDMCS	Detection limit 12 ng Se	70
4	Me_2Se (9.8)	Me_3As (1.5), Me_3Sb (12), Me_4Sn (8.4), CH_3I (7.6)	GC-TCD, 70°C, 20% DBS on $NaCl/SO_4$ /phosphate		90
5	Me_2Se	Et_2Se, Pr_2Se, Me_2Se_2, Et_2Se_2, Pr_2Se_2, MeSeSeEt, EtSeSePr, EtSeCN	GC-FID or ECD	See Table 1, item 5	80
6	Et_2Se	See item 2	GC-Si-90 ID		76
7	Et_2Se (5)	Et_2O (1), EtI (2)	GC-TCD, 20% silicone rubber on Chromaton N-AW-DMCS		91
8	Et_2Se	See item 5	GC-FID or ECD	See Table 1, item 5	80

(*Contd.*)

TABLE 2. (*Contd.*)

Item no.	Selenide	Separated from	Method	Remarks	Ref.
9	Et_2Se	Ph_2Se, piazselenol, 2,3-dihydro-3-azabenzoselenophene	GC-FPD, TP, 5% PEGA on 80/100 Chromosorb W AW		89
10	Pr_2Se	See item 2	GC-Sr-90 ID		76
11	Pr_2Se	See item 5	GC-FID or ECD	See Table 1, item 5	80
12	Bu_2Se	See item 2	GC-Sr-90 ID		76
13	$(PhCH_2)_2Se$ (26)	1,1-Dimethylselenourea (10)	HPLC-AA (graphite furnace), 196 nm, Partisil-PXS-ODS, $MeOH/H_2O$ (2:1)		72
14	PhSeMe	See item 2	GC-Sr-90 ID		76
15	PhSeEt	See item 2	GC-Sr-90 ID		76
16	Ph_2Se	Ph_2O, Ph_2S, other Se and Te compounds	TLC-alumina	See Table 3, items 2, 3	87 88
17	Ph_2Se	See item 9	GC-FID		89

[a] AA: Atomic Absorption Spectrometry; DBS: DodecylBenzeneSulphonate; ECD: Electron Capture Detector; FID: Flame Ionization Detector; GC: Gas Chromatography; Sr-90 ID: Sr-90 Ionization Detector.

[b] Numbers in parentheses represent retention times in minutes.

providing a high sulphur background with carbon disulphide[93].

The paper and thin-layer chromatographic behaviour of several aromatic ditellurides was investigated with the goal to separate reaction mixtures, identify products and isolate products. Diaryl tellurides were efficiently separated from tellurium tetrachloride, diaryltellurium dihalides, aryltellurium trihalides and triorganyltelluronium halides. The separation of organic Po compounds from the corresponding Te compounds was generally not possible with these methods. The systems investigated and pertinent references are listed in Table 3.

Diethyl telluride was separated from diethyl ether and ethyl iodide by gas chromatography on silicone rubber/Chromaton. A thermal conductivity detector was used[91].

G. Diorganyl-selenium and -tellurium Dihalides, R_2YX_2

Diarylselenium dichlorides and dibromides were determined by a volumetric procedure. Upon shaking the dihalides, R_2SeX_2 (R, X: Ph, Cl; Ph, Br; 4-Tol, Br)[78,101], $RR'SeX_2$ (R, R', X: Ph, 4-Tol, Cl; Ph, 4-BrC_6H_4, Br; 4-Tol, Ph, Br) or dibenzoselenophene dibromide[102] with aqueous KI, iodine was liberated. The iodine was titrated with sodium thiosulphate solution to the starch end-point.

To determine Se, 9 M HCl solutions of selenite were reacted with acetophenone to form an organic Se compound, which might have been bis(benzoylmethyl)selenium dichloride. The organic Se compound was extracted and the extract analysed by gas chromatography employing an electron-capture detector[102].

The thin-layer and paper chromatographic separations of diaryltellurium dichlorides from organic S, Se and Po compounds, other organic Te compounds and tellurium tetrachloride are summarized in Table 4.

H. Triorganyl-selenonium and -telluronium Salts

Milligram amounts of triarylselenonium salts, $(4\text{-}RC_6H_4)_3Se^+X^-$ (R, X: H, Cl; Me, Cl; Me, HSO_4) were determined in aqueous solutions of pH 1–13 by spectrophotometry at 227 nm (Ph derivative, $\varepsilon = 18{,}400$) or 232 nm (Tol derivatives, $\varepsilon = 30{,}900$)[103].

Data relating the thin-layer[81,87,88] and paper chromatographic[95] separation of triphenylselenonium tetrafluoroborate[88] and of triaryltelluronium salts from other organic chalcogen compounds are summarized in Table 5.

I. Selenoamino Acids and Related Compounds

Se with properties similar to S replaces S in S-containing amino acids forming selenoamino acids such as selenocystine and selenomethionine. Selenoamino acids occur naturally. The separation of the seleno- from the thio-amino acids and other amino acids was achieved by ion-exchange chromatography using amino acid analysers. Paper chromatography generally did not separate selenoamino acids from the corresponding S compounds. However, selenomethionine was successfully separated from methionine by thin-layer chromatography on silica gel[119]. Trimethylsilylated selenocystine and selenomethionine had gas chromatographic retention times different from those of the corresponding S compounds[115].

Several aminoalkyl selenides and diselenides related to selenoamino acids [seleno(homo)cystamine, seleno(homo)lanthionamine, selenocystathionamine, carboxymethylselenocysteamine] were separated from each other and the corresponding S derivatives by ion-exchange chromatography[116,117]. A dipeptide, glutamyl-*Se*-methylselenocysteine[123], had a significantly longer retention time than the S-peptide on a Dowex 1-X4 column. The paper chromatographic behaviour of the selenols, thiols,

TABLE 3. Separation, identification and determination of diorganyl tellurides by thin-layer, paper and gas chromatography[a]

Item no.	Telluride	Separated from	Method	Remarks	Ref.
1	Et_2Te (8)[b]	EtI (3.5), Et_2O (1)[b]	GC-TCD		91
2	Ph_2Te	(*o*-Tol)$_2$Te (0.61), (*m*-Tol)$_2$Te (0.54), (*p*-Tol)$_2$Te (0.54), (2,5-Xyl)$_2$Te (0.62), (*p*-An)$_2$Te (0.54), (1-Naph)$_2$Te (0.33), Ph_2O (0.59), Ph_2S (0.60)	TLC, alumina, pet. ether	Visualization with I_2 vapour	87
3	Ph_2Te	Ph_2S, Ph_2Se, Ph_2SCl_2, Ph_2SeCl_2, Ph_2TeCl_2, $Ph_3Y^+BF_4^-$ (Y = S, Se, Te)	TLC, Silufol UV-254, C_6H_6/EtOAc/H_2CO(?)(4:4:1)	Seven compounds sepd., visualization with 0.02% bromocresol green in EtOH	88
4	Ph_2Te (0.55)[c]	$TeCl_4$ (0.0)	TLC, alumina, pet. ether	Separation of ^{127m}Te compounds	94
5	Ph_2Te (0.20)	Ph_2TeCl_2 (0.67), Ph_3TeCl (0.96), Ph_3TeI (0.90)	PC, Me_2CO/MeOH/H_2O (4:3:2), several other solvent systems investigated	Po compounds have same R_f as Te compounds	95
6	Ph_2Te (0.95)	$TeCl_4$ (0.0), $PhTeCl_3$ (0.08), Ph_2TeCl_2 (0.54), Ph_3TeCl (0.32)	TLC, alumina, C_6H_6/EtOH/MeCOOH/H_2O (44:11:3.5:1)	Several other solvent systems investigated	81
7	(*p*-Tol)$_2$Te (0.64)	(*o*-Tol)$_2$Te (0.71), (*m*-Tol)$_2$Te (0.67)	TLC, alumina, solvent not reported	Visualized by spraying with aq. $KMnO_4$	96
8	(*p*-Tol)$_2$Te (0.0)	R_2TeCl_2 (0.40), $RTeCl_3$ (0.60), R_3TeCl (0.90)	PC, MeOH/H_2O (3:1)	Paper treated with 2% butyl sebacate/MeOH	97
9	(*p*-Tol)$_2$Te (1.0)	$TeCl_4$ (0.0), R_2TeCl_2, $RTeCl_3$, R_3TeCl (1.0)	PC, $CHCl_3$	Without sebacate	97

10	(*p*-Tol)$_2$Te (1.0)	TeCl$_4$, R$_2$TeCl$_2$, RTeCl$_3$, R$_3$TeCl (0.0)	PC, pet. ether	Without sebacate	97
11	(*p*-Tol)$_2$Te (0.76)	R$_2$TeF$_2$ (0.40), R$_2$TeCl$_2$ (0.58), R$_2$TeBr$_2$ (0.49), R$_2$TeI$_2$ (0.43), R$_3$TeCl (0.08), R$_3$TeI (0.21)	PC, EtOAc, paper treated with DMF	Po derivatives have R_f similar to Te compounds	98
12	(*m*-Tol)$_2$Te	See item 7	TLC, alumina		96
13	(*m*-Tol)$_2$Te	See item 2	TLC, alumina, pet. ether		87
14	(*o*-Tol)$_2$Te	See item 7	TLC, alumina		96
15	(*o*-Tol)$_2$Te	See item 2	TLC, alumina, pet. ether		87
16	(*p*-An)$_2$Te (0.66)	R$_2$TeF$_2$ (0.42), R$_2$TeCl$_2$ (0.59), R$_3$TeCl (0.12), R$_3$TeBr (0.13), R$_3$TeI (0.17)	PC, EtOAc, paper treated with DMF	Po compounds have R_f similar to Te compounds	99
17	(*p*-An)$_2$Te	See item 2	TLC, alumina, pet. ether		87
18	(2,5-Xyl)$_2$Te	See item 2	TLC, alumina, pet. ether		87
19	(1-Naph)$_2$Te (0.63)	R$_2$TeF$_2$ (0.50), R$_2$TeCl$_2$ (0.45), R$_2$TeBr$_2$ (0.50), R$_2$TeI$_2$ (0.69), R$_3$TeCl (0.09), R$_3$TeBr (0.02), R$_3$TeI (0.010), R$_3$TeCl·HgCl$_2$ (0.0)	PC, EtOAc, paper treated with DMF	Po compounds have R_f similar to Te compounds	100
20	(1-Naph)$_2$Te	See item 2	TLC, alumina, pet. ether		87

[a] GC: Gas Chromatography; PC: Paper Chromatography; TCD: Thermal Conductivity Detector; TLC: Thin-Layer Chromatography.

[b] Retention time.

[c] Numbers (O.XY) represent R_f values.

TABLE 4. Separation, identification and determination of diorganyl-selenium/tellurium dihalides by paper and thin-layer chromatography[a]

Item no.	Dihalide	Separated from	Method	Remarks	Ref.
1	Ph_2SeCl_2	Ph_2Y, $Ph_3Y^+BF_4^-$ (Y = S, Se, Te) Ph_2SCl_2, Ph_2TeCl_2	TLC, Silufol UV-254, C_6H_6/EtOAc/H_2CO(?) (4:4:1)	Seven compounds separated, visualization with 0.02% bromocresol green in EtOH	88
2	Ph_2TeCl_2	See item 1	See item 1	See item 1	88
3	Ph_2TeCl_2	Ph_2Te, Ph_3TeX[b]	PC, Me_2CO/MeOH/H_2O (4:3:2)	See Table 3, item 5	95
4	Ph_2TeCl_2	$TeCl_4$, $PhTeCl_3$, Ph_3TeCl	TLC, alumina	See Table 3, item 6	81
5	Ph_2TeCl_2 (0.49)[c]	(*o*-Tol)$_2$TeCl$_2$ (0.25), (*m*-Tol)$_2$TeCl$_2$ (0.67), (*p*-Tol)$_2$TeCl$_2$ (0.49), (*p*-Tol)$_3$TeCl (0.80)	TLC, alumina, EtOAc/MeOH (3:1)		87
6	Ph_2TeCl_2 (0.68)	(*p*-Tol)$_2$TeCl$_2$ (0.73), (*p*-Tol)$_3$TeCl (0.22), Ph_3TeCl (0.27)	TLC, alumina, C_6H_6/EtOH (4:1)	C_6H_6/EtOH (9:1) also used	87
7	(*p*-Tol)$_2$TeF$_2$	R_2Te, R_2TeX_2, R_3TeX	PC, EtOAc	See Table 3, item 11	98
8	(*p*-Tol)$_2$TeCl$_2$	R_2Te, $RTeCl_3$, R_3TeCl	PC, MeOH/H_2O (3:1)	See Table 3, item 8	97
9	(*p*-Tol)$_2$TeCl$_2$ (1.0)	$TeCl_4$ (0.0)	PC, $CHCl_3$	See Table 3, item 9	97
10	(*p*-Tol)$_2$TeCl$_2$ (0.0)	R_2Te (1.0)	PC, pet. ether	See Table 3, item 10	97

11	(*p*-Tol)$_2$TeCl$_2$	R$_2$Te, R$_2$TeX$_2$, R$_3$TeX	PC, EtOAc	See Table 3, item 11	98
12	(*p*-Tol)$_2$TeCl$_2$	See items 5, 6	TLC, alumina		87
13	(*p*-Tol)$_2$TeBr$_2$	R$_2$Te, R$_2$TeX$_2$, R$_3$TeX	PC, EtOAc	See Table 3, item 11	98
14	(*p*-Tol)$_2$TeI$_2$	R$_2$Te, R$_2$TeX$_2$, R$_3$TeX	PC, EtOAc	See Table 3, item 11	98
15	(*m*-Tol)$_2$TeCl$_2$	See item 5	PC, alumina		87
16	(*o*-Tol)$_2$TeCl$_2$	See item 5	PC, alumina		87
17	(*p*-An)$_2$TeF$_2$	R$_2$TeCl$_2$, R$_3$TeX	PC, EtOAc	See Table 3, item 16	99
18	(*p*-An)$_2$TeCl$_2$	R$_2$TeF$_2$, R$_3$TeX	PC, EtOAc	See Table 3, item 16	99
19	(1-Naph)$_2$TeF$_2$	R$_2$TeX$_2$, R$_3$TeX	PC, EtOAc	See Table 3, item 19	100
20	(1-Naph)$_2$TeCl$_2$	R$_2$TeX$_2$, R$_3$TeX	PC, EtOAc	See Table 3, item 19	100
21	(1-Naph)$_2$TeBr$_2$	R$_2$TeX$_2$, R$_3$TeX	PC, EtOAc	See Table 3, item 19	100
22	(1-Naph)$_2$TeI$_2$	R$_2$TeX$_2$, R$_3$TeX	PC, EtOAc	See Table 3, item 19	100

[a] PC: Paper Chromatography; TLC: Thin-Layer Chromatography.
[b] X = other halides. Numbers represent R_f values.

TABLE 5. Separation and identification of triaryl-telluronium and -selenonium compounds[a]

Item no.	$R_3Te^+X^-$	Separated from	Method	Remarks	Ref.
1	Ph_3TeCl	R_2TeCl_2, R_3TeI	PC, $Me_2CO/MeOH$	See Table 3, item 5	95
2	Ph_3TeCl	$TeCl_4$, $RTeCl_3$, R_2TeCl_2	TLC, alumina	See Table 3, item 6	81
3	Ph_3TeI	R_2TeCl_2, R_3TeCl	PC, $Me_2CO/MeOH$	See Table 3, item 5	95
4	Ph_3TeBF_4	Ph_2Y, Ph_2YCl_2, Ph_3YBF_4 ($Y = S$, Se, Te)	TLC, Silufol UV-254	See Table 3, item 3	88
5	Ph_3SeBF_4	Ph_2Y, Ph_2YCl_2, Ph_3YBF_4 ($Y = S$, Se, Te)	TLC, Silufol UV-254	See Table 3, item 3	88
6	*p*-Tol_3TeCl	R_2Te, R_2TeCl_2, $RTeCl_3$, $TeCl_4$	PC, $MeOH/H_2O$, $CHCl_3$, pet. ether, EtOAc	See Table 3, items 8, 9, 10, 11	97 98
7	*p*-Tol_3TeI	R_2TeX_2, R_3TeCl	PC, EtOAc	See Table 3, item 1	98
8	*p*-An_3TeX	R_2TeF_2, R_2TeCl_2, R_3TeX	PC, EtOAc	See Table 3, item 16	99
9	1-$Naph_3TeX$	R_2TeX_2, R_3TeX, $R_3TeCl \cdot HgCl_2$	PC, EtOAc	See Table 3, item 19	100

[a] PC: Paper Chromatography; TLC: Thin-Layer Chromatography.

selenides, sulphides, diselenides and disulphides related to pantethine, coenzyme A, 4-phosphopantethine and dephosphocoenzyme A was investigated[77].

The results of these investigations of selenoamino acids and related compounds are summarized in Table 6.

J. Diorganyl Selenoxides, R_2SeO

Diaryl selenoxides reacted with aq. KI in 6 M H_2SO_4 solution. The liberated iodine was titrated with sodium thiosulphate to the starch end-point. This reaction converts the selenoxides to selenides. The equivalent mass for selenoxides is half the molecular mass[78]. Although only bis(4-ethoxyphenyl) selenoxide was determined, the method should be applicable to other selenoxides and perhaps to telluroxides.

Four methods for the microdetermination of selenoxides were investigated. Potentiometric titrations of selenoxides dissolved in acetic anhydride with perchloric acid gave acceptable results[125,126]. The iodometric method[78] was found to be erratic and unreliable in the presence of compounds with other functional groups[125]. Selenoxides oxidized iron(II) to iron(III) in acidic methanolic ferroammonium thiocyanate solution. The intensely coloured iron(III) thiocyanate complex was determined photometrically. The instability of the iron(II) thiocyanate solution proved to be a serious disadvantage for routine application of this method[125]. The degree of inhibition of the hydrolysis of urea by urease was found to be proportional to the concentration of selenoxides. The inhibition constants are compound-specific. It might be possible to determine an inhibitory compound in the presence of others[125]. These methods were used to determine diphenyl selenoxide and 2-(phthalimido)ethyl methyl selenoxide[125].

K. Selenourea

Selenourea was determined in sulphite solutions buffered with $NaHCO_3$ by addition of 0.1 N iodine solution to oxidize selenium to selenite. After addition of acetic acid the excess iodine was titrated with thiosulphate solution. The selenite was then determined iodometrically in HCl solution. An appropriate modification of this procedure allowed the analysis of mixtures containing selenourea and selenosulphate[127].

1,1-Dimethylselenourea was separated from dibenzyl selenide by high-pressure liquid chromatography using a graphite furnace atomic absorption spectrometer as a Se-specific detector[74] (Section III. F, Table 2, item 13).

L. Selenophene, Tellurophene and Related Compounds

The molar responses relative to benzene and the effective carbon numbers of selenophene, tellurophene and their 2-acetyl derivatives were determined with a gas chromatograph – flame ionization detector system. The molar responses were approximately half that of benzene[128].

The equivalent mass of benzoselenophene dibromide was determined by treating the dibromide with a H_2SO_4 solution of KI and titrating the liberated iodine with thiosulphate solution[78].

The gas chromatographic peak caused by 2,5-dimethyl-3-azabenzoselenophene was identified by doping the gas stream with carbon disulphide. Se peaks turned negative, but S peaks remained positive[92].

2,3-Dihydro-3-azabenzoselenophene was separated by gas chromatography from diethyl selenide, diphenyl selenide and piazselenol[89] (Section III. F; Table 2, item 9).

TABLE 6. Separation, identification and determination of selenoamino acids and related compounds[a]

Item no.	Compound	Separated from	Method	Ref.
1	*Se*-Methylselenocysteine (0.48)[b] $MeSeCH_2CH(NH_2)COOH$	Selenocystine (0.14), selenomethionine (0.55), cystine (0.14), methionine (0.55); S compounds not separated from corresponding Se compounds	DPC, BuOH/pyr./H_2O (1:1:1); several other solvent systems investigated	104
2	*Se*-Methylselenocysteine	Cystine, homocystine, lanthionine, cystathionine, djenkolic acid, methionine, methionine sulphoxide, *S*-methylcysteine sulphoxide; not separated from *S*-methylcysteine	PC (2 dim.), HCO_2H/*t*-BuOH/H_2O (3:14:3), EtOH/BuOH/H_2O/(*c*-Hex)$_2$NH 10:10:5:2)	105
3	*Se*-Methylselenocysteine (115)[c]	Selenocystine (201), selenomethionine (210), selenocystathionine (203), selenohomocystine (305), corresponding S compounds, other amino acids	AAA, Aminex A-4, NaC, 56°C	106
4	*Se*-Methylselenocysteine (121)[c]	*S*-Methylcysteine (99), selenocystine (157), selenomethionine (170), selenoethionine (186), *Se*-benzylselenocysteine (282), and corresponding S compounds	AAA, Beckman P-28 resin, NaC with Brij, pentachlorophenol, thiodiglycolic reagent, 55°C	107
5	*Se*-Carboxymethylselenocysteine (78)[d] $HOOCCH_2SeCH_2CH(NH_2)COOH$	*S*-Carboxymethylcysteine (60), aspartic acid (68), threonine (72)	AAA, Aminex A-6, NaC, 30°C	108
6	*Se*-Benzylselenocysteine $PhCH_2SeCH_2CH(NH_2)COOH$	See item 4	AAA	107
7	*Se*-(*N*-Ethyl)succinimidoselenocysteine (0.66)[b]	Selenocystine (0.17), cystine (0.16), cysteic acid (0.20), *N*-ethylsuccinimidocysteine (0.66)	PC, EtOH/*t*-BuOH/HCO_2H/H_2O (12:4:1:3)	109
8	Selenocystine $[HOOCCH(NH_2)CH_2]_2Se_2$	See item 7	PC	109

9	Selenocystine	See item 1	DPC	104
10	Selenocystine	See item 3	AAA	106
11	Selenocystine (157)[c]	Cystine (134) and compounds in item 4	AAA	107
12	Selenocystine (410)[c]	Selenomethionine (455), cystine (368), methionine (420), isoleucine (423), leucine (442)	AAA, 8% divinylbenzene–styrene copolymer, NaC, 33°C	110
13	Selenocystine (20)[d]	Methionine (20), leucine (84), Selenomethionine (76) (time of buffer change: 0)	AAA, 8% divinylbenzene–styrene copolymer, NaC	111
14	Selenocystine	R_f values determined in various solvents	TLC, cellulose, PC	112
15	Selenocystine (45)[d]	Valine (36), methionine (62), isoleucine (65), leucine (82), selenomethionine (90)	AAA, Beckman PA-35, NaC, 30°C	113
16	Selenocystine (0.08)[b] oxidized with hydrogen peroxide	Selenomethionine (ox.) (0.22), methionine (0.55), cystine (0.04)	PC, $BuOH/AcOH/H_2O$ (4:1:1); other solvents used also	114
17	$[Me_3SiOOCCH(NH_2)CH_2]_2Se_2$ silylated selenocystine (15.8)[d]	$[Me_3SiOOCCH(NH_2)CH_2]_2S_2$ (9.8) $Me_3SiOOCCH(NH_2)CH_2$—SSe—$CH_2CH(NH_2)COOSiMe_3$ (15.8)	GC-FID, 170°C, 2% SE-30 on 90/100 Anakrom SD	115
18	$[HOOCCH(NH_2)CH_2]_2SeS$ (137)[c]	Selenocystine (143), cystine (130)	AAA, see item 4, without thiodiglycolic reagent	107
19	$HOOCCH(NH_2)CH_2SeSeCH_2CH_2COOH$ (146)[c]	Selenocystine (139)	AAA, see item 4, without thiodiglycolic reagent	107
20	*Se*-Carboxymethylselenocysteamine $HOOCCH_2$—Se—$CH_2CH_2NH_2$	Corresponding S compound	AAA, Aminex A-6, NaC, 50°C PC, $BuOH/AcOH/H_2O$ (4:1:5)	116

(*Contd.*)

TABLE 6. (*Contd.*)

Item no.	Compound	Separated from	Method	Ref.
21	Selenocystamine (163, 97*)^d $(H_2NCH_2CH_2)_2Se_2$	Selenohomocystamine ($\underline{58}$, $\underline{45}$*), selenolanthionamine (124, 93*), selenocystathionamine (82, 63*), selenohomolanthionamine (47, 44*) and corresponding S compounds (ret. time of S compounds marked*)	AAA, Aminex A-5, 2.35 M pot. citrate pH 5.6, then 0.2M NaOH; underlined ret. times relative to time of buffer change	117
22	Selenohomocystamine $(H_2NCH_2CH_2CH_2)_2Se_2$	See item 21	AAA, Aminex A-5	117
23	Selenalanthionamine $(H_2NCH_2CH_2)_2Se_2$	See item 21	AAA, Aminex A-5	117
24	Selenocystathionamine $H_2NCH_2CH_2—Se—CH_2CH_2CH_2NH_2$	See item 21	AAA, Aminex A-5	117
25	Selenohomolanthionamine $(H_2NCH_2CH_2CH_2)_2Se$	See item 21	AAA, Aminex A-5	117
26	Selenohomocystine $[HOOCCH(NH_2)CH_2CH_2]_2Se$	See item 3	AAA, Aminex A-4, NaC	106
27	Selenomethionine $MeSeCH_2CH_2CH(NH_2)COOH$	See item 3	AAA, Aminex A-4, NaC	106
28	Selenomethionine	See item 1; not separated from S compound	DPC	104
29	Selenomethionine	See item 4	AAA, Beckman P-28, NaC	107
30	Selenomethionine	See item 12	AAA	110
31	Selenomethionine	See item 13	AAA	111
32	Selenomethionine	See item 15	AAA, P-35 resin, NaC	113
33	Selenomethionine	Not separated from methonine	DPC, $BuOH/pyr./H_2O$ (1:1:1)	118

34	Selenomethionine (0.41)^b	Methionine (0.32)	TLC, silica gel, *i*-PrOH/BuOH/H_2O (1:3:1)	119
35	Selenomethionine (0.22) oxidized	Methionine (0.55), see item 16	PC	114
36	$Me_3SiOOCCH(NH_2)CH_2CH_2SeCH_3$ (3.8)^d silylated selenomethionine	Sil. methionine (2.8), sil. methionine sulphoxide (10.5), sil. methionine sulphone (14.3)	GC-FID, SE-30 on 80/100 Anakrom SD, 117°C	115
37	Selenoethionine $EtSeCH_2CH_2CH(NH_2)COOH$	See item 4	AAA, Beckman P-28, NaC	107
38	Selenocystathionine $HOOCCH(NH_2)CH_2SeCH_2CH_2CH(NH_2)COOH$	See item 3	AAA, Aminex A-4, NaC	106
39	Selenalysine (51) $H_2NCH_2CH_2SeCH_2CH(NH_2)COOH$	Lysine (43), thialysine (46), histidine (53)	AAA, Aminex A-5, 30°C, 0.35M Na citrate, pH 5.28	120
40	Selenalysine	Lysine, thialysine: only one spot, no separation; distinguishable with various spray reagents	PC, 10 mobile phases investigated	120
41	3-Selenaproline (34)^d	4-Selenaproline (37), 3-thiaproline (30), 4-thiaproline (34), proline (42)	AAA, Durum DC-2A, 54°C, NaC, pH 3.25	121
42	3-Selenaproline (0.66)^b	4-Selenaproline (0.36), 3-thiaproline (0.63), 4-thiaproline (0.59)	PC, $EtOH/NH_3(25\%)/H_2O$ (20:2:4)	121
43	4-Selenaproline	See items 41, 42	AAA, PC	121
44	4-Selenaproline (62)^d	4-Thiaproline (53), proline (68)	AAA, Aminex A-6, 50°C, 0.2N Na citrate, pH 3.25	122
45	4-Selenaproline (0.20)^b	4-Thiaproline (0.45)	PC, collidine/lutidine (1:1), water-saturated	122

(Contd.)

TABLE 6. (*Contd.*)

Item no.	Compound	Separated from	Method	Ref.
46	γ-L-Glutamyl-*Se*-methylseleno L-cysteine (163)[d]	Corresponding S-peptide (134), *Se*-methylselenocysteine (310)	AAA, Dowex 1-X4 (acetate form) pyr./acetate buffer pH 4 (0.1M acetate)	123
47	Panteth(e)ine	—SeH (0.61)[b], —SH (0.63), Se_2 (0.86), S_2 (0.72)	PC, $BuOH/AcOH/H_2O$ (5:2:1)	77
48	4′-Phosphopanteth(e)ine	—SeH (0.72)[b], —SH (0.67), Se_2 (0.50), S_2 (0.50)	PC, see item 47	77
49	Coenzyme A	—SeH (0.34)[b], —SH (0.36), Se_2 (0.10), S_2 (0.10)	PC, EtOH/0.5M NH_4OAc (3:2), pH 4	77
50	Benzoylcoenzyme A	Se (0.59)[b], S (0.63)	PC, EtOH/0.5M NaOAc (3:2), pH 4	77
51	Dephosphocoenzyme A	—SeH (—), —SH (0.48), Se_2 (0.25), S_2 (0.23)	PC, see item 49	77
52	Selenoxytocin	Oxytocin; no separation	TLC, silica gel; Gel Filtration Sephadex G-25, 0.2M AcOH	124

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[a] AAA: Amino Acid Analyser; DPC: Descending Paper Chromatography; NaC: Na Citrate buffer, 0.2M, pH 3.25, then 4.25; PC: Paper Chromatography; TLC: Thin-Layer Chromatography.

[b] R_f values.

[c] Elution volume (mL).

[d] Retention time (min).

M. Piazselenols

Piazselenols are five-membered heterocyclic compounds which form when aromatic *ortho*-diamines condense with selenites. The absorption and fluorescence properties of piazselenols were exploited for the determination of Se. Piazselenols in contrast to selenite are soluble in non-polar organic solvents and can be extracted, for instance with hexane, toluene, chloroform or cyclohexane, from aqueous solutions. The extracts can then be analysed by gas chromatography employing electron capture detectors[129-134], flame photometric detectors[89,135] or a microwave emission detector[136]. The preconcentration achieved by the extraction, the separation of the piazselenol from interfering compounds by gas chromatography and the sensitivity of the detectors make it possible to determine Se at concentrations of 0.1 μg/L. The absolute detection limits are in the low nanogram range. The sensitivity of the methods is influenced by the substituents present in the piazselenol. The relative sensitivities of piazselenols derived from diaminonaphthalene and substituted diaminobenzenes were investigated by Shimoishi[132].

Piazselenol was separated by gas chromatography from diethyl selenide, diphenyl selenide and 2,3-dihydro-3-azabenzoselenophene[89] (Section III. F; Table 2, item 9).

The piazselenol formed from selenite and diaminonaphthalene was extracted with cyclohexane. The extract was chromatographed on C-18 reverse-phase TLC plates ($EtOH/H_2O/AcOH$ 65:35:1) and silica gel plates (ethyl acetate/toluene 1:4). Se at nanogram levels was quantitated by densitometry[137].

Piazselenol, 5-chloro, 5-nitro- and benz-piazselenol (from 2,3-diaminonaphthalene[138,139]) were separated from excess reagents by reverse-phase (Nucleosil C-18[138], Bondapak C-18[139]) high-pressure liquid chromatography with methanol/water, acetonitrile/water[138] or ethanol/water[139] as mobile phases. With ultraviolet or fluorometric detection Se was determined in the nano- to pico-gram range[138].

N. Selenium and Tellurium Diethyldithiocarbamates, $(Et_2NCSS)_2Y$

Inorganic Se/Te compounds react with diethyldithiocarbamates to form compounds extractable with chloroform. Dithiocarbamates are formed by many cations. High-pressure liquid chromatography using reverse-phase columns allowed the separation of the Se[140,141] and Te[141] compounds from other dithiocarbamates. With ultraviolet spectroscopic detectors one microgram of Se/Te was detected[141].

Tellurium diethyldithiocarbamate was separated on silica gel thin layers, the spot extracted with methanol and Te determined in the extract by graphite furnace atomic absorption spectrometry[142].

O. Trialkylsilyl Selenides/Tellurides and Related Compounds

The compounds $(Et_3M)_2Y$ (Y = Te, Se, S) were separated by gas chromatography with a detector based on heat conductivity. The column material was 20% Apiezon L on silanized Chromosorb W. The retention time increased with increasing boiling points of the compounds[143]. Bis(trimethylsilyl) selenone [$(Me_3Si)_2SeO_2$] formed from selenite and *N*,*O*-bis(trimethylsilyl)acetamide, is a volatile, stable compound, which was used to determine Se by gas chromatography with flame ionization detection[144].

IV. POLAROGRAPHIC AND OTHER ELECTROCHEMICAL METHODS

Polarography has been applied extensively for the determination of inorganic Se[18-25]. Although several organic Se compounds have been the subject of polarographic studies, few methods were developed which are suitable for quantitative determinations. Most of the investigations explored the mechanisms of reduction of the Se compounds and compared their reduction behaviour with that of the corresponding S compounds.

Benzeneselenols gave under various conditions a single reduction wave. The half-wave potential was dependent on the pH of the medium and the substituents in the benzene ring[145]. Nygard investigated the polarographic reduction of bis(carboxyalkyl) diselenides, $[HOOC(CH_2)_n]_2Se_2$ ($n = 1$[146,147], 2–4[148,149]), diphenyl diselenide[150], 1,2-diselenacyclopentane[151] and its 4,4-bis(hydroxymethyl)[152,154], 4-carboxy[153] and 3-(4′-carboxybutyl)[152] derivatives, 4-carboxy-1-thia-2-selenacyclopentane[147,153], 3,6-dicarboxy-1,2-diselenacyclohexane[152], 4,5-dicarboxy-1,2-diselenacyclohexane[152] and 2,2-bis(hydroxymethyl)-1,3-propanediseleninic acid[147,154]. Information about the electrode processes was gained from direct-current polarographic curves, electrocapillary curves and oscillopolarographic investigations. The diselenides, R_2Se_2, form initially the mercury compounds $(RSe)_2Hg$ or RSeHg which are subsequently reduced to selenols, RSeH, by transfer of one electron per Se atom[147]. The diseleninic acid is first irreversibly reduced to the selenium–mercury compound which in a subsequent reversible step is transformed to the diselenol[147,154] The polarographic reduction of 2-aminoethylselenosulphuric acid is preceded by the formation of RSeHg and sulphite and finally yields 2-aminoethaneselenol[155].

Selenocystine and selenocysteine were investigated by several polarographic methods and the properties of the Se compounds compared with those of the corresponding S derivatives[148,156,157]. Selenocystine can be determined by cathodic stripping voltammetry in dilute aqueous acid. The detection limit for selenocystine is 5×10^{-10} M in the presence of 100-fold amounts of cystine and cysteine[158]. Selenocystine causes catalytic prewaves in the polarographic reduction of cobalt[159] and nickel[160]. The prewaves are probably produced by complexes formed between the metal ions and selenocysteine[159,160]. Selenocystamine [bis(2-aminoethyl) diselenide] gave polarographic waves more positive than cystamine. The diselenide can be distinguished from the disulphide in the same solution[161].

An oscillopolarographic investigation of selenourea proved that the reduction of selenourea yielded selenide ion which reacted with mercury. Selenourea is reduced at a potential 140 mV more negative than thiourea. The detection limit for selenourea is 5×10^{-6} M[162,163].

Substituted 2-nitroselenophenes can be determined polarographically at concentrations of 10^{-5} M[164]. The general features of the polarographic reduction of substituted 2-nitroselenophenes are similar to those of thiophenes and furans[165]. AC polarographic studies of heteroacene quinones in acetonitrile containing the 2,5-diphenylselenophene ring showed that the reduction proceeded in two one-electron steps[166].

Polarographic investigations of 2,1,3-selenadiazole[167], benzoselenadiazole[168–174], benzoselenadiazoles substituted in the 4- or 5-position[174], pyridinoselenadiazole[175] and dioxopyrimidinoselenadiazole[175] in aqueous medium and in dimethylformamide established that a radical anion is first formed which is subsequently reduced to the *ortho*-diamine and selenide.

The selenadiazoles obtained from 3,3′,4,4′-tetraaminobiphenyl and selenite were used for the polarographic determination of Se[176–178]. A sensitivity of one microgram Se per litre was achieved with single sweep polarography[178]. With 4-chlorobenzoselenadiazole and differential pulse polarography the detection limit was 0.4 microgram Se per litre[179].

The polarographic reduction of bis(4-methoxyphenyl) ditelluride produced 4-methoxybenzenetellurol[180] Bis(4-methoxyphenyl)tellurium oxide yielded under conditions of classical and oscillographic polarography bis(4-methoxyphenyl) telluride in an irreversible reaction[181].

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CHAPTER 6

Nuclear magnetic resonance and electron spin resonance studies of organic selenium and tellurium compounds

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I. INTRODUCTION

Every element in Group VI in the Periodic Table possesses at least one magnetically active isotope[1]. (Table 1 lists the NMR properties of these nuclei and compares them to those of the ^{1}H and ^{13}C nuclei.) However, the two lighter elements, O and S, both possess only quadrupolar nuclei (Table 1) and the dominant isotopes of the elements, ^{16}O and ^{32}S, have zero spin. Although the number of studies using ^{17}O-NMR spectroscopy has increased considerably with the advent of pulsed Fourier transform (FT) techniques, ^{33}S-NMR spectroscopy continues to be difficult experimentally, due to the quadrupolar spin ($I = 3/2$) and the low natural abundance (0.76%). On the other hand, Se and Te both possess spin-$\frac{1}{2}$ nuclei with adequate natural abundance (^{77}Se and ^{125}Te) such that NMR experiments using pulsed FT methods to observe these nuclei are relatively routine. However, only in the last five years have researchers begun to extensively investigate the NMR parameters of organoselenium and organotellurium compounds using pulsed FT ^{77}Se- and ^{125}Te-NMR spectroscopy.

Because the material has not been reviewed previously, this article will concentrate heavily on NMR studies utilizing the ^{77}Se and ^{125}Te nuclei. ^{1}H-NMR studies have been reviewed previously[2] and, because of the small chemical shift range, they have not been found to be very informative. ^{13}C-NMR investigations of organoselenium and organotel-

TABLE 1. NMR properties of the Group VI nuclei[a]

Isotope	Spin	Natural abundance (%)	NMR frequency (MHz)	Relative receptivity[b] R^{P}	R^{C}
^{1}H	1/2	99.985	100.1	1.000	5.68×10^{3}
^{13}C	1/2	1.108	25.1	1.76×10^{-4}	1.00
^{17}O	5/2	0.037	13.6	1.08×10^{-5}	6.11×10^{-2}
^{33}S	3/2	0.76	7.7	1.71×10^{-5}	9.73×10^{-2}
^{77}Se	1/2	7.58	19.1	5.26×10^{-4}	2.98
^{123}Te	1/2	0.87	26.2	1.57×10^{-4}	0.88
^{125}Te	1/2	6.99	31.5	2.21×10^{-3}	12.5

[a] Data taken from Ref. 1.

[b] Receptivity relative to ^{1}H is given as R^{P} and relative to ^{13}C is given as R^{C}.

lurium compounds are fairly numerous and will be dealt with where they complement the ^{77}Se and ^{125}Te studies or are in some other way especially noteworthy. A discussion and comprehensive listing of ^{13}C chemical shifts and other carbon parameters in organoselenium and organotellurium compounds is beyond the scope of this article.

In searching the literature, every attempt has been made to review publications through June 1983. Not every paper may be referenced, but certainly the large majority are discussed or referenced in some way. This article is divided into two parts. The first and largest part of the paper deals with NMR studies and the second part deals with ESR studies. As mentioned previously, material reviewing ^{77}Se- and ^{125}Te-NMR studies has not appeared since the large explosion of pulsed FT data has begun. To demonstrate how recent most of the data are, it is interesting to note that a 1978 book[1] covering NMR studies of all nuclei in a very comprehensive manner devoted only ten pages to ^{77}Se-NMR spectroscopy and only five papers were referenced[3-7] which had utilized pulsed FT methods. Only two pages described ^{125}Te-NMR spectroscopy and there were no publications describing direct observation of ^{125}Te resonances. Accordingly, it was felt that efficient use could be made of tables of ^{77}Se and ^{125}Te chemical shifts classified according to type of compound. The chemical shift ranges of both of these nuclei are very large (~ 3000 ppm for ^{77}Se and ~ 7000 ppm for ^{125}Te) and it is hoped that, in addition to the discussion in this chapter, the reader will find it instructive to refer to the chemical shift values given for various classes of organoselenium and organotellurium compounds. Because the chemical shift range is so large for these nuclei and because these shifts are sensitive to various factors, in some cases more than one value has been reported for the same molecule. Every attempt has been made to report all values in the tables and to comment on any discrepancies. Also, where possible, a comparison of Se and Te values with corresponding O and/or S parameters has been made.

II. NMR STUDIES

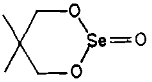
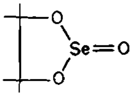
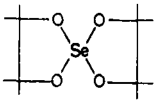
A. Organoselenium Compounds

1. *Relaxation times*

The problems of the relatively low natural abundance and relatively low NMR receptivity of ^{77}Se with respect to the proton have been minimized with the advent of FT NMR spectrometers and techniques, through which substantial gains in the signal-to-noise ratio over conventional continuous wave NMR spectroscopy may be realized. To take full advantage of the FT method, a knowledge of the inherent spin-lattice relaxation time, T_1, of the Se nucleus is desirable since it influences the time duration of the experiments via the recycle time between pulses[8,9]. The T_1 values can also provide valuable information concerning molecular dynamics and interactions, molecular structure, conformation and composition. It is always advantageous, when studying any particular nucleus, to be forearmed with a knowledge of the range of T_1 values of the nucleus in a number of functional forms and under a variety of conditions (e.g. temperature, solvent, concentration). Furthermore, it is also very important to determine which of the various mechanisms contribute to the overall spin-lattice relaxation of the nucleus[8,9].

In 1977–79 several studies[10-14] appeared which reported the first investigations of ^{77}Se spin-lattice relaxation times. Values for T_1 of representative compounds are shown in Table 2. Several important conclusions emerged from these and later studies[15,16]. First, the dipole–dipole (DD) relaxation mechanism which is so important in ^{13}C-NMR spectroscopy[17,18] is almost non-existent in Se compounds. For ^{77}Se, a maximum Nuclear Overhauser Enhancement (NOE)[19] of 2.6 is possible, but for only one compound has any

TABLE 2. ^{77}Se spin-lattice relaxation times, T_1, for representative compounds

Compound	T_1(s)	Temp. (°C)	Conditions	Ref.
H_2Se	0.7	34	1.0M, D_2O	11
	0.34	35	40% (v/v), $CDCl_3$	11
MeSeH	1.3	40	20% (v/v), $(CD_3)_2CO$	11
EtSeH	1.7	40	20% (v/v), $CDCl_3$	11
$C_{10}H_{21}SeH$	1.9	42	20% (v/v), $CDCl_3$	11
$H_2N(CH_2)_2SeH$	7.1	32	0.5M, D_2O, pD 8.3	11
PhSeH	1.8	27	80% (v/v), C_6F_6	14
Me_2Se	7.5	32	20% (v/v), $CDCl_3$	11
	4.5	27	7.5M, CH_2Cl_2, 20% (v/v)	14
Bu_2Se	19.1	40	20% (v/v), $CDCl_3$	11
$(C_8H_{17})_2Se$	10.4	41	20% (v/v), $CDCl_3$	11
i-Pr_2Se	8.7	41	20% (v/v), $CDCl_3$	11
$MeSe(CH_2)_2NH_2$	8.4	43	0.5M, $CDCl_3$	11
D,L-$MeSe(CH_2)_2CH(NH_2)CO_2H$	13.5	34	0.1M, D_2O, pD 4	11
$MeSeCH_2SeMe$	13.9	29	30% (v/v), $CDCl_3$	16
$MeSe(CH_2)_2SeMe$	14.4	29	30% (v/v), $CDCl_3$	16
$MeSe(CH_2)_3SeMe$	12.9	29	30% (v/v), $CDCl_3$	16
$(MeSe—)_2$	9.0	45	0.5M, $CDCl_3$	11
$(PhSe—)_2$	20.0	45	0.5M, $CDCl_3$	11
	16.0	[a]	3.0M, 20% (v/v), C_6F_6	14
$(PhCH_2Se—)_2$	27.0	55	0.5M, $CDCl_3$	11
$(C_{10}H_{21}Se—)_2$	21.0	43	0.5M, $CDCl_3$	11
Me_3SeI	13.7	32	1.0M, D_2O, pD 7	11
$Me_2Se(Br)CH_2CO_2Et$	1.8	32	0.5M, $CDCl_3$	11
$Me_2NC(Se)NH_2$	8.6	55	0.5M, D_2O, pD 4	11
Me_2SeO	8.9	30	0.5M, D_2O, pH 7	11
$(Me_2CHO)_2SeO$	11.9	[a]	[a]	15
$(CF_3CH_2O)_2SeO$	13.1	[a]	[a]	15
	7.4	[a]	[a]	15
	6.7	[a]	[a]	15
	10.8	[a]	[a]	15
NaSeMe	16.3	43	1.0M, D_2O	11
Na_2SeO_4	16.8	15	0.5M, D_2O, pH 6.6	11
	10.2	[a]	0.5m, H_2O	13
Na_2SeO_3	10.7	[a]	1.0m, H_2O	13
H_2SeO_3	2.1	12	1.0M, D_2O, pH 9.6	11
	8.5	10	1.0M, D_2O, pH 1.5	11
	1.4	[a]	4.0m, D_2O	13
$NaHSeO_3$	0.34	[a]	4.0m, H_2O	13
$Zn(Se_2CNEt_2)_2$	4.4	24	1.0M, $CDCl_3$	12
$Pd[Se_2CN(Bu$-$i)_2]_2$	1.4	27	0.43M, $CHCl_3$	12
$Et_2NH_2Se_2CNEt_2$	2.7	−8	0.87M, $CDCl_3$	12

[a] Value not given.

significant enhancement been reported (4 M aqueous Na_2SeO_3, NOE = 0.4[13]). Second, for small Se-containing molecules, the spin-rotation (SR) relaxation mechanism dominates the spin-lattice relaxation and as the size of the molecule increases, the chemical shift anisotropy mechanism (CSA) becomes increasingly important[11,12,16].

These findings have important implications concerning the future of ^{77}Se-NMR spectroscopy, particularly if this nucleus is studied in large, macromolecular, biological systems as well as higher molecular weight organic molecules. The relaxation times which have been reported thus far are not extremely long (~ 1–30 s) and thus ^{77}Se-NMR spectroscopy should be able to be utilized as a routine tool for characterization. Also, in higher molecular weight systems where CSA is the dominant relaxation rate ($1/T_1$) the use of high-field spectrometers will be very beneficial since the CSA mechanism is proportional to the square of the external magnetic field[20]. As yet, no variable field T_1 studies have been reported for ^{77}Se to determine quantitatively the contributions of the SR and CSA mechanisms and experiments of this type are needed.

2. *Chemical shifts*

It is not within the purview of this article to thoroughly discuss the theory of chemical shifts. However, it is useful to discuss chemical shift theory in a rather specific way as it relates to ^{77}Se. The chemical shift reflects the distribution of electrons surrounding the observed nucleus and is, in general, a sensitive probe for characterization of the bonding in a molecule. Although considerable progress has been made in the recent past towards a refined theory of nuclear shielding, the *ab initio* calculation of chemical shifts still constitutes a formidable problem, and satisfactory correlation with experimental data remains limited to relatively small molecules containing light atoms, which unfortunately are of little practical importance to most chemists. This is certainly the case for Se where no published attempts toward a unified chemical shift theory are available. Thus we will endeavour to discuss chemical shifts in chemically relevant terms and interpret these shifts, where possible, using empirical substituent effects.

For any magnetically active nucleus in the presence of an external field, H_0, the effective field, H'_0, is given by

$$H'_0 = H_0 - H_0\sigma = H_0(1 - \sigma) \qquad (1)$$

$$\sigma = \frac{H_0 - H'_0}{H_0} \qquad (2)$$

The factor σ is called the magnetic shielding constant for the nucleus under observation and characterizes the electronic and chemical environment of that nucleus. The magnitude of the chemical shift is determined by this parameter which can be further subdivided into three different types of shielding as shown in equation (3).

$$\sigma = \sigma^{\text{dia}} + \sigma^{\text{para}} + \sigma^{\text{N}} \qquad (3)$$

Here σ^{dia} represents contributions from local diamagnetic effects, σ^{para} is the shielding term arising from electronic circulations on the observed atom and σ^{N} represents neighbouring-group anisotropy effects, i.e. fields arising from electronic circulations around atoms surrounding the observed nucleus. The diamagnetic term decreases with the distance r between the nucleus and circulating electrons and is therefore dominant for atoms with s electrons only. The σ^{N} term is dependent on the nature and geometry of neighbouring atoms and is independent of the nature of the observed nucleus. The paramagnetic term σ^{para} is zero for nuclei with spherical distributions of electrons. However, for Se, which has a valence-shell electron configuration of $4s^24p^4$, a non-spherical distribution of electrons exists and variations in paramagnetic terms are expected to be the dominant contributor to Se chemical shifts. The paramagnetic term σ^{para} for Se is related to several factors as shown in expression (4)[21]

$$\sigma^{\text{para}} \propto -\frac{\langle r^{-3}\rangle_{4p}}{\Delta E}\Sigma Q \tag{4}$$

where $\langle r^{-3}\rangle_{4p}$ is the mean inverse cube of the radius of the 4p orbitals, the Q terms (obtained from the charge density-bond order matrix) denote the imbalance of charge in the valence shell of Se and ΔE is an effective excitation energy. The above is a somewhat drastic approximation of a more rigorous formulation but will suffice for our purposes.

From expression (4), it is clear that the *deshielding* of Se will increase (*a*) as the paramagnetic circulation gets closer to the nucleus, i.e. the larger the radial factor $\langle r^{-3}\rangle_{4p}$, (*b*) as the asymmetry of the valence electron cloud increases, i.e. the greater the ΣQ term and (*c*) as ΔE becomes smaller and excitation becomes easier.

An increase in the electron-withdrawing ability of the groups attached to Se should decrease the value of r, thereby increasing $\langle r^{-3}\rangle$ and increasing the deshielding. Such a correlation is indeed shown by the ^{77}Se chemical shifts for a series of Me derivatives[22] in which the Se shielding increases in the order MeSeOOH < $MeSeCl_3$ < Me_2SeO < Me_2SeCl_2 < Me_2SeBr_2 < Me_2Se_2 < Me_3Se^+ < Me_2Se < MeSeH < $MeSe^-$. This is the order of decreasing electronegativity of the groups attached to Se. A similar order is obtained when the chemical shifts of a series of phenyl selenenyl derivatives is compared[23]. For example, the shielding increases in the order PhSeOOH < PhSeCl < PhSeBr < PhSeSPh < PhSeSePh < PhSeMe < PhSeH < $PhSe^-$.

Deviations from spherical symmetry of the electron cloud occurs in molecules having low-lying electronic excited states which mix with the ground state to yield non-zero matrix elements of the magnetic moment operator. The ΔE term tends to decrease as the asymmetry of the molecules increases so that the ΣQ and ΔE^{-1} terms tend to act in the same way. In general, whenever the chemical shift of a diselenide is compared to that of the corresponding selenide, a deshielding of Se is observed[22]. This has been attributed to the influence of the low-energy electronic band associated with the diselenide moiety, i.e. to a small value of ΔE.

In this regard, it has been shown that in some organoselenium compounds, particularly selones (which contain carbon–selenium double bonds, $\rangle$C=Se), there is a correlation of the ^{77}Se chemical shift with the wavelength λ of the band in the visible spectrum[24]. The major contribution to the chemical shifts comes from the deshielding of Se by the $n \rightarrow \pi^*$ circulation of lone-pair electrons in the π^* orbitals of the C=Se group. In fact, the deshielding of Se in selones increases as the $n \rightarrow \pi^*$ band moves to longer wavelength. This can be understood by expression (4) since the larger the value of λ, the smaller the excitation energy ΔE and thus the greater the deshielding of the Se nucleus.

a. Medium effects. (*i*) Solvent effects. ^{77}Se-NMR chemical shifts are very susceptible to solvent effects. The solvent dependence of ^{77}Se-NMR shifts can vary by up to 50 ppm in many organoselenium compounds[23,25]. (Although not as high as several hundred ppm as indicated by Wong and coworkers[26] in reference to the ^{77}Se-NMR shifts of selenophosphorus compounds studied by Dean[27]; in this case the solvent (SO_2) forms a complex with the selenophosphorus compound.) While this property may be exploited for studies of many molecular properties, comparison of chemical shift data from different sources is made correspondingly more difficult. The solvent shifts[28,29] of the ^{77}Se resonance of 5% solutions of Me_2Se in 20 solvents are presented in Table 3. These shifts cover a range of approximately 22 ppm. Deshielding of Se resonances is observed in going from polar solvents such as dimethyl sulphoxide to non-polar solvents such as cyclohexane and carbon tetrachloride. Employing a linear solvation energy relationship and the data of Table 3, Taft recently demonstrated that in non-chlorinated solvents, ^{77}Se solvent shifts in Me_2Se are influenced primarily by the dipolarity of the solvent[30]. Solvent shifts have been

TABLE 3. ^{77}Se solvent shifts of Me_2Se

Solvent	Chemical shift (ppm)	Standard	Ref.
Cyclohexane	4.5; 7.3	*a*; *b*	28; 29
Carbon tetrachloride	2.1; 5.46	*a*; *b*	28; 29
Triethylamine	0.4	*a*	28
Mesitylene	0.3	*a*	28
Diethyl ether	−2.8	*a*	28
Benzene	−3.2; −0.58	*a*; *b*	28; 29
N,*N*-Dimethylaniline	−4.2	*a*	28
Nitrobenzene	−5.4	*a*	28
Pyridine	−5.5	*a*	28
Acetic acid	−6.7	*a*	28
Phenylacetonitrile	−7.0	*a*	28
Methylene chloride	−7.2; −4.50	*a*; *b*	28; 29
Chloroform	−7.6; −4.86	*a*; *b*	28; 29
Methanol	−8.3; −4.34	*a*; *b*	28; 29
Acetonitrile	−8.5	*b*	29
Hexamethylphosphoramide	−9.4	*a*	28
Acetone	−9.8; −6.30	*a*; *b*	28; 29
Dimethylformamide	−11.9	*a*	28
Nitromethane	−13.4	*a*	28
Dimethyl sulphoxide	−14.9; −14.33	*a*; *b*	28; 29

[a] Relative to neat Me_2Se (shifts are reported for 5% mol solution).
[b] Relative to Me_2Se in $CDCl_3$ (60% v/v); all samples 5% (v/v) in the specified solvent.

observed for alkyl and aryl selenides[23,28], diselenides[23] and methyl selenocyanate[28]. From this discussion it is clear that solvent effects are significant in ^{77}Se-NMR studies, making it imperative to specify the solvent in which ^{77}Se spectra are obtained.

(*ii*) Concentration effects. Dilution shifts may reach a magnitude of several ppm. The ^{77}Se-NMR resonance of neat Me_2Se is shielded by 9 ppm upon dilution in $CDCl_3$ (1.25% v/v)[29]. Shifts of similar magnitude have been observed for other alkyl selenides and diselenides[23] whereas the shifts of diaryl diselenides show much smaller concentration dependence. The concentration dependence of the chemical shift probably accounts, at least in part, for discrepancies of reported chemical shifts which have appeared in the literature when Me_2Se has been used as the reference. For example, reported ^{77}Se chemical shifts for dimethyl diselenide are 275 and 281 ppm, and for dibenzyl diselenide, $(PhCH_2Se)_2$, 402 and 412 ppm. In these two studies[11,22] neat Me_2Se and 1.0 M Me_2Se in $CDCl_3$, respectively, were used as reference standards. A constant shift independent of concentration can be attained by using very dilute samples, which, in some cases, could be time-consuming because of the large number of repetitive scans which would be required to obtain a spectrum. Again, for reproducibility between laboratories, it is important to specify the concentrations of the sample used in the study.

(*iii*) pH effects. Selenols, RSeH, in general, are relatively acidic and can be easily deprotonated. For example, 2-aminoethaneselenol has been found to be completely in the zwitterionic form at pH 7–10, in contrast to 2-aminoethanethiol, which is only 60% zwitterionic at pH 10[31] When the selenolate anion is formed, the ^{77}Se resonance of the selenol is shielded by approximately 200 ppm. A typical weak acid titration plot has been obtained for the change in ^{77}Se-NMR chemical shifts of selenocysteamine, $H_2NCH_2CH_2SeH$, as a function of pH[11].

(*iv*) Temperature effects. The temperature dependence of ^{77}Se chemical shifts of Se compounds was first noted by Lardon[32] in 1972 and by Odom, Dawson and Ellis[11] in 1979. Subsequently it has been reported for selenides[23,29], diselenides[23] and selenocarbonyl[26] ($R_2C{=}Se$)compounds. The temperature dependence of the ^{77}Se chemical shifts of $(CH_3)_2Se$ in $CDCl_3$ is approximately 2.5 ppm over the range of 222–323 K[29]. The temperature dependence of selones, $R_2C{=}Se$, is found to be 0.34–0.48 ppm K^{-1}. Over the temperature range 287–313 K, the variation of ^{77}Se shifts with temperature is reported to be linear[26]. Aryl diselenides[32] are reported to have a temperature dependence of 0.4 ppm K^{-1}. In all cases a deshielding of Se is observed. Diselenides and selones are highly coloured compounds which would be expected to have small excitation energies, ΔE, the value of which would decrease with increasing temperature. As noted previously, a smaller value of ΔE would reduce the shielding of Se.

b. ^{77}Se chemical shift referencing. This area has been a somewhat vexing problem. There has been no universal agreement on a reference standard. The earliest studies employed either neat dimethyl selenide[22], Me_2Se, or seleninyl chloride[33], $SeOCl_2$, as a reference. More recently, ^{77}Se FT NMR studies have been reported using aqueous selenous acid[34,35], H_2SeO_3, selenophene[3–6] and 4,4′-dimethyldiphenyldiselenide[36], $(4\text{-}CH_3C_6H_4Se)_2$, as well as the two standards mentioned above. Since, as noted, Se chemical shifts are susceptible to solvent effects, reproducibility is best attained by using an external standard which appears to be a general consensus. A proposal that a solution of Me_2Se in $CDCl_3$ (60% v/v) be accepted as universal reference standard for ^{77}Se chemical shifts has appeared in the literature[29]. The rationale for doing so is that (1) Me_2Se resonates at a frequency which is close to one extreme of the chemical shift range, (2) Me_2Se is inexpensive and commercially available and (3) a spectrum of Me_2Se can be obtained with a good signal-to-noise ratio in one pulse on any of the commercially available FT instruments. The magnetic field of a magnet of an FT instrument is generally 'shimmed' to high homogeneity by locking to a ^2H resonance signal and adjusting the current in the shim coils until maximum signal and resolution are achieved. This process requires repetitive acquisition of the spectrum of the observed nucleus. Thus, the 60% Me_2Se in $CDCl_3$ provides both the ^2H lock signal and sufficient signal-to-noise to achieve maximum homogeneity of the magnetic field in a series of one-pulse acquisitions.

c. Classes of compounds. The tables are organized according to chemical shift values, i.e. from the most shielded resonance to the most deshielded resonance for that particular class of compounds. In cases where there are substituted phenyl rings the parent compound is given first and all derivatives of that parent are then presented in the order stated above. To standardize ^{77}Se chemical shift values in this chapter, they are tabulated with respect to the reported value of Me_2Se in $CDCl_3$ (60% v/v). In the tables we have attempted to present values which may be compared in as consistent a manner as possible. However, in many cases experimental conditions have not been specified clearly, or more commonly, investigators were probably not aware that the resonance positions of their reference standards were so sensitive to variable conditions. Thus, to avoid confusion, in those investigations where values are reported with respect to Me_2Se as a standard reference, we have tabulated the original values irrespective of the conditions employed, whereas, for the values which are referenced to standards other than Me_2Se, relevant conversion factors are employed with respect to Me_2Se in $CDCl_3$ (60% v/v). For the reader's convenience, the conversion constants employed for other reference materials are given as footnotes in each table.

(*i*) Selenols and selenolates. The chemical shift data for selenols and selenolates are presented in Table 4. The total chemical shift range is approximately 600 ppm with the most shielded ^{77}Se resonance being that in the selenolate $MeSe^-\ Na^+$ and the most deshielded resonance occurring in CF_3SeH. As expected, selenolates are more shielded than the corresponding selenol, usually by ~200 ppm. For example, the ^{77}Se chemical shifts of MeSeH and $MeSe^-\ Na^+$ are -130 and -330 ppm, respectively. The increased shielding in selenolates occurs as a result of the increased electron density around the Se

TABLE 4. ^{77}Se chemical shifts of selenols and selenolates

Compound	Chemical shift (ppm)	Standard	Solvent	Ref.
$MeSe^- Na^+$	$-332; -330$	*a*;*b*	H_2O	22;11
H_2Se	-288	*b*	D_2O	11
$HSeCH_2CH_2NH_2$	-212	*b*	D_2O, pD = 8.3	11
$EtSe^- Na^+$	-150	*a*	H_2O	22
DL-$HSeCH_2CH(NH_2)COOH$	-141	*b*	D_2O, pD = 5	11
MeSeH	$-116; -130$	*a*;*b*	Neat; $CDCl_3$	22;11
C_6F_5SeH	-16	*a*	Not specified	37
$C_{10}H_{21}SeH$	-7	*b*	$CDCl_3$	11
i-$PrSe^- Na^+$	8.7	*a*	H_2O	22
EtSeH	39;41	*b*	$CDCl_3$; Me_2CO	11
$PhCH_2SeH$	107	*a*	CH_2Cl_2	22
t-$BuSe^- Na^+$	129	*a*	H_2O	22
PhSeH	145	*a*	Neat	22
o-AnSeH	84	*a*	Neat	22
o-TolSeH	112	*a*	Neat	22
o-ClC_6H_4SeH	158	*a*	Neat	22
o-FC_6H_4SeH	191	*a*	Neat	22
m-TolSeH	144	*a*	Neat	22
m-AnSeH	153	*a*	Neat	22
m-$CF_3C_6H_4SeH$	159	*a*	Neat	22
m-FC_6H_4SeH	164	*a*	Neat	22
m-ClC_6H_4SeH	167	*a*	Neat	22
p-AnSeH	122	*a*	Neat	22
p-TolSeH	128	*a*	Neat	22
p-FC_6H_4SeH	141	*a*	Neat	22
p-ClC_6H_4SeH	142	*a*	Neat	22
i-PrSeH	159	*a*	Neat	22
t-BuSeH	278	*a*	Neat	22
CF_3SeH	287	*c*	C_6F_6	41

[a] Relative to neat Me_2Se.
[b] Relative to 1.0M Me_2Se in $CDCl_3$.
[c] Relative to Me_2Se in C_6D_6.

nucleus causing an increase in the 4p radial distance. Thus the $\langle r^{-3}\rangle_{4p}$ factor of expression (4) decreases. A comparison of the data for MeSeH, $PhCH_2SeH$ and PhSeH shows that the replacement of a Me group by a $PhCH_2$ group deshields the Se nucleus by ~ 220 ppm whereas the deshielding caused by substitution of a Ph group is ~ 280 ppm, presumably due to the increased electronegativity of the sp^2-hybridized C atom in the Ph group. Interestingly, introduction of a C_6F_5 group shields the Se nucleus as evidenced by a 168 ppm chemical shifts difference between selenophenol, PhSeH, and pentafluoroselenophenol, C_6F_5SeH. In this case the greater electronegativity of the ring F atoms should lead to a positive charge on the sigma framework of the polyfluoroaromatic ring, making it a stronger inductive acceptor than the Ph group. However, an increased nuclear shielding has been found in polyfluoroaromatic compounds with respect to their hydrocarbon analogues. Thus, the CF_3 group which exhibits a strong inductive effect deshields Se, whereas the C_6F_5 group shields it. This shielding has been discussed[37] in terms of a decreased conjugation between the unshared electron pair of the Se and the π system of the perfluorinated benzene ring. Reduced conjugation of the unshared electron pair of S with the π system of the polyfluoroaryl ring is confirmed by X-ray fluorescent spectral data for organic S compounds[38]. A similar dependence may also be expected for the Se derivatives.

McFarlane and Wood[22], who were the first to report ^{77}Se chemical shift data for a variety of organoselenium compounds, observed that, in general, Se resonances are deshielded as the electronegativity of the substituent attached to Se increases when the overall range of substituent electronegativities is relatively large. However, when substituents had similar electronegativity values, as, for example, when alkyl groups were varied, the relationship broke down. Thus, in the alkyl selenols and selenolates (RSeH and RSe^-), the shielding effect of the group increases in the order t-Bu < n-Pr < Et < Me which is opposite to that expected if the Se chemical shifts were dominated by the inductive effect of the alkyl groups. As will be seen later in this chapter, the same trend is observed with dialkyl selenides, R_2Se, aryl alkyl selenides, ArSeR, dialkyl diselenides, R_2Se_2, and similar behaviour has been observed in ^{31}P chemical shifts of trialkylphosphines[39]. An explanation for this reverse shielding phenomenon has been proposed[40] and will be discussed in the section concerning Se chemical shifts of selenides.

Due to the large chemical shift range of ^{77}Se, NMR studies of this nucleus should be a powerful technique to study the transmission of electronic substituent effects. McFarlane and Wood[22] carried out such a study for *meta-* and *para*-substituted phenyl selenols and reported a poor correlation of ^{77}Se chemical shifts with Hammett σ constants of the substituents. The lack of a good fit was attributed to H-bond formation in selenols which these investigators felt could affect the Se shielding by more than 20 ppm. This is significant considering that the total chemical shift range covered in the compounds studied was ~45 ppm. It should also be noted that, as yet, no additional definitive studies demonstrating significant H-bonding to Se have appeared.

(*ii*) Dialkyl selenides. ^{77}Se chemical shifts of dialkyl selenides are reported in Table 5. When hydrogen atoms of the methyl groups of Me_2Se are successively replaced by Me groups, a deshielding of approximately 100 ppm per H atom replaced is observed (e.g., Me_2Se (0 ppm), MeSeEt (108 ppm), Et_2Se (217 ppm), MeSeBu-t (294 ppm), $(i\text{-}Pr)_2Se$ (432 ppm) and $(t\text{-}Bu)_2Se$ (601 ppm)). The replacement of the methyl H by a Ph group causes a deshielding of ~ 170 ppm per replacement, e.g. Me_2Se (0 ppm), $PhCH_2SeMe$ (173 ppm), $(PhCH_2)_2Se$ (333 ppm). Although replacement of H by a more electronegative F atom causes a considerable deshielding, the replacement by a Cl (less electronegative than F) causes even greater deshielding. For example, the ^{77}Se chemical shifts of Se in CF_3SeCH_3, CF_3SeCF_3, CF_3SeCF_2Cl, $CF_3SeCFCl_2$ and CF_3SeCCl_3 are 370, 717, 815, 927 and 953 ppm, respectively.

The ^{77}Se-NMR studies of a large number of substituted *Se*-benzylselenoalkanoic acids ($XC_6H_4CH_2Se(CH_2)_nCOOH$, where $n = 1-10$) are presented in Table 6. The shifts caused by *meta* and *para* substituents have been correlated with Hammett's σ values; however, in our opinion there were not enough substituents studied to obtain a meaningful correlation. It is interesting to note that a maximum ^{77}Se shielding occurs for the butyric acid derivatives ($n = 3$) and it has been proposed that this could perhaps be due to the interaction between the free electron pairs on the carbonyl group and empty Se valence-shell d orbitals[5].

Previously, the abnormal behaviour of the ^{77}Se chemicals shifts in alkyl selenols, selenolates, selenides and diselenides was mentioned (*vide supra*). Briefly, for selenols, a deshielding of ~ 120 ppm is observed as H is replaced by Me in the series MeSeH, EtSeH, i-PrSeH, t-BuSeH and a similar trend is observed for selenolates. In alkyl selenides, the analogous substitution deshields the Se resonance by ~ 110 ppm per replacement by a Me group for the series Me_2Se, MeSeEt, Et_2Se, MeSeBu-t, $(i\text{-}Pr)_2Se$, $(t\text{-}Bu)_2Se$. In dialkyl diselenides a similar, but smaller (~65 ppm per replacement) deshielding is observed in the ^{77}Se chemical shifts of MeSeSeMe, EtSeSeEt, i-PrSeSe-Pr-i, t-BuSeSeBu-t. In all cases, each Me group contributes an additive deshielding to the ^{77}Se resonance which is surprisingly large for a relatively small change in the electronic nature and electronegativity of these groups.

A clearer understanding of this effect and its origin can be obtained by more closely

TABLE 5. ^{77}Se chemical shifts of dialkyl selenides

Compound	Chemical shift (ppm)	Standard	Solvent	Ref.
Me_2Se	0	*a*	$CDCl_3$	27
$MeSeCH_2CH_2NH_2$	44	*c*	$CDCl_3$	11
DL-$MeSeCH_2CH_2CH(NH_2)COOH$	75	*c*	D_2O(pD 4)	11
MeSeEt	108	*b*	CH_2Cl_2	22
Bu_2Se	167	*c*	$CDCl_3$	11
$(C_8H_{17})_2Se$	168	*c*	$CDCl_3$	11
$PhCH_2SeMe$	173	*b*	$CDCl_3$	7
Et_2Se	217; 236.6	*d*; *b*	Neat; neat	34; 22
$CF_3SeHgCl$	267.9	*e*	CH_3OH	33
MeSeBu-*t*	294	*b*	Neat	22
$(PhCH_2)_2Se$	328.5; 333	*f*; *b*	$(CD_3)_2CO$; $CDCl_3$	5; 7
$(o\text{-}ClC_6H_4CH_2)_2Se$	302.4	*f*	$(CD_3)_2CO$	5
$(m\text{-}ClC_6H_4CH_2)_2Se$	330.2	*f*	$(CD_3)_2CO$	5
$(m\text{-}BrC_6H_4CH_2)_2Se$	331.5	*f*	$(CD_3)_2CO$	5
$(p\text{-}ClC_6H_4CH_2)_2Se$	331.9	*f*	$(CD_3)_2CO$	5
$(p\text{-}BrC_6H_4CH_2)_2Se$	338.0	*f*	$(CD_3)_2CO$	5
$(o,p\text{-}Cl_2C_6H_3CH_2)_2Se$	309.2	*f*	$(CD_3)_2CO$	5
$(CF_3Se)_2Hg$	337.4	*e*	MeOH	33
CF_3SeMe	370	*g*	C_6D_6	41
$(i\text{-}Pr)_2Se$	432; 436	*c*; *d*	$CDCl_3$; $CDCl_3$	11; 22
$(CF_3)_2Se$	697.9; 717; 724.6	*e*; *g*; *e*	Neat; C_6D_6; not specified	33; 41; 52
CF_3SeCF_2Cl	799.6; 815	*e*; *g*	Not specified; C_6D_6	52; 41
$CF_3SeCFCl_2$	910.6; 927	*e*; *g*	Not specified; C_6D_6	52; 41
CF_3SeCCl_3	953	*g*	C_6D_6	41

[a] Relative to Me_2Se in $CDCl_3$ (60% v/v).

[b] Relative to neat Me_2Se.

[c] Relative to 1.0M Me_2Se in $CDCl_3$.

[d] Aq. H_2SeO_3 was used as a reference; chemical shift values have been converted relative to Me_2Se in $CDCl_3$ (60% v/v) using the expression $\delta[Me_2Se] = \delta[H_2SeO_3\ (aq.)] - 1285.6$.

[e] $SeOCl_2$ was used as a reference; chemical shift values have been converted relative to Me_2Se in $CDCl_3$ (60% v/v) using the expression $\delta[Me_2Se] = \delta[SeOCl_2] - 1482.6$.

[f] Selenophene in $(CD_3)_2CO$ (20%) was used as a reference; chemical shift values have been converted relative to Me_2Se in $CDCl_3$ (60% v/v) using the expression $\delta(Me_2Se) = \delta(\text{selenophene}) - 608.6$.

[g] Relative to Me_2Se in C_6D_6.

examining solvent effects on ^{77}Se chemical shifts[40]. As pointed out earlier in this chapter, substantial solvent-induced ^{77}Se chemical shifts have been observed. The shifts have been reported to range up to 40–50 ppm for alkyl selenides and diselenides and diamagnetic susceptibility contributions are small compared to these shifts. It should be noted that the extreme values for these solvent shifts for low molecular weight alkyl selenides and diselenides occur for the solvents trifluoroacetic acid (maximum shielding) and diiodomethane (maximum deshielding)[40].

In an attempt to understand the ^{77}Se solvent-induced chemical shifts with respect to some particular property of the solvent, the shifts have been correlated with the following parameters: (1) the refractive index of the solvent, (2) the molar polarizability of the solvent and (3) the ratio of the molar polarizability of the solvent to its molar volume[40].

TABLE 6. ^{77}Se chemical shifts of *Se*-benzylselenoalkanoic acids[a,b]

Compound	Chemical shift (ppm)	Compound	Chemical shift (ppm)
$PhCH_2Se(CH_2)_3COOH$	243.3	$4\text{-}BrC_6H_4CH_2Se(CH_2)_9COOH$	253.2
$4\text{-}BrC_6H_4CH_2Se(CH_2)_3COOH$	250.1	$4\text{-}NO_2C_6H_4CH_2Se(CH_2)_9COOH$	265.5
$4\text{-}NO_2C_6H_4CH_2Se(CH_2)_3COOH$	263.4	$2,4\text{-}Cl_2C_6H_3CH_2Se(CH_2)_9COOH$	245.9
$PhCH_2Se(CH_2)_7COOH$	247.2	$PhCH_2Se(CH_2)_4COOH$	264.4
$4\text{-}MeC_6H_4CH_2Se(CH_2)_7COOH$	245.9	$4\text{-}MeC_6H_4CH_2Se(CH_2)_4COOH$	245.1
$4\text{-}BrC_6H_4CH_2Se(CH_2)_7COOH$	253.5	$4\text{-}BrC_6H_4CH_2Se(CH_2)_4COOH$	252.4
$PhCH_2Se(CH_2)_{10}COOH$	247.2	$4\text{-}NO_2C_6H_4CH_2Se(CH_2)_4COOH$	264.7
$2\text{-}ClC_6H_4CH_2Se(CH_2)_{10}COOH$	242.0	$PhCH_2Se(CH_2)_2COOH$	266.8
$2\text{-}BrC_6H_4CH_2Se(CH_2)_{10}COOH$	242.8	$2\text{-}ClC_6H_4CH_2Se(CH_2)_2COOH$	261.1
$2\text{-}FC_6H_4CH_2Se(CH_2)_{10}COOH$	247.7	$2\text{-}BrC_6H_4CH_2Se(CH_2)_2COOH$	262.1
$2\text{-}NO_2C_6H_4CH_2Se(CH_2)_{10}COOH$	261.6	$2\text{-}FC_6H_4CH_2Se(CH_2)_2COOH$	266.8
$3\text{-}FC_6H_4CH_2Se(CH_2)_{10}COOH$	251.7	$2\text{-}NO_2C_6H_4CH_2Se(CH_2)_2COOH$	280.9
$3\text{-}ClC_6H_4CH_2Se(CH_2)_{10}COOH$	253.5	$3\text{-}FC_6H_4CH_2Se(CH_2)_2COOH$	271.8
$3\text{-}BrC_6H_4CH_2Se(CH_2)_{10}COOH$	254.0	$3\text{-}ClC_6H_4CH_2Se(CH_2)_2COOH$	272.8
$3\text{-}NO_2C_6H_4CH_2Se(CH_2)_{10}COOH$	259.8	$3\text{-}BrC_6H_4CH_2Se(CH_2)_2COOH$	273.4
$4\text{-}FC_6H_4CH_2Se(CH_2)_{10}COOH$	249.6	$3\text{-}NO_2C_6H_4CH_2Se(CH_2)_2COOH$	278.8
$4\text{-}ClC_6H_4CH_2Se(CH_2)_{10}COOH$	251.0	$4\text{-}FC_6H_4CH_2Se(CH_2)_2COOH$	269.6
$4\text{-}NO_2C_6H_4CH_2Se(CH_2)_{10}COOH$	265.8	$4\text{-}ClC_6H_4CH_2Se(CH_2)_2COOH$	272.6
$2,4\text{-}Cl_2C_6H_3CH_2Se(CH_2)_{10}COOH$	246.2	$4\text{-}BrC_6H_4CH_2Se(CH_2)_2COOH$	273.1
$PhCH_2Se(CH_2)_5COOH$	247.5	$4\text{-}NO_2C_6H_4CH_2Se(CH_2)_2COOH$	285.1
$4\text{-}BrC_6H_4CH_2Se(CH_2)_5COOH$	253.5	$2,4\text{-}Cl_2C_6H_3CH_2Se(CH_2)_2COOH$	265.0
$4\text{-}NO_2C_6H_4CH_2Se(CH_2)_5COOH$	265.3	$PhCH_2SeCH_2COOH$	291.1
$PhCH_2Se(CH_2)_6COOH$	247.5	$2\text{-}ClC_6H_4CH_2SeCH_2COOH$	277.8
$4\text{-}BrC_6H_4CH_2Se(CH_2)_6COOH$	253.5	$2\text{-}BrC_6H_4CH_2SeCH_2COOH$	279.9
$4\text{-}NO_2C_6H_4CH_2Se(CH_2)_6COOH$	265.3	$2\text{-}FC_6H_4CH_2SeCH_2COOH$	283.0
$PhCH_2Se(CH_2)_8COOH$	247.5	$2\text{-}NO_2C_6H_4CH_2SeCH_2COOH$	300.8
$4\text{-}NO_2C_6H_4CH_2Se(CH_2)_8COOH$	265.3	$3\text{-}FC_6H_4CH_2SeCH_2COOH$	296.0
$PhCH_2Se(CH_2)_9COOH$	247.7	$3\text{-}BrC_6H_4CH_2SeCH_2COOH$	296.9
$2\text{-}ClC_6H_4CH_2Se(CH_2)_9COOH$	242.0	$3\text{-}ClC_6H_4CH_2SeCH_2COOH$	297.4
$2\text{-}BrC_6H_4CH_2Se(CH_2)_9COOH$	242.8	$3\text{-}NO_2C_6H_4CH_2SeCH_2COOH$	302.9
$2\text{-}FC_6H_4CH_2Se(CH_2)_9COOH$	248.3	$4\text{-}MeC_6H_4CH_2SeCH_2COOH$	288.5
$3\text{-}FC_6H_4CH_2Se(CH_2)_9COOH$	251.4	$4\text{-}FC_6H_4CH_2SeCH_2COOH$	294.5
$3\text{-}ClC_6H_4CH_2Se(CH_2)_9COOH$	253.5	$4\text{-}ClC_6H_4CH_2SeCH_2COOH$	297.7
$3\text{-}BrC_6H_4CH_2Se(CH_2)_9COOH$	254.0	$4\text{-}BrC_6H_4CH_2SeCH_2COOH$	297.7
$4\text{-}FC_6H_4CH_2Se(CH_2)_9COOH$	249.3	$4\text{-}NO_2C_6H_4CH_2SeCH_2COOH$	306.5
$4\text{-}ClC_6H_4CH_2Se(CH_2)_9COOH$	252.7	$2,4\text{-}Cl_2C_6H_3CH_2SeCH_2COOH$	282.8

[a] Solvent C_6D_6 (20% solutions). Chemical shifts were reported relative to selenophene; converted to Me_2Se in $CDCl_3$ (60% v/v) using the relationship $\delta(Me_2Se) = \delta(\text{selenophene}) - 608.6$.

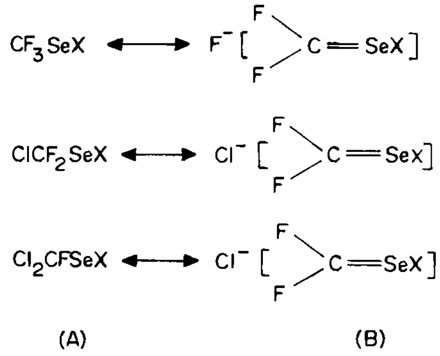
[b] Ref. 5.

Although none of these parameters individually yields an excellent correlation, all three reproduce the overall trend of the data with the refractive index being the parameter which most successfully correlates with the solvent shifts. For example, CF_3COOH has the lowest value of refractive index and CH_2I_2 has the highest value of the solvents studied[42]. Thus polarizability and dispersion forces clearly figure predominantly (although perhaps not exclusively) in the intermolecular interactions causing these shifts. Se, with its relatively large size and two unshared pairs of electrons should be highly polarizable and should interact significantly with highly polarizable solvents.

With such an intermolecular polarizability concept in mind, it is rather easy to extrapolate to an *intramolecular* situation where dispersion forces within a molecule could be exerted by neighbouring alkyl groups and influence Se shielding. Alkyl groups have been shown to be very polarizable in the gas phase in that they stabilize a negative or a positive charge[43]. This polarizability effect is based on the charge-induced dipole interaction and attenuates rapidly with distance (proportional to r^{-4}) between the centres of polarizability and of charge. Since the polarizability of a molecule is an additive property[44], successive additions of a Me group at a fixed distance should exert nearly the same influence. Thus, in going from MeSeMe → MeSeEt → EtSeEt → MeSeBu-*t* → *i*-PrSePr-*i*, successive replacement of a Me group at a fixed distance disperses the electron density at the highly polarizable Se atom by about the same magnitude which in turn increases the $\langle r^{-3} \rangle$ factor (r decreases) as well as the asymmetry factor, ΣQ, in expression (4). The net result is an increased deshielding of about equal magnitude in each case. The deshielding observed in alkyl selenols and selenolates can be explained in a similar manner as the methyl hydrogens in methyl selenol (or selenolate) are successively replaced by Me groups.

In molecules where the alkyl group is *n*-Pr, a *shielding* of Se is observed relative to the case where the alkyl group is Et. For example, this is seen in the compounds PhSeMe (202 ppm), PhSeEt (322 ppm), PhSePr-*i* (424 ppm), PhSeBu-*t* (521 ppm) and PhSePr-*n* (285 ppm). This shielding in *n*-Pr derivatives can be understood due to the fact that a Me group is now introduced two C atoms away from the Se and thus the dispersion effect introduced by an extra Me group is very small compared to that in PhSe-Pr-*i*. In addition, introduction of a Me group in the γ-position with respect to the Se atom causes shielding by the 'γ-effect', which is well known and accepted in ^{13}C-NMR spectroscopy[45]. Confirmation of this γ-effect in Se-NMR spectroscopy is further established by comparing the ^{77}Se chemical shifts of (1) PhSeBu-*i* (264 ppm) and PhSeBu-*n* (288 ppm) and of (2) PhSeBu-*s* (394 ppm) and PhSePr-*i* (424 ppm). In the first case the *i*-Bu derivative has two γ-carbons with respect to Se whereas the *n*-Bu derivative has only one such carbon; thus an increased shielding of 24 ppm is observed with the *i*-Bu derivative. In the second case introduction of a γ-carbon in the *i*-Pr compound yields a *s*-Bu derivative and causes a shielding of 30 ppm. The replacement of a methyl H of the *n*-Pr group by an alkyl group has virtually no effect on the Se shielding, as e.g. in PhSePr-*n* (285 ppm) and PhSeBu-*n* (288 ppm) and in n-Bu_2Se (167 ppm) and $(n\text{-}C_8H_{17})_2Se$ (168 ppm). Thus, intramolecular dispersion effects of neighbouring alkyl groups have a great influence on the shielding of the Se nucleus. Such an effect is also observed in the gas-phase acidities (also an intrinsic property) of alcohols[43]. The observed order of gas-phase acidities of alkyl alcohols is *t*-BuOH > *i*-PrOH > EtOH > MeOH > H_2O which is reversed from that found in solution. In fact, it has been suggested that the solution order is an artifact and does not represent any intrinsic property of these molecules.

Another example where a group which is less electronegative (i.e. has lower electron-withdrawing ability) influences the shielding of ^{77}Se in the reverse manner is the observed increased deshielding in going from $CF_3SeCH_3 \rightarrow CF_3SeCF_2Cl \rightarrow CF_3SeCFCl_2 \rightarrow CF_3SeCCl_3$. Gombler explained[41] this phenomenon by considering C—F and C—Cl hyperconjugation so that mesomeric structures **A** and **B** contribute to the shielding of Se.



Although hyperconjugation involving the —CF_3 group was proposed[46] as early as 1950, serious reservations have been expressed and reviewed[47–49] concerning this concept and conclusions have also been advanced that C—F hyperconjugation does *not* play a significant role in the stability or reactivity of aliphatic organofluorine compounds or aromatic compounds with perfluoroalkyl substituents. In this regard, it should be noted that in halogen-substituted acetic acid molecules, gas-phase acidities increase in the order $FCH_2COOH < ClCH_2COOH < BrCH_2COOH$ which is the reverse of the order in aqueous solution[50]. This acidity order can be explained by comparing the polarizability of the halogen substituents. The atomic polarizabilities of F, Cl and Br are 0.53, 2.61 and 3.79 Å^3, respectively[51]. Thus it was proposed that the more polarizable atom can better stabilize a charge on the O in the acetate anion. In the Se compounds above, the more polarizable Cl atom can polarize the electron density on the polarizable Se atom more effectively than F. Polarization of the Se electron density causes an increase in the ΣQ and $\langle r^{-3} \rangle$ factors in expression (4), thereby increasing the deshielding at the Se nucleus.

(*iii*) Alkyl aryl selenides. ^{77}Se chemical shifts of alkyl aryl selenides are shown in Table 7. The ^{77}Se resonance in MeSePh is deshielded by ~200 ppm when compared to that in Me_2Se. Again, deshielding of Se is incremented by ~120 ppm when the Me group is replaced by Et, *i*-Pr and *t*-Bu groups. Table 7 also provides the ^{77}Se chemical shifts for a range of substituted selenoanisoles, XC_6H_4SeMe. The shifts in the *para* series[53] cover a range of ~50 ppm as the substituent is varied from —NMe_2 to —NO_2. The direction of the shifts is normal, i.e. electron donors cause upfield shifts and electron acceptors cause downfield shifts. The ^{77}Se chemical shifts of these substituted selenoanisoles have been examined rather carefully in an attempt to understand their origin. Although single-parameter equations of the Hammett or Brown–Okamoto type have been used extensively to derive relationships between Substituent Chemical Shift (SCS) values and substituent parameters (σ constants) in order to obtain one or more transmission coefficients (commonly denoted by ρ), Dual Substituent Parameter (DSP) equations have also been successfully used[54,55]. In the DSP method, the SCS values are related to a linear combination of previously defined polar and resonance substituent parameters (σ_I and $\bar{\sigma}_R$, respectively) as shown in equation (5):

$$\mathrm{SCS} = \rho_I \sigma_I + \rho_R \bar{\sigma}_R \qquad (5)$$

The symbol $\bar{\sigma}_R$ denotes the fact that any one of four resonance scales (σ_R^-, σ_R^0, σ_R^{BA}, σ_R^+) may be used for a given correlation. It is usual practice to perform four separate correlations, each with a different resonance scale, and then to utilize the one which yields the best fit to the experimental data. The main advantage of the DSP method over single-parameter treatments is that it allows the calculation of separate transmission coefficients for resonance and polar effects. The 'goodness of fit' of a DSP correlation is judged from the '*f*'

TABLE 7. ^{77}Se chemical shifts of alkyl aryl selenides[a]

Compound	Chemical shift (ppm)	Solvent	Ref.
1-NaphSeMe	155	CDCl$_3$	7
2-NaphSeMe	202	CDCl$_3$	7
PhSeMe	197	CDCl$_3$	57
	202	CH$_2$Cl$_2$	22
	202	CDCl$_3$	58
	202	Neat	53
	203	CDCl$_3$	7
o-AnSeMe	150	CH$_2$Cl$_2$	22
o-TolSeMe	162	CH$_2$Cl$_2$	22
o-ClC$_6$H$_4$SeMe	201	CH$_2$Cl$_2$	22
o-NaOOCC$_6$H$_4$Me	225	50% aq. MeOH	58
o-MeOOCC$_6$H$_4$SeMe	259; 265	CDCl$_3$; CDCl$_3$	59; 58
o-CH(O)C$_6$H$_4$SeMe	267	CDCl$_3$	59
o-HOOCC$_6$H$_4$SeMe	272	CDCl$_3$	58
o-AcC$_6$H$_4$SeMe	282	CDCl$_3$	59
o-NO$_2$C$_6$H$_4$SeMe	292.1	Neat	53
m-TolSeMe	199; 200	CH$_2$Cl$_2$; neat	22; 53
m-AnSeMe	207	Neat	53
m-FC$_6$H$_4$SeMe	214	Neat	53
m-CF$_3$C$_6$H$_4$SeMe	217	Neat	53
m-ClC$_6$H$_4$SeMe	215; 217.7	CH$_2$Cl$_2$; neat	22; 53
m-BrC$_6$H$_4$SeMe	219.8	Neat	53
m-NO$_2$C$_6$H$_4$SeMe	225.6	Neat	53
p-Me$_2$NC$_6$H$_4$SeMe	181.2	Neat	53
p-NH$_2$C$_6$H$_4$SeMe	182.0	Neat	53
p-AnSeMe	189.5; 191	Neat; CDCl$_3$	53; 22
p-TolSeMe	196.1; 197	Neat; neat	53; 22
p-FC$_6$H$_4$SeMe	200; 200.0	CH$_2$Cl$_2$; neat	22; 53
p-ClC$_6$H$_4$SeMe	203; 203.6	CH$_2$Cl$_2$; neat	22; 53
p-MeOOCC$_6$H$_4$SeMe	218.1	Neat	53
p-NO$_2$C$_6$H$_4$SeMe	233.4	Neat	53
PhSeBu-*i*	264	CDCl$_3$	57
PhSePr-*n*	285	CDCl$_3$	57
PhSeBu-*n*	288	CDCl$_3$	57
PhSeEt	322	CDCl$_3$	57
	326	CDCl$_3$	7
	327	CH$_2$Cl$_2$	22
o-TolSeEt	276	CH$_2$Cl$_2$	22
o-AnSeEt	362	CH$_2$Cl$_2$	22
m-AnSeEt	331	Neat	22
m-ClC$_6$H$_4$SeEt	336	CH$_2$Cl$_2$	22
m-CF$_3$C$_6$H$_4$SeEt	340	Neat	22
p-AnSeEt	318	CH$_2$Cl$_2$	22
p-TolSeEt	323	Neat	22
p-FC$_6$H$_4$SeEt	324	CH$_2$Cl$_2$	22
PhSeBu-*s*	394	CDCl$_3$	57
PhSePr-*i*	424	CDCl$_3$	57
o-AnSePr-*i*	355	CH$_2$Cl$_2$	22
PhSeBu-*t*	521	CDCl$_3$	57

[a] All chemical shifts are relative to neat Me$_2$Se.

value where

$$f = \mathrm{SD}/\mathrm{RMS} \tag{6}$$

Here, SD is the standard deviation of the fit and RMS represents the root mean square value of the experimental data. In practice, $f = 0.0$–0.1 represents excellent correlation, $f = 0.1$–0.2 is felt to be moderately good correlation and f values of 0.3 and greater represent only crude trends[56].

In the substituted selenoanisoles, a DSP analysis of the ^{77}Se chemical shifts as the substituent is varied indicates that the shifts are precisely related to substituent electronic effects and the following equations are obtained[56]:

$$\textit{ortho}\text{: SCS} = 47\sigma_{\mathrm{I}} + 137\sigma_{\mathrm{R}}^{-} \qquad f = 0.21 \tag{7}$$

$$\textit{meta}\text{: SCS} = 34\sigma_{\mathrm{I}} + 8\sigma_{\mathrm{R}}^{\mathrm{BA}} \qquad f = 0.14 \tag{8}$$

$$\textit{para}\text{: SCS} = 32\sigma_{\mathrm{I}} + 52\sigma_{\mathrm{R}}^{0} \qquad f = 0.17 \tag{9}$$

It is interesting to note that, while 'good' correlations are obtained, the ρ_{I} values for the *meta* and *para* transmission coefficients are similar but the ρ_{R} values differ substantially.

(*iv*) Diaryl selenides. Gronowitz and coworkers carried out a systematic ^{77}Se-NMR study[6] of the effect of substituents on the Se chemical shift in 4,4′-disubstituted diphenyl selenides (Table 8). The ^{77}Se shifts vary in a regular way with the character of the substituents, i.e. electron-donating groups cause upfield shifts and electron-attracting groups induce downfield shifts. A good linear correlation was obtained when the ^{77}Se shifts were plotted against the σ_p^+ values of Swain and Lupton or with the σ_p values of Hammett. A linear correlation was also found between ^{77}Se chemical shifts and ^{19}F

TABLE 8. ^{77}Se chemical shifts of diaryl selenides

Compound	Chemical shift (ppm)	Standard	Solvent	Ref.
$(C_6F_5)_2Se$	110	*a*	Not specified	37
$(4\text{-}CF_3C_6F_4)_2Se$	179	*a*	Not specified	37
$PhSeC_6F_5$	265	*a*	Not specified	37
Ph_2Se	402;414.5	*a*;*b*	$CDCl_3$;$CDCl_3$:DMSO	7;6
$(o\text{-}NaOOCC_6H_4)_2Se$	435	*c*	50% aq. MeOH	58
$(o\text{-}MeOOCC_6H_4)_2Se$	469	*c*	$CDCl_3$	58
$(o\text{-}HOOCC_6H_4)_2Se$	479	*c*	$CDCl_3$	58
$(p\text{-}H_2NC_6H_4)_2Se$	373.4	*b*	$CDCl_3$:DMSO (1:1)	6
$p\text{-}An_2Se$	387.5	*b*	$CDCl_3$:DMSO (1:1)	6
$(p\text{-}PhOC_6H_4)_2Se$	393.8	*b*	$CDCl_3$:DMSO (1:1)	6
$p\text{-}Tol_2Se$	399.3	*b*	$CDCl_3$:DMSO (1:1)	6
$(p\text{-}IC_6H_4)_2Se$	402.2	*b*	$CDCl_3$:DMSO (1:1)	6
$(p\text{-}MeSC_6H_4)_2Se$	404.0	*b*	$CDCl_3$:DMSO (1:1)	6
$(p\text{-}FC_6H_4)_2Se$	404.8	*b*	$CDCl_3$:DMSO (1:1)	6
$(p\text{-}BrC_6H_4)_2Se$	408.4	*b*	$CDCl_3$:DMSO (1:1)	6
$(p\text{-}ClC_6H_4)_2Se$	411.8	*b*	$CDCl_3$:DMSO (1:1)	6
$(p\text{-}HOOCC_6H_4)_2Se$	428.6	*b*	$CDCl_3$:DMSO (1:1)	6
$(p\text{-}AcC_6H_4)_2Se$	429.9	*b*	$CDCl_3$:DMSO (1:1)	6
$(p\text{-}NO_2C_6H_4)_2Se$	439.3	*b*	$CDCl_3$:DMSO (1:1)	6

[a] Relative to neat Me_2Se.

[b] Reported relative to selenophene; converted to Me_2Se in $CDCl_3$ (60% v/v) using the relationship $\delta(Me_2Se) = \delta(\text{selenophene}) - 608.6$.

chemical shifts of 4-substituted fluorobenzenes with the ^{77}Se shifts being approximately 2.5 times more sensitive than the ^{19}F shifts. Again it can be seen from the data in Table 8 that the introduction of a perfluorinated benzene ring causes a shielding of the Se nucleus compared to the parent hydrogen compound. For example, compare the ^{77}Se chemical shifts of Ph_2Se (402 ppm), $PhSeC_6F_5$ (265 ppm) and $(C_6F_5)_2Se$ (110 ppm).

(*v*) Alkyl diselenides. ^{77}Se chemical shifts of dialkyl and alkyl aryl diselenides are provided in Table 9. As mentioned previously, a deshielding of approximately 65 ppm is observed in going from $Me_2Se_2 \rightarrow Et_2Se_2 \rightarrow i\text{-}Pr_2Se_2 \rightarrow t\text{-}Bu_2Se_2$. The magnitude of the deshielding is considerably less than that observed in alkyl selenides, as, for example, Me_2Se (0 ppm) and Et_2Se (217 ppm). This smaller deshielding in diselenides has been discussed in terms of the difference in the site where substitution takes place[40]. In going from Me_2Se to Et_2Se, the substitution takes place at each of the α-carbons, whereas in going from Me_2Se_2 to Et_2Se_2, each of the Me groups is introduced at the α-position with respect to one Se atom and at the β-position with respect to the second Se atom. Thus, in diethyl diselenide each of the Se atoms has a Me group in the γ-position, which induces a shielding of Se by the γ-effect (*vide supra*). Therefore, in going from $Me_2Se_2 \rightarrow Et_2Se_2 \rightarrow i\text{-}Pr_2Se_2 \rightarrow t\text{-}Bu_2Se_2$, each new Me group induces deshielding of the β-Se by a dispersion effect and shielding of the distant Se by the γ-effect, resulting in inducing a smaller

TABLE 9. ^{77}Se chemical shifts of alkyl diselenides

Compound	Chemical shift (ppm)	Standard	Solvent	Ref.
Dialkyl				
$(MeSe)_2$	268.3; 270; 275; 275; 281	*a; b; c; d; e*	$CDCl_3$; neat; neat; $CDCl_3$; $CDCl_3$	40; 32; 22; 7; 11
$(C_{10}H_{21}Se)_2$	316	*e*	$CDCl_3$	11
$(EtSe)_2$	319; 333.5; 339	*b; a; c*	Neat; $CDCl_3$; neat	32; 40: 22
$(PhCH_2Se)_2$	401.4; 402; 412	*f; d; e*	$CDCl_3$: DMSO (1:1); $CDCl_3$; $CDCl_3$	5; 7; 11
$(2\text{-}ClC_6H_4CH_2Se)_2$	395.1	*f*	$CDCl_3$: DMSO (1:1)	5
$(2\text{-}BrC_6H_4CH_2Se)_2$	395.9	*f*	$CDCl_3$: DMSO (1:1)	5
$(4\text{-}FC_6H_4CH_2Se)_2$	403.0	*f*	$CDCl_3$: DMSO (1:1)	5
$(4\text{-}ClC_6H_4CH_2Se)_2$	407.9	*f*	$CDCl_3$: DMSO (1:1)	5
$(4\text{-}BrC_6H_4CH_2Se)_2$	408.2	*f*	$CDCl_3$: DMSO (1:1)	5
$(2,4\text{-}Cl_2C_6H_3CH_2Se)_2$	398.8	*f*	$CDCl_3$: DMSO (1:1)	5
$(i\text{-}PrSe)_2$	401.9; 407	*c*	$CDCl_3$; neat	40, 22
$(t\text{-}BuSe)_2$	493	*c*	Neat	22
$(CF_3Se)_2$	528; 531; 550	*c; g; h*	Not specified; neat; C_6D_6	37, 33, 41
Alkyl aryl				
PhSe*SeMe	445(*), 294	*c*	Neat	22

[a] Relative to Me_2Se in $CDCl_3$ (60% v/v).

[b] Aq. H_2SeO_3 was used as a reference; chemical shift values have been converted relative to Me_2Se in $CDCl_3$ (60% v/v) using the expression $\delta[Me_2Se] = \delta[H_2SeO_3(aq.)] - 1285.6$.

[c] Relative to neat Me_2Se.

[d] Relative to Me_2Se in $CDCl_3$.

[e] Relative to 1.0M Me_2Se in $CDCl_3$.

[f] Selenophene in $(CD_3)_2CO$ (20%) was used as a reference; chemical shift values have been converted relative to Me_2Se in $CDCl_3$ (60% v/v) using the expression $\delta(Me_2Se) = \delta(\text{selenophene}) - 608.6$.

[g] $SeOCl_2$ was used as a reference; chemical shift values have been converted relative to Me_2Se in $CDCl_3$ (60% v/v) using the expression $\delta(Me_2Se) = \delta(SeOCl_2) - 1482.6$.

[h] Relative to Me_2Se in C_6D_6.

TABLE 10. ^{77}Se chemical shifts of diaryl diselenides, $R^1C_6H_4Se^*SeC_6H_4R^2$[a]

R^1	R^2	Chemical shift (ppm)
H	H	464.1
2-NO_2	2-NO_2	485.0
4-OMe	2-NO_2	352.2(*), 618.6
4-Me	2-NO_2	353.1(*), 596.4
4-H	2-NO_2	356.9(*), 583.6; 357(*), 584[b]
4-NO_2	2-NO_2	372.9(*), 565.7
4-COOMe	4-COOMe	451.4
4-NO_2	4-NO_2	455.8
4-CN	4-CN	457.5
4-OMe	4-H	462.0(*), 505.9
4-Me	4-H	462.0(*), 478.2
4-I	4-I	470.5
4-Me	4-Me	475.7
4-Br	4-Br	475.9
4-Cl	4-Cl	478.2
4-F	4-F	493.5
4-OMe	4-OMe	505.8

[a] Relative to Me_2Se in $CDCl_3$ (60% v/v); solvent $CDCl_3$; Ref. 60.
[b] Relative to Me_2Se; solvent $CDCl_3$; Ref. 61.

magnitude of deshielding compared to that observed in the alkyl selenide series. A similar effect has also been seen in ditellurides, which will be discussed in more detail later in this chapter.

(*vi*) Diaryl diselenides. ^{77}Se chemical shifts of symmetrical and unsymmetrical diaryl diselenides are presented in Table 10. For the symmetrical diselenides, ^{77}Se shifts of 4-substituted derivatives containing strongly electron-accepting groups, strongly electron-donating groups as well as substituents of intermediate character such as Me and halogens have been reported[60]. The total chemical shift range covered is ~ 55 ppm. Correlation of ^{77}Se shifts with substituent constants of the Hammett and Brown–Okamoto type is poor and a negative slope is obtained. Thus, electron-withdrawing groups shield the ^{77}Se resonance whereas electron-donating groups deshield the ^{77}Se resonance. From the ^{77}Se chemical shifts of unsymmetrical diselenides it can be seen that electron-withdrawing substituents induce deshielding of the proximate Se atom but induce shielding of the distant Se atom. For example, compare *p*-AnSe*SePh (462(*) ppm, 505.9 ppm) and PhSeSePh (464.1 ppm), in which introduction of an OMe group in the 4-position of diphenyl diselenide deshields the distant Se by 41.8 ppm whereas the proximate Se resonance is *shielded*, but only by ~ 2 ppm. Thus the main effect of a substituent is to affect the distant Se. The reason(s) for this rather unusual chemical shift behaviour certainly require and deserve further study.

(*vii*) Selenenyl sulphides. The large majority of selenenyl sulphides which have been studied by ^{77}Se-NMR spectroscopy (Table 11) were investigated as model compounds for biological systems which had Se covalently bound to thio groups by using the reactant 6,6′-diselenobis-(3-nitrobenzoic acid)[62]. Even though the compounds are relatively similar, the total chemical shift range is over 320 ppm with the most shielded system being $4\text{-}NO_2C_6H_4SeSBu\text{-}t$ and the most deshielded being $2\text{-}NO_2C_6H_4SeSCN$. The Se resonance in these compounds is generally deshielded with respect to the corresponding diselenides presumably due to the slightly greater electronegativity of S compared to Se. For example, the ^{77}Se chemical shift of Ph_2Se_2 (464 ppm) is 62 ppm shielded from

TABLE 11. ^{77}Se chemical shifts of selenenyl sulphides

Compound	Chemical shift (ppm)	Standard	Solvent	Ref.
$4\text{-}NO_2C_6H_4SeSBu\text{-}t$	416.6	*a*	$CDCl_3$	62
$PhSeSCH_2Ph$	475.0	*a*	$CDCl_3$	62
$2\text{-}NO_2,4\text{-}BrC_6H_3SeSBu\text{-}t$	514.6	*a*	$CDCl_3$	62
PhSeSPh	526.0	*a*	$CDCl_3$	62
$2\text{-}NO_2C_6H_4SeSEt$	563.7	*a*	$CDCl_3$	62
$2\text{-}NO_2C_6H_4SeSCH_2CH_2COOH$	565.7	*a*	$CDCl_3$	62
$2\text{-}NO_2C_6H_4SeSBu\text{-}n$	573.1	*a*	$CDCl_3$	62
PhSeSMe	574.0	*b*	Not specified	22
$2\text{-}NO_2C_6H_4SeSCH_2CH_2OH$	574.6	*a*	$CDCl_3$	62
$2\text{-}NO_2C_6H_4SeSC_{16}H_{33}$	574.7	*a*	$CDCl_3$	62
$2\text{-}NO_2C_6H_4SeSCH_2Ph$	577.0	*a*	$CDCl_3$	62
$2\text{-}NO_2,4\text{-}BrC_6H_3SeSCH_2Ph$	584.6	*a*	$CDCl_3$	62
CF_3SeSCF_3	590	*c*	C_6D_6	41
$2,4\text{-}(NO_2)_2C_6H_3SeSEt$	593.9	*a*	$CDCl_3$	62
$2,4\text{-}(NO_2)_2C_6H_3SeSCH_2Ph$	607.5	*a*	$CDCl_3$	62
$2\text{-}NO_2C_6H_4SeSCH_2COOH$	609.8	*a*	$CDCl_3$	62
$2\text{-}NO_2C_6H_4SeSPh$	618.8	*a*	$CDCl_3$	62
$2\text{-}NO_2C_6H_4SeS(4\text{-}NO_2C_6H_4)$	588.9	*a*	$CDCl_3$	62
$2\text{-}NO_2C_6H_4SeS(4\text{-}Tol)$	632.3	*a*	$CDCl_3$	62
$2\text{-}NO_2C_6H_4SeS(4\text{-}FC_6H_4)$	641.7	*a*	$CDCl_3$	62
$2\text{-}NO_2C_6H_4SeS(4\text{-}An)$	660.9	*a*	$CDCl_3$	62
$2\text{-}NO_2,4\text{-}BrC_6H_3SeS(4\text{-}Tol)$	639.9	*a*	$CDCl_3$	62
$2,4\text{-}(NO_2)_2C_6H_3SeS(4\text{-}Tol)$	668.9	*a*	$CDCl_3$	62
CF_3SeSCF_2Cl	620	*c*	C_6D_6	41
$CF_3SeSCFCl_2$	656	*c*	C_6D_6	41
$CF_3SeSCCl_3$	680	*c*	C_6D_6	41
$2\text{-}NO_2C_6H_4SeSCN$	737.7	*a*	$CDCl_3$	62

[a] Relative to Me_2Se in $CDCl_3$ (60% v/v).
[b] Relative to neat Me_2Se.
[c] Relative to Me_2Se in C_6D_6.

PhSeSPh (526 ppm). Since many of these compounds were studied as model systems, the Se had a Ph group attached. Introduction of an electron-withdrawing group (e.g. —NO_2) in the *ortho* or *para* position deshielded the Se resonance. Interestingly, when a *para* substituent was introduced on a Ph ring bound to S, behaviour of the ^{77}Se chemical shift was opposite to that expected. For example, a NO_2 group on the sulphur Ph ring caused a shielding of the Se while electron donors (in a mesomeric sense) effected a deshielding of the Se resonance. This same effect has been noticed in unsymmetrical diselenides (Table 10).

(*viii*) Seleno esters. The ^{77}Se chemical shifts for this class of compounds are shown in Table 12. Replacement of a Me group in dimethyl selenide by a benzoyl group, —COPh, leads to a deshielding of the ^{77}Se resonance by 445 ppm. Baiwir and coworkers found that the ^{77}Se chemical shifts of *ortho*-substituted butyl selenobenzoates varied in a linear manner with the electronegativities of the substituents if the substituents were halogens[63]. The ^{77}Se chemical shifts of 4-substituted phenyl selenobenzoates, $4\text{-}XC_6H_4SeCOPh$, were found to vary in a regular manner with the electronic properties of the substituent[64]. The total chemical shift range for this series covers approximately 28 ppm, only half as much as that observed for 4-substituted selenoanisoles. The observed ^{77}Se chemical shifts and the ^{13}C chemical shifts of the *ipso* and carbonyl carbon were evaluated with the Dual Substituent Parameter analysis (Taft) and all the correlations were found to be

TABLE 12. *^{77}Se chemical shifts of seleno esters,* ArCOSeR

Compound	Chemical shift (ppm)	Standard	Ref.
BzSeMe	445.0	*a*	63
BzSeBu	517.0	*a*	63
2-IC$_6$H$_4$COSeBu	562.3	*a*	63
2-BrC$_6$H$_4$COSeBu	566.2	*a*	63
2-ClC$_6$H$_4$COSeBu	569.4	*a*	63
2-FC$_6$H$_4$COSeBu(*trans*)	576.2	*a*	63
2-FC$_6$H$_4$COSeBu (*cis*)	582.3	*a*	63
2-MeC$_6$H$_4$COSeBu	590.6	*a*	63
BzSePh	627.6;641.5	*a;b*	63;64
BzSe(2-An)	549.5	*a*	64
BzSe(2-Tol)	593.5	*a*	63
BzSe(4-NMe$_2$C$_6$H$_4$)	622.9	*b*	64
BzSe(4-An)	628.9	*b*	64
BzSe(4-Tol)	633.1;634.4	*c;b*	36;64
BzSe(4-FC$_6$H$_4$)	634.4	*b*	64
BzSe(4-ClC$_6$H$_4$)	637.0	*b*	64
BzSe(4-BrC$_6$H$_4$)	637.4	*b*	64
BzSe(4-EtOOCC$_6$H$_4$)	642.3	*b*	64
BzSe(4-AcC$_6$H$_4$)	642.7	*b*	64
BzSe(4-NO$_2$C$_6$H$_4$)	645.7	*b*	64
BzSe(4-CNC$_6$H$_4$)	650.4	*b*	64
2-IC$_6$H$_4$COSe(2-An)	595.4	*a*	63
2-BrC$_6$H$_4$COSe(2-Tol)	636.6	*a*	63
2-MeSeC$_6$H$_4$COSePh	640.8	*a*	63
2-MeSC$_6$H$_4$COSePh	650.7	*a*	63
2-IC$_6$H$_4$COSePh	668.0	*a*	63
2-ClC$_6$H$_4$COSePh	674.1	*a*	63
2-AnCOSePh	700.2	*a*	63
4-OctOC$_6$H$_4$COSe(4-PenC$_6$H$_4$)	618.9	*c*	36
4-AnCOSe(4-Tol)	620.5	*c*	36
AcSePh	660.0	*a*	63

[a] Relative to Me$_2$Se in CDCl$_3$; solvent CDCl$_3$.

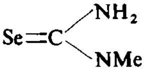
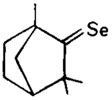
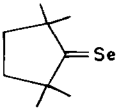
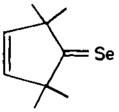
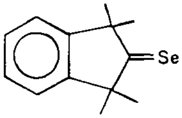
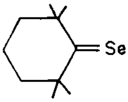
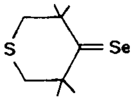
[b] Relative to Me$_2$Se in CDCl$_3$ (60% v/v); solvent CDCl$_3$.

[c] (4-TolSe)$_2$ in CDCl$_3$ (~ 10%) was used as a reference; chemical shifts values have been converted relative to Me$_2$Se in CDCl$_3$ (60% v/v) using the expression $\delta[\mathrm{Me_2Se}] = \delta[(\text{4-TolSe})_2] - 475.7$; solvent CDCl$_3$.

discriminatory towards the σ_R^+ resonance scales. Mesomeric donors were found to interact well with the Ph ring. Thus it is proposed that the selenobenzoato moiety, —SeCOPh, is acting as an electron-deficient group and that the delocalization of electron density of Se onto carbonyl O takes place via an n_{Se}–π^*_{Se} interaction.

(*ix*) Compounds containing C=Se double bonds. ^{77}Se chemical shifts of compounds containing C=Se double bonds are spread over a very broad range (Table 13). The ^{77}Se chemical shift of COSe is most shielded at − 447 ppm and the Se resonance in (t-Bu)$_2$CSe is the most deshielded at 2131 ppm. In fact, the chemical shifts of compounds containing the C=Se moiety appear as a class to have a larger chemical shift range than any other type of Se compound. Cullen and coworkers[24], Gombler[65] and Wong, Guziec and Moustakis[26] found a linear correlation, with two exceptions, between the ^{77}Se shifts and λ_{max} of the $n \rightarrow \pi^*$ transition. As the ΔE term appears well correlated with the energies of the $n \rightarrow \pi^*$ transition, the correlation between ^{77}Se chemical shifts and λ_{max} ($n \rightarrow \pi^*$) clearly shows that the ^{77}Se chemical shift is dominated by the local paramagnetic screening term, σ^{para}. Wong, Guziec and Moustakis[26] have also determined ^{17}O chemical shifts of the corresponding carbonyl compounds and found that the correlation of ^{77}Se chemical shifts

TABLE 13. ^{77}Se chemical shifts of C=Se compounds

Compound	Chemical shift (ppm)	Standard	Solvent	Ref.
Se=C=O	−447	*a*	C_6D_6	65
Se=C=S	102	*a*	C_6D_6	65
 $Se{=}C(NH_2)(NMe_2)$	147	*b*	D_2O, pD 4	11
$Se{=}C(NH_2)_2$	195	*a*	C_6D_6	65
Se=C=Se	331	*a*	C_6D_6	65
Se=C(*t*-Bu)NMe_2	640	c	$CDCl_3$	24
$Se{=}CF_2$	688	*a*	C_6D_6	65
Se=C(Ph)NMe_2	733	*c*	$CDCl_3$	24
Se=C(Ph)OEt	915	*c*	$CDCl_3$	24
	1613	*c*	$CDCl_3$	24
	1737	*c*	$CDCl_3$	26
	1803	*c*	$CDCl_3$	24
	1844; 1849	*c*; *a*	$CDCl_3$; C_6D_6	24; 65
	2034	*c*	$CDCl_3$	26
	2135	*c*	$CDCl_3$	24
Se=C(Bu-*t*)$_2$	2131; 2162	*c*; *a*	$CDCl_3$; C_6D_6	24; 65

[a] Relative to Me_2Se in C_6D_6.
[b] Relative to 1.0M Me_2Se in $CDCl_3$.
[c] Internal standard Ph_3PSe; converted to Me_2Se in $CDCl_3$ (60% v/v) using the relationship $\delta(Me_2Se) = \delta(Ph_3PSe) + 263$.

of selones and ^{17}O chemical shifts of the corresponding ketones is excellent.

(*x*) Selenocyanates. Se resonances of selenocyanates fall in the range of 125–509 ppm (Table 14). The CN group exhibits a surprisingly small deshielding effect on the Se chemical shift in these compounds. In fact, it is much smaller than might be expected on the

TABLE 14. ^{77}Se chemical shifts of selenocyanates

Compound	Chemical shift (ppm)	Standard	Solvent	Ref.
Alkyl derivatives				
$MeSeCN$	125	*a*	$CDCl_3$	7
$PhCH_2SeCN$	291; 299.9	*a*; *b*	$CDCl_3$; $(CD_3)_2CO$	7, 5
$2\text{-}ClC_6H_4CH_2SeCN$	284.7	*b*	$(CD_3)_2CO$	5
$2\text{-}BrC_6H_4CH_2SeCN$	285.0	*b*	$(CD_3)_2CO$	5
$2\text{-}FC_6H_4CH_2SeCN$	295.7	*b*	$(CD_3)_2CO$	5
$3\text{-}FC_6H_4CH_2SeCN$	305.8	*b*	$(CD_3)_2CO$	5
$3\text{-}ClC_6H_4CH_2SeCN$	309.0	*b*	$(CD_3)_2CO$	5
$3\text{-}BrC_6H_4CH_2SeCN$	309.8	*b*	$(CD_3)_2CO$	5
$4\text{-}FC_6H_4CH_2SeCN$	306.4	*b*	$(CD_3)_2CO$	5
$4\text{-}ClC_6H_4CH_2SeCN$	309.3	*b*	$(CD_3)_2CO$	5
$4\text{-}BrC_6H_4CH_2SeCN$	309.3	*b*	$(CD_3)_2CO$	5
$2,4\text{-}Cl_2C_6H_3CH_2SeCN$	291.8	*b*	$(CD_3)_2CO$	5
CF_3SeCN	509	*a*	C_6D_6	41
Aryl derivatives				
$PhSeCN$	320.8; 322.3	*c*; *a*	$CDCl_3$; neat	60, 67
$2\text{-}MeOC(O)C_6H_4SeCN$	394	*a*	$CDCl_3$	59
$2\text{-}NO_2C_6H_4SeCN$	413; 417	*d*; *c*	$CDCl_3$; $CDCl_3$	61, 68
$2\text{-}HC(O)C_6H_4SeCN$	423	*a*	$CDCl_3$	59
$2\text{-}AcC_6H_4SeCN$	434	*a*	$CDCl_3$	59
4-AnSeCN	305.0; 308.8	*a*; *c*	$CDCl_3$; $CDCl_3$	67, 60
4-TolSeCN	313.0	*c*	$CDCl_3$	60
$4\text{-}FC_6H_4SeCN$	318.3	*c*	$CDCl_3$	60
$4\text{-}ClC_6H_4SeCN$	321.0	*c*	$CDCl_3$	60
$4\text{-}BrC_6H_4SeCN$	321.7	*c*	$CDCl_3$	60
$4\text{-}EtOC(O)C_6H_4SeCN$	329.4	*c*	$CDCl_3$	60
$4\text{-}AcC_6H_4SeCN$	329.9	*c*	$CDCl_3$	60
$4\text{-}MeOC(O)C_6H_4SeCN$	330; 330.5	*a*; *c*	$CDCl_3$; $CDCl_3$	7; 60
$4\text{-}NO_2C_6H_4SeCN$	338.8; 340	*c*; *a*	$CDCl_3$; $CDCl_3$	60; 67
$4\text{-}CNC_6H_4SeCN$	341.8	*c*	$CDCl_3$	60
$2,4\text{-}(NO_2)_2C_6H_3SeCN$	449	*c*	$CDCl_3$	68

[a] Relative to neat Me_2Se.

[b] Selenophene in $(CD_3)_2CO$ (20%) was used as a reference; chemical shift values have been converted relative to Me_2Se in $CDCl_3$ (60% v/v) using the expression $\delta(Me_2Se) = \delta(\text{selenophene}) - 608.6$.

[c] Relative to Me_2Se in $CDCl_3$ (60% v/v).

[d] Relative to Me_2Se in $CDCl_3$ (concentration not specified).

basis of its electron-withdrawing power (i.e. its electronegativity) as well as by comparison with the ^{77}Se chemical shifts of selenoisocyanates and selenoisothiocyanates (see Table 22). The deshielding induced by the CN group on the ^{77}Se chemical shift is approximately of the same magnitude as that induced by an acetylenic group[28]. Although the CN group and the $C{\equiv}C$ bond are isoelectronic, the more polar CN group would be expected to induce a larger deshielding if inductive polarization dominates. Thus other factors must contribute substantially in the case of triply bonded groupings. Similar behaviour of the CN group is observed in the α-carbon chemical shifts of alkyl cyanides[66].

The ^{77}Se chemical shifts of *para*-substituted aryl selenocyanates vary in a regular way with the character of the substituent[60], i.e. electron-donating groups cause shielding and electron-withdrawing groups cause deshielding. The shifts cover a range of approximately 33 ppm (becoming more deshielded from —Me to —CN), which is similar to the range observed for the substituent effect on the Se chemical shifts of *para*-substituted phenyl selenobenzoates (27.5 ppm). A Dual Substituent Parameter analysis of the shift data support the concept that the level of π interaction between the —SeCN group and the Ph ring is approximately 1.5 times the level of polar effects ($\rho_R/\rho_I = 1.49$)[60].

(*xi*) Selenenyl halides. This class of compounds includes mono-, di- and tri-halides and thus a relatively broad range of chemical shifts is observed (Table 15). Although, as expected, replacement of a hydrogen by a halogen induces a large deshielding, further introduction of halogens will reverse the trend. This can be seen when comparing the ^{77}Se chemical shifts of CF_3SeH (287 ppm), CF_3SeCl (1077 ppm) and CF_3SeCl_3 (890 ppm). It should be noted that this behaviour is also observed in the ^{119}Sn chemical shifts of alkyltin halides and in the ^{13}C chemical shifts of alkyl halides when the halogens are Br and I.

In a recent study[41] of trifluoromethyl selenenyl halides, a plot of the ^{77}Se chemical shift of the selenenyl derivative CF_3SeX (where X = Cl, Br, CN, H, Ag) vs. the electronegativity of the substituent X yielded a relatively straight line although there is some question concerning the scientific validity of this plot. All substituent electronegativity values were chosen from one scale, except that for the CN group which was taken from a separate scale. Electronegativity scales are internally consistent but values from different scales should not be mixed as has been done in this case. Thus, with respect to a correlation with electronegativity, there is reason to believe that the ^{77}Se chemical shift for CF_3SeCN may be anomalous.

TABLE 15. ^{77}Se chemical shifts of selenenyl halides[a]

Compound	Chemical shift (ppm)	Solvent	Ref.
Alkyl derivatives			
Me_2SeBr_2	389	CH_2Cl_2	22
Me_2SeCl_2	448	CH_2Cl_2	22
Et_2SeBr_2	540	CCl_4	22
i-Pr_2SeBr_2	742	CCl_4	22
$(CF_3)_2SeF_2$	830	C_6D_6	41
CF_3SeBr	886	C_6D_6	41
MeSeCl	890	CH_2Cl_2	22
CF_3SeCl_3	953	C_6D_6	41
$EtSeCl_3$	995	CH_2Cl_2	22
CF_3SeCl	1077	C_6D_6	41
Aryl derivatives			
Ph_2SeCl_2	586	$CDCl_3$	22
C_6F_5SeCl	812	Not specified	39
PhSeBr	869.0	$CDCl_3$	68
2-$NO_2C_6H_4SeBr$	908;912	$CDCl_3$;$CDCl_3$	61;68
2-CH(O)C_6H_4SeBr	1019	$CDCl_3$	59
2-AcC_6H_4SeBr	1029	$CDCl_3$	59
2-MeOC(O)C_6H_4SeBr	1042	$CDCl_3$	59
4-$NO_2C_6H_4SeBr$	823.0	$CDCl_3$	68
4-TolSeBr	876.9	$CDCl_3$	68
4-AnSeBr	887.7	$CDCl_3$	68
2,4-$(NO_2)_2C_6H_3SeBr$	897.6	$CDCl_3$	68
PhSeCl	1042	$CDCl_3$	68
2-$NO_2C_6H_4SeCl$	999	$CDCl_3$	68
2-MeOC(O)C_6H_4SeCl	1017	$CDCl_3$	59
2-AcC_6H_4SeCl	1087	$CDCl_3$	59
2-HC(O)C_6H_4SeCl	1097	$CDCl_3$	59

[a] Chemical shifts are reported relative to Me_2Se.

Similar to the above study, a plot of ^{77}Se chemical shifts of *o*-nitrophenyl selenenyl compounds, *o*-$NO_2C_6H_4SeX$ (where the first element of the X group is O, Cl, Br, N, S, Se, C), vs. the electronegativities of X yields two straight lines. One line represents the substituents X = C, N and O and has a different slope than the line where X = Cl, Br, Se and S.

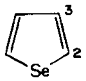
(*xii*) Heterocyclic selenium compounds. ^{77}Se NMR parameters for a series of 2- and 3-substituted selenophenes are presented in Table 16. Acceptable linear correlations were observed between the substituent-caused ^{77}Se shifts of 2-substituted selenophenes and similarly *ortho*-positioned ^{13}C shifts when carbonyl-containing derivatives and 2-nitroselenophene were excluded[4]. The substituent-caused ^{77}Se shifts in the 3-substituted derivatives behaved as if the substituents were in the para position rather than in the *meta* position and these ^{77}Se shifts were approximately six times larger than ^{13}C shifts of similarly positioned carbons. The ^{77}Se shifts are much smaller than expected for the 2-CHO group and furthermore an upfield shift was observed even though the 2-CHO group is electron-withdrawing. Although the difference between the ^{77}Se shift caused by the CN group (712.9 ppm) and the CHO group (602.2 ppm) is substantial, the ^{13}C chemical shifts of the 3-carbon are almost the same (11.5 ppm and 10.5 ppm from the chemical shift of the 3-carbon of selenophene, respectively) The anomalous ^{77}Se shifts of 2-carbonyl derivatives were explained by invoking through-space bonding between empty Se d orbitals and the carbonyl O lone pair in the *cis* conformation of the 2-carbonyl derivatives. A similar through-space d orbital interaction was also suggested to occur for 2-nitroselenophene, while this interaction is absent in 2-cyanoselenophene.

In addition to the substituted selenophenes discussed above, a series of mono- and di-substituted benzo[b]selenophenes have been studied and their ^{77}Se chemical shifts are listed in Table 17 and 18, respectively[69]. The general trends observed in the monosubstituted benzo[*b*]selenophenes are the same as those observed in the corresponding selenophenes. As observed in the selenophenes, nitro- and carbonyl-containing derivatives show relatively lower deshielding of Se resonances. No correlation has been established between the ^{77}Se chemical shifts in 2- and 3-substituted benzo[*b*]selenophenes. In disubstituted derivatives, additivity rules do not usually hold; however, a linear correlation has been established between the ^{77}Se chemical shifts of 2-substituted benzo[*b*]selenophenes and those of the corresponding 2,3-disubstituted derivatives when the 3-substituent is Me. In these compounds, the observed shifts are in good agreement with the shifts calculated by additivity.

Additional heterocyclic compounds of Se and their ^{77}Se chemical shifts are listed in Tables 19 and 20.

(*xiii*) Selenium–oxygen compounds. ^{77}Se chemical shifts of Se compounds containing a Se–O–C moiety are presented in Table 21. In general, the presence of a neighbouring O causes a large deshielding of Se and thus this class of compounds exhibits the most deshielded Se resonances among the organoselenium compounds with certain exceptions (e.g. some C=Se compounds, *vide supra*). It is interesting to note that the replacement of a Me group by a Ph group in methylseleninic acid, MeSeOOH, leads to a shielding (−40 ppm) rather than the expected deshielding of the Se nucleus; e.g. MeSeOOH (1216 ppm), PhSeOOH (1173 ppm), 3-TolSeOOH (1176 ppm). Actually the Se chemical shift in this class of compounds appears to be less sensitive to the changes in the structure of the neighbouring groups than most of the classes of compounds which we have discussed. For example, the ^{77}Se chemical shift difference between $PhCH_2SeOOH$ and MeSeOOH is only 19 ppm and that between $(MeO)_2SeO_2$ and $(EtO)_2SeO_2$ is only 6 ppm. In the former series, RSeOOH, the Se atom has one non-bonded pair of electrons and in the latter series, R_2SeO_2, the Se atom has no lone pairs. Moreover, for the transition $(MeO)_2SeO \rightarrow (MeO)_2SeO_2$ an increased shielding of Se of approximately 290 ppm is observed. Therefore, it appears that Se shielding is less sensitive to changes in substituents

TABLE 16. ^{77}Se chemical shifts of substituted selenophenes[a,b]

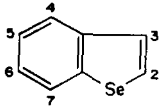


Substituent	Chemical shift (ppm)	Substituent	Chemical shift (ppm)
2-F	513.2	2-Br	674.6
2-OMe	517.3	2-CN	712.9
2-OAc	576.2	2-I	721.2
2-CH(Me)OAc	590.5	3-OMe	527.9
2-CH_2OH	600	3-Me	593.4
2-CHO	602.2	3-Cl	622.2
2-H	608.6	3-SMe	628.1
2-Me	612.4	3-Br	646.7
2-NO_2	614.2	3-COOH	652.1
2-Ac	620.3	3-Ac	653.4
2-COOMe	633.0	3-NO_2	654.4
2-COOH	634.8	3-CHO	663.9
2-Cl	649.8	3-CN	667.0
2-SMe	650.3	3-I	681.0
2-$CONMe_2$	650.9		

[a] Solvent C_6D_6 (20% solutions). Chemical shifts are reported relative to selenophene; converted to Me_2Se in $CDCl_3$ (60% v/v) using the relationship $\delta(Me_2Se) = \delta(\text{selenophene}) - 608.6$.

[b] Ref. 4.

TABLE 17. ^{77}Se chemical shifts of substituted benzo[*b*]selenophenes[a,b]

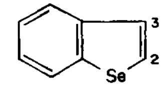


Compound	Chemical shift (ppm)	Compound	Chemical shift (ppm)
2-CHO	509.5	2-CN	604.6
2-CH_2OH	517	2-I	639.1
2-CH_2CN	517.1	3-OMe	425.7
2-NO_2	517.8	3-NHAc	454.9
2-Ac	527.4	3-Me	493.5
2-H	529.6	3-CH_2CN	497.3
2-CH_2SeCH_2COOH	531.3	3-Cl	508.6
2-CONHMe	536	3-CH_2SeCH_2COOH	510.2
2-COOEt	536.6	3-Ac	518.6
2-COOMe	537.7	3-SMe	526.7
2-COSMe	537.7	3-NO_2	531.4
2-Me	538.6	3-Br	533.7
2-CH_2Ph	538.8	3-SeMe	542.3
2-Bz	544.8	3-CHO	544.8
2-$CONMe_2$	564.1	3-Ph	555.1
2-SMe	569.2	3-CN	559.6
2-Cl	577.1	4-NO_2	553.9
2-SeMe	580.3	5-NO_2	562.0
2-$Se(CH_2)_2COOH$	587.6	7-NO_2	618.1
2-Br	601.1		

[a] Solvent $CDCl_3$. Chemical shifts are reported relative to benzo[*b*]selenophene; converted to Me_2Se in $CDCl_3$ (60% v/v) using the relationship $\delta(Me_2Se) = \delta$(benzo[*b*]selenophene) − 529.6.

[b] Ref. 69.

TABLE 18. ^{77}Se chemical shifts of disubstituted benzo[*b*]selenophenes[a,b]

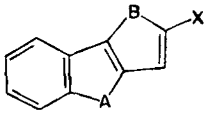


Substituents	Chemical shift (ppm)	Substituent	Chemical shift (ppm)
2-COOEt, 3-OH	465.1	2-Bz, 3-Me	549.8
2-Ac, 3-OAc	481.6	2-SeMe, 3-Me	552.8
2-Me, 3-OAc	484.0	2-Cl, 3-Me	553.4
2-NO_2, 3-Br	484.1	2-CH_2Ph, 3-CHO	560.9
2-COOEt, 3-OAc	487.8	2-Me, 3-Br	561.5
2-NHCOMe, 3-Me	488.7	2-Me, 3-Ac	564.0
2-CHO, 3-Me	497.2	2-SMe, 3-Ac	566.3
2-COOEt, 3-OMe	498.2	2-SeMe, 3-Ac	569.7
2-CH_2OH, 3-Me	500.7	2-Me, 3-COOMe	570.3
2-OAc, 3-Ac	515.4	2-Br, 3-Me	573.9
2-Me, 3-Me	520.3	2-COOEt, 3-Br	573.9
2-Ac, 3-Me	521.2	2-CN, 3-Me	575.8
2-COOMe, 3-Me	526.8	2-Ac, 3-SeMe	582.1
2-$CONMe_2$, 3-Me	527.7	2-Me, 3-CN	582.4
2-$CONH_2$, 3-Me	534.9	2-SeMe, 3-CHO	591.6
2-COOMe, 3-NO_2	536.9	2-Me, 3-I	599.8
2-CHO, 3-SPh	537.7	2-Ac, 3-OH	601.6
2-Me, 3-$CONH_2$	539.7	2-SPh, 3-CHO	602.7
2-SMe, 3-Me	540.7	2-I, 3-Me	614.8
2-OH, 3-Ac	540.8	2-Br, 3-Br	615.9
2-CHO, 3-Br	544.3	2-Br, 3-CHO	622.9
2-CHO, 3-SeMe	549.6		

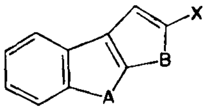
[a] Solvent $CDCl_3$. Chemical shifts are reported relative to benzo[*b*]selenophene; converted to Me_2Se in $CDCl_3$ (60% v/v) using the relationship $\delta(Me_2Se) = \delta(\text{benzo}[b]\text{selenophene}) - 529.6$.

[b] Ref. 69.

TABLE 19. ^{77}Se chemical shifts of S–Se and Se–Se isosteres of benzopentalene[a]



trans

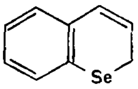


cis

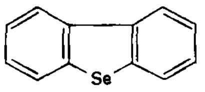
A–B	X = H		X = Ac		X = CHO		X = Br		X = Me		X = NO_2	
	A	B	A	B	A	B	A	B	A	B	A	B
Se–Se (*cis*)	499.7	583.4	521.5	597.1	525.0	583.8	515.6	655.6	498.2	595.8	550.2	599.6
Se–Se (*trans*)	486.7	549.6	494.9	588.8	486.6	549.4	508.5	634.0	488.6	555.3	524.4	563.2
Se–S (*cis*)	475.4	—	491.4	—	496.1	—	495.8	—	475.2	—	526.0	—
Se–S (*trans*)	459.4	—	465.2	—	468.8	—	479.7	—	457.2	—	504.5	—
S–Se (*cis*)	—	555.1	—	565.7	—	553.1	—	628.9	—	567.3	—	573.7
S–Se (*trans*)	—	525.8	—	533.9	—	519.8	—	611.0	—	525.5	—	541.3

[a] Relative to neat Me_2Se; solvent $CDCl_3$; Ref. 70.

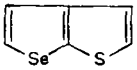
TABLE 20. ^{77}Se chemical shifts of other heterocycles containing selenium



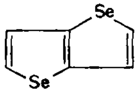
(1)



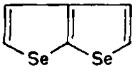
(2)



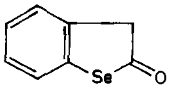
(3)



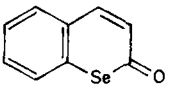
(4)



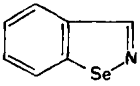
(5)



(6)



(7)



(8)

Compound	Chemical shift (ppm)	Standard	Solvent	Ref.
1	157	*a*	$CDCl_3$	7
2	451	*a*	$CDCl_3$	7
3	545	*a*	$CDCl_3$	7
4	552.6	*b*	$(CD_3)_2CO$	71
5	581	*a*	$CDCl_3$	7
6	584	*a*	$CDCl_3$	7
7	654	*a*	$CDCl_3$	7
8	1013	*a*	$CDCl_3$	7

[a] Relative to neat Me_2Se.

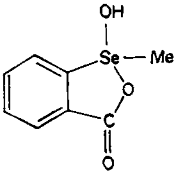
[b] Selenophene in $(CD_3)_2CO$ was used as a reference; chemical shift values have been converted relative to Me_2Se in $CDCl_3$ (60% v/v) using the expression $\delta(Me_2Se) = \delta(\text{selenophene}) - 608.6$.

in compounds in which Se does not have lone pairs, like R_2SeO_2, and much more sensitive in compounds in which Se has two non-bonded electron pairs, like alkyl selenides and dialkyl diselenides. This, of course, fits well with the polarizability concept discussed earlier in this chapter.

(*xiv*) Miscellaneous selenium compounds. A substantial deshielding of Se is observed in going from selenides to selenonium salts. The magnitude of this deshielding depends both upon the nature of the added alkyl group and the groups already present. Thus the formation of Me_3Se^+ from Me_2Se is accompanied by a deshielding of 253 ppm, whereas when Me_2EtSe^+ is formed from MeSeEt the deshielding is only 183 ppm (Table 22). Similarly the transformation $Et_2Se \rightarrow Et_3Se^+I^-$ and $Me_2Se \rightarrow Me_2EtSe^+I^-$ are accompanied by deshieldings of 144 and 291 ppm.

d. Isotope effects. Several groups have studied the effect of isotopes on ^{77}Se nuclear shielding. Actually, the first isotope effect involving Se was observed on the F chemical shift in ^{19}F-NMR spectroscopy in several Se–F compounds[74]. The first example of Se isotope effects on ^{77}Se shielding was that of Jakobsen and Hansen in a study[75] of the ^{77}Se-NMR spectrum of Me_2Se_2 in which four well-resolved lines due to the naturally occurring isotopic species $Me^{77}Se{-}^{n}SeMe$, where $n = 76$, 78, 80 and 82, were observed (natural abundances of selenium isotopes are: ^{74}Se, 0.96%; ^{76}Se, 9.12%; ^{77}Se, 7.5%; ^{78}Se, 23.61%; ^{80}Se, 49.61%; ^{82}Se, 8.85%). An increase by two mass units in Se mass was found to induce a

TABLE 21. ^{77}Se chemical shifts of selenium–oxygen compounds

Compound	Chemical shift (ppm)	Standard	Solvent	Ref.
$PhSe(OCH_2Ph)_2Me$	672	*a*	$CDCl_3$	58
	799	*c*	MeOH	58
Me_2SeO	812	*a*	H_2O	22
$2\text{-}HOOCC_6H_4Se(ONa)Me$	830	*a*	MeOH	58
PhSe(O)Me	832	*a*	$CDCl_3$	58
$2\text{-}MeOC(O)C_6H_4Se(O)Me$	852	*a*	$CDCl_3$	58
Ph_2SeO	863	*a*	$CDCl_3$	58
$(EtO)_2SeO_2$	1047	*a*	CH_2Cl_2	22
$(MeO)_2SeO_2$	1053	*a*	CH_2Cl_2	22
$(CF_3)_2SeO$	1095	*a*	C_6D_6	41
MeSeOOH	1216	*a*	Neat	22
$PhCH_2SeOOH$	1235	*b*	$(CD_3)_2SO$	72
$2\text{-}ClC_6H_4CH_2SeOOH$	1228.5	*b*	$(CD_3)_2SO$	72
$2\text{-}FC_6H_4CH_2SeOOH$	1228.7	*b*	$(CD_3)_2SO$	72
$2\text{-}BrC_6H_4CH_2SeOOH$	1230.8	*b*	$(CD_3)_2SO$	72
$2\text{-}TolCH_2SeOOH$	1240.5	*b*	$(CD_3)_2SO$	72
$3\text{-}BrC_6H_4CH_2SeOOH$	1228.2	*b*	$(CD_3)_2SO$	72
$3\text{-}FC_6H_4CH_2SeOOH$	1231.1	*b*	$(CD_3)_2SO$	72
$3\text{-}ClC_6H_4CH_2SeOOH$	1232.6	*b*	$(CD_3)_2SO$	72
$3\text{-}TolCH_2SeOOH$	1234.1	*b*	$(CD_3)_2SO$	72
$4\text{-}ClC_6H_4CH_2SeOOH$	1226.8	*b*	$(CD_3)_2SO$	72
$4\text{-}BrC_6H_4CH_2SeOOH$	1228.9	*b*	$(CD_3)_2SO$	72
$4\text{-}TolCH_2SeOOH$	1229.8	*b*	$(CD_3)_2SO$	72
$4\text{-}FC_6H_4CH_2SeOOH$	1231.7	*b*	$(CD_3)_2SO$	72
$2,4\text{-}Cl_2C_6H_3CH_2SeOOH$	1227.1	*b*	$(CD_3)_2SO$	72
PhSeOONa	1173	*c*	D_2O	23
3-TolSeOOH	1176.7	*b*	$(CD_3)_2SO$	72
4-TolSeOOH	1175.9	*b*	$(CD_3)_2SO$	72
$(MeO)_2SeO$	1339	*a*	Neat	22

[a] Relative to neat Me_2Se.

[b] Selenophene in $(CD_3)_2CO$ (20%) was used as a reference; chemical shift values have been converted relative to Me_2Se in $CDCl_3$ (60% v/v) using the expression $\delta(Me_2Se) = \delta(\text{selenophene}) - 608.6$.

[c] Relative to Me_2Se in $CDCl_3$ (60% v/v).

shift of 2.62×10^{-2} ppm (0.50 Hz at 19.09 MHz). In this same study[75], 2-deuteroselenophene exhibited a ^{77}Se chemical shift 32.1 Hz to lower frequency from that of the hydrogen compound which was a two-bond isotope shift of 1.682 ppm. Also, in the same sample of selenophene a one-bond ^{13}C (^{12}C) isotope effect of 0.257 ppm (4.9 Hz) on the ^{77}Se chemical shift was determined from the ^{13}C satellite doublet.

The largest secondary isotope shift ever observed in high-resolution NMR spectroscopy was reported for the ^{77}Se spectrum of a liquid mixture of H_2Se, HDSe and D_2Se[76]. The isotope shift per D atom is 7.02 ppm (133 Hz at 18.95 MHz) to lower frequency and in the

TABLE 22. ^{77}Se chemical shifts of miscellaneous organoselenium compounds

Compound	Chemical shift (ppm)	Standard	Solvent	Ref.
CF_3SeAg	26	*a*	Pyridine	41
$Me_3Se^+ I^-$	253	*b*	H_2O	22
$Et_2MeSe^+ I^-$	325	*b*	H_2O	22
$PhSeCH_2CH{=}CH_2$	321.9	*b*	Not specified	73
$4\text{-}MeOC_6H_4SeCH_2CH{=}CH_2$	313.5	*b*	Not specified	73
$4\text{-}NO_2C_6H_4SeCH_2CH{=}CH_2$	344.1	*b*	Not specified	73
$4\text{-}AnSe^+ Me_2I^-$	325	*b*	H_2O	22
$PhSeCH{=}CHCl$ (*trans*)	368.6	*b*	Not specified	73
$4\text{-}AnSeCH{=}CHCl$ (*trans*)	361.8	*b*	Not specified	73
$4\text{-}TolSeCH{=}CHCl$ (*trans*)	364.6	*b*	Not specified	73
$4\text{-}ClC_6H_4SeCH{=}CHCl$ (*trans*)	366.3	*b*	Not specified	73
$4\text{-}BrC_6H_4SeCH{=}CHCl$ (*trans*)	366.5	*b*	Not specified	73
$4\text{-}NO_2C_6H_4SeCH{=}CHCl$ (*trans*)	377.0	*b*	Not specified	73
$PhSeC_3H_3Cl_2$ (cyclo)	370.2	*b*	Not specified	73
$4\text{-}AnSeC_3H_3Cl_2$ (cyclo)	356.8	*b*	Not specified	73
$4\text{-}TolSeC_3H_3Cl_2$ (cyclo)	362.9	*b*	Not specified	73
$4\text{-}ClC_6H_4SeC_3H_3Cl_2$ (cyclo)	370.5	*b*	Not specified	73
$4\text{-}BrC_6H_4SeC_3H_3Cl_2$ (cyclo)	371.5	*b*	Not specified	73
$4\text{-}NO_2C_6H_4SeC_3H_3Cl_2$ (cyclo)	396.8	*b*	Not specified	73
$Et_3Se^+ I^-$	377	*b*	H_2O	22
$PhSeCH{=}CH_2$	395.5	*b*	Not specified	73
$4\text{-}AnSeCH{=}CH_2$	386.7	*b*	Not specified	73
$4\text{-}TolSeCH{=}CH_2$	390.9	*b*	Not specified	73
$4\text{-}ClC_6H_4SeCH{=}CH_2$	395.4	*b*	Not specified	73
$4\text{-}BrC_6H_4SeCH{=}CH_2$	396.0	*b*	Not specified	73
$4\text{-}NO_2C_6H_4SeCH{=}CH_2$	404.9	*b*	Not specified	73
$(CF_3Se)_3As$	505	*a*	C_6D_6	41
$(CF_3Se)_3P$	541	*a*	C_6D_6	41
$CF_3SeSO_2CF_2Cl$	975	*a*	C_6D_6	41
$CF_3SeSO_2CFCl_2$	976	*a*	C_6D_6	41
$CF_3SeSO_2CF_3$	984	*a*	C_6D_6	41
CF_3SeNSO	1091	*a*	C_6D_6	41
CF_3SeNCO	1104	*a*	C_6D_6	41
$CF_3SeNPPh_3$	1112	*a*	C_6D_6	41
$(CF_3Se)_3N$	1617	*a*	C_6D_6	41

[a] Relative to Me_2Se in C_6D_6.
[b] Relative to neat Me_2Se.

^{1}H-coupled ^{77}Se spectrum each resonance is fully separated from resonances of the other isotopomers. In this study primary and secondary isotope effects on the $^{77}Se{-}^1H$ coupling constants were also observed.

In two other recent reports, Gombler reported further studies on C and Se isotope effects on ^{77}Se nuclear shielding[77,78]. ^{13}C isotope effects were measured for 30 organoselenium compounds and were found to range from 0.012 ppm in CF_3SeCl to 1.099 ppm in $Se{=}C(Bu\text{-}t)_2$[77]. Several important findings were (1) the magnitude of the isotope shift could be correlated with C—Se bond distance, (2) appreciable substituent effects were observed in closely related compounds, (3) there was no general correlation between the electronegativity of the substituent and the isotope shift and (4) the isotope shift could be temperature-dependent. In the study of the effect of Se isotopes on ^{77}Se shielding[78], the compounds $(CF_3)_2Se_2$, Me_2Se_2 and $CF_3SeSeMe$ were investigated.

Jakobsen's earlier work on Me_2Se_2 was essentially confirmed, although instead of a constant isotope shift it was found that the isotope shift per unit mass difference decreased with increasing mass of the Se isotopes. A very interesting observation was that the ^{77}Se spectrum of the MeSe group of $CF_3SeSeMe$ exhibited a fine splitting for each isotopomer which was attributed to the occurrence of two conformers. This suggests a relatively high barrier to rotation around the Se—Se bond in this molecule and why this should be so is not clear. This molecule and its ^{77}Se-NMR spectrum deserve further study.

3. *Coupling constants*

Spin–spin coupling constants involving ^{77}Se have been measured for a relatively large number of nuclei and this area has been reviewed relatively recently[79]. Of primary importance in this review are ^{77}Se–^{13}C and ^{77}Se–^{77}Se coupling constants in organoselenium compounds although ^{77}Se–^{1}H coupling constants deserve mention. A large number of ^{77}Se–^{1}H coupling constants have been reported and the area has not been reviewed since 1973[2]. However, in the intervening years, nothing more of substance has been uncovered. Of particular interest is the possible use of coupling constants to probe structure and bonding and ^{77}Se–^{1}H couplings appear to be sensitive to stereochemistry[80–82].

Although fewer ^{77}Se–^{13}C coupling constants have been reported, they are increasingly being investigated with regard to structure and bonding in organoselenium compounds. McFarlane and coworkers[83] were the first to study ^{77}Se–^{13}C coupling constants in a variety of organoselenium compounds in which the Se atom had from zero to three unshared electron pairs. These coupling constants ranged from -13.0 Hz in $MeSeO_3^-$ K^+ to -123 Hz in $PhSe^-$ K^+ and the sign was always negative. It was suggested that, in general, a coupling constant of more than 45 Hz was indicative of a direct Se—C bond but the variety of factors affecting the magnitudes of the couplings would make it difficult to use them as structural probes. However, Reich demonstrated[82] that two-bond Se–C coupling constants in a selenide, a selenoxide, a selenium salt and a selenonium ylide in which the Se is part of a dihydrobenzoselenophene system are stereospecific. More recently one-bond Se–C coupling constants were found[58] to be useful in distinguishing between selenuranes (61–65 Hz) and selenoxides (77–81 Hz) and, in an attempt to further understand the factors influencing the Se–C spin–spin coupling, a series of diorganyl selenides, RSeR′, was investigated[84]. The conclusions of this study[84] were that the Fermi contact term is the principal contributor to one-bond and two-bond Se–C couplings and that $^{1}J(^{77}Se-^{13}C)$ can be used to estimate the bond order of the Se—C bond as well as the conformation of the selenide. It remains to be seen if this will be the case in a large number of systems.

That the Fermi contact contribution is important in Se–C spin–spin coupling in compounds containing a C=Se bond was demonstrated in 1981 by Gombler[65] as the couplings exhibited a strong dependence on the s character of the C atom. As expected, coupling constants between Se and C in these doubly bonded molecules are larger (>200 Hz) with the largest coupling constant being 286.9 Hz for COSe. Wong and coworkers[24,26,85] have also studied a series of selenocarbonyl compounds and confirm that the Fermi contact interaction is dominant in determining $^{1}J(^{77}Se-^{13}C)$. They also reported[26] that where the selenocarbonyl moiety is part of a ring system, due to a change in the s character of the C atom in the C=Se group, the smaller the CC(Se)C angle, the larger the one-bond Se–C coupling constant.

Se–Se coupling constants have understandably received even less attention than Se–C coupling constants. First, the particular compound must possess chemically non-equivalent Se atoms (i.e. $J(^{77}Se-^{77}Se)$ cannot be determined in a symmetrical diselenide) and second, the number of molecules in any diselenide sample possessing two ^{77}Se nuclei will be small (0.56%) and thus, the $^{77}Se-^{77}Se$ coupling constant determination must be from satellites and will be time-consuming. The first measurement of the sign and magnitude of a $^{77}Se-^{77}Se$ spin coupling constant was reported by McFarlane[86] in PhSeSeMe ($+22 \pm 4$ Hz). With the exception of $^{77}Se-^{77}Se$ coupling constants which have been measured in polyatomic inorganic cations[87] containing Se and Te, only one report has appeared[61] in the literature describing the determination of these couplings. The compounds were unsymmetrical diselenides and, in agreement with McFarlane's report, the values were less than 20 Hz. Attempts were also made to determine two- and three-bond $^{77}Se-^{77}Se$ coupling constants but these were unsuccessful and the values were said to be less than 2 Hz. Recent work in this laboratory[88] has resulted in the measurement of several $^{1}J(^{77}Se-^{77}Se)$ values in unsymmetrical diorganyl diselenides. These values range from 2.7 Hz in *t*-BuSeSeMe to 36.3 Hz in *n*-BuSeSeMe. Using enriched ^{77}Se we have also obtained a value of 64 Hz in *o*-$NO_2C_6H_4$SeSeCN for the one-bond $^{77}Se-^{77}Se$ coupling constant[68]. Also, Johannsen has recently observed $^{3}J(^{77}Se-^{77}Se)$ values in a series of substituted tetraselenafulvalenes and used the magnitude of this homonuclear coupling constant to distinguish between *cis* and *trans* isomers[89]. The *cis* orientation resulted in relatively large values of the coupling constant (80–100 Hz) while the *trans* geometry yielded much smaller values (10–25 Hz). Clearly, more extensive studies of this parameter and its relationship to molecular and electronic structure should be rewarding.

B. Organotellurium Compounds

1. Relaxation times

In general, progress in Te-NMR spectroscopy has lagged somewhat behind that in ^{77}Se-NMR spectroscopy. However, in the last 2–3 years publications involving ^{125}Te-NMR studies have increased dramatically, although ^{125}Te relaxation times have not been studied nearly so thoroughly. One reason for this may be that researchers have felt that what has been found for Se will also hold true for Te, but the few preliminary studies which have appeared[15,90–93,114] demonstrate that spin-lattice relaxation times for ^{125}Te are approximately 6–7 times shorter than those of ^{77}Se in analogous compounds (Table 23). It has been shown that the spin rotation mechanism is the dominant mechanism for small Te-containing molecules. It has not yet been demonstrated that the chemical shift anisotropy mechanism may be important in larger organotellurium molecules as has been shown for ^{77}Se.

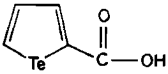
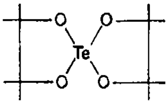
2. Chemical shifts

Like Se, the chemical shift pattern of Te compounds is considered to be dominated by the paramagnetic term of the chemical shift equation. The paramagnetic term for Te is given by the following proportionality:

$$\sigma_{\mathrm{Te}}^{\mathrm{para}} \propto \frac{-\langle r^{-3}\rangle_{5\mathrm{p}}}{\Delta E}\Sigma Q \qquad (10)$$

Expressions (4) and (10) predict that if the ΣQ terms for Se and Te are the same in analogous compounds, a plot of $\delta_{^{125}\mathrm{Te}}$ vs. $\delta_{^{77}\mathrm{Se}}$ should be a straight line with a slope of $\langle r^{-3}\rangle_{5\mathrm{p(Te)}}\cdot\Delta E_{\mathrm{Se}}/\langle r^{-3}\rangle_{4\mathrm{p(Se)}}\cdot\Delta E_{\mathrm{Te}}$. Such a plot has been found to be linear with a slope of 1.7–1.8[57,94]. Whereas a part of this can be attributed to the ratio of $\langle r^{-3}\rangle_{5\mathrm{p(Te)}}/\langle r^{-3}\rangle_{4\mathrm{p(Se)}} \simeq 1.25$[94], there is still an unexplained factor which must come from the difference in the ΔE values. It is difficult to obtain a reasonable estimate of ΔE for Se and Te; however, changes in these ΔE values should roughly parallel those found

TABLE 23. ^{125}Te spin-lattice relaxation times, T_1

Compound	T_1 (s)	Temp. (°C)	Conditions	Ref.
Me_2Te	0.58	26	90%, C_6D_6	92
Et_2Te	1.1	30	2M, $CDCl_3$	91
	~3	*a*	$(CD_3)_2CO$	114
$Te(OCHMe_2)_4$	2.23	*a*	*a*	15
$Te(OCH_2CF_3)_4$	1.57	*a*	*a*	15
	2.99	*a*	*a*	15
p-Tol_2Te_2	1.4	26	$CDCl_3$	93
$(p$-$EtOC_6H_4)_2Te_2$	1.7	26	$CDCl_3$	93
Te	0.04	26	Oleum	92
$TeCl_4$	0.8	26	12N, HCl	92
K_2TeO_3	2.5[b]	27	4N, D_2O	90
Na_2TeO_4	1.95	26	10%, HNO_3	92

[a] Not specified.
[b] $T_2 = 0.31$ s.

for absorption maxima, $\lambda_{\max}$, in the UV–visible spectrum. Therefore, it seems reasonable to take $\Delta E_{Te}/\Delta E_{Se} \simeq \lambda_{Te}/\lambda_{Se}$. The value of the latter ratio has been found to be ~1.25[94]. A calculated value of the slope of the plot of $\delta_{^{125}Te}$ vs. $\delta_{^{77}Se}$ is 1.5–1.6; hence the agreement is reasonable in view of the approximations involved in the preceding treatment. In general, trends in ^{125}Te shielding are very similar to those found for analogous Se compounds and thus, a separate detailed discussion for each class of compounds, as for Se compounds, is scarcely warranted.

Dimethyl telluride appears to be the reference of choice for reported ^{125}Te chemical shifts although 4,4′-dimethyldiphenyl ditelluride[36,95–97] and bis[diethyldithiocarbamato]tellurium(II)[98,99] have also been used. To standardize ^{125}Te chemical shift values in this chapter, they are reported with respect to the literature value of Me_2Te (neat). This creates some discrepancies between our values and some values found in the literature[57,105] since there is a definite concentration effect on the chemical shift of Me_2Te in solution (e.g. 20 ppm difference between neat Me_2Te and dilute solutions of Me_2Te in $CDCl_3$[102]). As was pointed out previously for Me_2Se, the chemical shift value of the Te reference standard, Me_2Te, is also solvent-dependent. The magnitude of the solvent shift of Me_2Te is approximately twice that of the Se standard[100]. These solvent shifts are provided in Table 24.

^{125}Te chemical shifts have also been found to be concentration-dependent. For example, a 2M solution of Me_2Te_2 in benzene gave $\delta_{^{125}Te} = 303$ ppm and on dilution changed monotonically to 293 ppm at a concentration of 0.02M[94]. It has been found that $\lambda_{\max}$ for Me_2Te_2 decreases from 410 to 385 nm on dilution in hexane and other solvents, and other tellurides behave similarly[94]. Interestingly, the value of $\lambda_{\max}$ for Me_2Se_2 was unaffected by dilution.

a. Tellurides. ^{125}Te chemical shifts of dialkyl, alkyl aryl and diaryl tellurides are given in

TABLE 24. ^{125}Te solvent shifts of Me_2Te[a]

Solvent	Chemical shift (ppm)	Solvent	Chemical shift (ppm)
Et_3N	5.9	Me_2CO	−12.7
CCl_4	0.9	CH_2Cl_2	−14.9
Et_2O	−0.2	Me_2NCHO	−18.6
C_6H_6	−3.1	$CHCl_3$	−18.8
$PhNO_2$	−7.1	$MeNO_2$	−20.6
C_5H_5N	−9.4	Me_2SO	−26.4
MeOH	−10.4		

[a] Relative to neat Me_2Te; solutions are 5 mole%; Ref. 100.

TABLE 25. ^{125}Te chemical shifts of dialkyl tellurides[a]

Compound	Chemical shift (ppm)	Solvent	Ref.
$(Me_3Sn)_2Te$	−1214	CH_2Cl_2	101
$(Me_3Si)_2Te$	−43	$CDCl_3$	97
MeTePen-*neo*	5	$CDCl_3$	57
(*neo*-Pen)$_2$Te	25	$CDCl_3$	57
MeTeBu-*i*	44	$CDCl_3$	57
neo-PenTeBu-*i*	92	$CDCl_3$	57
MeTePr-*n*	95	$CDCl_3$	57
MeTeBu-*n*	103	$CDCl_3$	57
(*i*-Bu)$_2$Te	113	$CDCl_3$	57
neo-PenTePr-*n*	120	$CDCl_3$	57
neo-PenTeBu-*n*	128	$CDCl_3$	57
n-PrTeBu-*i*	163	$CDCl_3$	57
MeTeEt	165	$CDCl_3$	57
n-BuTeBu-*i*	171	$CDCl_3$	57
EtTePen-*neo*	191	$CDCl_3$	57
n-Pr$_2$Te	213	$CDCl_3$	57
$(Me_3Si(CH_2)_3)_2Te$[b]	221	Not specified	98
n-PrTeBu-*n*	222	$CDCl_3$	57
n-Bu$_2$Te	228	$CDCl_3$	57
n-Pen$_2$Te	230	$CDCl_3$	57
$(C_{16}H_{33})_2Te$[b]	232	$CDCl_3$	102
EtTeBu-*i*	234	$CDCl_3$	57
$(Me_2CHCH_2CH_2)_2Te$	241	$CDCl_3$	57
MeTeBu-*s*	246	$CDCl_3$	57
$(PhCH_2CH_2)_2Te$	277	CH_2Cl_2	99
EtTePr-*n*	285	$CDCl_3$	57
s-BuTePen-*neo*	287	$CDCl_3$	57
EtTeBu-*n*	292	$CDCl_3$	57
MeTePr-*i*	322	$CDCl_3$	57
i-BuTeBu-*s*	332	$CDCl_3$	57
i-PrTePen-*neo*	351	$CDCl_3$	57
EtTeEt	356;380;392	$CDCl_3$;C_6H_6;$CDCl_3$	57;94;91
n-PrTeBu-*s*	381	$CDCl_3$	57
n-BuTeBu-*s*	388	$CDCl_3$	57
i-PrTeBu-*i*	394	$CDCl_3$	57
n-PrTePr-*i*	445	$CDCl_3$	57

(Contd.)

TABLE 25. (*Contd.*)

Compound	Chemical shift (ppm)	Solvent	Ref.
EtTeBu-*s*	449	$CDCl_3$	57
i-PrTeBu-*n*	451	$CDCl_3$	57
MeTeBu-*t*	479	$CDCl_3$	57
t-BuTePen-*neo*	504	$CDCl_3$	57
EtTePr-*i*	512	$CDCl_3$	57
i-BuTeBu-*t*	554	$CDCl_3$	57
$(s\text{-Bu})_2Te$	558	$CDCl_3$	57
$(s\text{-Pen})_2Te$	564	$CDCl_3$	57
n-PrTeBu-*t*	602	$CDCl_3$	57
n-BuTeBu-*t*	608	$CDCl_3$	57
i-PrTeBu-*s*	618	$CDCl_3$	57
EtTeBu-*t*	670	$CDCl_3$	57
$(i\text{-Pr})_2Te$	676; 707	$CDCl_3$; CH_2Cl_2	57; 94
s-BuTeBu-*t*	786	$CDCl_3$	57
i-PrTeBu-*t*	846	$CDCl_3$	57
$(t\text{-Bu})_2Te$	979	$CDCl_3$	57
$(CF_3)_2Te$	1368	CH_3CN	41
CF_3TeCF_2Cl	1566	CH_3CN	41

[a] Chemical shifts reported relative to neat Me_2Te.

[b] Chemical shifts reported relative to bis(diethyldithiocarbamato)tellurium(II); converted relative to neat Me_2Te using the expression $\delta[Me_2Te] = \delta[\text{bis(diethyldithiocarbamato)tellurium(II)}] - 833.6$.

Tables 25, 26 and 27, respectively. The effect of replacing α-hydrogens by alkyl groups on the ^{125}Te chemical shifts parallels that observed in the ^{77}Se chemical shifts for analogous Se compounds. A deshielding of Te is observed when hydrogens in Me_2Te are replaced by Me groups as shown, for example, in the following series: (1) MeTeMe (0 ppm), MeTeEt (165 ppm), MeTePr-*i* (322 ppm), MeTeBu-*t* (477 ppm); (2) EtTeMe (165 ppm), EtTeEt (356 ppm), EtSePr-*i* (512 ppm), EtTeBu-*t* (670 ppm); (3) *i*-PrTePr-*i* (676), *i*-PrTeBu-*t* (846) and (4) *t*-BuTeBu-*t* (979 ppm). The chemical shift values of all possible Me derivatives of Me_2Te are considered above and in each case the deshielding introduced per replacement of a H atom by a Me group is approximately 165 ppm. Furthermore, the shielding caused by the introduction of a γ-carbon in tellurides can be clearly seen in the ^{125}Te chemical shifts if the following compounds are compared, i.e. MeTeEt (156 ppm), MeTePr (95), MeTeBu-*i* (44 ppm), MeTePen-*neo* (5 ppm). Thus, the replacement of one hydrogen atom on the β-carbon of the Et group in MeTeEt by a Me group introduces a shielding of 70 ppm. Further replacement introduces additional shielding although the magnitude of the shielding decreases. A small deshielding is observed if alkyl substitution takes place at the γ-carbon and alkyl substitution more remote to Te than the γ-carbon has little or no effect on the ^{125}Te chemical shifts, e.g. (1) MeTePr (95 ppm), MeTeBu (103 ppm); (2) Bu_2Te (228 ppm), $(C_{16}H_{33})_2Te$ (232 ppm).

The effect of alkyl substitution on the ^{125}Te chemical shifts for methyl phenyl telluride is consistent with that observed with Me_2Te. Thus, for alkyl phenyl tellurides, the most shielded Te resonance is found in methyl phenyl telluride and the most deshielded resonance is observed for *t*-butyl phenyl telluride. ^{125}Te chemical shifts for *ortho*-, *meta*- and *para*-substituted telluroanisoles are provided in Table 26. There have not been enough substituents studied to meaningfully evaluate the data.

b. Ditellurides. ^{125}Te chemical shifts of dialkyl, alkyl aryl and diaryl ditellurides are

TABLE 26. ^{125}Te chemical shifts of alkyl aryl tellurides[a]

Compound	Chemical shift (ppm)	Solvent	Ref.
PhTeMe	329; 330	$CDCl_3$; $CHCl_3$	57; 100
2-AnTeMe	205	$CDCl_3$	102
2-TolTeMe	221	$CDCl_3$	102
3-TolTeMe	324	$CDCl_3$	102
3-AnTeMe	341	$CDCl_3$	102
3-FC_6H_4TeMe	355	$CDCl_3$	102
4-$EtOC_6H_4$TeMe	317	$CDCl_3$	102
4-AnTeMe	318; 321	$CDCl_3$; CCl_4	102; 100
4-TolTeMe	318; 329	$CDCl_3$; CCl_4	102; 100
4-$PhOC_6H_4$TeMe	326	$CDCl_3$	102
4-FC_6H_4TeMe	336	$CDCl_3$	102
4-ClC_6H_4TeMe	338	$CDCl_3$	102
PhTeBu-*i*	409	$CDCl_3$	57
PhTePr-*n*	460	$CDCl_3$	57
PhTeBu-*n*	468	$CDCl_3$	57
2-$OHCC_6H_4$TeBu-*n*	517	$CDCl_3$	104
PhTeEt	532; 549	$CDCl_3$; CCl_4	102; 100
PhTeBu-*s*	640	$CDCl_3$	102
PhTePr-*i*	702; 719	$CDCl_3$; CCl_4	102; 100

[a] Relative to neat Me_2Te.

TABLE 27. ^{125}Te chemical shifts of diaryl tellurides[a]

Compound	Chemical shift (ppm)	Solvent	Ref.
Ph_2Te	688; 688	CH_2Cl_2; $CDCl_3$	94; 102
2-An_2Te	445	$CDCl_3$	102
2-AnTePh	579	$CDCl_3$	102
4-Tol_2Te	660; 663	$CDCl_3$; CH_2Cl_2	102; 103
4-AnTePh	664; 668	$CDCl_3$; CH_2Cl_2	102; 104
4-BrC_6H_4TePh	699	CH_2Cl_2	104
$(2,4,6\text{-}Me_3C_6H_2)_2Te$	612	$CDCl_3$	91
$(2\text{-Naph})_2Te$	692	$CDCl_3$	102

[a] Relative to neat Me_2Te.

given in Tables 28, 29 and 30, respectively. ^{125}Te magnetic shielding of dialkyl ditellurides closely parallels that of Se in analogous diselenides, but the sensitivity to changes in alkyl groups is even greater. For example, compare Me_2Te_2 (49 ppm), Et_2Te_2 (166 ppm), *i*-Pr_2Te_2 (293 ppm) and *t*-Bu_2Te_2 (477 ppm). The deshielding effect per replacement of a H atom by a Me group is approximately 120 ppm compared to 65 ppm in the ^{77}Se chemical shifts of analogous Se compounds. As previously discussed in the ^{77}Se-NMR section using Et_2Se_2 as an example, the influence of each Me group is two-fold, (1) to induce deshielding of the proximate Se by the dispersion (or polarizability) effect and (2) to cause shielding of the distant Se by the γ-effect. The same effects are found for Te shielding in dialkyl ditellurides. It can be seen further if the shifts of the following ditellurides are compared: MeTeTeMe (49 ppm), MeTe*TeEt (-48 ppm(*), 264 ppm), MeTe*TePr-*i* (-94 ppm(*), 435 ppm), MeTe*TeBu-*t* (-68 ppm(*), 597 ppm). In these compounds the Te bonded to

TABLE 28. ^{125}Te chemical shifts of dialkyl ditellurides[a]

Compound	Chemical shift (ppm)	Compound	Chemical shift (ppm)
MeTe*TeBu-_s_	−108(*), 130	_n_-BuTe*TeBu-_t_	71(*), 522
MeTe*TePr-_i_	−94(*), 435	(_i_-BuTe)$_2$	79
_s_-BuTeTe*Pen-_neo_	−79(*), 353	EtTeTe*Pr-_n_	88(*), 182
MeTe*TeBu-_t_	−68(*), 597	EtTeTe*Bu-_n_	97(*), 183
_i_-PrTeTe*Pen-_neo_	−65(*), 415	(_n_-PrTe)$_2$	105
MeTe*TeEt	−48(*), 264	EtTe*TeBu-_s_	105(*), 276
_t_-BuTeTe*Pen-_neo_	−45(*), 577	_n_-PrTe*TeBu-_n_	195(*), 112
MeTe*TePr-_n_	−31(*), 185	(_n_-BuTe)$_2$	113
MeTe*TeBu-_n_	−31(*), 193	$(C_{10}H_{21}Te)_2$	113
EtTeTe*Pen-_neo_	−25(*), 249	$(C_9H_{19}Te)_2$	114
_i_-BuTe*TeBu-_s_	−19(*), 315	$(C_{18}H_{37}Te)_2$	114
_n_-PrTeTe*Pen-_neo_	−9(*), 172	$(C_5H_{11}Te)_2$	115
_n_-BuTeTe*Pen-_neo_	−8(*), 181	$(C_6H_{13}Te)_2$	117
_i_-PrTeTe*Bu-_i_	−6(*), 378	$(C_{11}H_{23}Te)_2$	117
MeTeTe*Bu-_i_	−4(*), 130	EtTe*TePr-_i_	118(*), 337
_i_-BuTe*TeBu-_t_	16(*), 545	$(C_8H_{17}Te)_2$	118
_i_-BuTeTe*Pen-_neo_	17(*), 122	$(Me_2CHCH_2CH_2Te)_2$	120
_n_-PrTe*TeBu-_s_	30(*), 291	$(C_7H_{15}Te)_2$	120
EtTeTe*Bu-_i_	37(*), 208	EtTe*TeBu-_t_	135(*), 503
_n_-BuTe*TeBu-_s_	37(*), 292	(EtTe)$_2$	166; 188[b]
MeTe*TePen-_neo_	42(*), 72	(_t_-BuTe)$_2$	223
_n_-PrTe*TePr-_i_	44(*), 354	_i_-PrTeTe*Bu-_s_	236(*), 281
(MeTe)$_2$	49; 63[b]	_s_-BuTe*TeBu-_t_	249(*), 460
_i_-PrTeTe*Bu-_n_	51(*), 355	(_i_-PrTe)$_2$	293; 303[b]
_n_-PrTeTe*Bu-_i_	53(*), 131	_i_-PrTe*TeBu-_t_	305(*), 470
_i_-BuTe*TeBu-_n_	53(*), 138	(_s_-BuTe)$_2$	477
(_neo_-PenTe)$_2$	60	$(HOOCCH_2Te)_2$	538[c]
_n_-PrTe*TeBu-_t_	63(*), 520	$(CF_3Te)_2$	686[d]

[a] Relative to neat Me_2Te; solvent $CDCl_3$ unless otherwise indicated; Ref. 105.
[b] Solvent CH_2Cl_2; Ref. 94.
[c] Solvent Me_2SO; Ref. 103.
[d] Solvent C_6D_6; Ref. 41.

the Me group is shielded by successive methylation of the distant Me group, whereas the shielding of the remote Te decreases progressively. The Te atom remote to the Me group does not have any γ-atom and thus experiences only the deshielding caused by the dispersion effect of the alkyl group in going from $Me_2Te_2 \rightarrow \rightarrow \rightarrow$ MeTeTeBu-_t_. On the other hand, the Me-bonded Te experiences a net shielding from the two opposing effects (shielding from the γ-effect and deshielding from the dispersion effect). The magnitude of the net shielding decreases with additional alkylation (actually, a deshielding is observed in going from MeTeTePr-_i_ → MeTeTeBu-_t_).

Unlike diselenides, dialkyl[105] and diaryl[93] ditellurides apparently undergo exchange reactions between two symmetrical ditellurides. The exchange is slow on the ^{125}Te-NMR time-scale and, consequently, four ^{125}Te resonances were observed in the spectra of solutions initially containing two symmetrical ditellurides, one resonance corresponding to the Te in each symmetric ditelluride and two resonances representing the non-equivalent Te atoms of the unsymmetric ditelluride. Thus, O'Brien and coworkers[105] were able to report the ^{125}Te chemical shifts of 36 unsymmetrical dialkyl ditellurides by initially preparing nine symmetrical dialkyl ditellurides. Such an exchange is also shown

TABLE 29. ^{125}Te chemical shifts of alkyl aryl ditellurides[a]

Compound	Chemical shift (ppm)	Ref.
MeTe*TePh	95(*), 384	105
i-BuTe*TePh	170(*), 331	105
n-PrTe*TePh	223(*), 305	102
n-BuTe*TePh	226(*), 304	102
EtTe*TePh	295(*), 289	102

[a] Relative to neat Me_2Te, solvent $CDCl_3$.

TABLE 30. ^{125}Te chemical shift of diaryl ditellurides, $XC_6H_4TeTeC_6H_4X'$[a]

X = X'	Chemical shift (ppm)	Solvent	Ref.
H	420; 421	$CDCl_3$; $CDCl_3$	102; 93
2-OMe	168	$CDCl_3$	106
2-F	255	$CDCl_3$	102
2-Cl	312	$CDCl_3$	102
2-SPh	325	$CDCl_3$	102
2-COOEt	411; 414	$CDCl_3$; $CDCl_3$	102; 106
2-CHO	423	$CDCl_3$	106
2-Ac	473	$CDCl_3$	102
2-Me	495	$CDCl_3$	102
3-Me	416	$CDCl_3$	102
3-F	444	$CDCl_3$	102
3-OMe	435	$CDCl_3$	102
4-Me	427; 432.2; 433	$CDCl_3$; $CDCl_3$; $CDCl_3$	102; 93; 106
4-SPh	434	$CDCl_3$	102
4-Br	442	$CDCl_3$	102
4-Cl	447; 452	$CDCl_3$; $CDCl_3$	102; 93
4-OPh	449	$CDCl_3$	102
4-OEt	455; 456	$CDCl_3$; $CDCl_3$	102; 93
4-F	457; 458	$CDCl_3$; $CDCl_3$	102; 106
4-Me_2N	466	$CDCl_3$	102

X	X'	Chemical shift (ppm)	Solvent	Ref.
4-Me*	4-Cl	433.9(*); 456.3	$CDCl_3$	93
4-Me*	4-OEt	436.8(*); 446.9	$CDCl_3$	93
4-Cl*	4-OEt	444.3(*); 475.2	$CDCl_3$	93

Compound	Chemical shift (ppm)	Solvent	Ref.
$(2\text{-Thiophenyl})_2Te_2$	264	$CDCl_3$	93
$(1\text{-Naph})_2Te_2$	336	$CDCl_3$	102
$(2\text{-Naph})_2Te_2$	438	$CDCl_3$	102

[a] Relative to neat Me_2Te.

to occur in diaryl ditellurides and between dialkyl and diaryl ditellurides. Granger and coworkers[93] have shown that the exchange is a thermal process. The substituent effect on the ^{125}Te chemical shifts of *para*-substituted diaryl ditellurides has been shown to be consistent with that observed on the ^{77}Se chemical shifts for *para*-substituted diaryl diselenides. Thus electron-donating groups (in a mesomeric sense) deshield the Te resonance in diaryl ditellurides. However, mesomeric withdrawing groups have not been studied in sufficient number to enable a good comparison.

Finally, it should be noted that ^{125}Te chemical shifts of diaryl ditellurides have been found to be concentration-dependent[93], more so than the ^{77}Se chemical shifts for analogous diaryl diselenides. Also, the assignment[93] of the Te resonances for unsymmetrical diaryl ditellurides is not consistent with the reported values of ^{77}Se resonances for the analogous unsymmetrical diaryl diselenides[60]. Thus, saturation transfer or labelling experiments should be performed to assign the Te resonances unequivocally in these unsymmetrical ditellurides.

c. Tellurium halides. ^{125}Te chemical shifts of alkyl and aryl tellurium halides (mono-, di- and tri-) are reported in Tables 31, 32 and 33. From the chemical shift data it is apparent that introduction of halogens bonded to Te causes a deshielding of the Te nucleus. For example, a deshielding of 293 ppm is observed in going from Ph_2Te (688 ppm) to Ph_2TeCl_2 (981 ppm) and deshielding of 749 ppm is seen in going from Me_2Te to Me_2TeCl_2. Thus, Cl has a relatively greater effect on the shielding of Te in the alkyl derivative than the aryl derivative. Large solvent shifts of the order of 400 ppm have been reported in this class of compounds. The observed chemical shift values of $PhTeCl_3$ and $PhTeBr_3$ in a benzene/toluene mixture are 900 and 892 ppm, respectively[107], whereas in CH_2Cl_2 : Me_2SO (1 : 1) the corresponding values are 1229 and 1193 ppm, respectively[104]. Similarly, the effect of solvent on the shielding of Te is also observed in dihalides, e.g. chemical shifts of Me_2TeCl_2 and Me_2TeBr_2 in CH_2Cl_2 are 749 and 669 ppm[94], respectively, and in toluene these are 1218 and 858 ppm[107], respectively. Although there is

TABLE 31. ^{125}Te chemical shifts of aryl- and alkyl-tellurium trihalides[a]

Compound	Chemical shift (ppm)	Solvent	Ref.
$MeTeBr_3$	647	$C_6H_6/PhCH_3$	107
$MeTeCl_3$	758	$C_6H_6/PhCH_3$	107
$EtTeBr_3$	849	$C_6H_6/PhCH_3$	107
$(Cl_3TeCH_2CO)_2O$	864	Me_2SO	103
$PhTeBr_3$	892; 1193	$C_6H_6/PhCH_3$; $CH_2Cl_2 : Me_2SO(2:1)$	107; 104
$EtTeCl_3$	900	$C_6H_6/PhCH_3$	107
$PhTeCl_3$	917; 1229	$C_6H_6/PhCH_3$; $CH_2Cl_2 : Me_2SO(2:1)$	107; 104
$PhTeI_3$	1101	$CH_2Cl_2 : Me_2SO(2:1)$	104
4-$AnTeI_3$	1078	$CH_2Cl_2 : Me_2SO(1:1)$	104
4-$AnTeBr_3$	1204	$CH_2Cl_2 : Me_2SO(2:1)$	104
$(Cl_3Te)_2CH_2$	1198	Me_2SO	103
4-$BrC_6H_4TeCl_3$	1208	$CH_2Cl_2 : Me_2SO(1:1)$	104
4-$ClC_6H_4TeCl_3$	1208	$CH_2Cl_2 : Me_2SO(1:1)$	104
4-$PhOC_6H_4TeCl_3$	1226	$CH_2Cl_2 : Me_2SO(1:1)$	104
4-$TolTeCl_3$	1234	$CDCl_3 : Me_2SO(1:1)$	104
4-$AnTeCl_3$	1246	Me_2SO	104

[a] Relative to neat Me_2Te.

TABLE 32. ^{125}Te chemical shifts of diorganyl tellurium dihalides, R_2TeX_2[a]

Compound	Chemical shift (ppm)	Solvent	Ref.
Me_2TeBr_2	669;858	CH_2Cl_2;$PhCH_3$	94;107
$PhTeMeI_2$	698	CH_2Cl_2	103
4-$TolTeMeI_2$	663	CH_2Cl_2	103
4-$AnTeMeI_2$	664	CH_2Cl_2	103
4-$EtOC_6H_4TeMeI_2$	670	CH_2Cl_2	103
Me_2TeCl_2	749;1218	CH_2Cl_2;$PhCH_3$	94;107
Et_2TeBr_2	879;1153	CH_2Cl_2;$PhCH_3$	94;107
Ph_2TeCl_2	981;917	CH_2Cl_2;$PhCH_3$	103
4-$TolTe(Ph)Cl_2$	1070.6	CH_2Cl_2	104
4-$BrC_6H_4Te(Ph)Cl_2$	1079.6	CH_2Cl_2	104
i-Pr_2TeBr_2	1105	CH_2Cl_2	94
$(CF_3)_2TeCl_2$	1114	MeCN	41
$(CF_3)_2TeBr_2$	1180	MeCN	41
$(CF_3)_2TeF_2$	1187	MeCN	41
Ph_2TeBr_2	1481;1508;890	THF;$CDCl_3$; $PhCH_3$	91;102;107
4-Tol_2TeBr_2	905	$CDCl_3$	102

[a] Relative to neat Me_2Te.

TABLE 33. ^{125}Te chemical shifts of triorganyl tellurium halides, R_3TeX[a]

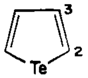
Compound	Chemical Shifts (ppm)	Solvent	Ref.
Me_3TeI	443	Me_2SO-d_6	94
$Et_2TeMeBr$	470	D_2O	94
$PhTeMe_2I$	550	Me_2SO	103
4-$EtC_6H_4TeMe_2I$	542	Me_2SO	103
4-$AnTeMe_2I$	550	Me_2SO	103
Et_3TeBr	573	D_2O	94
Ph_2TeMeI	595	Me_2SO	103
2-Tol_2TeMeI	580	Me_2SO	103
$(Et_3Te^*)_2(TeCl_4Br_2)$	598.4(*), 1365.4	CH_2Cl_2 : Me_2SO(1:2)	104
$(Et_3Te^*)_2(TeBr_6)$	603.5(*), 1347.7	CH_2Cl_2 : Me_2SO(1:2)	104
i-Pr_2TeMeI	630	D_2O	94

[a] Relative to neat Me_2Te.

no explanation provided for this very substantial solvent effect observed for the ^{125}Te chemical shift of these halides, we find it hard to rationalize the ^{125}Te shifts of this class of compounds based on simple inductive and solvent effects.

From the results of many cryoscopic studies[108] it has been suggested that $MeTeCl_3$ exists as a mixture of monomers and dimers in benzene and that $MeTeBr_3$ is more associated than $MeTeCl_3$. Thus, equilibria involving higher aggregates are more important for $MeTeBr_3$. Perhaps due to the different degree of oligomerization in various solvents, the state of aggregation may play an important role in determining the shielding of Te in these compounds. Even the ^{1}H-NMR spectrum of $MeTeCl_3$ exhibited a pronounced solvent dependence[108]. A peak was found at 2.83 ppm in benzene, while this resonance occurred at 3.70 ppm in CH_2Cl_2. Clearly large solvent effects will make it rather difficult to interpret the shielding behaviour of Te in the organic tellurium halides. A consideration of shifts in the same solvent should enable a more valid comparison of various effects on ^{125}Te chemical shifts. The four diiodides, $XC_6H_4TeMeI_2$, have chemical shifts in the region 663–698 ppm (Table 32). The shielding of Te in the two diarylmethyl tellurium iodides (Table 33) increases (580 and 595 ppm), indicating that the Te nucleus becomes more shielded when I is replaced by an aryl group. The replacement of aryl by Me causes further shielding. The chemical shifts of the three aryl dimethyltellurium iodides are

TABLE 34. ^{125}Te chemical shifts of substituted tellurophenes[a]



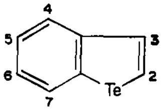
Compound	Chemical shift (ppm)
2-CH_2OH	764
2-H	782; 782[b]
2-CHO	789
2-Ac	· 813
2-COOEt	820
2-COOH	848; 861[c]
2-Cl	905
2-Br	949

[a] Tellurophene in $(CD_3)_2CO$ was used as a reference; chemical shift values have been converted relative to neat Me_2Te using the expression $\delta(Me_2Te) = \delta(\text{tellurophene}) - 782$; solvent $(CD_3)_2CO$; Ref. 109.

[b] Relative to neat Me_2Te; solvent $(CD_3)_2CO$; Ref. 100.

[c] Ref. 102.

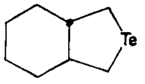
TABLE 35. ^{125}Te chemical shifts of substituted benzo[*b*]tellurophenes[a]



Compound	Chemical shift (ppm)	Compound	Chemical shift (ppm)
2-CH_2OH	721	2-SMe	839
2-H	727	2-Cl	868
2-CHO	727	2-Br	911
2-Me	750	2-CN	952
2-Ac	751	3-Me	659
2-COOH	764	3-CH_2COOH	680
2-$CONH_2$	764	3-CH_2OH	683
2-CONHMe	765	3-CH_2CN	709
2-COCl	769	3-Cl	721
2-COOEt	774	3-CHO	750
2-COOMe	775	3-Br	762
2-COPh	786	3-CN	787
2-$CONMe_2$	830		

[a] Relative to neat Me_2Te; Ref. 110.

TABLE 36. ^{125}Te chemical shifts of other heterocycles containing tellurium[a]



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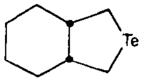

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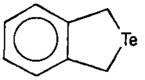

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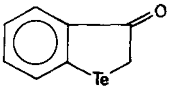

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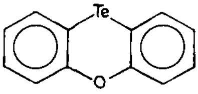

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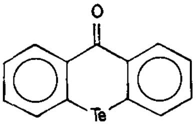

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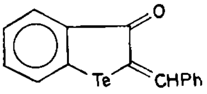

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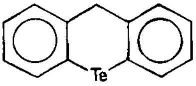

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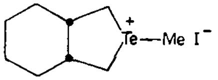

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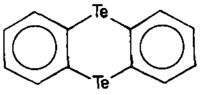

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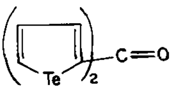

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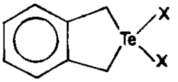


(20)

(a) X = Cl, Cl
(b) X = Br, Cl
(c) X = Br, Br
(d) X = I, I

Compound	Chemical shift (ppm)	Solvent	Ref.
9	175	—	111
10	209	—	111
11	269[c]	$(CD_3)_2NCHO$	98
12	383[b]	$CDCl_3$	95
13	424[b]	$CDCl_3$	95
14	468[b]	$CDCl_3$	95
15	501	$CDCl_3$	95
16	512[b]	$CDCl_3$	95
17	630	—	111
18	888	Not specified	112
19	901[b]	$CDCl_3$	96
20a	994[c]	$(CD_3)_2NCHO$	98
20b	972[c]	$(CD_3)_2NCHO$	98
20c	940[c]	$(CD_3)_2NCHO$	98
20d	831[c]	$(CD_3)_2NCHO$	98

[a] Relative to neat Me_2Te.

[b] $(4\text{-}TolTe)_2$ in $CDCl_3$ was used as a reference; chemical shift values have been converted relative to neat Me_2Te using the expression $\delta(Me_2Te) = \delta(4\text{-}TolTe)_2 - 427$.

[c] Chemical shifts reported relative to bis(diethyldithiocarbamato)tellurium(II); converted relative to neat Me_2Te using the expression $\delta[Me_2Te] = \delta[\text{bis(diethyldithiocarbamato)tellurium(II)}] - 833.6$.

in the region 542–550 ppm whereas the value for trimethyl tellurium iodide is 443 ppm. As expected, a shielding of Te is observed in going from $PhTeCl_3 \rightarrow PhTeBr_3 \rightarrow PhTeI_3$.

d. Heterocyclic tellurium compounds. ^{125}Te chemical shifts of 2-substituted tellurophenes are reported in Table 34. When the substituent-caused shifts of the eight tellurophenes (substituent: 2-Cl, 2-Br, 2-CH_2OH, 2-CHO, 2-Ac, 2-COOH, 2-COOMe, H) were plotted[109] against the ^{77}Se chemical shifts of the same set of selenophene derivatives, a good linear correlation was observed. This should be an indication that the transmission of substituent effects follows the same mechanism in the two analogous heterocyclic systems. Furthermore, the slope of the regression line showed that Te is 2.44 times more sensitive to substituent effects than Se in this type of organic compound[109]. Te chemical shifts for substituted benzo[*b*]tellurophenes[110] and other heterocyclic Te compounds are given in Tables 35 and 36, respectively.

e. Miscellaneous tellurium compounds. The ^{125}Te chemical shifts of miscellaneous compounds are shown in Table 37, whereas Table 38 provides the ^{125}Te chemical shifts of alkenyl and alkynyl tellurides. The presence of two chemically different Te atoms in tellurenyl tellurinyl selenides, RTeSeTe(O)R, was indicated[106] by two widely separated ^{125}Te-NMR resonances (Table 37). One resonance was the same as that observed for the corresponding ditelluride whereas the second was observed approximately 600 ppm further deshielded. The magnitude of the deshielding effect would be expected for a Te—O bond. It is interesting to note that even in these compounds mesomeric donors deshield both Te nuclei, although the magnitude of the deshielding is smaller for the telurinyl Te(Te—O). It has been reported [106] that when a solution containing two aryl tellurenyl

TABLE 37. ^{125}Te chemical shifts of miscellaneous compounds containing tellurium[a]

Compound	Chemical shift (ppm)	Solvent	Ref.
(PhTe*)Se(TeBz)	431(*), 1014	$CDCl_3$	106
(2-AnTe*)Se(2-AnTe(O))	159(*), 931	$CDCl_3$	106
(4-TolTe*)Se(4-TolTe(O))	424(*), 1010	$CDCl_3$	106
(4-AnTe*)Se(4-AnTe(O))	455(*), 1012	$CDCl_3$	106
(4-FC_6H_4Te*)Se(4-FC_6H_4Te(O))	456(*), 1027	$CDCl_3$	106
MeTeSeMe	512	C_6H_6	94
i-PrTeSeMe	816	CH_2Cl_2	94
(4-OctC_6H_4C(O))Te(4-PenC_6H_4)	899.9^{b}	$CDCl_3$	36
(4-AnC(O))Te(4-Tol)	904.7^{b}	$CDCl_3$	36
(2-EtOOCC_6H_4Te)$_2$Se	907	$CDCl_3$	106
BzTe(4-Tol)	929.4^{b}	$CDCl_3$	36
(2-CHOC_6H_4Te)$_2$Se	1120	$CDCl_3$	106
($OCH_2CMe_2CH_2O$)$_2$Te	1355^{c}	Not specified	15
((CF_3)$_2$CHO)$_4$Te	1394^{c}	Not specified	15
(CF_3CH_2O)$_4$Te	1463^{c}	Not specified	15
(EtO)$_4$Te	1503^{c}	Not specified	15
(MeO)$_4$Te	1510^{c}	Not specified	15
(*i*-PrO)$_4$Te	1523^{c}	Not specified	15
(*i*-BuO)$_4$Te	1525^{c}	Not specified	15
($OCMe_2CMe_2O$)$_2$Te	1526	Not specified	15
(OCH_2CH_2O)$_2$Te	1601^{c}	Not specified	15

[a] Relative to neat Me_2Te unless otherwise specified.

[b] $(4\text{-}TolTe)_2$ in $CDCl_3$ was used as a reference; chemical shift values have been converted relative to neat Me_2Te using the expression $\delta[Me_2Te] = \delta[(4\text{-}TolTe)_2] - 427$.

[c] Relative to 2.0M Me_2Te in C_6D_6.

TABLE 38. ^{125}Te chemical shifts of alkenyl and alkynyl[a] tellurides

Compound	Chemical shift (ppm)	Solvent	Ref.
$MeTeC{\equiv}CBu$	159.1	Neat	100
$MeTeC{\equiv}CCH{=}CH_2$	174	Neat	100
$PhTeC{\equiv}CPh$	475	$CDCl_3$	102
4-$TolTeC{\equiv}CH$	483.7	CCl_4	100
4-$FC_6H_4TeC{\equiv}CH$	499.0	CCl_4	100
4-$ClC_6H_4TeC{\equiv}CH$	503.1	CCl_4	100
$(CH_2{=}CH)_2Te$	529.9	CCl_4	100
$PhTeCH{=}CH_2$	615.3	CCl_4	100
4-$AnTeCH{=}CH_2$	596.3	CCl_4	100
4-$BrC_6H_4TeCH{=}CH_2$	621.0	CCl_4	100
4-$TolTeCH{=}CHOCOEt$	743.9	CCl_4	100
4-$TolTeC(Ph){=}CHCHO$	918.0	CCl_4	100

[a]Relative to neat Me_2Te.

aryltellurinyl selenides was examined by ^{125}Te-NMR, a rapid exchange similar to the exchange reported for diaryl ditellurides appeared to occur. It can also be noted that the replacement of a Te in Me_2Te_2 by a Se (i.e. MeTeSeMe) caused a deshielding of Te by 449 ppm[94]. A similar deshielding (425 ppm) was observed[94] in going from MeTeTePr-*i* → MeSeTePr-*i*. A deshielding of similar magnitude was observed[106] in the aryl derivatives, e.g. (o-$CHOC_6H_4Te)_2$ (423 ppm), (o-$CHOC_6H_4Te)_2Se$ (1120 ppm).

To date there have been no published reports dealing with isotope effects in ^{125}Te- or ^{123}Te-NMR spectroscopy.

3. *Coupling constants*

As a general rule, spin–spin coupling constants involving Te are about 2–3 times greater than the same coupling constants involving Se. Although coupling constants of Te to other magnetically active nuclei have not been studied in any great detail, coupling to ^{1}H, ^{13}C, ^{19}F, ^{31}P, ^{77}Se, ^{119}Sn, ^{129}Xe and ^{195}Pt have been reported and these were recently reviewed[113]. Analogously to Se, our primary concern will be Te–C and Te–Te spin–spin coupling, although the fact that the ^{125}Te nucleus couples strongly with ^{1}H allowed McFarlane to obtain Te chemical shifts of organotellurium compounds by heteronuclear double resonance over a decade ago[94,103]. At the same time two- and three-bond ^{125}Te–^{1}H coupling constants were obtained and published[94,103]. These values were generally between 20 and 30 Hz.

More recently, by use of selective population transfer experiments, the sign of ^{2}J(Te–H) and ^{3}J(Te–H) in 2-tellurophenecarboxylic acid were shown[114] to be negative while the one-bond J(Te–C) coupling constant was positive. In this same report[114], a personal communication from Jakobsen was cited in which the J(Te–C) one-bond coupling in the parent tellurophene was also found to be positive. Also, relatively recently, reports of Te–C coupling constants have appeared for various organotellurium compounds although the value for Me_2Te had appeared[115,116] as early as 1967. The mechanism which contributes to Te–C coupling has not been thoroughly studied although in a follow-up study to the sign determinations discussed above, Martin and coworkers[117] determined ^{125}Te–^{13}C coupling constants in 2-substituted tellurophenes. Based on a comparison of Se–C and Te–C coupling constants in analogous compounds, it was postulated[117] that, in addition to the Fermi contact term, orbital and spin-dipolar terms also contributed significantly to these couplings. Interestingly, in perhaps the most complete study to date of ^{13}C parameters of organotellurium compounds, Chadha and Miller[104] assume that Te–C coupling is dominated by the Fermi contact term. In their study, a linear relationship between $\Delta\delta(^{13}C_1)$ and $^1J(Te–C)$ is observed and different straight lines are found for phenyl- and *p*-methoxyphenyl-tellurium compounds. On this basis, and the fact that there is an approximate linear relationship between $^1J(Te–C)$ and ^{125}Te Mossbauer isomer shift values, it was postulated[104] that one-bond Te–C coupling constants depend primarily on the s electron density at the Te nucleus. No correlation between the magnitude of one-bond and two-bond Te–C couplings was evident, leading to the postulate[104] that the two-bond couplings are dependent on complex steric and electronic factors.

With the exception of the determination of Te–Te coupling constants in polyatomic cations[87,118] only one report has appeared describing the determination of this parameter in organotellurium compounds. Granger and coworkers[93] reported $J(^{125}Te–^{125}Te)$ values for two unsymmetrical ditellurides and found that, because of exchange, the magnitude of this coupling may change with solvent and concentration.

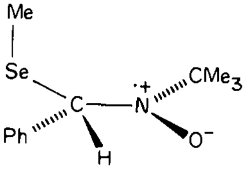
Several Se–Te coupling constants have been reported although most of these are from polyatomic cations[87,118]. Two of these coupling constants are published for organic compounds[106].

III. ESR STUDIES

A. Organoselenium Compounds

In 1964, Shimazu and Tappel[119] first found that Se-amino acids are much better protectors *in vitro* against ionizing radiations than the analogous S-amino acids and this was later confirmed *in vivo* by Breccia and coworkers[120]. To explain these results, it was suggested that Se-containing compounds were able to stabilize free radicals better than the thio analogues. Even though the hypothesis that Se-amino acids are able to stabilize free radicals was advanced some time ago, to date there have been only a few reports concerned with electron spin resonance (ESR) studies of organoselenium radicals and, with the exception of a Se–Te compound, we are not aware of a single study describing the ESR of organotellurium compounds.

No radicals could be detected by ESR spectroscopy when Me_2Se_2 was photolysed in hydrocarbon solvents nor when mixtures of MeSeH and di-*t*-butyl peroxide were photolysed[121]. This is hardly unexpected since alkoxy radicals[122] and alkylthiyl radicals[123,124] in solution are also undetected by the ESR technique[125]. This is due to the fact that these radicals have orbitally degenerate (or nearly degenerate) ground states which lead, by spin-orbit coupling, to a markedly anisotropic *g* factor. As a consequence, these radicals have very short relaxation times and hence extremely broad lines[122–124]. However, a radical that appeared to be MeSe· was trapped when Me_2Se was photolysed in the presence of *t*-butyl phenyl nitrone. The adduct had a well-resolved ESR spectrum[121],



(21)

the parameters for which are $g = 2.0097$, $a^N = 13.5G$, $a^H(1H) = 2.06G$ and $a^H(3H) = 0.85G$ at $-50°C$. On the basis of these parameters structure **21** was assigned to the adduct. No adduct was identified when 2-methyl-2-nitrosopropane or 1,1-di-t-butylethylene were used as spin traps. However, di-t-butyl selenoketone gave a short-lived adduct ($t_{1/2} = 0.5$ s at $-80°C$) having $g = 2.0026$ to which the structure $MeSeSe\dot{C}(t\text{-}Bu)_2$ was assigned. With di-t-butyl thioketone at $-105°C$, a weak signal due to $MeS\dot{C}(t\text{-}Bu)_2$ could be obtained together with an even weaker signal at $g = 2.0056$ which was attributed to $MeSeS\dot{C}(t\text{-}Bu)_2$[121].

The ESR spectrum[126] of a γ-irradiated single crystal of Me_2Se at $-196°C$ consisted of lines from more than one radical. The main spectrum (^{even}Se) showed hyperfine coupling to twelve equivalent protons. The analysis is what would be expected for a radical cation dimer of Me_2Se, i.e. $Me_2SeSeMe_2{}^{+\cdot}$. Dimer radical cations of the congeneric species $Me_2SSMe_2^{+\cdot}$ have been detected by ESR studies during chemical oxidation of Me_2S in aqueous solution[127]. The identification of this radical cation dimer of Me_2Se was completed by the observation of ^{77}Se satellite spectra at several different orientations of the crystal. The relative intensities in the ^{77}Se spectrum were in agreement with a hyperfine interaction involving two anisotropically equivalent Se atoms ($a^H(12H) = 4.9$ G). From the principal values and the direction cosines of the ^{77}Se hyperfine and g tensors, the structure of the dimer radical cation was interpreted as a centrosymmetrical dimer, with the unpaired electron occupying an antibonding (σ^*) orbital formed almost entirely from the p_σ orbitals of the two Se atoms. The results seemed to rule out the possibility of any significant d orbital participation in the bonding[126].

That dimerization of the dimethyl selenide radical cation can be avoided was shown by using a γ-irradiation technique which generated the monomer radical cations by positive charge transfer to the parent molecules dispersed in a Freon matrix[128]. Thus, the ESR spectrum of the dimethyl selenide radical cation, generated in a Freon solution[129], consisted of a seven-line pattern with a binomial intensity distribution with the parameter $a^H(6H) = 15.6$ G. The ^1H coupling constant for the monomer species is about three times greater than that for the dimer species. Assuming that the spin population is shared between the Se orbitals in going from monomer to dimer without any significant change of orbital hybridization, a ratio of 2 would be expected if the ^1H coupling in the Me groups were determined only by the local spin densities in the orbitals of the adjacent Se atom. It was proposed that the admixture of a Me group orbital into the heavy atom orbitals of a dimeric radical species is determined by the character of the molecular orbital (MO) formed between the heavy atoms. If the MO containing the unpaired electron is antibonding, the Me group admixture coefficients into the two heavy atom orbitals will have opposite signs resulting in considerable cancellation and a much lower spin density at the Me hydrogens in the dimer than half the value for the monomeric species. Since the MO which contains the odd electron in $Me_2SeSeMe_2^{+\cdot}$ is antibonding (σ^*) the results are clearly in accord with this proposal[129].

All attempts at the direct observation by ESR spectroscopy of unhindered β-selenoalkyl radicals formed by hydrogen atom abstraction from Me_2Se, Et_2Se, n-BuSeBu-t, MeSePh and Me_2Se_2 were unsuccessful[121]. In contrast to the unhindered β-selenoalkyls, well-resolved ESR spectra of hindered β-selenoalkyl radical species $R_nXSe\dot{C}(t\text{-}Bu)_2$ (where X = C,S,Se) were obtained when transient radicals $R_nX\cdot$ were added to di-t-butyl selenoketone[130,131].

The ESR parameters for a series of $R_nXSe\dot{C}(t\text{-}Bu)_2$ radicals are listed in Table 39. The failure to detect unhindered β-selenoalkyl radicals (which were shown to be produced by spin-trapping experiments) was attributed to the conformation adopted by these radicals. It was proposed that the hindered radicals adopt a conformation in which the unpaired electron interacts only weakly with the Se nucleus because a Se unshared pair of electrons lies in the C_α-$2p_z$ nodal plane. The unhindered radicals presumably adopt a conformation

TABLE 39. ESR parameters for $R_nXSeC_\alpha(t\text{-Bu})_2$ radicals[a]

R_nX	g	$a(^{13}C_\alpha)$(G)	$a(^{77}Se)$(G)	a^X(G)	Temp. range (°C)
Me	2.0021	49.5	23.7	19.00	30 to − 100
t-Bu	2.0019	48.5	21.3	*b*	20 to − 150
F_3C	2.0005	46.5	36.6	*b*	30 to − 130
Cl_3C	2.0020	45.5	46.5	*b*	− 20 to − 70
Ph	2.0030	49.5	18.7	*b*	30 to − 50
C_6F_5	2.0026	*b*	*b*	*b*	− 20 only
Me_3CO	2.0024	38.4	66.3	*b*	0 to − 100
$(Me_2CHCH_2)_2(Me)CO$	2.0024	*b*	64.2	*b*	− 70 only
t-BuS	2.0014	41.1	59.4	*b*	20 to − 80
n-BuS	2.0018	*b*	65.8	*b*	− 110 only
CF_3S	2.0024	*b*	*b*	*b*	− 10 to − 80
$(t\text{-Bu})_2CHSe$	2.0022	*b*	39.22	65.06	− 110 only
MeSe	2.0026	*b*	*b*	*b*	− 120 only

[a] Unless otherwise noted, parameters are reported in *n*-pentane or isopentane at − 50°C and they are essentially invariant over the range of temperatures studied.

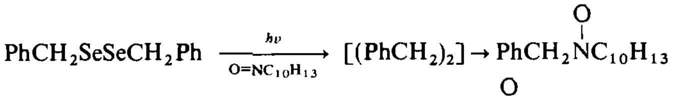
[b] Poorly resolved.

in which the Se lone pair is eclipsed by the C_α-$2p_z$ orbital and the resultant strong interaction with the Se nucleus leads to a line-broadening both by the spin-rotation and the spin-orbit mechanisms.

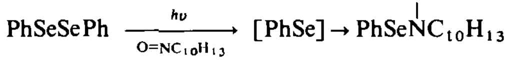
The formation of γ-selenoalkyl radicals presented no major problems provided the intervening β-atom was not carbon[121]. Thus, the $MeSeSe\dot{C}(t\text{-Bu})_2$ and $MeSeS\dot{C}(t\text{-Bu})_2$ radicals could be formed by the addition of the MeSe· radical to the selenoketone and thioketone (for ESR parameters, see Table 39). However, no γ-selenoalkyl radicals having a β-carbon could be detected by ESR spectroscopy[121]. The failure to detect these radicals was attributed to a facile and probably exothermic β-scission reaction, i.e.

$$R_nXSeCH_2\dot{C}H_2 \rightarrow R_nXSe\cdot + CH_2{=}CH_2 \qquad (11)$$

From chemical observation, Chu and coworkers[132] proposed that both Se—Se and Se—C scissions occur in dibenzyl diselenide photolysis. Brown and coworkers[133] had considered that for the same compound the cleavage of the Se—Se bond was more important than that of the Se—C bond, and a similar result had been reported for Et_2Se_2[134]. Franzi and Geoffroy[135] concluded from their results that diphenyl diselenide and dibenzyl diselenide, when subjected to UV irradiation in the presence of the spin-trapping reagent nitrosodurene, probably reacted by different mechanisms.



$$\mathrm{PhCH_2SeSeCH_2Ph} \xrightarrow[\mathrm{O{=}NC_{10}H_{13}}]{h\nu} [(\mathrm{PhCH_2})_2] \rightarrow \mathrm{PhCH_2}\overset{\mathrm{O}}{\overset{|}{\mathrm{N}}}\mathrm{C_{10}H_{13}} \qquad (12)$$



$$\mathrm{PhSeSePh} \xrightarrow[\mathrm{O{=}NC_{10}H_{13}}]{h\nu} [\mathrm{PhSe}] \rightarrow \mathrm{PhSe}\overset{\mathrm{O}}{\overset{|}{\mathrm{N}}}\mathrm{C_{10}H_{13}} \qquad (13)$$

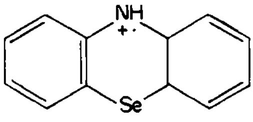
Equation (12) involves C—Se scission and a subsequent formation of $\dot{S}eSeCH_2Ph$, which was not detected by ESR spectroscopy. The spectrum obtained for $PhSeN(O)C_{10}H_{13}$ was characterized by a high g value, which indicated some spin delocalization into the Se atom ($g = 2.0098$, $a(^{14}N) = 18.8$ G, $a(^{77}Se) = 8.7$ G). An ESR spectrum was also observed for o-$NO_2C_6H_4SeN(O)C_{10}H_{13}$ during photolysis of $(o\text{-}NO_2C_6H_4Se)_2$ in the presence of nitrosodurene. The electron-attracting group increased the nitrogen participation in the $NO(\pi)$ orbital and thus decreased the nitrogen contribution in the $NO(\pi^*)$ orbital which contained the unpaired electron. The diminution of the $^{14}N\text{-}2p_z$ spin density involved a smaller spin polarization of the ^{77}Se s electrons, resulting in a smaller value of $a(^{77}Se)$ ($g = 2.0075$), $a(^{14}N) = 16.5$ G, $a(^{77}Se) = 7.8$ G)[135].

It has been shown that irradiation of Ph_3SeX (X = Cl, Br)[136,137] and of R_2SeO_2[138] lead respectively to the formation of $Ph_2\dot{S}eX$ and $R\dot{S}eO_2$. The X-irradiation of a single crystal of Ph_3SeCl produced a radical showing hyperfine interaction with ^{35}Cl and ^{77}Se. Through the principal values of g and the hyperfine coupling tensors, it was proposed that the totality of the spin was shared between the Cl and Se atoms and that, for these two atoms, the unpaired electron was confined in a p orbital. The calculated spin distribution for $Ph_2\dot{S}eCl$ trapped in Ph_3SeCl was $\rho_z(^{35}Cl) = 0.24$, $\rho_x(^{77}Se) = -0.09$ and $\rho_z(^{77}Se) = 0.72$. The X-irradiation of single crystals of Ph_3SeBr leads to the formation of a radical identified as $Ph_2\dot{S}eBr$. Using the magnetic hyperfine interaction or the quadrupolar interaction, the value calculated for $\rho_z(Br)$ was found to be the same (0.27). Thus, when $Ph_2\dot{S}eCl$ trapped in Ph_3SeCl was compared with $Ph_2\dot{S}eBr$ trapped in Ph_3SeBr, it appeared that substitution of Cl by Br led to a slight increase in the spin density of the halogen. This difference was further evident when $Ph_2\dot{S}eCl$ trapped in Ph_3SeCl was compared with $Ph_2\dot{S}eBr$ trapped in Ph_2SeBr_2 [$\rho_z(Br) = 0.47$][137]. This behaviour is in accordance with an antibonding character of the orbital containing the unpaired electron. From the analysis of the data it was concluded that the σ^* orbital was oriented perpendicular to the CSeC plane. The ESR parameters for the $Ph_2\dot{S}eCl$ radical trapped in Ph_2SeBr_2 have also been provided and the spin distribution was again found to be very sensitive to the nature of the host matrix[137].

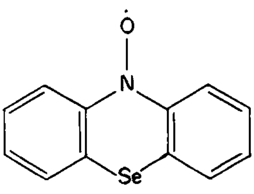
The first ESR study of an organic seleninyl radical trapped in a single-crystal matrix was reported by Franzi and coworkers[139], when they produced the radical $Ph\dot{S}eO$ by irradiating diphenyl selenoxide, Ph_2SeO. From the analysis of the hyperfine interaction with ^{77}Se it was concluded that the unpaired electron was mainly localized (~ 80%) in a Se $4p_x$ orbital. The reported ESR parameters are very similar to those obtained for $Ph_2\dot{A}s$ and from that it was estimated that the p_x orbital was probably perpendicular to the CSeO plane. The spin density on the Se atom in the phenylseleninyl radical, $Ph\dot{S}eO$, was calculated to be twice as much as that reported in the phenylselenenoyl radical, $Ph\dot{S}eO_2$[139].

Radical anions of 2,2,4,4-tetramethyl-3-pentaneselone, $t\text{-}Bu_2C{=}Se$, and 1,1,3,3-tetramethyl-2-indaneselone were produced by one-electron electroreduction and were studied by ESR spectroscopy[140]. From the values of the ^{13}C hyperfine coupling constants, it was concluded that the spin density was located at the central carbon atom. The ESR parameters were similar to those obtained for the corresponding thioketyl radical anions. For the thioketyl molecules a temperature dependence of the ^{13}C hyperfine coupling constants was observed which indicated the presence of a planar geometry for these radical anions.

The ESR spectra of cation radicals (**22**) and nitroxide radicals (**23**) derived from phenoselenazine have been reported[141]. Hyperfine splittings from ^{77}Se have been observed and these are employed in the evaluation of the unpaired electron density



(**22**)



(**23**)

distributions. For the cation radical it has been concluded that spin-rotation relaxation caused an appreciable contribution to the line-width of the ESR spectrum in solution at room temperature. The ESR spectra of several Se-containing anion radicals from 2,1,3-benzoselanediazole and the corresponding perfluorocompound have been reported. No ^{77}Se satellite lines have been reported for these compounds.

The radical cations generated from the peri-bridged naphthalenes $C_{10}H_6XY$, where XY = SS, SSe, STe, SeSe, SeTe are found to be stable at room temperature except when XY = TeTe for which no ESR signal could be detected even at 200 K[142]. The ESR spectra of other compounds showed line-widths increasing in the sequence S < Se < Te. From the 17 lines observed for the disulphide radical cation, only a quintet remained in the selenothiol derivative. It was still recognizable in the ESR spectrum of $C_{10}H_6SeSe^{+\cdot}$ but could no longer be detected for $C_{10}H_6SeTe^{+\cdot}$ (only one broad line was observed). The g values of the radical cations generated increased from 2.0086 (XY = SS) to 2.0409 (SY = SeTe).

The formation and stabilization of free radicals in X-irradiated S- and Se-amino acids have been investigated by ESR spectroscopy[143]. It was difficult to identify radical species from powder spectra; therefore, speculative interpretations have been made based on studies on the related compounds. Se-Cystine and Se-methionine at 295 K showed very similar ESR spectra, whereas Se-ethionine exhibited a very different one. The spectra of Se-cystine and Se-methionine were poorly resolved whereas Se-ethionine showed a well-resolved spectrum. It was speculated that the main radicals in Se-cystine and Se-methionine were $RSeSe\dot{C}HR'$ and $MeSe\dot{C}HR''$. For Se-cystine the spectrum at 100 K showed a signal in the low-field region and was attributed to the $RS\dot{e}$ radical. On warming the low-field signal disappeared very quickly and the spectrum changed to that observed at 295 K.

Finally, with regard to ESR studies of organoselenium compounds, brief mention should be made of studies of biological systems which normally contain S but which have had Se substituted for labile S. ESR studies of such seleno biomolecules include ^{77}Se- and ^{80}Se-replaced putidaredoxin and adrenodoxin[144–146], Se-containing parsley ferredoxin[147] and *N,N*-dimethylselenocysteamine iron(III) complexes of bleomycin and hemoglobin[148].

B. Organotellurium Compounds

To our knowledge, there have been no published reports concerning ESR studies of organotellurium compounds.

IV. ACKNOWLEDGEMENTS

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The Chemistry of Organic
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CHAPTER 7

Mass spectrometry of organic selenium and tellurium compounds

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I. INTRODUCTION

The number of scientific papers concerning the mass spectra of organic Se and Te compounds has grown in parallel with the increasing interest in such compounds in the last decade. Among the reasons for the growing interest are the use of Se and Te and related species in chemical synthesis[1], the potential of these compounds for antitumour and antileptospire activity[2], the development of molecules in the organic conductor class[3], and the study of the mass spectral behaviour of compounds which contain the Group VIa metals in a rational series.

Because of the decline in activity in 'main-group element' chemistry and the concentration of inorganic chemists upon transition-metal complexes and organometallic species, most of the work in this area has been performed from the organic chemistry perspective. But the general organic chemistry view of the organo-selenium and -tellurium class is likely to consist of the opinion that these compounds by-and-large emulate their S analogues except insofar as the heavier species are less stable and hence more difficult to prepare. Although this is generally true, we shall see examples in this review where large differences in the gas-phase ion chemistry of Se- and Te-containing compounds occur in comparison to their S analogues.

The rich isotopic mixture for both Se and Te provides advantages and drawbacks. 'Fingerprinting' is more detailed in the mass spectra, and the discernment of the presence and number of atoms of Se or Te present in a species is usually quite direct. Ideal mass distributions for combinations of two or more chalcogens in the same species, even including a halogen or two, have been reported by several authors[4–6]. On the other hand, the presence of species containing one less or one additional H atom and the contributions by ^{13}C etc. mixed into the isotopic distributions can complicate the spectra. Therefore, most authors thoughtfully convert their data to a basis consistent with the presence of only ^{80}Se or ^{130}Te. Deconvolution techniques are useful and often essential for this purpose. A recent example of the analytical use of isotopic ratios is the quantitation of selenocysteine in glutathione peroxidase[7].

The generally reduced stability of Se- and Te-containing compounds, by comparison to the O- and S-containing analogues, has two effects. First, use of a direct inlet method becomes desirable since decompositions and rearrangements can result during attempts at chromatographic separation and purification. Secondly, low mass ions, corresponding to such species as CH_3Se or C_3HSe, which may be produced prior to ionization as a result of attempts to vaporize samples, are rather typically observed in the spectra. (Metastable ion studies can rule out these species as resulting from the fragmentation of heavier ions.)

A few other features of the mass spectra rather commonly occur for Se- and Te-containing organics: (1) combinations of molecular groupings leading to *m/z* ratios greater than that of the parent ion, very often at $[M + 80]^+$ when Se is involved; (2) the relatively larger tendency of ions to lose chalcogen, even to 'extrude' chalcogen from the middle of a group or from a ring system; and (3) the subsequent propensity of chalcogen atoms to combine to give species of the general formula $Se^{+\cdot}$ or $Te^{+\cdot}$.

The natural expectation that Se—C and, even more so, Te—C bonds would be more easily broken than their C—O and C—S counterparts is most often borne out in the fragmentation behaviours upon electron ionization. But some instances of surprising resilience of C—Se are encountered. Cases where the parent ion is too unstable to be detected are rare but do occur: e.g. alkyl selenides and tellurides.

Nearly all workers who have reported mass spectral studies of organic Se and Te compounds have made use of electron ionization (usually at high energy, 70 eV) and low-resolution mass analysis. In those cases, the proposed fragmentation mechanisms and ion structures should be viewed as entirely speculative. However, studies are beginning to appear which have involved high mass resolution to confirm elemental compositions, metastable ion studies to verify pathways, and isotopic labelling to shore-up mechanisms. Most metastable ion studies are somewhat haphazard; that is, only those metastable ions which appear in the normal mass spectra are used. With the advent of tandem mass spectrometry instruments[8] including reverse geometry and triple sector quadrupoles, more detailed investigations of decomposition pathways are urged and should appear. Moreover, standard high-resolution instruments of forward geometry can be modified with linked scanning capabilities[9] to permit studies of metastable ions unencumbered by normal ions which usually overlap severely in conventional spectra.

Other ionization modes may be useful for certain organic Se and Te compounds. Complex acyclic materials such as alkyl selenides and tellurides give low abundance molecular ions. These substances may be profitably ionized by using chemical ionization, field ionization or field desorption. Very few examples of the use of these more gentle methods of ionization have been published to date. The utility of fast atom bombardment[10] and field desorption will no doubt be realized for thermally sensitive or ionic compounds in the Se and Te series. One example compound is benzeneseleninic acid which decomposes under normal solid sample handling. Finally, negative ion mass spectra may be very useful for structure studies and for determining molecular masses. This approach has also been slighted as we were able to find only one report of organoselenium compounds in which negative ions were investigated. Nevertheless, it is expected that the recent advances in technique in mass spectrometry will have a salutary effect on future studies of organic-Se and Te compounds.

In the review which follows, we begin with a discussion of the ionization of and the charge localization in organic compounds containing Se and Te. This is intended to serve as an introduction to the chemistry of gas-phase ions of these compounds. These sections are followed by a review of the mass spectra of compound types, beginning with acyclic selenides and tellurides and moving toward complex heterocycles. The review includes papers published up to early 1984.

A. Ionization Energies

The first event in producing a mass spectrum is ionization, usually to form a radical cation. The initially formed radical cation may exist in various excited states, but internal conversion to a vibrationally excited ground state should occur very rapidly. Fragmentation is then viewed to involve the ground state of the ion. Therefore, it is of interest to consider the nature of the lowest energy ionization of Se- and Te-containing organic molecules before discussing their mass spectral fragmentations.

The lowest energy ionization of various dimethyl chalcogenides has been measured by using photoelectron spectroscopy (PES), and assigned to ionization from the chalcogen lone pair[11,12]. The trend of ionization potentials for Me_2X is 10.04, 8.71, 8.40 and 7.89 eV for X = O, S, Se and Te, respectively. The decreasing electronegativity of X as we go from O to Te destabilizes the n molecular orbital and is responsible for the trend. Similar variations were found for a series of compounds $(MH_3)_2X$ where M = C, Si, Ge, and X = S, Se, Te[13].

The lowest energy ionization of the series PhXMe also smoothly decreases as X is varied from O to Te[14]. Again, the most facile ionization is that of the n electrons of X except for PhOMe where π electron ionization is more favoured.

For a series of disubstituted benzenes RC_6H_4SeMe, where R = NH_2, OMe, SMe and SeMe and is substituted *ortho*, *meta* and *para* to the SeMe, little difference can be seen in the lowest ionization energies[15]. Again, electrons in the n orbital of the Se are most readily removed. Little interaction occurs between the two substituents, apparently because of the non-planar structures of these disubstituted molecules. On the other hand, the lowest ionization potential of p-$MeOC_6H_4OMe$ is determined by π_s orbitals of the benzene ring and not by the chalcogen.

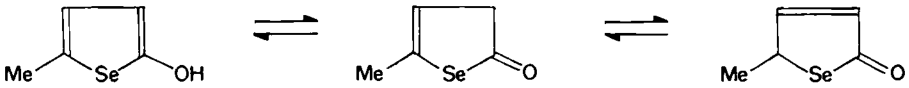
Simple cyclic molecules, $(CH_2)_4X$, also show a smooth decrease in the ionizing energy as we go from O to Te[16]. The ionization is thought to involve an n_π molecular orbital which is perpendicular to the C—X—C plane and thus reflects the electronegativity of X. The trend of values 9.53, 8.42, 8.14 and 7.73 eV for X = O, S, Se and Te, respectively, parallels nicely that observed for the Me_2X series.

The picture is more complex for the series furan, thiophene, selenophene and tellurophene: *IE* = 8.99, 9.12, 9.01 and 8.60 eV, respectively, as determined by using electron ionization[17]. It was concluded by using PES that the highest occupied molecular orbital (HOMO) of tellurophene is π_2 whereas the other analogues have π_3 as the HOMO. The π_2 MO involves bonding between carbon atoms and antibonding between the heteroatom and carbons whereas π_3 is almost exclusively C—C bonding and, thus, its energy is nearly independent of the heteroatom. Low-energy ionization of selenophene, as of furan and thiophene, does not involve the n electrons of the chalcogen.

This inversion of π_2 and π_3 molecular orbitals in tellurophene was verified by a PES study of a large series of substituted furans, thiophenes, selenophenes and tellurophenes[18]. The π_2 is inevitably the HOMO for all tellurophenes, but π_3 is of highest energy for all others.

The PES of benzo[*b*]selenophene and benzo[*b*]tellurophene have also been measured and compared with those of benzofuran, benzothiophene, indole and indene[19]. The HOMO for benzo[*b*]tellurophene is highly localized on the heteroatom and has an ionization energy of 7.76 eV whereas the HOMO ionization energy for the benzo[*b*]selenophene is 8.03 eV.

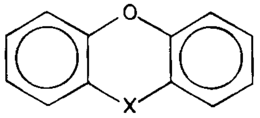
Ionization energies determined by electron ionization have been used to determine the extent of tautomerism of various substituted selenophenes (see equation 1) in the gas phase[20-22]. The strategy involved comparisons of the ionization energy of the unknown with various model or reference compounds which exist in either a keto or enol form. For both 2- and 3-hydroxyselenophenes, the keto form is preferred whereas 3-thio-substituted selenophenes exist preferentially in the thiol (enol) form.



(1) (2) (3) (1)

Ionization energies from mass spectrometric measurements have also been used as correlates for understanding electrophilic substitution reactions on selenophene[23]. It was concluded that variation of reactivity with substituent effects is similar to that of thiophene.

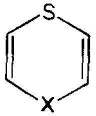
The lowest ionization energies for a series of phenoxachalcogenins (**4**), where X = O, S, Se and Te, were determined by using PES and found to be nearly identical whatever the



(**4**)

identity of X[24]. If the molecules were planar, the π MOs would become progressively destabilized as the mass of X was increased. Since this was not the case, it was postulated that the centre ring is not planar, and π interactions with the chalcogen and the aromatic rings are reduced. This conclusion is in agreement with interpretations drawn from dipole moment data[24].

The lowest ionization energies of various non-benzofused analogues (**5**), where X = O, S, Se and Te, also do not vary significantly for various identities of X, which indicates that the favoured ionization does not principally involve the chalcogen atom[25]. This is not true for various $(MeO)_3PX$ compounds where X = O, S and Se[26]. The lowest ionization energy drops in the order 10.82, 9.16 and 8.67 eV for X = O, S and Se, respectively, which can be interpreted in terms of favoured ionization of the n electrons of the X atom.



(**5**)

A unique application of PES has been the proof of the structure of 6-fulveneselone, a product of the pyrolysis of 1,2,3-benzoselenadiazole[27]. The first ionization potential of 8.34 eV is lower than for the S analogue and the lowest of known fulvene-like analogues. However, a reversal is found for tetramethyltetraselenafulvalenewhose HOMO is stabilized ($IE = 6.58$ eV) with respect to the tetrathia compound ($IE = 6.40$ eV)[28].

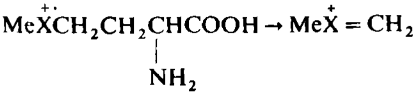
In summary, caution should be exercised in viewing the positive charge localized on Se or Te in ionized organic molecules containing these atoms. This seems to be an accurate picture for selenides and tellurides, but it clearly is not for more complex molecules. The role of localization of charge in triggering fragmentation reactions is discussed in the next section.

B. Role of Charge Localization in Fragmentation

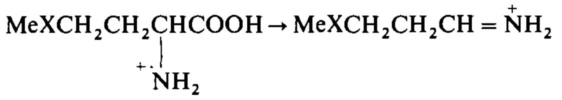
The replacement of an O or S atom by Se in an organic molecule may result in a lowered ionization energy. For example, the ionization energies for Me_2O, Me_2S, Me_2Se and Me_2Te are 10.0 eV, 8.71 eV, 8.40 eV and 7.93 eV[12]. This has presented theorists in mass spectrometry with an opportunity to examine the widely held concept of 'charge localization'. It has been hypothesized that the unimolecular dissociations of gas-phase radical cations are triggered or initiated by the nearby presence of a charged site. For example, the loss of R in the series of compounds $MeXCH_2R$, where X is a chalcogen, is due to the ionization of the chalcogen (equation 2).

$$Me\overset{+\cdot}{X}CH_2R \rightarrow Me\overset{+}{X}{=}CH_2 + R\cdot \qquad (2)$$

A now classic example of the use of charge localization theory is the explanation of the mass spectra of methionine and selenomethionine. Svec and Junk[29] postulated that the reason for the higher intensity of $C_2H_5X^+$ (X = Se, S) is the preferred charge localization on S or Se rather than N (equations 3 and 4). The ionization energy of Se non-bonding electrons in molecules such as selenomethionine is ca. 8.6 eV compared to ca. 10 eV for nitrogen non-bonding electrons.



$$Me\overset{+\cdot}{X}CH_2CH_2\underset{\displaystyle NH_2}{\underset{|}{C}}HCOOH \rightarrow Me\overset{+}{X} = CH_2 \qquad (3)$$



$$\mathrm{MeXCH_2CH_2\underset{{}^{+\cdot}NH_2}{\underset{|}{C}}HCOOH \rightarrow MeXCH_2CH_2CH=\overset{+}{N}H_2} \qquad (4)$$

However, Bentley and coworkers[30] have shown conclusively by means of metastable ion measurements and low energy spectra that $C_2H_5X^+$ is not produced by direct decomposition of the molecular ion but rather by some circuitous routes such as loss of H_2O followed by expulsion of methyl radical, CO and finally HCN. The loss of water has an appearance energy lower than the ionization energy of the non-bonding electrons of $—NH_2$ or —COOH, and, thus, the charge triggering or localization of charge on the NH_2 or COOH moieties is not a necessary prerequisite for the decomposition. In other words, the decomposition takes place 'thermally' from the vibrationally excited ground electronic state of methionine or selenomethionine, an explanation fully in accord with the quasiequilibrium theory of mass spectra.

Van den Heuvel and Nibbering[31] have shown that the corresponding multistep process leading to $C_2H_5S^+$ from ionized methionine contributes little to the intensity of this ion actually observed in the mass spectrum. This serves as an appropriate caution that metastable-denoted fragmentation routes may 'refer to processes which contribute to the intensities of peaks to only a minor extent...'. Furthermore, they were able to rationalize the decomposition route of the methionine radical cation by invoking charge localization on nitrogen. Bentley and coworkers[30] anticipated this type of rationalization by noting that the triggering approach does have the notable properties of 'flexibility and vagueness'. The criticism is undeserved, in part, because there is no doubt that charge localization is a valuable predictive and didactic tool in the hands of the practicing mass spectroscopist. Nevertheless, it is now clear that the Svec and Junk explanation of the relatively intense $C_2H_5Se^+$ ion in the mass spectrum of selenomethionine is incorrect.

Budzikiewicz and Pesch[32] have also addressed this problem of charge localization by a study of a well-chosen set of homologues $CH_3X(CH_2)_nNH_2$ where X = O, S or Se. Here, as for methionine and selenomethionine, little $C_2H_5X^+$ is obtained; the major ions produced in the mass spectral decompositions contain N, viz. $CH_2{=}NH_2^+$. The direct cleavage to give $CH_3\overset{+}{X}{=}CH_2$ is probably not favoured energetically when X = Se because of the difficulty in forming a C—Se double bond. The ionization energy and appearance energy for production of $CH_2{=}NH_2^+$ were measured as a function of the number of intervening methylene groups between Se and NH_2 (see Table 1). As can be seen from the table, the *IE* is nearly the same for all homologues and is principally determined by the orbital energy of the chalcogen. The appearance energy for $CH_2{=}NH_2^+$ is between 9 and 10 eV, which is above the ionization energy of *n*-propylamine (*IE* = 9.1 eV) but suspiciously, and perhaps fortuitously, close to the *AE* of $CH_2{=}NH_2^+$ from $CH_3CH_2CH_2NH_2$ (*AE* = 9.7 eV).

There are two notable exceptions; the homologues for which $n = 3$ have appearance energies significantly lower and nearly equal to the ionization energies. One explanation, favoured by Budzikiewicz and Pesch, is that charge exchange from Se to N can now occur

TABLE 1. Ionization (*IE*) and appearance energies (*AE*) for the homologous series of compounds: $CH_3X(CH_2)_nCH_2NH_2$

	X = S		X = Se	
n	*IE*	*AE*	*IE*	*AE*
1	8.4	8.9	8.4	9.8
2	8.5	9.7	8.3	9.5
3	8.4	8.4	8.3	8.3
4	8.5	10.1	8.3	10.0

via a six-membered ring, a transition state of lower energy than those which would be possible for the other homologues. Thus, transfer and localization of charge on the N triggers the fragmentation to produce $CH_2{=}NH_2^+$.

An alternate explanation rests upon the unusual stability of the neutrals formed along with $CH_2{=}NH_2^+$ when $n = 3$; e.g. $CH_3XCH_2^{\cdot}$ and $CH_2{=}CH_2$ or a cyclic structure. If this is so, then the question must be addressed as to why no unusual stability pertains when Se or S is replaced by oxygen. Thus, the question of charge localization remains an open one. In our view, because it provides a means of conveniently interpreting spectra of Se-containing molecules, the concept should be retained on a utilitarian basis until more solid evidence to require its rejection is generated.

II. MASS SPECTRA

A. Alkyl Selenides and Tellurides

Agenas, in a 1973 review of the mass spectrometry of Se compounds[33], discussed the Se analogues of ethers. The mass spectra of several prototypic compounds, e.g. diethylselenium, dibenzylselenium, diphenylselenium as well as more complex species such as selenodialkanoic acids, selenomethionines, 3,3′-diindolyl selenide, 3,3′-di(l-methylindolyl)selenide and mixed side-chain compounds such as selenocyanatobenzene were presented. Typical decomposition reactions of the selenides included progressive loss of alkyl groups, H migration and alkene (e.g. C_2H_4) loss, and loss of RSe, HSe or Se itself.

For cyclic analogues such as selenolane and tellurolane with five-membered saturated rings various eliminations leading to three-membered rings were most commonly reported, although cyclic structures had to be inferred.

More recently, Rebane[34] used deuterium substitution to demonstrate supplemental skeletal rearrangements which implied that Se extrusion and carbon–carbon bond formation took place. Thus, the one-step loss of C_2H_4 from dimethylselenium was confirmed by metastable ion studies. The base peak in the mass spectrum of this compound corresponded to $MeSe^+$; successive losses of hydrogens from $MeSe^+$, leading finally to $CSe^{+\cdot}$, were posited as well. The most common decomposition reaction for higher molecular weight dialkyl selenides was the cleavage of a C—Se bond accompanied by migration of H to Se to give $RSeH^{+\cdot}$. This process is rare for O- or S-containing analogues. Other ions resulted from fragmentations involving the alkyl groups.

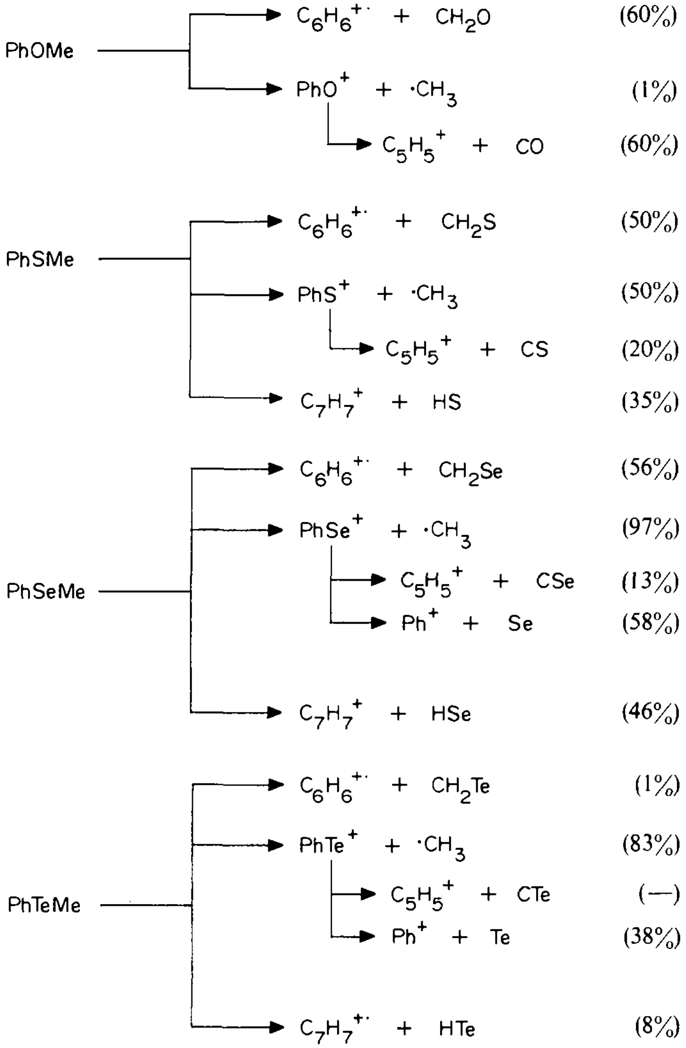
Budzikiewicz and Pesch[32] reported the spectra of several dialkylselenium compounds, all possessing one Me group on the Se. They, along with others, observed the disfavour of the Se compounds for α-cleavage. However, their assertion that this is due to the impossibility of a Se=C double bond (to form, say, $MeSe{=}CH_2^+$) is, at best, of qualitative value, since the appearance of such a species has been reported by other workers. They also studied the decomposition of $MeSe(CH_2)_nNH_2$ as was discussed in the previous section.

The mass spectra of $(C_2F_5)_2Te$, $MeTeC_2F_5$, $(CF_3)_2Te$ and of CF_3TeMe were reported by Denniston and Martin[35]. They noticed no interchange of H and F in the mixed fluorine–hydrogen compounds. For the perfluorinated bis-ethyltellurium, Paige and Passmore[36] have similarly reported only the parent ion and an expected fragmentation pattern.

B. Alkyl Aryl Selenides and Tellurides

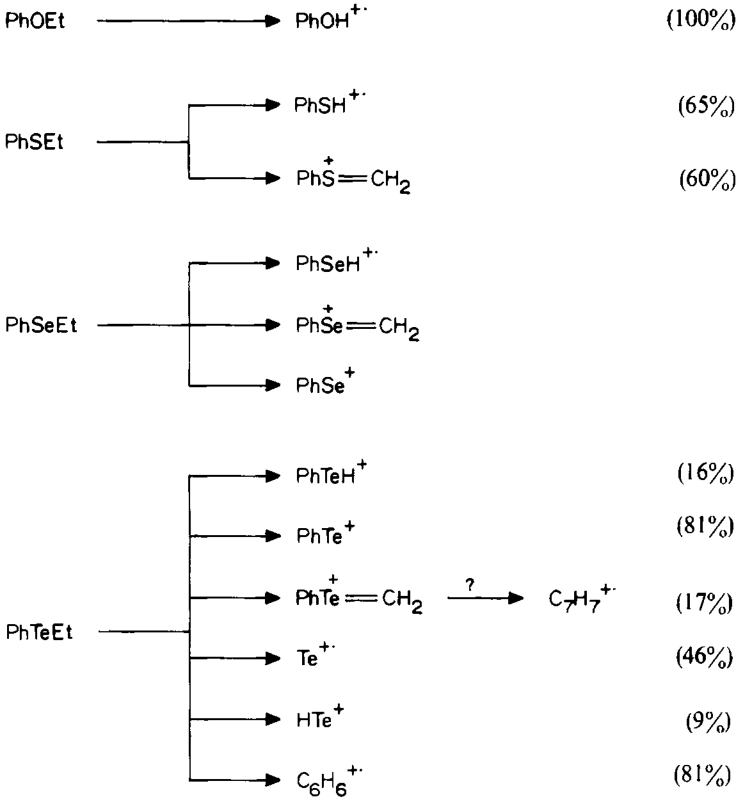
Rebane[37,38], Greiner and coworkers[39] and Busse and coworkers[40] have added to our knowledge of the mixed alkyl aryl ether analogues. Thus, it is now possible to make comparisons of behaviour descending the Group VI column. For phenyl methyl ether and its analogues, the parent ion is invariably the base peak in the mass spectra. For the ether proper, the familiar losses of formaldehyde and $CH_3 + CO$ are equally dominant (ca. 60%). For the sulphide, loss of SCH_2 (ca. 50%) still occurs, but new processes involving loss of Me radical (ca. 50%) and of HS expulsion (ca. 35%) enter in. With the selenide, the processes insinuated into the scheme by replacement of O by S grow in importance, and, by the time the telluride is reached, Me radical loss is entirely dominant. These results are summarized in Scheme 1 for comparison.

A similar comparison of the phenyl ethyl ether and its analogues (see Scheme 2) first shows, for the ether itself, the familiar expulsion of ethene and production of the $PhOH^{+\cdot}$ ion (via the so-called the phenetole rearrangement) which provides the base peak in the spectrum. While the same sort of process occurs for the sulphide, the $PhS{=}CH_2^+$ ion, by loss of a Me radical, is nearly as important. With the replacement of S by Se, yet another



SCHEME 1

process, loss of a Et radical, becomes significant. Finally, for phenyl ethyl tellurium, the important ions (parent ion = 100%) are: Ph^+ (108%, perhaps by progressive loss of Et and Te), $PhTe^+$ (83% loss of Et radical), $C_6H_6{}^{+\cdot}$ (1% loss of ethene and Te), $Te^{+\cdot}$ (46.0%), HTe^+ (8.6%) and $C_7H_7^+$ (17.2%). This latter species may be viewed as a product of reductive elimination of Te from $PhTeCH_2^+$. The rearrangement to give $PhTeH^{+\cdot}$ still occurs, but it is relatively unimportant.



SCHEME 2

Greiner and coworkers[39] reported the fragmentations of ionized ether analogues involving Ph and Et groups substituted by CN or CO_2Me groups. α-Cleavage to produce $Ar—X{=}CH_2^+$ (X = O, S, Se, Te) was encouraged by the substituent groups; $PhXH^{+\cdot}$ fragment ions lost CX to give $C_5H_6^{+\cdot}$ when X = O or S. Production of PhX^+ became important for X = Se or Te as for the PhXMe and PhXEt series discussed above.

Busse and coworkers[40] also noted the presence of low molecular weight species of the class TeC_pH_q ($p = 1$–4, $q = 1,2$) in the mass spectra of alkyl phenyl tellurides. These fragment ions were found to derive their hydrogens from the Ph ring as was proved by studies of deuterium-labelled analogues. The $MeTe^+$ ion from methyl phenyl telluride contained exclusively the Me group on the Te of the parent compound with no H/D exchange reactions preempting this simple cleavage reaction.

C. Diaryl Selenides and Tellurides

Fewer studies have been carried out on diaryl selenides and tellurides, although some information has arisen as a result of studies upon the dichalcogenides (*vide infra*). Rebane[41] has supplied data concerning bis(substituted phenyl)selenium. He has reported that the main fragmentations involve scission at the Se atom although loss of the substituents on the Ph ring is also typical. Most interesting are the strong tendency to extrude the Se entirely, presumably giving rise to a substituted biphenyl species, the tendency to undergo rearrangements towards expanded aromatic rings (tropylium ion, for example) or even to undergo a process such as that shown in equation (5).

$$(MeC_6H_4)_2Se^{+\cdot} \xrightarrow{-2\,Me} (C_6H_4)_2Se^{+\cdot} \xrightarrow{-Se} (C_6H_4)_2^{+\cdot} \qquad (5)$$

Albeck and Shaik[4] reported studies on Ph_2Te, *p*-An_2Te and their dichlorides and dibromides. The most notable features for the dihalides (halogen bounded to Te) were the losses of the halogens leading to the species already noted for the simple diaryl compounds. Based on metastable ion studies, they were able to demonstrate that the dihalides were also capable of the stepwise loss of aryl groups giving rise to $ArTeCl^{+\cdot}$ and $TeCl^{+}$, for example, but since the initial step was invariably loss of $Cl^{\cdot}$, no $ArTeCl_2^{+}$ was observed.

D. Cyclic Selenides and Tellurides

Rebane[34] reported the mass spectrum of the saturated cyclic selenane, $C_5H_{10}Se$. An important process was the fracture of both Se—C bonds, allowing the elimination of HSe after an H atom migration so that the resulting ion has the formula $C_5H_9^{+}$. An entirely parallel pattern has been reported for the selenacyclopentane[42], but this behaviour is foreign to the corresponding S analogues. Additional modes involved elimination of one-, two-, and three-carbon atom fragments giving rise to $C_4H_7Se^{+}$, $C_3H_6Se^{+\cdot}$, $C_3H_3Se^{+}$, $C_2H_4Se^{+\cdot}$, $C_2H_5^{+}$ and $CH_2Se^{+\cdot}$, the last arising at least in part via a succession of C_2H_4 eliminations. $CHSe^{+}$, HSe^{+} and $Se^{+\cdot}$ ions, typical of aliphatic Se compounds, were also observed here.

Kulkarni and coworkers[43] reported detailed studies of a series of saturated heterocyclic hexanes analogous to 1,4-dioxane. Important decompositions resulted in cyclic intermediate ions by elimination of C_2H_4 and CH_2X where X = chalcogen. The formation of $C_2H_4X^{+\cdot}$ and $C_2H_5^{+}$ ions was also important. As would be anticipated, there was considerable variation among the different members of the series and a fairly regular trend was often observed.

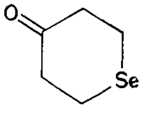
In the case of 1,4-dioxane itself, the most abundant ion was $C_2H_4^{+\cdot}$, the parent ion lagging at 77% and the ion resulting from loss of formaldehyde at 59%. For all other members of the series studied, the parent ion was the most abundant and the occurrence of $C_2H_4^{+\cdot}$ was at less than 10% except for the 1,4-dithiane (80%). Loss of formaldehyde dropped off in importance as one O atom was successively replaced with S, Se or Te; of course, loss of formaldehyde was impossible in the absence of O, but no formaldehyde analogue figured significantly among the species ejected from the parent ions. The authors suggested that a difficulty in forming the resultant cyclic intermediates militates against these eliminations for those species bearing the heavier chalcogens.

Especially in the cases involving the heavier chalcogens, the fragment ions retained the chalcogen atom because, apparently, of the capacity of the chalcogen for stabilizing positive charge through a greater ability to share electrons or to be polarized.

Formation of $H_2C{=}X^{+\cdot}$ via C_3H_6O loss assumed the most importance for OC_4H_8S (99%) and for OC_4H_8Se (85%), dropping off thereafter for OC_4H_8Te (13%). The dithiane (49%) and to a lesser extent the diselenane (17%) produced a similar $CH_2X^{+\cdot}$ ion.

Production of $C_2H_4X^{+\cdot}$ was of little importance for the low molecular weight members of the series, but their direct production by loss of C_2H_4O became very important when X = Se (90%) or Te (44%). Hydrogen migration and loss of C_2H_3O led to $C_2H_5X^+$ [X = S (66%), Se (51%) and Te (0.7%)]. For 1,4-dithiane, the $C_2H_2^+$ peak was again fairly large at 53%.

Nanjappan and coworkers[44] have published recently a study of an extensive series of 4-selenanones (**6**) with both alkyl and aryl substituents on the ring carbon atoms. In addition to cleavage reactions involving ring carbons, loss of CO occurred to form presumably a five-membered cyclic selenide, a process not found for 4-thianones.



(**6**)

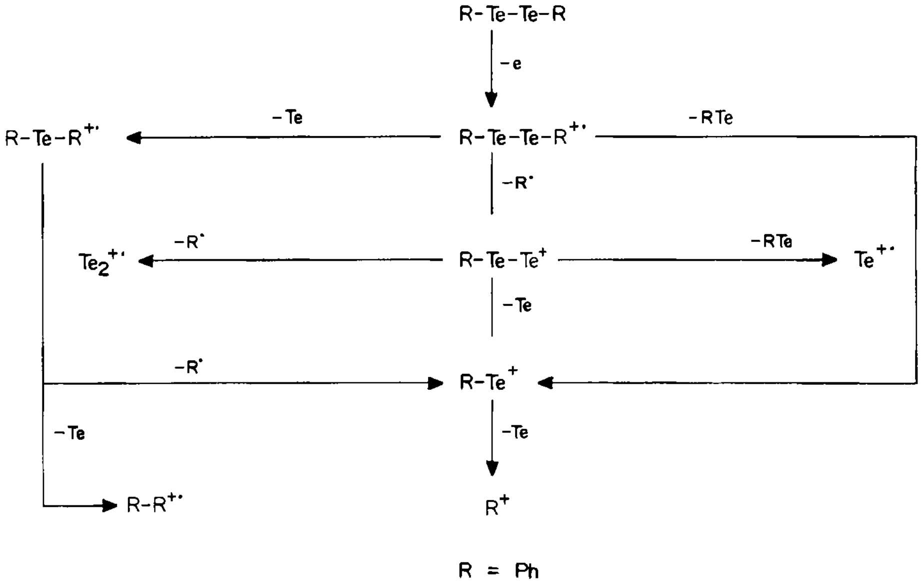
E. Diselenides and Ditellurides

Reactions of tetrafluoroethylene with $Se_8(AsF_6)_2$ and with $Se_8(Sb_2F_{11})$ were carried out by Desjardin and Passmore[45]. Among the unusual perfluorinated alkylselenium compounds which were discovered and studied using mass spectrometry were $(F_5C_2Se)_2$, $(F_5C_2Se)_2Se$, their Me analogues and some oxyfluoro species tracing from chemical contaminants.

The triselenium species gave rise to $F_4C_2Se_3C_2F_5^{+\cdot}$, and $F_4C_2Se_3^{+\cdot}$ along with species typical of the diselenium version of the compound (*vide infra*). In light of the occurrence of triselenium species in mass spectra of samples where only diselenium species are supposed to exist, it is not clear whether real quantities of a neutral triselenium compound were actually prepared, although the excess of Se present would certainly allow for this. The reports of the mass spectrometry of the triselenium species are sketchy, but the spectra do show that F atom loss and the fracture of F—C as well as C—Se bonds, while the Se_3 group remains intact, both occur.

In the spectrum arising from $(F_5C_2Se)_2$, the most abundant ion is CF_3^+ (100%); other important fluorocarbon fragments are $C_2F_5^+$(37%) and $C_2F_4^{+\cdot}$ (23%). As for Se-containing species, the parent ion (26%), $[M - C_2F_5]^+$ (36%), $SeC_2F_5^+$ (5%), $F_4C_2Se^{+\cdot}$ (7%), $Se_2C_2F_4^{+\cdot}$ (8%), $SeCF^+$ (17%) and $Se_2^{+\cdot}$ (39%) appear with notable abundances. Many less abundant species appear to have arisen possibly by loss of a fluorine atom, breaking a C—F bond. The ion at *m/z* 379 (1%) certainly corresponds to $[M - F]^+$. This information together with the albeit slight presence of species such as $F_2CSe_2^{+\cdot}$, $FCSe_2^{+\cdot}$, and $SeC^{+\cdot}$ serve as a warning that fragmentations depend upon factors aside from inherent or relative strengths of bonds such as Se—C or C—F.

Irgolic and Haller[5] have presented and discussed the mass spectra of symmetrical diaryl ditellurides where the aryl groups were XC_6H_4(X = 4-Me, 3-F, 4-F, 4-Br, 4-Ph). In most cases, the parent ion was most abundant, but for the bis(fluorophenyl) and bis(bromophenyl) compounds, the $ArTe^{+\cdot}$ species were the most favoured; for bis(4-biphenylyl) ditelluride the parent ion was of low abundance and the dominant species was $Ar^{+\cdot}$. All of the spectra exhibited the foreseeable species $Ar_2Te^{+\cdot}$, $ArTe_2^+$, $ArTe^+$, $Ar_2^{+\cdot}$, Ar^+, $Te_2^{+\cdot}$ and $Te^{+\cdot}$ (cf. Scheme 3). In addition, the species $Ar_2Te_3^{+\cdot}$ was noted in several of the spectra. Whether this arose from a tritelluride impurity in the initial compound or from thermolytic rearrangement reactions upon evaporation into the ionization region or upon electron ionization is not known. Again, low intensity peaks corresponding to



SCHEME 3

TeC$_n$H ($n = 2$–5) were observed. Also, typically, species such as ArTe$_2$H$^{+\cdot}$, ArTeH$^{+\cdot}$, Te$_2$H$^+$ and TeH$^+$ were present. Finally, smaller hydrocarbon fragments, attributable to decomposition and possible rearrangements of Ar$^+$ and Ar$_2^{+\cdot}$ were observed. Therefore, the authors noted that, with the exception of HS loss from disulphides, which is not found for Se and Te cases, the spectra of the diaryl disulphides, diselenides and ditellurides are largely the same.

For the decomposition of ionized bis(4-bromophenyl) ditelluride, the presence of a C$_7$H$_7$Te$^+$ species was noted. Although unexplained, it is reminiscent of C$_7$H$_7$Te$^+$ observed in the spectrum of PhTeEt and must necessarily result from some rearrangement process or processes.

Dance and McWhinnie[46] studied a similar group of R$_2$Te$_2$ compounds but with R = Ph, *p*-Tol, *p*-An, *p*-EtOC$_6$H$_4$, *p*-PhOC$_6$H$_4$ or C$_6$F$_5$. These spectra presumably exhibited the features as described by Irgolic and Haller[5]. Dance and McWhinnie performed appearance energy measurements which permitted them to argue for the production of R$_2$Te$^{+\cdot}$ by the fragmentation of R$_2$Te$_2^{+\cdot}$ rather than via thermolysis on the sample introduction probe. The curvature of the ionizing energy vs. intensity curves for RTe$^+$ was cited as an argument in favour of two routes for production of this ion from the parent R$_2$Te$_2^{+\cdot}$—the first by rupture of the Te—Te bond and the second by progressive loss of Te, then R. They suggested that both the Te—C and Te—Te bonds have bond strengths of the order of 290 kJ mol^{-1}, thus supporting the low-energy pathway represented by Te extrusion.

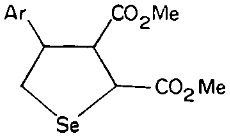
Another interesting feature of this work involved the physical mixing of two different diaryl ditelluride species prior to admission to the sample introduction probe and ionization. In addition to the spectral features anticipated from each component of the mixture, evidence for mixed species such as PhTeTeC$_6$H$_4$OPh$^{+\cdot}$ and PhTeC$_6$H$_4$OPh$^{+\cdot}$ was noted, in spite of their lack of success in preparing the corresponding unsymmetrical neutral ditelluride molecules.

Finally, these workers also prepared and studied the series Ph_3SnTeR (R = Ph, *p*-An, *p*-$EtOC_6H_4$, *p*-$PhOC_6H_4$) and also observed a parent ion for $(n\text{-}Bu)_3SnTePh$, all of which might be considered 'pseudo-ditellurides'. Appearance energies for some ionic species and the note that $Ph_6Sn_2^{+\cdot}$ was observed from thermolysis were the limits of information provided.

Continuing their pursuits of the 1960s, Buu-Hoi and coworkers[47] studied the mass spectra of RTeTeR′ compounds, most of them with R = R′ (R = Ph, *p*-Tol, α,α′-Naph, β,β′-Naph). Parent ions were obtained for these compounds, presumably because the aryl groups provided sufficient stabilization for the positive charge. Many of the features of the spectra were expected, e.g. the stepwise extrusion of Te atoms leading to $RTeR'^{+\cdot}$ and $RR'^{+\cdot}$ species. However, there was no evidence presented for the symmetric fracture of the parent ion at the Te—Te bond. The spectra of these compounds qualitatively, if not quantitatively, emulated those of the analogous Se compounds. However, the counterparts of species such as C_3HSe^+ and CHSe, species which are typical in the Se systems, were not reported here.

F. Other Selenides

Shafiee and coworkers[48–57] have prepared a number of Se-containing compounds and have used mass spectrometry to characterize them, chiefly by observing the parent ion and noting the intensity pattern appropriate for the isotopic distribution of Se. In one study[48], the mass spectra of a group of related compounds were studied. They can be interpreted as discussed below although no demonstration of the fragmentations or supporting data are available.



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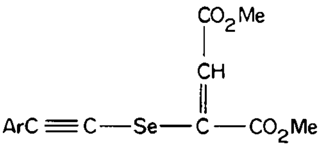
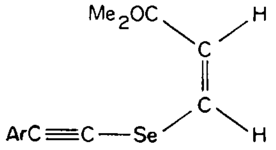


$$ArC{\equiv}C{-}Se{-}\overset{\overset{\displaystyle CO_2Me}{|}}{\overset{\displaystyle CH}{\overset{\|}{C}}}{-}CO_2Me$$

(8)



(9)

For all of these compounds Ar = *p*-Tol. Progressive losses from the parent ion at *m*/*z* 338 for **7** gave rise to daughter peaks at *m*/*z* 307 (loss of MeO), *m*/*z* 275 (loss of CH_4O from *m*/*z* 307), *m*/*z* 219 (loss of two CO) and *m*/*z* 139 (loss of Se). The isomer, **8**, appeared to lose Me (giving *m*/*z* 323) and $(CCOOMe)_2$ followed by Se (giving *m*/*z* 195 and 115), and also to undergo a rearrangement yielding *m*/*z* 146 which corresponds to $ArC{\equiv}COMe^{+\cdot}$. Compound **9** with parent ion at *m*/*z* 280 apparently lost OMe (giving *m*/*z* 249), $SeCHCHCO_2Me$ (giving *m*/*z* 115) and $CHCHCO_2Me$ (giving *m*/*z* 195). In addition, the $ArC{\equiv}COMe$ radical cation (*m*/*z* 146) is again produced along with ions at *m*/*z* 209 corresponding to $ArC{\equiv}C{-}Se{-}CH_2^{+\cdot}$ and at *m*/*z* 129 corresponding to $ArC{\equiv}C{-}CH_2^{+\cdot}$.

G. Dialkyl Selenoxides

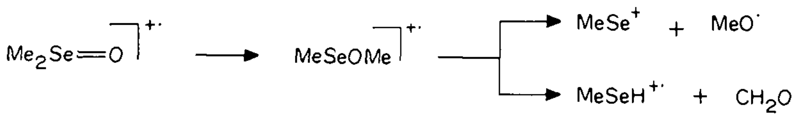
Dialkyl selenoxides are the Se analogues of sulphoxides, and their mass spectra have been investigated by Rebane[38]. Dimethyl selenoxide gives an intense molecular ion upon ionization, but the molecular ion intensity drops precipitously for higher homologues such as diethyl, dipropyl, etc. The mass spectra of these latter compounds are dominated by alkyl and alkenyl ions. For example, the most abundant fragments produced in the decomposition of dibutyl selenoxide are $C_4H_9^+$ and its decomposition products $C_3H_5^+$ and $C_2H_5^+$. Unlike $Me_2Se{=}O$ and $Ph(Me)Se{=}O$ which give abundant fragments corresponding to $MeSeO^+$ and $PhSeO^+$, the higher dialkyl selenoxides give very low-abundance ions corresponding to $C_nH_{2n+1}SeO^+$.

This is also true of the dialkyl selenides themselves. The relative abundances of RSe^+ are surprisingly low compared to R^+ (R = Et, Pr, Bu). From this we may conclude that the ionization potentials of the alkyl selenide and alkyl selenoxide radicals are higher than those of the alkyl radical, i.e.:

$$Et^{\cdot}\ (IE = 8.4\,eV) < EtSe^{\cdot} \text{ and } EtSeO^{\cdot} \tag{6}$$

$$Pr^{\cdot}\ (IE = 8.1\,eV) < PrSe^{\cdot} \text{ and } PrSeO^{\cdot} \tag{7}$$

There exist interesting rearrangement reactions of the dialkyl selenoxide radical cations which compete only weakly with the decomposition to produce alkyl ions. The rearrangement processes are most noteworthy for MeSeOMe. In addition to the rearrangement of H followed by loss of OH, losses of MeO and CH_2O to give $MeSe^+$ and $MeSeH^{+\cdot}$, respectively, have been observed. These latter ions must originate in a rearrangement (termed a selenoxide–selenate rearrangement) (see equation 8). The relative abundances of $MeSe^+$ and MeO^+ are comparable, which may mean that the ionization potential of MeSe is approximately equal to that of MeO. However, it is possible that these ions are produced by rearrangement to give CH_2OH^+, for example.



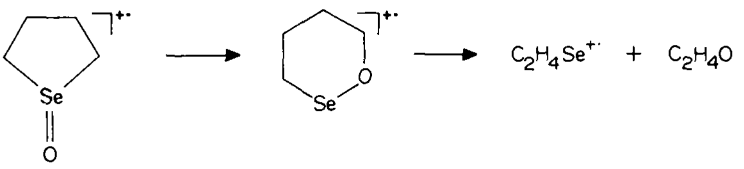
(8)

The corresponding selenoxide–selenate rearrangement occurs for diethyl, dipropyl and dibutyl selenoxides, but it is of little consequence. The mass spectrum of $Pr_2Se{=}O$ shows a weak molecular ion, loss of O, OH and C_3H_6. The losses of OH and of the olefin are also found in the decompositions of the corresponding sulphoxides.

The dibenzyl compound shows the loss of C_7H_6 (which corresponds to C_3H_6 loss for dipropyl), loss of O and a low abundance selenoxide–selenate rearrangement. Specifically, losses of $PhCH_2Se$ and $PhCH_2O$ constitute less than 5% of the total ion current.

H. Cyclic Selenoxides

Compared to the acyclic compounds, the five- and six-membered ring selenoxides show considerably more abundant molecular ions[38]. Losses of O, OH and C_2H_4 all imply no rearrangement. However, the low intensity losses of SeH and C_2H_4O require a prior rearrangement, presumably selenoxide-to cyclic selenate (equation 9). The corresponding process is less important for the six-membered ring, probably because expansions to seven-membered rings are less likely.



(9)

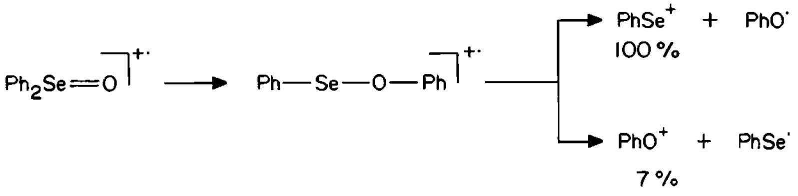
I. Alkyl Aryl Selenoxides

Methyl phenyl selenoxide undergoes a very facile rearrangement to form *m/z* 94 (base peak) by expulsion of neutral CH_2Se[38]. Again, this can be accounted for by the selenoxide-selenate rearrangement involving preferential Ph migration (equation 10). The corresponding rearrangement also occurs from methyl phenyl sulphoxide, but it is considerably less facile. The other decompositions of Ph(Me)Se=O radical cations are the expected ones: loss of Me and O. Following loss of O, the expulsion of SeH to give $C_7H_7^+$ is found, just as for PhSeMe.

$$\mathrm{Ph(Me)Se{=}O}\rceil^{+\cdot} \rightarrow \mathrm{PhOSeMe}\rceil^{+\cdot} \rightarrow \mathrm{PhOH}\rceil^{+\cdot} \qquad (10)$$

J. Diaryl Selenoxides

Here skeletal rearrangements totally dominate, which is consistent with the high aptitude of Ph groups for migration to electron-deficient centres[38]. First of all, one sees abundant loss of Se (reminiscent of the diaryl selenides) to give, in the case of diphenyl selenoxide, $PhOPh^{+\cdot}$. the expected loss of O is observed and expulsion of Se again gives $Ph—Ph^{+\cdot}$. However, the most intense ion is $PhSe^+$ (equation 11). Weakly competitive is the formation of PhO^+ as is expected in view of the greater ability of PhSe to accommodate a positive charge. The loss of H_2O is reasonably facile and must be accompanied by an interesting rearrangement; Rebane has suggested the pathway as shown in equation (12). The rearrangement to selenate finds precedent in $Ph_2S{=}O$ with PhS^+ as one of the most abundant fragments formed in its decomposition. The comparable rearrangement also occurs for substituted diphenyl selenoxides and is probably general for all diaryl selenoxides.



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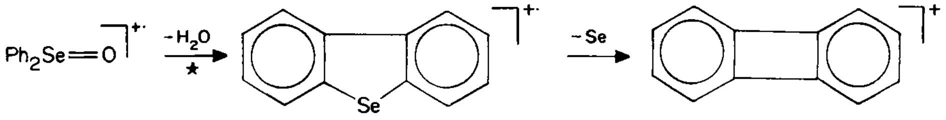
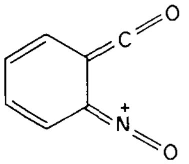


(12)

K. Oxygen Atom Transfer Reactions: Rearrangements to Selenoxides

Certain molecules containing S and *o*-$NO_2C_6H_4$ groups undergo novel oxygen-transfer reactions upon electron ionization (see equation 13). Martens and coworkers[58] have recently investigated the scope of this reaction by replacing the S atom with Se. For example, the radical cation of the Se analogue of the compound pictured decomposes to two ions, **10** and **11**, which must arise via an oxygen transfer. The most abundant ion (100% rel. abund.) is SeC_6H_4Me, which is formed by simple α-cleavage.

$$o\text{-}\mathrm{O_2NC_6H_4C({=}O)SC_6H_4Me}\rceil^{+\cdot} \longrightarrow \mathrm{O{=}\overset{+}{S}—C_6H_4Me} \qquad (13)$$

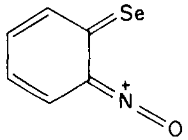


$O{=}SeC_6H_4Me$

(10)
21% rel. abund.

(11)
95% rel. abund.

A more stringent test of the generality of the reaction is the mass spectral decomposition of *o*-nitrophenyl *p*-tolyl selenide (equation 14). The indicated fragmentation is very facile which shows

o-$O_2NC_6H_4SeTol$-$p]^{+\cdot}$ ⟶  (14)

that oxygen transfer can occur via a five-centred transition state. When the Se is replaced by S, the reaction is not observed; rather the unusual loss of SO_2 is found instead.

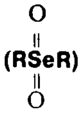
The authors pointed out that the intermediacy of a selenoxide which would then rearrange to a selenate cannot be ruled out. We have reviewed a number of examples which implicate clearly the latter process. Therefore, a possible mechanism is as shown by equation (15).

$$o\text{-}O_2NC_6H_4SeTol\text{-}p^{+\cdot} \rightarrow o\text{-}ONC_6H_4Se(=O)Tol\text{-}p^{+\cdot} \rightarrow$$
$$o\text{-}ONC_6H_4SeOTol\text{-}p^{+\cdot} \qquad (15)$$

If the Se is replaced by SeO, again the rearrangement of O occurs with expulsion of C_7H_7O, to give the most intense ion in the mass spectrum. The corresponding sulphoxide radical cation does not undergo this loss of C_7H_7O, but oxygen-transfer reactions must still pertain as losses of SO_2, SO_3 and HSO_3 (the last gives rise to the most abundant ion) are conspicuous.

The aromatic ring might be regarded as necessary to orient the *o*-nitro group properly for oxygen transfer, but this is not so for acyclic S-containing nitro compounds. However, the radical cation of $O_2NCH_2CH_2COSeTol$ does not decompose by loss of C_7H_7O; instead, an interesting rearrangement to form $[HOSeC_6H_4CH_3]^{+\cdot}$ occurs.

Martens and coworkers[58] concluded that the generalization that S and Se compounds show analogous behaviour is suspect. The compounds they studied are the most dramatic examples which support their conclusion, but additional examples are reviewed here that show that mass spectral decompositions of Se-containing compounds are related but not identical to those of S analogues.

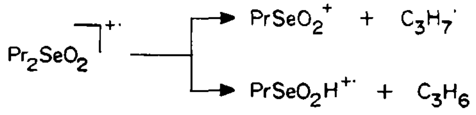


L. Dialkyl Selenones ($R\overset{O}{\underset{O}{Se}}R$)

The mass spectra of this class of compounds have been principally investigated by Rebane[59]. Only dimethyl selenone gives an abundant molecular ion; for the diethyl homologue, the molecular ion is barely visible, and for higher dialkyl homologues, the molecular ion is so low in abundance as to preclude inclusion in the bar graph spectrum.

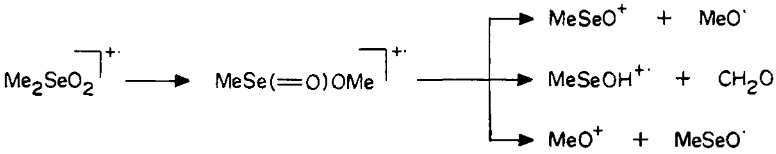
Clearly alternative methods of ionization, such as chemical or field ionization, will be required for obtaining unambiguous molecular weight information of even moderately complex dialkyl selenones. This precipitous decline in molecular ion abundance and the higher propensity to produce alkyl ions is also a property of sulphones, selenoxides and selenides (*vide supra*).

The principal decomposition reactions of the diethyl selenones and higher homologues is to produce alkyl ions. Just as for the selenoxides, the fragmentation to ions carrying the Se atom is overshadowed by the high abundance of alkyl cations. Nevertheless, some diagnostic ions of higher mass are produced by loss of an alkyl group or by rearrangement of H followed by loss of an alkene (see equation 16). These decomposition reactions are characteristic of the selenides and the selenoxides as well.



(16)

Isomerization of dialkyl selenones to dialkyl seleninates must occur for these compounds as evidenced by losses of CH_2O, CH_3O and formation of CH_3O^+ from the molecular ion of dimethyl selenone (equation 17). A second Me migration either before, concurrent with, or following loss of MeO and Me was also postulated to account for the consecutive loss of CH_2O (equations 18 and 19) and was substantiated by observation of the appropriate metastable ions.



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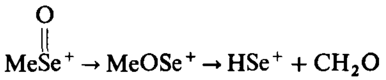
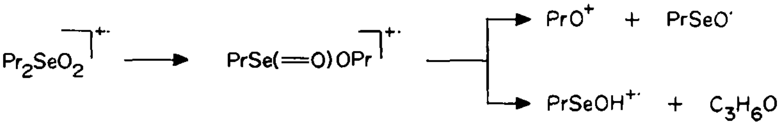


$$\overset{O}{\overset{\|}{MeSe^+}} \rightarrow MeOSe^+ \rightarrow HSe^+ + CH_2O \qquad (18)$$

$$MeSeO_2^+ \rightarrow MeOSeO^+ \rightarrow HSeO^+ + CH_2O \qquad (19)$$

The mass spectrum of dimethyl sulphone serves as an interesting contrast to that of dimethyl selenone. The sulphone decomposes principally by loss of Me, and the losses of MeO, CH_2O and formation of MeO^+ are only weakly competitive. Replacement of S by Se apparently lowers the activation energy for the selenone–seleninate rearrangement such that this process is highly competitive with the simple cleavage to expel a methyl group.

The higher molecular weight homologues also undergo the selenone to seleninate rearrangement, but the principal fragmentations of the isomerized ion no longer include expulsion of the alkoxy radical. For example, dipropyl selenone decomposes to give roughly comparable amounts of PrO^+ and $PrSeOH^{+\cdot}$ (equation 20). Apparent loss of O_2



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either as such or via a two-step process is also characteristic of higher homologues, but it is not possible to rule out trace quantities of the dialkyl selenides being present initially or formed thermally on the sample introduction probe of the mass spectrometer.

A unique rearrangement occurs for the dibutyl selenone. Apparently a double hydrogen rearrangement occurs with expulsion of $C_4H_7^{\cdot}$, which is followed by loss of $C_4H_9^{\cdot}$ (equation 21).

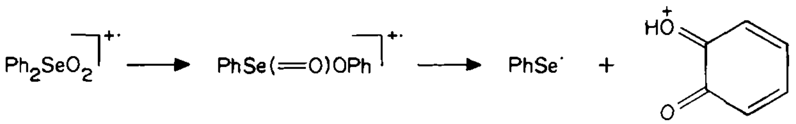
$$\left.\mathrm{Bu_2SeO_2}\right]^{+\cdot} \longrightarrow \left.\mathrm{BuSe(OH)_2CH_2CH{=}CHCH_3}\right]^{+\cdot} \longrightarrow \left.\mathrm{BuSe(OH)_2}\right]^{+} \longrightarrow \left.\mathrm{Se(OH)_2}\right]^{+\cdot} \qquad (21)$$

M. Diaryl Selenones (Ar_2SeO_2)

Diaryl selenones undergo extensive rearrangement reactions, similar to diaryl selenoxides, an observation not unexpected given the greater migratory aptitude of aryl groups. These rearrangements find precedent in diaryl sulphone mass spectral reactions as well. Thus, the base peak in the mass spectrum of diphenyl selenone arises by elimination of $PhO^{\cdot}$. Furthermore, PhO^+ formation presumably occurs in competition with the elimination of $PhO^{\cdot}$ (equation 22). Both of these fragment ions undergo consecutive decarbonylation reactions to give the abundant $C_5H_5Se^+$ and $C_5H_5^+$ daughters, respectively.

$$\left.\mathrm{Ph_2SeO_2}\right]^{+\cdot} \longrightarrow \left.\mathrm{PhOSe({=}O)Ph}\right]^{+\cdot} \longrightarrow \begin{cases} \mathrm{PhSeO} \\ \mathrm{PhO^+} \end{cases} \qquad (22)$$

Reductive elimination of SeO_2, of Se following loss of O_2 (or O + O) and of SeO are other noteworthy features of the decomposition reactions of the diaryl selenones and appear to be general processes. Finally, all of the diaryl selenones investigated by Rebane show losses of $ArSe^{\cdot}$. This interesting rearrangement may be a route to protonated *o*-quinoid structures as pictured for the diphenyl compound in equation (23). Evidence for this hypothesis is the stepwise elimination of two CO molecules from the presumed *o*-quinoid ion, as confirmed by detection of appropriate metastable ions.



(23)

N. Organo-selenium and -tellurium Dihalides

Several organoselenium dihalides, R_2SeX_2 (R = Me, Pr, Ph; X = Cl, Br), as reported by Rebane[37], provided quite untrammelled mass spectra. Loss of a halogen was the first process in all cases studied, and that reaction was so facile that a parent ion was often not observed; $X_2^{+\cdot}$ was also very weak or not observed. The $[M - X]^+$ ion, in one common mode of fragmentation, eliminated the second halogen, thus presumably providing an organic selenide radical cation identical to that directly available by ionizing the neutral selenide; it presumably would be capable of the same fragmentations. The other mode of fragmentation, in which the remaining halogen stays with the Se, involved fracture of one or both Se—C bonds, or cleavage of a C—C bond α to the Se, with or without an associated H migration.

Mass spectra of dihalides of cyclic selenides have also been investigated by Rebane[37] and by Kulkarni and coworkers[43].

Futekov and coworkers[60] reported in passing that several compounds of the type R_2SeCl_2, in which R represents a monochloro, saturated alkyl group, cyclic or not, presented mass spectra exhibiting the parent ion as well as successive losses of Cl and of HCl. Their suggestion that the departing halogen and hydrohalogen species arose from the hydrocarbon portions and were not attached to the Se is probably an untenable speculation in light of the work of Rebane just mentioned.

Dimethyltellurium diiodides and tetraiodides were studied by Smith and Thayer[61]. The highest mass ions they observed in both cases were those of $Me_2TeI^{+\cdot}$ and a trace of TeI_2^+. The major ion corresponded to $I_2^{+\cdot}$ and other ions corresponding to $MeTeI^+$, TeI^+, Me_2Te^+, $MeTe^+$, MeI^+, $Te^{+\cdot}$ and I^+ testified to the rather straightforward decompositions induced by electron ionization of these molecules.

O. Selenium Ylides

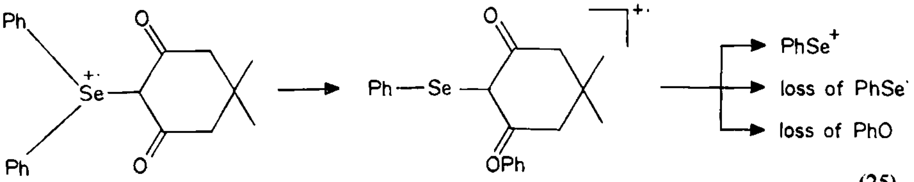
A brief description of the mass spectrum of (diacetylmethylene) diphenylselenurane was reported by Wei and coworkers[62]. Other than loss of Me group and loss of the complete diacetylmethylene groups, the spectrum exhibited the features of diphenyl selenurane; viz.: $Ar_2Se^{+\cdot}$, $ArSe^+$, $Ar_2^{+\cdot}$ and Ar^+.

A more complete study of the mass spectra of selenium ylides was made by Terent'ev and coworkers[63]. They observed the parent ion for all seven of the ylides which they studied; in fact, the molecular ion was quite abundant possibly because of ready ionization at the anionic site (equation 24).

$$R_2\overset{+}{Se}—\bar{C}R_2 \rightarrow R_2\overset{+}{Se}—\dot{C}R_2 + e^- \qquad (24)$$

Invariably, the main fragment ions corresponded to the rupture of the ylide bond ($R^1R^2Se—C$) accompanied by H transfer from R^1R^2 when $R^1R^2 = —C_4H_8—$. Thus, species such as $R^1R^2Se^{+\cdot}$, $R^1Se = R^2H^+$, R^1Se^+ etc. could be explained.

More striking was the transfer of Ph from Se to the O of the anion moiety which was postulated to explain the losses of PhSe and PhO and the formation of $PhSe^+$ (equation 25). Various explicable purely organic species were also observed, but $SeH_2^{+\cdot}$, $RSeO^+$, $RSeOH^{+\cdot}$ and $RSeH^{+\cdot}$ ions were not observed even though these are characteristic of selenides and selenoxides.



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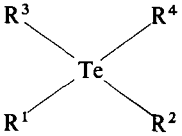
P. Diorganotellurium Dicarboxylates

A fairly thorough study of the mass spectra of some diorganotellurium dicarboxylates was reported by Adley and coworkers[64] (see Scheme 4). The carboxylate groups were either acetate or benzoate; the organo groups were: Ph, *p*-An, or *p*-$EtOC_6H_4$. Among the general features were: (1) The parent ions never exceeded 0.05% Σ_{40} and mostly were not observed. Alternate ionization methods are recommended for these compounds. (2) Purely organic ions were important in the spectra, particularly species such as the biphenyl ion. (3) Loss of one complete carboxylate group from the parent ion always occurred and the resulting ion generally showed loss of the second carboxylate group as part of its fragmentation pattern. (4) By contrast, loss of an aryl group was not favoured, particularly when the aryl group was Ph. (5) By shedding of various groups and Te extrusion, some arylcarboxylate ions (e.g. $PhOAc^+$) were observed. (6) Small fragments such as $TeCH_2^+$ turned up, but were not important in the spectra.



$R^1 = R^2 = Ph$
$R^3 = R^4 = CO_2Me$

$R^1 = R^2 = p\text{-}An$
$R^3 = R^4 = CO_2Me$

$R^1 = R^2 = Ph$
$R^3 = R^4 = CO_2Ph$

$R^1 = Ph$, $R^2 = p\text{-}PhOC_6H_4$
$R^3 = R^4 = CO_2Me$

$R^1 = R^2 = —C_4H_8—$
$R^3 = R^4 = CO_2Me$

$R^1R^2 = —C_4H_8—$
$R^3 = R^4 = CO_2Ph$

SCHEME 4

Additionally, Adley and coworkers ordered the groups according to their facility to detach from the central Te atom: acetate ≈ benzoate > p-$EtOC_6H_4$ ≈ p-An > Ph. Disubstituted tellurium ions, observed in the course of decomposition of the tetrasubstituted species or by direct ionization of the disubstituted neutrals, behaved similarly. However, the trisubstituted species, again arising in the fragmentation of the tetrasubstituted species, behaved somewhat differently. Most interestingly, the loss of acetate, for example, was not a single-step process but rather required loss of ketene followed by loss of OH, whereas the loss of benzoate was direct.

Necessarily, some rearrangements must occur to account for the formation of biphenyl and other ions with two originally ligated groups conjoined: the conversion of $PhCOOTeAr^{+\cdot}$ to $PhTeAr^{+\cdot}$ with loss of CO_2, loss of RCO_2 from $C_4H_8TeOCOR^+$, as well as the loss of C_2H_4 from $biaryl^{+\cdot}$ ions.

Q. Seleninic Acids and Selenocyanates

The first report of the mass spectra of methaneseleninic acid, CH_3SeO_2H, its methyl ester, and benzeneseleninic acid, $PhSeO_2H$, and its methyl ester was made by Rebane[65] in 1974. As for selenones and selenoxides, methaneseleninic acid rearranged after electron ionization to yield $[MeOSeOH]^{+\cdot}$ and MeO and CH_2O were then lost. The other decompositions were predictable. Similar rearrangements occurred for benzeneseleninic acid en route to formation of $[C_6H_6O]^{+\cdot}$, for example, and for a variety of substituted benzeneseleninic acids. Although the molecular ions were of low abundance, they were detectable, and the mass spectra were consistent with the structures of the acids and esters.

More recently, the mass spectra of the benzeneseleninic acid class were reported again in two papers by Benedetti and coworkers[66,67]. No mention was made of the earlier work of Rebane. By far the most notable feature of the mass spectra of these compounds was that they were dominated by peaks corresponding to diphenyl diselenide ions and their daughter fragments. The spectra were totally different to those reported by Rebane[65]. The fragment ions were presumed to arise via a probe reaction prior to ionization. After ionization, the fragmentation behaviour of the diphenyl diselenide ion was that already discussed. Of lesser importance was the occurrence and the fragmentation of $Ph_2SeO^{+\cdot}$-type species, giving $PhSeO^+$ and $PhSeOH^{+\cdot}$, for example. Again, these were analogous to the selenoxide–selenate rearrangements discussed earlier.

Regardless of the presence of a substituent (X = m-Cl, p-Cl, m-Br, p-Br, m-NO_2, p-NO_2, *p*-Me) on the Ph ring or of the position of the substituent, the principal fragmentation mechanisms remained the same. The authors cited several species such as $XC_6H_4Se^+$, $XC_6H_4^+$, $C_6H_4^{+\cdot}$ as possible daughters of an originally ionized acid molecule. However, peaks corresponding to these ions had slight intensities in the spectrum and the ions may have originated by other decomposition routes. Low intensity peaks in appropriate multiplets were observed at *m/z* ratios ascribable to $XC_6H_4SeOC_6H_4X$ moieties. This species surely arises as part of the thermally induced probe reactions.

The appearance of ions with masses appropriate to $C_6H_4OH^+$, $XC_6H_5^{+\cdot}$ and $XC_6H_4OH^{+\cdot}$ argued for a possible parent acid molecular ion (not seen in the spectrum) which rapidly eliminated SeO and then lost either CO or X. The loss of SeO was supported by metastable ion studies.

In the case of the nitro-substituted benzeneseleninic acids only, the steps of formation of selenoxide ion via a 1,2-shift of $NO_2C_6H_4$ group to O, then loss of NO_2 groups and Se to give $C_6H_4OC_6H_4^{+\cdot}$ (possibly a dibenzofuran radical cation) was supported by a metastable ion. This ion was not observed by Rebane in his earlier study[65]. The dramatic differences in spectra reported by these two authors point to the requirement of careful sample handling during sample introduction into the mass spectrometer. We suggest that a more reliable way of mass spectral analysis of these seleninic acids would be to employ fast atom bombardment.

Finally, Benedetti and coworkers[67] presented a study of the mass spectrum of *m*-nitrophenyl selenocyanate. This compound presented a very abundant molecular ion and subsequent fragments. Here too, the diselenide and its fragment ions were present, but at much reduced abundance when compared to the seleninic acids. The selenocyanate parent ion itself fragmented by rather expected routes: initial loss of CN, NO_2 or Se followed by subsequent losses such as CN, NO_2, Se, CO, NO, HCN. A variety of small-mass hydrocarbon ions as well as the species C_3HSe and HCSe were explained in the authors' proposed decomposition reaction schemes.

R. Carbonate Analogues

Dimethyl carbonate analogues with S and/or Se were studied by Drager and Gattow[6]. It is worth recalling that, after ionization, MeOCOOMe itself primarily ejects H and neutral CO_2 to yield $CH_2{=}OMe^+$. Although the charged species $CS_2^{+\cdot}$ was observed in the spectrum of MeSCSSMe, it is unlikely that the $CS_2^{+\cdot}$ arose directly from the molecular ion. Since the ionization potential of neutral Me_2S is about 8.7 eV, and that of neutral CS_2 is about 10 eV, the charge of a parent ion should be retained by the Me_2S fragment rather than by the CS_2 portion. Rather, we propose that the origin of CS_2^+ was by loss of Me from $MeSC{=}S^+$.

For the case of MeSeCSSMe, the expected preferential cleavage of the Se—C bond was observed, giving $S{=}CSMe^+$ as the base peak in the spectrum. Again this species ejected $Me^\cdot$ to give $CS_2^{+\cdot}$. Because the alternate route involving initial loss of MeS by cleavage of a C—S bond to produce $S{=}C{=}\overset{+}{S}eMe$ is less significant, only a small peak due to $SeCS^{+\cdot}$ was expected and was observed. There is no reason to believe that the Se atom in the original molecule does not bear a Me group.

The compound Me_2CSSe_2, according to expectation and to the NMR spectrum, shows both Se atoms bearing Me groups. The high abundance of $SeCS^{+\cdot}$ in the decompositions is explicable regardless of S and Se positions, but were the structure of the parent ion $MeSeCSeSMe^+$, there should be at least some fracture of a C—S bond giving rise to $MeSeCSe^+$ which in turn ought to yield $CSe_2^{+\cdot}$. However, no $MeSeCSe^+$ was observed. With two Se atoms present in the parent, the occurrence of the species $Se_2^{+\cdot}$, Se_2Me^+ and $(MeSe)_2^{+\cdot}$ is not startling.

When the compound Me_2CSe_3 is ionized, the parent ion is not so abundant as in the previous cases; CSe_2^{+} becomes the base peak. In all of these cases, the lower mass region contains several of the by-now-familiar fragments such as $SeCH_x^{+}$($x = 1$–3).

S. Urea Analogues

Kirkien and coworkers[68] extended their study of the mass spectra of numerous *N*-substituted ureas and thioureas to include five selenoureas, and two related selenothiocarbamic esters. In addition to graphical representations of the actual spectra, they presented a tabular summary of the features they considered important in comparable $R^1R^2NCXNR^3R^4$ compounds (X = O, Se; R = H, Me, Ph). There appears to be some disagreement between the numbers shown in their Table 2 and the data found in their references (in particular, the *m/z* and relative intensity data for $H_2NCSNHPh$ and for $Me_2NCSNHPh$). Nonetheless, the reader may find the article useful in identifying spectra or in rationalizing spectra of related compounds.

A few generalizations can be drawn from their table: there is a very strong tendency to produce a $R^1R^2NH^{+\cdot}$ species when at least one of the R groups is Ph. By contrast, evidence for the same sort of species when the R groups are H or Me is minimal or vanishingly small. The S analogue species exhibit the greatest tendency to form intact molecular ions. Falling outside the authors' standard set of fragmentation behaviors is the loss of SePh from $Me_2NCSeNHPh$ to give the base peak at *m/z* 71. Expulsion of HSe is also notable. On the other hand, the 1,1-diphenyl analogue, $H_2NCSeNPh_2$, shows loss of HSe, H_2Se and SePh, but derives its base peak from the *m/z* 51 ion, a standard fragment of the Ph group.

The other 'standard fragmentation behaviours' must involve cleavage at the carbonyl C—N bond, with the charge apportioned to either of the resulting fragments and with or without H migration in either direction. Needless to say, most of the observed fragments can be fitted to such a set of behaviour patterns, especially when migration of H or R groups to the O or chalcogen atom is added to the list of possibilities. Some of the same patterns were observed, in part, in the fragmentation patterns of the selenothiocarbamates although some rather more complicated mechanisms would have to be invoked to explain the prominent occurrence of $[M - SeMe]^+$ for $Me_2NCSeSMe$ or of $PhCN^+$ from PhHNCSeSMe.

The authors concluded that the Se compounds generally emulate the S analogues more closely than the O analogues, particularly as R group migration to Se is involved, and that the charge of the molecular ion must be 'largely centred on the selenium atom'.

T. Selenophenes and Tellurophenes

When one turns to the mass spectrometric behaviour of this aromatic class of organochalcogen compounds, it is found that Fringuelli and Taticchi[69] have provided a

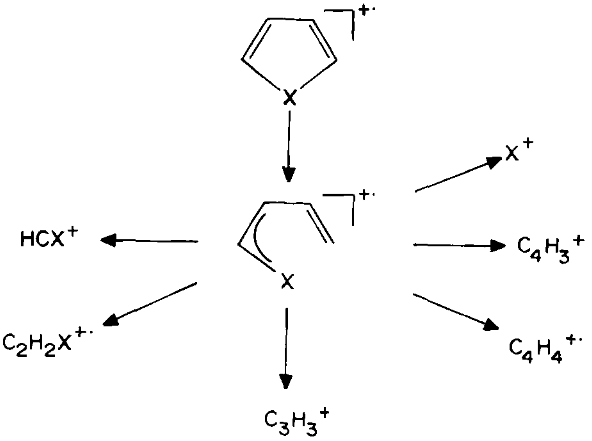
TABLE 2. Percent total ionization between *m/z* 29 and $M^{+\cdot}$

	C_4H_4O	C_4H_4S	C_4H_4Se	C_4H_4Te
$M^{+\cdot}$	26.8	30.4	44.8	44.4
$[M - CHX]^+$	43.2	8.3	3.3	0.4
$[M - C_3H_3]^+$	6.8	17.5	5.2	1.1
$[M - C_2H_2]^{+\cdot}$	3.0	19.7	16.6	4.1
$[M - HX]^{+\cdot}$		1.1	5.7	6.6
X^+			4.8	21.6
$[M - X]^+$			0.8	3.8
$[M - H]^+$				2.0

useful comparison by a study of the furan to tellurophene series of model compounds. The principal fragmentations noted for the unsubstituted members of the series are summarized in Table 2.

That S and Se exhibit the most closely similar behaviours within this family is aptly illustrated by these data. Fairly regular variation in a single direction is exhibited for the most part. Only Se and Te atoms show any propensity to be eliminated as monatomic neutrals or by retaining the charge as monatomic cations.

This authors were able to suggest a few decay routes which rationalize the observed spectra (Scheme 5).



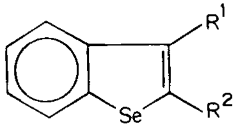
SCHEME 5

A parallel statement by Barton and coworkers[70] regarding the furan class with chalcogen replacement reads: 'Thus there is a great variety in the modes of decomposition of excited Group VI heterocyclopentadienes, but at the same time there is a high degree of continuity in going from furans to tellurophenes with selenophenes providing a key link in that continuity at the interface of the non-metallic elements of the group with the metallic members of the group.'

Further, Barton's group reported the mass spectra of selenophenes and tellurophenes with a Ph group substituted in either the 2- or 3-position, and mono- or tri-substituted with D. Of two important observations, one was that a compound substituted with a Ph group, regardless of location, gives a mass spectrum with the same fragmentations as those of the unsubstituted heterocycles except for the straightforward offset of some peaks by 77 units due to the presence of Ph; the other was that the photolytic decompositions of these parent molecules are also dominated by the loss of Se, or of Se and HCSe.

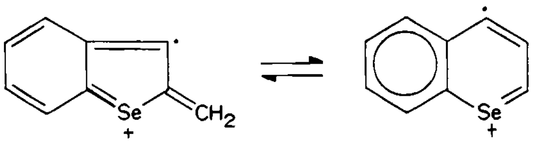
U. Benzoselenophenes and Related Compounds

A set of 18 disubstituted benzo[*b*]selenophenes (**12**) substituted in the 2- and 3-positions was studied by Croisy and coworkers[71]. When either R^1 or R^2 = Me, the molecular ions were the most abundant ions seen. Where the substitution was appropriate, rearrangements in the category of '*ortho* effects' occurred just as for other 1,2-disubstituted aromatic compounds. For example when R^2 = Me and R^1 = CO_2H or CO_2Me, losses of H_2O or MeOH were found. In a consecutive reaction, loss of CO occurred to give **13** which was postulated to undergo expansion to give the interesting radical cation **14** (equation 26).



(12)

When $R^1 = OH$ and $R^2 = CO_2Et$, the '*ortho* effect' rearrangement led to elimination of EtOH which was followed by expulsion of two molecules of CO to yield **15**. The structures are purely speculative as little supporting evidence involving isotopic labelling, metastable or collisional activation spectra of the ions was obtained.



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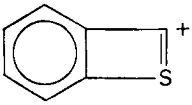
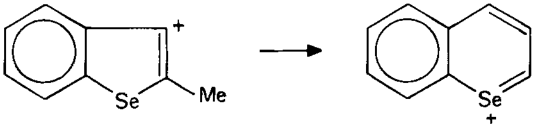


(13) **(14)** **(15)**

Closed-shell ions possibly of similar structure were found as products in many of the mass spectral decompositions of substituted selenophenes. For example, when $R^1 = COR$ and $R^2 = Me$, the expected losses of R followed by CO occurred to give ion **16** which might undergo ring-expansion to **17**, a rearrangement entirely analogous to the tolyl–tropylium ion interconversion. Losses of H from the Me group of Me-substituted selenophenes might also be accompanied or followed by a similar ring-expansion to give substituted selenopyrylium ions. Additional evidence from metastable ions or collisional activation spectroscopy and from isotopic labelling should be gathered before the ring-expansion hypothesis is accepted.



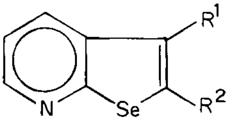
(27)

(16) **(17)**

Isomers which involve interchange of the substituents R^1 and R^2 could be detected in some cases by comparison of quantitative peak intensities in the mass spectrum. The consecutive losses of R and CO were more prevalent when COR was R^2 than when it is R^1 (in **12**).

It is noteworthy that loss of Se from these disubstituted selenophenes was *not* observed except when a second Se atom was introduced into a side-chain of the molecule. This contrasts with the mass spectrum of the parent or unsubstituted benzoselenophene. The chemistry of disubstituted benzoselenophenes is entirely analogous to other 1,2-disubstituted aromatics. The decomposition reaction to expel Se is preempted by other, more standard, fragmentation processes such as *ortho* effects, loss of substituents, etc.

Croisy and coworkers[2] have also reported the mass spectra of 13 selenolo[2,3-b]pyridines (**18**) including the parent compound and mono- and di-substituted analogues. The unsubstituted compound, like selenophene, gave the molecular ion as the most abundant species. For **18** and selenophene, ca. 50% of the total ion current was carried by



(18)

the molecular ion. Fragmentation of **18** was a composite of that of selenophene and quinoline; i.e. losses of C_2H_2, HCN and Se were observed, the latter being in 36% relative abundance.

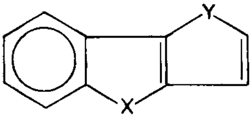
Me-substituted **18** showed more extensive fragmentation when ionized. The expected loss of H might be followed by ring-expansion. Losses of Se and HSe (possibly in two steps) were still observed. Substitution with COR, where R = H, Me or OEt, led to fragmentation by loss of R to give abundant $ArCO^+$ ions which then decarbonylated to form Ar^+. No loss of Se was observed, presumably because the decomposition reactions involving COR were of lower critical energy.

The compound with an OEt substituent gave an unexpected mass spectrum. Unlike ethyl aryl ethers, no loss of C_2H_4 to give ArOH was found. Instead losses of Et and OC_2H_4 occurred. No explanation has been put forth.

For disubstituted compounds such as those with $R^1 = OH$ and $R^2 = CO_2Et$, the expected loss of EtOH ('*ortho* effect') occurred, just as for the corresponding benzoselenophene, to give the most abundant ion in the spectrum. This type of rearrangement was not found when $R^1 = Me$ and $R^2 = CO_2Et$, however.

The decomposition reactions of these substituted compounds are also typical of mono- and di-substituted aromatic molecules, and they have low energy barriers which preempt the loss of Se which is so prevalent for the unsubstituted prototype.

The mass spectra of some tricyclic analogues **19** and **20** where X and Y = S or Se have been studied by Jacquignon and coworkers[72]. The molecular ions were relatively stable yet losses of Se were facile processes. When X = S and Y = Se, the greatest propensity to lose Se was found ($[M - Se]^{+\cdot}$ carried ca. 20% of the total ion current). When Se and S were interchanged (X = Se, Y = S), loss of Se was somewhat attenuated, which may suggest that the selenophene ring is more stabilized when fused to two other aromatic rings.



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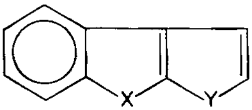

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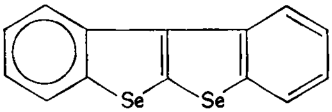
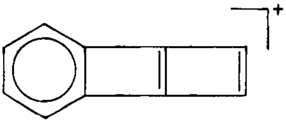


(21)

When X = Y = Se, consecutive losses of both Se atoms were observed, and this was the major decomposition route for this ionized compound. Losses of two Se atoms were also characteristic of **21**[73]. The structural possibilities for the $[M - 2Se]^{+\cdot}$ are intriguing. Could it be **22**, a benzyne analogue of naphthalene (**23**) or diethynyl benzene (**24**)?



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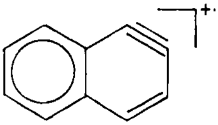
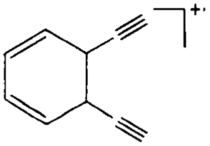


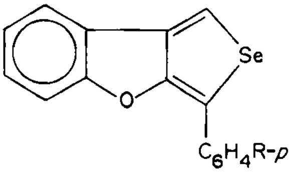
(23)



(24)

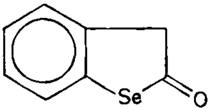
Other fragmentations such as losses of C_2H_2, CS or CSe compete only weakly for this series of compounds. Once again the ability of unsubstituted selenophene radical cations to undergo reductive elimination of the Se is seen.

Shafiee and Behnam[51] prepared a series of seleno[3,4-*b*]benzofurans (**25**), but the mass spectrum of only one member of the series (R = OMe) was reported. The molecular ion was the most abundant.

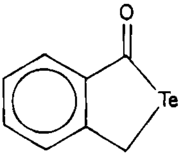


(**25**)

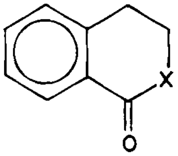
Evers and coworkers[74] reported the preparation of a number of benzochalcogenophenones, and mass spectra were obtained for several compounds. In the case of the benzo[*b*]selenophene-2(3*H*)-ones (**26**), a selenolactone model, and closely related structures, the mass spectral behaviour was characterized by the strong presence of the parent ion, the loss of the monocarbon species, either CO or HCO, and of Se.



(**26**)

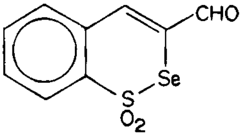


(**27**)



(**28**)

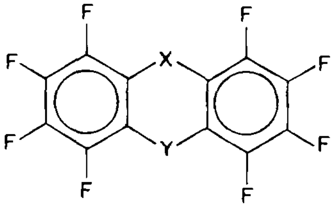
In the case of $^1H,^3H$-benzo[*c*]tellurophen-1-one (2-tellurophthalide) (**27**) Loth-Compere and coworkers[75] were able to ascertain that the expulsion of monatomic Te generally preceded the loss of CO or HCO. Their comparison of the fragmentations of the Te-, Se- and S-containing analogues of **28** illustrated anew the pivotal position of Se. Se approximated the behaviour of S in participating in a retro-Diels–Alder reaction via emission of CH_2S or CH_2Se (like the familiar formaldehyde loss), or in suffering the loss of CO or of HCO while the Te compound showed one-fourth to one-half the propensity for these decay routes. On the other hand, both Se and Te species were capable of producing $C_8H_8^{+\cdot}$ and $C_9H_4O^{+\cdot}$. Indeed, $C_8H_8^{+\cdot}$, presumably the cyclooctatetraene radical cation, was the most abundant in the decomposition of the Te compound. As has been often observed, the chalcogens can be viewed to exhibit metallic behaviour by exiting from the species to which they had been bound. For example, this process of reductive elimination is also exhibited by Se- and Te-containing heteroaromatics.



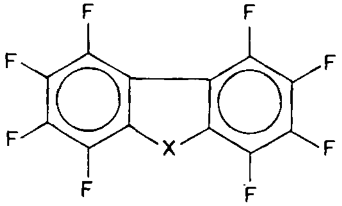
(**29**)

Van Coppenolle and Renson[76] reported a molecular ion for a selenosulphone (**29**) which lost an SO_2 molecule and gave an ion corresponding in formula and fragmentation to that obtained directly from formyl-2-benzo[*b*]selenophene.

Cohen and coworkers[77] presented considerable detail concerning the mass spectra of two classes of compounds, represented by **30** and **31**, which are related in their mass spectra even more than they may appear to be according to their structures.



(30)
X = Y = S
X = Y = Se
X = S, Y = Se



(31)
X = S, Se, Te

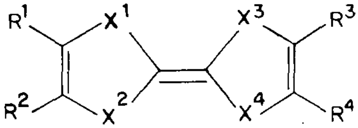
Through the use particularly of metastable studies, the authors were able to discern many implications in the spectra of these species. For compound **30** with one or two S atoms, the ion current was distributed broadly among various ions, but these need not concern us here. When two or even one atom of Se was present, the spectra were more straightforward. For example, with X = Y = Se, the major ion resulted from loss of Se from the parent ion. The parent ion itself, $[M - Se]^{+\cdot}$, $[M - 2Se]^{+\cdot}$ and $Se_2^{+\cdot}$ accounted for 73% of the total ion current. When X = S and Y = Se, the parent ion was relatively abundant, but the ion $[M - Se]^{+\cdot}$ provided the base peak and these two peaks alone accounted for nearly 75% of the total ion current.

For compounds of structure **31** the parent ions were so dominant as to account for over half of the ion current. The S compound showed the greatest stability of its parent ion, but the Se and Te analogues demonstrated increasing tendencies to lose neutral Se or Te atoms (10.2% and 17.1%, respectively, of the total ion current). Other ion current was attributable to a myriad of species which had diminished numbers of C and F atoms with or without chalcogens.

The substantial degree of fragmentation via loss of Se is once again cited by these authors as a reflection or indicator of a relatively weak C—Se bond strength. This must be tempered by the observation that loss of Se is more favoured when there is an S atom across from it than when two Se atoms are present. In part, this probably reflects the greater stability of the tricyclic product when the S atom is a part of the central ring. It is also bemusing to note the authors' comment: 'Another common reaction is the loss of neutral F' among the many metastable-ion-supported fragmentations of fluorocarbon groupings, with or without a chalcogen. What, if anything, does this suggest regarding strength of the C—F bond?

V. Fulvalene and Pentalene Analogues

The mass spectra of Se analogues of tetrathiofulvalenes (TTF) (**32**) were reported by Andersen and coworkers[3]. In these compounds, all of, or two of, the S atoms, symmetrically or not, across the inversion centre of the molecular core, were replaced by Se. Various substituent groups were attached to the periphery of the molecules.



(32)

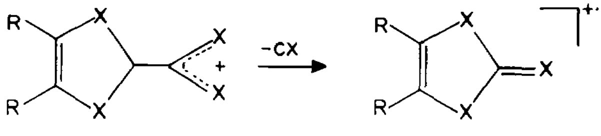
(a) All $R = H$; all $X = Se$
(b) All $R = Me$; all $X = Se$
(c) All $R = Me$; $X^1, X^3 = S$; $X^2, X^4 = Se$
(d) All $R = Me$; $X^1, X^4 = S$; $X^2, X^3 = Se$
(e) $R^1, R^3 = H$; $R^2, R^4 = Me$; all $X = Se$
(f) $R^1, R^4 = H$; $R^2, R^3 = Me$; all $X = Se$
(g) $R^1, R^3 = H$; $R^2, R^4 = Ph$; all $X = Se$
(h) $R^1, R^4 = H$; $R^2, R^3 = Ph$; all $X = Se$
(i) $R^1, R^3 = H$; $R^2, R^4 = Me$; $X^1, X^3 = S$; $X^2, X^4 = Se$
(j) $R^1, R^3 = H$; $R^2, R^4 = Me$; $X^1, X^4 = S$; $X^2, X^3 = Se$
(k) $R^1R^2 = —(CH_2)_3—$; $R^3R^4 = —(CH_2)_3—$; all $X = Se$
(l) $R^1R^2 = —(CH_2)_3—$; $R^3R^4 = —(CH_2)_3—$; $X^1, X^3 = S$; $X^2, X^4 = Se$
(m) $R^1R^2 = —(CH_2)_3—$; $R^3R^4 = —(CH_2)_3—$; $X^1, X^4 = S$; $X^2, X^3 = Se$

This thorough study made good use of field ionization (FI); the observation of only the molecular ions in the FI spectra demonstrated the high purity of the samples. Thus, the electron impact spectra were open to interpretation without fear of being misled by peaks arising from impurities or from prior thermolysis.

A number of fundamental patterns were observed. As is the case for many other compounds, the ease of elimination of Se was greater than for S. But this Se loss, commonly observed in Se organics, was only of 1–6% relative abundance for this class. The loss of C_2R_2 was most important for the tetraseleno class, less so for the dithiadiseleno class, and least important for the tetrathia class, in support of the idea that the C—Se bond is relatively fragile. Although the loss of SCR had a relative abundance up to 43%, no loss of SeCR occurred detectably.

The authors pictured the primary products as originating either directly from the parent ion or via parallel routes, all substantiated by metastable ion studies.

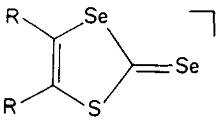
One particularly noteworthy rearrangement reaction takes place (see equation 28) starting with the $[M - C_2R_2]^{+\cdot}$ fragment 33. When the diselenodithia compound is



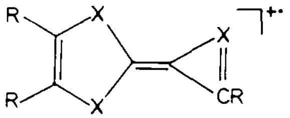
(28)

(33) **(34)**

involved, the only product is 35. The intermediate species can be viewed as reacting with a preferred migration of a five-membered ring moiety onto the Se atom, followed by elimination of CS. A second intermediate 36 is formed from the parent ion by initial loss of XCR. It subsequently loses C_2R. Since no corresponding loss of SeCR was observed, this route must be blocked for the tetraseleno analogues.

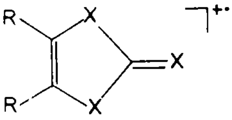


(35)



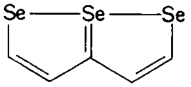
(36)

Undoubtedly, an important factor in the fragmentation of the TTF-type compounds is the production of species **37**, the stability of which has already been demonstrated by the mass spectra of the corresponding neutrals, which invariably show the molecular ion as the most abundant.

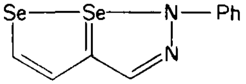


(37)

A small group of rather unusual, conjugated fused ring structure species was studied by Moller and coworkers[78]. The two basic structures are shown as **38** and **39**. Part of the incentive for studying this group of compounds arose from the linear arrangement of the chalcogen atoms and the implied three-centre, four-electron bonding. Some possible reflection of these unusual features was anticipated in the mass spectra. What was observed for **38** and derivatives was a very abundant molecular ion, often providing the base peak of the spectrum; the inevitable loss of Se_2, confirmed by a metastable ion, occurred in parallel with or followed by losses of Se or HSe. Note that there was no loss of S_2 by the S analogues for which, rather, losses of SH, S_2H and S_2H_2 were observed.

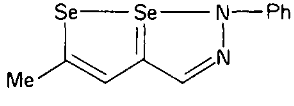


(38)
1,6,6aλ^4-Triselenapentalene

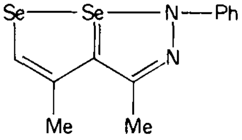


(39)
Phenyl-1,6aλ^4-diselena-5,6-diazapentalene

For the class of compounds represented by **39**, about 50% of the molecular ions fragmented to give Ph^+ when the N atom bore a Ph group. For compound **40**, losses of Se_2 and PhN_2 led to the formation of $C_5H_5^+$. However, for compound **41**, only a trace of $C_6H_7^+$ was observed.

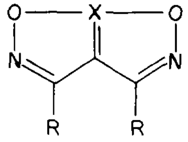


(40)



(41)

A rather interesting class of compounds (**42**) was studied by Perrier and coworkers[79]. By analogy with the symmetric trithiapentalenes, this 2,5-diaza-1,6-dioxa-6aλ^4-thiapentalene and its Se and Te analogues are presumed to be bicyclic with the chalcogen atom assuming a tetravalent role.



(42)
R = H, Me
X = S, Se, Te

The stability of these species upon electron ionization is reflected in the high abundance of the molecular ion, which generally, gives the base peak. The formulae for the parent compounds are thereby demonstrated.

All species, after ionization, are capable of loss of first one and then a second NO molecule, leading to a cyclopropenone-type stoichiometry and, perhaps, structure. It is this $HC_3HTe^{+\cdot}$ species which provides the most abundant ion in the spectrum arising when R = H and X = Te.

A possible but less favoured alternative to the loss of the second NO is the loss of XO although it is about equally likely that the charge will remain with the XO as with the organic moiety.

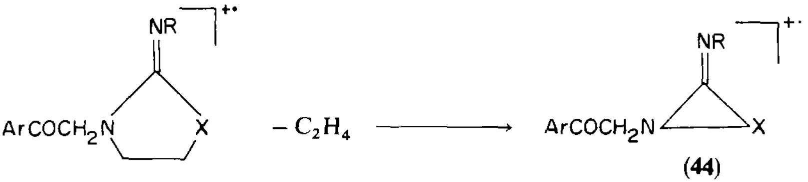
Loss of HCNO is observed when R = H, but there is no observed loss of MeCNO.

Finally, a few unusual decomposition reactions are observed: loss of HO when R = Me, X = Se and the appearance of $HC{\equiv}S^+$ or $HC{\equiv}Se^+$, but not $HC{\equiv}Te^+$, and of $H_3CC{\equiv}Se^+$. All in all, the spectra of this group are very similar to each other.

W. Complex Heterocyclic Compounds

In the category of the more complex monocyclic compounds, Jham and coworkers[80] have discussed some substituted thiazoles and the analogous selenazoles. They reported no major differences in the electron ionization mass spectral behaviour relating to the substitution of Se for S.

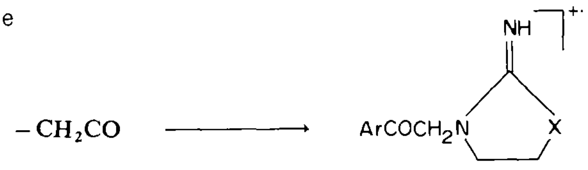
In addition to the predictable fragmentation behaviour such as release of Ph$^{\cdot}$, Ph$^+$, PhCO or PhCO$^+$, etc., the following were presented, based on metastable ion evidence and deuterium replacements of O—H and N—H hydrogens (equations 29–32).



(43) (44) (29)

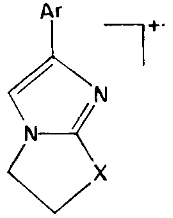
X = S, Se

If R = Ac:



(45) (30)

If R = H: $-\ H_2O \longrightarrow$

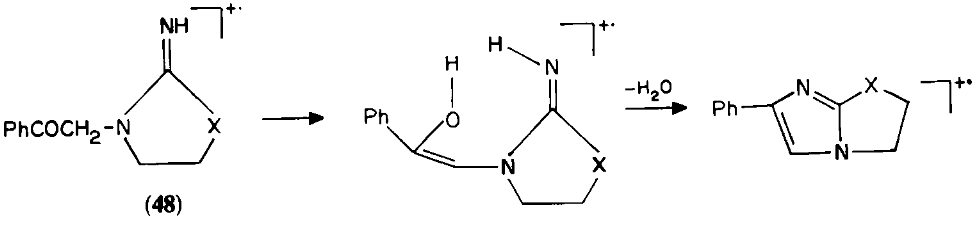


(46) (31)

If R = H: $-[H_2O, C_2H_4, HCN] \longrightarrow Ar{-}C{\equiv}C{-}N{=}X$ (32)

(47)

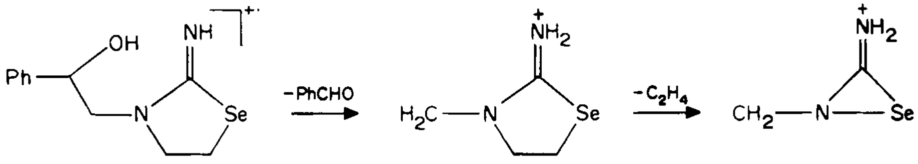
The rather startling loss of water from **49** was proposed to proceed via the mechanism in equation (33) leading to a highly conjugated, stabilized species. Replacement of an imine hydrogen by an alkyl group caused the water elimination to shut down, an observation in accord with the proposed mechanism. It is interesting to note that, in the case where R = Ac, a fragmentation specific for that species, elimination of CH_2CO with an H migration, should produce a species identical to the parent ion where R = H originally, except for possible differences in energy. Nonetheless, the authors did not report evidence for the novel water elimination from the $[M - CH_2CO]^{+\cdot}$ which was reported for the parent compound where R = H. Whether this process indeed does not occur when R originally equals Ac or the data relating to this process have been omitted by the authors is not clear.



(48) (49) (50)

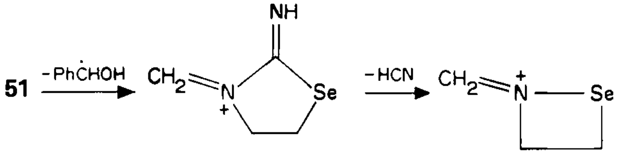
(33)

Both the Se and S compounds with R = H have, as the base peak in their respective mass spectra, ions which correspond in fact to an approximately 50/50 mixture of isobars arrived at through separate pathways: the first involved progressive loss of aldehyde and ethene (see equation 34); the second loss of PhCHOH and hydrogen cyanide (see equation 35).



(51) (52) (53)

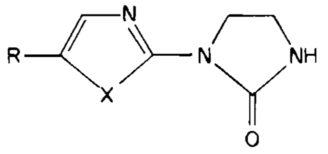
(34)



(54) (55)

(35)

For the class of compounds of type **56** it was postulated that the initial fragmentations, confined to the ring adjoining that containing the chalcogen, consisted of the ordinary eliminations of isocyanate-type species. These all appeared to originate in the cleavage of the C—N bond between the carbonyl carbon and the adjoining tertiary nitrogen.



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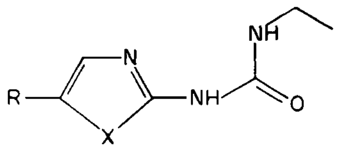
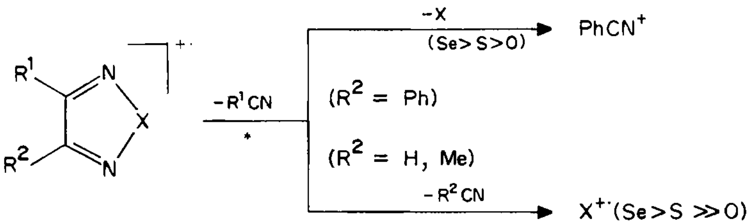


(57)

Similarly, compounds typified by **57** kept the chalcogen-containing ring system intact in all of the initial fragmentations of the parent ions so that no Se-specific chemistry was noted.

A thorough study of the mass spectra of 1,2,5-selenadiazoles, together with their O and S analogues, was carried out by Pedersen and Moller[81]. They worked at the lowest possible probe temperatures to minimize thermal decomposition of the samples, employed metastable defocusing techniques to support virtually all of their fragmentation pathways, and used exact mass measurements to ascertain the chemical formula of $C_5H_2N^{+\cdot}$ for m/z 76 which previously had been posited to be the benzyne ion.

Most of the important features of the observed spectra with the exception of the propensity for the ionized O-containing compounds to undergo NO emission are summarized by equation (36). In comparison, NS emission was observed only barely, and NSe not at all, from their respective analogous species.



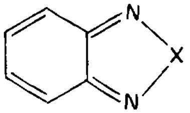
(58)

(36)

The molecular ions always appeared quite strongly, sometimes providing the most abundant species. To be noted is the consistent first fragmentation step of the loss of RCN. The chemical formula for the resulting species is $RCNX^{+\cdot}$ (X = O, S, Se). The authors raised the question of the structure of this species. The loss of X, which was strongest for Se of course, would appear to call for a simple cleavage of the N—X bond. However, other fragmentation products such as losses of CX and HCN neutrals argued for the rearrangement of RCNX$^{+\cdot}$. Comparison with spectra from PhNCX molecules did not completely answer the question, which remains open at this point.

In the presence of a Ph group, the charge of the ions tended to be retained on the organic moiety producing high abundances of species such as PhCN$^{+\cdot}$ and Ph^{+}. In the absence of a Ph substituent, the tendency for the charge to reside on those species containing S, and even more so, Se, was enhanced. Thus, when $R^1 = R^2 = H$, the dominant fragmentation was by progressive emission of HCN groups. Similarly, when $R^1R^2 = —C_4H_4—$, loss of HCN was by far the most important fragmentation process.

Arshadi[82] also studied the mass spectra of the 1,3-benzodiazoles with O, S and Se in the 2-position and found results parallel to those of Pedersen and Moller[81]. However, he also investigated the negative ions of these species—an unusual approach when it comes to organoselenium compounds although the author points out the propensity of these and similar compounds for electron capture and formation of molecular anions.

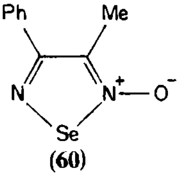


(59)
X = O, S, Se

All of the various species **59** exhibited formation of molecular anions at relatively high pressures (9×10^{-5} Torr) where there is an abundance of secondary electrons with approximately thermal energy. However, even at low pressure (1×10^{-6} Torr), the Se compound was able to form molecular anions in significant quantities (38% relative intensity).

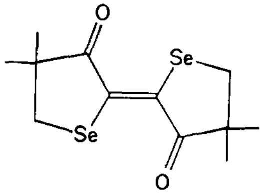
Dissociative electron capture processes produced very abundant amounts of CN$^-$ ion for all species under all circumstances, generally providing the base peak in the spectrum. In addition, the oxygen compound showed loss of NO from the parent anion, formation of CNO$^-$, and of very small amounts of O$^-$; the Se analogue predominantly gave CN$^-$ and Se$^-$ ions; and the S analogue was intermediate between the O- and Se-containing species in its behaviour.

Following the study of 1,2,5-selenadiazoles[81], Pedersen[83] reported the synthesis and mass spectra of some substituted 1,2,5-selenadiazole *N*-oxides. He found that the position of *N*-oxide could be detected; for example, **60** underwent a facile loss of MeCNO and little MeCN elimination was seen.



(60)

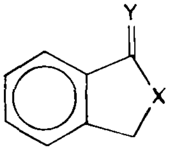
A particulaly straightforward fragmentation scheme largely appears to be followed by the molecular ion of **61** as reported by Fitjer and Luttke[84]. Although the base peak was provided by $C_3H_5^+$, the molecular ion showed a 79% relative abundance. The molecular ion mainly underwent a cycloreversion, expelling C_4H_8 (isobutene), followed by loss of CO. The second ring then emulated the first leading to formation of $Se_2C_2^{+\cdot}$, of undetermined structure. Besides a peak for $C_4H_8Se^{+\cdot}$, only hydrocarbon fragments, including that yielding the base peak, were to be found in the decompositions.



(61)

trans-3,3′-Dioxo-4,4,4′,4′-tetramethyl-2,2′-biselenolanylidene

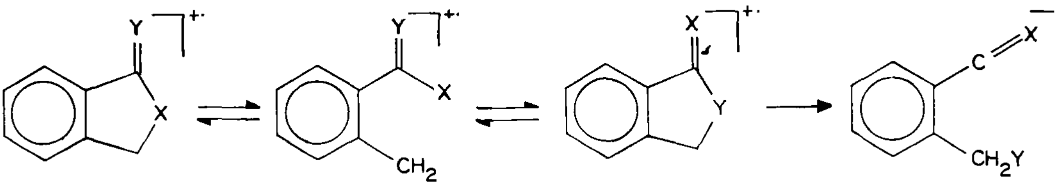
The mass spectra of phthalide, together with some S and Se analogues (**62**) were reported and discussed by McMurray and coworkers[85]. They observed that when both X and Y = O, the abundant parent ion gave rise to relatively abundant species (40–50% compared to the parent ion) corresponding to the loss of CHO and subsequent loss of CO, forming Ph^+ ion.



(62)

When both X and Y = S, the predominant decomposition of the abundant parent ion was via loss of CS and CHS, mimicking the O prototype. However, loss of monatomic S became significant here, along with some loss of CS_2, which introduced a route not observed when X = Y = O.

Compounds with mixed chalcogens, corresponding to X = O, Y = S, or X = S, Y = O, gave nearly identical spectra when ionized. Loss of CO, loss of CHO or CO then H, some loss of COS and a trace of S loss were all observed. The authors explained the near-identity of the spectra on the basis of a facile interchange of the X and Y atoms (see equation 37).

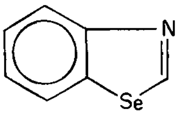


(63) **(64)** **(65)** **(66)** (37)

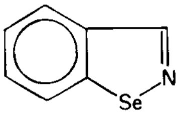
A similar interchange occurred when X = Se and Y = S or X = S and Y = Se; the spectra were nearly identical. Here, loss of Se was so pronounced as to give rise to the most abundant ion with the parent ion at only 40% relative abundance.

All of the fragmentations of this group of species can be explained by the authors' fragmentation schemes which invoke no unusual processes beyond the isomerization of the parent ion prior to decompositions.

The electron ionization induced decompositions of some model benzoselenazoles (**67**) and benzoisoselenazole (**68**) have been investigated by Croisy and coworkers[86]. It is informative to compare their spectra with benzothiazoles and benzoisothiazole (also reported in this paper) as well as with benzoselenophene itself (*vide supra*).



(67)



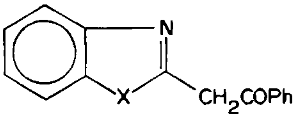
(68)

Both of the parent compounds underwent loss of HCN after ionization to yield $C_6H_4Se^{+\cdot}$ which then eliminated Se to give $C_6H_4^{+\cdot}$. In competition with this process was the expected reductive elimination of Se, which was considerably more favoured (by a factor of seven times) for the isoselenazole. Benzoselenophene also showed elimination of Se, but the corresponding benzoisothiazole and benzothiazole give barely detectable losses of S.

The loss of HCN shifted to an elimination of MeCN for both 2-methylbenzoselenadiazole and 3-methylbenzoisoselenazole. The loss of Se, CSe and H were competitive but the differences in the abundances in $[M - Se]^+$ could no longer be observed.

Replacing the Me groups with Ph groups led to expulsion of PhCN instead of MeCN. The isoselenazole now showed considerably more loss of Se and HSe (presumably in two steps) which permitted ready distinction of the two isomers.

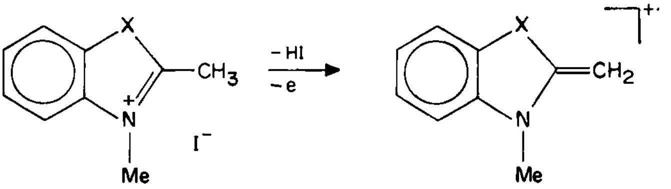
The mass spectrometric fragmentations of several 2-acylmethylbenzo-thia- and -selenazoles (**69**) were reported by Ciurdaru and coworkers[87] whose work was distinguished by the use of high-resolution as well as metastable ion studies. For these compounds very little of the fragmentation was determined by the presence of S or Se. Beyond the loss of PhCO, exhibited by all of the analogues studied, the Se-containing compound showed loss of Se which was not reflective of the other two compounds.



(69)

X = O, S, Se, NH (imidazoles)

Very similar fragmentations were found by Bologa and coworkers[88] when they attempted to introduce quaternary nitrogen salts of the structure **70** into the mass spectrometer. The salts lost HI and then evaporated and were ionized, presumably to give **71**. A preferred method for these compounds would be fast atom bombardment. Once again, with X = O, the principal decomposition was loss of CO, when X = S the loss was of SH and when X = Se the loss was of Se itself. Exact masses and the study of metastable species were used to advantage again in this study.



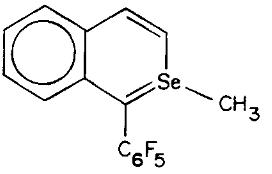
(38)

(70)

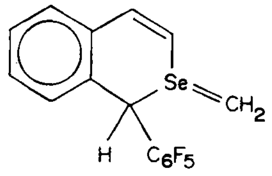
X = O, S, Se

(71)

Stackhouse and coworkers[89], in a report of the first example of a selenabenzene (**72**), presented its mass spectrum and those of related synthetic products (e.g. **73**). The mass spectrum was used to provide a fingerprint and to confirm the mass of the parent molecule through the parent ion. They presented no analysis of the mass spectra but it would appear that among the fragmentations were found some familiar and anticipated routes such as the loss of Se, and of H_xSe.

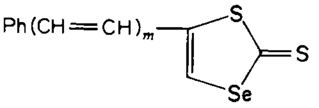


(72)

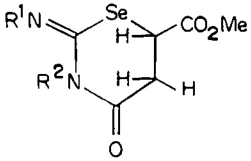


(73)

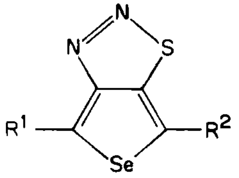
A number of complex heterocyclic organic molecules containing Se have been subjected to mass spectrometric examination by Shafiee working with a number of different colleagues[48–57]. This work was inspired chiefly by the pharmacological potentialities of the compounds, and so the mass spectral information was sought primarily to provide a molecular mass and a 'fingerprint' of each compound. Therefore, little more than the m/z of the parent ion, perhaps along with masses of a few other prominent ions, devoid of interpretation, was offered. The compounds which were reported have structures **74–97**.



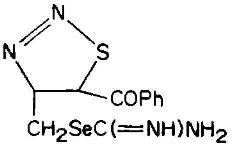
(74) $m = 1$: 5-Styryl-2-thioxo-1,3-thiaselenole[55]
(75) $m = 2$: 5-(4-Phenyl-1,3-butadienyl)-2-thioxo-1,3-thiaselenole[55]



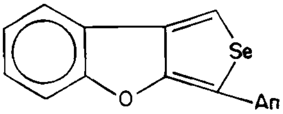
(76)
Methyl 2-amino-3,4,5,6-tetrahydro-4-oxo-2*H*-1,3-selenazine-6-carboxylate[49]



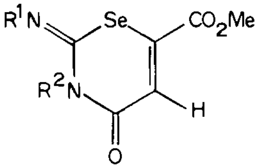
(77) $R^1 = H$, $R^2 = Ph$: 6-Phenylselenolo[3,4-*d*] [1,2,3]thiadiazole[50]
(78) $R^1 = Ph$, $R^2 = H$: 4-Phenylselenolo[3,4-*d*] [1,2,3]thiadiazole[50]



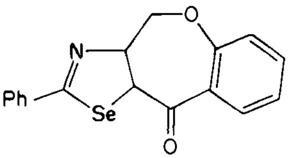
(79)
4-Isoselenoureidomethyl-5-benzoyl-[1,2,3]thiadiazole[50]



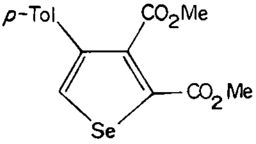
(80)
4-*p*-Methoxyphenylselenolo[3,4-*b*]benzofuran[51]



(81)
$R^1 = R^2 = H$: Methyl 2-imino-3,4-dihydro-4-oxo-2*H*-1,3-selenazine-6-carboxylate[49]
$R^1 = R^2 = Ph$: Methyl 2-phenylimino-3-phenyl-3,4-dihydro-4-oxo-2*H*-1,3-selenazine-6-carboxylate[49]



(82)
2-Phenyl-4,10-dihydro-10-oxo[1]benzoxepino[3,4-*d*]selenazole[57]



(83)
Dimethyl 4-*p*-tolylselenophene-2,3-dicarboxylate[48]

$p\text{-TolC}\equiv\text{C—Se—C(CO}_2\text{Me)=CHCO}_2\text{Me}$

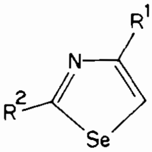
(84)

Dimethyl 2-(2-*p*-tolylethynylselenomercapto)-1,2-ethenedicarboxylate[48]

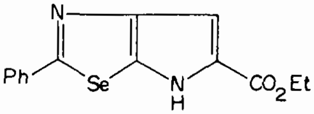
$p\text{-TolC}\equiv\text{C—Se—CH=CHCO}_2\text{Me}$

(85)

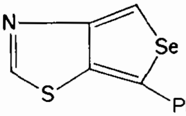
Methyl *cis*-3-(2-tolylethynylselenomercapto)acrylate[48]



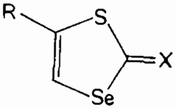
(86) $R^1 = CH_2Cl$, CH_2OH, HCO; R^2 = Ph: 2-Phenyl-4-chloromethylselenazole[53]
(87) $R^1 = CH_2OH$, R^2 = Ph: 2-Phenyl-4-hydroxymethylselenazole[53]
(88) R^1 = CHO, R^2 = H: 2-Phenyl-4-formylselenazole[53]



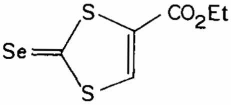
(89)
Ethyl 2-phenylpyrrolo[3,2-*d*]selenazole-5-carboxylate[53]



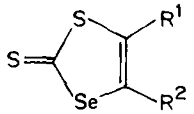
(90)
6-Phenylselenolo[3,4-*d*]thiazole[52]



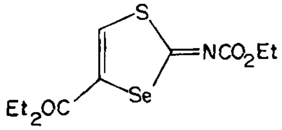
(91) R = Ph, X = $CHCO_2Et$: 2-Phenyl-ω-carbethoxy-1,4-thiaselenafulvene[54]
(92) R = $CHMe_2$, X = NPh: 5-Isopropyl-2-phenylimino-1,3-thiaselenole[54]
(93) R = Me, X = NCO_2Et: 5-Methyl-2-carbethoxyimino-1,3-thiaselenole[54]



(94)
4-Carbethoxy-2-selenoxo-1,3-dithiole[56]



(**95**) $R^1 = CO_2Et$, $R^2 = H$: 5-Carbethoxy-2-thioxo-1,3-thiaselenole[56]
(**96**) $R^1 = H$, $R^2 = CO_2Et$: 4-Carbethoxy-2-thioxo-1,3-thiaselenole[56]



(**97**)
4-Carbethoxy-2-carbethoximino-1,3-thiaselenole[56]

X. Organometallic Compounds Involving Transition Metals

Chaudhuri and coworkers[90–92] carried out mass spectrometric studies of a class of compounds which involve chalcogen together with manganese and iron carbonyl species. In the case of species of the general formulae $Fe_2(CO)_6X_2$($X = S$, Se) and $Fe_3(CO)_9X'_2$ ($X' = S$, Se, Te), the parent ion appeared in all cases; its abundance increased with the atomic weight of X or X′ but was much greater for the diiron species than for the trisiron ones. In all cases, the base peak was provided by the ions resulting from the complete shedding of CO molecules and with iron and chalcogen atoms retained. Thereafter, progressive losses occurred, first of X, then of Fe for $Fe_2X_2^+$, or of Fe, then both X and another Fe ultimately resulting in monatomic Fe^+[90]. These results were well supported by studies of metastable species.

In the case of the species $[Mn(CO)_4SeCF_3]_2$ and $[Fe(CO)_3SeCF_3]_2$[91] the molecular ion was observed and successive losses of six carbonyl groups led to $(CF_2Se)_2Fe_2$. An ion corresponding to $CF_3SeFe_2F^+$ indicated occurrence of a transfer of F from C to metal; this turned out to be standard in the decomposition of these compounds. A different placement of the charge led to $SeCF_2^{+\cdot}$ which appeared as 'one of the strongest ions' in the mass spectra of these two metal carbonyl species.

For $CF_3SeFe(CO)_2C_5H_5$, a similar pattern was followed. Beginning with the parent ion, progressive losses were observed as follows: $-CO$, $-CO$, $-SeCF_2$, $-F$, $-C_2H_2$ and $-C_3H_3$. Chaudhuri and his coworkers[92] presented a thorough mass spectrometric study of compounds of the class $[CF_3XMn(CO)_4]_2$, $[CF_3XFe(CO)_3]_2$ ($X = S$, Se), $CF_3SeFe(CO)_2C_5H_5$ and $CF_3SCr(NO)_2C_5H_5$. Low-abundance molecular ions were observed for both the $[CF_3XMn(CO)_4]_2$ compounds. The molecular ions lost three CO groups in a single step, another CO, and then XCF_2 with an accompanying F atom shift to the Mn. The resultant fragment, $[CF_3XMn_2(CO)_4F]^+$ lost the remaining CO groups stepwise, then another XCF_2 unit which gave $[Mn_2F_2]^{+\cdot}$. This lost its F atoms, one by one, then an Mn atom leading to the Mn^+ ion. Little distinction between the S and Se cases was to be noted.

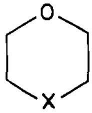
For the iron compounds $[CF_3SFe(CO)_3]_2$ and $[CF_3SeFe(CO)_3]_2$, the molecular ions were again present but sparse. The preferred decompositions proceeded via the progressive loss of all six CO groups and progressive loss of XCF_2 groups, leading to species containing only Fe and F atoms: $[Fe_2F_2]^{+\cdot} \rightarrow [Fe_2F]^+ \rightarrow [Fe]^+$.

III. SUMMARY

An examination of the mass spectra of organic Se and Te compounds presents the opportunity to test whether their chemical properties can be understood in analogy with those of corresponding O and S analogues. In general, smooth variations occur for the reactivity of gas-phase radical cations. Starting with alkyl selenide radical cations, $RSeR^{+\cdot}$, losses of R to give RSe^+ and hydrogen rearrangements to yield $RSeH^{+\cdot}$ are foreshadowed by the chemistry of S analogues, but these reactions are not seen when S or Se is replaced by O. Diselenides and ditellurides react similarly to disulphides. The aryl alkyl chalcogenides ArXR, constitute a useful system for making detailed comparisons. For PhXMe, the propensity for loss of CH_2X smoothly drops whereas production of PhX^+ smoothly increases as one goes from O to Te. For PhXEt, the common rearrangement to expel C_2H_4 is dominant for X = O, but is barely detectable for X = Te. Replacement of O with Se or Te presumably opens up new low-energy pathways, such as formation of PhX^+.

The ability to expel X increases smoothly from X = O to X = Te for ArXAr, a process which may be viewed as a reductive elimination and which occurs commonly in the fragmentations of Se and Te compounds. As expected, the elimination is only important for compounds containing the more metal-like chalcogens.

Periodic variations are also seen for cyclic chalcogenides. Notable is the smooth decrease in the facility of **98** to undergo cycloreversion reactions to expel CH_2O or C_3H_6O as X is varied from O to Te.



(98)

Various oxidized organoselenides have been extensively studied, and examples include selenoxides and selenones. Noteworthy is a facile rearrangement which usually involves

$$PhSe(=O)Me \rightarrow Ph—O—SeMe \qquad (39)$$

aryl transfer from Se to O (equation 39), which is termed as a selenoxide–selenate rearrangement. Hints of this rearrangement are found by examining the decompositions of the corresponding sulphoxides and sulphones. Oxygen transfer from a nitro group to Se followed by the selenoxide–selenate rearrangement may be the explanation for the abundant loss of C_7H_7O from **99**. For **99** and related compounds, the variation of chemical properties is abrupt rather than smooth as the S-containing analogues show absolutely no sign of this interesting rearrangement. This abrupt change, however, appears to be an exception, not the rule.

$$o\text{-}O_2NC_6H_4SeTol\text{-}p \qquad \mathbf{(99)}$$

Examination of the mass spectra of various heteroaromatics also reveals smooth variations of decomposition reactions. Loss of CHX smoothly drops off as one proceeds from furan to tellurophene whereas the reductive elimination of Te from tellurophene is foreshadowed by the fragmentation of selenophene. For benzoselenophene, benzoselenazole, benzoisoselenazole and selenolo[2,3-*b*]pyridines, reductive elimination of Se is always important. The reactions of substituted benzoselenophenes, however, involve decompositions which are determined by the nature of substituents rather than the presence of the Se. The mass spectra are entirely similar to the corresponding benzofurans and benzothiophenes. Apparently, the energy requirement for substituent-driven processes is lower than that of the reductive elimination. Systematic variations can also be found for the mass spectral decompositions of selenadiazoles, 2,5-diazoles substituted with O, S or Se in the 1-position, and other heterocycles.

Besides the selenone/selenate-type rearrangement, two other rearrangements are noteworthy for Se-containing compounds, and they merit further study. The exchange of heteroatoms in the S and Se analogues of phthalide (see equation 37) and the C—Se interchange which occurs for various selenofulvalenes (see equation 28) are characterized by transfer of organic moieties to the Se. An interesting question is whether these processes pertain when these species are in solution under one-electron oxidation conditions.

Final remarks are focused on the mass spectrometric techniques used in the studies reviewed here. Most compounds have been ionized by using electron beams and that works reasonably well. It is recommended that materials which give low-abundance molecular ions be reinvestigated by using newer methods such as field ionization, field desorption and fast atom bombardment, or by electron attachment to give radical anions. Two reports show clearly the advantages of field ionization and negative ions[3,82]. Many, but not all, fragmentation pathways and ion structures are speculative. Future studies should include metastable ion measurements, collisional activation and tandem mass spectrometry (MS/MS) to remove some of the uncertainties associated with the mechanisms given in this review.

IV. ACKNOWLEDGEMENT

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The Chemistry of Organic
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CHAPTER 8

Radiation chemistry of organic selenium and tellurium compounds

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I. INTRODUCTION

The heaviest elements of the sulphur subgroups—Se, Te and Po—have been less intensively studied than either O or S; consequently the radiation chemistry of Se- and Te-containing compounds has been less exploited. Nevertheless, the interest in radiation effects, particularly in Se-containing compounds has increased in recent years, as, on the one hand, the identification of radiation damage is helpful in understanding the part played by Se in radioprotection, and on the other, such studies enable a direct comparison with the more important element S. The organic Te-containing compounds could be important in relation to hot-atom chemistry.

II. SELENIUM COMPOUNDS

A. Antiradiation Effects in Chemical and Biological Systems

Radiation chemical studies on Se-containing compounds were recently performed in connection with the role played by these compounds as radioprotectors.

Many chemical substances can act as modifiers of radiation damage (i.e. radioprotectors and radiosensitizers) in chemical and biological systems and it is well known that the most important class of radioprotective agents is the S-containing compounds[1].

Compounds in which Se replaces S are also of interest in relation to the phenomenon of radiobiological protection. Some chemical and biological features of Se- and S-containing compounds appear to be similar, but some differences are observed[2–4]. The atomic rays and the solvation abilities of S and Se analogues are rather similar. S is a typical metalloid and can expand its electron shell, but does so with some difficulty; Se presents some metallic properties and the expansion of the electron shells is easier. Their compounds are therefore quite different in terms of electronic distribution and chemical reactivity. For example, in conjugated systems, the C—Se bond is more polarized than the C—S bond. The differences in the bond polarization are reflected in the different reactivities of the systems in analogous series of compounds.

Se-containing compounds are generally very reactive, especially in redox processes. The Se—Se bond is less stable than the S—S bond and it is easily cleaved in various reversible reactions. In the last few years the biochemistry of Se has also developed extensively due to the role of Se as an essential micronutrient element. Recently it has been shown that some enzyme-catalysed redox reactions require the participation of Se-containing proteins, and a detailed review on this subject has been published[5].

Considerations concerning mainly ionization potentials, bond strengths and electropositivities suggest that compounds in which Se replaces S should be good radioprotective agents. Some attempts made in the past to test this assumption have not always met with success. The first Se-containing compound tested for radioprotective ability was selenophenol. When administered to mice i.p. (0.2 or 0.4 mg per kg body weight) in olive oil 10 minutes before X-irradiation, this compound was found by Bacq and coworkers to be ineffective[6].

Shimazu and Tappel[7,8] have compared the radioprotection, in model systems, offered by the Se-containing amino acids, selenocystine and selenomethionine, with that of the known radioprotectors, cystine, 2-aminoethylthiopseudourea dihydrochloride and 2-aminoethanethiol hydrochloride. The selenoamino acids were found to protect different amino acids and the enzymes ribonuclease and yeast-alcohol deydrogenase against ionizing radiation better than the S-containing compounds. The strong radioresistance of selenomethionine was attributed to its ability to form stable radical intermediates which can combine with free H atoms or electrons to restore the molecule to its original state.

This behaviour could be linked to the biological role of Se and in particular to its antioxidant action. However, in these and in other *in vitro* experiments, the Se levels were very much higher than those commonly present in normal tissues and cells and often the pH values were outside the physiological range[9].

In other related experiments, Dickson and Tappel[10] explored the effects of the selenoamino acids, as compared to the analogous thioamino acids, on the activation and the activity of the sulphydryl enzymes papain and glyceraldeyde-3-phosphate dehydrogenase. They observed that the selenoamino acids bind reversibly to the thiol groups of the enzymes to form substrate-displaceable complexes which protect the enzymes against oxidative inactivation.

The synthesis of some potential antiradiation Se compounds, analogues of the well-known radioprotective drugs, are reported in the literature: 2-aminoethaneselenol (selenocysteamine) hydrochloride[11], bis(2-aminoethyl) diselenide(selenocystamine) dihydrochloride[11,12], 2-aminoethaneselenosulphuric acid[11] and 2-aminoethyl selenopseudourea dihydrobromide[13]. None of these compounds showed any protective activity[3].

The radioprotective activities of selenourea[14] and of selenocystine, selenomethionine, selenoxanthene, selenoxanthone, selenochromone and colloidal Se[15] in rats exposed at sublethal (600 R), lethal (750 R) and superlethal doses (900 R) have been reported. All these substances show activity similar to that of cysteine and, in some instances, superior to it. This results in reduction in mortality, of some clinical symptoms of radiation injury and of the severity of haematological syndrome (depression of white cell count and of neutrophiles in blood). Moreover, other experiments have shown that the preadministration of selenourea in rats modifies favourably other biochemical changes induced by ionizing radiation[16].

The parameters investigated in the last paper were the total protein content and the protein pattern of serum and some changes in the activity of plasma enzymes like alkaline phosphatase (AP), glutamate oxalacetate transaminase (GOT) and glutamate pyruvate transaminase (GPT).

The distribution of ^{75}Se after 6 hours to 14 days from labelled selenourea in rat organs has been determined after i.p. administration[17]. The distribution of ^{75}Se varied depending upon the amount of Se and was strictly related to the physiological activity of the organs and to the catabolism of selenourea. At the highest levels of administered selenourea, chemical and radiochemical toxicity phenomena were observed[18].

The rates of incorporation of seleno analogues of cystine, methionine, cystamine and taurine, as well as their toxicities have also been investigated in rats[19,20]. Generally, the highest values of incorporation of all the tested compounds occurred in the liver with a fast metabolic exchange, while the blood values remained practicallly constant from three hours to one week. The toxic effects were estimated from the survival, the general clinical conditions and the qualitative changes in the components of the red and white blood-cell series.

With selenourea, selenocystine and selenomethionine the retention of Se in blood constituents and its distribution at the subcellular levels of the liver have been studied[15]. For all compounds the blood radioactivity was concentrated in the red cells, while that in the plasma was low. In the subcellular fractions of the liver, the ^{75}Se was distributed mainly in the non-protein-soluble fraction, in the microsomes and in the nuclei. There was practically none in the protein and in the mitochondria. The microsomes should be the initial point of Se incorporation into proteins and should therefore be the first to utilize the organoselenium compounds and the elementary Se. The high activity of the nuclei was probably due to elementary Se formed by decomposition of the compound and precipitated with the nuclear fraction. The radioactivity of the soluble fraction was due to the presence of intact organoselenium compounds, as tested by chromatography.

Inorganic seleno compounds have also been reported to exhibit radioprotection in animals. Sodium selenate, when administered to rats one hour postirradiation (800 R) at 4.2–4.6 mg/kg i.p., followed by an additional 80% subcutaneously, resulted in the survival of all the animals[21]. Sodium selenite, administered *per os* to male Swiss albino mice, using a dose of 0.05 mg/kg day for ten consecutive days prior to their 500 R irradiation, increased their survival rates in the 15th day after irradiation[22]. Other experiments have demonstrated the protective effects of Se against teratogenic and carcinogenic effects[23].

The radioprotective characteristics of sodium selenite on rats have also been investigated[24]. It was ascertained that the sodium selenite in combination with vitamins A and E has radioprotective ability. The greatest protective effect was achieved by introduction of the combination of sodium selenite with the vitamins A and E half an hour before irradiation. The possible mechanism of the radioprotective effect has been discussed on the base of the antioxidizing characteristics of Se and vitamin E and on their influence on the subcellular particles, specifically on lysozomes.

The radioprotective properties of Se in 2-amino ethylisoselenouronium bromide–hydrobromide, 2-aminoselenoazoline and the Se analogue of mercaptoethylguanidine were investigated in white mice[25]. A radioprotective effectiveness, comparable with classical thiol radioprotectors, was manifested by 2-aminoselenoazoline. In the other two compounds, on the contrary, a synergism of toxicity and radiation was observed.

The time dependence of the distribution of ^{75}Se-labelled 2-aminoselenoazoline in the organisms of rats and mice was followed[26]. By comparison of the results obtained with the previous study of radioprotective properties of this compound, its efficiency was shown to be dependent on the actual concentration in tissues.

Se-containing compounds have also been reported to act as radioprotectors in cellular and molecular systems.

The ability of various Se heterocycles to protect ATP from losing orthophosphate on irradiation has been studied by Brucker and Bulka[27]. Only 2-amino-4,5-dimethylselenazole hydrochloride acted as radioprotector. Other 2-aminoselenazoles, as well as selenocarbazide and acetoselenosemicarbazone, did not show any radioprotective ability for *Phycomyces blakesleeanus*, but on the contrary showed some sensitizing effect[28].

Selenourea has been reported to protect amino acids from radiation damage in aqueous solution and in the solid state[29] by serving as an efficient free-radical scavenger[30]. Similar behaviour in selenourea, as well as in selenocystine and selenomethionine, was observed for enzyme systems, i.e. ribonuclease[31] and yeast-alcohol dehydrogenase[32].

The inactivation of ribonuclease was strongly reduced by the presence of the Se-containing additive. In view of the high reactivity of selenourea, selenocystine and selenomethionine with primary water radicals, as deduced from the radiation chemical data, the radioprotective effect could be explained on the basis of a simple competition between organic Se compounds and ribonuclease for the radicals themselves.

In contrast with the results obtained from multicellular systems, when cultures of *E. coli* B/r were irradiated in the presence of selenourea, they show an increased survival when irradiated in air, and the opposite effect in nitrogen[33]. The anoxic sensitization was explained by the presence of colloidal Se which is the main product of selenourea radiolysis, while selenourea itself is a most active protector in the presence of O_2, confirming the general trend found for Se-containing compounds in mammalian systems.

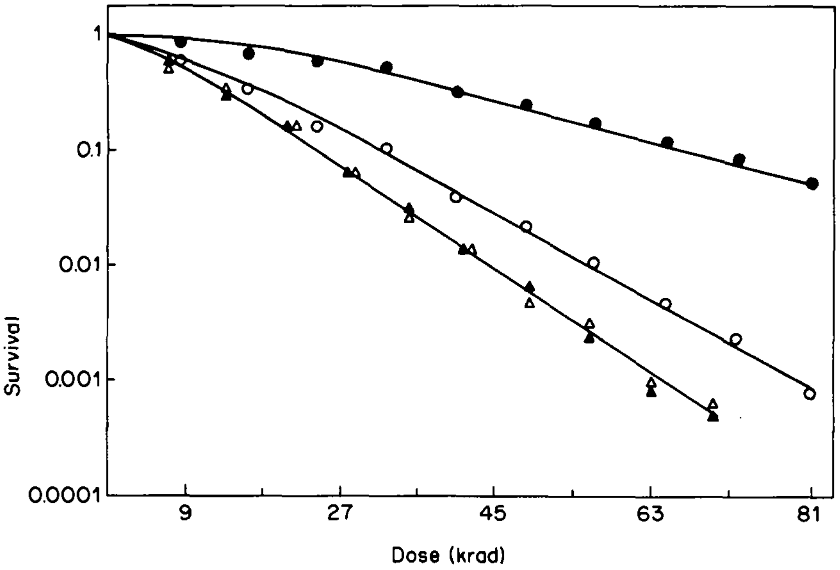


FIGURE 1. Survival of *E. Coli* B/r irradiated with X-rays in the presence of colloidal Se: ●——● control and ○——○ colloidal Se in N_2, ▲—▲ control and △—△ colloidal Se in air. Reproduced with permission from Ref. 33

TABLE 1. Radioprotective effects of Se-containing compounds on various biological systems

Compound	Test system	End-point	Ref.
Molecular			
Selenocystine,	Amino acids	Chemical degradation	7,8
Selenomethionine	Enzymes (ribonuclease, yeast-alcohol-dehydrogenase)	Loss of catalytic activity	
Selenourea	Amino acids	Chemical degradation and inhibition of ESR signals	29
Selenourea	Yeast-alcohol dehydrogenase	Loss of catalytic activity	32
Selenourea, Selenocystine, Selenomethionine	Ribonuclease	Loss of catalytic activity	31
Selenocyanate	Enzymes (ribonuclease, lysozime, α-chymotrypsin, alcohol dehydrogenases)	Loss of catalytic activity	35
Selenium dioxide	Enzymes (ribonuclease, lysozime, α-chymotrypsin, alcohol dehydrogenases)	Loss of catalytic activity	37
Colloidal Se	Yeast-alcohol dehydrogenase	Loss of catalytic activity	32
2-Amino-4,5-dimethyl-selenazole; HCl	ATP	Loss of ortophosphate	27
Cellular			
Selenourea	*E. coli* B/r	Cell survival	32,33
Colloidal Se	*E. coli* B/r	Cell survival	32,33
2-Aminoselenazoles, Selenocarbazide, Acetoselenosemicarbazone	*Phycomyces blakesleeamus*	Spore survival	28
Multicellular organisms			
Selenourea	Rats	30 days survival, haematological syndrome	14
Selenourea	Rats	Protein and enzyme parameters	16
Selenocystine, Selenomethionine, Selenoxanthene, Selenoxanthone, Selenochromone	Rats	30 days survival, haematological syndrome	15
Sodium selenate	Rats	30 days survival	21
Sodium selenite	Mice	15 days survival	22
Sodium selenite (+ vitamins A and E)	Rats	30 days survival	24
Selenophenol	Mice	30 days survival	6
2-Aminoselenoazoline, Selenium-2-aminoethyl-isoselenouronium bromide–HBr, Selenoethylguanidine	Mice	30 days survival	25
2-Aminoethaneselenol (selenocysteamine)·HCl	Mice	30 days survival	39
Bis(2-aminoethyl) diselenide (selenocystamine)·2 HCl	Mice	30 days survival	3
2-Aminoethaneselenosulphuric acid	Mice	30 days survival	39
2-Aminoethylselenopseudourea·2 HBr	Mice	30 days survival	3

Figure 1 shows the sensitizing activity of colloidal Se on bacterial systems. In particular the data emphasize that colloidal Se has no effect in air but it shows appreciable sensitization in the absence of O_2. Although colloidal Se does not appear to have any possible practical application, mainly because of its toxicity and instability, it exhibits a type of radiosensitization which could contribute to an understanding of mechanisms of anoxic sensitization[34]. Colloidal Se forms as the result of chemical and physical actions on aqueous solutions of selenourea. The hydrosols of elementary Se are made up by micellae which may contain different numbers of atoms. The micellae tend to grow sedimenting amorphous red Se which then goes over into the grey form. The elementary Se particles are rather unlikely to be involved in an intracellular sensitization mechanisms just because of their size, and therefore one is inclined to postulate an extracellular mechanism in which the free-radical cleavage and reformation of —Se—Se— bonds is likely to play a role. The sensitization is probably due to the formation, from irradiated colloidal Se, of short-lived species acting in processes occurring extracellularly.

It should be noted that the two inorganic secondary radicals $(CNSe)_2^-$[35] and SeO_3^-[36], derived from the radiation-induced oxidation of $CNSe^-$ and SeO_2, show on the inactivation of some enzymes a dose-modifying effect which is related to the specificity of attack of the secondary radical towards certain amino acids and to the structure of the protein itself[31,35,37] (see also Section II.B).

A series of 2-substituted selenoazolidines have been synthesized as potential radioprotective agents[38].

A comprehensive survey of the radioprotective activity reported so far for a variety of systems of different biological organization and end-groups is given in Table 1. With multicellular organisms only a few compounds have apparently been tested. However, one can try a tentative extrapolation to such organisms, based on the information concerning mechanisms of action obtained with molecular and single-cell systems.

B. Radiation Chemistry of Selenium Compounds

Understanding of the radiation chemistry of Se-containing compounds is especially important in order to explain their role in radioprotection and to permit a comparison with the S analogues. Identification of the transient species and radiolysis products arising from Se compounds and knowledge of the nature of their reactions with biologically interesting compounds should help to explain the radioprotection offered by these compounds.

All these studies are far from being exhaustive since the instability of many Se compounds with consequent analytical difficulties does not permit accurate experiments of steady-state radiolysis.

The most suitable techniques for studying such systems are pulse radiolysis and electron spin resonance spectroscopy and most papers deal with these subjects. In particular, pulse radiolysis uses a short intense pulse of radiation to induce the initial physicochemical damage and fast recording techniques (i.e. absorption kinetic spectrophotometry with oscillographic output) to investigate the short-lived chemical species produced and to follow their subsequent reaction pathway[40].

Unlike photochemistry, where the incident energy is absorbed by a particular chromophore, the absorption of ionizing radiation energy occurs non-selectively and, in dilute solution, exclusively by the solvent. The most important transient species formed in water or in aqueous solutions are OH radicals, H atoms and the hydrated electron (e_{aq}^-), which are the precursors of the subsequent chemical damage.

When aqueous solutions of Se-containing compounds are pulse-irradiated, an intense transient absorption with a maximum from 380 to 450 nm is produced (Figure 2). In all cases this absorption is attributed to radicals where Se atom (or atoms) is (or are) involved.

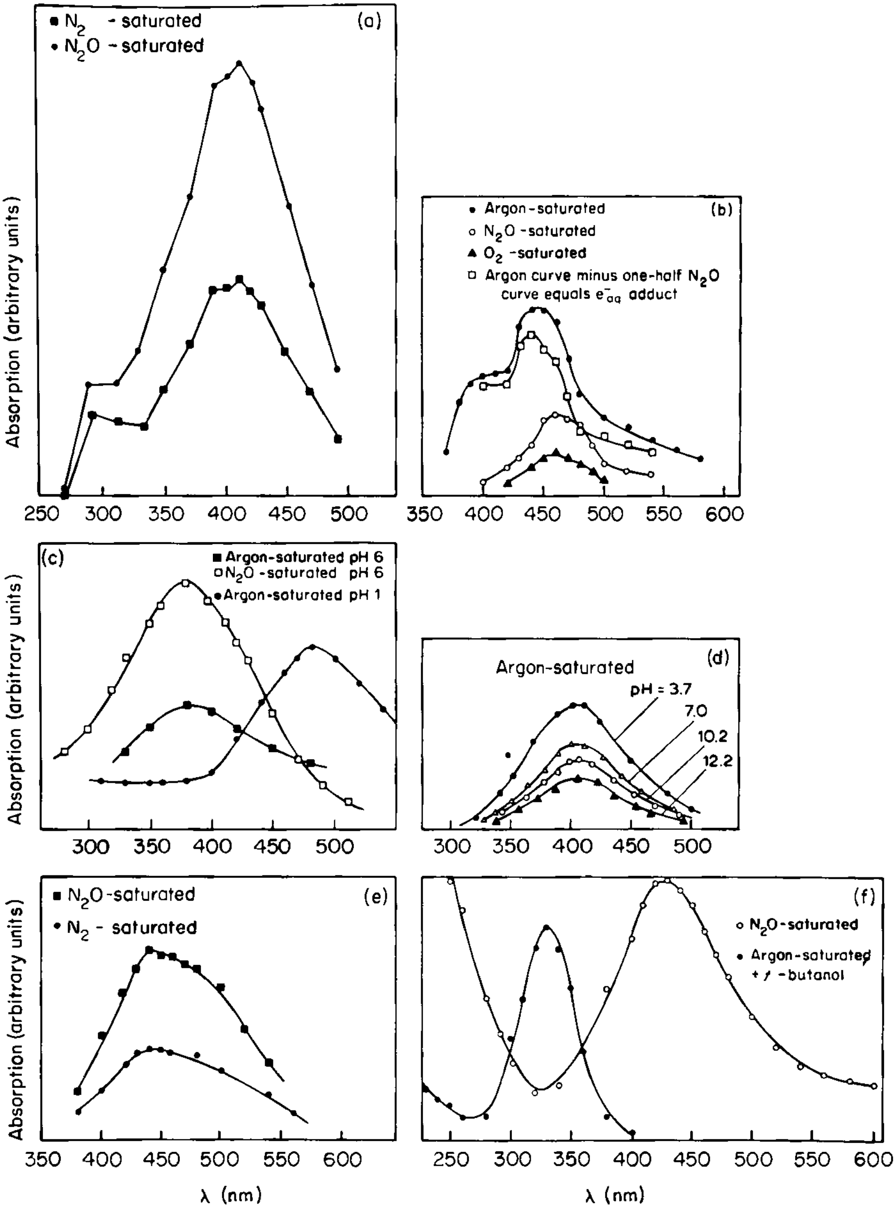


FIGURE 2. Transient absorption spectra from aqueous solutions containing seleno derivatives. (a) selenourea[41] (b) selenocystine[42] (c) selenomethionine[43] (d) selenidric acid[44] (e) selenocyanate[35] and (f) selenium dioxide[36]. A spectrum similar to (c) was obtained in the case of selenoethionine[45]. Reproduced with permission from the above references

Radicals which absorb in a similar spectral region have been identified for S-containing compounds[46].

The most studied and best understood is the radiation chemistry of selenourea[41]. The main results obtained from pulse radiolysis of selenourea are summarized in Table 2, which gives the features of the transient absorption spectra, Table 3 which gives the

TABLE 2. Transient spectra on irradiation of selenourea solutions

Transient absorption maximum	410 nm
Extinction coefficient (410 nm)	8.7×10^3
Effect of N_2O on absorption	Increased by a factor of 2
Effect of acid pH	Increased by a factor of 2
Effect of O_2	Reduced by a factor of 0.2
Effect of OH scavenger	Strongly reduced
Effect of solute	Not in accordance with a radical scavenging process

TABLE 3. Characteristics of the 410 nm absorption decay in selenourea pulse radiolysis

Always second order in N_2O-saturated and neutral solution ($k = 5.7 \times 10^9 M^{-1} s^{-1}$)
The rate increases as the ionic strength increases
No effect of hundredfold increase in selenourea concentration
Nearly second-order in N_2-saturated and neutral solution ($k = 1.4 \times 10^{10} M^{-1} s^{-1}$)
Pseudo-first-order in O_2-saturated solution.
(average value of the bimolecular rate constant between the transient and molecular oxygen, ($k = 1.2 \times 10^8 M^{-1} s^{-1}$)

TABLE 4. Rate constants for the reaction of selenourea with primary water radicals[a]

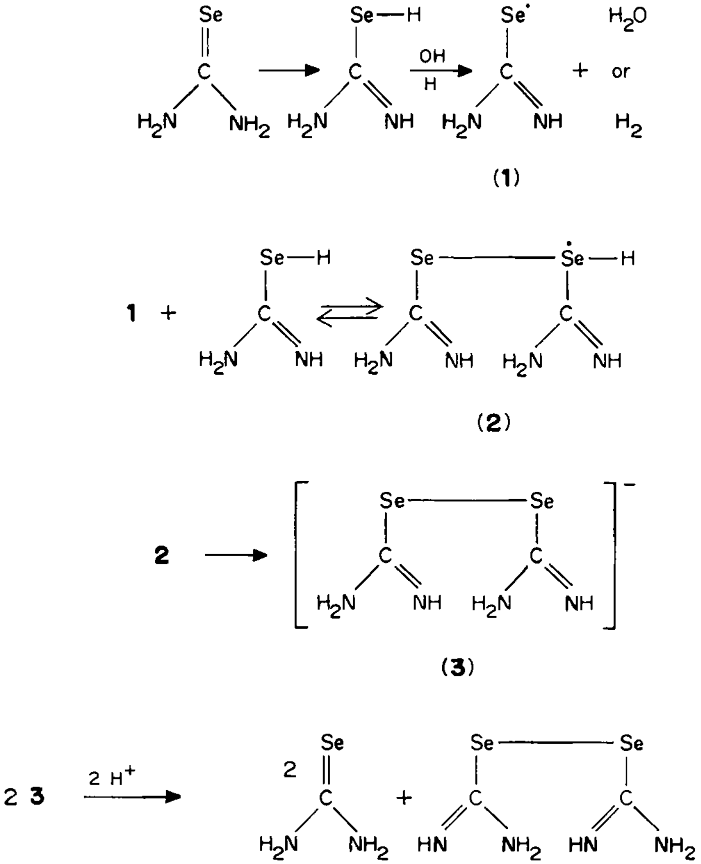
Reaction	Method used to determine k	$k(M^{-1}s^{-1})$
Selenourea + e_{aq}^-	Decay of e_{aq}^- at 700 nm, in N_2-saturated, neutral solution	4.0×10^9 (independent of pH in the range 6–11)
Selenourea + OH	Competition with CNS^-, in N_2O-saturated, neutral solution	7.2×10^9
	Competition with EtOH in N_2O-saturated, neutral solution	6.8×10^9
	Competition with MeOH in N_2O-saturated, neutral solution	6.5×10^9
	Bleaching at 250 nm	6.9×10^9
	Direct build up of 410 nm absorption in N_2O-saturated, neutral solution	5.5×10^9
Selenourea + H	Competition with EtOH in N_2O-saturated, neutral solution	7.5×10^8
	Competition with MeOH in N_2O-saturated, neutral solution	6.4×10^8
	Direct build up of 410 nm absorption in N_2-saturated, acid and concentrated solution	6.3×10^8

[a] Reproduced with permission from Ref. 41.

characteristics of the transient absorption decay and Table 4 which gives the rate constants for the reaction of selenourea with primary water radicals.

From the above data and from the data in the tables both the OH radical and the hydrogen atom give rise to the same radical species when reacting with selenourea. The radical formed by this reaction with a strong absorption band at 410 nm is shown to be a charged complex involving two selenourea molecules.

The reaction involves the abstraction of one H atom from the —SeH group of the pseudoenol form of the compound, followed by the association with another molecule of selenourea in an equilibrium reaction (Scheme 1).



SCHEME 1

The radical species decays with the reformation of two selenourea molecules and the formation of the condensed dimer. The latter is very unstable and serves as a precursor of the red Se found under all experimental conditions.

The structure of α,α′-diselenobisformamidinium cation, derived from selenourea oxidation product has been determined by X-ray structural analysis[47].

Table 4 shows the high reactivity of selenourea towards the primary radicals of water radiolysis. Selenourea is superior to urea and thiourea in competing for these free radicals.

TABLE 5. Radiolytic products from γ-irradiation of 3×10^{-4} M selenocystine in aqueous solutions[a]

Dose (rads)	Deaerated solutions	Deaerated solutions + 0.1 M CH_3OH	N_2O-saturated solutions
1×10^5	G(—Se—cystine) = 0.65	G(—Se—cystine) = 0.38	G(—Se—cystine) = 0.87
	Colloidal Se($G = 0.40$)	Colloidal Se($G = 0.20$)	Colloidal Se($G = 0.70$)
	Alanine ($G < 0.1$)	Alanine ($G = 0.24$)	Alanine ($G < 0.1$)
	Serine ($G < 0.01$)		Serine ($G < 0.1$)
	Selenocysteine seleninic acid (traces)	Selenocysteine seleninic acid (traces)	Selenocysteine seleninic acid (traces)
	Unidentified product containing Se	Unidentified product containing Se	Three unidentified products containing Se
2×20^5	G(—Se—cystine) = 0.55	G(—Se—cystine) = 0.40	G(—Se—cystine) = 0.84
	Colloidal Se ($G = 0.50$)	Colloidal Se ($G = 0.30$)	Colloidal Se ($G = 0.70$)
	Alanine ($G < 0.1$)	Alanine ($G = 0.24$)	Alanine ($G < 0.1$)
	Serine ($G < 0.01$)	—	Serine ($G < 0.1$)
	Selenocysteine seleninic acid (traces)	Selenocysteine seleninic acid (traces)	Selenocysteine seleninic acid (traces)
	Unidentified product containing Se	Unidentified product containing Se	Three unidentified products containing Se

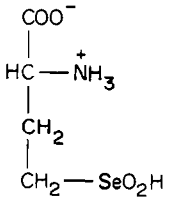
[a] Reproduced with permission from Ref. 42.

The order of reactivity with radicals in the series of ureas seems to parallel their known radioprotective activity in biological systems. The ability of a secondary radical to form a relatively inert complex may also have some bearing on the protective efficiency of the parent molecule.

The high reactivity of selenourea with free radicals is also found in the irradiation of organic compounds in the solid state, where the presence of selenourea suppresses the formation of stable free radicals by an amount proportional to its concentration[29]. The fact that neutron activation has proved a good method for labelling selenourea with ^{75}Se with high yield[48], although the recoil of the (n, γ) reaction has sufficient energy to break the Se—C bond, reflects the efficiency of Se as a radical scavenger.

Gamma and pulse radiolysis of selenoamino acids have been reported and mechanisms of the radiation–degradation processes can be suggested.

Table 5 shows some radiolytic products derived from γ-irradiation of selenocystine[42,49]. The main product is elementary Se, which is produced with a yield proportional to selenocystine decomposition. Some amino acids not containing Se are present, as well as the oxidation product selenocysteine seleninic acid (4). Deamination and decarboxylation reactions occur but they have not been followed quantitatively.



$COO^- - CH(\overset{+}{N}H_3) - CH_2 - CH_2 - SeO_2H$

(4)

Tables 6 and 7 show some radiolytic products derived from γ-radiolysis of selenomethionine[50,51]. The main radiation–degradation reactions of selenomethionine include, in addition to decarboxylation and deamination, reactions leading to cleavage of the Se bonds accompanied by formation of volatile compounds, as well as recombination reactions, which prevail in a nitrogen atmosphere. In oxygen, oxidation reactions take place on Se, on the carbon skeleton and on the cleaved groups.

Some of these degradation products have been found, although to a lower extent, during the storage of radiopharmaceutical selenomethionine labelled with ^{75}Se, due to self-radiolytic processes[51,52].

The pulse radiolysis results demonstrate the high reactivity of selenocystine and selenomethionine with the hydrated electron and the hydroxyl radical. The rate constants (Table 8) are higher than for other aliphatic amino acids[53] and are of the same order of

TABLE 6. Radiolytic products from γ-irradiation of selenomethionine[50]

Deaerated solution	N_2O-saturated solution	O_2-saturated solution
G(—selenomethionine) = 1.4	G(—selenomethionine) = 5.2	G(—selenomethionine) = 5.7
Ammonia (G = 0.52)	Ammonia (G = 1.2)	Ammonia (G = 1.5)
Selenohomolanthionine	(No other product was tested)	Selenomethionine oxide
Selenohomocysteine		Homoserine
Me_2Se		Aspartic acid
Me_2Se_2		Methylselenous acids
		Selenous acids

TABLE 7. Radiolytic products from γ-irradiation of selenomethionine (1 Mrad)[51]

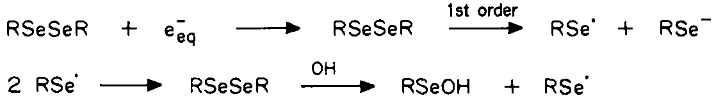
Deaerated solution	Air solution
Undestroyed selenomethionine (30%)	Undestroyed selenomethionine (30%)
Inorganic Se and highly oxidized selenomethionine (7.0%)	Inorganic Se and highly oxidized selenomethionine (15%)
Selenomethionine oxide (43%)	Selenomethionine oxide (11%)
Other decomposition products (5.0%)	Other decomposition products (negligible at this dose and about 10% at 2 Mrad)

TABLE 8. Rate constants for the reaction of e_{aq}^- and OH with selenoamino acids

Reaction	pH	Method used	$k(\mathrm{M}^{-1}\mathrm{s}^{-1})$	Ref.
Selenocystine + e_{aq}^-	6.0	Decay of e_{aq}^- at 700 nm	7.6×10^9	42
	11.5		3.9×10^9	42
Selenomethionine + e_{aq}^-	7.0	Decay of e_{aq}^- at 700 nm	1.8×10^9	43
Selenocystine + OH	7.0	Direct build-up of the transient absorption in N_2O	1.0×10^{10}	42
	7.0	Competition with CNS^- in N_2O	1.7×10^{10}	42
Selenomethionine + OH	7.0	Direct build-up of the transient absorption in N_2O	1.3×10^{10}	43

magnitude of those of thioamino acids[54]. The compound selenodicysteine shows similarly a high rate constant for scavenging OH radicals[55].

The product of the reaction of e_{aq}^- with selenomethionine has no significant absorption in the ultraviolet and visible region. The most likely reaction of e_{aq}^- with selenocystine occurs at the —Se—Se— group and gives rise to a transient absorption with a maximum at 400 nm. The reaction scheme is shown in Scheme 2[42].



$$\mathrm{RSeSeR} + e_{eq}^- \longrightarrow \overset{-}{\mathrm{RSeSeR}} \xrightarrow{\text{1st order}} \mathrm{RSe}^{\bullet} + \mathrm{RSe}^-$$

$$2\,\mathrm{RSe}^{\bullet} \longrightarrow \mathrm{RSeSeR} \xrightarrow{\mathrm{OH}} \mathrm{RSeOH} + \mathrm{RSe}^{\bullet}$$

SCHEME 2

The electron adduct decays in an equilibrium reaction and the radical RSe$^{\bullet}$ is responsible for the absorption peak at 460 nm. A back-reaction should occur with reformation of selenocystine and this would explain the low values of *G*(—RSeSeR) in γ-radiolysis experiments.

As OH radicals also generate a transient absorption at 460 nm, a possible mechanism is indicated in Scheme 2. Such mechanism is in conformity with the γ-radiolysis experiments, as RSeOH could be the precursor of the Se analogue of cysteine sulphinic acid.

In the case of selenomethionine, the OH attack occurs at the Se atom with the formation of transient absorption at 380 nm.

The decay of this radical is complex due to the existence of concurrent reactions, and it requires a special kinetic treatment[56]. The exponential decay observed at low doses may be due to a unimolecular decomposition or to an internal rearrangement; the bimolecular reaction, observed at high doses, probably involves neutral radicals.

In conclusion, from the steady-state and pulse radiolysis data, the degradation of both selenoamino acids is mainly due to OH attack; meanwhile the e_{aq} are partially scavenged by Se atoms with less damage to the molecule.

TABLE 9. Radical yields by X-ray irradiation of thio- and seleno-amino acids at 295 K and 100 K[a]

Compound	295 K	100 K
Cysteine	0.3	1.1
Cystine	2.5	2.1
Methionine	1.0	1.7
Ethionine	1.4	0.8
Se-cystine	0.02	0.1
Se-methionine	0.3	0.2
Se-ethionine	0.4	0.1

[a] Reproduced with permission from Ref. 58.

The relative radiation stability of both selenoamino acids may be ascribed to a repair mechanism and to back-reactions during the irradiation process. Likewise in the case of selenourea steady-state radiolysis the dose dependence is initially linear with a sharp kink at the higher doses, attributed to a self-repair mechanism[29].

Of particular interest in this context are the comparative ESR studies by Colombetti and coworkers on the radiation resistance of thio- and seleno-amino acids in the solid state[57,58]. The formation and the stabilization of free radicals in X-ray irradiated thio- and seleno-amino acids have been investigated by ESR in an attempt to identify the main radical species present. A low free-radical yield was found in irradiated Se compounds, indicating the presence of repair mechanisms (Table 9). The radicals formed in these compounds probably react readily with H atoms or electrons, returning to the original molecule or forming non-radical species. Another possibility is that the absorbed energy is utilized to break bonds to Se, which are readily reformed.

In support of this hypothesis are some polarographic results[59] which demonstrate that the dissociation–formation rate of bonds to Se is higher than for the S bonds.

Comparison of some spectroscopic properties of selenoamino acids[60] with those of their thio analogues show important structural modifications which could be related to the different reactivity and radiation response of the compounds.

The substitution of S by Se results in a bathochromic shift of the UV absorption band and this is due to the higher excitability of the unbound electron pairs of the Se atom with respect to S. This should favour a greater chemical reactivity for selenoamino acids, as was indeed observed in pulse radiolysis for the process concerning the reactivity with water free radicals.

From IR spectra, the substitution of Se for S in methionine/selenomethionine results in a weakening of the C—C bonds of the side-chain and of the bond between the heteroatom and the Me group. The different radiation response of the two amino acids[50,51] may be explained in the light of these results.

The role of some Se-containing compounds in the transfer of excitation energy produced by ionizing radiation has also been investigated in order to give a more complete picture of radiation effects on such compounds.

In particular, the technique of pulse radiolysis has been applied to the study of luminescence phenomena of the radioprotective compound selenoxanthene in the crystalline form[61]. The spectral distributions of the radiation-induced luminescence have been studied as a function of time and temperature giving information about the disposition and the fate of excitation energy produced by ionizing radiation. Selenoxanthene is an extremely efficient luminescent material as may be expected from its aromatic structure. No fluorescent emission was found following pulse irradiation. Only a single sharp phosphorescence peak at 500 nm was observed. An oscillogram of the decay of

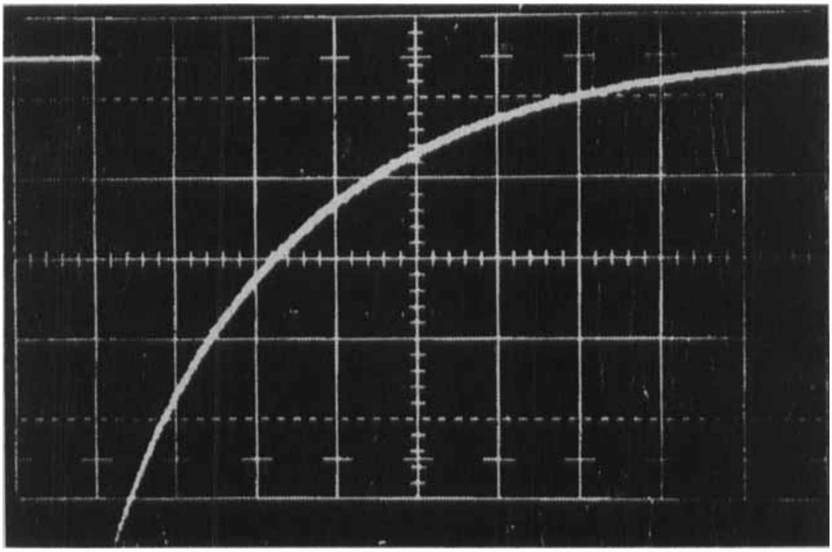


FIGURE 3. Decay of the phosphorescence from irradiated selenoxanthene at 490 nm. Sample temperature, 95 K, time-scale 50 μs cm⁻¹. Reproduced with permission from Ref. 61

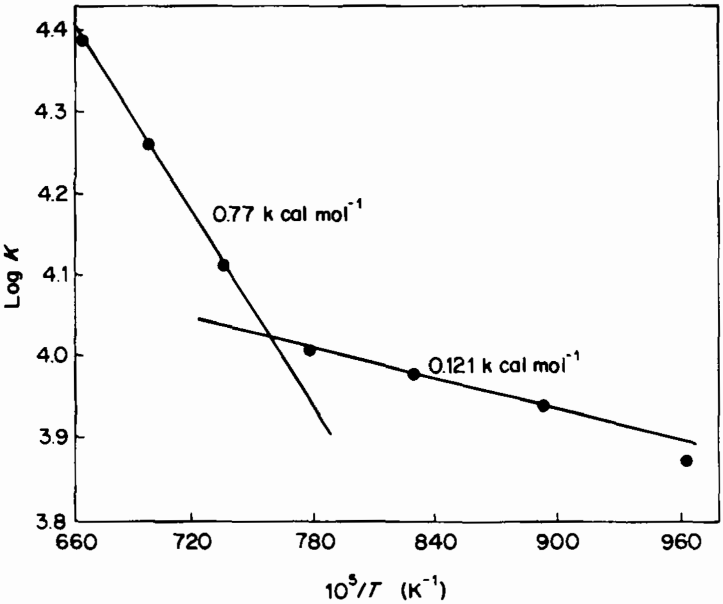


FIGURE 4. Arrhenius plot for the temperature-sensitive phosphorescence decay of selenoxanthene emission. Reproduced with permission from Ref. 61

this phosphorescence is shown in Figure 3. Below 150 K this decay is exponential but the half-life is strongly dependent on the temperature of the sample. The emission decay rate as a function of temperature can be plotted in the form of an Arrhenius plot as shown in Figure 4.

It is obvious from these data that there must be at least two temperature-sensitive quenching reactions in competition with the phosphorescence decay. The activation energies for these two quenching reactions were calculated to be 0.77 and 0.12 kcal mol^{-1}.

The fluorescent efficiencies of compounds excited by ionizing radiation are in the order xanthene > thioxanthene > selenoxanthene, with marked differences between them, whereas the phosphorescent efficiences are in the reverse order. The luminescence yields, defined as the proportion of the absorbed energy which is reemitted, are shown in Table 10.

The enhanced intersystem crossing within the molecule, promoted by the high atomic number of Se, could explain why at low temperature the total luminescence yields of selenoxanthene and xanthene are within an order of magnitude but the emission from xanthene is 99% fluorescence. At room temperature, the total luminescence yields of xanthene and thioxanthene are reduced slightly, while the phosphorescence yield of selenoxanthene is dramatically decreased. As intersystem crossing is very fast compared with the lifetime of the triplet state the transfer of energy to the triplet state probably still occurs but it is followed by dissipation of the energy before light emission. At room temperature the triplet energy level of selenoxanthene is also lower than that of thioxanthene and many other organic molecules of biological interest (i.e. nucleic acids). It is possible that the action of Se in radioprotection is to promote the transfer of electronic excitation energy away from the initial site of energy absorption to the n,π^* triplet states associated with the Se atom. On the basis of this hypothesis, the molecule containing the Se could act as an innocuous 'energy sink' in some vital part of the cell.

The ESR technique has contributed to the study of radiation damage in Se-containing compounds, giving information on the structure of radicals trapped in irradiated molecules.

Geoffroy studied the irradiation and ESR analysis of single crystals of Ph_3SeCl[62] and of diphenylselenone (Ph_2SeO_2)[63]. The identification of the radicals was made by comparison with the homologous thio radicals, and the radiation mechanism aspects were discussed.

Some radiation-induced Se-containing free radicals have found applications in biochemical problems. Radiation-induced oxidizing free radicals have been introduced by Adams and coworkers[64,65] and are now used extensively as selective probes in identifying sites of radical attack at essential amino acid residues in proteins[66].

The primary radicals formed in water radiolysis, e_{aq}^-, OH and H, damage biomolecules, and enzymes in particular, in a non-specific way, because these species can attack many sites of the molecule. In contrast, secondary radicals, derived from the introduction of

TABLE 10. Luminescence yields at 95 and 295 K[a]

Compound	Fluorescence		Phosphorescence	
	95 K	295 K	95 K	295 K
Xanthene	6×10^{-3} (2×10^{-5})	2×10^{-3}	3.5×10^{-5}	—
Thioxanthene	2.5×10^{-3} (2.8×10^{-4})	1.8×10^{-3} (1.5×10^{-4})	4.4×10^{-3}	4.1×10^{-5}
Selenoxanthene	—	—	3.0×10^{-2}	1.0×10^{-5}

[a] Reproduced with permission from Ref. 61.

TABLE 11. Absorption maxima and bimolecular rate constants, k, with amino acids for Se-containing secondary radicals

		$k(\mathrm{M}^{-1}\mathrm{s}^{-1})$					
Radical anion	λ_{max}(nm)	Cysteine	Methionine	Tyrosine	Tryptophan	Histidine	Ref.
$(CNSe)_2^{-\cdot}$	440	6.8×10^7	$< 1 \times 10^7$	1×10^7	1×10^7	$< 1 \times 10^7$	35
$SeO_3^{-\cdot}$	430	—	1.2×10^8	1.1×10^9	3.3×10^9	4.3×10^7	36,37

another solute into the solution which competes as a radical scavenger, can attack specific functional groups and could be, therefore, useful reagents for the identification of residues related to the biological activity.

The secondary radicals of different redox properties derived from halide or pseudohalide ions, or from carbonate and selenate ions, have been shown to be of potential interest as selective reagents. These ions react with OH quantitatively and rapidly according to the reactions:

$$X^- + OH^{\cdot} \longrightarrow X^{\cdot} + OH^- \qquad X^- = Cl^-, Br^-, I^-, CNS^-, CNSe^-$$

$$X^{\cdot} + X^- \rightleftharpoons X_2^-$$

$$Y^{2-} + OH^{\cdot} \longrightarrow Y^- + OH^- \qquad Y^{2-} = CO_3^{2-}, SeO_3^{2-}$$

The secondary radicals derived from the pulse radiolysis of selenocyanate[35] and selenium dioxide[36] answer the need for a good selective secondary radical. Table 11 shows the absorption maximum for each radical and the bimolecular rate constants with some amino acids. Both radicals present strong transient absorption spectra, so their reactions can be observed directly. They react rapidly with amino acids containing residues involved in the composition of the active site of enzymes.

Some of the rate constants are pH-dependent due to the ionic equilibria in the particular amino acids and the solute system[36]. Furthermore, the absorption spectra of the reaction products between the secondary radicals and the amino acids studied by means of pulse radiolysis are typical and characteristic of the precise amino acid involved in the reaction.

The combination of pulse radiolysis data, i.e. the rate constants and the spectral characteristics, and the data derived from the assay of biological activity measured under comparable conditions, can give useful information on the composition of the active site of simple and complex enzymes.

The effects of $SeCN^{-\cdot}$[35] and $SeO_3^{-\cdot}$[37] on the inactivation of some enzymes (ribonuclease, lysozime, α-chymotrypsin, alcohol dehydrogenases, etc.) are consistent with the present knowledge of the structure of the catalytic site and of the crucial role played by the amino acid residues.

III. TELLURIUM COMPOUNDS

The radiation chemistry of inorganic Te compounds has mainly been studied by Haissinsky and coworkers[67-69]. They have described some results on the γ-radiolysis of acid solutions of Te(IV) and Te(VI). The apparent existence of a 'quasiequilibrium' between these two valency states is pointed out and a mechanism of radiolytic oxidation of Te(IV) and reduction of Te(VI) is proposed.

The rate constants of the reactions: (1) Te(IV) + OH and (2) Te(VI) + H have been determined by competition with the H_2O_2 + OH and H_2O_2 + H reactions: $k_1 = 4.7 \times$

$10^6 M^{-1}s^{-1}$ and $k_2 = 1.05 \times 10^8 M^{-1}s^{-1}$, respectively. In deaerated solutions neither the oxidation nor the reduction is complete, but after a sufficient irradiation a 'quasiequilibrium' state is apparently established. It is shown that this is due to competition between the Te compounds and the stable radiolytic products (H_2O_2, O_2,H_2) for the free OH radicals and the H atoms.

Other detailed studies on the radiation-induced reactions of Te compounds have been performed by a Japanese group[70,71]. γ-ray-induced reactions of Te(IV) and Te(VI) in sulphuric acid solutions have been investigated by using double tracers for the element[71]. The results are interpreted on the basis of reactions of solutes with H, OH, H_2 and H_2O_2 which are the primary species in acid solutions. The direct absorption of γ-rays in H_2SO_4 is neglected as the concentration of H_2SO_4 is much lower than that of water. The experimental data support a sequence in which the unstable valence states Te(III) and Te(V) play an important role in the reaction mechanisms.

The radiation damage of solid $TeCl_4$ irradiated by fast protons (600 MeV) was investigated by the use of the combined methods of microfiltration and neutron activation analysis[72]. The results indicate that the radiolytic decomposition is negligible compared to other types of decomposition (i.e. thermal effects). The final products of any decomposition of solid $TeCl_4$ may be $TeCl_2$, elementary Cl and elementary Te. As the dichloride probably does not exist in the solid state[73], the amount of elementary Te in the tetrachloride is a measure of the degree of decomposition of this compound. An estimation of the pure radiolytic decomposition shows good agreement with the experimental data.

The organotellurium compounds are of potential importance in the chemistry of hot atoms. Te has several radioisotopes, which can be prepared artificially and can be utilized to study the chemical effects associated with nuclear transformations such as (n,γ) reactions on ^{126}Te, ^{128}Te and ^{130}Te, isomeric transitions (^{129}Te m → ^{129}Te) and β-disintegration of ^{131}Te m, ^{131}Te and ^{132}Te.

It is well known that nuclear processes are associated with radiolysis of the target during irradiation inside the reactor or with the effect of rays emitted during the nuclear disintegration or the nuclear deexcitation.

These facts imply the necessity of a good knowledge of the radiation resistance of the organotellurium compounds.

Studies of this type have been carried out by Llabador [74,75].

The role of the energy and charge-transfer processes which occur during the reactions of ^{131}I formed by β–γ decay of ^{132}Te in mixtures of ^{132}Te-labelled and unlabelled diphenyltellurium (Ph_2Te) and dibutyltellurium (Bu_2Te) has been determined[74]. The results show that the radiolysis of the organotellurium molecules in the autoradiation zone is mainly due to energy-transfer processes involving highly excited states.

The products formed during the γ-radiolysis of Ph_2Te, in the pure state and in benzene solution, have been analysed by gas chromatography[75]. In the pure compound, the main products are benzene, biphenyl and diphenylditelluride. The yield of the latter decreases markedly in the presence of oxygen. In no case is elementary Te found. The proposed primary process involves the rupture of a C—Te bond.

IV. CONCLUDING REMARKS

The radiation chemistry of Se-containing compounds has been much more investigated than that of Te-containing compounds. This fact is explained by the possible role played by Se compounds in chemical radioprotection, and by the interest in development of drugs that, when given before exposure to lethal ionizing radiation, can prolong the life of the irradiated organism. Se-containing compounds are certainly not the best and most versatile radioprotective agents. Their toxicity and chemical instability do not permit their practical application. The best and most effective antiradiation drugs are probably those containing S in their molecules.

However, Se compounds do show a type of radioprotection which could contribute to an understanding of phenomena of radiobiological interest. These compounds exhibit radioprotective ability in many chemical and biological systems, but it is not known whether they act by the same mechanism at all levels of organization.

Since free-radical mechanisms involving transient species from Se compounds acting on chemical or biological structures are important in the radiobiological phenomena, the radiochemical investigations have contributed to the elucidation of these mechanisms. In particular the studies on the pulse radiolysis of some Se-containing organic molecules have shown the chemical nature and reactivity of free radicals which could be active in the radioprotective events. However, our knowledge of the radiobiology and radiochemistry of Se compounds is quite incomplete and most of the different aspects of the field are still wide open to investigation.

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CHAPTER 9

Selenium-stabilized carbenium ions and free radicals

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I. INTRODUCTION

Since the discovery of selenium by Berzelius some 150 years ago its organic chemistry has developed considerably, especially in the years 1920–1950 and during the last decade[1,2]. It has been recognized only recently that divalent Se is able to stabilize positively charged, negatively charged and radical centres located at the α-position. Therefore, selenium closely resembles in this respect its congener sulphur. While α-selenocarbanions have already proved to be extremely useful synthetic intermediates, the use of their cationic and radical counterparts is currently under investigation. The aim of this chapter is to give an overview of what is presently known about Se-stabilized carbenium ions and radicals.

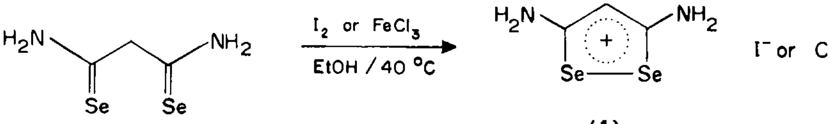
II. SELENIUM-STABILIZED CARBENIUM IONS

A. Cyclic Selenocarbenium Ions

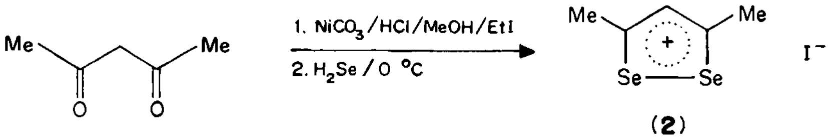
Besides being cyclic all these cations have the common feature of containing additional structural features which contribute to their stabilization. Some of them are aromatic in the sense that they formally possess a delocalized π sextet; others bear substituents such as $—NH_2$ or $—NMe_2$.

1. 1,2-Diselenolylium ions

The 3,5-diamino-1,2-diselenolylium ion (**1**) was described first[3] in this series. It can be prepared in 76% yield by iodine or iron (III) chloride oxidation of diselenomalonamide[4] in ethanol solution (equation 1) and isolated as a yellow crystalline solid. Both the chloride and iodide salts are so stable that they decompose (without melting) only when heated to 200 °C. 3,5-Dimethyl-1,2-diselenolylium salts (**2**) have also been prepared by a completely different method[5,6] (equation 2).

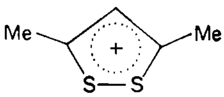


(1) (1)



(2) (2)

The close similarity of the spectral properties of cations **1** and **2** to those of the corresponding 1,2-dithiolylium systems[3-7] led the authors to the conclusion that the two types of cations must also have similar structures. Table 1 illustrates UV and a few of the IR absorptions of **2** as compared to those of the 3,5-dimethyl-1,2-dithiolylium ion (**3**).



(3)

The crystal structures of several differently substituted 1,2-dithiolylium cations have been determined [8-11]. These ions all appear to be planar with all the ring-forming bonds being intermediate between single and double bond lengths[11,12]. The close structural similarity between **2** and **3** suggests therefore that 1,2-diselenolylium ions also have delocalized 6 π electron structure. Presumably, the relatively high thermal stability of **1** and **2** as well as their inertness towards halide and alcohol nucleophiles are also due to this aromatic character. It is worth noting in this connection that non-empirical calculations using linear combinations of gaussian orbitals on the parent 1,2-dithiolylium cation[13] have shown that almost all the positive charge is shared by the S and H atoms and quite

TABLE 1. IR and UV absorptions of **2** and **3**

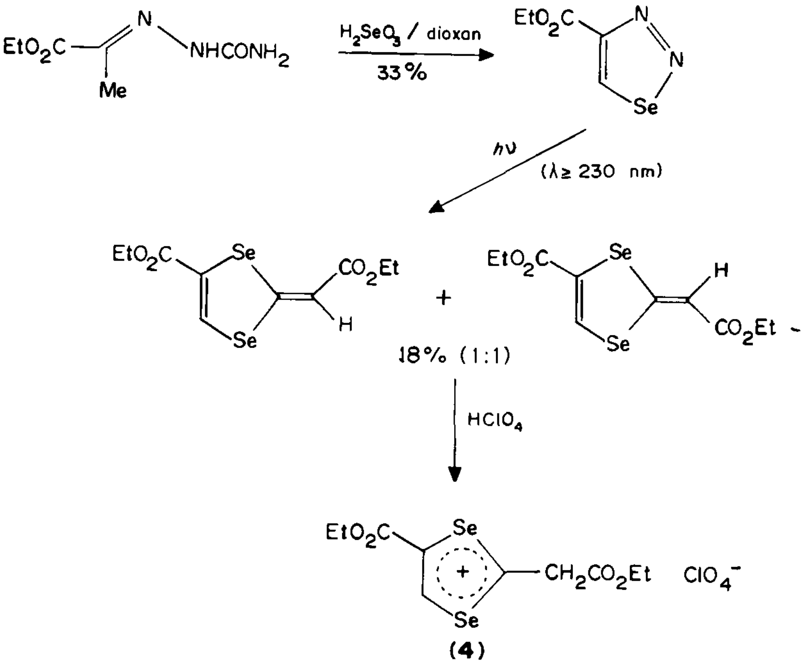
IR[5,7]				UV[a 6]			
3		**2**		**3**		**2**	
$\tilde{\nu}$(cm^{-1})	Assignment	$\tilde{\nu}$(cm^{-1})	Assignment	λ_{max}	log ε	λ_{max}	log ε
1476	ν(C—C)	1465	ν(C—C)				
1318	ν(C—C)	1340	ν(C—C)	265	3.89	300	3.75
1232	δ(C—H)	1240	δ(C—H)				
1204	ν(C—CH$_3$)	1170	ν(C—CH$_3$)	288	4.00	320	3.81
1092	ν(C—CH$_3$) + ν(C—S)	1000	ν(C—CH$_3$) + ν(C—Se)				
697	ν(C—S)	600	ν(C—Se)				

[a] In 1M HCl solution.

surprisingly, all the ring C atoms bear net negative charges. Again, if a similar situation holds for 1,2-diselenolylium systems, it explains their lack of reactivity towards common nucleophiles.

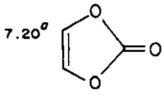
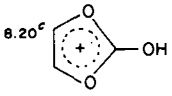
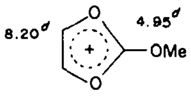
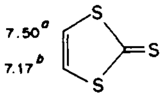
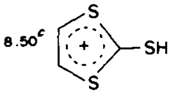
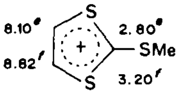
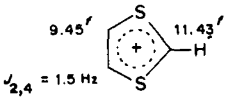
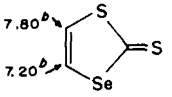
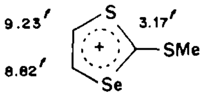
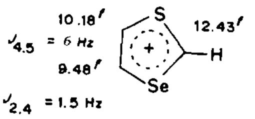
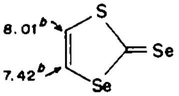
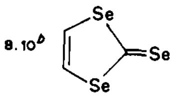
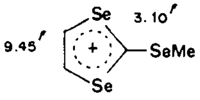
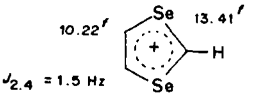
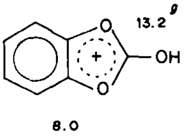
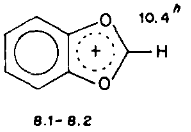
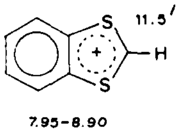
2. *1,3-Diselenol-2-ylium ions*

Two methods are now available for the preparation of 1,3-diselenolylium salts (**4**). Meier and Menzel[14] obtained a precursor of **4** by photolysis of 4-carboethoxy-1,2,3-



SCHEME 1

TABLE 2. Selected ^{1}H-NMR data for 1,3-dichalcogenolylium ions

 **(10)**	 **(11)**	 **(12)**	———
 **(13)**	 **(14)**	 **(15)**	 **(16)**
 **(17)**	———	 **(18)**	 **(19)**
 **(20)**	———	———	———
 **(7)**	———	 **(8)**	 **(9)**
 **(21)**	 **(22)**	 **(23)**	

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[a] In SO_2 solution, external (capillary) $SiMe_4$.[18]

[b] In $CDCl_3$ internal $SiMe_4$[16].

[c] In FSO_3H-SbF_5-SO_2 at −60 °C[18].

[d] In H_3CF-SbF_5-SO_2 at −40 °C[18].

[e] Stable iodide salt in SO_2 solution at −40 °C[18].

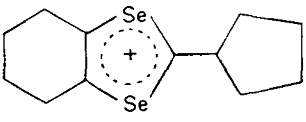
[f] In DMSO-d_6[16]

[g] In FSO_3H-SbF_5-SO_2ClF at −80 °C[18].

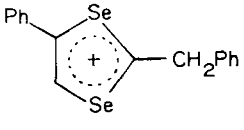
[h] In FSO_3H-SO_2 at −70 °C[18].

[i] In CD_3CN at room temperature[18].

selenadiazole; the sequence is outlined in Scheme 1. However, perchlorate 4 decomposed during NMR measurements. Changing the protonation medium ($CDCl_3$/CF_3COOH instead of $HClO_4$), as well as the ring substituents, has the effect of slowing down the decomposition rate sufficiently to permit NMR measurements. Thus the trifluoroacetate salts of 2-cyclopentyl-4,5-tetramethylene-1,3-diselenolylium (5) and 2-benzyl-4-phenyl-1,3-diselenolylium (6) ions could be observed[15] in solution.

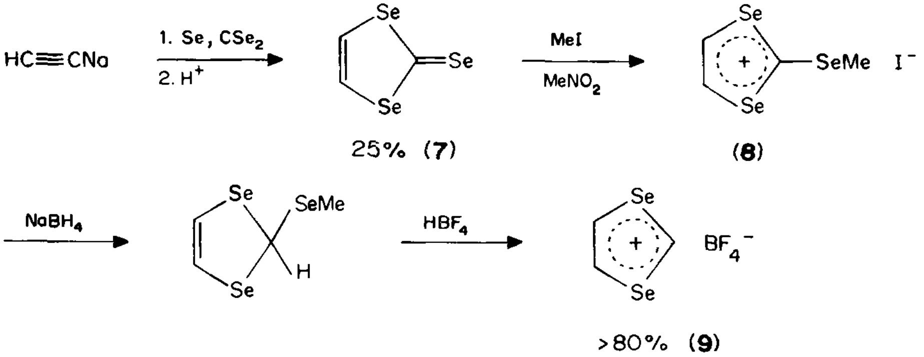


(5)



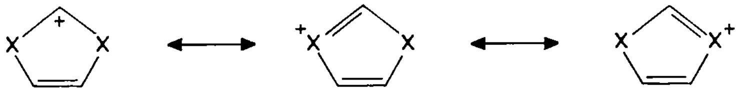
(6)

The method of Engler and Patel[16] is more versatile with regard to the nature of the heteroatoms (S, Se or Se, Se) present in the five-membered ring. However, it is less flexible with regard to the substituents on C(4) or C(5) (Scheme 2). Starting from 1,3-diselenole-2-selone (7) or from 1,3-thiaselenole-2-selone (or from 2-thione)[17], 1,3-diselenolylium (9) or 1,3-thiaselenolylium salts can be obtained. These compounds appear to be more stable thermally than compounds **4**, **5** and **6**.



SCHEME 2

Although UV and IR absorptions have been provided[16] for some of the compounds, the most relevant information about their electronic structure has been obtained from ^1H- and ^{13}C-NMR data[15,18]. Proton chemical shifts are available for a fair number of 1,3-dichalcogenolylium systems (Table 2). Direct comparisons are however difficult, not only because data for 1,3-dioxol-2-ylium ions are missing, but also because the solvent effects are in many cases too large to be ignored. The most striking examples of this are the 0.33 ppm difference for the vinyl protons of **13** in SO_2 or $CDCl_3$ solution and the 0.72 ppm difference for the vinyl protons of **15** in SO_2 at $-40\,°C$ or in DMSO-d_6 at room temperature. Nevertheless, **16** and **9** have been measured in the same solvent and the vinyl and methine protons are shifted downfield by 0.77 ppm and 2 ppm, respectively on going from **16** to **9**. It has been concluded[16] that the greater displacement to low field of the methine proton is a consequence of more positive charge being on C(2) in **9** than in **16**, and that resonance structures **B** and **C** are less important than A in the case of **9** compared with **16**. The picture is less clear however, if one compares other pairs of data in Table 2.



A **B** **C**

Conversion of vinylene carbonate (**10**) to the cation **12** brings about a downfield shift of 1.0 ppm for the vinyl protons. The same transformation results in a downfield shift of ca. 1.6 ppm for the change from **13** to **15** and of ca. 1.35 ppm for the change from **7** to **8**. Even taking into account the important solvent effects, it seems difficult to rationalize the same sort of downfield shift for **8** in terms of dominant resonance structure **A**. Also, comparing the methine proton chemical shifts of **22** and **23** and those of **16**, **19** and **9** it is intriguing to see that replacement of two O atoms by two S atoms brings about the same difference of ca. 1 ppm in the chemical shift as does the replacement of one S atom by Se.

It is not our purpose to deny the better positive-charge-stablizing ability of S compared with Se, but we feel that the existing data do not exclude the simultaneous operation of rather significant ring current effects through the O, S and Se analogues.

On the other hand, Table 3 presents some pertinent[13] C-NMR data for 1,3-dioxol-2-ylium and 1,3-diselenol-2-ylium ions. With the exception of **11**, **12**, **14** and **15** there is a general trend of increasing chemical shifts for the C(2) carbon atoms on going from O to S to Se derivatives. Thus one finds a $\Delta\delta$ of 14.5 ppm between **22** and **23**, 26.3 ppm between **25** and **5** and 24.2 ppm between **28** and **6**. Increasing C(2) chemical shifts point to more and more localized and increasing positive charge on that carbon and one could therefore conclude not only that the aromatic character decreases in the order O > S > Se, but also that it is eventually negligible for the thio and seleno cations[15]. The same sort of conclusion is arrived at when one considers $\Delta\delta$ values of C(4) carbon atoms in couples like **10** and **11** or **13** and **14**. There is only a small change in C(4) chemical shift on protonation of vinylene carbonate (**10**) and vinylene trithiocarbonate (**13**). Actually, the largest part of the change may be due to a solvent effect[15,18], which indicates that in the case of trisubstituted ions like **11** and **14** charge delocalization onto C(4) and C(5) is indeed negligibly small.

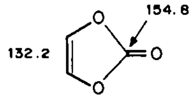
The situation appears even more complicated in the case of disubstituted ions **25**, **28**, **5** and **6**, where $\Delta\delta \sim 30$ ppm (free of solvent effect) for C(4) of the ion and its corresponding precursor. Taking into account the small differences in C(4) chemical shifts between the thio and seleno precursors (**24**, **26**, **27** and **29**) it is difficult to explain the above relatively large values solely in terms of localized positive charge on C(2), especially for the Se derivatives **5** and **6**.

In summary, the question of charge delocalization and aromatic character of 1,3-diselenol-2-ylium ions remains open to dispute until X-ray structure data are available for these species.

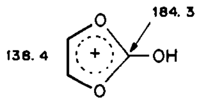
3. *1,3-Diselenolan-2-ylium and 1,3-thiaselenolan-2-ylium ions*

A number of saturated cyclic Se-stabilized carbenium ions bearing *N*,*N*′-dialkylamino or *N*,*N*′-arylalkylamino substituents on the positively charged C atom have also been prepared as their dimethyltin (IV) tribromide salts (Scheme 3). These compounds can also be regarded as imminium salts. In agreement with this view compounds **30**–**34** exhibit the ν(C—N) absorptions in the IR at relatively high frequencies (1520–1588 cm^{-1}), suggesting thereby high percentages of double-bond character of the C—N bonds[19]. Also, the *N*-Me protons of 2-(dimethylamino)-1,3-thiaselenolan-2-ylium (**30**) and 2-(dimethylamino)-1,3-thiaselenan-2-ylium (**31**) ions appear as two singlets in the ^{1}H-NMR spectrum at room

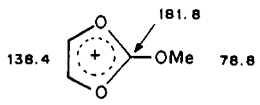
TABLE 3. Selected ^{13}C chemical shift of 1,3-dichalcogenolylium ions



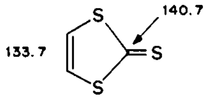
(**10**)



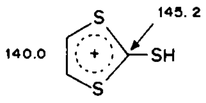
(**11**)



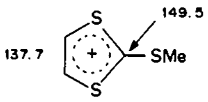
(**12**)



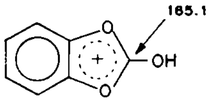
(**13**)



(**14**)



(**15**)



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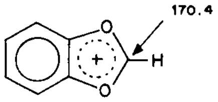
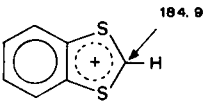
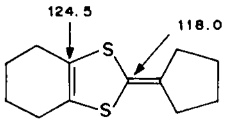


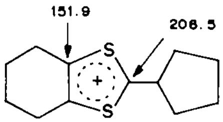
(**22**)



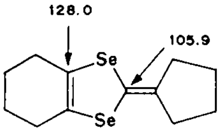
(**23**)



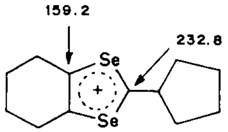
(**24**)



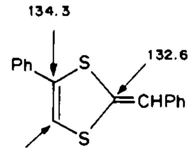
(**25**)



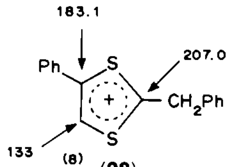
(**26**)



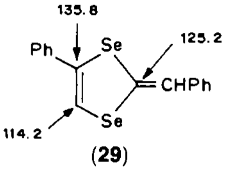
(**5**)



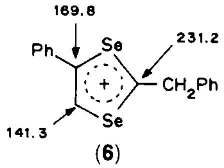
(**27**)



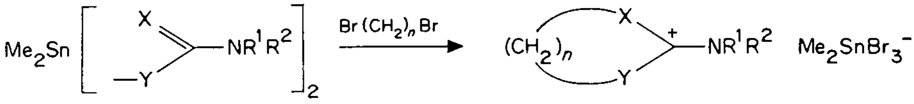
(**28**)



(**29**)



(**6**)



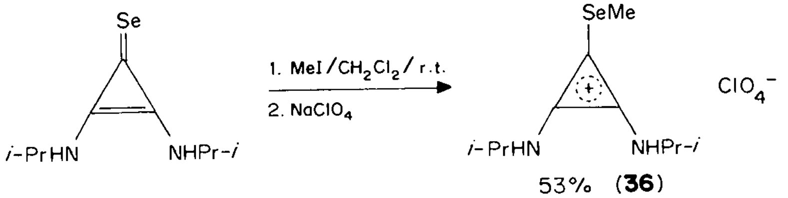
(30) $n = 2$;	X = S, Y = Se;	$R^1 = R^2 = Me$
(31) $n = 3$;	X = S, Y = Se;	$R^1 = R^2 = Me$
(32) $n = 2$;	X = Y = Se;	$R^1 = R^2 = Me$
(33) $n = 3$;	X = Y = Se;	$R^1 = R^2 = Me$
(34) $n = 2$;	X = Y = Se;	$R^1 = Ph$, $R^2 = Me$
(35) $n = 2$;	X = Y = S;	$R^1 = R^2 = Me$

SCHEME 3

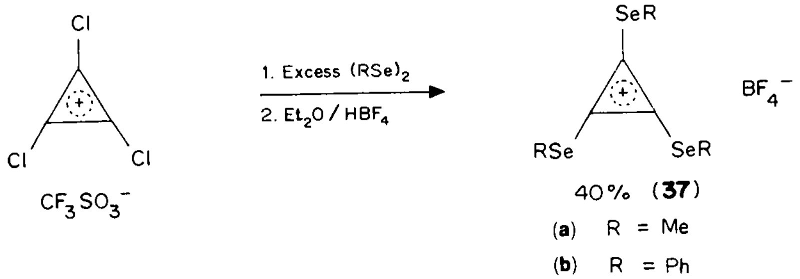
temperature. This has been attributed to hindered rotation around the C—N bond. Interestingly, in compounds **32**, **33** and **34** and their dithio analogue **35** the *N*-Me protons appear as singlets. It is unclear at present whether the apparent lower barrier to rotation about the C—N bond is due to a more efficient delocalization of the positive charge in **32**–**35**. In any case this peculiar behaviour of the mixed cations **30** and **31** deserves more detailed investigation.

4. *Miscellaneous cationic systems*

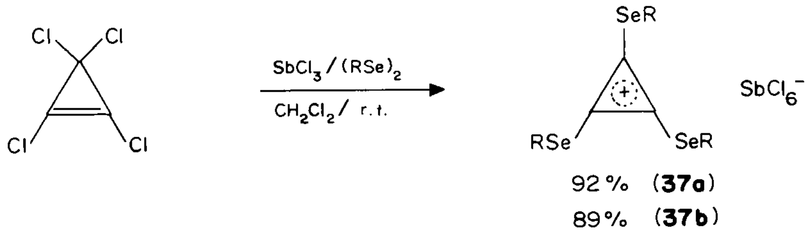
Bis (isopropylamino)methylselenocyclopropenylium perchlorate (**36**) has been prepared[20] according to equation (3) and tris(alkylseleno) and -(arylseleno)-cyclopropenylium salts (**37**) have been obtained according to equations (4)–(6)[21–23]



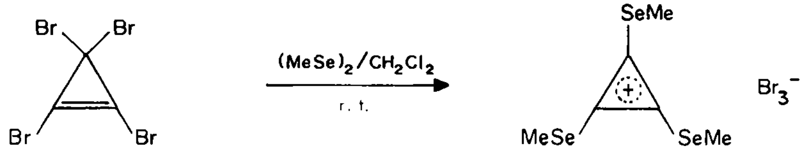
(3)



(4)



(5)

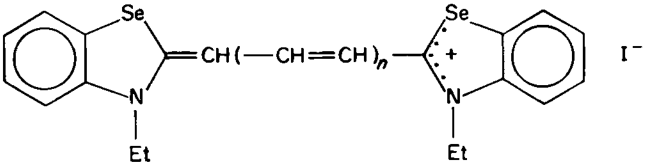


(6)

92% (**37a**)

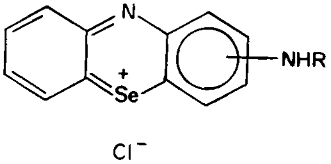
Tris(methyltelluro)cyclopropenylium salts can also be prepared by a method analogous to that of equation (4). While the thio and seleno derivatives very closely resemble each other in stability and in their spectroscopic properties, the telluro analogues appear to be much more labile. Although no attempt has been made to evaluate the contribution of the alkylthio or alkylseleno groups in these systems to the total stabilization, it should not be very high since trihalogenocyclopropenylium ions are equally stable.

A large number of aromatic heterocyclic cationic systems have been described, such as selenocyanine (**38**), selenazinium (**39**) and selenoxanthylium (**40**) dyes[24] or selenopyrylium (**41**) and selenochromylium (**42**) salts[25-27].

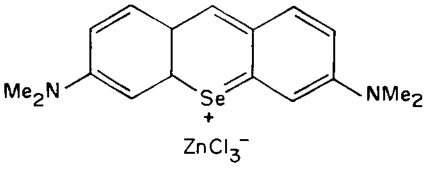


(**38**)

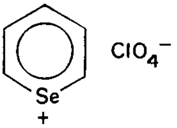
n = 0, 1, 2, 3



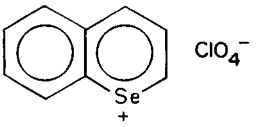
(**39**)



(**40**)



(**41**)



(**42**)

In all these cases the UV-visible spectra alone provide convincing evidence for a efficient delocalization of the positive charge through the Se atom.

B. Aliphatic Selenocarbenium Ions

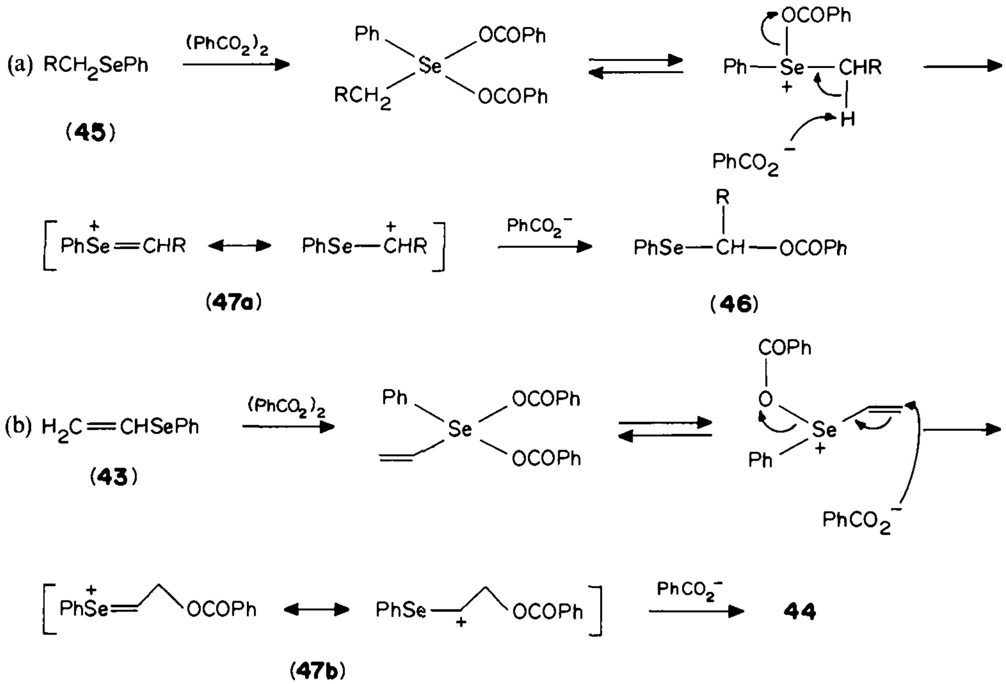
1. *Monoselenocarbenium ions*

Although these species have not yet been isolated and characterized structurally, there are good reasons to believe in their existence. The first line of evidence arises from the observation of a number of reactions which appear to be the seleno analogues of the well-documented Pummerer rearrangement for thio compounds[28,29].

In an attempt to polymerize phenyl vinyl selenide (**43**) in the presence of benzoyl peroxide Okamoto and coworkers[30] isolated crystalline **44** in 56% yield (equation 7). Treatment of alkyl phenyl selenides (**45**) under the same reaction conditions yielded (50–92%) α-benzoyloxyalkyl phenyl selenides (**46**)[31].

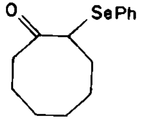
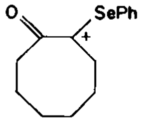
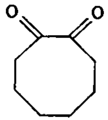
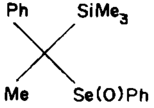
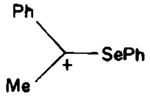
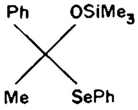
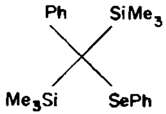
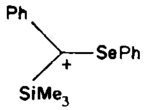
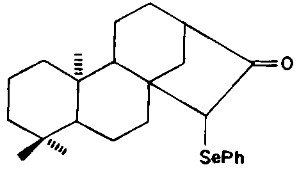
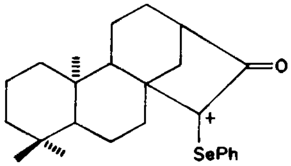
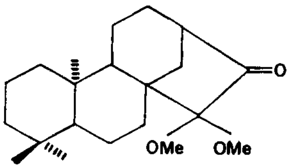
$$\underset{(\mathbf{43})}{\mathrm{PhSeCH{=}CH_2}} + (\mathrm{PhCOO})_2 \xrightarrow[\text{reflux}]{\mathrm{CCl_4}} \underset{(\mathbf{44})}{\mathrm{PhSeCH(OCOPh)CH_2OCOPh}}$$

Both reactions have been rationalized[31] by postulating the initial formation of a dibenzoyloxyselenurane which decomposes on heating to the corresponding ion pair and then leads to products via a Se-stabilized carbenium ion (**47**) as shown in Scheme 4. Starting from methyl phenyl selenide the corresponding selenurane was isolated in 92% yield[31]. Similarly alkyl phenyl selenides have on treatment with peracids been transformed to α-acyloxyphenyl selenides via Pummerer rearrangement[32]. Other interesting examples of this type of reaction are included in Table 4. It should be noted that in Scheme 4 and Table 4 we have represented the key intermediates as free α-selenocarbenium ions. However, another mechanistic possibility is that at least some of the seleno-Pummerer rearrangements mentioned above proceed in a concerted manner without involving carbenium ions.



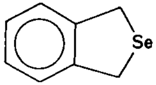
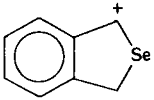
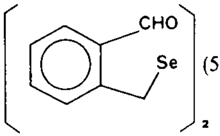
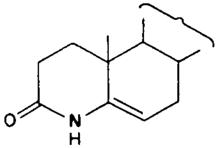
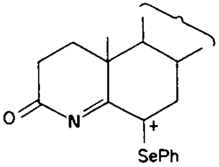
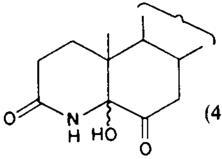
SCHEME 4

TABLE 4. Examples of the seleno-Pummerer rearrangement

Starting material	Conditions	Key intermediate	Products (yield, %)	Ref.
MeSe(O)Me	AcOH/60 °C	$MeSeCH_2^+$	$MeSeCH_2OAc$ (29)	33
	$O_3/CH_2Cl_2/-78\,°C \rightarrow$ r.t.		 (43)	34
	THF/i-Pr_2NH/r.t.		 + PhC(O)Me (22)	35
	H_2O_2/CH_2Cl_2/r.t.		$PhC(O)SiMe_3$ (46)	35
$(Me(CH_2)_4C(O)CH(Me)Se)_2$	O_3/AcOEt/25 °C	$Me(CH_2)_4C(O)\overset{+}{C}(Me)Se$—	$Me(CH_2)_4C(O)C(O)Me$ (34)	36
	$Tl(NO_3)_3$/MeOH/24 h			37

(*Contd.*)

TABLE 4 (*Contd.*)

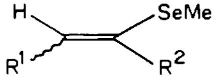
Starting material	Conditions	Key intermediate	Products (yield, %)	Ref.
	H_2O_2/AcOH		 (58)	38
	$(PhSeO)_2O/CH_2Cl_2$/r.t.		 (40)	39, 40

The second line of evidence for substantial stabilization of a positive charge by an adjacent selenyl moiety stems from investigations of the mechanism of acidic hydrolysis of vinyl selenides **48**[41] and **49**[42,43]. It has been established that all the aryl vinyl selenides **48** undergo hydrolysis according to the conventional mechanism characteristic for vinyl ethers and vinyl sulphides. A slow protonation of the olefinic β-carbon atom is followed by hydration of the intermediate arylselenocarbenium ion **50**. By using the correlation equation for the protonation of alkenes[44,45] McClelland and Leung were able to estimate[41] the following σ_p^+ constants: $\sigma_p^+(\mathrm{PhO}) = -0.62$, $\sigma_p^+(\mathrm{PhS}) = -0.54$ and $\sigma_p^+(\mathrm{PhSe}) = -0.47$. The value for the phenylseleno group is comparable to that of the cyclopropyl group[46].

$H_2C{=}CHSeC_6H_4X$

(48)

X = 4-MeO, 4-Me, H, 4-F, 4-Br, 4-Cl, 3-Cl, 4-CF_3, 4-NO_2



(49)

(a) R^1 = *n*-Dec; R^2 = Me

(b) R^1 = H; R^2 = 4-XC_6H_4;
X = MeO, Me, H, Cl, NO_2

In the case of vinyl selenides **49b** the hydrolysis rate constants do not correlate with the σ^+ parameters, but they obey a Yukawa–Tsuno-type equation[43]. This can be interpreted as the result of a cross-conjugative competition between ArX and SeMe for delocalization of the positive charge in **51**.

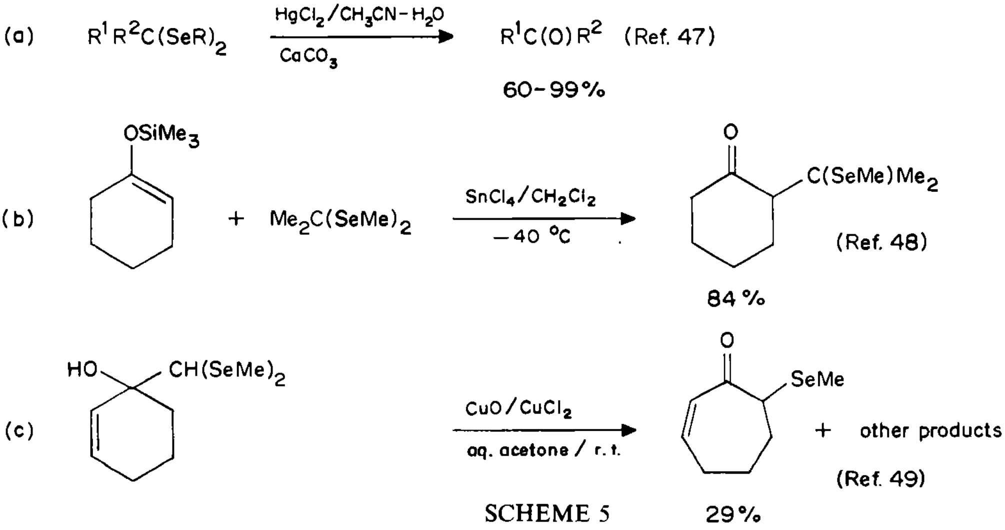
$Me\overset{+}{C}HSeC_6H_4X$

(50)

$R^1CH_2\overset{+}{C}(SeMe)C_6H_4X$

(51)

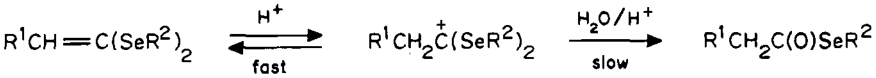
Finally, a few other reactions in which α-selenocarbenium ions are the most likely intermediates have also been carried out in our laboratory (Scheme 5)[47–49]. Reactions (a) and (b) proved to be synthetically useful[47,48].



SCHEME 5

2. Bis(seleno)carbenium ions

Acidic hydrolysis of ketene selenoacetals (**52**) (Scheme 6) provided[50] the first examples of bis(seleno)carbenium ions (**53**). From the mechanistic point of view it is of interest to note that there is a progressive changeover from a rate-limiting protonation to a rapid preequilibrium protonation of the double bond on going from **48** to **49** to **52**. Preequilibrium protonation was likewise observed during hydrolysis of ketene thioacetals[51]. Subsequently a few cations of the type **53** were also prepared and isolated[52] as their hexahaloantimonate salts (Scheme 7).

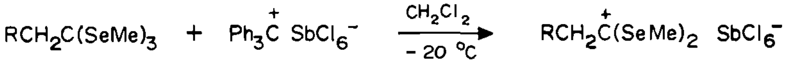


$R^1CH{=}C(SeR^2)_2 \underset{fast}{\overset{H^+}{\rightleftharpoons}} R^1CH_2\overset{+}{C}(SeR^2)_2 \xrightarrow[slow]{H_2O/H^+} R^1CH_2C(O)SeR^2$

(**52**)
R^1,R^2 = Me, Ph

(**53**)
(**a**) $R^1 = R^2$ = Me
(**b**) R^1 = Ph, R^2 = Me

SCHEME 6

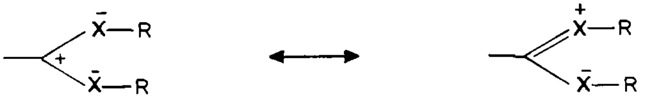


$RCH_2C(SeMe)_3 + Ph_3\overset{+}{C}\ SbCl_6^- \xrightarrow[-20\ °C]{CH_2Cl_2} RCH_2\overset{+}{C}(SeMe)_2\ SbCl_6^-$

R = Me 85%
R = Ph 80%

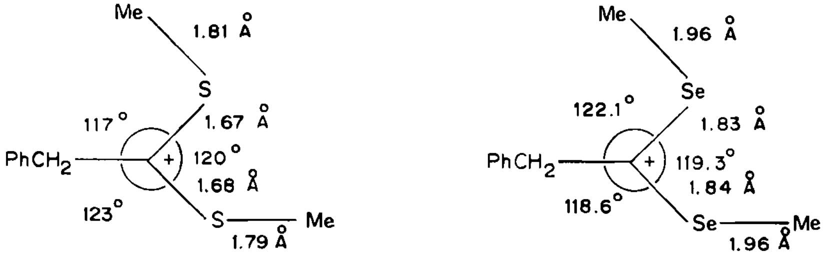
SCHEME 7

Bis(methylseleno)benzylcarbenium hexachloroantimonate (**53b**) has been structurally investigated by ^1H- and ^{13}C-NMR as well as by X-ray diffraction and compared to its bis (methylthio) analogue[52]. ^1H-NMR spectra (room temperature, CD_3CN solution) of these two compounds appeared to be identical within a few hundredths of a ppm. No significant conclusion can therefore be drawn from ^1H chemical shifts. However, the shapes of both the SMe and the SeMe signals were temperature-dependent and this was attributed to hindered rotation about the C^+—S and C^+—Se bonds. The corresponding Arrhenius activation energies are 14.3 ± 2 and 12.7 ± 2 kcal mol^{-1} respectively. The available values for the oxo derivatives range from 8 to 15 kcal mol^{-1}. Thus, the rotational barriers appear to be roughly identical for all three types of carbenium ions, suggesting thereby a very large contribution from resonance structures **54**, even in the case of X = Se.



(**54**)
X = O, S, Se

Although ^{13}C resonances for C^+ occur at a rather low field (263.4 ppm for **53b** and 244.5 ppm for its thio analogue), the above idea gains considerable support from X-ray structural data, especially from the bond distances (Scheme 8). The bond angles around the positive carbon atom show that both cations are essentially planar with virtually no distortion of the regular triangular structure. More striking is the finding that the C^+—S and C^+—Se bond distances are considerably reduced with respect to the corresponding single bond lengths of 1.81 Å (C—S) and 1.98 Å (C—Se). (Note that the C═S and C═Se bond lengths are 1.54–1.61 Å and 1.67 Å, respectively.) This undoubtedly shows that Se-containing substituents are able to stabilize a neighbouring positive charge and that the mechanism of this stabilization involves non-negligible conjugative interaction.



SCHEME 8

The latter results shed some light also on the 1,2-diselenolylium and 1,3-diselenolylium ions as well as on other 'aromatic' Se-containing cationic systems discussed in the preceding sections.

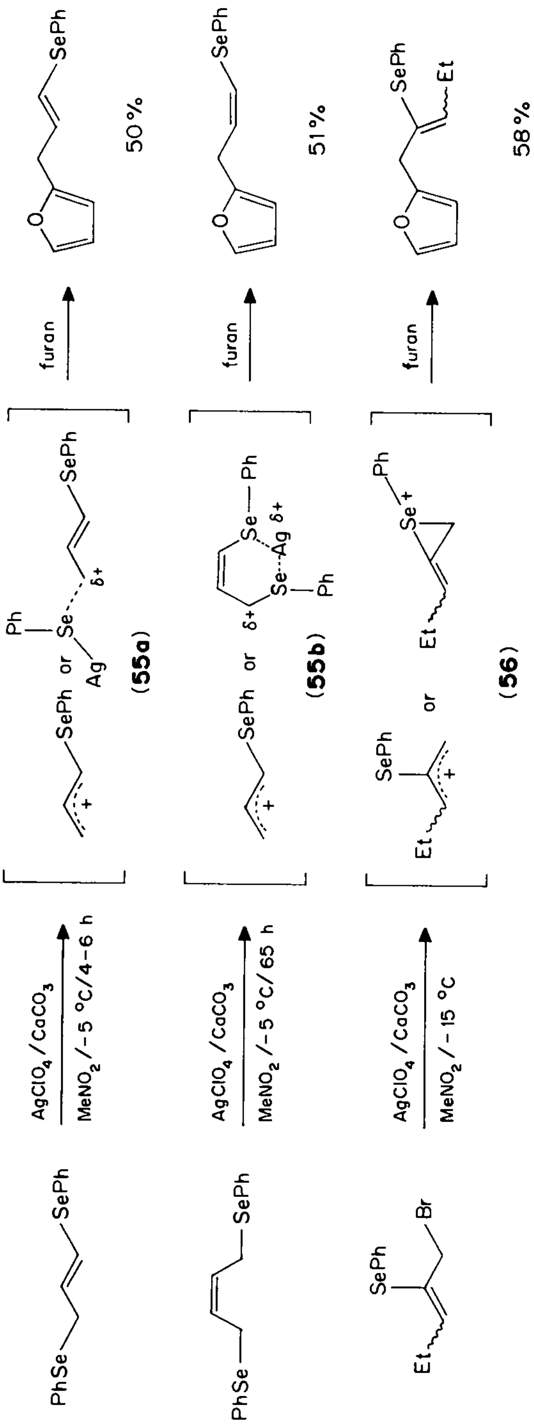
3. *1-Seleno- and 2-seleno-allyl cations*

The presence of the allylic delocalization should in principle make these monoselenated species more stable than their saturated analogues. However, the preliminary work so far carried out suggests that both 1-seleno- and 2-seleno-allyl cations **55** and **56** must possess some structural peculiarities which are responsible for the observed reactivities[53,54] illustrated in Scheme 9. The fact that *E*- and *Z*-1,3-bis(phenylseleno)propenes react with furan with a remarkable retention of the initial double-bond configuration, as well as the notable difference in the reaction rates, suggest more complex intermediates such as **55a** and **55b** instead of the fully delocalized free allylcarbenium ion. Similarly, the intermediacy of alkylideneseleniranium ion **56** could explain that 1-bromo-2-(phenylseleno)-2-pentene gives no cycloaddition at all and that C(1) of the starting material is the exclusive site of attachment to the furan ring. However, these structures are proposed only tentatively in order to rationalize the observed results; more work is necessary to fully characterize the nature of the intermediates.

III. α-SELENO FREE RADICALS

The field of Se-containing radicals is much less well documented than that of Se-containing anions or cations. A large part of the existing work has been devoted to radical anions or radical cations, so that at present time only a very limited number of papers deal with neutral α-seleno free radicals. The best method for investigating radicals is by ESR and the following discussion will mainly be centred on the results obtained by this technique.

Radical anions **57** and **58** derived from heteroaromatic Se compounds have been prepared by one-electron transfer to the parent heterocycle from anions, alkali metals or from an electrode[55–59]. Neutral and cation radicals derived from phenoselenazine[56,60] (**59** and **62**), from phenoxselenin[56,61] (**60**), from dibenzodiselenin[61], (**61**), from 9-phenylselenoxanthene[62], (**63**) and phenoselenazine nitroxide[56,60] (**64**) have also been generated in solution and studied by ESR. Hyperfine coupling constants a_i and g values for these species are presented in Table 5. In terms of resonance theory the extent of delocalization of the odd electron of a radical is a measure of its stability. In so far as the hyperfine splitting constants a_i are linearly connected to spin densities, the magnitude of the splitting by[77] Se should in principle give a measure of the contribution of Se atoms to the stabilization of radical species. On the other hand, semiempirical theory has been



(55a)

(55b)

(56)

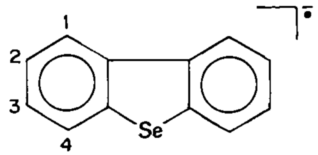
SCHEME 9

TABLE 5. Hyperfine coupling constants a_i (G) and g values of heteroaromatic seleno radicals

		a_i								
Species	i =	Se	N	C(1)	C(2)	C(3)	C(4)	g	Solvent	Ref.
57		—		4.27	1.02	5.27	1.02	—	DME	55
		5.44		4.21	1.03	5.18	1.03	2.0030	DME	56
58		—	5.97	1.99	1.99			—	DMSO–*t*-BuOH	57
		4.9	5.79	2.48	1.65			2.0063	DME	56
		—	5.79	2.48	1.65			—	DME	58
		—	5.67	1.88	1.88			—	DME	59[a]
59		25.0	6.17	1.18	0.40	2.50	0.40	2.0161	Nitroethane	56,60
60		39.5		—	—	—	—	2.0228	Nitroethane	56,61
61		—		—	—	—	—	2.0315		61
62		10.9	6.96	3.82	1.00	2.86	0.100	2.0104	Benzene	56
63		—		3.70	0.59	3.70	0.59	—	THF	62
64		7.70	9.26	2.15	0.64	2.12	0.64	2.0071	Benzene	60

[a] Variation of a_i with the solvent was also reported.

suggested[63] and successfully applied[56] to correlate isotropic g shifts with spin densities and spin-orbit coupling constants. Therefore, experimentally determined g values can also give valuable information on the stabilization of radicals by a heteroatom. This is especially true for Se whose spin-orbit coupling constant is large compared to that of S (1688 and 382 cm^{-1} for Se and S, respectively). Inspection of Table 5 then shows that a large ^{77}Se coupling constant (a_{Se}) is associated with a large g value (species **59, 60, 62**) and vice-versa. It is interesting to note that a_{Se} and g values are also strongly dependent on the charge of the radical. Anion radicals **57** and **58** exhibit the lowest ^{77}Se coupling, neutral phenoselenazine radical **62** and nitroxide **64** have intermediate values, while cation radicals **59–61** have the highest ^{77}Se coupling constants. The same trend is observed for the corresponding g values. Gilbert and coworkers have derived spin densities ρ^{π} for **59** as well as its oxo and thio analogues using HMO and McLachlan calculations[56,60], which in the case of **59** reproduced correctly all the observed coupling constants including a_{Se}. The calculations also appeared quite adequate for the other seleno cation radicals. The calculated spin densities can therefore be considered correct also in the case of phenoxazine and phenothiazine cation radicals, with the result $\rho^{\pi}_{\mathrm{Se}} \geqslant \rho^{\pi}_{\mathrm{S}} > \rho^{\pi}_{\mathrm{O}}$ (0.198, 0.179 and 0.086, respectively, using McLachlan calculations). The method also applies for neutral radicals and yields the same trend with considerably lower spin densities ($\rho^{\pi}_{\mathrm{X}} = 0.085$; 0.076 and 0.046 for X = Se, S and O, respectively), but it fails in the case of radical anions **57** and **58**. The reasons for this failure are not clear[56] but it seems quite certain that the spin densities on Se in these anionic species are very low, as confirmed by the coupling constants and g values of Table 5.



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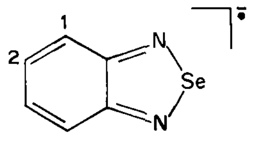

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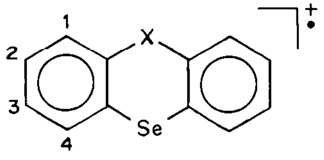
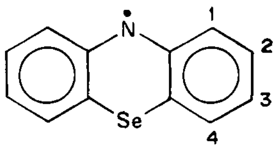


(59) X = NH
(60) X = O
(61) X = Se



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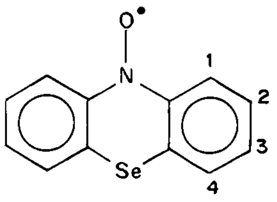

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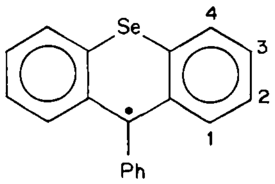
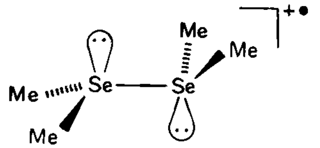


(63)

It therefore appears reasonable to conclude that the unpaired electron of neutral and cation radicals derived from heteroaromatic molecules is efficiently delocalized onto Se. However, at present, it is not possible to make a statement about the relative stability of the oxo, thio and seleno species.

Selenuranyl-type radicals are relevent to the problem of radical stabilization by Se because in a way they make the link between the aromatic species discussed above and the carbon radicals bearing α-seleno substituents.

The dimer radical cation of dimethyl selenide (**65**) was obtained by γ-irradiation of a single crystal at − 196 °C and investigated by ESR spectroscopy[64]. Dialkyl selenides have also been found[65] to react with various radicals to produce the neutral selenuranyl radicals **66**. Se-containing heterapentalenes[66] react with tri-*n*-butylstannyl to produce radicals such as **67** and **68**. In the absence of conjugation one expects high spin densities on the Se atoms of **65** and **66**. This is confirmed by both the isotropic g values and the hyperfine coupling constants to ^{77}Se ($g = 2.0344$, $a_{Se} = 108$ G for **64**; $g = 2.0206$, $a_{Se} = 162.6$ G for **66** where $R^1 = R^2 =$ 1-adamantyl, X = *t*-BuC(O)S). As can be judged from the g values a similar spin distribution holds in radical **68** ($g = 2.0169$), while in the persistent radical **67** a very small part, if any, of the odd electron resides on Se ($g = 2.0047$).



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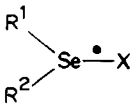

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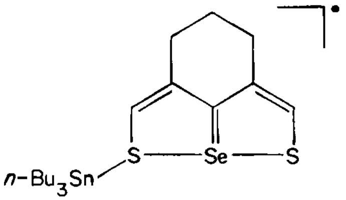

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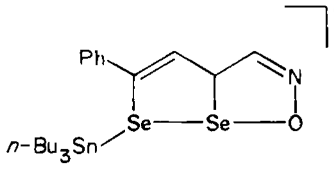
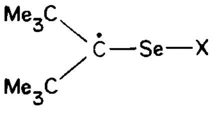


(68)

It is of importance to note that the ESR spectrum of **65** at − 196 °C also contained lines at higher field which were attributed[64] to carbon-centred radicals, mainly $MeSeCH_2\cdot$, but it was not possible to analyse this portion of the spectrum in detail. On the other hand Scaiano and Ingold have described[67] the easy generation of hindered α-selenoalkyl radicals **69** by the reaction of radicals X· with di-*t*-butyl selenoketone in hydrocarbon solution.

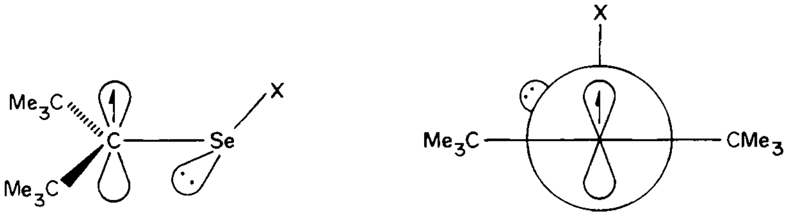


(69)

	X	g	$a_{Se}(G)$
(a)	Me	2.0021	24.6
(b)	*t*-Bu	2.0020	21.3
(c)	CF_3	2.0005	36.6
(d)	*t*-BuO	2.0024	65.0
(e)	Me_3Sn	2.0043	10.9

However, all attempts at the direct observation of unhindered α-selenoradicals formed in solution by hydrogen abstraction from dimethyl selenide, diethyl selenide, methyl phenyl selenide or dimethyl diselenide and under a variety of experimental conditions were unsuccessful[68]. Yet, spin trapping experiments using di-*t*-butyl thioketone provided good evidence that methylselenomethyl ($MeSeCH_2\cdot$) and 1-ethyseleno-1-ethyl ($EtSe\dot{C}HMe$) radicals were indeed efficiently formed. The authors suggested that their failure to detect unhindered alkylselenoalkyl radicals was due to the operation of both the spin-rotation and the spin-orbit line broadening mechanisms. Thus it was estimated[68] that the line width for $MeSeCH_2\cdot$ should be ca. 6.6 G arising from spin rotation alone, while some of the radicals **69** have line widths as small as 0.1–0.2 G.

This great difference in line widths between hindered and unhindered α-selenoalkyl radicals has been attributed to conformational effects. The preferred conformation of **69** is given by **70** and that of $MeSeCH_2\cdot$ by **71**. The unpaired electron in **70** cannot be appreciably delocalized onto the Se atom, hence the low *g* values (see **69**) and sharp lines. In contrast, delocalization in **71** can be efficient and causes very important line broadening, and such radicals cannot be observed in solution.



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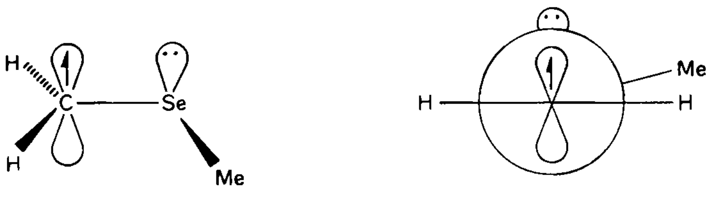
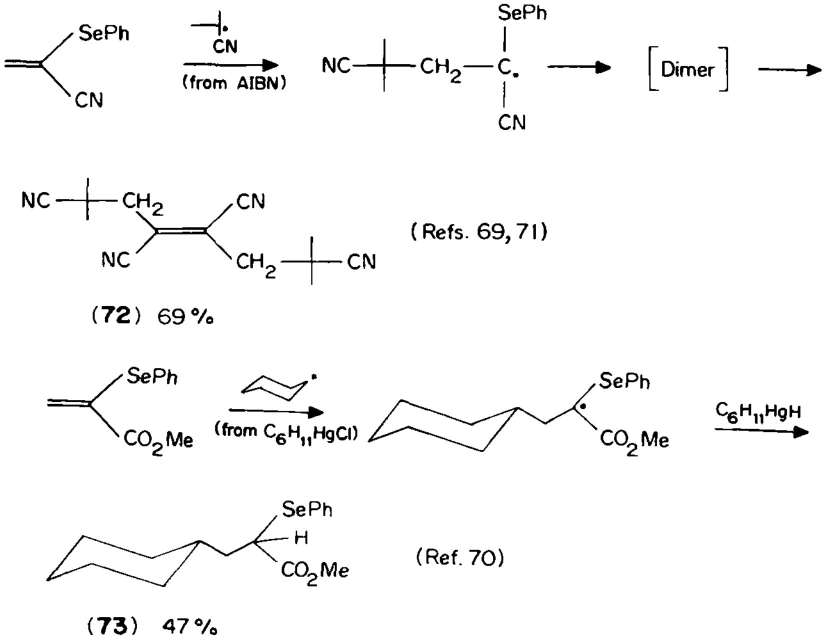


(71)

The last series of examples illustrating the stabilization of carbon radicals by adjacent seleno substituents comes from studies of the addition of radicals to 1, 1-disubstituted olefins (equation 8). It has been found that the formation and stability of the adduct

$$H_2C{=}CXY + R\cdot \rightarrow RCH_2\dot{C}XY \qquad (8)$$

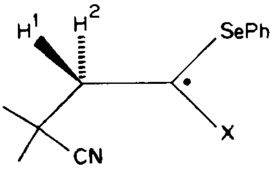
radicals are highly dependent on the nature of the geminal substituents of the starting olefin, and that olefins bearing one electron-attracting and one electron-donating group on the same sp^2 carbon react far more easily and yield the most stable adduct radicals. Furthermore, the latter radicals do not undergo polymerization or hydrogen abstraction, but rather they trap another radical or dimerize[69]. Scheme 10 features two examples of such reactions involving 'captodative'-stabilized α-phenylseleno radicals[69–71]. From competition and rate measurements it was also possible to establish the relative rate of



SCHEME 10

formation of adduct radicals. The figures of Table 6 clearly demonstrate the beneficial effect of the phenylseleno group on the rate of reaction which, of course, also depends on the nature of the electron-attracting group and of the reacting radical species. However, recent results suggest that these additions proceed via very early transition states, and the observed rate differences arise primarily from polar effects of the substituents X and Y on the transition state rather than from their radical stabilizing abilities[72].

α-Phenylseleno radicals (**74**) have also been studied[73] by ESR. Isotropic *g* factors indicate by themselves that in all cases the Se atom carries a significant amount of spin density, and thereby confirm, at least to some extent, the results of kinetic measurements as well as the conclusions arrived at in the cases of aromatic neutral and cation radicals. There is no doubt, however, that additional experimental evidence such as ^{77}Se hyperfine coupling and appropriate theoretical treatment are necessary for a closer and more quantitative evaluation of the radical-stabilizing ability of α-selenyl moieties.



(**74**)

X	g	a_1	a_2	$(a_1 + a_2)$	a_F
CF_3	2.0107	10.75	10.75	—	24.5
S(O)Ph	2.0095	8.55	13.16	—	—
SO_2Et	2.0119	—	—	19.65	—
SO_2Ph	2.0113	—	—	19.19	—

TABLE 6. Relative rates of addition of cyclohexyl and isobutyronitrile radicals to *gem*-disubstituted olefins[a]

R	X	Y	Rel. rate
C_6H_{11}[70 b]	SePh	CO_2Me	62
	Ph	CO_2Et	40
	$SCMe_3$	CO_2Me	35
	Me	CO_2Me	4.7
	OMe	CO_2Me	1 .
IBN[72 c]	SePh	CO_2Me	6.9
	SePh	SO_2Ph	1.5
	OMe	CO_2Me	1
	SePh	S(O)Ph	0.5
	SePh	CF_3	0.4

[a] Cf. equation (8).
[b] At 20 °C in CH_2Cl_2.
[c] At 70 °C in benzene; IBN = isobutyronitrile.

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The Chemistry of Organic
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CHAPTER 10

Selenium- and tellurium-containing organic polymers

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I. INTRODUCTION

Recently, the considerable interest in Se- and Te-containing polymers[1,2] has been greatly enhanced by the observation of the highly conductive properties of modified polyarylyene sulphides. The most promising polymer among the latter is the commercially available poly(thio-1,4-phenylene), PPS (**1**). The polymer becomes highly conducting on exposure to strong oxidants[3]. The strong similarity between S and Se has often been a lead in investigating chalcogen analogues of S compounds.

The C—Se bond is much weaker than the C—S bond and the C—Te bond is even weaker than the C—Se bond. Thus, although Se- and Te-containing polymers may be prepared by using methods similar to those containing S, the synthetic routes for Se- and Te-containing polymers are more limited.

There are three general synthetic routes for producing Se-containing polymers (please note that in this chapter the symbol —R—denotes a divalent alkylene or arylene radical):

(1) *Polycondensation of alkyl or aryl dihalide compounds*:

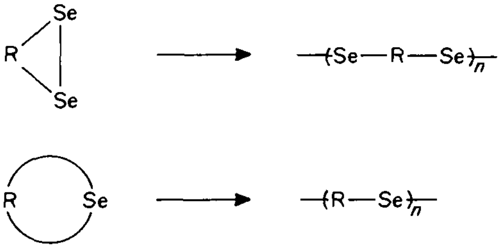
$$X{-}R{-}X \;+\; Na_2Se \longrightarrow -\!\!\left(R{-}Se\right)_n\!\!-$$

$$X{-}R{-}X \;+\; Na_2Se_2 \longrightarrow -\!\!\left(R{-}Se_2\right)_n\!\!-$$

(2) *Hydrolysis and oxidation of alkyl- or aryl-diselenocyanates in an alkaline medium*:

$$NCSe{-}R{-}SeCN \longrightarrow HOSe{-}R{-}SeOH \longrightarrow -\!\!\left(Se{-}R{-}Se\right)_n\!\!-$$

(3) *Ring-opening polymerization of Se-containing cyclic oligomers*: Methods (1) and (2) are the most generally utilized for synthesis of Se-containing polymers. However, these methods often yield both Se-containing cyclic oligomers as well as linear polymers. The third method involves the ring-opening polymerization of the Se-containing cyclic oligomers obtained by methods (1) and (2).



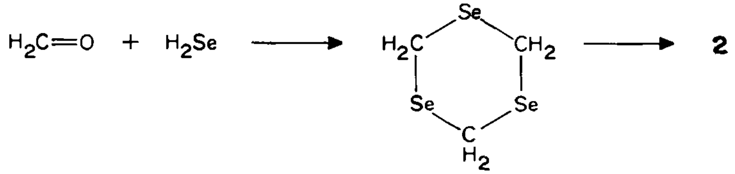
II. ORGANOSELENIUM POLYMERS CONTAINING A MONOSELENIDE CHAIN

A. Poly(selenoalkylene)s, $-\!\!\left(C_nH_{2n}Se\right)\!\!-_n$

1. *Poly(selenomethylene),* $-\!\!\left(CH_2Se\right)\!\!-_n$ *(**2**)*

This is one of the most widely investigated organoselenium polymers with respect to both its synthesis and its physical properties.

In 1915 Vanino and Schinner found that on passing H_2Se into an aqueous solution of formaldehyde in dilute HCl, a pasty solid was obtained[4]. The structure of this compound was later determined as cyclic trimer[5]. Various polymers **2** were obtained from the ring-opening polymerization of the trimer with cationic initiation[6,7] or in the solid state by γ-irradiation[8]. Prince and Bremer reported that **2** could also be prepared in 76% yield without the intermediate cyclic oligomers from the reaction of CH_2Br_2 with Na_2Se in ethyl acetate[9].



Two crystalline structures of **2**, one hexagonal and one orthorhombic, were obtained and their occurrence was found to be dependent on the polymerization conditions. In particular, the polycondensation method[9] and the ring-opening polymerization[6] gave the hexagonal structure, while solid-state irradiation or solid-state cationic polymerization (BF_3–etherate catalyst at 180 °C) of triselenane yielded an orthorhombic polymer[10]. The two crystalline systems of **2** give rise to a monotropic dimorphic system with an orthorhombic to hexagonal transition temperature near the melting range of the hexagonal polymer (185–190 °C). It is very interesting that the same monotropic dimorphism, orthorhombic–hexagonal, observed in polymer **2**, appears also in polyoxymethylene[11].

Prince and Bremer reported that **2** had an electrical conductivity of $6.72 \times 10^{-4}\ \Omega^{-1}\,cm^{-1}$ at 25°C[9]. However, Sandrolini and coworkers who reinvestigated the conductivity of **2** synthesized by various methods found in contrast to Prince and Bremer's data, that none of the samples of **2** studied showed conductivity values exceeding $7.5 \times 10^{13}\ \Omega^{-1}\ cm^{-1}$ [10].

2. *Poly(selenoalkylene)s*

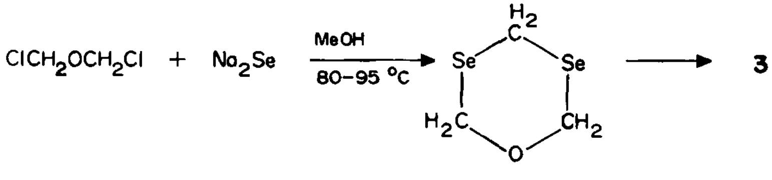
The reaction of *vic*-dihaloethanes with Na_2Se in DMSO of DMF did not produce any polymeric compounds, but rather produced ethylene and Se: The elimination reaction was stereospecific, thus *d,l*-2,3-dibromobutane gave 90% *cis*-butene-2[13]. Longer chain α,ω-dibromoalkanes react readily with Na_2Se to produce the corresponding cyclic seleno hydrocarbons. However, Morgan and Burstall found that 1,3-dibromopropane and Na_2Se gave only a small proportion of cycloselenopropane, the main product being a low molecular weight polymer, $-\!(C_3H_6Se)\!-_6$, m.p. 38–40 °C[14]. They also obtained poly(selenohexylene), $-\!(C_6H_{12}Se)\!-_n$ ($n \sim 12$), m.p. 36–37 °C, by reacting the corresponding dibromide with Na_2Se[14]. This polymer was thermally stable up to 200 °C, but on further heating to 220 °C, it depolymerized without loss of Se giving 2-methylcycloselenopentane.

$$XCH_2{-}CH_2X + Na_2Se \longrightarrow CH_2{=}CH_2 + 2\,NaX + Se$$

Okamoto and coworkers had prepared these polymers according to the literature procedures and found that the electric conductivities were in the range of $\sim 10^{-14}\,\Omega^{-1}\,cm^{-1}$ [15].

B. Oxygen- and Selenium-containing Polymer

The O- and Se-containing linear copolymer, $-\!(CH_2O(CH_2Se)_2)\!-_n$ (**3**), m.p. 195–198 °C, was formed by the cationic (BF_3–etherate) ring-opening polymerization of 1,3,5-



oxadiselenane, prepared by the reaction of α,α′-dichlorodimethyl ether with Na_2Se in methanol[12].

C. Poly(seleno-*p*-xylene), $-\!\!(CH_2C_6H_5CH_2Se)\!\!-_n$ (4)

The reaction of α,α′-dichloro-*p*-xylene with Na_2Se in refluxing ethyl acetate yielded the pale yellow polymer **4**. The polymer was slightly soluble in boiling pyridine, DMSO and DMF; it was found to have a narrow melting point, 174–175 °C, but the molecular weight was not determined[15].

D. Poly(seleno-1,4-phenylene), $-\!\!(C_6H_4Se)\!\!-_n$ (PPSe) (5)

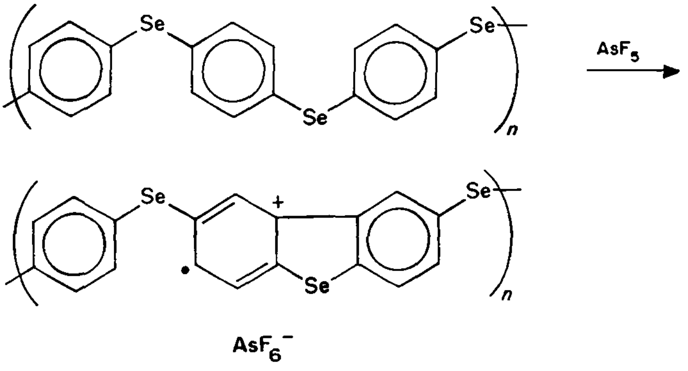
The polymer **5**, which is an analogue of poly(thio-1,4-phenylene) (PPS), has recently been investigated with respect to synthetic methods and physical properties, particularly electric properties.

Cava and coworkers reported that **5** was synthesized from bis(4-bromophenyl) diselenide by reaction with electrolytic copper in refluxing *n*-hexanol-pyridine[16]. Sandman and coworkers found that **5** could also be easily obtained in 80% yield from the reaction between *p*-dibromobenzene with Na_2Se in DMF[17].

The polymer obtained was yellow and melted at 220 °C. Elemental analysis showed that the polymer contained bromine and, assuming that both ends of the polymer chain were bromine atoms, the molecular weight of the polymer was calculated to be about 10,000 ($n = 60$). The polymer was partially crystalline and its density was 2.05–2.15 g cm^{-3}. The structure was found to be isomorphous to that for PPS[13].

Tanaka and coworkers also prepared **5** ($n \sim 25$), m.p. 250 °C, from the reaction of *p*-dibromobenzene with Na_2Se in *N*-methylpyrrolidone in a sealed tube at 180 °C[19]. The polymer obtained was thermally stable up to 350 °C in a N_2 atmosphere and yielded a residue of 46% upon heating to 500 °C. The electric properties of **5** and the modified polymers prepared by different investigators are summarized in Table 1.

The conductivities of the doped **5** varied. However, Sandman and coworkers[18] showed that doping of **5** with AsF_5 led to an insulator–conductor transformation and this was accompanied by structural cross-linking and apparent dibenzoselenophene formation which is analogous to processes occurring for PPS[3].



E. Poly(seleno-4,4′-biphenylene), $-\!\!(C_6H_4C_6H_4Se)\!\!-_n$ (6)

Tanaka and coworkers have prepared **6** in a sealed tube using 4,4′-diiodobiphenyl with Na_2Se in *N*-methylpyrrolidone[19]. The polymerization degree *n* was calculated as $n \sim 24$ by the determination of the iodine end-groups. **6** was also synthesized by the polycondensation reaction of the Grignard reagent of bis(4-bromophenylselenide) with 2,2′-

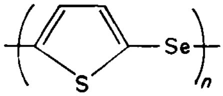
TABLE 1. Electric conductivities of PPSe

Dopant	Conductivity ($\Omega^{-1}cm^{-1}$)	T°(C)	Ref.
None	8.3×10^{-3}	50	17
AsF_5	10^{-6}	25	14
	10^{-8} (after 24h)	25	14
AsF_5	10^{-2}–10^{-3} (40–45% weight increase)	25	16
SO_3^-	1.5×10^{-7}	25	17
BF_3	3.4×10^{-8}	25	17
I_2	7.1×10^{-12}	25	17
SbF_5	1.3×10^{10}	25	17

bipyridine nickel dichloride. The molecular weight of the **6** thus prepared was found to be much lower than that of **6** prepared by the former method[19]. Okamoto and coworkers found that **6** was obtained from the reaction of the Grignard reagent of 4,4'-diiodobenzene with Se followed by oxidation[15].

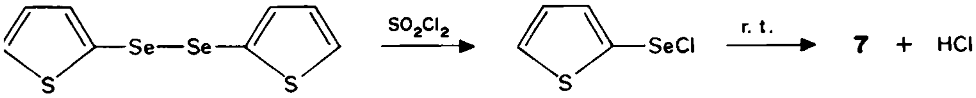
The electrical conductivities of **6** as well as of the doped polymer were in the range of $10^{-2}\ \Omega^{-1}\ cm^{-1}$ [19].

F. Poly(seleno-2,5-thienylene) (7)

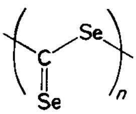


(7)

2,2'-Dithienyl diselenide was treated with SO_2Cl_2 in CH_2Cl_2 in a N_2 atmosphere and the resulting 2-thienylselenyl chloride was then polymerized into **7** in 87% yield. The polymer obtained was a cream-coloured powder and softened at 220–235 °C. A preliminary result showed that the conductivity of **7** was not appreciable and changed after doping with AsF_5[16].



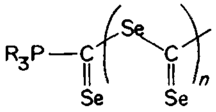
G. Poly(carbon diselenide) (8)



(8)

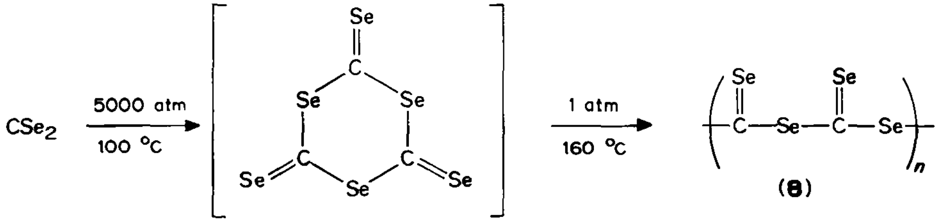
CSe_2 was reported to yield a black solid at a rate of about 1% per month at room temperature[20,21]. The structure of the solid was investigated by IR over the range of 4000–50 cm^{-1} and found to have a linear polymeric structure similar to that of poly(carbon disulphide)[22].

Jensen and Nielsen have reported that when the complex of CSe_2 and a trialkylphosphine was allowed to stand, it was transformed to a brown-red semisolid from which a dark crystalline material was isolated. The following structure was suggested[23]:



Okamoto and Wojciechowski found that when a CSe_2 solution in CH_2Cl_2 or dioxane was pressurized to about 5000 atm and heated at 100 °C for 20 h a black solid was obtained in 95% yield. When the solid was further heated under reduced pressure, it was transformed into another black solid at around 160 °C. The results of IR and electrical conductivity measurements suggested that CSe_2 was first trimerized into a cyclic compound, which was then polymerized upon heating at 160 °C to yield a linear polymer **8**. The **8** obtained was found to be amorphous by X-ray diffraction, similar to poly(carbon disulphide) and its electrical conductivity was $10^{-3}\,\Omega^{-1}\,cm^{-1}$ at room temperature[24].

The copolymerization of CSe_2 with CS_2 or CSeS was investigated under a higher pressure, ~6000 atm. However, only Se-containing solids were isolated[24].



(8)

III. ORGANOSELENIUM POLYMERS CONTAINING A DISELENIDE CHAIN

The Se—Se bond is weaker than the S—S bond. The bond energies are 44 and 50.9 kcal mol^{-1}, respectively. Therefore, the Se—Se bond can be easily cleaved and various reversible reactions can be observed. The polymer containing Se—Se bonds may be synthesized by similar reactions to those decribed for the organic monoselenide polymer.

A. Poly(diselenoalkylene)s, $-\!\!(C_nH_{2n}Se_2)\!\!-_n$

1. *Poly(diselenomethylene),* $-\!\!(CH_2Se_2)\!\!-_n$ *(**9**)*

The reaction of H_2Se with formaldehyde in aqueous solution produced poly(selenomethylene) (**2**). However, Prince and Bremer found that under anhydrous conditions, formaldehyde and Na_2Se reacted to give **9**[25]. Two crystalline forms were found to exist with a transition temperature of about 120 °C. The crystalline red–brown low-temperature solid **9** could be moulded at 70 °C under pressure and the conductivity was found to be $10^{-5}\,\Omega^{-1}\,cm^{-1}$. Paetzold and Knaust also obtained **9** in 98% yield by the reaction of dibromomethane and Na_2Se_2 in aqueous solution[26].

2. *Poly(diselenoethylene),* $-\!\!(C_2H_4Se_2)\!\!-_n$ *(**10**)*

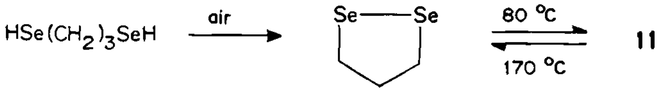
10 was prepared via a three-step process involving reaction of 1,2-dibromoethane with KSeCN followed by hydrolysis of the diselenocyanate formed with alkali or acid to produce the corresponding diselenol. The diselenol was then oxidized by air in aqueous alcohol to give **10**[15].

$$\mathrm{BrCH_2CH_2Br + 2\ KSeCN \longrightarrow NCSeCH_2CH_2SeCN \xrightarrow[alc.]{KOH} HSeCH_2CH_2SeH \xrightarrow{air} \mathbf{10}}$$

The **10** obtained was insoluble in all common organic solvents and had a melting point of 120 °C. The electrical conductivity was $10^{-13}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ and no photoconductivity was detected. The polymer was thermally stable at room temperature, but it decomposed into ethylene and Se at around 225 °C.

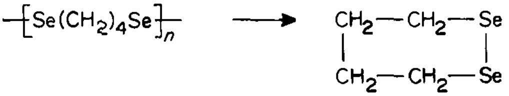
3. *Poly(1,3-diselenopropylene),* $\mathrm{-\!\!\left(C_3H_6Se_2\right)\!\!-_n}$ *(**11**)*

When 1,3-propylenediselenol, obtained by the method described above, was oxidized with air, a cyclotrimethylene 1,2-diselenide was obtained instead of the polymeric material[27,28]. The cyclic monomer was polymerized upon heating to 80 °C, but when the **11** obtained was further heated to 170 °C, it was depolymerized to the original cyclic monomer[27,28]. The polymer was insoluble in organic solvent.

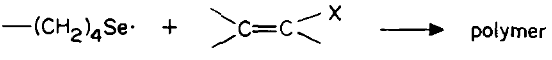


4. *Poly(1,4-diselenotetramethylene),* $\mathrm{-\!\!\left(C_4H_8Se_2\right)\!\!-_n}$ *(**12**)*

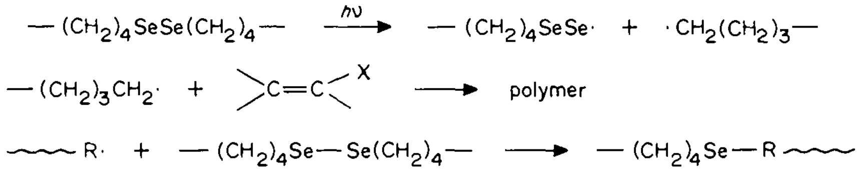
The polymer **12** was obtained by air oxidation of 1,4-butanediselenocyanate[29,30]. Brown and Gillman reported in detail the properties of **12**, which was obtained from this precursor[31]. The polymer was purified by dissolving it in warm chloroform and then cooling the solution at 0 °C, and it melted at 38–39 °C with decomposition. The molecular weight was found to be 516 in a freshly prepared $\mathrm{CHBr_3}$ solution using a cryoscopic method. However, when the solution was heated at 60 °C in the dark for 24 h, the molecular weight was decreased and ultimately reached a steady value of 209.7, which is close to the value of 214.0 expected for 1,2-diselenotetramethylene. A similar decrease in the molecular weight with time was also detected by viscosity measurements. The UV spectrum of a freshly prepared solution of **12** in $\mathrm{CHCl_3}$ gave an absorption maximum at 308 nm which is characteristic of the Se—Se bond in linear diselenide. On allowing the solution to stand at 60 °C in the presence or absence of air, the peak at 308 nm disappeared while a new maximum at 364 nm appeared. The latter absorption is characteristic of the Se—Se bond in the cyclic 1,2-diselenide. These observations suggested that the polymer was depolymerized to give the cyclic monomer. The depolymerization was found to obey first-order kinetics with $k = 2.75 \times 10^{-5}\,\mathrm{s}^{-1}$ at 60 °C in $\mathrm{CHCl_3}$ and $8.96 \times 10^{-5}\,\mathrm{s}^{-1}$ at room temperature by irradiation with 366 nm. Since the depolymerization might involve the formation of radicals, the polymerization of various vinyl monomers in the presence of **12** was investigated by Brown and Gillman[31]. The vinyl monomers studied included styrene, methyl methacrylate, vinyl acetate and acrylonitrile. However, the alkylselenium radicals produced thermally did not initiate the polymerization of these vinyl monomers



$$\mathrm{-(CH_2)_4Se{-}Se(CH_2)_4- \longrightarrow -(CH_2)_4Se\cdot + \cdot Se(CH_2)_4-}$$

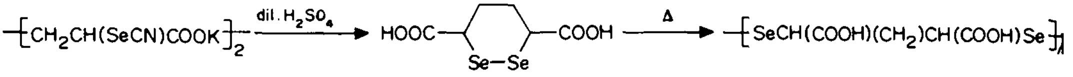


(except possibly for methyl methacrylate). However under photodepolymerization conditions (360 nm at 25 °C), the polymerizations of these vinyl monomers were accelerated in the presence of **12**, and the degree of polymerization was decreased. This behaviour resembles that of linear disulphides which show little activity as thermal initiators of vinyl polymerization but which are excellent photoinitiators[32]. Since the Se end-radicals were not capable of initiating the polymerization of monomers, the results might be explained if the light was absorbed by the Se—Se bond, but the adjacent C—Se bond was broken. The resulting methylene radical might initiate the polymerization of the monomers and then the growing polymer radical could react with the diselenide, with the polymer **12** acting as a chain-transfer agent. Thus, this mechanism (Scheme 1) explains the decrease in the degree of the polymerization in the presence of **12**.

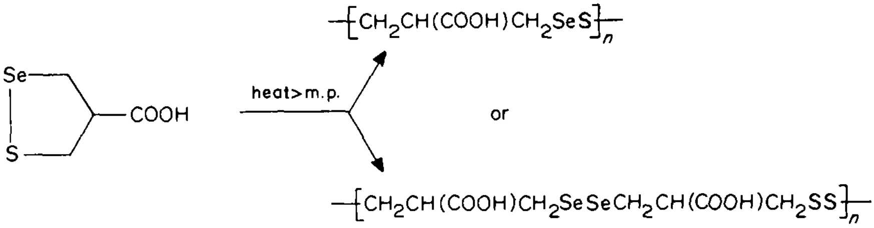


SCHEME 1

A carboxylic-acid-substituted poly(diselenoalkylene) can be prepared by the ring-opening polymerization of the corresponding substituted cyclodiselenide. Fredga reported the preparation of a cyclodiselenide–dicarboxylic acid which was readily converted to a functionalized diselenoalkylene polymer[33].

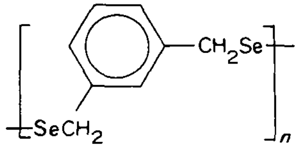


A Se—S bond in a cyclic compound was also found to be polymerized by ring opening. Bergson and Biezais reported that 1-thia-2-selenolane-4-carboxylic acid was polymerized at just above its melting point, to a polymeric material for which two possible alternative structures have been proposed, as shown in Scheme 2[34].



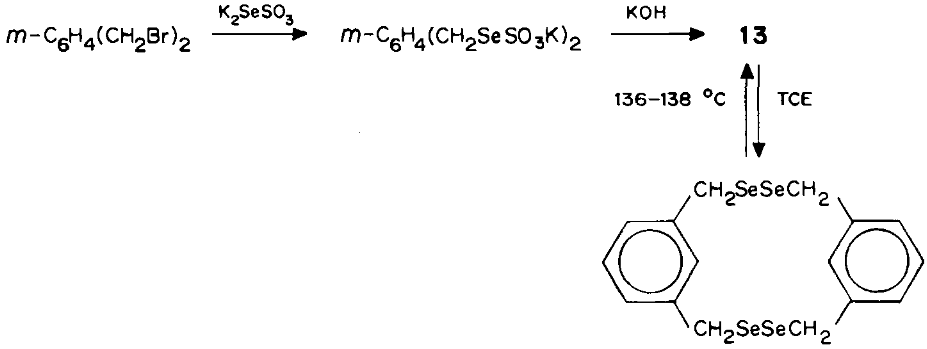
SCHEME 2

B. Poly (α,α′-diseleno-*m*-xylene) (13)



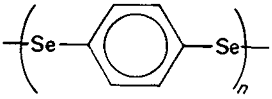
(13)

Günther and Salzman have reported that benzylic polydiselenides can be produced fairly readily via a thermal polymerization of a cyclic dimer[35]. The polymer **13** was obtained as a yellow amorphous powder. When a solution of **13** in 1,1,2,2-tetrachloroethane (TCE) was heated at 80–100 °C for several days it depolymerized into the cyclic dimer (Scheme 3) which was insoluble in organic solvents.



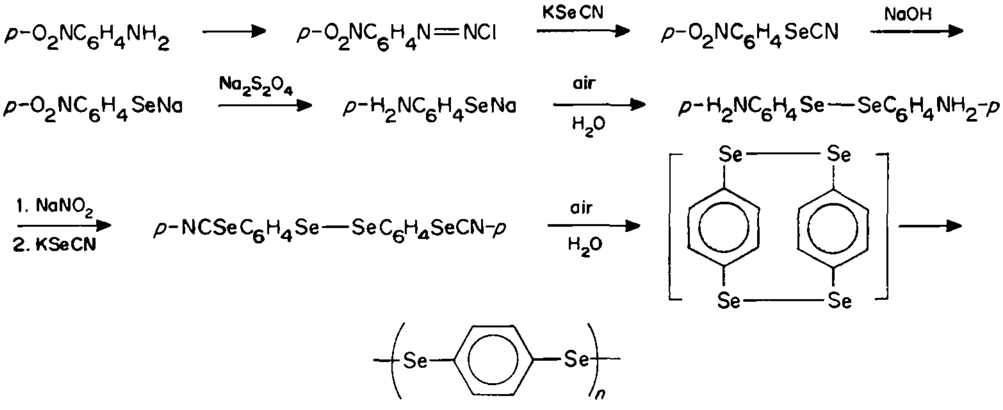
SCHEME 3

C. Poly(1,4-diselenophenylene) (14)



(14)

The aromatic Se—C bond is generally more stable than that of the aliphatic Se—C bond. Keimatsu and Satoda[36] first prepared **14** in 1935 and Okamoto and coworkers later modified their method[15]. The synthetic route is shown in Scheme 4. The possible precursor of the polymer, paraselenocyclophane, could not be isolated. The **14** obtained melted at 248 °C and was stable up to 400 °C in a N_2 atmosphere.



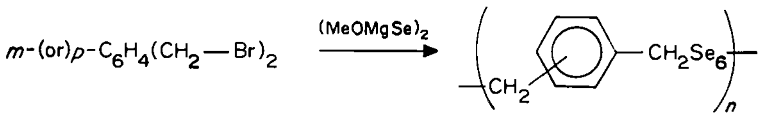
(14)

SCHEME 4

Günther and Saltzman also obtained **14** (m.p. 252–256 °C) and showed that it was a crystalline tetramer (mol. wt. 930) of *p*-phenylene diselenide [35]. Okamoto and coworkers also concluded by mass spectrometric analysis that **14** was the cyclic tetramer and found that the oligomer had an electrical conductivity in the range of $10^{-13}\,\Omega^{-1}\,\text{cm}^{-1}$ [15].

IV. POLYSELENIUM-CONTAINING POLYMERS, $-\!\!(\text{RSe}_x)\!\!-_n$

It has occasionally been found that the reactions of dihaloalkanes with diselenide reagents yield unexpectedly products with a high Se content. For example, Günther and Saltzman observed that reaction of α,α′-dibromo-(*m*- and *p*-)xylenes with bis(methoxymagnesium) diselenide produced a polymer containing six equivalents of Se per xylene moiety[35]. They have shown that the result is reproducible and have accounted for the product by suggesting a possible reaction between the initial product, a diselenide, with elemental Se. It was suggested that Se can be incorporated into the chain containing the Se—Se bond and this alloying process was investigated on the diselenide.



Günther and Saltzman showed that when the cyclic dimer shown in Scheme 3 was heated with elemental Se at 220–230 °C, 15 additional equivalents of Se per monomer unit were readily assimilated into the chain and the polyselenide compound was thermally stable to 140 °C, but on further heating, it disproportionated with deposition of grey Se. However, reheating the mixture to 220 °C reproduced the original alloy[35].

V. ORGANOTELLURIUM POLYMERS

Organotellurium compounds are generally less well known than organoselenium compounds. Only a few organotellurium polymers have been reported in the literature. Organic tellurides and ditellurides may be prepared by the reaction of alkyl or aryl halides with Na_2Te and Na_2Te_2. However, Russo and Credali noted that it was not possible to prepare a cyclic oligomer or a polymer of telluroformaldehyde by a synthetic route analogous to that used for the preparation of poly(selenomethylene)[11].

Livingston and Krosec reported the first polymer containing Te as part of a chain[37]. They reacted diphenyltellurium dichloride with dicarboxylic acid silver salts and obtained a polymer ($R = C_3H_6$) having a molecular weight of ~ 3860.

$$\text{Ph}_2\text{TeCl}_2 + \text{AgOOC—R—COOAg} \longrightarrow -\!\!\left[\text{Te(Ph}_2\text{)OOC—R—COOTe(Ph}_2\text{)}\right]\!\!-_n + \text{AgCl}$$

$$R = C_2H_4\,,\ C_3H_6$$

The Te analogue of PPS and PPSe, poly(telluro-1,4-phenylene), $-\!\!(C_6H_4Te)\!\!-_n$(**15**), was synthesized by Sandman and coworkers by the reaction of *p*-diidobenzene with Na_2Te in DMF at 110–120 °C in 70% yield[38]. The infrared spectrum of **15** is superimposable on that of PPS between 4000 and 600 cm^{-1} while the bands at 550 and 475 cm^{-1} in PPS are shifted to 489 and 465 cm^{-1} in **15**. The molecular weight was calculated from the iodine content to be about 8000, and the polymer decomposed at 162–170 °C.

The electrical conductivity of **15** at room temperature was $10^{-11}\,\Omega^{-1}\,\text{cm}^{-1}$. When **15** was exposed to iodine vapour, the weight was increased by 150% and the conductivity increased to 10^{-8}–$10^{-6}\,\Omega^{-1}\,cm^{-1}$. The large increase in weight was accounted for by the formation of tetracoordinate Te in the polymer, by attachment of two iodines to each Te atom. This species was transformed back to **15** by reaction with Na_2S. When **15** was treated with AsF_5, the tan colour initially turned to black and then returned to tan. The conductivity did not increase appreciably. The IR spectrum of this material after NH_3 treatment and salt removal revealed that structural modification had occurred in **15**. Polymer **15** was decomposed by $SbCl_5$ in CH_2Cl_2 at 0 °C[18].

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CHAPTER 11

Organometallic compounds with selenium and tellurium atoms bonded to main group elements of Groups IIIa, IVa and Va

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I. INTRODUCTION

This chapter is concerned with developments which have taken place in recent years and which describe organometallic compounds bearing X—Se or X—Te bonds; specifically, X = B, Al, Ga, In, Tl from Group IIIa, X = Si, Ge, Sn, Pb from Group IVa and X = P, As, Sb, Bi from Group Va. Compounds containing C—Se or C—Te bonds are not included in this chapter. They form the major portion of the other chapters which make up this volume.

Compounds of the type which form the subject of this chapter are relatively few in number. The literature is not extensive. Among the reasons for the relative paucity of literature references in this field is the fact that many X—Se and X—Te bonds are thermodynamically, and often photochemically, unstable.

The reader should consult the 'Annual Surveys on Tellurium' prepared by Irgolic which appear regularly in the *Journal of Organometallic Chemistry*. Unfortunately, 'Annual Surveys on Selenium' have not appeared as part of this series. A very useful review entitled 'The Ligand Chemistry of Tellurium' by Gysling[1] furnishes the reader with a detailed coverage of Te—M bonded compounds in which M is a transition metal.

II. COMPOUNDS CONTAINING AN X—Se OR X—Te BOND WHERE X IS A GROUP IIIa ELEMENT

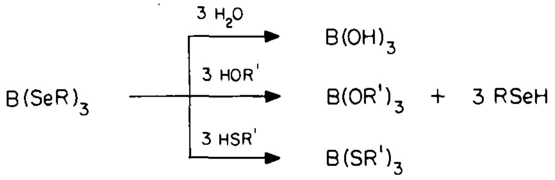
A. Compounds Containing a B—Se or B—Te Bond

Alkaneselenols or benzeneselenol undergo reaction with boron trihalides in carbon disulphide to give tris(organoseleno)boranes[2]. The alkyl derivatives, $B(SeR)_3$ (R = Et, *i*-Pr, *n*-Bu), are pale yellow liquids, whereas tris(phenylseleno)borane, $B(SePh)_3$, is a white solid. The compounds can also be prepared from the selenolates.

$$BY_3 + 3\,NaSeR \longrightarrow B(SeR)_3 + 3\,NaY$$

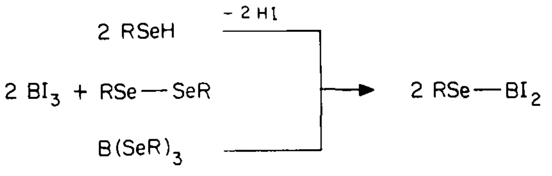
$$Y = Cl, Br, I$$

The B—Se bond is ruptured by nucleophilic protic reagents.



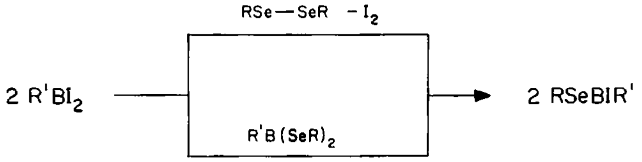
Siebert and Ospici[3] have described the synthesis of alkylseleno(diiodo)boranes, $RSe—BI_2$, (alkylseleno)alkyliodoboranes, RSe—BR'I, and other derivatives of the type $(MeSe)_nBR'_{3-n}$ where $n = 1,2$ and R' = Me, Ph.

For the synthesis of the diiodoboranes, the following reactions have been utilized. The



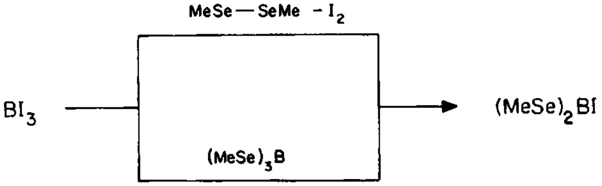
R = Me, Ph

monoiodoborane derivatives are prepared by the reaction between a diiodo(organyl)borane and a diselenide or a (diorganylseleno)organylborane. The term 'organyl' is used in this chapter to include both alkyl and aryl substituents. The reaction between



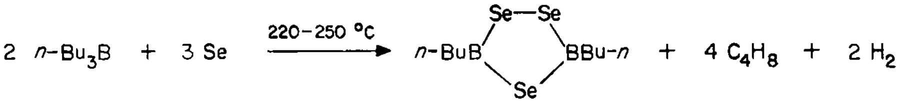
R = Me , 1-Pr ; R' = Me, Ph

triiodoborane and a diselenide or tri(organylseleno)borane gives the iododi-



(organylseleno)borane. The reactions are carried out in carbon disulphide under a nitrogen atmosphere. Methylselenoboranes of the composition MeSe—BI$_2$ and MeSe—B(Me)I form stable trimers. However, (MeSe)$_2$BI, MeSe—B(Ph)I and (MeSe)$_n$BR'$_{3-n}$ (R' = Me, Ph) are monomeric. The ^{11}B-NMR chemical shift observed for the trimer, [MeSe—BMeI]$_3$, is 11.1 ppm. This is consistent with an sp^3-hybridized boron atom.

The synthesis of 1,2,4,3,5-triselenadiborolanes has been described by Siebert and Riegel[4]. This ring system has been synthesized in a variety of ways. The reaction between tri(*n*-butyl)borane and elemental Se yields the ring system shown below. Elemental Se also



undergoes reactions with various boranes to yield derivatives having the same ring system.

$$2\ \mathrm{RBI_2} + 3\ \mathrm{Se} \longrightarrow (\mathrm{RB})_2\mathrm{Se}_3 + 2\ \mathrm{I_2}$$

R = Me, Ph

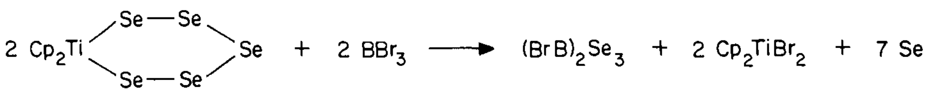
$$(c\text{-HexBH}_2)_2 + 3\ \mathrm{Se} \xrightarrow{\Delta} (c\text{-HexB})_2\mathrm{Se}_3 + 2\ \mathrm{H_2}$$

$$2\left[(n\text{-Pr})_2\mathrm{BH}\right]_2 + 3\ \mathrm{Se} \xrightarrow{\Delta} (n\text{-PrB})_2\mathrm{Se}_3 + 2\ (n\text{-Pr})_3\mathrm{B} + 2\ \mathrm{H_2}$$

The B—Se bonded compound, PhSe—BI$_2$, disproportionates at room temperature to yield the diphenyl derivative. The reaction between boron tribomide and dicyclopen-

$$3\ \mathrm{PhSe{-}BI_2} \longrightarrow \mathrm{(PhB)_2Se_3} + \mathrm{PhBI_2} + 2\ \mathrm{I_2}$$

tadienyltitanium pentaselenide (Cp_2TiSe_5) gives the Br-substituted derivative. NMR



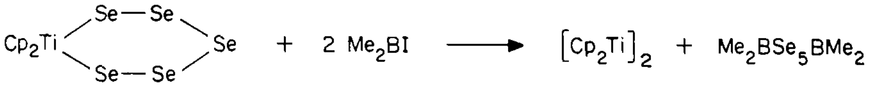
chemical shifts for some of the triselenadiborolanes are given in Table 1.

B—Se—B bonds are formed by the reaction between dimethyltin selenide and dimethylboron iodide in carbon disulphide[5]. The product is removed by vacuum

$$2\ \mathrm{R_2BI} + \mathrm{Me_2SnMe} \longrightarrow \mathrm{R_2B{-}Se{-}BR_2} + \mathrm{Me_2SnI_2}$$

distillation from the solvent. Compounds of the same type shown have been isolated for R = *c*-Hex or Ph. When R = Me or *n*-Bu the product polymerizes to $(RBSe)_n$.

Compounds having B—Se—B bonds are prepared in two ways. The first utilizes the reaction between $(Cp_2)TiSe_5$ and Me_2BI in carbon disulphide at room temperature.



$$\mathrm{Me_2BSe_5BMe_2} \xrightarrow{35\ ^\circ\mathrm{C}} \mathrm{Me_2BSe{-}SeBMe_2} + 3/8\ \mathrm{Se_8}$$

The second procedure involves the reaction between a borolane and elemental Se. Thus, 3-methylborolane reacts with elemental Se at 120–140 °C to give bis(3-methylboranyl) diselenide.

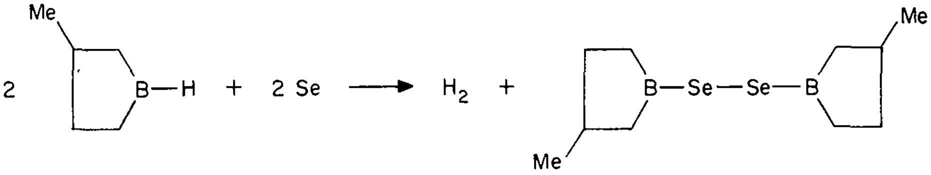
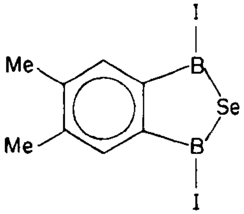


TABLE 1. NMR chemical shifts for triselenadiborolanes $(RB)_2Se_3$

R	NMR chemical shift, (ppm)
Me	– 0.93 (s)
n-Pr	– 1.16 (m); – 1.75 (m)
n-Bu	– 1.2 (m)
Ph	– 7.8 (m)
p-Tol	– 2.45 (6,s); – 7.22 (4d); – 7.83 (4,d), *J* = 8 Hz

The heterocyclic system, 1,2,5-selenadiborolene, has also been reported[6]. Polymeric iodoboron selenide, $-\!\!(-BISe-\!\!)_n$, is first prepared by the reaction between BI_3 and Se at 140 °C. This polymer, when heated with $3,4\text{-}Me_2C_6H_3BI_2$, gives yellow crystals of xyleno-1,2,5-selenadiborolene diiodide.



Bregadze and coworkers have reported[7] that B-mercurated and B-thalliated carboranes undergo reaction with elemental Se and Te to give carboranyl derivatives having B—Se or B—Te bonds. The following example illustrates the reaction. The same investigators report that the monotelluride is formed in the reaction between [*m*-carboranyl(9)]thallium bis(trisfluoroacetate) with Te in dimethylformamide in the presence of iodide. The carboranyl derivatives of Se and Te are solids which melt at temperatures > 200 °C.

$$(C_2H_2B_{10}H_9)_2Hg \;+\; X \xrightarrow{270\text{-}300\ ^\circ C} (C_2H_2B_{10}H_9)_2X_n$$

$$X = Se,\ n = 2\ ;\ X = Te\ ,\ n = 1$$

$$(CF_3CO_2)_2TlB_{10}H_9C_2H_2 \;+\; Te \xrightarrow[DMF]{I^-} (C_2H_2B_{10}H_9)_2Te$$

Clive and Menchen[8-10] have utilized tris(phenylseleno)borane, $(PhSe)_3B$, for organic functional group interconversions. This reagent is a reasonably stable crystalline solid, first reported by Schmidt and Block[11]. It readily undergoes reaction with carbonyl compounds to yield selenoacetals which are easily reduced by organotin hydrides. The reaction sequence utilized by Clive and Menchen is summarized below. Besides the deoxygenation of carbonyl compounds, the reagents $(PhSe)_3B$, $MeSe_3B$ and $(n\text{-}BuB)_2Se_3$ deoxygenate sulphoxides efficiently. NMR evidence suggests that the formation of a selenosulphoxide, R_2SSe, as an intermediate is *not* involved. These investigators have suggested the initial formation of the following species:

$$R^1R^2C{=}O \;+\; (PhSe)_3B \longrightarrow R^1R^2C(SePh)_2 \xrightarrow{Ph_3SnH} R^1R^2CH_2$$

$$R^1R^2C{=}\overset{+}{O}{-}\overset{-}{B}(SeR)_3 \quad \text{and} \quad R^1R^2C(SeR)OB\!\!<\!\Big\}$$

B. Compounds Containing a Al—Se, Al—Te, Ga—Se or Ga—Te Bond

Coates[12] has described the formation of adducts between Me_3Ga or Me_3Al and Me_2Se or Me_2Te. The following liquid adducts were prepared: $Me_3\overset{-}{Ga}—\overset{+}{Se}Me_2$, $Me_3\overset{-}{Ga}—\overset{+}{Se}Me_2$, $Me_3\overset{-}{Al}—\overset{+}{Se}Me_2$ and $Me_3\overset{-}{Al}—\overset{+}{Te}Me_2$. Coates found the $Me_3\overset{-}{Ga}—\overset{+}{Se}Me_2$ adduct to be more stable than that formed with Me_2S. The greater stability was attributed in part to contributions arising from double-bonded structures of the type $Me_3Ga{=\!=}SeMe_2$.

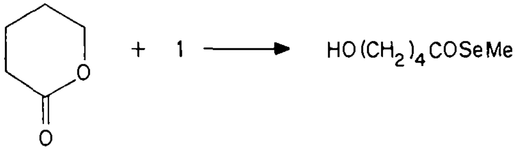
The Al—Se bond has been the subject of only limited investigations. The air-sensitive compound, $K[MeSe(AlMe_3)_3]\cdot 2\,C_6H_6$ is prepared[13] by the thermal decomposition, in a sealed tube, of $K(Al_2Me_6SeCN)\cdot n\,C_6H_6$ at 80 °C. The crystal structure reveals that the Se atom is tetrahedrally coordinated. The Al—Se bond lengths average 2.578(5) Å and the Se—C bond distance is 1.93(2) Å.

The reaction between Me_3Al and powdered Se in toluene gives dimethylaluminium methylselenolate (**1**)[14]. The compound is prepared *in situ* and reacts with esters to give

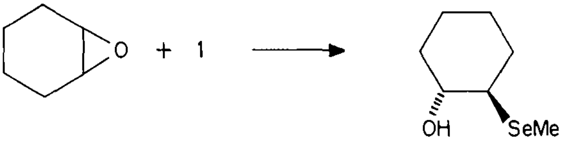
$$Me_3Al \;+\; Se \;.\; \xrightarrow[2\ h]{\Delta\ ,\ \text{toluene}} \; \underset{(\mathbf{1})}{Me_2AlSeMe}$$

$$PhCOOMe \;+\; 1 \;\longrightarrow\; PhCOSeMe$$

methyl selenol esters in good yield. With δ-lactones **1** reacts to give the δ-hydroxy selenol



ester. With epoxides **1** gives methylseleno alcohols.



III. COMPOUNDS CONTAINING AN X—Se OR X—Te BOND WHERE X IS A GROUP IVa ELEMENT

A. Compounds Containing a Si—Se or Si—Te Bond

Trisilylamine reacts readily with hydrogen selenide[15] and analagous reactions take place with *N*-methyldisilyamine. If air is eliminated, the salts are stable at room

$$(H_3Si)_3N \;+\; 2\,H_2Se \;\longrightarrow\; Se(SiH_3)_2 \;+\; H_3SiSe^-\;NH_4^+$$

$$2\,(H_3Si)_2NMe \;+\; 3\,H_2Se \;\longrightarrow\; Se(SiH_3)_2 \;+\; 2\,H_3SiSe^-\;NH_3Me^+$$

$$H_3SiNMe_2 \;+\; H_2Se \;\longrightarrow\; H_3SiSe^-\;\overset{+}{N}H_2Me_2$$

$$H_4\overset{+}{N}\ \overset{-}{Se}SiH_3 \;+\; MeI \;\longrightarrow\; NH_4I \;+\; MeSeSiH_3$$

temperature for about a day. Infrared spectra suggest the presence of H_3SiSe^- anions in the crystal lattice. The salts react slowly with methyl iodide and among the products formed is silyl methyl selenide. With trimethylsilyl chloride, a Si—Se—Si derivative is formed in 50% yield. With F_2PBr the expected $F_2PSeSiH_3$ is not formed. Instead, the

$$H_4\overset{+}{N}\ \overset{-}{Se}SiH_3 \;+\; Me_3SiCl \;\longrightarrow\; NH_4Cl \;+\; Me_3SiSeSiH_3$$

phosphine selenide, $F_2P(Se)SiH_3$, is obtained. The ammonium salts undergo reaction with MeCOCl with the formation of a variety of products among which is $(H_3Si)_2Se$, $(MeCO)_2Se$ and $MeCOSeSiH_3$.

Anderson and coworkers[16] have reported on the synthesis of a number of methylseleno derivatives of the elements of Group IVa. Methaneselenol undergoes reaction with chloromethylsilanes in the presence of Me_3N to give methylselenosilanes in yields up to

$$Me_{4-n}SiCl_n \;+\; n\,MeSeH \;+\; n\,Me_3N \;\longrightarrow\; Me_{4-n}Si(SeMe)_n \;+\; n\,Me_3NHCl$$

70%. A second method involves an interesting reagent prepared by these investigators, i.e. lithium tetra(methylseleno)aluminate. The latter undergoes reaction with trimethylstannyl halides to give yields of the desired products. The third synthetic method described by

$$LiAlH_4 \;+\; 4\ MeSeH \;\longrightarrow\; 4\ H_2 \;+\; LiAl(SeMe)_4$$

$$LiAl(SeMe)_4 \;+\; 4\ Me_3MX \;\longrightarrow\; 4\ Me_3MSeMe \;+\; LiX \;+\; AlX_3$$

$$M = Si, Ge, Sn\ ;\quad X = Br, Cl$$

these workers involves the reaction between Si—N, Ge—N or Sn—N bonded compounds and methaneselenol.

$$Me_3MMe_2 \;+\; MeSeH \;\longrightarrow\; Me_3MSeMe \;+\; Me_2NH$$

$$M = Si, Ge, Sn$$

Methylseleno(trimethyl)silane can be utilized as a starting material for the synthesis of the Ge and Sn derivatives. The driving force for these reactions is attributed by these

$$n\,Me_3SiSeMe \;+\; Me_{4-n}MX_n \;\longrightarrow\; Me_{4-n}M(SeMe)_n \;+\; n\,Me_3SiX$$

$$M = Ge, Sn\ ;\ n = 1\text{-}4\ ;\ X = \text{halogen}$$

investigators to the 'hardness' of Si and the 'softness' of Se, Ge and Sn. The 'harder' halogens form stronger bonds to Si, while the heavier Group IV metals and Se prefer a mutual 'soft–soft' interaction. The exchange reaction does not occur with Me_3PbCl. In this latter case only decomposition products are formed.

NMR studies give evidence of long-range ^1H–^{77}Se NMR couplings. The NMR data and the results of the reaction studies by these investigators are summarized in Table 2, 3 and 4.

Barker and coworkers[17] have utilized the exchange reaction which takes place between the Si—Se and Ge—Cl bonds for the preparation of Ge—Se bonded molecules. A rapid

TABLE 2. The ^{1}H-NMR parameters for the series $Me_{4-n}M(SeMe)_n$ (M = Si, Ge, Sn; $n = 1$–4)[a,b]

Compound	δ(SeMe)	δ(MMe)	$\lvert J(HC^{77}Se)\rvert$	$\lvert J(HCM^{77}Se)$	$\lvert J(^{13}CH)\rvert(M)$	$\lvert J(^{13}CH)\rvert(Se)$	$\lvert J(MCH)\rvert$	$\lvert J(MSeCH)\rvert$
$Me_3SiSeMe$	1.70	0.36	9.8	3.9	122	141	8.1	3.6
$Me_2Si(SeMe)_2$	1.78	0.62	10.5	4.2	122	143	7.8	4.2
$MeSi(SeMe)_3$	1.84	0.93	10.5	3.3	123	143	7.8	5.4
$Si(SeMe)_4$	2.00	—	10.5	—	—	145	—	5.7
$Me_3GeSeMe$	1.78	0.55	10.2	3.6	128	143	—	
$Me_2Ge(SeMe)_2$	1.85	0.85	10.5	2.7	131	142	—	
$MeGe(SeMe)_3$	1.95	1.22	10.8	2.1	131	141	—	
$Ge(SeMe)_4$	2.04	—	10.9	—	—	144	—	
$Me_3SnSeMe$	1.83	0.52	10.5	4.1	131	144	57.8 53.5	33.3 31.5
$Me_2Sn(SeMe)_2$	1.90	0.74	10.8	4.2	132	144	57.2 55.4	37.4 36.2
$MeSn(SeMe)_3$	2.05	1.12	10.8	4.0	132	143	59.7 57.3	46.1 43.9
$Sn(SeMe)_4$	2.09	—	10.8	—	—	141	—	54.0 52.2

[a] All spectra recorded at room temperature; δ in ppm (±0.02) downfield from internal tetramethylsilane; J in Hz(±0.2 for $J < 12$; ±1 for $J > 12$).

[b] Reproduced with permission from Ref. 16.

TABLE 3. The ^{1}H-NMR parameters of some chloro(methyl)seleno derivatives of Si and Ge[a,b]

Compound	δ(SeMe)	δ(MMe)	$\|J(HC^{77}Se)\|$	$\|J(HCM^{77}Se)\|$	$\|J(^{13}CH)\|(M)$	$\|J(^{13}CH)\|(Se)$	$\|J(MCH)\|$
$Me_2SiCl(SeMe)$	1.83	0.66	9.6	3.1	123	145	7.2
$MeSiCl(SeMe)_2$	1.90	0.99	9.9	3.0	122	144	n.o.
$MeSiCl_2(SeMe)$	2.15	1.04	9.7	3.0	122	144	n.o.
$SiCl(SeMe)_3$	2.08	—	10.2	—	—	144	—
$SiCl_2(SeMe)_2$	2.13	—	10.6	—	—	144	—
$SiCl_3(SeMe)$	2.23	—	10.4	—	—	144	—
$Me_2GeCl(SeMe)$	1.99	1.01	9.9	2.4	129	141	—
$MeGeCl(SeMe)_2$	2.03	1.38	9.8	1.8	130	144	—
$MeGeCl_2(SeMe)$	2.19	1.52	10.5	1.8	131	144	—
$GeCl(SeMe)_3$	2.16	—	10.5	—	—	144	—
$GeCl_2(SeMe)_2$	2.26	—	10.5	—	—	145	—
$GeCl_3(SeMe)$	2.44	—	10.0	—	—	144	—

[a] All spectra recorded at room temperature on equilibrium mixtures; δ in ppm ($\pm$ 0.02) downfield from internal tetramethylsilane; J in Hz ($\pm$ 0.1 for $J < 12$; $\pm$ 1 for $J > 12$).

[b] Reproduced with permission from Ref. 16.

TABLE 4. Reactions of methylseleno(trimethyl)silane with halides[d]

Halide	[Halide] (mmol)	[$Me_3SiSeMe$] (mmol)	Reaction time (h)	Product	[Product] (mmol)	[$Me_3SiSeMe$] (mmol)	[Me_3SiCl] (mmol)	
Me_2SiCl_2	0.2	0.5	ca. 170	No reaction		0.5		
$MeSiCl_3$	0.2	0.7	ca. 170	No reaction		0.7	—	
$SiCl_4$	1.0	4.5	72	$Si(SeMe)_4$	0.95	0.5	4.0	
Me_3GeBr	0.6	0.5	0.5	$Me_3GeSeMe$	0.47	Trace	0.49[a]	Me_3GeBr
Me_2GeF_2	0.5	1.1	1.0	$Me_2Ge(SeMe)_2$	0.5	1.0	*ca.*1.0[b]	
$MeGeCl_3$	0.4	1.4	2.0	$MeGe(SeMe)_3$	0.38	ca 0.2	1.2	
$GeCl_4$	0.4	2.0	2.0	$Ge(SeMe)_4$	0.36	0.5	1.5	
Me_3SnCl	0.4	0.5	1.0	$Me_3SnSeMe$	0.38	Trace	0.4	Trace of yellow solid
Me_2SnCl_2	0.9	2.0	1.0	$Me_2Sn(SeMe)_2$	0.86	Trace	1.75	
$MeSnCl_3$	0.8	2.5	1.0	$MeSn(SeMe)_3$	0.75	0.2	2.3	
$SnCl_4$	0.5	2.3	1.0	$Sn(SeMe)_4$	0.45	0.5	2.0	
SiH_3Br	1.0	0.6	1.0	SiH_3SeMe	*c*	—	*c*	SiH_3Br (0.4 mmol)
HBr	0.7	0.5	1.0	HSeMe	0.48	—	49[a]	HBr (0.2 mmol)

[a] Me_3SiBr. [b] Me_3SiF. [c] Inseparable mixture of SiH_3SeMe and Me_3SiBr (approximately equimolar by NMR).

[d] Reproduced with permission from Ref. 16.

$$\mathrm{MeGeH_2Cl + Me_3SiSeMe \longrightarrow MeGeH_2SeMe + Me_3SiCl}$$

exchange takes place when an excess of halogenogermane undergoes reaction with $Me_3SiSeMe$. Evidence of the formation of $H_2Ge(SeMe)_2$ was obtained, but the compound was not characterized due to its extreme instability. $MeGeH_2SeMe$ and $Me_2GeHSeMe$ were prepared by the direct combination of the reactants at − 196 °C. The reaction mixture was taken to room temperature for 15 min and the components were separated by trap-to-trap fractionation. The componenets were identified by ^{1}H-NMR as well as IR and Raman spectroscopy. However, the Si—Se and Ge—Se vibrations were not reported.

The preparation of Te—Si and Te—Ge bonded species has been described by Drake and Hemmings[18]. Lithium organotellurolates, LiTeR(R = Me, Ph), are prepared by the addition of elemental Te to the organolithium reagent in THF. The THF is removed by distillation at reduced pressure and the Cl—Si reagent is added to the residual solid. Trimethyl(methyltelluro)silane and trimethyl(phenyltelluro)silane are isolated as pure compounds.

$$\mathrm{Me_3SiCl + LiTeR \xrightarrow{R.T.} Me_3SiTeR + LiCl}$$

$$\mathrm{R = Me,\ Ph}$$

They have been characterized by elemental analysis, mass spectrometry, ^{1}H-NMR and vibrational spectroscopy. Both fluorogermanes and chlorostannanes undergo quantitative exchange reactions with the Si—Te derivatives to give tellurogermanes and tellurostannanes.

$$\mathrm{Me_3SiTeMe + H_3GeF \longrightarrow H_3GeTeMe + Me_3SiF}$$

$$\mathrm{Me_3SiTePh + Me_3SnCl \longrightarrow Me_3SnTePh + Me_3SiCl}$$

The tellurosilanes are sensitive to protolytic cleavage and make possible the synthesis of the otherwise unavailable arenetellurols. On prolonged storage or when subjected to laser

$$\mathrm{2\ Me_3SiTePh + H_2O \longrightarrow (Me_3Si)_2O + PhTeH}$$

excitation, the derivatives display a variety of decomposition routes which are summarized below.

$$\mathrm{2\ Me_3SnTeMe \longrightarrow (Me_3Sn)_2Te + Me_2Te}$$

$$\mathrm{2\ H_3GeTeMe \longrightarrow (H_3Ge)_2Te + Me_2Te}$$

$$\mathrm{2\ H_3SiTeMe \longrightarrow H_2Si(TeMe)_2 + SiH_4}$$

The following tentative assignments have been made for the M—Te vibrational frequencies: ν(Si—Te) 327, 227 cm^{-1}; ν(Ge—Te) 257, 238 and 258, 233; ν(Sn—Te) 248, 177.

Charov and coworkers[19] have prepared compounds of the type Et_3ESeLi(E = Si, Ge) as follows: The reaction is run in hexane and the following crystalline compounds are

$$\mathrm{EtLi + \left[(Et)_3E\right]_2Se \longrightarrow Et_4E + Et_3ESeLi}$$

$$\mathrm{E = Si,\ Ge}$$

obtained: $(Et_3SiSeLi)_4$, $(Et_3SiTeLi)_4$, $(Et_3GeSeLi)_{4.3}$ and $[(i\text{-}Pr)_3GeSeLi]_x$. When treated with haloalkanes the lithium compounds yield E—Se(or Te)—R bonded derivatives.

$$Et_3GeSeLi + n\text{-}BuCl \longrightarrow LiCl + Et_3GeSeBu\text{-}n$$

The compounds $Et_3SiSeBu\text{-}n$, $Et_3SiTeBu\text{-}n$, $Et_3GeSeBu\text{-}n$ and $(i\text{-}Pr)_3GeSeBu\text{-}n$ are liquids at room temperature.

Diselenides, following initial treatment with sodium, which presumably converts them to the selenolates, react readily with chlorosilanes[20,21].

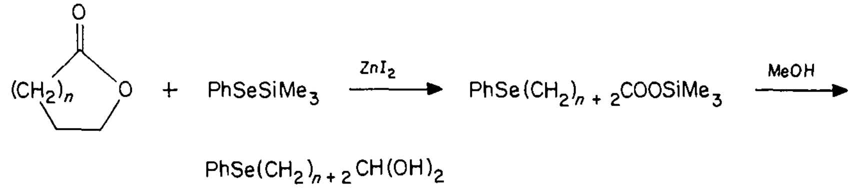
$$PhSeSePh + 2\ Na \longrightarrow PhSeNa$$

$$PhSeNa + ClSiMe_3 \longrightarrow PhSeSiMe_3$$

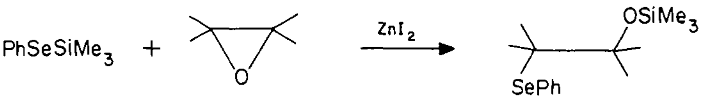
The product, $PhSeSiMe_3$, reacts with alkyl acetates (and also with lactones) in the presence of ZnI_2[22].

$$ROAc + PhSeSiMe_3 \longrightarrow RSePh$$

This reaction allows for the introduction of the phenylseleno group into an organic molecule. The reaction with a lactone, carried out in acetonitrile or toluene, is described as follows:



The same reagent also undergoes reaction with epoxides in the presence of ZnI_2 or n-BuLi[23].

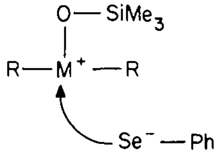


Detty[24] has demonstrated that phenylselenotrimethylsilane is a useful reagent for the gentle reduction (deoxygenation) of sulphoxides, selenoxides and telluroxides. The reaction depicted below is generally applicable. The reaction is successful with a variety of

$$R_2M\rightarrow O + 2\ PhSeSiMe_3 \longrightarrow R_2M + (PhSe)_2 + (Me_3Si)_2O$$

$$M = S,\ Se,\ Te$$

functional groups. Detty describes a mechanism in which the oxide oxygen attacks the $SiMe_3$ group to give the onium species together with the phenylselenide anion shown below. Attack by the phenylselenide anion on the onium compound results in the displacement of Me_3SiO^- and formation of the onium species, R_2M^+—SePh. The Me_3SiO^- could attack a second mole of $PhSeSiMe_3$ to give $Me_3SiOSiMe_3$ and $PhSe^-$.



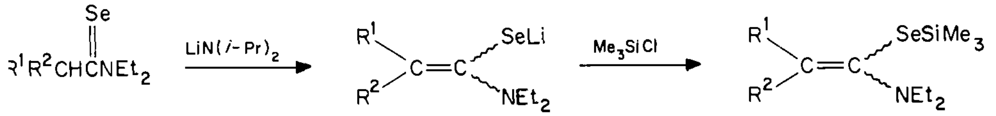
The addition of iodine to phenylselenotrimethylsilane produces trimethylsilyl iodide and diphenyldiselenide[25]. Because of the utility of Me_3SiI in organic synthesis, this has

$$PhSeSiMe_3 + \tfrac{1}{2} I_2 \longrightarrow (PhSe)_2 + Me_3SiI$$

been described as a useful method for its preparation. The reaction between phenylselenotrimethylsilane and alcohols has been recommended for the synthesis of benzeneselenol[26].

$$PhSeSiMe_3 + MeOH \longrightarrow PhSeH + Me_3SiOMe$$

Selenoamides undergo reaction with lithium diisopropylamide in tetrahydrofuran to give the eneselenolates which, on trimethylsilylation, give the vinylselenosilane[27].



$R^1 = R^2 =$ H, Me, Et, *t*-Bu

When decamethylcyclopentasilane dissolved in decalin containing a 10% molar excess of Se is heated to 190 °C for 10 h a quantitative yield of the six-membered ring, *c*-$(Me_2Si)_5Se$, is obtained[28]. The mass spectrum gives a strong parent ion peak and the ^{1}H-NMR shows three singlets at δ0.496, 0.172 and 0.200 ppm in a 2:2:1 ratio, respectively. Insertion by Se into the Si—Si bond of $(Me_2Si)_6$ does not take place.

A similar study has been reported by Hengge and Schuster[29] Octamethylcyclotetrasilane undergoes a reaction with Se in benzene at 80 °C to give the five-membered ring system, *c*-$(Me_2Si)_4Se$. The ν(Si—Se) vibration is observed at 368 (Raman) and 348 cm^{-1} (IR).

Praefcke and Weichsel[30] have described the syntheses of 4-methylphenylseleno- and 4-methylphenyltelluro-trimethylsilane. The synthesis if fairly straightforward. The appropriate Grignard reagent is treated with Se or Te to give the arylchalcogenomagnesium

$$p\text{-Tol—Y—MgBr} + SiMe_3Cl \longrightarrow p\text{-Tol—Y—SiMe}_3 + MgBrCl$$

$$Y = Se, Te$$

bromide. The latter, with trimethylsilyl chloride, gives the desired compound. Both the Se and Te compounds are colourless oils.

Bis(trifluorosilyl)tellurium has been prepared by the condensation of Te vapours in an atmosphere of $SiF_3\cdot$ radicals generated from hexafluorodisilane in a low-temperature glow discharge[31]. The compound is unstable at room temperature. It reacts with water and polar organic solvents. It can be vaporized at −30 °C in vacuo without decomposition. The ^{19}F-NMR spectrum at −45 °C gives a singlet at 102.0 ppm from $CFCl_3$ with $J(^{125}Te—F) = 210$ Hz. The $Si_2F_6Te^+$ ion is present in the mass spectrum.

B. Compounds Containing a Ge—Se or Ge—Te Bond

Elemental Se or Te react with trialkylgermanes at high temperatures[32] to form the unstable R_3GeXH compounds (X = Se, Te). The exchange reaction between $(C_6F_5)_3GeBr$

$$R_3GeH \ + \ X \xrightarrow{\Delta} R_3GeXH$$

$$X = Se, Te$$

and $(Et_3Ge)_2Se$ is carried out at 150 °C for 35 h. Fractionation of the mixture at reduced pressure gives $(C_6F_5)_3GeSeGeEt_3$ in 66% yield. When $(C_6F_5)_3GeBr$ and $(Et_3Ge)_2$ are heated at 150 °C for 32 h and the products are separated *in vacuo*, $[(C_6F_5)_3Ge]_2$ Se is obtained[33]. In this work, the synthesis of a Ge—Se—Sn bonded compound is also described.

The reaction between $(C_6F_5)_3GeSeGeEt_3$ and Ph_3SnBr in toluene at 100 °C for 2 h gives Et_3GeBr and a solid residue. The residue, recrystallized from hexane, was identified as $(C_6F_5)_3GeSeSn(C_6F_5)_3$.

The four-membered ring systems *c*-2,2,4,4-tetra-(*t*-butyl)-1,3-diselena-2,4-digermane and the analagous 1,3-ditellura compound have been described[34]. The hydride, $[(t\text{-}Bu)_2GeH]_2$ is prepared by the reaction between $GeCl_4$ and excess *t*-BuLi. It reacts with elemental Se to give orange cystals of the four-membered Ge—Se heterocycle or pale green crystals of the Ge—Te heterocycle. Mass spectral data suggest the formation of *c*-3,3,5,5-tetra-(*t*-butyl)-1,2,4-triselena-3,5-digermane as a secondary product during the reaction with elemental Se.

The oxidative addition of $(R_3Ge)_2Cd$ to vanadocene gives organobimetallic compounds of the type $Cp_2V(GeR_3)$. Se inserts easily into the V—Ge bond to give $Cp_2V(SeGeR_3)$[35].

Phenyl(triphenylgermyl)tellurium(II) has been synthesized by Gardner and coworkers[36]. Diphenyl ditelluride in benzene–ethanol is converted to PhTeNa by reduction with sodium borohydride followed by the addition of sodium hydroxide. The addition of triphenylgermanium chloride, followed by work-up, gives a yellow solid, analysed as $PhTeGePh_3$. In a similar manner *p*-$TolTeGePh_3$ and *p*-$AnTeGePh_3$ can also be prepared. In this study, the following M—Te vibrational frequences (cm^{-1}) have been identified by Raman spectroscopy: M = Ge 173, 182; M = Sn 161, 164, 168; M = Pb 147, 154, 153, 156. In derivatives of the type $(Ar_3M)_2Te$, the ν(M—Te) vibrations have been reported as follows: M = Ge 167; M = Sn 153; M = Pb 113. For $(Me_3M)_2Te$, the following assignments were made for ν(M—Te): M = Ge 236; M = Sn 191; M = Pb 161.

C. Compounds Containing a Sn—Se or Sn—Te Bond

Dialkyltin oxides undergo a neutralization reaction with benzeneselenol, and dialkyltin dihalides in the presence of triethylamine react with benzeneselenol to give organotin benzeneselenolates[37], Some reported physical properties of these compounds are the

$$R_2SnO \ + \ 2\ PhSeH \longrightarrow R_2Sn(SePh)_2 \ + \ H_2O$$

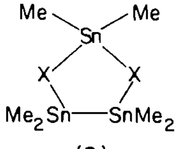
$$R_2SnCl_2 \ + \ 2\ PhSeH \ + \ 2\ Et_3N \longrightarrow R_2Sn(SePh)_2 \ + \ 2\ Et_3NHCl$$

following: *n*-$Bu_2Sn(SePh)_2$, orange oil, ν(Sn—Se) 305 and 275 cm^{-1}; *n*-$Bu_3SnSePh$, red–orange oil, ν(Sn—Se) 295; $Et_2Sn(SePh)_2$, red–orange oil, ν(Sn—Se) 328 and 309; $Ph_3Sn(SePh)\cdot 4\ Me_2CO$, white solid, ν(Sn—Se) 339; $Me_2Sn(SePh)_2$, yellow oil, ν(Sn—Se) 305 and 285.

Japanese workers[38] have described *N*,*N*-dialkylselenocarbamate complexes of tin(IV) The reaction of a dialkyltin dihalide with the dimethylammonium salt of R_2NCSeO in dry benzene gives derivatives of the type $R^1_2Sn(OSeCNR_2)_2$. The stereochemical configurations of these compounds is uncertain. The fundamental stretching frequencies, ν(Sn—Se), were reported to occur in the range 322–343 cm^{-1}.

A number of heterocyclic systems which have Sn—Se bonds have been described[39–45].

2,4,5-Hexamethyl-1,3-diselena-2,4,5-tristannolane (**2a**) and its Te analogue (**2b**) were prepared[39] by the reaction of dimethyltin dihydride in ether:dimethylformamide (30:1/v/v) with elemental Se or Te under N_2.

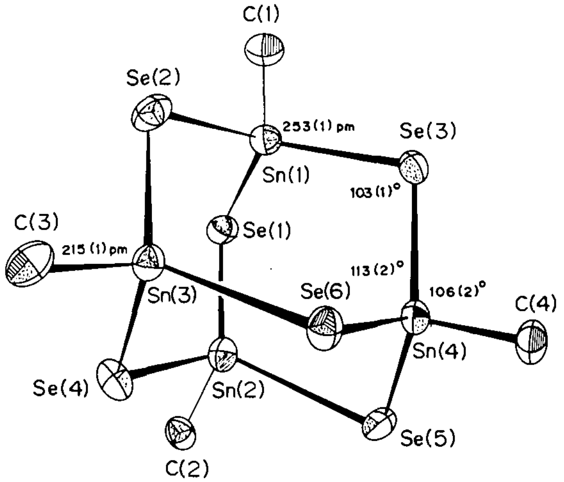


(2)

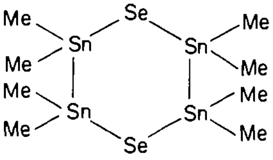
(a) X = Se

(b) X = Te

The compound $(MeSn)_4Se_6$ has an adamantane-type of structure[41]. It is prepared by the reaction of $MeSnBr_3$ with NaSeH in aqueous media. The crystal structure of the molecule has been determined and its structure is shown below.



Tetramethyl-1,2-dichlorodistannane and sodium selenide react in aqueous solution, to form 2,2,3,3,5,5,6,6-octamethyl-1-4-diselena-2,3,5,6-tetrastannane (**3**)[42]. The Sn—Se stretching vibration is located in the 217–255 cm^{-1} region. Vibrational analysis excludes a chain conformation for this six-membered ring.



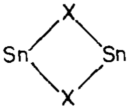
(**3**)

Four-membered cyclic ring systems having two Sn—Se or Sn—Te bonds have been reported[40,43]. The reaction is described by the following equation:

$$2\,(t\text{-Bu})_2\text{SnCl}_2 + 2\,\text{Na}_2\text{X} \longrightarrow 4\,\text{NaCl} + \left[(t\text{-Bu})_2\text{SnX}\right]_2$$

$$\text{X} = \text{Se, Te}$$

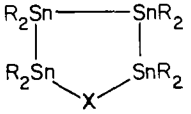
The four-membered ring:



is planar and the Sn—Se distance is 2.55 Å.

The six-membered ring compound, $(\text{Me}_2\text{SnSe})_3$, has been prepared and its structure determined[44]. The measured Sn—Se bond distances are reported as 2.51, 2.54 and 2.54 Å. The molecules have a twist-boat conformation.

Sn–Se and Sn–Te five-membered ring compounds (4) have been reported[45]. These are prepared by the reaction between $(t\text{-Bu}_2\text{Sn})_4\text{I}_2$ and H_2Se or H_2Te. The crystal structures have been determined and the rings are almost planar. An unusual feature of these heterocyclic compounds is their long Sn—Sn bond distances.



(4)

X = Se, Te

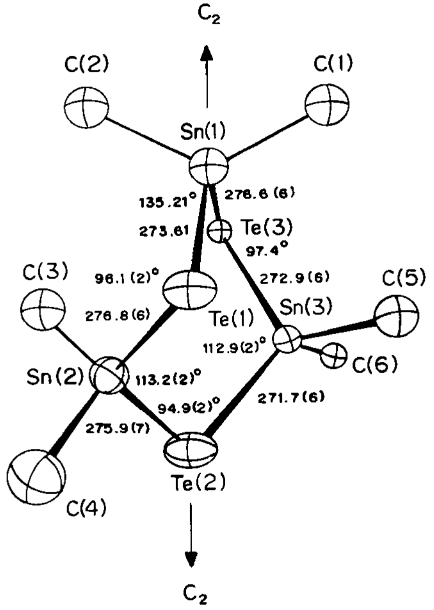
R = *t*-Bu

Diphenyl ditelluride and triphenyltin hydride react at 60–70 °C to give Ph_3SnTePh. In a similar way $\text{Ph}_3\text{SnTe}(\text{C}_6\text{H}_4\text{OR-}p)$ (R = Me, Et, Ph) can be prepared[46]. The reaction of $(t\text{-Bu})_3\text{SnH}$ with $(\text{ArTe})_2$ gives a red oil which, from mass spectral observation, shows the presence of $[(t\text{-Bu})_3\text{SnTePh}]^+$. Mössbauer measurements show that the sign of the ^{119}Sn quadrupole splitting is negative.

The six-membered heterocycle, 2,2,4,4,6,6-hexamethylcyclotristannatellurane, a Sn_3Te_3 ring system, has been prepared by Blecher and Dräger[47], as follows:

$$3\,\text{Me}_2\text{SnCl}_2 + 3\,\text{NaHTe} \xrightarrow{\text{H}_2\text{O}} \left[\text{Me}_2\text{SnTe}\right]_3 + 3\,\text{NaCl} + 3\,\text{HCl}$$

Its structure is shown below. Analagous molecules had been synthesized earlier by Blecher and Mathiasch[48] by the reaction between dimethyltin hydride and elemental S, Se or Te.



D. Compounds Containing the Pb—Se Bond

Several Pb—X (X = Se, Te) bonded compounds have been described in the preceding sections of this chapter. Only a limited amount of additional work has been carried out.

The hexacarbonyls of Cr, Mo and W undergo a photochemical displacement of CO by

$$M(CO)_6 + C_4H_8O \longrightarrow (CO)_5MOC_4H_8 + CO$$

$$M = Cr, Mo, W$$

tetrahydrofuran, C_4H_8O. The C_4H_8O can be displaced by $(Me_3M')_2Se$, where M' is Ge, Sn or Pb:

$$(CO)_5MOC_4H_8 + (Me_3M')_2Se \longrightarrow (CO)_5MSe(M'Me_3)_2 + C_4H_8O$$

The compound $(Me_3Pb)_2Se$ is prepared by the reaction of MePbCl with Na_2Se in dry benzene[49].

IV. COMPOUNDS CONTAINING AN X—Se OR X—Te BOND WHERE X IS A GROUP Va ELEMENT

A. Compounds Containing a P—Se or P—Te Bond

A number of reviews have appeared which cover developments in this area up until about 1971. Selenothiophosphates and diselenophosphates and their transition-metal complexes are described in a review by Wasson and coauthors[50].

Kuchen and Knop[51] have described the reaction between tetraethyldiphosphine disulphide, sodium selenide and Se which gives sodium diethylphosphoselenothioate (**5**).

$$\mathrm{Et_2P(S}\text{—}\mathrm{P(S)Et_2} + \mathrm{Na_2Se} + \mathrm{Se} \longrightarrow 2\ \underset{\mathbf{(5)}}{\mathrm{Et_2PSSe^-\ Na^+}}$$

Compound **5** can also be prepared by the reaction between diethylchlorophosphine sulphide or selenide with NaHSe or NaHs, respectively. Diethylchlorophosphine

$$\mathrm{Et_2P(S)Cl} + \mathrm{NaHSe} \longrightarrow \mathbf{5}$$

$$\mathrm{Et_2P(Se)Cl} + \mathrm{NaHS} \longrightarrow \mathbf{5}$$

$$\mathrm{Et_2P(Se)Cl} + 2\ \mathrm{NaHSe} \longrightarrow \mathbf{5} + \mathrm{NaCl} + \mathrm{H_2Se}$$

undergoes nucleophilic addition by Se to give the selenide. Trialkylphosphines add Se to

$$\mathrm{Et_2PCl} + \mathrm{Se} \longrightarrow \mathrm{Et_2P(Se)Cl}$$

form phosphine selenides[52,53]. In acetonitrile, the reaction between triarylphosphines and KSeCN gives triarylphosphine selenides[54].

$$\mathrm{R_3P} + \mathrm{Se} \longrightarrow \mathrm{R_3PSe}$$

A review entiled 'The Chemistry of Selenium-bearing Organometallic Derivatives of Group Va Elements' was published in 1972[55]. This review covers the reactions of P_2Se_5 with alcohols and amines, compounds of the type R_3MX ($X = Se, Te$; $M = P, As, Sb$), R_2AsSeR' derivatives and the addition of H_2Se and selenols to Vaska's compounds. This report now proceeds to more recent developments.

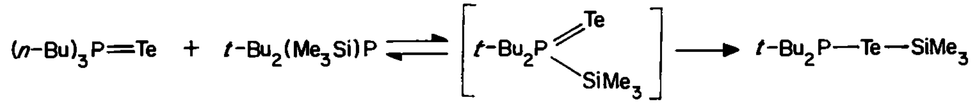
Austad and coworkers[56] were able to prepare a triphenylphosphine telluride–triphenylphosphine adduct which was found to be quite stable. Previously, trialklphosphine tellurides had been found to be quite unstable[57]. These workers found that triphenylphosphine and tetraphenylarsonium tellurocyanate in pure acetonitrile, in the presence of lithium perchlorate, react to give a yellow precipitate identified as Ph_3PTePh. Te—P 'short distances' in this adduct (the crystals are disordered) range from 2.270 to 2.424 Å. Each formula unit is found to contain a linear P—Te—P configuration. Other Scandinavian investigators[58] have prepared tris(morpholino)phosphine telluride by the reaction between tris(morpholino)phosphine and $TeCN^-$. In this compound the P—Te bond distance is 2.356 Å.

Du Mont[59] has found that phosphine tellurides behave as kinetically labile Te complexes in the presence of an excess of the phosphine. On the ^{1}H- and ^{31}P-NMR time-scale, even at room temperature, all PR_3Te/PR'_3 systems which have been investigated display fast Te transfer reactions which have been termed 'fluxional redox systems'. Such an equilibrium is illustrated by the following equation:

$$\mathrm{R_3P{=}Te} + \mathrm{R'_3P} \rightleftharpoons \mathrm{R'_3P{=}Te} + \mathrm{R_3P}$$

R, R' = alkyl, dialkylamino, sometimes aryl

However, as found by du Mont, if Te is transferred from tri-*n*-butylphosphine telluride to di-*t*-butyl(trimethylsilyl)phosphine, the transfer of Te to silylphosphine is followed by a rapid insertion of Te into the P—Si bond.



In an analogous manner, elemental Te reacts with P—Si, P—Ge and P—Sn bonded compounds.

$$t\text{-Bu}_2\text{P—XMe}_3 + \text{Te} \longrightarrow t\text{-Bu}_2\text{P—Te—XMe}_3$$

$$\text{X} = \text{Si}, \text{Ge}, \text{Sn}$$

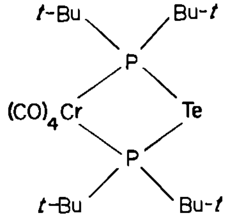
The compounds, t-Bu_2P—Te—XMe_3 are detected in solution by ^{31}P-NMR and ^{119}Sn-NMR spectroscopy. In a few hours, the following redistribution equilibria occur:

$$2\ t\text{-Bu}_2\text{P—Te—XMe}_3 \rightleftharpoons (\text{Me}_3\text{X})_2\text{Te} + (t\text{-Bu})_2\text{P—Te—P(Bu-}t)_2$$

The R_2P—Te—PR_2 type compounds are identified by ^{1}H- and ^{31}P-NMR spectroscopy. They are pale yellow in colour and have been termed 'tellurophosphinous anhydrides'.

^{125}Te-NMR chemical shifts and coupling constants $^1J(^{125}\text{Te}-^{31}\text{P})$ have been reported by du Mont and Kroth[60]. In R_3PTe/PR'_3 mixtures only ^{125}Te singlets are observed. This is taken as evidence of a rapid Te migration. In tellurophosphines such as R—Te—PR'_2 well-resolved doublets arising from $^1J(^{125}\text{Te}-^{31}\text{P})$ coupling is noted. If $R = PR'_2$, such doublets give rise to triplets. The ^{125}Te-NMR data reported by these investigators are as follows: compound, $\delta(^{125}\text{Te})$(ppm), ^1J(Te–P)(Hz); all chemical shifts are relative to (p-$MeC_6H_4Te)_2$ as a standard – (t-Bu)$_3$PTe, – 480(s), 1600; (t-Bu)$_3$PTe/(t-Bu)$_3$P, – 481 (s); (n-Bu)$_3$PTe/(n-Bu)$_3$P, – 512(s); Te[P(Bu-t)$_2$]$_2$, – 574(t), 451; Te[P(Bu-t)$_2$]$_2$·Cr(CO)$_4$, + 142, 324; Te[P(Pr-i)$_2$]$_2$, – 704(t), 324, Me$_3$Si—Te—P(Bu-t)$_2$, – 772(d), 384; p-TolTe—P(Bu-t)$_2$, – 542(d), 532; p-TolTe—P(Bu-t)$_2$·Ni(CO)$_3$, – 396(d), 651; p-TolTe-P(Pr-i)$_2$, – 588(d), 556; (Me$_3$Si)$_2$Te, – 460(s).

Tellurium bis(di-t-butyl)phosphine displaces norbornadiene from $C_7H_8Cr(CO)_4$ to give a red crystalline solid, **6**, with a four-membered CrP_2Te cyclic group[61]. A nickel compound p-TolTeP(Bu-t)$_2$Ni(CO)$_3$ can also be prepared. In the chromium compound, the ^{125}Te chemical shift is + 142 ppm(t) and $^1J(^{125}\text{Te}-^{31}\text{P})$ is 324 Hz.



(6)

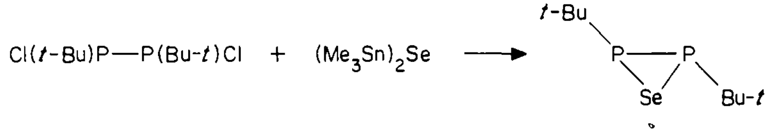
Bergesen and coworkers[62] have prepared a series of compounds of the type $(R_2N)_3P$, $(R_2N)_3PX$(X = O, S, Se, Te) and $(R_2N)_3As$. In these compounds, R_2N is morpholine(Mor), piperidine, pyrrole, Me_2N, Et_2N and (n-Pr)$_2$N. In the vast majority of cases, the ^{13}C-NMR chemical shifts are found to be insensitive to whether the central atom is P or As and relatively insensitive to the nature of X in the pentacovalent series. For example, in the series Mor_3P, Mor_3PO, Mor_3PS, Mor_3PSe and Mor_3PTe, the ^{13}C-NMR shifts of the carbons attached to the nitrogen atom are, respectively, 47.4, 45.4, 46.5 and

47.5 ppm. These values are within 2 ppm of those of the parent amines. In Mor_3P and Mor_3As, the corresponding shifts are 47.1 and 47.4 ppm, respectively.

Among the pentacovalent phosphorus species, a slight, but distinct downfield trend is noted with increasing size of the chalogen atom. To quote the investigators: 'A compensation between sterically induced upfield shifts and varying downfield shifts due to differences in the electron withdrawing power of the chalcogen atom may well be the cause of the small effects observed in the present study'.

Among the tervalent compounds which have been studied, a small, but generally observed downfield shift is noted (1–2 ppm) in going from the phosphines to the arsines. This modest effect is attributed to the fact that the As atom, being less electronegative, deshields the amino carbon atoms more effectively relative to the P atom.

A cyclic three-membered selenadiphosphorane ring system has been synthesized by Baudler and coworkers[63]. The reagents are 1,2-di-*t*-butyl-1,2-dichlorodiphosphine and bis(trimethylstannyl) selenide. The reaction is carried out in boiling THF. Based on NMR spectral evidence, the alkyl groups assume a *trans* configuration.



B. Compounds Containing As—Se, As—Te and Other P—Se or P—Te Bonds

A detailed NMR(^1H, ^{19}F) spectroscopic investigation of the cleavage of element–element bonds by Me_3SnH in ligands coordinated to $Cr(CO)_5$ and $Mo(CO)_5$ has been published by Grobe and Le Van[64]. The coordinated ligands are of the type $R_2XXR'_2$ and R_2XGR', where X is P or As and G is S, Se or Te. The rate of reaction of the coordinated ligands is much slower than that of the free ligands. In Table 5 are listed the results by these workers for compounds containing an XGR′ bond.

Emeléus and coworkers[65] introduced trifluoromethylselenobis(trifluoromethyl)-phosphines and -arsines. The reactions used for the syntheses of these compounds are given below.

$$2\ (CF_3)_2PI + (CF_3Se)_2Hg \longrightarrow HgI_2 + 2\ (CF_3)_2PSeCF_3$$

$$2\ (CF_3)_2AsI + (CF_3Se)_2Hg \longrightarrow HgI_2 + 2\ (CF_3)_2AsSeCF_3$$

The reaction was carried out in sealed glass ampoules for 72 h. The precipitated red mercuric oxide was separated by filtration and the colourless liquid products were separated by vacuum distillation. Heptafluoropropylselenobis(trifluoromethyl)arsine was also prepared from bis(heptafluoropropylseleno)mercury and iodobis(trifluromethyl)arsine.

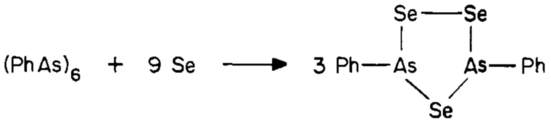
The conformations of tris(phenylthio)-, tris(phenylseleno)- and tris(phenyltelluro)-arsines as well as of the $Me_2As(XPh)$ derivatives (X = S, Se, Te) have been studied by ^1H-NMR and UPS (ultiaviolet photoelectron spectroscopy)[66]. It was concluded that (in benezene solution) (*a*) in all the compounds studied the As is pyramidal; (*b*) the $As(XPh)_3$ molecules are symmetric; (*c*) the twisting angle about the As—X bond is close to zero; (*d*) the Ph—X bond is directed toward the external of the pyramid; (*e*) the Ph rings are symmetrically twisted at an angle of about 40° with respect to the As—X—C plane in the tris(phenylchalcogeno)arsines and (*f*) the bond moments, As(L)—X, where L is the electron lone pair, have been determined to be 0.35 D, 0.30 D and 0.28 D for X = S, Se and Te, respectively. It is concluded from these measurements that there is a virtual absence of resonance contributions.

TABLE 5. Cleavage reactions of complexes of the type $Cr(CO)_5R_2XGR'$ and $MO(CO)_5R_2XGR'$ by Me_3SnH[64]

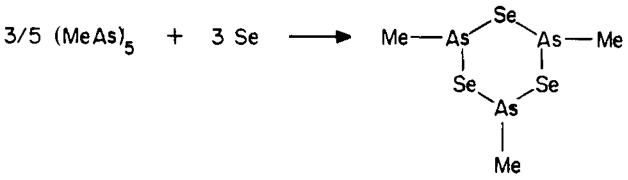
Reactant	Reaction temp. (°C)	Products
$Cr(CO)_5Me_2PSeMe$	20	$Cr(CO)_5Me_2PH$, $Me_3SnSeMe$
$Cr(CO)_5Me_2AsSeMe$	20	$Cr(CO)_5Me_2AsSnMe_3$
$Cr(CO)_5(CF_3)_2PSeMe$	<0	$Cr(CO)_5(CF_3)_2PH$, $Me_3SnSeMe$
	>0	$Cr(CO)_5(CF_3)_2SnMe_3$, $Cr(CO)_5(CF_3)_2PH$
$Cr(CO)_5Me_2AsSeCF_3$	20	$Cr(CO)_5Me_2AsH$, $CF_3SeSnMe_3$
$Mo(CO)_5Me_2PSeMe$	20	$Mo(CO)_5Me_2PH$ $Me_3SnSeMe$
$Mo(CO)_5Me_2AsSeMe$	20	$Mo(CO)_5Me_2AsSnMe_3$
$Mo(CO)_5(CF_3)_2PSeMe$	-10–0	$Mo(CO)_5(CF_3)_2PH$, $Me_3SnSeMe$
	>0	$Mo(CO)_5(CF_3)_2PSnMe_3$, Me_3SnF
$Mo(CO)_5(CF_3)_2PTeMe$	-40–0	$Mo(CO)_5(CF_3)_2PH$, $Me_3SnTeMe$
	>0	$Mo(CO)_5(CF_3)_2PSnMe_3$, Me_3SnF
$Mo(CO)_5Me_2AsSeCF_3$	0–20	$Mo(CO)_5Me_2AsH$, $CF_3SeSnMe_3$

The ^{1}H-NMR chemical shifts of the *ortho*, *meta* and *para* protons move slightly downfield with decreasing electronegativity of the X atom. This is in agreement with the decreasing ability of the chalcogen atoms to transfer charge from the lone-pair electrons into the aromatic ring as the atomic number increases.

Herrmann[67] has described the synthesis of the five-membered and six-membered heterocyclic systems, 1,4-diarsa-2,3,5-triselenacyclopentane (**7**) and 1,3,5-triarsa-2,4,6-triselenacyclohexane (**8**). The preparation involves the reaction between elemental Se and either hexaphenylcyclohexylarsine or pentamethylcyclopentaarsine. Compound **7** is prepared by heating the reactants at 220 °C and crystallization from benzene in the form of orange–yellow crystals. Compound **8** is obtained as yellowish crystals by heating the reactants at 180 °C. Details about the geometries have not been obtained.

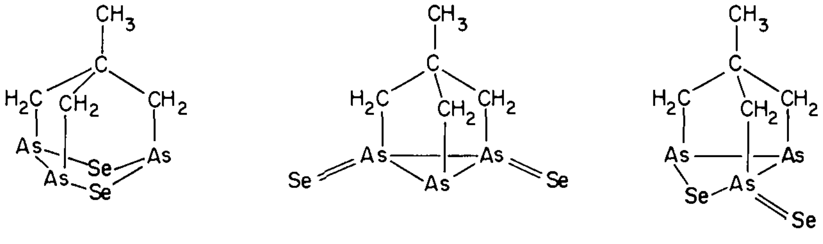


(**7**)



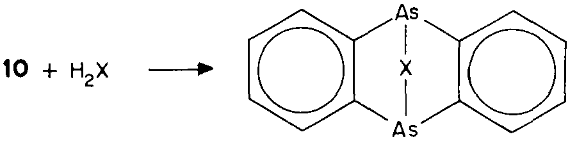
(**8**)

Ellerman and Lietz[68] have described the preparation of the reagent, 1,1,1-tris(diiodoarsinomethyl)ethane $(I_2AsCH_2)_3CMe$. When it reacts with NaSeH, the cage compound $Me(C(CH_2As)_3Se_2$ (**9**) is obtained. Of the three structures (A, B, C) proposed for **9** structure A is considered to be the most likely.



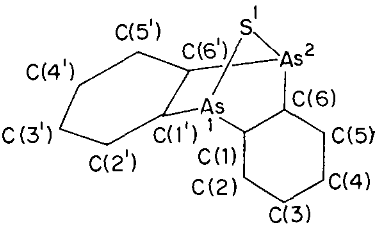
(9)

All four members of the 5,10-epichalcogenodihydroarsanthrene series have been prepared[69]. The epithio, episeleno and epitelluro compounds are prepared by saturating a solution of 5,10-dichloro-5,10-dihydroarsanthrene (10) in ethanol with H_2S, H_2Se or H_2Te.



X = S, Se, Te

The structure of the epithio compound has been determined crystallographically and is shown below. The 5,10-episeleno and 5,10-epitelluro analogues have closely related cell constants, but they are not isomorphous. The investigators are of the opinion that the Se and Te analogues have structures very similar to that shown for the thio compound.



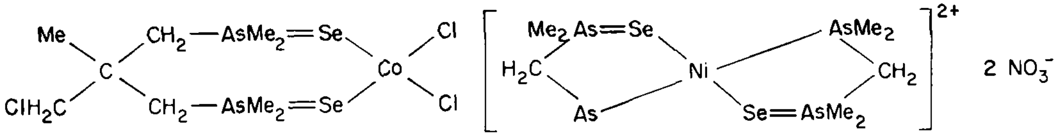
Chi and Kober[70] have prepared, by the oxidation of the parent arsines with Se, di- and tri-tertiary arsine selenides. Typical examples of the types of compounds prepared are shown below.

$$\mathrm{N[CH_2CH_2AsMe_2]_3 \xrightarrow{Se} N[CH_2CH_2As(Se)Me_2]_3}$$

$$\mathrm{ClCH_2C(Me)[CH_2AsMe_2]_2 \xrightarrow{Se} ClCH_2C(Me)[CH_2As(Se)Me_2]_2}$$

$$\mathrm{(ClCH_2)_2C[CH_2AsMe_2]_2 \xrightarrow{Se} (ClCH_2)_2C[CH_2As(Se)Me_2]_2}$$

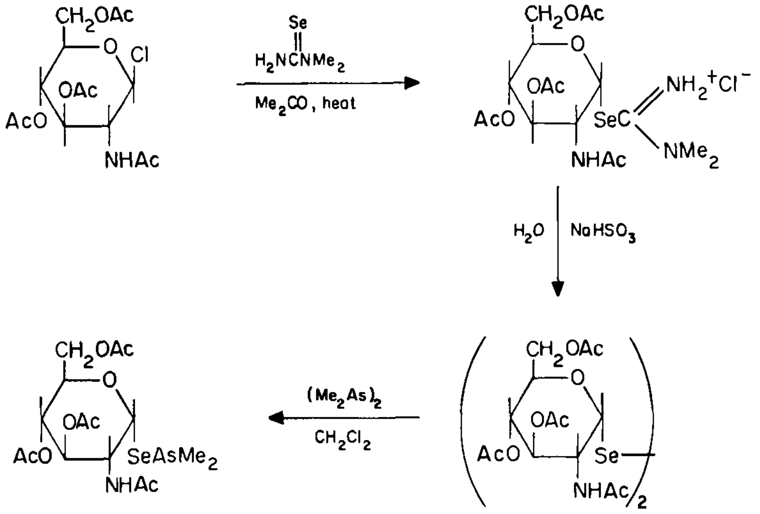
The coordination compounds shown below were also prepared.



The As—O—C bond is hydrolytically unstable, but the As—S—C and As—Se—C bonds are hydrolytically quite stable. This has led Zingaro to the conclusion that although monosaccharide esters of arsenic acid have never been successfully prepared it should be possible to prepare thio- or seleno-sugar esters of arsinous acids. The synthesis of 1- and 6-*S*- and -*Se*-arsinous acid esters have been reviewed[71]. A typical reaction procedure is that described for the synthesis of 2,3,4,6-tetra-*O*-acetyl-1-*SE*-dimethylarsino-β-D-galactopyranose[72].

Acetobromogalactose is treated with selenourea which displaces bromine at C(1) to give the selenoureide. Reduction of the selenoureide by bisulphite or borohydride followed by air oxidation gives the galactosyl-1–1′-diselenide. The diselenide is cleaved by $Me_2AsAsMe_2$ under nitrogen to give the acetylated 1-*Se*-dimethylarsinogalactose compound.

Another example of such a reaction, for the synthesis of derivatives of 2-amino-2-deoxy-D-glucopyranose, is given in Scheme 1[73].



SCHEME 1

V. ACKNOWLEDGEMENT

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The Chemistry of Organic
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CHAPTER 12

Synthesis and uses of isotopically labelled selenium and tellurium compounds

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I. INTRODUCTION

Selenium and tellurium have many stable and radioactive isotopes. For example, the stable isotopes of selenium, with their natural abundances, are ^{74}Se (0.87%), ^{76}Se (9.02%), ^{77}Se (7.58%), ^{78}Se (23.52%), ^{80}Se (49.82%) and ^{82}Se (9.19%), while ^{72}Se, ^{73}Se, ^{75}Se and ^{77m}Se are the main radioactive isotopes. Tellurium has 8 different stable isotopes and more than 10 radioisotopes[1]. Among the most often used are ^{75}Se (half-life: 118.5 days), ^{123m}Te (half-life: 117 days), ^{127m}Te (half-life: 109 days) and ^{132}Te (half-life: 78 h)[1]. Positron-emitting ^{73}Se may be useful for imaging human body organs by what is called PETT (positron emission transaxial tomography), but it has not yet been put into use.

Most of the radioactively labelled selenium and tellurium compounds discussed in this chapter have been used for biochemical studies and radiomedical research, whereas the deuteriated compounds have been used for infrared, Raman, microwave and nuclear magnetic resonance spectroscopic studies. Very rarely, these isotopes have also been used for studying organic reaction mechanisms. Accordingly, our attention will be focused on the preparation of these isotopically labelled compounds and their biochemical and medicinal uses.

II. PREPARATION OF ISOTOPICALLY LABELLED SELENIUM AND TELLURIUM COMPOUNDS

A. Inorganic Selenium and Tellurium Compounds Labelled with Radioactive Isotopes

Commercially available radioactive elemental selenium and tellurium, selenium dioxide, alkali selenite and tellurite can be reduced to radioactive Na_2Se_2, Na_2Se, NaSeH, Na_2Te and NaTeH, which are versatile reagents for the synthesis of a variety of radioactive organic selenium and tellurium compounds, since these reagents are extremely strong nucleophiles which by S_N2 processes can readily displace halides and tosyloxy groups attached to carbon. This is mainly due to the softness of these reagents which have donor orbitals (HOMOs) of quite high energy levels[2] and even behave as potential reducing agents[3].

Radioactive selenium can readily be reduced with sodium borohydride to sodium selenide and sodium diselenide (equation 1)[4,5].

$$^{75}\mathrm{Se} \xrightarrow{\mathrm{NaBH_4}} \mathrm{Na^{75}SeH} \xrightarrow{^{75}\mathrm{Se}} (\mathrm{Na^{75}Se})_2 \qquad (1)$$

Radioactive elemental selenium is also often reduced by metallic sodium in liquid ammonia to generate sodium diselenide which in turn reacts with various alkylating agents *in situ* to afford dialkyl diselenide labelled with ^{75}Se (equation 2)[6-9].

$$2\ {}^{75}\mathrm{Se} + 2\ \mathrm{Na} \xrightarrow{\text{liq. } \mathrm{NH_3}} \mathrm{Na_2Se_2} \qquad (2)$$

Kronrád and coworkers reduced ${}^{75}SeO_2$ with stannous chloride and phosphoric acid to gaseous hydrogen selenide, $H_2{}^{75}Se$, which can be driven into the reactor containing a suitable electrophilic reagents by a stream of nitrogen (equation 3)[10].

$${}^{75}\mathrm{SeO_2} + 3\ \mathrm{Sn^{2+}} + 6\ \mathrm{H^+} \longrightarrow \mathrm{H_2{}^{75}Se} + 3\ \mathrm{Sn^{4+}} + 2\ \mathrm{H_2O} \qquad (3)$$

Sadek, Basmadjian and Ice reduced radioactive selenious acid with sodium borohydride in an aqueous buffer solution by adjusting the final pH at 6.5–7.0 to obtain $Na^{75}SeH$ quantitatively. Under these reaction conditions evolution of highly toxic hydrogen selenide and the formation of $Na_2{}^{75}Se$ can be avoided[11].

Radioactive elemental selenium obtained by treatment of $Na_2{}^{75}SeO_3$ with sulphur dioxide was shown to be reduced to potassium diselenide, which can be converted to ^{75}Se-labelled dialkyl diselenides upon treatment with alkyl halides or tosylates *in situ* (equation 4)[12].

$$\mathrm{Na_2{}^{75}SeO_3} \xrightarrow{\mathrm{SO_2/H^+}} {}^{75}\mathrm{Se} \xrightarrow{\mathrm{K_2SO_3}} \mathrm{K_2{}^{75}Se_2} \qquad (4)$$

^{127m}Te-labelled elemental tellurium was prepared by treating radioactive sodium tellurite with hydrogen bromide and subsequent addition of stannous chloride and natural tellurium as an entraining agent. The radioactive tellurium so obtained was purified by sublimation and can be converted to ^{127m}Te-labelled tellurium tetrachloride by direct contact with chlorine gas (equation 5)[13].

$$\mathrm{Na_2{}^{127m}TeO_3} \xrightarrow{\mathrm{HBr,\ SnCl_2}} {}^{127m}\mathrm{Te} \xrightarrow{\mathrm{Cl_2}} {}^{127m}\mathrm{TeCl_4} \qquad (5)$$

B. Selenols, Diselenides, Selenides and Tellurides

1. *Acyclic compounds*

Methaneselenol-d_4 was prepared by the following sequence of reactions: treatment of dimethyl sulphate-d_6 with sodium diselenide gave dimethyl diselenide-d_6 which was reduced with metallic sodium in liquid ammonia to obtain the desired compound (equation 6)[6,14,15]. Methaneselenol and methaneselenol-d_3 can be readily converted to CH_3SeD and CD_3SeD simply by treating with deuterium oxide[15].

$$\mathrm{Na_2Se_2} \xrightarrow{\mathrm{(CD_3)_2SO_4}} \mathrm{(CD_3Se)_2} \xrightarrow[\text{2. } \mathrm{H^+}]{\text{1. Na}} \mathrm{CD_3SeH} \xrightarrow{\mathrm{D_2O}/\text{gas phase}} \mathrm{CD_3SeD} \qquad (6)$$

Alkyllithium and Grignard reagents react readily with elemental selenium to afford the selenols (equation 7). Isotopically labelled selenols can be obtained if suitably labelled starting materials are used[16,17].

$$\mathrm{RMgX} + \mathrm{Se} \longrightarrow \mathrm{RSeMgX} \xrightarrow{\mathrm{H_2O/H^+}} \mathrm{RSeH} \tag{7}$$

Basmadjian, Hetzel and Ice synthesized ^{75}Se-labelled α-tolueneselenol and dibenzyl diselenide by treating benzyl chloride with ^{75}Se-labelled sodium hydrogen selenide or sodium diselenide, respectively (equation 8 and 9)[4]. The first method may be used to afford any non-symmetrical selenide. The same authors claim that ^{75}Se-labelled selenourea

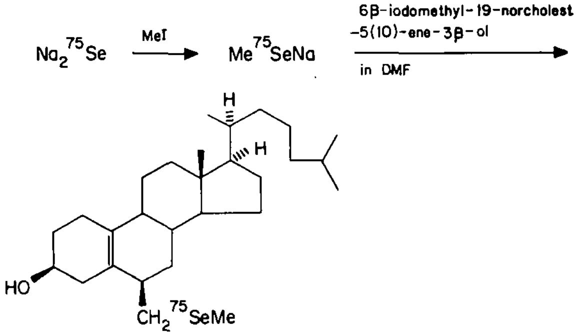
$$\mathrm{Na^{75}SeH} \xrightarrow{\mathrm{RX}} \mathrm{R^{75}SeH} \xrightarrow{\mathrm{R'X/B:}} \mathrm{R^{75}SeR'} \tag{8}$$

$$\mathrm{Na_2{}^{75}Se_2} \xrightarrow{\mathrm{2\ RX}} \mathrm{R_2{}^{75}Se_2} \tag{9}$$

derivatives, which can be readily obtained upon heating ^{75}Se-labelled sodium hydrogen selenide with substituted carbodiimides, are versatile reagents for preparation of ^{75}Se-labelled selenols (equation 10)[4].

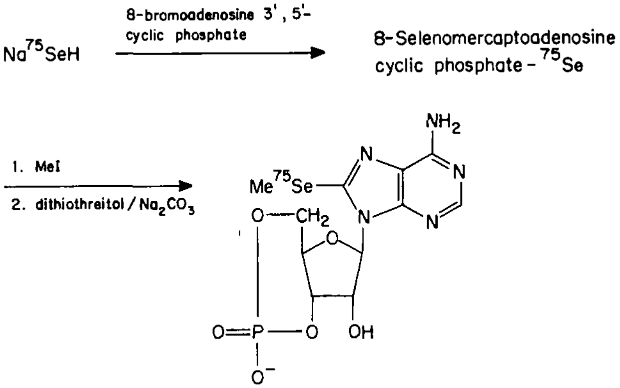
$$\mathrm{Na^{75}SeH} \xrightarrow{\mathrm{RN{=}C{=}NR}} \mathrm{RNHC({=}^{75}Se)NHR} \xrightarrow{\mathrm{R'X}} \mathrm{RNH\overset{+}{C}(^{75}SeR')NHR\ X^-} \xrightarrow{\mathrm{H_2O}} \mathrm{R'^{75}SeH} \tag{10}$$

Monks and coworkers prepared 6β-(alkylseleno-^{75}Se-methyl)norcholestane[7] (**1**) and ^{75}Se-labelled 8-methylselenoadenosine 3′,5′-cyclic phosphate[18] (**2**) by the reaction sequence shown in equations (11) and (12).



(**1**)

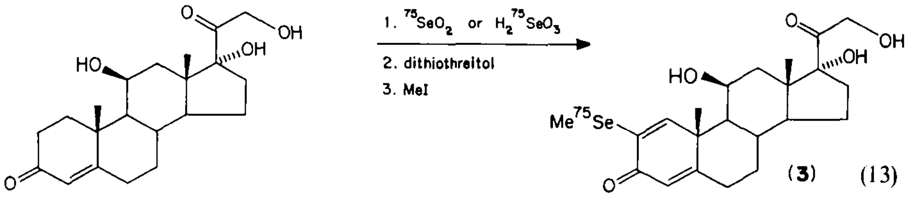
(11)



(**2**)

(12)

Chambers and coworkers prepared ^{75}Se-labelled 2-methylselenoprednisolone (**3**) by treating cortisol with ^{75}Se-labelled selenium dioxide as shown in equation (13)[19].



(**3**) (13)

Monks and coworkers studied two routes for the preparation of ^{75}Se-labelled steroids. One route involves conversion of a hydroxyl group in the steroids at the 3, 6, 17, 19 or 21 position to the corresponding methaneselenyl group as shown in equation (14)[20]. The

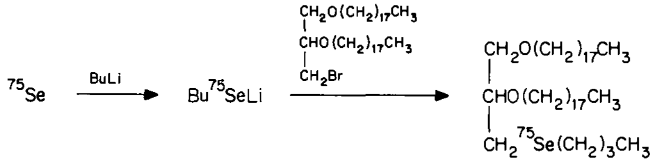
$$\text{Steroid—OH} \xrightarrow{\text{TsCl}} \text{Steroid—OTs} \xrightarrow{K^{75}SeCN} \text{Steroid—}^{75}\text{SeCN} \xrightarrow{\text{1. dithiothreitol 2. MeI or } Me_2SO_4} \text{Steroid—}^{75}\text{SeMe}\ (\mathbf{4}) \qquad (14)$$

second route involves conversion of steroids bearing a carbonyl group at the 3, 6, 17 or 20 position into oximes having a radioactive selenium-containing group as shown in equation (15)[20].

$$\text{Steroid=O} \xrightarrow{H_2NOCH_2COOH} \text{Steroid=}NOCH_2COOH \xrightarrow{ClCOOBu\text{-}i\,/Et_3N}$$

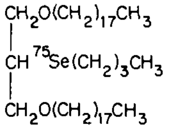
$$\xrightarrow[\text{or } Me^{75}SeCH_2CH_2NH_2]{Me^{75}SeCH_2CH_2CH(NH_2)COOH} \begin{array}{c} \text{Steroid=}NOCH_2CONHCH(COOH)CH_2CH_2{}^{75}SeMe \\ (\mathbf{5}) \\ \text{or} \\ \text{Steroid=}NOCH_2CONHCH_2CH_2{}^{75}SeMe \\ (\mathbf{5a}) \end{array} \qquad (15)$$

Otto prepared ^{75}Se-labelled glycerine triethers (**6a** and **6b**) by the method shown for **6a** in equation (16)[21]. They also showed that when ^{123m}Te was used instead of ^{75}Se in the above synthetic procedure, ^{123m}Te-labelled glycerine triethers, e.g. **7**, could be obtained[21].



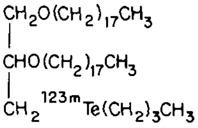
$$^{75}Se \xrightarrow{\text{BuLi}} Bu^{75}SeLi \xrightarrow{\begin{array}{l} CH_2O(CH_2)_{17}CH_3 \\ | \\ CHO(CH_2)_{17}CH_3 \\ | \\ CH_2Br \end{array}} \begin{array}{l} CH_2O(CH_2)_{17}CH_3 \\ | \\ CHO(CH_2)_{17}CH_3 \\ | \\ CH_2{}^{75}Se(CH_2)_3CH_3 \end{array} \qquad (16)$$

(**6a**)



$$\begin{array}{l} CH_2O(CH_2)_{17}CH_3 \\ | \\ CH{}^{75}Se(CH_2)_3CH_3 \\ | \\ CH_2O(CH_2)_{17}CH_3 \end{array}$$

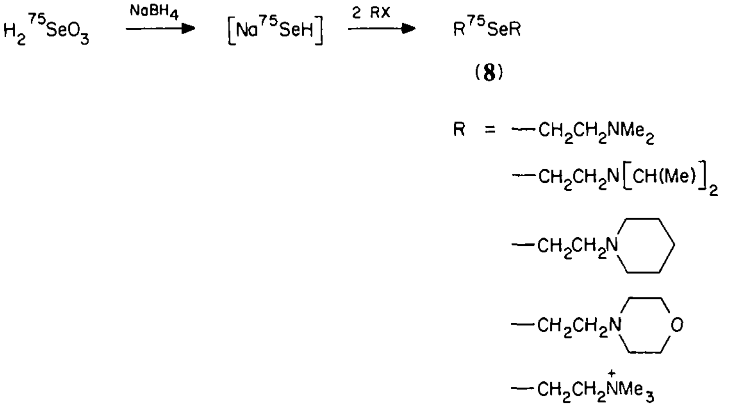
(**6b**)



$$\begin{array}{l} CH_2O(CH_2)_{17}CH_3 \\ | \\ CHO(CH_2)_{17}CH_3 \\ | \\ CH_2{}^{123m}Te(CH_2)_3CH_3 \end{array}$$

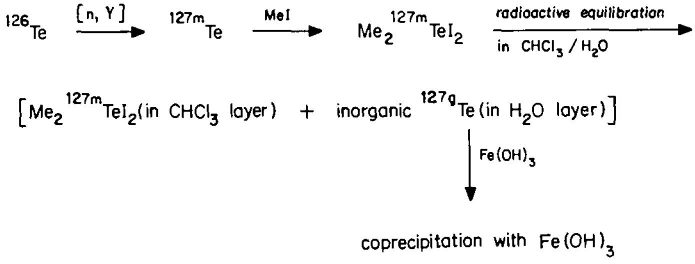
(**7**)

Kung and Blau synthesized ^{75}Se-labelled tertiary amines (**8**) by reducing ^{75}Se-labelled selenious acid with sodium borohydride and subsequent treatment of the intermediate formed with *N*,*N*-substituted aminoethyl chloride (equation 17)[22].



(17)

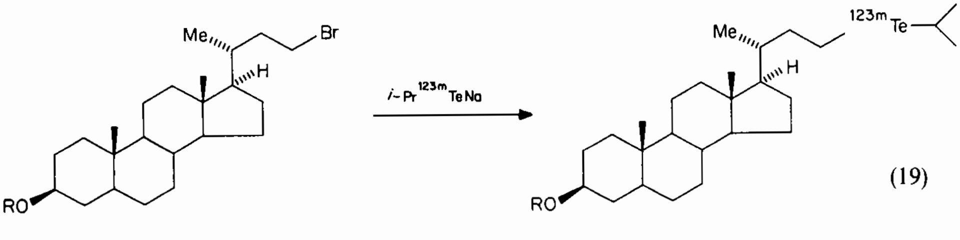
Carrillo and Nassiff succeeded in the separation of ^{127m}Te/^{127g}Te obtained by [n, γ] reaction of a sample enriched with ^{126}Te. The elemental tellurium containing a mixture of radioactive isotopes obtained by the neutron irradiation was converted to dimethyltellurium iodide, which was then dissolved in an organic solvent and kept until radioactive equilibrium was attained. At this stage, ^{127g}Te (half-life: 9.4 h), formed from ^{127m}Te (half-life: 109 days) during the radioactive equilibration, was shown to have changed through recoil reaction to inorganic tellurium which could be separated by coprecipitation with ferric hydroxide from other isotopes of organic form contained in the organic layer (equation 18)[23].



(18)

Adloff and Adloff prepared radioactive ^{132}Te-labelled diphenyltellurium dichloride by displacement of mercury from diphenylmercury by ^{132}Te under nitrogen and subsequent treatment with chlorine[24].

The ^{123m}Te-labelled norchorane derivative **10** was prepared by the reaction of bromonorcholane (**9**) with ^{123m}Te-labelled isopropyl telluride in an alkaline solution (equation 19)[25].



(9) (10)

(19)

Knapp and coworkers prepared ^{123m}Te-labelled isosters of palmitoleic acid and oleic acid, i.e. 9-tellura-^{123m}Te-pentadecanoic acid (**11a**) and 9-tellura-^{123m}Te-heptadecanoic acid (**11b**), respectively, by the synthetic route shown in equation (20)[26]. 17-

$$n\text{-}C_nH_{2n+1}{}^{123m}TeNa \xrightarrow[\substack{2.\ H_2O/OH^- \\ 3.\ H^+}]{1.\ Br(CH_2)_7COOCH_3} n\text{-}C_nH_{2n+1}{}^{123m}Te(CH_2)_7COOH \qquad (20)$$

(**11**)

(**a**) $n = 6$

(**b**) $n = 8$

[^{123m}Te]tellura-9-octadecenoic acid (**13a**) was prepared by Basmadjian and coworkers through the two routes shown in equation (21)[27]. The four ^{123m}Te-labelled hexadecenoic acid analogues **13b–e** were synthesized in the same manner[27].

$$\begin{tikzcd}
BrCH_2(CH_2)_5CH{=}CH(CH_2)_6CH_2COO^-\ Na^+ \arrow[d, "Na^{123m}TeH"'] \arrow[dr, "Na_2{}^{123m}Te_2"] & \\
& {[Na^+\ {}^-OOCCH_2(CH_2)_6CH{=}CH(CH_2)_5CH_2Te]_2} \arrow[dl, "NaBH_4"] \\
Na^{123m}TeCH_2(CH_2)_5CH{=}CH(CH_2)_6CH_2COO^-\ Na^+ \arrow[d, "MeI"] & \\
Me^{123m}TeCH_2(CH_2)_5CH{=}CH(CH_2)_6CH_2COO^-\ Na^+ &
\end{tikzcd}$$

(**12**)

(21)

(**13a**)

$Et^{123m}TeCH_2(CH_2)_5CH{=\!=}CH(CH_2)_6CH_2COOH$ **(13b)**

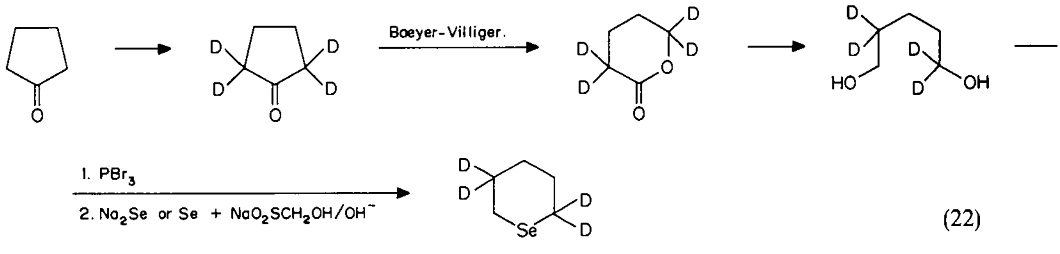
$Pr^{123m}TeCH_2(CH_2)_5CH{=\!=}CH(CH_2)_6CH_2COOH$ **(13c)**

$Me_2{}^{123m}\overset{+}{Te}(CH_2)_5CH{=\!=}CH(CH_2)_6CH_2COOH\ Cl^-$ **(13d)**

$Me(CH_2)_{15}{}^{123m}TeCH_2COOH$ **(13e)**

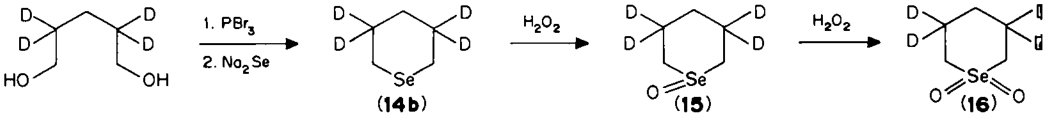
2. Cyclic compounds

Lambert and coworkers synthesized several deuteriated selenanes (**14a–c**)[28–30] by treating suitable deuteriated 1,5-dibromopentanes with sodium selenide or a mixture of sodium formaldehydesulphoxylate and elemental selenium according to the procedure developed by McCullough and Lefohn (equations 22–24)[31]. In the latter process elemental selenium is believed to be reduced to form sodium selenide in the initial step of the reaction[31].



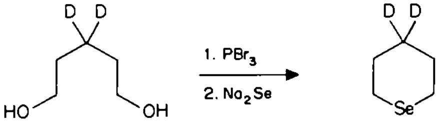
(14a)

(22)



(14b) **(15)** **(16)**

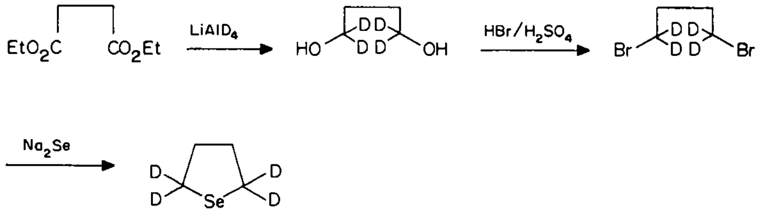
(23)



(14c)

(24)

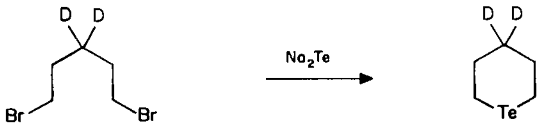
Meanwhile, Russian chemists prepared 2,2,5,5-tetradeuterioselenolane (**17**) as shown in equation (25)[32].



(17)

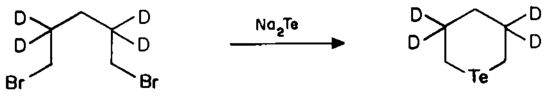
(25)

Lambert and coworkers also synthesized 4,4-dideuteriotellurane (**18a**) and 3,3,5,5-tetradeuteriotellurane (**18b**) by the reaction between the corresponding deuteriated 1,5-dibromopentane and sodium telluride (equations 26 and 27)[28].



(18a)

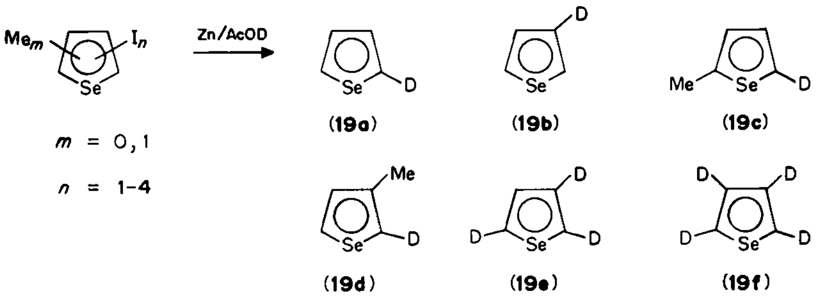
(26)



(18b)

(27)

Several deuteriated selenophenes (**19a–f**) were prepared by Magdesieva and coworkers by treating the corresponding iodoselenophenes with zinc and AcOD (equation 28)[33].



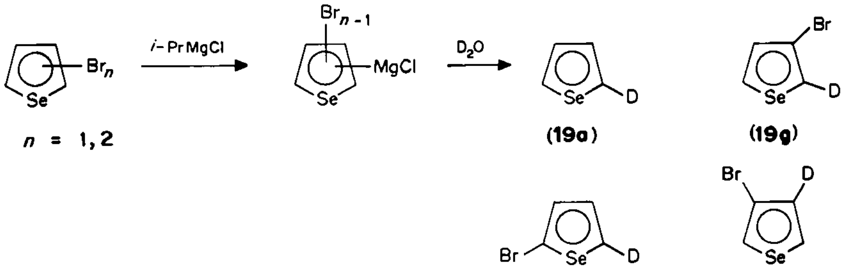
m = 0, 1

n = 1–4

(19a) **(19b)** **(19c)** **(19d)** **(19e)** **(19f)**

(28)

Martin and coworkers obtained deuteriated selenophenes (**19a,g–i**) by quenching the corresponding Grignard reagents with D_2O (equation 29)[34].

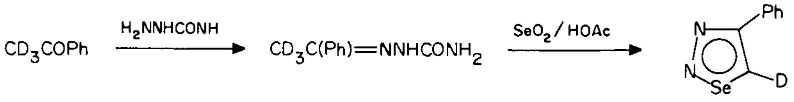


n = 1, 2

(19a) **(19g)** **(19h)** **(19i)**

(29)

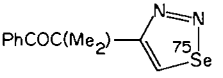
4-Phenyl-5-deuterio-1,2,3-selenodiazole (**20**) was prepared by the reaction of the semicarbazone of acetophenone-d_3 with selenium dioxide (equation 30)[35]. Hanson and



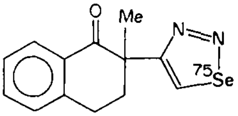
(30)

(20)

Davis reported that the synthesis of ^{75}Se-labelled 4-substituted 1,2,3-selenadiazoles, **21** and **22**, could be achieved by cyclization of appropriate semicarbazones by the method shown in equation (30)[36].

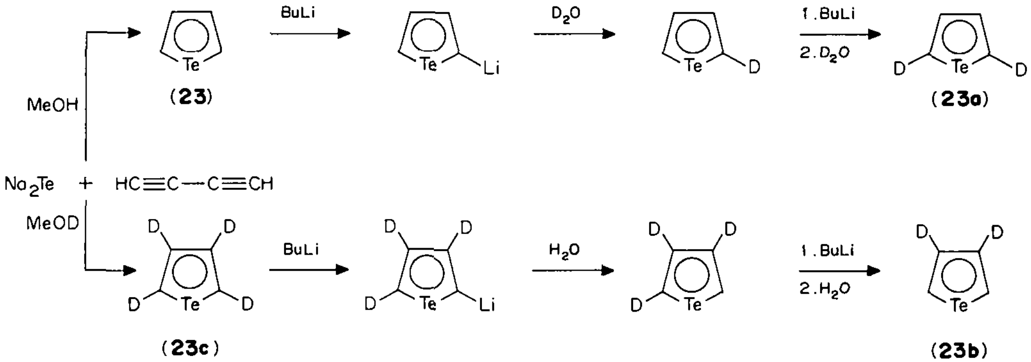


(21)



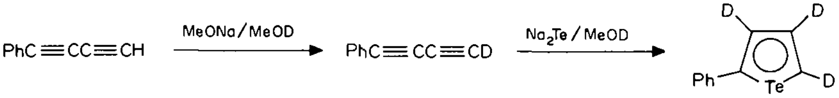
(22)

Paliani and coworkers synthesized tellurophene (**23**) and various deuteriated derivatives (**23a–c**) by the processes shown in equation (31)[37]. Barton and coworkers



(31)

prepared 2-phenyltellurophene-5-d_1 (**24a**) by initial lithiation of 2-phenyltellurophene and subsequent quenching of the lithiated compound by deuterium oxide, while 2-phenyltellurophene-3,4,5-d_3 (**24b**) was prepared as shown in equation (32)[38].



(32)

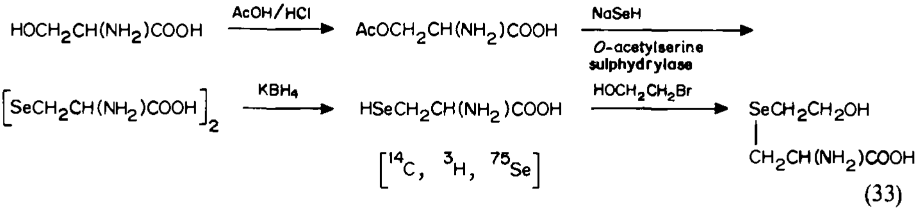
(24b)

3. *Amino acids*

Barak and Swanberg established a quantitative analytical method for estimating the amount of selenomethionine in biological samples such as serum, liver and muscle by coupling the techniques of paper chromatography and neutron activation analysis; this involves the irradiation of the sample with neutron flux to convert ^{76}Se to radioactive ^{77m}Se[39].

McConnell and coworkers irradiated selenomethionine, 6-selenoguanine and 6-selenopurine in a water-cooled compartment of a graphite reactor with a neutron flux of 7.5 × 10^{11} neutron cm^{-2} s^{-1} for 62h to obtain directly the corresponding ^{75}Se-labelled compounds. They claimed that no notable degradation of the starting substances was observed[40]. Later, however, Spencer and coworkers found that the neutron irradiation of selenocystine gave ^{75}Se-labelled selenocystine together with some degradation products via recombination of symmetrical halves of the molecule or by exchange with non-radioactive molecules found as cleavage products in the [n, γ] reaction as observed in the neutron irradiation of diphenyl selenide which had been known to give a mixture of radioactive diphenyl selenide and labelled diphenyl diselenide. These observations suggest that the [n,γ] process involves Se—Se bond rupture–recombination[41].

Dilworth reported a convenient enzymatic synthesis of isotopically labelled selenocysteine and its derivatives. At first serine was converted to *O*-acetylserine which was then incubated with *O*-acetylserine sulphydrylase at pH 7.2 in the presence of sodium hydrogen selenide to obtain selenocysteine which was converted to ^{75}Se-labelled selenocysteine via ^{75}Se-labelled selenocystine as shown in equation (33)[5]. When ^{14}C- or ^{3}H-labelled serine or ^{75}Se-labelled sodium hydrogen selenide was used as the starting material, the corresponding radioactive selenoamino acid was obtained[5].



$$HOCH_2CH(NH_2)COOH \xrightarrow{AcOH/HCl} AcOCH_2CH(NH_2)COOH \xrightarrow[O\text{-acetylserine sulphydrylase}]{NaSeH}$$

$$[SeCH_2CH(NH_2)COOH]_2 \xrightarrow{KBH_4} \underset{[^{14}C,\ ^{3}H,\ ^{75}Se]}{HSeCH_2CH(NH_2)COOH} \xrightarrow{HOCH_2CH_2Br} \begin{array}{l} SeCH_2CH_2OH \\ | \\ CH_2CH(NH_2)COOH \end{array}$$

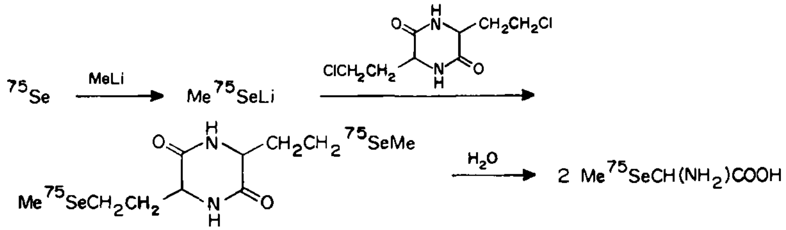
(33)

^{75}Se-labelled selenomethionine was prepared according to equation (34)[12].

$$(Me^{75}Se)_2 \xrightarrow{Na} Me^{75}SeNa \xrightarrow{BrCH_2CH_2CH(NH_2)COOMe}$$

$$Me^{75}SeCH_2CH_2CH(NH_2)COOMe \xrightarrow{H^+/H_2O} Me^{75}SeCH_2CH_2CH(NH_2)COOH \qquad (34)$$

Otto obtained ^{75}Se-labelled selenomethionine by treating ^{75}Se-labelled lithium methaneselenolate with bis(chloroethyl)dioxopiperazine and subsequent hydrolysis (equation 35)[42].



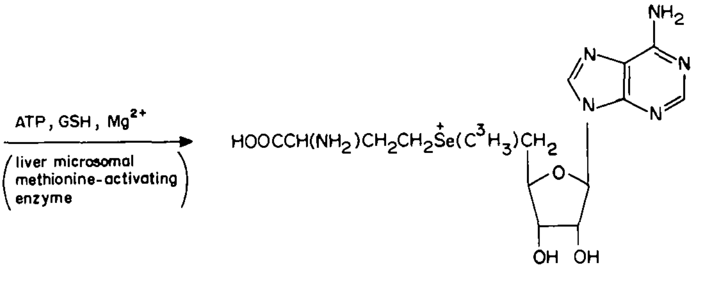
(35)

Racemic methyl-^{14}C-labelled selenomethionine and ethyl-^{14}C-labelled selenoethionine were readily prepared by treating racemic selenocysteine with ^{14}C-labelled alkyl iodides (equation 36)[43].

$$^{14}CH_3I + HSeCH_2CH_2CH(NH_2)COOH \longrightarrow {}^{14}CH_3SeCH_2CH_2CH(NH_2)COOH \qquad (36)$$

Bremer and Natori tritiated selenomethionine randomly by simple exposure of the compound to tritium gas [44]according to the procedure reported by Wilzbach[45]. ^3H-labelled selenomethionine was then converted to ^3H-labelled *Se*-adenosylselenomethionine (**25**) through the procedure developed by Cantoni and Durell (equation 37)[46].

$$CH_3SeCH_2CH_2CH(NH_2)COOH \xrightarrow{^3H_2} CH_3SeCH_2CH_2CH(NH_2)COOH\ [^3H]$$

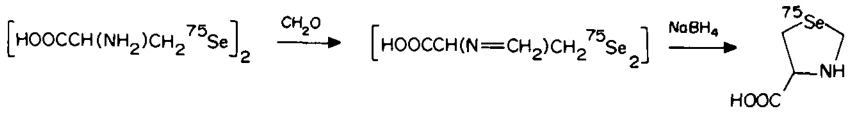


(**25**)

(37)

Blau reported a successful small-scale biosynthesis of radioactive selenocysteine and selenomethionine[47]. At first baker's yeast (*Saccharomyces cerevisa*) was grown in the presence of ^{75}Se-labelled selenous acid. Subsequent hydrolysis and ion exchange fractionation provided the desired ^{75}Se-labelled amino acids.

Wong and coworkers prepared ^{75}Se-labelled selenaproline (4-selenazolidine-1-^{75}Se-carboxylic acid) (**26**) by condensation of ^{75}Se-labelled L-selenocystine with formaldehyde after reduction with sodium borohydride as shown in equation (38)[48].



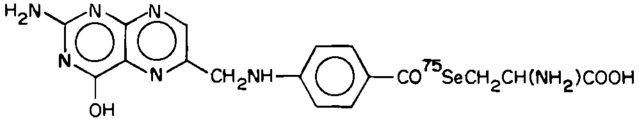
(**26**)

(38)

Monks prepared ^{75}Se-labelled derivatives of folates **28** and **29** as shown in equations (39) and (40)[8,9].

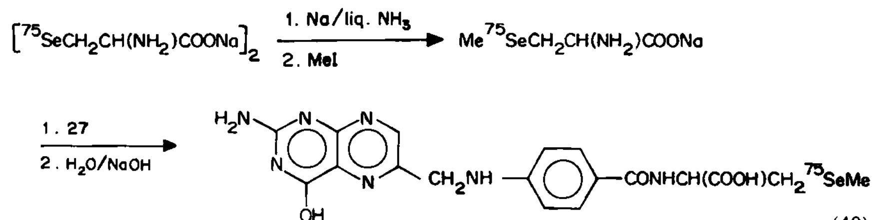
$$Na_2{}^{75}Se_2 \xrightarrow{ClCH_2CH(NH_2)COONa} [{}^{75}SeCH_2CH(NH_2)COONa]_2 \xrightarrow{Na/liq.\ NH_3}$$

$$Na^{75}SeCH_2CH(NH_2)COONa \xrightarrow[\text{2. } H_2O/NaOH \quad \text{3. } H^+]{\text{1. } N^{10}\text{-trifluoroacetylpteroyl isobutyl carbonate } (\mathbf{27})}$$



(28)

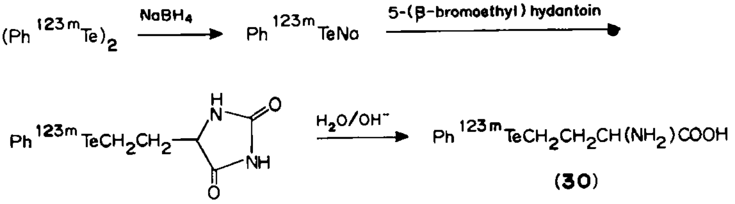
(39)



(29)

(40)

^{123m}Te-labelled racemic α-amino-γ-(phenyltelluro)butyric acid (**30**) was synthesized by Knapp and coworkers by alkaline hydrolysis of racemic 5-[β-(phenyltelluro)ethyl]hydantoin-^{123m}Te obtained as shown in equation (41)[49].



(30)

(41)

Celander and Celander isolated ^{75}Se-labelled urokinase from the urine of dogs after injecting $Na_2{}^{75}SeO_3$[50], while ^{75}Se-labelled fibrinogen was obtained from the plasma of dogs which were administered with $Na_2{}^{75}SeO_3$[51] or ^{75}Se-selenomethionine[52].

Insulin containing radioactive selenocystine was prepared by Tavaarwerk according to the following *in vivo* reaction[53]: Selenocystine labelled with ^{75}Se was injected into the tail vein of a rat. After one day, radioactive insulin was extracted from the rats pancreas and purified.

Leon and coworkers successfully prepared ^{75}Se-labelled plague murine toxins produced by *Pasteurella pestis*. The toxic proteins A and B were isolated from the soluble protein obtained from the cells grown in the presence of ^{75}Se-labelled selenomethionine[54].

Snake venom labelled with ^{75}Se was obtained from *Vipera ammodytes* one week after ^{75}Se-labelled selenomethionine was injected into the snake's stomach. The labelled snake venom exhibited the same electrophoretic behaviour as non-labelled venom[55].

The technique of labelling proteins with ^{75}Se has also been applied to immunological research[56–60]. For example, Engler and coworkers obtained highly radioactive ^{75}Se-labelled glycoproteins, i.e. hepatoglobin and α_2-macroglobulin, formed by acute-phase reaction of the inflammatory process caused by turpentine[57]. Rats were injected with ^{75}Se-selenomethionine one day after treating with turpentine. Five and a half hours later the blood of the animals was collected and the radioactive glycoproteins were isolated from the plasma[57].

In vivo labelling of living lymphocytes with ^{75}Se was performed through incubation of mice or rat lymphocytes with ^{75}Se-selenomethionine[61,62].

Meanwhile, highly specific labelling of viral proteins was achieved by Enzmann, who revealed that viruses incorporated ^{75}Se-selenomethionine in culture, during their protein synthesis[63].

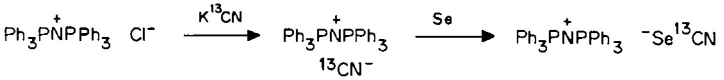
Kishore and coworkers labelled the living cells of *Pseudomonas aeruginosa* and *Staphylococcus aureus* with ^{75}Se by growing the bacteria in trypticase soy in the presence of ^{75}Se-labelled selenomethionine[64].

4. Miscellaneous

Kronrád and Hladik prepared ^{75}Se-labelled selenourea by treating ^{75}Se-labelled hydrogen selenide, obtained from the reaction shown in equation (3), with cyanamide (equation 42)[10b].

$$NCNH_2 + H_2{}^{75}Se \longrightarrow {}^{75}Se{=}C(NH_2)_2 \qquad (42)$$

Martinsen and Songstad obtained bis(triphenylphosphine)imminium selenocyanate-^{13}C by the reaction of ^{13}C-labelled cyanide with elemental selenium (equation 43)[65].



$$Ph_3\overset{+}{P}NPPh_3\ Cl^- \xrightarrow{K^{13}CN} \underset{^{13}CN^-}{Ph_3\overset{+}{P}NPPh_3} \xrightarrow{Se} Ph_3\overset{+}{P}NPPh_3\ {}^-Se^{13}CN \qquad (43)$$

Sulphur atoms in acid-labile sulphur–iron clusters of bacterial origin were found to be replaced by selenium in an ESR study of these enzymes. Putidaredoxin isolated from *Pseudomonas putida* is a protein of mol. wt. 12,000 containing two atoms each of acid-labile sulphur and iron. Selenium-containing homologues of this iron protein labelled with ^{80}Se (97 atom%) and ^{77}Se (87 atom%) containing a small amount of radioactive ^{75}Se were prepared by treating putidaredoxin apoprotein with ammonium selenide enriched with the desired isotope and ferrous iron in the presence of 2-mercaptoethanol under argon. Both the selenium and iron contents of the modified protein were two atoms per mole of the enzyme[66]. Fee and Palmer prepared $^{32}S^{57}Fe$, $^{80}Se^{56}Fe$, $^{77}Se^{56}Fe$ and $^{80}Se^{57}Fe$ homologues of parsley ferredoxin (native enzyme: $^{32}S^{56}Fe$). They treated the apoenzyme with a mixture of ^{80}Se (80 atom%)- or ^{77}Se (88 atom%)-labelled Na_2SeO_3 containing a small amount of $Na_2{}^{75}SeO_3$ and excess dithiothreitol in a buffer solution under helium, and subsequently with ^{56}Fe or ^{57}Fe (90 atom%) citrate. The apoprotein was prepared by precipitation with trichloroacetic acid, while the isotopically labelled Na_2SeO_3 was prepared by the reaction of enriched isotopic elemental selenium with nitric acid[67]. Similarly, Mukai and coworkers prepared ^{80}Se- or ^{77}Se-containing selenium homologues of adrenodoxin isolated from beef adrenal gland[68]. Displacement of labile sulphur atoms in these native non-haemeiron proteins with selenium changed little the nature of the original enzymes, e.g. the enzymes modified with selenium were found to retain about 80% of the native enzyme activity in all three cases above.

III. USES OF ISOTOPICALLY LABELLED SELENIUM AND TELLURIUM COMPOUNDS

A. Physicochemical Uses

1. Infrared and Raman spectroscopy

Harvey and coworkers recorded IR spectra of light and heavy methaneselenols[15] and dimethyl diselenides[6]. They assigned absorption bands at 3027 cm^{-1} (CH_3SeH, CH_3SeD)

and 2270 cm^{-1} (CD_3SeH, CD_3SeD) for antisymmetrical stretching vibrations, while absorption bands at 2955 cm^{-1} (CH_3SeH, CH_3SeD), 2194 cm^{-1} (CD_3SeH) and 2148 cm^{-1} (CD_3SeD) were taken to be due to symmetrical C—H stretching vibrations. The following bands were assigned for Se—H or Se—D stretching vibrations: 2330 cm^{-1} (CH_3SeH), 2323 cm^{-1} (CD_3SeH) and 1680 cm^{-1} (CH_3SeD, CD_3SeD). The absorption bands due to the antisymmetrical stretching vibrations of the C—H or C—D bond for dimethyl diselenide were found to be located at 3027 cm^{-1} for $(CH_3Se)_2$, and at 2273 and 2258 cm^{-1} for $(CD_3Se)_2$. The symmetrical stretching vibration of the C—H bond was at 2940 cm^{-1} for $(CH_3Se)_2$, while that of the C—D bond was at 2137 cm^{-1} for $(CD_3Se)_2$. These authors claimed the complete assignment of both the IR and Raman spectra of these compounds.

Magdesieva and coworkers recorded the IR and Raman spectra of selenophene and its deuteriated derivatives (**19a–f**) in the region of 400–3100 cm^{-1}[69,70]. The observed data were compared with the values of frequencies, force constants and intensities theoretically calculated. Magdesieva summarized C—H(D) stretching and deformation and 9 ring strecthing and deformation vibrations for light and heavy selenophenes together with those for thiophenes[71].

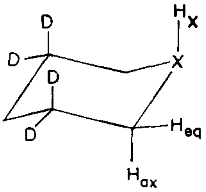
The infrared and Raman spectra of tellurophene (**23**) and the deuteriated tellurophenes (**23a–c**) have been studied by Italian investigators, who reported that the vibrational spectra of thiophene, selenophene and tellurophene are very similar, although somewhat different from that of furan[37]. They proposed that the spectral behaviour of five-membered aromatics containing one heteroatom can be attributed to the mass and the electronegativity of the heteroatom, the delocalization of π electrons, the geometry of the molecule and to the differences in vibrational coupling on the normal mode in these molecules. The increase in frequency of the ν_5 mode due to the symmetric stretching of the double bond in the order of thiophene, selenophene, tellurophene was explained in terms of the same decreasing order of aromaticity which increases the localization of the double bonds in the heterocycles.

2. *Microwave spectroscopy*

Earlier, planarity of selenophene had been a matter of controversy[72]. In order to clarify this problem, Pozdeev and coworkers recorded microwave spectra of selenophene and deuteriated selenophenes at −40 °C. 17 Selenophenes containing different isotopes such as ^{12}C, ^{13}C, ^{1}H, ^{2}H, ^{76}Se, ^{78}Se, ^{80}Se and ^{82}Se, were studied. The experimental results verified the planarity of the selenophene molecule[73].

3. *Nuclear magnetic resonance spectroscopy*

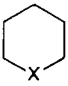
Lambert and coworkers achieved conformational characterization of protonated thiane, selenane and tellurane in $FSO_3H–SO_2$ by measuring NMR spectra of the deuteriated compounds. Vicinal coupling constants between H_X and the axial proton (J_{ax})

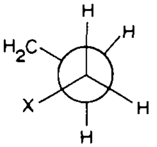


X = S, Se, Te

of 3,3,5,5-tetradeuterio heterocycles were found to be 14.1, 13.0 and 11.2 Hz for X = S, Se and Te, respectively. These values are similar to those found in piperidine (10.5 Hz), *N*-methylpiperidine (10.0 Hz) and *N*-methylpiperidine (11.3 Hz) in which the *N*-bound protons are axial, indicating that the protons attached to the Group IV heteroatoms are also at the axial position. Similarly,the values of J_{eq}, the coupling constant between H_X and H_{eq} for the Group IV heterocycles (2.3, 2.1 and 2.4 Hz for X = S, Se and Te, respectively) were found to be similar to those of the nitrogen heterocycles in accordance with the above results[28].

The same authors also studied the ring deformation of these heterocycles on the basis of the NMR data of 4,4-dideuterio heterocycles, and showed that the following three cases, i.e. **31**, **32** and **33**, can be diagnosed based on an *R* value which is equal to J_{trans}/J_{cis} and is independent of the electronegativity of X.





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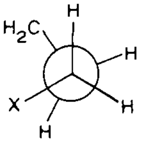

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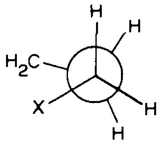


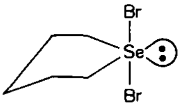
(33)

$R = J_{trans} / J_{cis}$ $R = 2$ $R > 2$ $R < 2$

R values were found to be 2.61, 2.74 and 2.76 for thiane-4-d$_2$, selenane-4-d$_2$ (**14c**) and tellurane-4-d$_2$ (**18a**), respectively. These values appear to indicate that the pseudo-equatorial protons are pushed more closely together as in **32** in these heterocycles[28].

Lambert and coworkers[30] determined the free energy barrier for the conformational reversal for six-membered heterocycyclic rings containing a Group IV heteroatom by analyzing the temperature-dependent proton NMR spectra of these heterocycles tetra-deuteriated at the 3- and 5-positions. The free energy for the ring reversal decreases with the increase of the size of the Group IV atoms, i.e. 10.3 kcal mol^{-1} at $-64\,°C$ for tetrahydropyrane, 9.4 kcal mol^{-1} at $-81\,°C$ for thiane, 8.2 kcal mol^{-1} at $-105\,°C$ for selenane (**14b**) and 7.3 kcal mol^{-1} at $-119\,°C$ for tellurane (**18b**). The barriers are well correlated with the torsional properties of the C—X bond. The same trend was observed for the corresponding oxides, i.e. 10.1 kcal mol^{-1} at $-70\,°C$ for thiane-1-oxide, 8.3 kcal mol^{-1} at $-102\,°C$ for selenane-1-oxide (**15**), 10.3 kcal mol^{-1} at $-63\,°C$ for thiane-1,1-dioxide and 6.7 kcal mol^{-1} at $-133\,°C$ for selenane-1,1-dioxide (**16**). They also found that in **15** the proportion of axial isomer (84%) is more than that in thiane-1-oxide (62%), since the increase of carbon–heteroatom bond length increases the 1,3- and 1,5-attractive interactions. For the same reason, in the *Se*-methylselenanium iodide, the Me group was found to be nearly exclusively axial, while in the *S*-methylthianium iodide the Me group was nearly completely equatorial[30].

Lambert and coworkers determined the structure of complexes between Group IV heterocycles and halogens by an NMR study using 4,4-dideuterio derivatives and 2,2,5,5-tetradeuterio heterocycles, and also by conductance measurements. In solution, selenane



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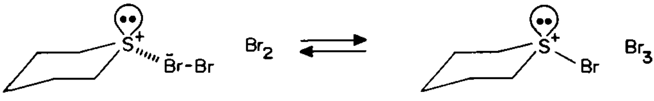


(35)

dibromide exists as a trigonal bipyramid (**34**), whereas selenane diiodide, thiane dibromide and thiane diiodide are in the form of a molecular complex like **35**[29].

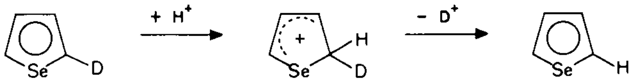
Gronowitz and coworkers determined the ^{1}H- and ^{13}C-NMR parameters for a series of selenophenes substituted at the 2- and 3-positions. The chemical shifts were linearly correlated with the reactivity parameters of Swain–Lupton's two-parameter equation. Deuteriated selenophenes were used for the chemical shift assignment[74].

Fringuelli and coworkers also used deuteriotellurophenes in an NMR study[75]. They discussed physicochemical properties involving NMR and chemical reactivities of tellurophene in comparison with those of other five-membered heteroaromatics containing a Group IV element[75].

B. Mechanistic Studies of the Reactions of Organic Selenium and Tellurium Compounds

1. Isotopic exchange

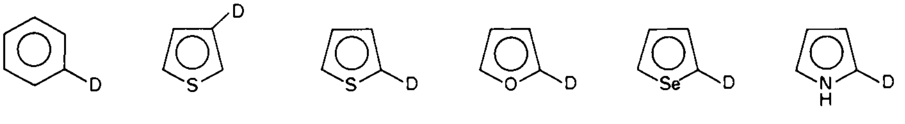
Magdesieva and coworkers investigated both acid- and base-catalysed D–H exchange reactions of 2- and 3-deuterioselenophene (**19a** and **b**), 2-deuterio-5-methylselenophene (**19c**) and 2-deuterio-3-methylselenophene (**19d**)[33b]. Electrophilic D–H exchange reactions were conducted in 4:1 mixture of acetic and trifluoroacetic acids at 25 °C. Relative rates were reported to be **19a**:**19c**:**19d** = 1:107:236, while the D–H exchange in **19b** was too slow to compete with the acid-catalysed degradation. The results clearly reveal that the rate of D–H exchange reaction is correlated with the stability of the protonated intermediate **36** (equation 44).



(**19a**) (**36**) (**19**)

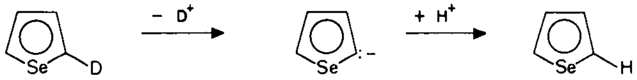
(44)

Schwetlick and Unverferth determined relative reactivities of different aromatics in the acid-catalysed D–H exchange[76]. Obviously, the rate appears to increase as the aromaticity of the heteroaromatics decreases as shown below. Magdesieva also discussed the relative reactivities of selenophene, thiophene and furan in both acid- and base-catalysed D–H exchange reactions at the α- and β-positions, on the basis of the abilities of electron pair donating effects of the heteroatoms[71].



k^{rel}	1	10^4	2×10^7	3×10^7	2×10^8	10^{15}

Magdesieva and coworkers also carried out alkaline D–H exchanges of deuterioselenophenes in t-BuOLi/DMSO or t-BuOK/in 70% t-BuOH and 30% diglyme at 25 °C. In the former system, the relative exchange rates were observed to be **19a**:**19c**:**19d**:**19b** = 1:

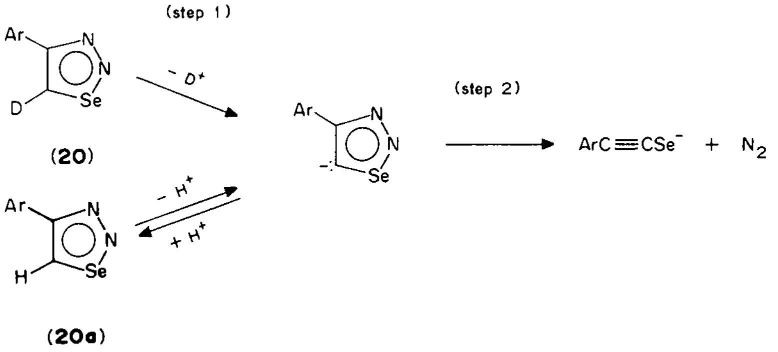


(**37**)

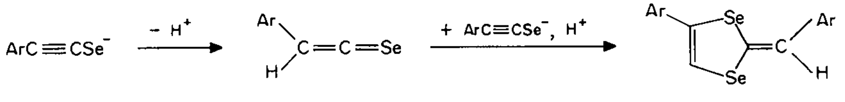
(45)

0.12: 0.05: 2.5 × 10^{-5}. These rates vary with the stability of the intermediary anion (**37**) as shown in equation (45)[33b,71].

Ghandehari and coworkers[35] investigated the mechanism of the base-catalysed decomposition of 4-aryl-substituted 1,2,3-selenodiazoles (**20a**) to give *para*-substituted phenylethynylselenolate (equation 46a)[38b] which eventually affords substituted 1,3-diselenafulvenes (**38**) by the reaction shown in equation (46b)[35]. They observed that an electronegative *para* substituent in the Ph group accelerates the reaction (46a) and the kinetic data were nicely correlated with the Hammett σ constants giving $\rho = +2.37$.



(46a)



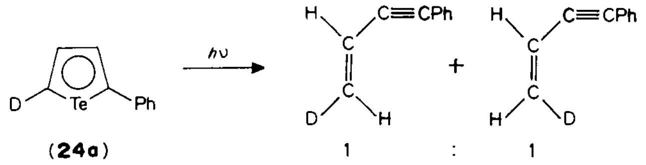
Ar = p-XC$_6$H$_4$

(**38**) (46b)

However, when 5-deuterio-4-phenyl-1,2,3-selenadiazole (**20**) was subjected to the reaction, the D–H exchange took place readily before the evolution of nitrogen gas was noticed. The value of $k_H/k_D = 2$ was observed for step 1, while no significant D–H kinetic isotope effect was observed in the overall reaction. Thus the authors concluded that step 1 is a fast equilibrium and the positive ρ value is due to the shift of the equilibrium by the electronegative substituents to the right, hence step 2 seems to be facilitated[35].

2. *Photochemical reaction*

Upon irradiation of 2-phenylselenophene, Barton and coworkers obtained a mixture of 3-phenylselenophene and 1-phenyl-2-vinylacetylene, while the latter product was the sole product in the irradiation of 2-phenyltellurophene (**24**). They studied the mechanism of the formation of phenylvinylacetylene using deuterium as the tracer[38a]. Photolysis of 2-phenyl-5-deuteriotellurophene (**24a**) in ether with a 300 nm lamp gave a 1:1 *syn anti* mixture of (2-deuteriovinyl)phenylacetylenes (equation 47). Similarly, a 1: 1 mixture of *syn*- and *anti*-



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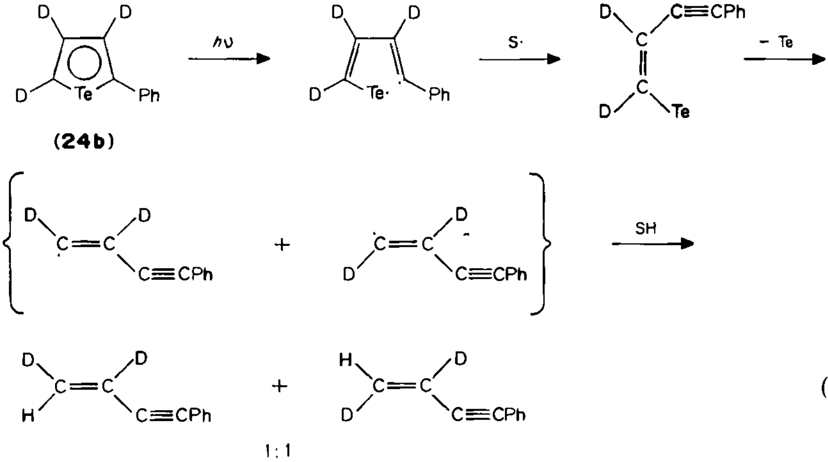


(24b)

(48)

1,2-dideuteriovinylphenylacetylenes, was afforded in the photolysis of 2-phenyl-3,4,5-trideuteriotellurophene(**24b**). This clearly demonstrates that the reaction involves intermolecular hydrogen transfer. These deuterium tracer results were rationalized by the mechanism shown in equation (48). Actually this is an extension of van Tamelen's general mechanism for the photochemistry of aromatic heterocyclopentadienes. The mechanism involves homolytic cleavage of the weakest C—Te linkage of the excited tellurophene followed by hydrogen abstraction by either a solvent radical or the photoexcited substrate. The subsequent second C—Te homolysis forms a phenylpropargylvinyl radical which then abstracts hydrogen from solvent giving the final products[38].

C. Biochemical Uses

Earlier, selenium compounds were regarded as only toxic to most living organisms. Later, especially by the use of isotopically labelled selenium compounds in biochemical studies, selenium was found to be an essential element.

1. *Metabolism of selenium and tellurium*

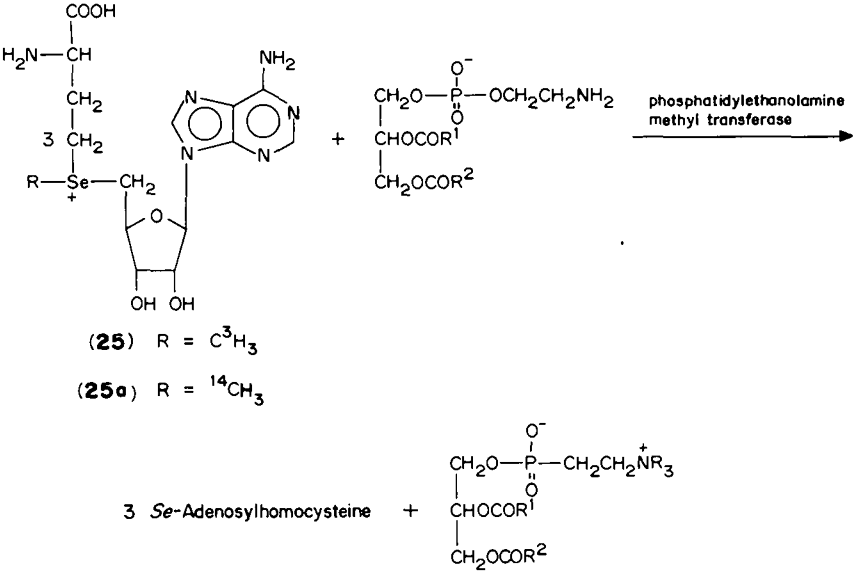
a. Selenium. Absorption, retention, distribution and excretion of selenium in living bodies have been tested very extensively with humans[78–81] animals[82–92], chickens[93–98], bacteria[99–100], etc. Usually ^{75}Se, a γ-emitter, is used because of its convenience in monitoring. This radioactive nuclide can be used from macro- to molecular level investigations. For example, by whole-body counting of ^{75}Se it is possible to determine its retention after administration of ^{75}Se-labelled substances[77]. On the other hand, molecular level investigation of a trace amount of ^{75}Se-containing metabolite is also possible as mentioned in the following sections.

When $Na_2{}^{75}SeO_3$ is administered to selenium-deficient animals or chickens, selenium is effectively absorbed in the body and retained for a long time. Generally, ^{75}Se is detected more in the liver, kidney and pancreas than in the muscles, heart, lungs and spleen. When $Na_2{}^{75}SeO_3$ was administered to cocks, the highest ^{75}Se concentration was found in the protein fraction of sperm after 16 days. The ^{75}Se was found to remain in a non-dialysable protein probably as selenocysteine[93]. The same trend was found in rats[84]. Janghorbani and coworkers found that chicken tissue which was fed with $Na_2{}^{74}SeO_3$ contained a sufficient amount of ^{74}Se to allow the use of these chicken for human feeding experiments by faecal monitoring of ^{74}Se with neutron activation analysis[98].

Some tracer experiments have revealed that the metabolisms of selenoamino acids are quite similar to those of the sulphur analogues. According to some evidence the metabolisms of both sulphur and selenium amino acids share the same enzyme systems[5,43,44,99–103]. Mudd and Cantoni found that selenomethionine is utilized better than methionine in the partially purified yeast methionine adenosyltransferase (MAT)-catalysed reaction with ATP, affording *Se*-adenosylselenomethionine and *S*-adenosylmethionine, respectively (equations 49 and 50)[102a]. Pan and Tarver found that methionine works 1.7 times more effectively than selenomethionine in the reaction with ATP which is catalysed by purified rat-liver methionine adenosyltransferase (equations 49 and 50), while the K_m value for the reaction with selenomethionine (equation 50) was found to be less than that for with methionine (equation 49).[102b]. Bremer and Natori showed that the methylating ability of ^{3}H-labelled *Se*-adenosylselenomethionine (**25**) is 1.4 times greater than *S*-adenosylmethionine in the phosphatidylcholine (**39**) synthesis (equation 51)[44]. This was further evidenced in the choline biosynthesis *in vivo* by Pan and coworkers, who revealed that ^{14}C-labelled selenomethionine (**25a**) is twice as efficient as methionine in the methylation of phosphatidylethanolamine to afford phosphatidylcholine (**39a**) in intact rat liver (equation 51)[43]. They demonstrated further that *Se*-adenosylselenomethionine (**25b**) can donate a Me group to RNA similarly to *S*-adenosylmethionine 43.

$$\mathrm{MeSCH_2CH_2CH(NH_2)COOH + ATP + H_2O \xrightarrow{MAT} P_i + P_iP_i} + \textit{S}\text{-adenosylmethionine} \qquad (49)$$

$$\mathrm{MeSeCH_2CH_2CH(NH_2)COOH + ATP + H_2O \xrightarrow{MAT} P_i + P_iP_i} + \textit{Se}\text{-adenosylselenomethionine} \qquad (50)$$



(**25**) R = C^3H_3

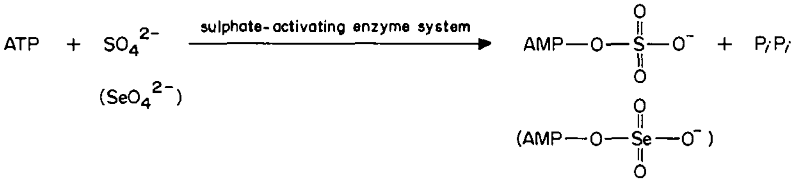
(**25a**) R = $^{14}CH_3$

(51)

(**39**) R = C^3H_3

(**39a**) R = $^{14}CH_3$

Wilson and Bandurski suggested that the sulphate-activating enzyme system to form adenosine monophosphate–sulphate from adenosine triphosphate (ATP) and sulphate can also promote the selenate activation in the same manner (equation 52)[103].



$$\mathrm{ATP} + \underset{(\mathrm{SeO_4}^{2-})}{\mathrm{SO_4}^{2-}} \xrightarrow{\text{sulphate-activating enzyme system}} \underset{\left(\mathrm{AMP{-}O{-}}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{Se}}}}\mathrm{{-}O^-}\right)}{\mathrm{AMP{-}O{-}}\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}\mathrm{{-}O^-}} + \mathrm{P_iP_i} \tag{52}$$

Spencer and Blau revealed that ^{75}Se-selenomethionine seems to come out from the hamster's intestine through the same route as for methionine[101].

Awwad and coworkers reported that when ^{75}Se-selenomethionine and ^{35}S-cystine are injected into rats, the formation of radioselenate is much less than that of radiosulphate, suggesting that the selenoamino acid is utilized for peptide synthesis better than thioamino acid[91].

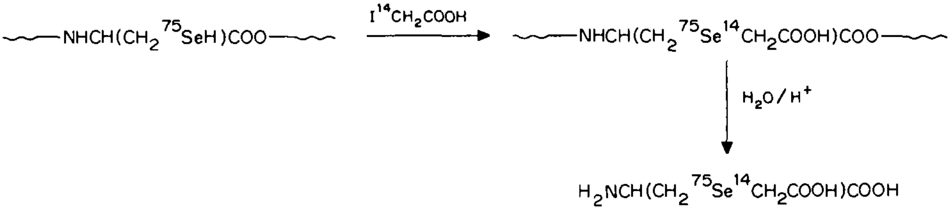
b. Tellurium. When $^{132}\mathrm{TeCl_4}$ is injected into a rat, the liver contains 20.17% of the ^{132}Te after 6 h, whereas a lesser amount of ^{132}Te is found in the bones (8.21%), kidneys (7.30%), lungs (2.23%), spleen (0.7%) and brain (0.37%)[104]. Russian investigators administered $^{127}\mathrm{TeCl_4}$ to rats in order to see the fate of the tellurium and several experimental results have been reported[105–112].

2. Selenoproteins

a. Glutathione peroxidase. Glutathione peroxidase (EC 1.11.1.9) is the only known mammalian enzyme which requires selenium. Glutathione peroxidase reduces poisonous hydrogen peroxide and a variety of lipid hydroperoxides formed by autooxidation to prevent the damage of components in living bodies, while vitamin E prevents the hydroperoxide formation. Rotruck and coworkers revealed by the use of ^{75}Se as tracer that selenium is an essential element of the glutathione peroxidase in erythrocytes. Erythrocytes were obtained from rats after they were injected with $\mathrm{Na_2{}^{75}SeO_3}$ for 2 or 4 weeks[113]. On the chromatograph of the supernatant prepared by haemolysis of the erythrocytes both the peaks of the enzyme activity and the selenium content appeared in the same position[113].

$$\left.\begin{array}{c}\mathrm{H_2O_2}\\ \text{or}\\ \mathrm{ROOH}\end{array}\right\} + 2\ \mathrm{GSH} \xrightarrow{\text{glutathione peroxidase}} \left.\begin{array}{c}\mathrm{H_2O}\\ \text{or}\\ \mathrm{ROH}\end{array}\right\} + \mathrm{GSSG} \tag{53}$$

Flohé and Günzler found that only the reduced form of glutathione peroxidase is inhibited by iodoacetic acid[114]. Thus Tappel and coworkers treated the reduced form of ^{75}Se-labelled glutathione peroxidase (obtained from rat liver pretreated with $\mathrm{Na_2{}^{75}SeO_3}$) with ^{14}C-labelled iodoacetic acid. Acid hydrolysis of the modified enzyme gave carboxymethylselenocysteine labelled with ^{75}Se and ^{14}C (equation 54). Since about 60–90% of the original selenium in the enzyme was recovered in the form of carboxymethylselenocysteine by this treatment, it was concluded that all of the selenium in the enzyme is in the form of selenocysteine. This was further confirmed by a similar procedure using ethyleneimine as an alkylating agent of the reduced form of glutathione peroxidase instead of iodoacetic acid[115].

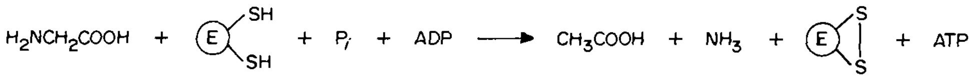


$$\text{NHCH(CH}_2{}^{75}\text{SeH)COO} \xrightarrow{\text{I}^{14}\text{CH}_2\text{COOH}} \text{NHCH(CH}_2{}^{75}\text{Se}^{14}\text{CH}_2\text{COOH)COO} \xrightarrow{\text{H}_2\text{O/H}^+} \text{H}_2\text{NCH(CH}_2{}^{75}\text{Se}^{14}\text{CH}_2\text{COOH)COOH}$$

(54)

Recently, in order to test which selenium compound would serve as the best precursor to stimulate glutathione peroxidase, human erthrocytes were cultured in the presence of $Na_2{}^{75}SeO_3$, $Na_2{}^{75}SeO_4$, ^{75}Se-selenocystine, ^{75}Se-selenomethionine and ^{75}Se-labelled foetal calf serum protein in vitro. Among these, selenocystine was found to give the highest increase in the glutathione peroxidase activity (79%). The foetal calf serum protein labelled with ^{75}Se also increased markedly the enzyme activity (47%), while selenite showed a very low stimulation (7%). Hence selenocystine is the compound most effectively utilized for the protein synthesis[116].

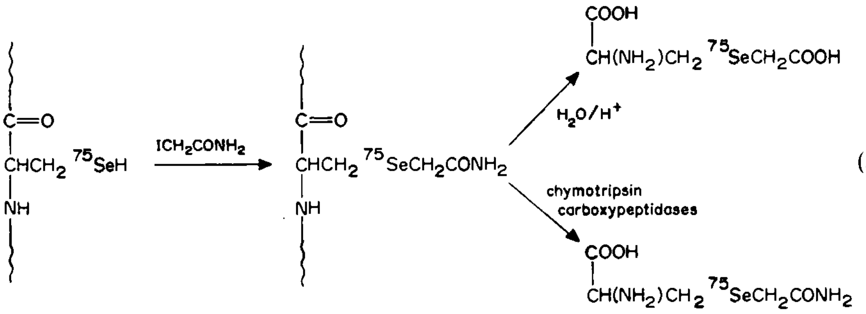
b. Glycine reductase. Glycine reductase which catalyses the reductive deamination of glycine (equation 55) has been found in bacteria, e.g. *Clostridium sticklandii.* The presence of selenite in the culture of the bacteria increases the glycine reductase activity of bacteria, but their growth is only increased slightly[117]. In this enzymic reaction, at least three proteins, called A, B, and C, seem to cooperate[117]. Stadtman and coworkers confirmed that in the purification of protein A obtained from bacteria grown in the presence of sodium selenite-^{75}Se, the ^{75}Se content and the activity of the enzyme increased in parallel, showing that protein A is a selenoprotein[118]. Later they treated the purified enzyme labelled with ^{75}Se, obtained above, with various alkylating agents, such as iodoacetamide, and hydrolysed it to amino acids by heating with HCl. Thus, they isolated both ^{75}Se-carboxymethylselenocysteine and *S*-carboxymethylcysteine from the hydrolysis mixture, indicating that both selenocysteine and cysteine are essential components. The enzyme (mol. wt. = 12,000–16,200) was found to contain 1 gram atom of Se per mole. The fully reduced enzyme possesses two sulphydryl groups in addition to the selenol group titrable with 5,5'-dithiobis(2-nitrobenzoic acid), Ellman's reagent[119].



(55)

c. Formic acid dehydrogenase. The presence of selenium-dependent formic acid dehydrogenase has been identified in *E. coli* and several anaerobic bacteria. These enzymes are known to contain acid-labile iron, molybdenum and cytochrome b besides selenium[117]. Shum and Murphy suggest the presence of selenium in *E. coli* formic acid dehydrogenase based on parallel increases of the ^{75}Se content and the activity during the purification of the enzyme[120]. Similarly, Andressen and Ljungdahl found that there is a correlation between the bound ^{75}Se and the enzyme activity in the formate dehydrogenase obtained from *Clostridium thermoaceticum* grown in the presence of $Na_2{}^{75}SeO_3$[121].

Jones, Dilworth and Stadtman grew *Methanococcus vannielii* in the presence of $Na_2{}^{75}SeO_3$ and isolated the formate dehydrogenase labelled with ^{75}Se from the bacteria, reduced and alkylated with iodoacetamide (equation 56). The alkylated enzyme was hydrolysed in two different ways. The acid hydrolysis gave ^{75}Se-labelled carboxymethyl selenocysteine, while the enzymic hydrolysis with chymotripsin followed by carboxypeptidase B and carboxypeptidase A-DEP afforded ^{75}Se-labelled carboximidomethylselenoeysteine. Thus, the formate dehydrogenase was firmly shown to contain selenocysteine[122].



(56)

d. Other proteins. Pedersen and coworkers successfully isolated a selenoprotein (mol. wt. = 10,000) from the muscle of Se-supplemented lambs. They injected lambs with $Na_2{}^{75}SeO_3$ and isolated a selenoprotein labelled with ^{75}Se from the muscle of the lambs. This protein could not be detected in the muscle of white muscle diseased lambs but was present in normal ones[123].

Imhoff and Andressen found that the activity of bacterial nicotinic acid hydroxylase (which catalyses the addition of water to the double bond of nicotinic acid, the initial step in the anaerobic fermentation of nictinic acid to propionate, acetate, NH_3 and CO_2) is increased by the addition of 10^{-7} M sodium selenite to the growth medium of *Clostridium barkeri*, suggesting that the enzyme is selenoprotein[124]. This was evidenced by a parallel increase of both the ^{75}Se radioactivity and the enzyme activity during the purification of the enzyme obtained from the bacteria grown in the presence of $Na_2{}^{75}SeO_3$[117].

Burk and Gregory isolated ^{75}Se-containing proteins from plasma (mol. wt. = 79,000) and liver (mol. wt. = 90,000) of pigs injected with $Na_2{}^{75}SeO_3$; however the biochemical function of these selenoproteins is not yet known[125].

3. Selenium-containing t-RNA

Recently, various naturally occurring t-RNAs containing selenium have been isolated from bacteria; for example, Hoffman and coworkers isolated a ^{75}Se-containing t-RNA from *E. coli* cultured in the presence of $Na_2{}^{75}SeO_3$. ^{75}Se-t-RNA was subjected to RNase digestion followed by chromatography. A selenium-containing component remained on the column, suggesting that selenium is not incorporated as a selenoaminoacyl-t-RNA but in the base of the t-RNA. This prediction has been proved by the isolation of ^{75}Se-labelled 4-selenouridine from the ^{75}Se-t-RNA after digestion of the latter with a mixture of bovine pancreatic RNase, snake venom phosphodiesterase and alkaline phosphatase[126].

Chen and Stadtman were able to isolate three varieties of ^{75}Se-containing t-RNA from *Clostridium sticklandii* grown in cultures supplemented with $Na_2{}^{75}SeO_3$ or ^{75}Se-selenocysteine. The selenium was shown to be located in the polynucleotide portion of the t-RNA but not as the alkali-labile selenocysteine[127].

4. Non-haemeiron proteins containing acid-labile sulphur

Non-haemeiron proteins containing two irons and two acid labile sulphurs are known to be widely present in a variety of living bodies. ESR has been shown to be a powerful tool to investigate how the odd electron is shared in the enzyme's active site which consists of cysteine sulphur and two acid-labile sulphur and iron atoms according to research groups who utilized selenium isotopes. The odd electron densities can be estimated from the ESR hyperfine structure. However, naturally occurring non-haemeiron proteins possess ^{32}S and ^{56}Fe which have unfortunately both the nuclear spin 0 and do not give any hyperfine splitting. Although the nuclear spin of ^{33}S is 3/2, ^{33}S gives seven hyperfine lines if two nuclei are involved. Therefore the analysis becomes very complicated[66], especially since only 50% enriched ^{33}S is available. Thus, one or two of the labile sulphur atoms have been substituted by ^{77}Se (nuclear spin = 1/2) and ^{80}Se (nuclear spin = 0) up to 80 atom% prior to ESR spectroscopic studies as mentioned in Section II.B.4. ^{57}Fe(nuclear spin = 1/2) is also a suitable isotope for this purpose.

Gunsalus and coworkers recorded ESR spectra of the reduced form of native (^{32}S), ^{80}Se and ^{77}Se containing reduced forms of putidaredoxin obtained from *Pseudomonas putida* and adrenodoxin obtained from pig and beef. A single ESR signal appeared at a low field for the ^{32}S^{32}S and ^{80}Se^{80}Se combinations whereas both enzymes with the ^{77}Se^{77}Se combination exhibited hyperfine splitting in the same region. This suggests that the unpaired electron is shared among the two iron and the two selenium atoms[66].

Fee and Palmer examined by ESR isotopic derivatives of parsley ferredoxin containing ^{32}S^{56}Fe, ^{32}S^{57}Fe, ^{80}Se^{56}Fe, ^{77}Se^{56}Fe and ^{80}Se^{57}Fe. They concluded that two labile sulphur and two iron atoms are present at the active centre of the enzyme and share the unpaired electron in the reduced form[67].

Mukai and coworkers also studied isotopic derivatives of adrenodoxin prepared from beef adrenal gland containing. ^{80}Se^{80}Se, ^{77}Se^{77}Se,^{80}Se^{32}S and ^{77}Se^{32}S combinations. They concluded that the paramagnetic centre of the enzyme with one sulphur and one selenium atom is more rhombohedral than those of the native adrenodoxin and its Se—Se derivative[68].

C. Medicinal Uses

1. Scintiscanning

Much attention has been paid to ^{75}Se-selenomethionine as a pancreas-imaging agent[12,49,128–136] and the method is now used clinically. Seven to eight times more selenomethionine-^{75}Se appeared in the pancreas of mice than in their liver 25–30 min after *in vivo* administration[131]. Cottrall and Taylor tested the influence of the pretreatments with a variety of agents on the uptake of ^{75}Se-selenomethionine by rat pancreas. Only propylthiouracil increased the pancreatic uptake of ^{75}Se-selenomethionine[134]. Selenomethionine-^{75}Se photoscan of the pancrease is useful for the detection of cancer which is difficult to diagnose by ordinary means[133]. Several papers have appeared on the effect on internal irradiation with ^{75}Se-selenomethionine on the endocrine systems[137–143]. Knapp and coworkers found that ^{123m}Te-labelled DL-α-amino-γ-(phenyltelluro)butyric acid (**30**) is a potential pancreatic imaging agent[49].

Kozák and coworkers reported that ^{75}Se-labelled 2-aminoisoselenouronium bromide is accumulated in myocardium and may be useful for scanning of myocardium[144]. Since the normal myocardial tissues utilize fatty acids as the energy source, ^{123m}Te-labelled fatty acid analogues (**11**) are useful as myocardial imaging agents[26]. The ^{123m}Te-labelled unsaturated fatty acid analogues (**13**)[27] and ^{75}Se- or ^{123m}Te-labelled glycerine triethers (**6, 7**)[21] are also useful in the determination of the fat absorption[21,27].

Di(β-dialkylaminoethyl) selenides (**8**) labelled with ^{75}Se[22] and 4-selenazolidine-1-^{75}Se-carboxylic acid (**26**) were examined as brain-imaging agents[48].

^{75}Se-labelled 4-substituted 1,2,3-selenadiazoles (**21, 22**) were tested for the possibility of adrenal gland imaging[36]. 6-Benzylseleno-19-norcholesterol and alkylselenanilide labelled with ^{75}Se are known to be specific for adrenal cortex and adrenal modula, respectively[4].

Parizek and Benes reported that trimethylselenium iodide labelled with ^{75}Se may be useful for nephrography[145]. Blottner and coworkers suggested the possibility of using 8-^{75}Se-substituted purine nucleosides for tumour-specific diagnosis[146]. A scientigraphic measurement of the relative concentration of ^{75}Se-labelled selenomethionine and radioactive colloidal ^{198}Au has been shown to detect primary and secondary liver cancers in patients[147].

2. *Miscellaneous*

^{75}Se-labelled selenomethionine can be used in immunological investigations [57–60,148]. For example, Gutman and coworkers labelled immunoglobins secreted by plasmacytomas with ^{75}Se-selenomethionine which binds to foetal calf serum protein so that it is releaseable by mercaptoethanol treatment[58]. Dosseto and coworkers labelled plasma membrane antigens of human and mouse lymphocytes with ^{75}Se-selenomethionine[59].

^{75}Se-selenomethionine was found to be a good isotopic marker for cell localization studies of lymphocytes[61,62] and erythrocytes[149,150]. ^{75}Se-selenomethionine has also been used for labelling of insulin[53], of platelets to determine their kinetics[151,152], of urokinase[50] and of fibrinogen[51,52,153]. Some muscle tumours were found to accumulate ^{75}Se-selenomethionine more than liver and muscle[154]. The Metabolism of ^{75}Se-selenomethionine has been shown to be useful in the diagnosis of some diseases[155–159].

Celander and coworkers achieved *in vivo* labelling of erythrocytes with ^{75}Se by injecting $Na_2{}^{75}SeO_3$ to a dog. ^{75}Se appeared to be bound to the haemoglobin[160].

Monks synthesized ^{75}Se-containing folate derivatives (**28**, **29**) for the saturation analysis of trace folates[8,9]. Steroid derivatives labelled with ^{75}Se (**1**, **3–5**, **10**) were applied for radioimmunological determination of steroid hormones[9,20], for the investigation of steroid metabolism and for imaging to detect disorders[7,25]. ^{75}Se-labelled cyclic nucleotide (**2**) was used for the saturation analysis of nucleotides[18].

IV. CONCLUSION

As mentioned in the introduction, the major portion of the research activities with isotopically labelled selenium and tellurium compounds is in the fields of biology and medical sciences, tracing the locations and the fates of these labelled compounds in living bodies. Only a few simple synthetic methods have been developed to prepare these labelled compounds. However, these compounds have contributed enormously to clarifying many of the biological functions of selenium compounds which are by now considered quite essential in living bodies. Thus, it is our hope that this review will be of some use for the overview of the various applications of the isotopically labelled selenium and tellurium compounds in biomedical studies.

V. REFERENCES

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The Chemistry of Organic
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CHAPTER 13

Selenium and tellurium heterocycles

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I. INTRODUCTION

The present chapter is devoted to the chemistry of organic Se/Te heterocycles. Generally, it will not take into account heterocycles derived from Se (IV) or Te(IV), to avoid overlap with another chapter of this book. For the same reason, it will discuss neither the physicochemical properties nor the photochemistry of Se/Te heterocycles.

The literature on the theory, preparation and applications of Se/Te heterocycles is too voluminous to enable an extensive coverage of the subject. This chapter will attempt to cover the most important advances in this field, mainly during the last few years, and through 1983. Earlier reviews include small chapters on Se heterocycles [1,2], and a complete coverage of the subject has been given in Klayman and Günther's book[3]. The chemistry of Te heterocycles has been described in detail in Cooper's book[4] as well as in Irgolic's book[5] and his annual reviews[6]. Information about Se/Te heterocycles can also be found in the *Specialist Periodical Reports of the Royal Society of Chemistry* (*London*)[7-10].

We must also note a review covering the years 1975–1979[11]. Special reviews devoted to particular Se or Te ring systems will be mentioned in the relevant chapters.

When information is available, comparison will be made with the corresponding S heterocycles. Differences between S and heavier chalcogen heterocycles are related to the greater size of Se/Te atoms, their greater polarizability, their lower electronegativity and their lower bond energies with other elements. These differences will sometimes lead to lower stability of Se/Te heterocycles, and to specific ring-opening or ring-transformation reactions.

This chapter will be divided according to the size of the ring systems. For a given size, it will successively follow the number of heteroatoms.

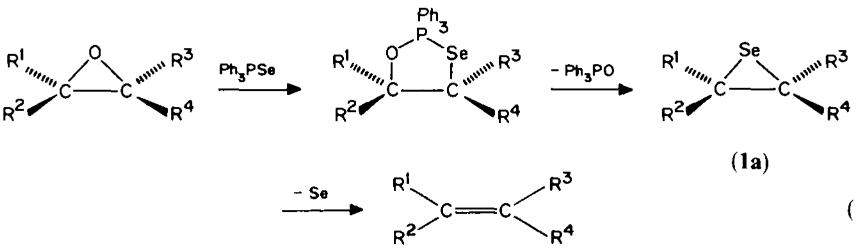
II. Se/Te THREE-MEMBERED RINGS

A. One Heteroatom in the Ring

1. *Seleniranes and telluriranes*

No seleniranes **Ia**, (episelenides) have been isolated, but they were tentatively assumed to be formed during flash photolysis of CSe_2–olefin mixtures[12], and their structure was confirmed by mass spectral assignments[13]. Seleniranes were also suggested as intermediates in the following reactions:

(*a*) In the stereospecific conversion of oxiranes to olefins with triphenylphosphine selenide[14] (equation 1), tri-*n*-butylphosphine selenide[15], phosphole and phospholene selenide[16] or potassium selenocyanate[17].



(**1a**)

(1)

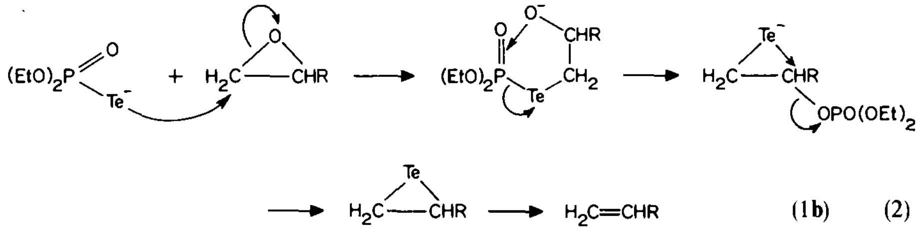
(*b*) In the cyclization of *para*-substituted phenylallyl selenides in boiling quinoline[18].

(*c*) In the conversion of bromohydrins to alkenes by potassium selenocyanate[19].

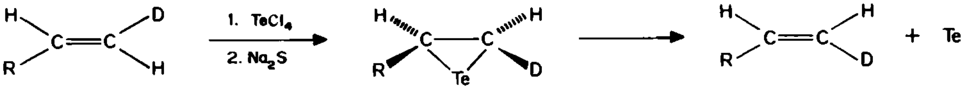
(*d*) In the conversion of 1,2-dibromoethane to ethylene with selenodithiocarbonate anion[20].

(*e*) In the desulphurization of thiiranes by 3-methyl-2-selenoxobenzothiazole[21]. These intermediates are thought to lose Se immediately.

Telluriranes **Ib**, also never isolated, were postulated as intermediates in the conversion of epoxides to alkenes by sodium *O*,*O*-diethylphosphorotellurate (equation 2)[22a], in the



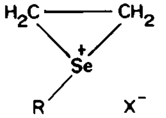
(**Ib**) (2)



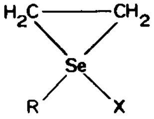
(3)

dehalogenation of α-haloketones by the same reagent[22b], and in the Na_2S reduction with olefin inversion of chloroalkyltellurium trichlorides, the addition products of $TeCl_4$ with alkenes (equation 3)[23,24]. The transient tellurirane **1b** (R = H) and its Me derivative were detected in the flash photolysis of dimethyl telluride in ethylene and propene, respectively[25].

2. *Seleniranium salts*



(2)



(3)

Thiiranium (episulphonium) ions are known to be very unstable[26]. The first long-lived thiiranium salt, stable for weeks below −10 °C, was synthezised in 1975[27]. Seleniranium salts were not isolated. Seleniranium intermediates **2** or their selenurane equivalent **3** are, however, invoked in the addition of selenium monochloride[28], *p*-tolueneselenenyl chloride[29], areneselenenyl hexafluorophosphate[30], methaneselenium trichloride[31], benzene and methaneselenenyl bromide[32–35] to alkenes. In one case[29], the isolation of a stable episelenurane was claimed, but this cyclic structure has been shown to be incorrect and is apparently the acyclic compound, **4**[36] (equation 4).

$$p\text{-MeC}_6\text{H}_4\text{SeCl} + \text{H}_2\text{C}{=}\text{CH}_2 \rightarrow \underset{\textbf{(4)}}{p\text{-MeC}_6\text{H}_4\text{SeCl}_2\text{CH}_2\text{CH}_2\text{Cl}} \qquad (4)$$

Seleniranium ions are also proposed as intermediates in the reaction of bis(2-bromoethyl) selenide with various nucleophiles[37].

3. *Seleniren and selenirenium salts*

Similarly to thiirens, seleniren intermediates are considered to be formed from the reaction of 1,2,3-selenadiazole with diiron enneacarbonyl[38,39] which forms complexes with the heterocycles and catalyses the elimination of N_2, and by photolysis[40,41]. Further irradiation results in a cleavage of this small ring to acetylene and selenoketene[40].

Selenirenium ions are believed to be intermediates in the electrophilic addition of areneselenenyl halides to alkynes[30,45,46a], according to spectroscopic, kinetic and stereochemical studies[45]. Not surprisingly, no selenirenium salt has been isolated up to now, since the first stable thiirenium compounds were isolated only recently. These are 1,2,3-trimethylthiirenium tetrafluoroborate, stable below −10 °C[42], and the 1-methyl-2,3-di-*t*-butyl analogue[43], stable for weeks at room temperature, and whose structure was confirmed by X-ray analysis[44].

Benzoseleniren has been detected by ESCA[46b], by IR spectroscopy[46c], and matrix-isolated as a short-lived intermediate in the pyrolysis and the photolysis of 1,2,3-benzoselenadiazole. It is rapidly rearranged to fulvene-6-selone.

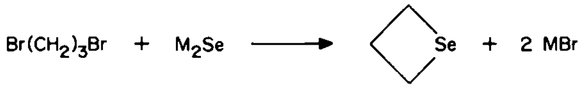
B. Two Heteroatoms in the Ring

Parallel to sulphur chemistry, unsuccessful attempts were made to obtain selenaziridines as intermediates in the treatment of oxaziridine with potassium selenoxanthate[47]. Selenaziridine and oxaselenirane were suggested as intermediates in the decomposition of 1,2-benzodithiole-3-selenoxoimide[48] and in the oxidation of 3-selenoxo-1,2-benzodithiole[49], respectively. This must be regarded with caution, since the structure of the last compound was demonstrated later to be an isomeric structure[511].

III. Se/Te FOUR-MEMBERED RINGS

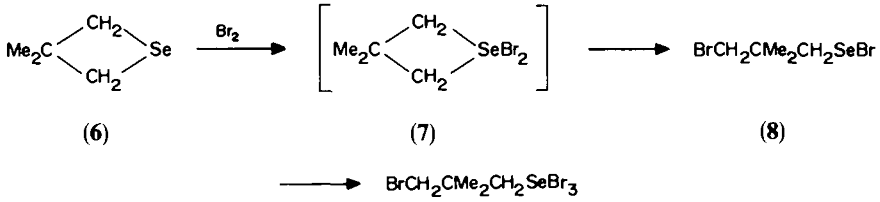
A. One Heteroatom in the Ring

Selenetane (**5**) itself is obtained in a low yield from 1,3-dibromopropane and alkali selenide[50] (equation 5). It is stable only in the dark when cooled and it polymerizes easily. The more stable 3,3-dimethyl derivative **6**, prepared under similar conditions[51] or with



(**5**) (5)

KSeCN as the nucleophilic salt[52], is stable up to 140 °C. Its Se dibromo derivative **7** is stable at temperatures below −20 °C. At more elevated temperatures there is a ring-opening to the 1-bromo-3-bromoseleno compound **8** which subsequently gives 1-bromo-3-tribromoseleno-2,2-dimethylpropane **9**[51,53a] (equation 6). Methyl iodide gives also ring-opening to 1-dimethyliodoseleno-2,2-dimethyl-3-iodopropane[52].



(**6**) (**7**) (**8**)

(**9**) (6)

Compound **6** is oxidized by H_2O_2 to a five-membered lactone of corresponding seleninic acid, rather than to a selenone[53a]. Selenetan-3-ol has also been prepared[53b].

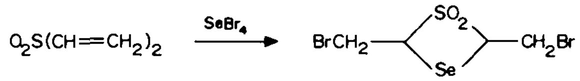
B. Two Heteroatoms in the Ring

1. One oxygen and one selenium

An oxaselenetane is suggested as intermediate in the oxidation of exocyclic alkenes with SeO_2/H_2O_2[54].

2. One sulphur and one selenium

A sulphone of thiaselenetane (**10**) was claimed to be obtained by the reaction of divinyl sulphone with $SeBr_4$, instead of the corresponding six-membered ring[55] (equation 7).

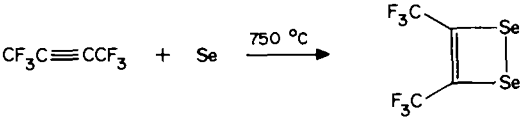


(10)

(7)

3. *Two selenium atoms*

a. In the 1,2-*position.* 3,4-Bis(trifluoromethyl)-1,2-diselenetene (**11**) has been prepared in 25% yield by pyrolysis of bis(trifluoromethyl)acetylene with Se vapour at 750 °C[56] (equation 8).

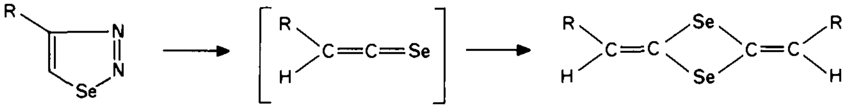


(11)

(8)

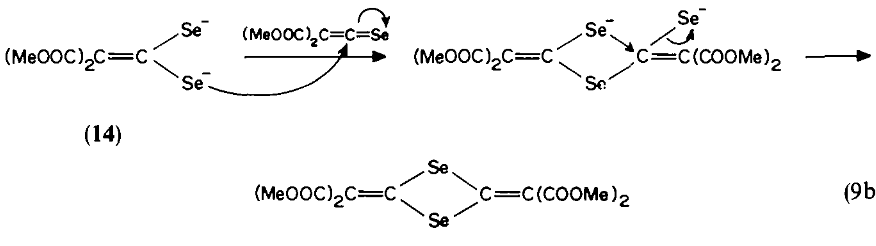
b. In the 1,3-*position.* Derivatives **13** and **15** of 2,4-bis(methylene)-1,3-diselenetane have been obtained by two different methods:

(*i*) Pyrolysis of 1,2,3-selenadiazoles at 500–600 °C[57], via a selenoketene **12** (equation 9a).



(12) **(13)**

(*ii*) Reaction of CSe_2 with dimethyl malonate[58], giving initially the intermediate **14** by a route parallel to that used in sulphur chemistry (equation 9b).

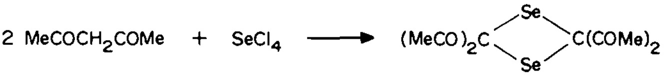


(14)

(15)

(9b)

2,2,4,4-Tetraacetyl-1,3-diselenetane (**16**) for which another structure was previously assigned[59] has been prepared from $SeCl_4$ and acetylacetone[60a] (equation 10).



(16)

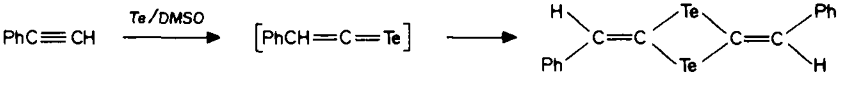
(10)

Hydrogen cyanide gives ring-opening to 3-cyanoseleno-2,4-pentanedione. 1,3-Diselenetane-2,4-diselenol diacetate is formed by treating acetyl chloride with H_2Se and $AlCl_3$[60b]. Perfluoro-1,3-diselenetane structures have been tentatively assigned to the pyrolysis product at 150 °C of the polymer $(CF_2Se)_n$[61], or to the reaction product of perfluoropropene with selenium and antimony pentafluoride[62a]. 2,2,4,4-Tetrakis(trifluoromethyl)-1,3-diselenetane is obtained from triphenylphosphine selenoxide and hexafluoroacetone[62b].

4. *Two tellurium atoms*

The first 1,3-ditelluretane system **17** was recently obtained by reaction of phenylacetylene and Te in DMSO[63-65,69]. The ditelluretane structure, which was previously believed to be a 1,4-ditellurafulvene ring[66], by analogy with known S and Se compounds[67,68], has been determined by ^{1}H-NMR, mass spectrometry and X-ray measurements.

Compound **17** and its *cis* isomer[64] may be considered as the cyclodimerization products of a transient telluroketene (equation 11).

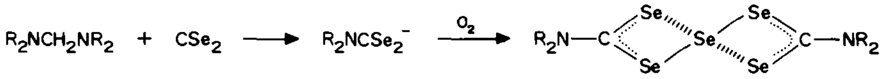


(11)

(17)

C. Three Heteroatoms in the Ring

A four-membered ring with three Se atoms **18**, regarded as a bis(diselenocarbamato)selenium(II) compound, and whose structure was proven by X-ray diffraction, is obtained from CSe_2 and tetrasubstituted methylene diamine[70] (equation 12).



(18) (12)

IV. Se/Te FIVE-MEMBERED RINGS

A. One Heteroatom: Selenophenes and Tellurophenes

1. *Monocyclic selenophenes and tellurophenes*

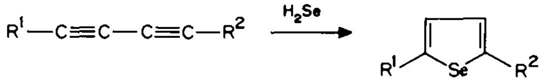
The chemistry of selenophene has been reviewed through 1950 by Hartough[71], for the period up to 1970 by Magdesieva[72] and by Magdesieva and Zefirov[73], and for the last decade by Hörnfeldt[74]. The chemistry of tellurophene has been completely covered up to 1975 by Fringuelli and coworkers[75]. A more condensed review was presented by Marino[76]. The current literature on selenophene and tellurophene has been continuously reviewed by Gronowitz in his biennial reviews on thiophene and Se/Te analogues[9] and for tellurophene in the annual surveys of Irgolic[6].

Selenophene and tellurophene complete with furan and thiophene a series of four stable aromatic systems. These systems differ mainly in their degree of reactivity, but generally display similar reactions. However the larger heteroatoms can be a centre of reactivity towards some reagents, and sometimes a centre of ring destruction.

In this chapter, we shall use the terms ‘selenienyl’ and ‘tellurienyl’ for the heterocyclic radicals, and for the corresponding condensed derivatives the prefixes ‘selenolo’ and ‘tellurolo’ will be added.

a. Synthesis. (*i*) *Selenophenes.* Selenophene or its homologues can be obtained by two main methods: from acyclic compounds, or from other ring systems. The first true synthesis of selenophene, a liquid (b.p. 100 °C, m.p. – 38 °C) of a disagreeable odour, in contrast to thiophene, was realized in 1927 by Mazza and Solazzo from acetylene and Se at high temperature[77]. The same methodology was later applied by Briscoe and coworkers[78,79] and by Umezawa[80,81]. Recently, Gronowitz and coworkers[82a] modified this reaction to a larger scale synthesis (150–200 g per day), in a 58% yield, by mixing Se with alumina under well-determined conditions. In this reaction, about 30 compounds were identified including 2- and 3-alkylselenophenes, biselenienyls and condensed ring systems. The yield of this reaction is now improved to 70%[82b]. Perveev and coworkers[83] used acetylenic epoxides to obtain alkyl-, vinyl- and hydroxyalkyl-selenophenes. Selenophene derivatives, e.g., alkyl-substituted selenophenes, were also obtained from paraffins[87,88], olefins or conjugated dienes with SeO_2[84–86] or metallic Se[87,88].

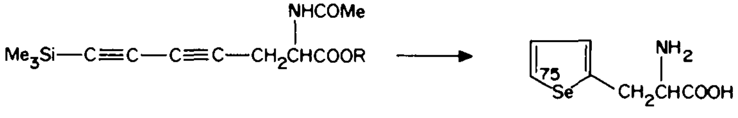
More elaborated syntheses start from a four-carbon chain. Substituted 1,3-diyne systems including the bis(trimethylsilyl) derivative, reacted with NaSeH or H_2Se in a general synthesis of 2,5-disubstituted selenophenes **19**[89,90] (equation 13). For example, 2,5-diphenyl- and 2,5-dihydroxymethyl-selenophenes were synthesized by this method.



(13)

(19)

Using the bis(trimethylsilyl) analogue ($R^1 = R^2 = SiMe_3$) leads, after hydrolysis, to the unsubstituted selenophene[91]. The monosilylated diyne **20** was used for the synthesis of ^{75}Se-labelled 2-selenienylalanine **21**[92] (equation 14). Vinylacetylene and Se also give selenophene as the main product (24%)[93].



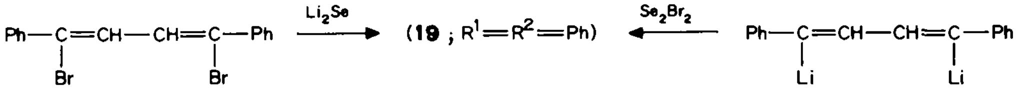
(14)

(20) **(21)**

2,5-Disubstituted selenophenes can also be obtained in a general way by the Paal-Knorr five-membered heterocycle synthesis from γ-diketones and phosphorus pentaselenide[94–96]. The first known derivative of a selenophene (2,5-dimethylselenophene, also named selenoxene, **19**, $R^1 = R^2 = Me$) was prepared by this method[96] (equation 15). The

$$R^1CO(CH_2)_2COR^2 \xrightarrow{P_4Se_{10}} \mathbf{19} \qquad (15)$$

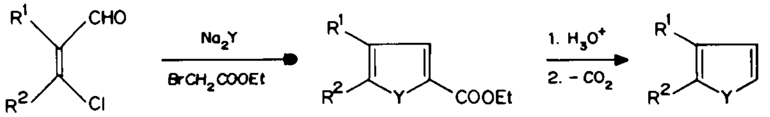
synthetic equivalents of γ-diketones, 1,4-dihalogeno-1,3-dienes, can also be used in reaction with Li_2Se. The reagents of the corresponding opposite polarities, i.e., 1,4-dilithiodienes and Se_2Br_2 were also used.[97a] (equation 16).



(16)

Starting from a molecule bearing a carbonyl and an alkyne group, low yields of 3-ethoxycarbonyl-2,5-dimethyl- or 5-methyl-2-phenyl-selenophenes are obtained[97b].

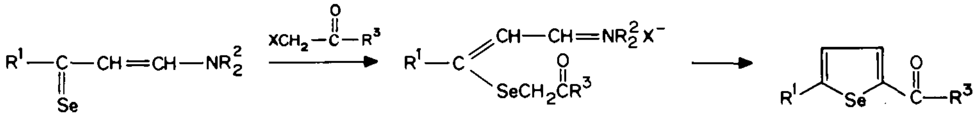
Another general ring-closure synthesis of selenophenes developed by Cagniant and coworkers consists of the Fiesselmann reaction involving β-chlorovinylaldehyde (**22**), Na_2Se and ethyl bromoacetate[98-100] (equation 17). Using the appropriate aldehyde **22** and α-bromopropionate gives 2,5-dimethylselenophene in a 40% yield[100].



(17)

(**22**)

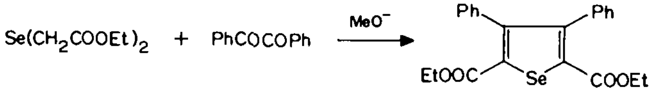
Liebscher and Hartmann developed a methodology, starting from 2-aminovinyl selenoketones (**23**) for the formation of 2-acylselenophenes **24**[101] (equation 18).



(**23**) (**24**)

(18)

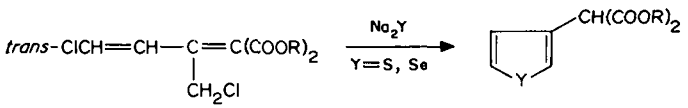
Selenophene derivatives **26** can be obtained from α-diketones by the Hinsberg ring-closure reaction[102], in mixture with mono- and di-decarboxylated heterocycles (equation 19).



(19)

(**25**) (**26**)

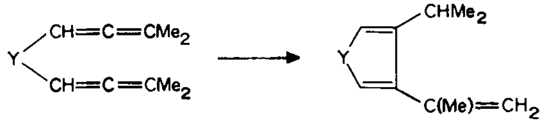
A recent novel method of synthesis of thiophene and selenophene consists of a double nucleophilic substitution of the dichloro precursor **27** to give either thienyl- or selenienyl-3-malonic ester **28**[103] (equation 20).



(20)

(**27**) (**28**)

Cycloaromatization of diallenyl chalcogenides **29** through a 6π electrocyclic ring-closure with a 1,5-hydride shift gives 3,4-disubstituted furans, thiophenes and selenophenes **30**[104] (equation 21).

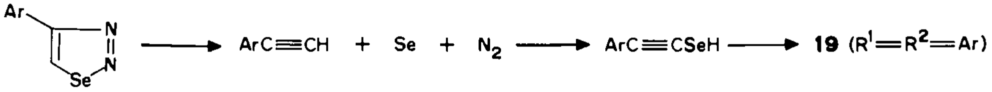


(21)

Y = O, S, Se

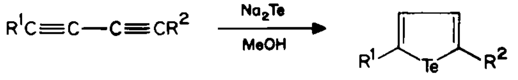
(29) **(30)**

Selenophene derivatives can also be obtained from furans and H_2Se[105,106], from pyrolysis of 4-aryl-1,2,3-selenadiazoles (**31**)[107,108], probably via intermediate monoaryl acetylene and Se, and the subsequent 2-arylethynyl selenol (equation 22), and from displacement of sulphone groups by Se[109].



(31) (22)

(*ii*) *Tellurophenes.* Unsuccessful attempts have been made to prepare tellurophene from acetylene or sodium succinate and aluminium telluride[110]. The first synthesis of the unsubstituted heterocycle was realized only in 1966 by Mack[111] using butadiyne and Na_2Te (equation 23). However, the procedure was first well described by Fringuelli and Taticchi in 1972[112,113], with yields of 37–50%. Tellurophene (**32**; $R^1 = R^2 = H$) is a light-yellow bad-smelling liquid (b.p. 151 °C, m.p. − 36 °C).

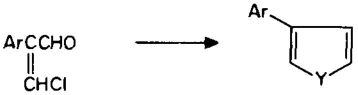


(23)

(32)

The use of the bis-silylated diyne seemed first to give a lower yield[114], but when Na_2Te solution was prepared from sodium formaldehyde sulphoxylate (rongalite), the yield improved to 59%[115]. 2-Phenyltellurophene was obtained by the same methodology[116]. Applying reaction 23 when $R^1 = R^2 = PhCH(OH)$ gives a bis(hydroxbenzyl)tellurophene which is the precursor of the synthesis of a tellurathiaporphyrine[117], a reaction parallel to that in the selenophene series[118a]. Recently, reaction of lithium and Se or Te on 3-methyl-3-butene-1-yne gave, after prototropy, a good yield of 3-methylselenophene and 3-methyltellurophene[118b]. The Fiesselmann reaction was also extended by Cagniant and coworkers to the tellurophene series, (equation 17; $R^1 = H, R^2 = t\text{-Bu}, Y = Te$) to give some mono and polycyclic tellurophenes in 35% yield[119]. Applied to arylacetic synthons, this method leads to 3-aryl-thiophenes,-selenophenes and -tellurophenes **33**[120] (equation 24).

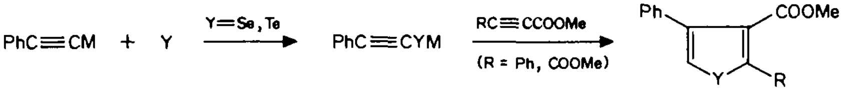
Tetraphenyltellurophene was also obtained in 1961, by the two alternative procedures described for selenophenes in equation (16) (right-hand side, $TeBr_4$ as the reagent[97]).



(24)

(33)

Selenophene[69,121] and tellurophene derivatives **34**[122] can also be obtained, among other products, by dipolar addition of acetylenic esters to phenylethynyl metal(M)-selenolate or tellurolate (equation 25).



(25)

(34)

2-Benzylidene-3-oxo-2,3-dihydrotellurophenes can sometimes be obtained from dialkynyl ketones and $(t\text{-}Bu_3Si)_2Te$, instead of the six-membered isomer telluropyrone[123]. This reaction will be discussed in the corresponding section.

b. Ground-state aromaticity: comparison with furan and thiophene. Selenophene and tellurophene show typical aromatic behaviour: they are more stable than the corresponding dienic compounds and tend to react by substitution rather than by addition. Like thiophene, selenophene does not give a normal Diels–Alder reaction, and loses Se when heated with maleic anhydride[124]. The geometry of these rings, determined by microwave spectral measurements[125,126], is planar and similar to that of furan and thiophene. The more characteristic variations for the four congeners are an increase of the Y—C (2) bond from furan to tellurophene (O: 1.362 Å; S: 1.714; Se: 1.855; Te: 2.005), and a decrease of the C(2)—Y—C(5) bond angle (O: 106.55°; S: 92.17; Se: 87.76; Te: 82.53)[76].

The ground-state aromaticity can be estimated by a study of seven different criteria, the more direct feature, i.e. the resonance energy, being not available: NMR dilution shifts experiments, observation of the effect of a 2-Me substituent on the heterocyclic proton NMR shifts, the difference of chemical shifts between α and β protons, the diamagnetic susceptibility exaltation, the sum of the bond orders, the Julg parameter and the mesomeric dipole moments[127]. These criteria, within their limit of validity, are in good agreement with one another, giving good linear relations from which empirical values of resonance energy can be estimated for selenophene (29 kcal mol^{-1}) and tellurophene (25 kcal mol^{-1}). All these criteria, but one, agree with the following order of ground-state aromaticity:

$$\text{thiophene} > \text{selenophene} > \text{tellurophene} > \text{furan}$$

For example, mesomeric dipole moments, which measure the π delocalization give the following values: O: 1.03 D; S: 1.35; Se: 1.29; Te: 1.17[128,129]. This sequence must be explained by taking into account an interplay of two opposite factors: the decrease of electronegativity from O to Te, which should favour the contribution of the lone pair of the heteroatom to the aromatic sextet, and the corresponding increase of the covalent radius, which is unfavourable to good overlap between the p orbitals of C(2) and of the heteroatom.

c. Electrophilic and nucleophilic substitution. (i) Kinetic and physicochemical results. Selenophene and tellurophene easily give electrophilic substitution and α-metalation. Electrophilic substitution in furan, thiophene, selenophene and pyrrole has been reviewed by Marino[130]. Quantitative studies of electrophilic substitution have been conducted with the four heterocycles in three reactions: formylation by phosgene and dimethylformamide, acetylation with acetic anhydride and $SnCl_4$, and trifluoroacetylation by trifluoroacetic anhydride[131,132]. In all three reactions, the reactivity sequence is: furan > tellurophene > selenophene > thiophene. The relative reactivities in this sequence are 107:36.8:3.64:1.0 for the formylation, 11.9:7.75:2.28:1.0 for the acetylation and 140:46.4:7.33:1.0 for the trifluoroacetylation[132].

Measurements of activation parameters in α-formylation show that the activation entropy $\Delta S^{\ddagger}$ can be regarded as constant, so that the relative rates are controlled by the activation enthalpies $\Delta H^{\ddagger}$. These activation enthalpies give a good linear correlation with the resonance energy of the four congeners, showing that the ground-state energy plays an important role in controlling the sequence of reactivity.

Thus, the more aromatic system should give the lower substitution rate and this is corroborated by the experimental data. The ability of a more polarizable heteroatom to delocalize the positive charge should also play a role in the stabilization of the transition complexes. That selenophene is more reactive than thiophene in electrophilic substitution reactions is confirmed by the determination of the ratios of competitive Vilsmeier–Haack formylation (S:Se = 20:80), and of Friedel–Crafts acetylation (S:Se = 25:75) in selenienyl-thienyl-methane[133]. Solvolysis in side-chain reactions[134] gives results in complete agreement with the electrophilic substitution, except for the inversion between furan and tellurophene. On the other hand, the solvolysis of 1-(2-aryl)ethyl acetate shows that tellurophene is less sensitive to substituents than selenophene, and more sensitive in electrophilic substitutions. By these side-chain reactions, a σ_{α}^{+} parameter has been determined for each heteroatom (O: −0.93; S: −0.79; Se: −0.88; Te: −0.92). The pK_as of the 2-carboxylic acids give a linear correlation with the electronegativity (O:3.16; S:3.53; Se:3.60; Te:3.97)[135] and with the $\nu_{C=O}$ in the IR spectra. The reaction constant ρ, determined from the pK_a of 2-carboxy-5-substituted heterocycles is equal for tellurophene, selenophene[136] and thiophene, indicating that the electronic effects of substituents are transmitted in the same manner in the three heterocycles.

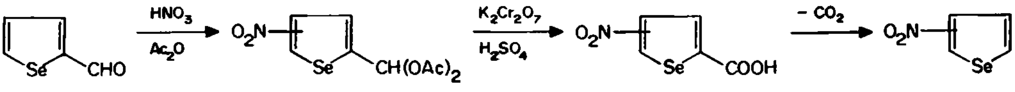
From the ionization constants, a σ-Hammett-like value can be calculated for the heteroatoms which are considered as endocyclic substituents of the —CH=CH— group in benzene. Their σ_{α} values (O: +1.04; S: +0.67; Se: +0.60; Te: +0.23) also appear to be a function of the electronegativity. The validity of the Hammett equation in selenophene confirms that 2,4- and 2,5-substituents can be considered as *meta*-like and *para*-like substituents, respectively; σ and σ^{-} constants were also evaluated for the 2-selenienyl and the 2-tellurienyl groups[137].

The increasing polarizability of the heteroatom, which is connected with increased stabilization of a negative charged transition state intermediate, should also play a role in the faster nucleophilic reactions of selenophene compared to thiophene. The nucleophilic substitution of 3-bromo-2-nitroselenophene by thiophenoxide ion is four times faster than that of the corresponding thiophene[138–141]. Some Meisenheimer complexes have been detected in the selenophene series[142–145].

(*ii*) *Synthetic results*. Very few organized studies were known in the selenophene series before Yur'ev and coworkers started their investigations in the fifties. More recent and systematic studies in this field are mainly due to the groups in Lund and in Rouen. Studies on tellurophene were started mainly by the group of Marino and Fringuelli in the seventies. Selenophene and tellurophene, like their congeners, undergo electrophilic substitution in the α- rather than in the β-position.

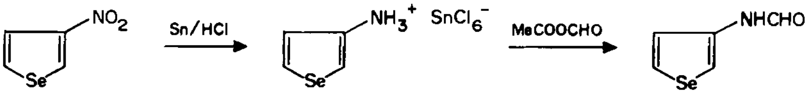
Selenophenes undergo electrophilic nitration, sulphonation, halogenation, mercuration, acylation, formylation, chloro- and amino-methylation and hydrogen exchange.

Nitration of selenophene with fuming nitric acid in acetic anhydride[146,147] or with nitric acid at −40 °C[148,149] occurs mainly in the α-position, with a total yield of 15–25%, giving a mixture of 85% 2-nitro and 15% 3-nitro isomer, which is very difficult to separate. When position 2 is occupied by an electron-withdrawing group (—NO_2, —CHO, —COMe), the nitration occurs mainly in position 4 and less (10–15%) in position 5[150,151]. For example, nitration of 2-formylselenophene by fuming HNO_3/H_2SO_4 gives 45% 2-formyl-4-nitroselenophene, 5% of its 5-nitro isomer and nearly 50% 2,4-dinitroselenophene. However, in acetic anhydride with 7% H_2SO_4, the NO_2 group enters only in position 5[150]. The 2- and 3-nitroselenophenes were prepared by decarboxylation of 2-carboxy-5-nitro- and 2-carboxy-4-nitro-selenophenes, the latter being easily obtained by oxidation of the corresponding formyl or acetyl-derivative[151a] (equation 26). 3-Nitroselenophene (**36**) can be reduced by Sn/HCl to 3-aminoselenophene hexachlorostannate (**37**). Isolation of the 3-amino base is impossible, but **37** can be acylated in 30% yield[148] to compound **38** (equation 27). The hexachlorostannate of the 2-amino isomer can be similarly obtained[148]. Aminoselenophenes are stabilized by an *ortho* electron-attracting substituent[149]. They can be obtained from activated bromo selenophenes via the azido derivative and its subsequent reduction[151b].



(**35**)

(26)



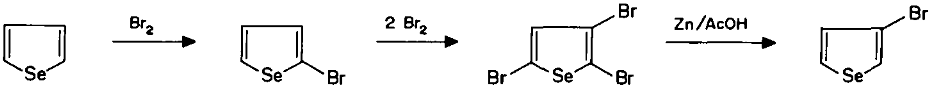
(**36**) (**37**) (**38**)

(27)

Sulphonation by sulphuric acid or pyridine SO_3[152] gives a 2-substituted sulphonic acid, identical with that obtained independently from 2-lithioselenophene and SO_2 followed by oxidation. 2-Formyl- and 2-carboxy-selenophenes are sulphonated mainly in position 5, rather than in the position 4, as in nitration. Sulphonyl derivatives, e.g. 2-selenophenesulphonamide, are obtained through this intermediate[152,153].

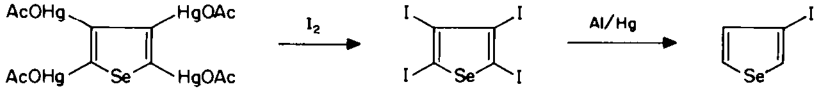
Chlorination of selenophene gives a mixture of 2-chloro- and 2,5-dichloro-selenophene, which, with chlorine in excess, leads to addition and substitution products[154]. Tetrachloroselenophene is obtained directly from Se and hexachlorobutadiene at 250 °C[155]. 2-Chloroselenophene is obtained in 60% yield from selenophene and sulphuryl chloride[154], and a fairly recent patent claims its preparation through dechlorination of tetrachloroselenophene by Na_2Te[156].

Bromination in CS_2 at − 20°C gives 2-bromoselenophene (**39**). Excess of bromine leads to 2,5-dibromo- and 2,3,5-tribromo-selenophene (**40**)[80]. The latter compound is the key intermediate in the preparation of 3-bromoselenophene (**41**) which cannot be obtained by direct monobromination; **41** is obtained from **40** by debromination with zinc in acetic acid[157] (equation 28). A recent simplified synthesis of **41** using the same methodology, but without isolating intermediates, has been described, with an overall yield of 61%[158]. A similar α,α′-debromination is realized starting from tetrabromoselenophene[159–161]. The product, 3,4-dibromoselenophene, is a starting material for 3,4-fusion on selenophene.



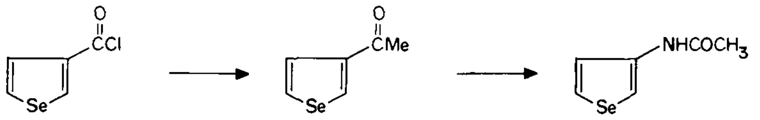
(39) (40) (41) (28)

Iodine can be introduced in the α-position of activated selenophenes with the aid of mercuric oxide[86,162], or through exchange with mercuri salts, which can enter directly by electrophilic substitution to the α-position of selenophene and substituted selenophenes[81c,88,94,163–165]. The HgX group is readily exchanged, not only by iodine, but by various halogens[88] and by the cyano group[94]. For example, from tetramercuriacetate **42**, tetraiodoselenophene (**43**) can be obtained, from which by reduction with aluminium amalgam 3-iodoselenophene (**44**) was obtained[163] (equation 29). From 2,5-dihaloselenophene the selenophene analogue of the electron acceptor TCNQ is prepared[166].



(42) (43) (44) (29)

Acylation can take place in the α-position under Friedel–Crafts conditions[81,167]. No diacylated selenophenes can be obtained, nor products of direct β-acylation on unsubstituted selenophenes. Hence, 3-acetylselenophene (**46**) is synthesized by standard malonate synthesis from the corresponding acid chloride **45**[157], the acid being obtained through 3-metalated selenophenes (see following section). **46** could be transformed to 3-acetylaminoselenophene (**47**) by the Schmidt reaction with a 75% yield[149] (equation 30).

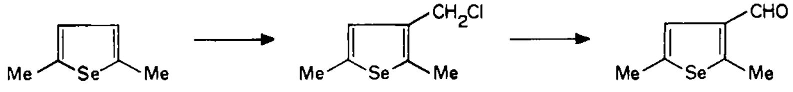


(45) (46) (47) (30)

α-Formylation is generally realized by the Vilsmeier–Haack reaction. The 2-formylselenophene obtained is the starting material for the 2-carboxy- and 2-hydroxymethyl-selenophenes[168]. 2-Methylselenophene gives formylation in position 5[169] and 3-methylselenophene, like compound **47**[149], gives the 2-formyl derivative[86,170,171]. 3-Formylselenophene is obtained through standard modifications of conveniently available 3-substituted selenophenes, e.g. by Sommelet reaction on 3-bromomethylselenophene[163], by reaction of DMF on 3-lithioselenophene[163] or by reduction of 3-cyanoselenophene[172]. Tri- and tetra-formylselenophenes can be obtained by a suitable combination of electrophilic formylation, halogen–metal exchange, reduction of nitriles, Kröhnke or Sommelet reaction and protection of existing groups[173–176].

Selenophene carboxaldehydes behave like typical aromatic aldehydes, undergoing the Darzens, Perkin, Claisen, Wittig and crotonic type condensations. 2-Vinylselenophene can also be obtained by reaction with MeMgBr[177].

Chloro-[178,179] and amino-methylation[180] also occur in the 2- and 2,5-positions. Direct β-chloromethylation can only be obtained with 2,5-disubstituted selenophenes. For example, 2,5-dimethylselenophene (**48**) which cannot be directly formylated, is chloromethylated in the β-position[181,182a] and the product **49** is transformed to the 3-formyl analogue **50** (equation 31). By aminomalonate synthesis 2- and 3-chloromethylselenophenes lead to the corresponding 2- and 3-selenienyl alanines[182b].



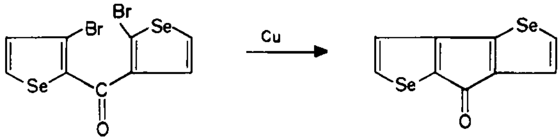
(48) **(49)** **(50)**

(31)

Finally, with powerful 3-substituted + M donating groups (—$NHCOCH_3$,—OCH_3) the electrophilic Kaufmann reaction (Br_2 + KSCN or KSeCN) can be realized in position 2, giving the corresponding 2-thiocyano- and 2-selenocyano-selenophenes[183,184]. The introduction of the groups —SCN and —SeCN in the β-position can, on the other hand, be achieved through diazotation of 3-amino-substituted selenophenes[185]. The groups directly introduced by electrophilic substitution can be transformed by standard methods to other appropriate functional groups, which can be used further for the synthesis of many selenienyl-substituted heterocycles. For example, 3-(2′-selenienyl)-pyrazoles or -isoxazoles can be obtained from 2-selenienylalkynyl ketones[186]; 2-(2′-selenienyl)-oxazolines and -thiazolidines[150,187] from 2-formylselenophene; 2-(2′-and 3′-selenienyl)-oxazoles, -thiazoles and -selenazoles from the corresponding 2- or 3-selenienylchalcogenoamides[188,189]; 3-selenienyl-1,2,4-oxadiazoles from selenienylamidoximes[190]; 2-selenienylpyrimidine from selenienylamidines[191] and 4-selenienyl-1,2,3,5-tetrazoles from cyanoselenophene or the corresponding imino esters[192a].

Very recently 2-selenienyl isosters of levamisole, an immuno-potentiating agent, were prepared for biological evaluation[192b].

It should be noted that Ullmann reaction on 3-bromo-2-selenienyl and 2- or 4-bromo-3-selenienyl ketones leads to bis-hetero-condensed cyclopentadienones **51**[193] (equation 32).

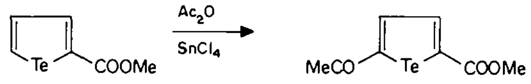


(51)

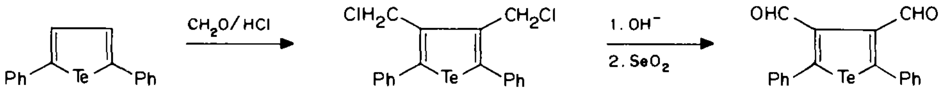
(32)

The chemistry of tellurophene is much less known. Tellurophene is fairly stable to air and light at room temperature; at 0 °C and in the dark, it can be stored for long periods[112]. Since tellurophene is decomposed by strong mineral acids, electrophilic substitution is conducted under moderate conditions. Because of the very high α/β ratio, only 2-substituted or 2,5-disubstituted tellurophenes could be obtained and no 3-monosubstituted tellurophenes are known except the 3-methyl derivative[118b].

Attempts to prepare 2-nitrotellurophene by nitration have been unsuccessful[75,113] and halogens give only 1,1-addition products on the Te atom[97,111,194]. Direct acylation with Ac_2O–$SnCl_4$[113] and with trifluoroacetic anhydride at − 75 °C[75] leads to 2-acetyl- and 2-trifluoroacetyl-tellurophene, respectively. 2,5-Dideuteriotellurophene can also be prepared from D_2SO_4/MeOD[111], and 2,5 bis(acetoxymercuri)tellurophene from mercuric acetate[111]. All other known 2-monosubstituted tellurophenes are obtained from 2-lithiotellurophene. 2-Methoxycarbonyltellurophene (**52**) has been acetylated in position 5 (equation 33), and 2,5-diphenyltellurophene (**54**) has been bis(chloromethylated) in positions 3 and 4, to give **55**. The latter compound was transformed to 3,4-diformyl-2,5-diphenyltellurophene (**56**) (equation 34) via the corresponding diol[195].



(52) (53) (33)

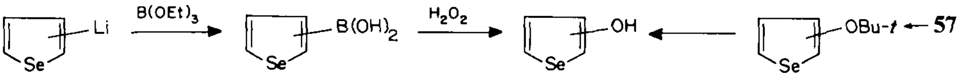


(54) (55) (56)

(34)

d. Metalated selenophenes and tellurophenes. (*i*) *Preparation and standard transformations.* Analogously to furan and thiophene, selenophene can be directly metalated in the α-position by organolithium compounds, through hydrogen–metal exchange[157]. α-Metalation can also be realized through halogen–metal exchange, e.g. from 2-iodoselenophene and phenyl-lithium[162] or -magnesium.

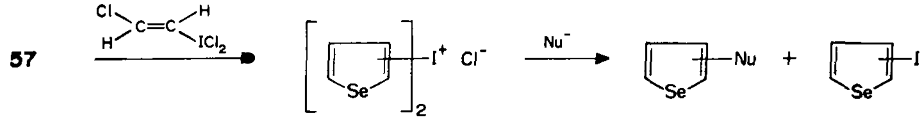
β-Metalation can only be achieved by reacting 3-halogeno(Br,I)selenophene and organolithium compounds at the temperature of dry ice[157,196]. 2-Selenienyl- and 3-selenienyl-lithium are valuable nucleophilic intermediates for the preparation of various 2- and 3-substituted selenophenes. In this way were obtained 2-[157] and 3-carboxyselenophenes[157,196] from CO_2, selenophene-2-sulphinic acid from SO_2[141,152], 3-formylselenophene from DMF[163,175], isomer-free 2- and 3-chloro- and 2- and 3-bromoselenophenes, respectively, from hexachloroethane at − 70 °C and ethylene bromide[197], and 2- and 3-selenopheneboronic acids **58** from triethylborate. These boronic acids are converted by oxidation to 2-[198–200] and 3-hydroxyselenophenes[199–201]. Compounds **59** are also accessible from the lithium compounds by reaction with *t*-butyl perbenzoate[198,200,201], followed by hydrolysis (equation 35). 2,5-Dihydroxyselenophene, regarded as the Se analogue of maleic anhydride, is obtained by this method[198].



(57) (58) (59) (35)

Reaction of sulphur on 2- and 3-lithioselenophenes gives the corresponding 2- and 3-mercaptoselenophenes[201]. The tautomerism of these hydroxy and mercapto compounds has been studied[200–203]: 2-hydroxyselenophene exists mainly as the α,β-unsaturated selenolactone form, 3-selenolene-2-one, and undergoes Michael addition[202]; 3-hydroxyselenophene and its 2,5-dimethyl analogue are present only in the keto form, 3-oxo-4-selenolene[201]. This is reminiscent of the corresponding furans, whereas the corresponding 2,5-dimethyl-3-hydroxythiophene shows 32% of the enol form[199]. The 2- and 3-mercaptoselenophenes, whose tautomerism was studied in the more stable methyl analogues, exist in the enethiol form, due to difficulties in the formation of thione groups[201,203]. The enol form in hydroxy compounds becomes preponderant in the stabilized *o*-acylated derivatives[204,205].

Reversed reactivity of selenienyllithium is obtained through iodonium salts **60**, by reaction with *trans*-iodosovinyl dichloride. This conversion to an electrophilic reagent is of great synthetic values for condensation with various nucleophiles, in order to obtain substituents which are difficult to prepare by other methods (equation 36). For example, with sodium nitrite in DMF 2- and 3-nitroselenophenes were obtained in 37 and 18% yield, respectively[206]. The nucleophile SCN^- gives 48% of 3-thiocyanoselenophene[207], but the reaction has failed in introducing the SeCN group.



(60) (36)

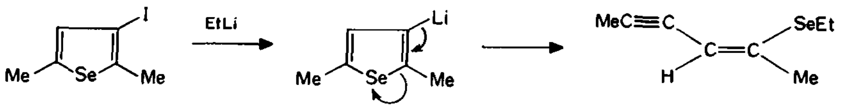
Direct α-metalation is also preponderant in substituted selenophenes. 3-Monosubstituted selenophenes such as 3-methoxy-[208] 3-cyano-[209] 3-diethoxymethyl-[175,209] and 3-*t*-butoxy-[205] are lithiated in position 2. A 2-substituted selenophene, like 2-cyanoselenophene, is lithiated in the second α-position[209]. To obtain β-metalation it is necessary to start from the corresponding bromo compound. 3-Bromoselenophene itself gives, depending on the reagent and temperature, either 3-lithioselenophene (BuLi, − 50°C), or 3-bromo-2-lithioselenophene[157]. 3,4-Dibromoselenophene gives β-lithiation to 3-bromo-4-lithioselenophene[159,176]. However, with a 2,3-dibromoselenophene, halogen–lithium exchange takes place preferentially on the 2-bromo atom[176]. Easy exchange in the α-position is used to obtain a 2,5-selenienylated polymer from a Grignard reagent and 2,5-dibromoselenophene via a poly-Wurtz reaction[210]. There is thus experimental evidence that selenophene is metalated in the same manner as thiophene.

2-Lithiotellurophene, easily obtained by α-metalation of the parent heterocycle[113], is the starting product for the synthesis of some 2-substituted tellurophenes. In this way were obtained 2-carboxytellurophene[113] (leading by diazomethane to 2-methoxycarbonyl tellurophene), 2-formyltellurophene (leading to 2-methyl, 2-hydroxymethyl- and 2-α-hydroxyethyl-tellurophenes[113]) and 2-dimethylcarboxamido-[211] and 2-methylthio-tellurophenes[212]. 2-Methyltellurophene is lithiated in the remaining α-position[113,213], giving 2,5-disubstituted tellurophenes. It was shown later that by carbonation of 2-lithiotellurophene di-tellurienyl ketone was obtained in 6% yield as a by-product[214].

2-Lithiotellurophene also gives di-α-tellurienyl telluride by reaction with Te[215], but does not lead to the 2-fluoro derivative from $FClO_3$, nor to the 2-nitro derivative from ethyl nitrate. The 2-chloro- and 2-bromo-tellurophenes were obtained by using the reversed methodology shown in equation (36), but the 2-nitro derivative was not obtained in this way[215]. 2-Copper derivatives and iodoarenes give coupling reactions to 2-aryltellurophenes[216]. No β-lithiotellurophene has been obtained so far.

(*ii*) *Ring-opening of lithium derivatives.* The first indication of abnormal behaviour in some selenophene derivatives towards organolithium compounds was the lack of coupling in the reaction of 2,5-dimethyl-3-iodoselenophene with ethyllithium, shown by the failure of subsequent treatment with copper chloride to give the corresponding biselenienyl[217] a reaction working well for the synthesis of bithienyls.

The isolation of the acyclic vinylacetylene **63** in 49% yield when 2,5-dimethyl-3-iodoselenophene (**61**) was treated with ethyllithium at − 70 °C was the evidence of a ring-opening of the selenophene ring (equation 37). The corresponding lithium derivative **62** was trapped in the same reaction at − 100 °C as the carboxylic acid. Consequently, it is very probable that **62** is the key intermediate of this ring-opening[218].

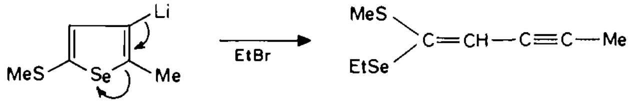


(37)

(61) (62) (63)

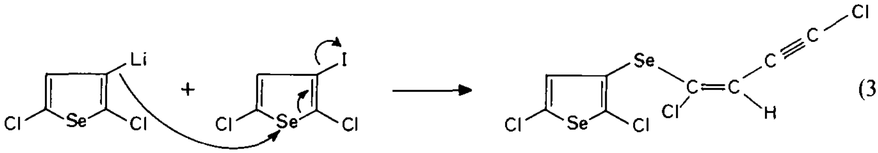
The corresponding thiophene derivative is much more stable and it decomposes only at room temperature, with complicated rearrangements. These facts have led to a careful comparison of the ring-opening of 3-lithiothiophene, -selenophene and -furan derivatives. The previous indication that 3-lithiothiophene gave some unsaturated aliphatic compounds[219] can be explained in this way. A mechanism which has been proposed to explain this ring-opening consists of a retro-Michael reaction from a carbanion situated in a position β to a heteroatom (equation 37). A similar bond-rupture is known for β-carbanions or vinyl ethers[220]. The ring-opening is trans-stereospecific giving the *Z*-compound, where the alkyne and the Se group are in *cis* positions, a conclusion also reached for 3-lithio-2-methylthiophene[221]. Although some 3-lithiofurans give this ring-opening (but not 3-lithiofuran itself which decomposes at − 5 °C), no pyrrole derivatives give this reaction.

A general review of the base-induced ring-opening of heterocycles[222] has led to a classification of three types of ring-opening. The preceding reaction belongs to the first group, named 'R.O.I' (Ring Opening Type I) which is extended to all eliminative ring-opening of β-carbanions. That the selenophene ring is less stable than the thiophene ring in this reaction is due to the greater size of the Se atom, rendering it more polarizable and reducing the bond energy between the heteroatom and carbon. Extension of this reaction to some 3-lithio-5-(methylthio)selenophenes **64** leads to the formation of a mixed thioselenoacetal of acetylenic ketene (**65**)[223], a compound difficult to prepare by other methods (equation 38). The R.O.I is easier with donor groups (for example Me groups) in positions 2 or 5. It was found to be easy, even in the sulphur series and was observed at − 70 °C for both 2-trimethylsilyl-3-lithio-thiophene and -selenophene[224]. It could therefore be anticipated that − I groups in the α-position should stabilize the 3-lithio intermediates. For example, 2,5-dichloro-3-lithioselenophene (**66**), prepared by abstraction of proton of 2,5-dichloroselenophene by lithium diethylamide is highly stable. However, when one tries to obtain this lithio compound by the classical method from 2,5-dichloro-3-iodoselenophene and ethyllithium, only the unstable ring-opening product (**67**) is formed[225] (equation 39). Its formation can be explained by reaction of the 3-lithio derivative on the unreacted 3-iodo precursor. It brings evidence of a second type of ring-opening (R.O.II), consisting of a heterophilic reaction (reaction on the heteroatom) of the lithium nucleophile, which can be of two different types. The first one, exemplified in the preceding reaction, consists of an eliminative R.O.II, and requires the presence of a good leaving group β to the heteroatom. To this R.O.II type belongs also the formation of Ph_2Se (in 54% yield) from tetrachloroselenophene and phenyllithium[226]. Due to the greater polarizability of Se, the heterophilic R.O.II reaction is easier in the selenophene than in the



(38)

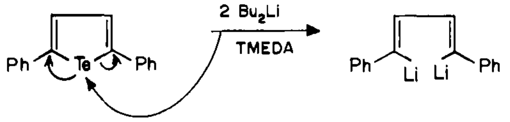
(64) **(65)**



(39)

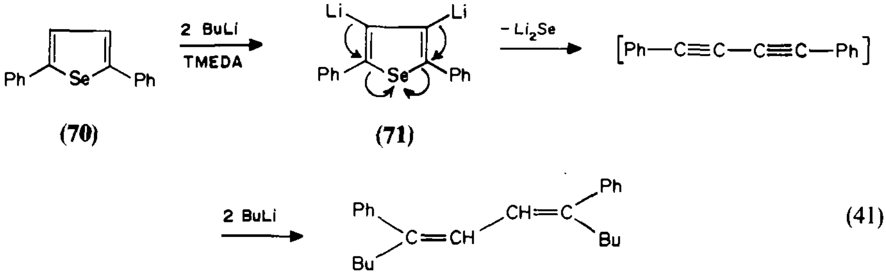
(66) **(67)**

thiophene series. But, contrary to the R.O.I, this eliminative R.O.II proves easier with electro-withdrawing groups. Consequently, even in the sulphur series, 3,4-dichloro 2,5-dimethoxythiophene shows this ring-opening reaction[227]. Another type of heterophilic ring-opening was demonstrated on 2,5-diphenyltellurophene (**68**)[228] and on fused selenophenes independently in Liège and in Moscow (see Sections IV.A.2 and IV.A.3). It consists of substitutive R.O.II with cleavage of the heteroatom–carbon bond and formation of a carbanion on this α-carbon (equation 40). The dilithio compound **69** was used to prepare a variety of 1,4-disubstituted butadienes. This reaction is normally easier with the largest and more polarizable heteroatom. A substitutive R.O.II was demonstrated later[229] in 2,5-dimethoxyselenophene, giving 55% yield of dibutyl selenide. This reaction failed in the corresponding thiophene. 2,5-Diphenylselenophene itself (**70**), the Se analogue of **68**, gives a ring-opening, which seems to be of the R.O.I eliminative type, since the isolation of 5,8-diphenyldodeca-5,7-diene (**72**) can only be explained by addition of butyllithium to intermediate 1,4-diphenylbutadiyne, probably formed by preliminary metalation in the β-position (equation 41)[229]. The substitutive R.O.II mechanism, which can also be viewed as a chalcogen–metal interconversion reaction, an



(40)

(68) **(69)**



(70) **(71)**

(41)

(72)

analogue to the halogen–metal interconversion, is thus very rare on heteroatoms which are part of an aromatic ring. However the Se–metal replacement has been described in a few examples of aromatic and heteroaromatic acyclic selenides. The third type of ring opening (R.O.III), starting from a lithium derivative on a side-chain, and where the cleavage is also realized in the β-position, is invoked in some lithiomethylthiophenes[222], but is not well documented up to now in the selenophene series.

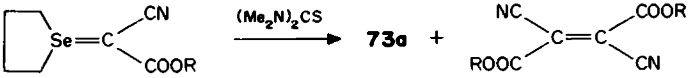
e. Hydrogenated selenophenes and tellurophenes. The chemistry of tetrahydroselenophene (selenolane) (**73a**) and tetrahydrotellurophene (**73b**) is similar to that of acyclic selenides and tellurides. The starting materials for their preparation are generally tetramethylene halides (equation 42). The most reliable method uses sodium chalcogenide:

(42)

(**a**) Y = Se
(**b**) Y = Te

(73)

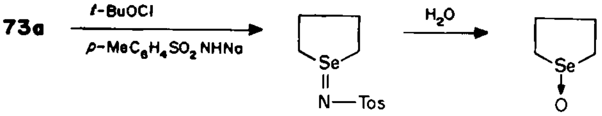
Na_2Se[230], Se + rongalite and NaOH[231] (Se + rongalite without NaOH forms a low-molecular-weight polymer, $(Se\text{-}(CH_2)_4\text{-}Se)_n$, which can lead to tetrahydroselenophene by heating[230] or the corresponding Te compounds[232]. Aluminium telluride gives a very low yield[233]), but Te at 130–140 °C can also be used[233,234]. Tetrahydroselenophene has also been prepared from tetrahydrofuran, Al_2O_3 and H_2Se at 400 °C[105] and in 97% yield from the stabilized selenonium ylid **74** (equation 43). The chalcogenide methodology was used



(74)

(43)

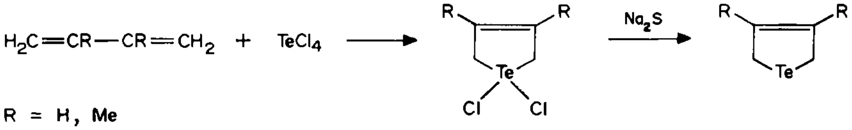
to prepare 2,5-dicarboxytetrahydroselenophene from α,α′-dibromoadipic acid[235], 4,4-dimethyl-3-oxo-tetrahydroselenophene[236] and 3,3′-bis-tetrahydrotellurienyl[237]. 2,5-Dihalomethyl-1,1-dihalotetrahydrotellurophenes were obtained from 1,5-hexadiene, using the ability of TeX_4 to add to alkenes[238]. The heteroatom of **73a**[230] and **73b**[233] can undergo addition reactions with halogen or MeI; when 1,1-dihalogenotetrahydrotellurophene is treated by SO_2, it gives back **73b**. The halogens on Te can be substituted by various nucleophiles (N_3^-, NCS^-, $NCSe^-$)[239]. Compound **73b** can be oxidized by air to the corresponding telluroxide[233]. Selenoxide **76** has been obtained by hydrolysis of selenium-*N*-tosylimide **75**[240] (equation 44).



(75) (76)

(44)

The dipole moments of **73a** and **73b** are lower than that of tetrahydrothiophene[241] (S: 1.89 D; Se: 1.81; Te: 1.63). The Se analogue of biotine has been synthesized, the Se being introduced by NaSeH through a pentacyclic lactone to give a corresponding selenolactone which is then transformed by standard methods to selenobiotine[242,243]. 2,5-Dihydrotellurophene and its 3,4-dimethyl analogue **78** were recently prepared from the corresponding butadienes and $TeCl_4$[244] (equation 45). The same reaction failed with $SeCl_4$ or $SeOCl_2$. **78** is detellurated by butyllithium, and the 1,1-dichloro precursor **77** reacts with arylmagnesium bromide to give a good synthetic micro-method for the preparation of diaryl tellurides.



(77) (78)

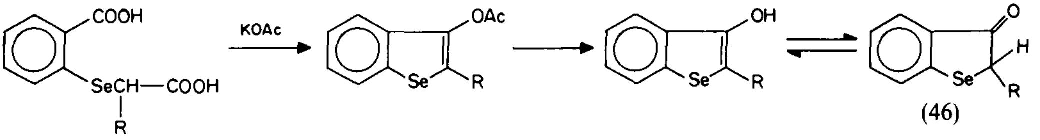
(45)

2. Benzoselenophenes and condensed analogues

A review of the chemistry of benzo(*b*)selenophene and benzo(*b*)tellurophene was published in 1975[245].

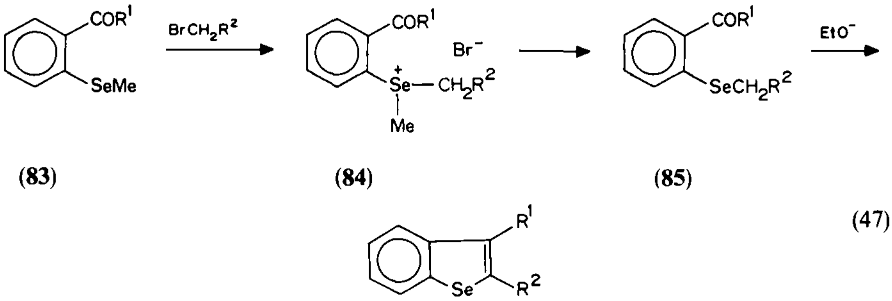
a. Benzo(b)*selenophene. (i) Synthesis.* Benzo(*b*)selenophene has been obtained, among other products and, often with very small yields, by reaction of Se with acetylene or phenylacetylene[77,246–248], by basic hydrolysis and oxidation of *o*-cyanoselenocinnamic acid[246], by reaction of SeO_2 with styrene[249] and by pyrolysis of *o*-ethylselenophenol[250]. Systematic methods of synthesis consist rarely of benzologation of selenophene. We can only note in this respect some ring-opening–ring-closure reactions of selenolo-(2,3-*c*)- or (3,2-*c*)-pyrylium cations by secondary amines to 5- or 6-dialkylamino- or hydroxy-benzoselenophenes[251,252]. The more general syntheses involve the building of the selenophene ring on the benzenic substrate.

Following the pyrolysis of diacids, unsubstituted[253,254] or substituted[255–260] Se analogues of indoxyl are prepared by the C(2)–C(3) ring-closure. The yields are improved by isolating the intermediate enol-acetate **80** (equation 46). Sodium amalgam[254], sodium borohydride or hypophosphorous acid reduction of **81** gives the corresponding benzo(*b*)selenophene[261]. By this general reaction naptho(2,3-*b*)selenophene was also prepared[262]. The alternative Dieckmann condensation of the corresponding diesters of **79** gives an α-keto ester, which is also directly reduced in high yields[261] to



(46)

(79) **(80)** **(81)** **(82)**



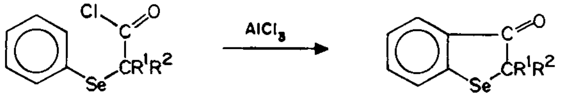
(83) **(84)** **(85)**

(47)

(86)

benzo(*b*)selenophene derivatives by $NaBH_4$, a reaction which can be extended to the O and S series[261]. A general C(2)–C(3) ring-closure can also be achieved by an intramolecular Perkin-like reaction from carbonyl compounds of type **85** where R^2 is an electron-withdrawing group (COOH, COOEt, CN, COR)[263] (equation 47). Contrary to the sulphur chemistry, there are some difficulties in using selenoglycolic acid or its salts as nucleophiles for synthesis of seleno ethers **85**, due to their instability. A rare example of their use consists of the synthesis of 5-nitrobenzo(*b*)selenophene[264]. Seleno ethers **85** can be obtained from an *o*-lithioacetal, Se and ethyl chloroacetate[265], but they are best prepared by alkylation of the selenoethers **83** to **84** and subsequent heating[263,266,267]. The ease of alkylation of the heteroatoms increases with the size of the chalcogen. The reaction works also with an acid cyanide to give 3-cyano-2-substituted benzo(*b*)selenophene[265].

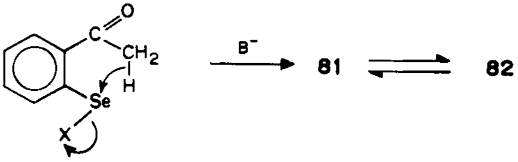
A C(3)–C(aromatic) ring-closure gives one of the most general preparations of benzo(*b*)thiophenes, by using acidic cyclodehydration of phenylthiomethyl ketones, aldehydes or acetals. However, it fails generally in the Se series, due to the cleavage of this type of selenium–aliphatic carbon bond in acidic conditions. A unique example, described in the literature[268], could not be repeated[260]. Electrophilic cyclization of acid chlorides to five-membered Se heterocycles is also very rare, and is only described in the cyclization of α-phenylselenopropionyl chloride (**87**; $R^1 = H$, $R^2 = Me$) to 2-methylselenoindoxyl (**88**)[269], and of oxalyl chloride monophenylseleno ester (**87**; $CR^1R^2 = C{=}O$) to 2,3-dioxo-2,3-dihydrobenzo(*b*)selenophene (selenanaphtenequinone)[270] (equation 48). A third type of C(3)–C(aromatic) ring-closure consists of a cyclization of phenylallyl selenides. It is realized only in quinoline solution and is thus different from the traditional Claisen rearrangement[18,271]. Depending on the nature of the allyl group this cyclization gives 2-methyl- or 2,2-dimethyl-2,3-dihydrobenzo(*b*)selenophene, but not a six-membered ring nor *o*-allylselenophenol. The selenoxide of 2,2-dimethyl-2,3-dihydrobenzo(*b*)selenophene gives, by ring-chain tautomerism, an unstable selenenic acid, trapped by intra- and inter-molecular reactions[272].



(**87**) (**88**)

(48)

Selenoindoxyls can be obtained by base-catalysed C(2)–Se cyclization of *o*-acetylselenenyl halide[260] or selenocyanate[273,274]. This cyclization is easier than in the the sulphur series due to the increasing size of the chalcogen and to its decreasing electronegativity (equation 49). Selenoindoxyl can also be similarly obtained from *o*-



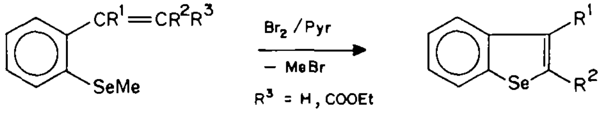
X = Cl, Br, CN

(**89**)

(49)

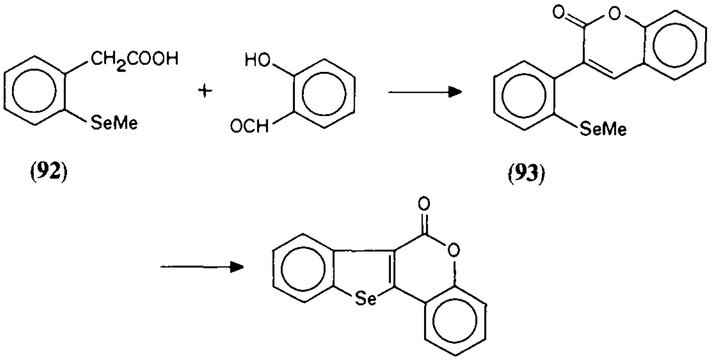
diazoacetylselenenyl bromide[275]. The tautomerism of selenoindoxyls has been the subject of discussion. The chemical behaviour of the compounds is consistent with ketonic behaviour. They form selenoaurones[276] with aromatic aldehydes and anils with nitrosodimethylaniline [followed by hydrolysis to 2,3-dioxo-2,3-dihydrobenzo(*b*)selenophene (selenanaphthene quinone)][253]. They are oxidized to selenoindigo (for a review on selenoindigoid dyes see Ref. 277) and give a positive Brady's test. On the other hand, enolic behaviour is shown by their solubility in NaOH, and by methylation and acetylation to *O*-substituted benzo(*b*)selenophenes[276]. Previous studies indicate that selenoindoxyl exists only in the keto form **82**[256,278]. A thorough investigation has shown by IR and NMR spectra the presence of the ketonic form in freshly distilled selenoindoxyl. However, an equilibrium was determined after more than a hundred hours. The equilibrium mixture consists of 13% of enol form in $CDCl_3$ solution, 21% enol in acetone-d_6 and 50% enol in DMSO-d_6[279]. The corresponding results for thioindoxyl are 2.4% of the enol form in $CDCl_3$, and 30% enol in acetone-d_6[280]. Substituents on the benzene ring modify the position of equilibrium and the rate of its achievement, but freshly prepared solutions are exclusively in the keto form. In DMSO solution, the equilibrium percentages of the enol form are: 4-MeO: 40%; 5-MeO: 80%; 5-NO_2: 100%. In this last example the value is obtained after 8 hours[279].

A C(2)–Se ring closure, by electrophilic substitution of selenenyl halides on styrenes, discovered during attempts to prepare selenocoumarine, was realized in pyridine solution (equation 50)[281]. A selenenyl bromide is an intermediate. This very general method can be



(90) **(91)**

(50)

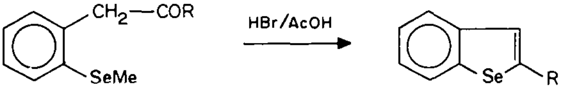


(92) **(93)**

(94)

(51)

applied to the synthesis of unsubstituted, 2- or 3-, or 2- and 3-substituted benzo(*b*)selenophenes[281], of homocycle-substituted benzo(*b*)selenophenes (4-NO_2, 5-NO_2, 7-NO_2, 6-Cl, 6-Br and their 2-Me derivatives)[282], and of some polycyclic derivatives, e.g. for the synthesis of the Se analogue of coumestan (**94**)[283] (equation 51). This method has been applied to the synthesis of benzo(*b*)thiophene: the intermediate sulphenyl halide was prepared by reaction of sulphuryl chloride on the corresponding thio ether[281].

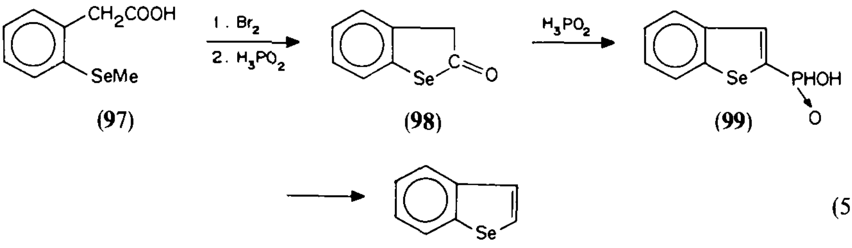


(95) **(96)**

(52)

Cyclodehydration of *o*-methylselenobenzyl ketones involves demethylation by HBr in acetic acid[284] (equation 52). This method has also been applied to the O and S congeners[284].

Cyclodehydration of demethylated *o*-methylselenophenylacetic acid results in selenolactonization. By this method 2-oxo-2,3-dihydrobenzo(*b*)selenophene (**98**), a lactone isomer of selenoindoxyl (**82**), was obtained in a one-pot reaction from *o*-methylselenophenylacetic acid (**97**) or its nitrile[283] (equation 53). Under more drastic

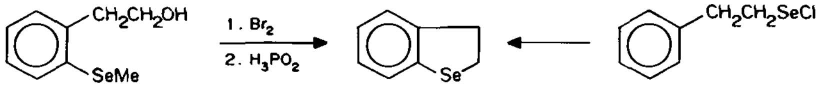


(97) **(98)** **(99)**

(53)

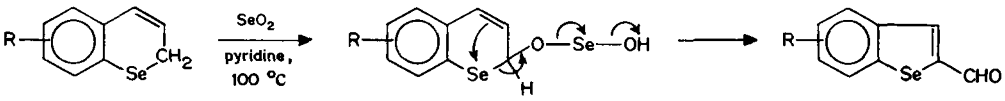
conditions, **98** gives a good yield of benzo(*b*)selenophene, through the 2-phosphinic acid **99** as intermediate. This lactonization method is applicable to the corresponding thiolactone derived from sulphenyl chloride. Selenolactone **98** undergoes ring-opening by conventional nucleophilic reagents, and reacts at the CH_2 by aldol condensation with benzaldehyde in ethanol–Et_3N solution. This is followed by ring-opening of the selenolactone and internal Michael addition of the SeH group, to give the ring-rearrangement product 2-phenyl-3-ethoxycarbonyl-2,3-dihydrobenzo(*b*)selenophene[283].

2,3-Dihydrobenzo(*b*)selenophene (**101**) is prepared in 45–50% yield by a one-pot H_3PO_2 reduction of *o*-bromoselenophenethyl alcohol, followed by cyclodehydration of the intermediate selenophenol[285] (equation 54). Compound **101** is difficult to obtain by other methods: electrophilic ring-closure of *β*-phenethylselenenyl chloride (**102**) gives a very low yield (5–10%); hydroboration or catalytic hydrogenation of benzo(*b*)selenophene, or Wolff–Kishner or Clemmensen reduction of selenoindoxyl failed[285]. Compound **101** can be quantitatively dehydrogenated by S to benzo(*b*)selenophene.



(**100**) (**101**) (**102**) (54)

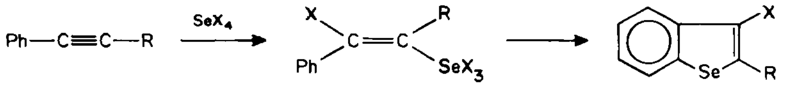
Allylic SeO_2 oxidation of selenochromenes **103** under well-chosen conditions gives rise to a ring-contraction leading to very good yields of 2-formylbenzo(*b*)selenophenes **105**[286], probably through an intermediate of type **104** (equation 55). In other solvents and at other temperatures 1-selenocoumarines, 1-selenochromones and diselenocinnamaldehydes are formed[286]. The ease of ring-contraction increases with the size of the chalcogen; for thiochromenes, the reaction is much more complex, giving also, depending on experimental conditions, dithiocinnamaldehyde-*S*,*S*-dioxide[287], 2-(2′-benzo(*b*)thienyl)-1-thiochromones[288] and a six-membered selenosultone by insertion of SeO_2[289] (Section V.B.2). The yields are lower for the corresponding ketones. MnO_2 oxidative hydrolysis of selenochromylium salts can also give **105**, through intermediates[290a] of a similar type. The intramolecular nucleophilic cyclization of *o*-(ethynyl)selenophenolate, obtained by *o*-lithiation of phenylacetylene and reaction with Se gives directly benzo(*b*)selenophene[290b].



(**103**) (**104**) (**105**)

(55)

$SeOCl_2$ cyclization of cinnamic acids by analogy with the $SOCl_2$–Krubsack cyclization has only been applied on hetarylpropenoic acids, and on diarylethylenes (Section IV.A.3).

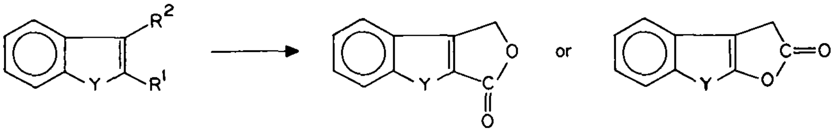


(**106**) (**107**) (**108**) (56)

C(aromatic)–Se cyclization by addition of $SeCl_4$ or $SeBr_4$ to acetylenic compounds (e.g. **106**) to give a Markownikoff-type addition compound **107** has been realized to give 3-halobenzo(*b*)selenophenes **108** (equation 56). By this method were obtained 2-phenyl-3-chloro-[291], 3-bromo-[292], 2,3-dibromo-[292], 2,3-dichloro-[292] and 3-chloro-2-methylbenzo(*b*)selenophenes[292]. This reaction was recently realized by phase-transfer catalysis[293]. By a similar reaction with selenium monochloride (Se_2Cl_2) 3-chloro-2-substituted-benzo(*b*)selenophenes (2-Ph, 2-Me, 2-*n*-Bu, 2-COOEt) were obtained, probably via a selenirenium ion[294]. By reaction of SeO_2 and HBr on phenylpropiolic acid or its *m*-methoxy derivative the 3-bromo-2-carboxy and 3-bromo-2-carboxy-5-methoxy-derivatives were obtained in yields of 28%[295] (compared with 63% in the corresponding sulphur series). Similarly, by the same reagent, 3-bromo-2-sulphonamido-benzo(*b*)selenophene was obtained in a 14% yield[296]. $SeBr_4$ can also give by addition to benzal or dibenzalacetone 3-bromo-2-acetyl or 2-cinnamoyl-2,3-dihydrobenzo(*b*)selenophene. The latter is dehydrohalogenated by MeONa to 2-cinnamoyl benzo(*b*)selenophene[297].

(*ii*) *Electrophilic substitution and standard transformations.* In parallel with its sulphur analogue benzo(*b*)selenophene undergoes preferential electrophilic substitution on the heterocycle. However, whereas mononitration gives isolated yields of 5% of the 2-nitro and 35% of the 3-nitro derivatives[298], acylation occurs preferentially in the 2-position[299,300] (2-acylation: 3-acylation = 9). This ratio is the opposite to that in the acetylation of benzo(*b*)thiophene, where the 2-acylation: 3-acylation ratio is 14: 86. The destabilization of the Wheland intermediate resulting from reaction in position 3, by a less efficient + E effect of Se is invoked[299]. Rieche or Vilsmeier formylation leads to high-melting-point compounds; chloromethylation by dichloromethyl methyl ether, followed by nitropropane reaction, leads however to a 7% yield of 3-formyl-benzo(*b*)selenophene[299].

Lewis acids alone can give two isomeric benzoselenophene dimers, 2- and 3-(2′-benzoselenienyl)-2,3-dihydrobenzoselenophene[300]. On the other hand, monobromination of benzo(*b*)selenophene by bromine in CCl_4[301] gives a 3:1 ratio of the 3- to 2-products[292]. Halogenation on Se occurs initially and 1,1,3-trihalogenated intermediates can be isolated. An important isotope effect on the β:α ratio is evidenced: for 3-deuterio-benzo(*b*)selenophene the preceding ratio is 3:2; for the 2-deuteriated isomer, it is 86:14. This could indicate that the reaction is not a traditional electrophilic substitution and thus suggests an intermediate bromonium ion as in alkenes, whose formation could be favoured by primary *Se*-dihalogenation which lowers the aromatic character. Excess of bromine gives successively 2,3-dibromo and 2,3,6-tribromo derivatives[292]. Pure 3-bromobenzo(*b*)selenophene can be obtained from the 2,3-dibromo derivative by reaction with Zn and AcOH (95% yield) or with butyllithium at −80 °C (80%). Monomethyl homologues of benzo(*b*)selenophene can be obtained, the 2-methyl isomer by a direct ring-closure of the corresponding α-methylated diacid **79** (R = Me)[256], from cyclodehydration following equation (52) or from Wolff–Kishner reduction of the 2-formyl derivative[302]. The 3-methyl isomer can be obtained by reaction of MeMgBr with selenoindoxyl[256], or best by direct ring-closure followed by decarboxylation of 2-acetylphenylselenoacetic acid, following equation (47). Electrophilic reactions (formylation[303], acylation[304], aroylation[304]), on these monomethyl benzo(*b*)selenophenes proceed easily on the neighbouring free heterocyclic position, leading by standard transformations to a variety of disubstituted benzo(*b*)selenophenes[303], such as the 2,3-dimethyl derivative, the 2,3-dicarboxy derivative and its corresponding 2,3-anhydride. From 2,3- or 3,2-acid alcohols (**109**; Y = Se) the corresponding lactones **110** and **111** (Y = Se) can be easily obtained (equation 57). In contrast, in the benzofuran series the corresponding **109a** or **109b** (Y = O) does not lactonize, and in the benzothiophene series, only the acid **109b** (Y = S) gives lactonization under these conditions. The lactone **110** (Y = S) can only be

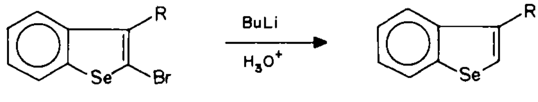


(109) **(110)** **(111)** (57)

(**a**) $R^1 = COOH, R^2 = CH_2OH$
(**b**) $R^1 = CH_2OH, R^2 = COOH$

obtained from the corresponding nitrile alcohol, but this reaction fails in the benzofuran series[305]. Electrophilic reactions can also lead to 2,3-disubstituted bromocarbonyl- or carboxybenzo(*b*)selenophenes.

Nucleophilic substitution of the bromine in the bromocarbonyl-activated compounds by thiolate or selenolate ion can be easily realized, leading to precursors for further cyclization to fused heterocycles[306]. This reaction leads to introduction of a S or Se atom into position 3 of the benzo(*b*)selenophenes. The 2-bromo-3-substituted derivatives can be debrominated by butyllithium, giving rise from the 2-bromo-3-diethoxymethyl compound (**112**; $R = CH(OEt)_2$) to the 3-formyl derivative (**113**; R = CHO), and successively to 3-carboxy-and 3-acetyl-benzo(*b*)selenophenes[299] (equation 58). The Se analogue of gramine (**113**; $R = CH_2NMe_2$) was obtained similarly from **112** ($R = CH_2NMe_2$)[307].

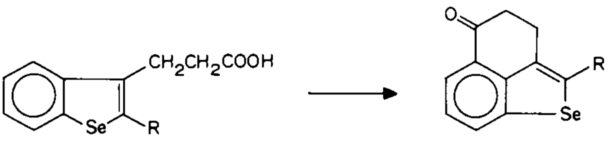


(58)

(**112**) (**113**)

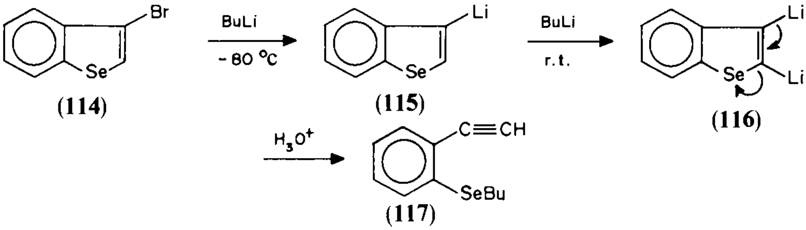
A Se analogue of tryptamine was prepared from the nitrile **113** ($R = CH_2CN$), which was obtained by a Wittig reaction on selenoindoxyl; the Se-analogue of tryptophane (**113**; $R = CH_2CH(NH_2)COOH$) was obtained from the 3-formylbenzo(*b*)selenophene via hippuric acid synthesis[307]. Corresponding isomers in position 2 were also synthesized. From selenotryptamine the Se analogues of desmethoxyharmaline, harmine and hexadehydroyohimbane can be obtained[308]; the Se analogue of serotonin (5-hydroxyselenotryptamine) can be prepared from 5-nitroselenoidoxyl in a similar way[309a]. In this same field, a benzoselenienyl glycine was obtained by direct electrophilic reaction on benzo(*b*)selenophene[309b].

Electrophilic substitution on the benzene ring takes place only when the 2- and 3-positions are occupied. For example, the 2,3-dimethyl-derivative is acylated in position 6[310]. In the same way β-(3-benzo(*b*)selenienyl)propionic acids can be cyclized at position 4 of the homocycle only if position 2 is occupied by a Me or halogen substituent as in the transformation **113a** → **113b**[311]. Note that the non-aromatic 2,3-dihydrobenzo(*b*)selenophene is also benzoylated in position 6[285].



(**113a**) (**113b**)

(*iii*) *Metalation and ring-opening reactions.* 2-Lithio-benzo(*b*)selenophene is easily obtained by direct metalation of the parent heterocycle. It is used for many transformations, e.g. for the synthesis of the pure 2-bromo derivative[299]. The 3-lithio isomer (**115**) is obtained by halogen–lithium interconversion of 3-bromobenzo(*b*)selenophene at −80 °C[312] (equation 59) and is stable for a long time at room temperature. It can be transformed with good yield to 3-bromo,3-carboxy- or 3-methyl-benzo(*b*)selenophenes. No lithium transfer is realized as in 3-lithiobenzo(*b*)thiophene. Treated by a second equivalent of butyllithium at 0 °C, it gives a ring-opening of eliminative R.O.I type. A study of the methylation products is in agreement with the formation of the intermediary 2,3-dilithio derivative (**116**). The latter is responsible for the ring-opening reaction, and its instability confirms the ease of the R.O.I transformation when electron density is increased in position 2 (equation 59). 3-Lithio-2-methyl-benzo(*b*)selenophene is also less stable and begins to ring-open after 4 h at room temperature. The formation of a 70% yield of the 2-carboxy derivative by treatment of **114** with 2.5 equivalents of phenyllithium, followed by carbonation can be explained by a ring-opening of **116**, carbonation of the resulting lithioacetylene and acidic ring-closure. This explanation takes into account the absence of 2-lithio-benzo(*b*)selenophene in the system, as demonstrated by a study of the methylation products[312].



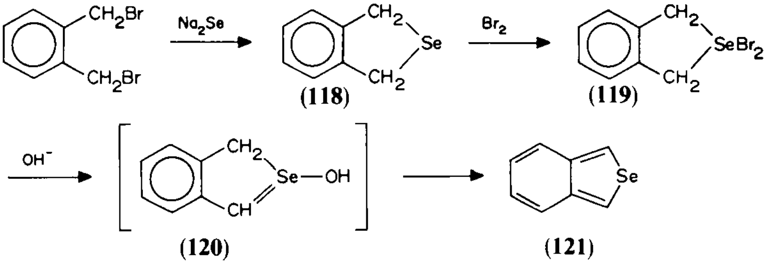
(59)

(*iv*) *Transformation and ring fusion on the homocycle.* The 4-, 5- and 7-nitro-benzo(*b*)selenophenes, obtained by direct ring-closure of conveniently nitrated precursors[264,298], give by reduction the corresponding 4-,5- and 7-amino derivatives. The 6-nitro isomer could not be prepared. The corresponding 6-amino derivative is obtained by reaction of potassium amide on the 6-bromo compound. These amino compounds have been used in the Bernthsen synthesis of acridines[313], in the Beyer–Combes and Skraup syntheses of quinolines, in the Ullmann–Fetiadjan cyclization of benzacridine derivatives of selenophene[314], and in the Fischer indole synthesis via the corresponding hydrazines. From 4,5-diamino-benzo(*b*)selenophene, quinoxalines, pyrroloquinoxalines, thiadiazoles and selenadiazoles condensed on the benzene ring were obtained[315].The 5-mercapto derivative, obtained from the 5-amino compound, has been used for the formation of a thiophene ring, giving a selenolobenzothiophene whose linear or angular structure is not firmly established[260].

(*v*) *Base-catalysed H/D exchange.* The stability of the carbanion α to the heteroatom has been tested by base-catalysed H/D exchange[316] in benzo-condensed furan and congeners. The ratios of *k*(exchange) values for the sequence S/Se/O are respectively, 7/1/2, indicating that, surprisingly in these systems, Se is less effective than O or S in stabilizing an α-carbanion. It can therefore be concluded that none of the preceding factors has a decisive contribution to this stabilization.

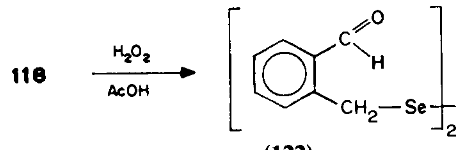
(*vi*) *Copolymerization.* Benzo(*b*)selenophene has been copolymerized as alkene with maleic anhydride. The ease of copolymerization indicates that, with respect to the aromatic character, it lies between benzothiophene and indole, and is completely different from benzofuran[317].

b. Benzo(c) *selenophene and derivatives.* The first synthesis of benzo(*c*)selenophene (**121**), a highly reactive *o*-quinonoid heterocycle whose substitution derivatives are unknown, was realized in 1976 by Saris and Cava[318] via a cold alkaline destruction of the dibromide **119** of 1,3-dihydrobenzo(*c*)selenophene (**118**) (2-selenaindane) (equation 60).



(60)

The selenoxide of **118**, readily available by oxidation of **118** with H_2O_2 in cold methanol, also liberated **121** when treated with 40% NaOH. Dehydration of the selenoxide hydrate, via the ylid **120**, should be a likely mechanism. **121** polymerizes easily in attempts to isolate it in a pure state. It gives the expected crystalline Se-containing adduct with tetracyanoethylene. Compound **118** has been thought to be oxidized to 2-selenophthalide by H_2O_2 in acetic acid[319], but in fact it gives 2,2′-diformyldibenzyl diselenide (**122**)[320] (equation 61). A possible mechanism should be a Pummerer rearrangement of the intermediate **120** followed by ring-chain tautomerism.

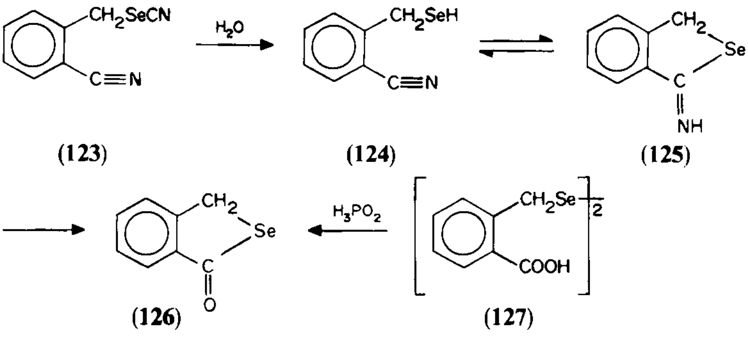


(122)

(61)

Chacko and coworkers[321] used the NMR J_{5-6}/J_{4-5} ratio (J ratio) as a measure of the degree of electronic delocalization in butadiene fragments. This ratio is 0.74 for **121** and is in the same range as for other benzo(*c*) five-membered heterocycles. This value is lower than for the isomeric (*b*) condensed congeners ($J_{ratio} = 0.9$), indicating a residual butadienic character, since $J = 0.52$ for cyclohexadiene. The annelation energies for (*c*) condensed systems are very low, indicating a low contribution of the benzene ring in the delocalization of the heterocycle.

The oxo compound **126** (2-selenophthalide) has been prepared by hydrolysis of the corresponding imino compound, 2-selenophthalimidine (**125**), a cyclic tautomer of **124**[322,323], by heating di(*o*-carboxybenzyl)diselenide (**127**) with 50% aqueous hypophosphorous acid[324] (equation 62) or by $AlCl_3$ cyclization of *o*-methylselenomethyl benzoyl chloride[11]. Compounds of type **123** can be transformed directly to the corresponding selenophthalide in a one-pot reaction with H_3PO_2[325]. The thione corresponding to **126** was obtained by treating **125** with hydrogen sulphide[323]. Dipole moments and relative basicities of the carbonyl group were studied in order to obtain information about the change in the electron density when replacing the O of phthalide by S and Se, in the ring as well as in the carbonyl group[326]. The 1,3-dioxo-1,3-dihydrobenzo(*c*)selenophene (2-selenophthalic anhydride) was obtained from phthaloyl dichloride, either with H_2Se in the presence of $AlCl_3$[327], or in 61% yield with Se and sodium borohydride in phase-transfer catalysis[328].

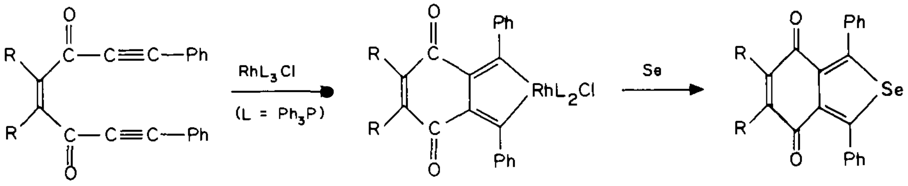


(123) **(124)** **(125)**

(126) **(127)**

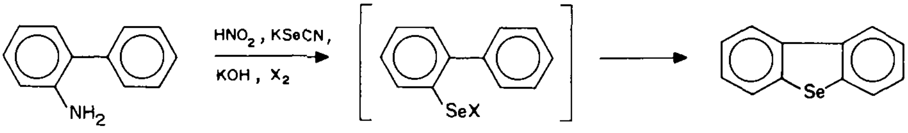
(62)

Some isobenzoselenophene quinones (**130**) and their O and S isologues were obtained by a general method starting from the reaction of bis-acetylenic γ-diketones **128** with tris(triphenylphosphine)rhodium(I) chloride and chalcogen[329–332] (equation 63).



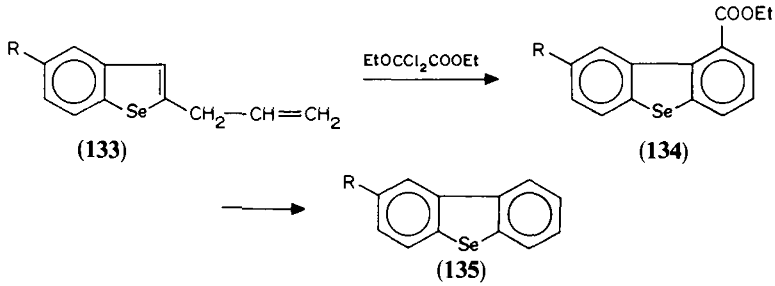
(128) (129) (130) (63)

c. Dibenzoselenophene and related compounds. Dibenzoselenophene (**132**) has been first prepared by cyclodehydration of diphenyl selenoxide with sodium amide[333]. Other syntheses giving low yields are a Pschorr reaction on diazotized diphenyl selenide or the heating treatment of *o*-biphenylselenium trihalide with KOH[334]. Better yields are obtained by cyclodehydrohalogenation of the unstable diphenylselenenyl halide **131**, prepared from *o*-aminobiphenyl[335] (equation 64). Analogously the selenium dichloride of phenyl 2-biphenylyl selenide gives 5-phenyldibenzoselenophenium chloride[336]. Dibenzoselenophene has also been obtained by heating dibenzothiophene *S,S*-dioxide with Se, from selenanthrene and copper-bronze[337], from the 2,2′-biphenylylenmercury tetramer and Se[338], or by Se insertion into biphenylene[339]. The selenanthrene route was also applied to the synthesis of perfluorodibenzoselenophene[340]. Dibenzoselenophene selenium-oxide was prepared from the selenium-dibromide by alkaline hydrolysis[341], or by direct oxidation with peracetic acid[337]. The *N*-tosylimide was also obtained from the parent heterocycle[338]. Dibenzoselenophene-*Se*-oxide can transfer oxygen photochemically to aryl alkyl sulphides[342]. Very few reactions have been tried on dibenzoselenophene. Nitration gives 2-nitro- and by subsequent reduction 2-aminodibenzoselenophene[343,344]. Friedel–Crafts reaction, followed by Haworth and Fischer synthesis, was realized[345,346] on position 2. Metalation was realized at position 4, and followed by carbonation it gave dibenzoselenophene carboxylic acid. Deselenization to biphenyl occurs with Raney nickel[347].



(131) (132) (64)

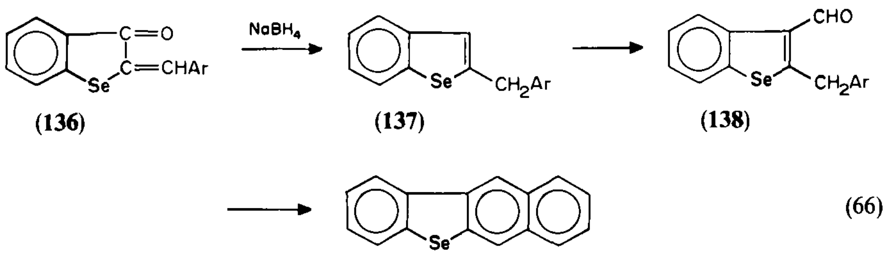
2-Allylbenzo(*b*)selenophenes **133**, prepared from the 2-lithio- and 2-lithio-5-methyl analogues, are cyclized, following Bradsher reaction with ethyl dichloroethoxy acetate, to 1-ethoxycarbonyldibenzoselenophene (**134**) and its 8-methyl analogue, which can be easily hydrolysed and decarboxylated[348] (equation 65).



(133) (134) (135) (65)

Esters **134** can be transformed in nine steps to the 1-γ-carboxypropyl derivatives which, after cyclization, Wolff–Kishner reduction and aromatization, lead to the tetracyclic benzo(*b*)naptho(1,2-*d*)selenophene[349].

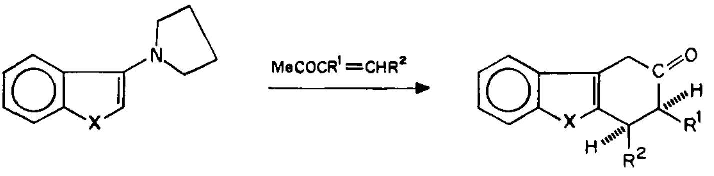
The 2,3-naptho isomer (**139**), and other Se analogues of benzo(*a*)anthracene and dibenzoanthracenes, were obtained by cyclodehydration of 2-benzyl- or 2-α-naphtylmethyl-3-formyl-benzo(*b*)selenophenes **138**, obtained in turn by Rieche formylation of the corresponding 2-benzyl compounds **137**. Compounds **137** are easily prepared by reduction of selenoaurones **136** (equation 66)[350]. A generalization of this reaction leads also to a Se analogue of cholanthrene[351].



(**136**) (**137**) (**138**)

(**139**) (66)

A Robinson–Stork stereospecific annelation of 3-pyrrolidino-benzo(*b*)selenophene or -benzofuran (**140**)[352] by methyl vinyl ketones gives a 2-oxo-1,2,3,4-tetrahydrodibenzoselenophene or its dibenzofuran analogue (**141**)[353] (equation 67).



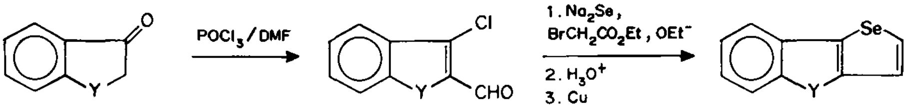
(67)

(**140**)
X = O, Se

(**141**)

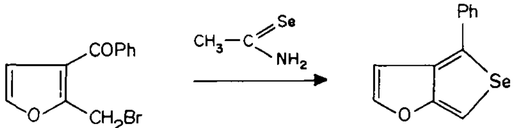
3. Hetero-condensed selenophenes

a. Selenophenes condensed to five-memberèd non-nitrogen heterocycles. (i) Selenolofurans. These are usually obtained from the oxygen heterocycle. For example, selenolo(3,2-*b*)benzofuran **144** (Y = O) was obtained by the general Fiesselmann–Hauptmann reaction of chlorovinyl aldehydes, Na_2Se and ethyl bromoacetate, followed by carbocyclization[354] (equation 68). However, this reaction has failed for the naptho (2,3-*b*)furan analogue of



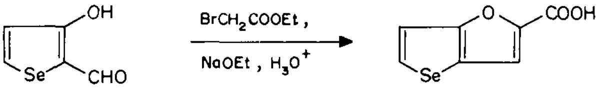
(**142**) (**143**) (**144**) (68)

143[355]. 2-Phenylselenolo(2,3-*b*)furan is obtained similarly, an imino intermediate being used instead of the formyl group[356,357]. 4-Phenylselenolo(3,4-*b*)furan (**146**)[358] and its (*d*)benzologue[359] are obtained from selenoacetamide with 2-bromomethyl-3-benzoylfuran (**145**) or benzofuran (equation 69). 2-Chloromethyl-3-formylbenzofuran gives no corresponding reaction.



(145) (146) (69)

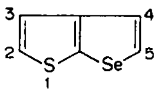
The 1*H*,3*H*-4,6-diphenyl derivative of the non-classical selenolo(3,4-*c*)furan is obtained by a Rhodium method similar to equation (63)[360]. Starting from a selenophene, in one case only a condensed derivative, i.e. the selenolo(3,2-*b*)furan derivative **148** is obtained[361] (equation 70). Decarboxylation of **148** has failed.



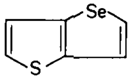
(147) (148) (70)

The three γ-lactones at the 2,3- and 3,4-positions of selenophene, regarded as oxodihydroselenolofurans, are obtained from the corresponding hydroxymethylcarboxyselenophenes[362].

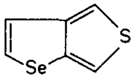
(*ii*) *Selenolothiophenes.* These have been more studied. There are four possible classical selenolothiophenes, where no tetracovalent S or Se atom appears in the noncharged structure: the (2,3-*b*) (**149**), (3,2-*b*) (**150**), (2,3-*c*) (**151**) and (3,4-*b*) (152) fused systems. Generally, their syntheses start from the more accessible thiophene compounds. **149**[363] and **150**[364] were prepared by a Perkin-like cyclization of the appropriate formyl thienylseleno acetates, in a reaction parallel to the last steps of equation (47). The 2-phenyl derivative of **149** was similarly prepared[356]. Two reviews have been published on the chemistry of these systems[365,366]. The direct preparation of its precursor 3-formyl 4-thienylselenoacetate failed, but **151** can be obtained from 3-methylseleno-4-formylthiophene[367].



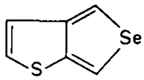
(**149**)



(**150**)

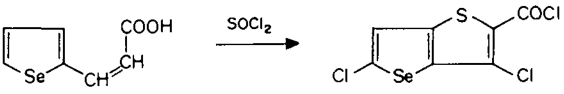


(**151**)

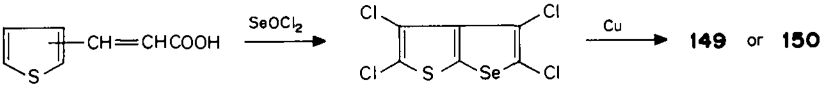


(**152**)

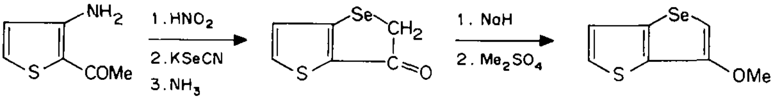
There are only a few recent publications in this field. Application of the $SOCl_2$ Krubsack method of cyclization of arylpropenoic acids to 2-[368,369] and 3-selenienylpropenoic acids[370] gives only the 2-chlorocarbonyl-3,5-dichloroselenolo(3,2-*b*)thiophene (**154**) or the corresponding (2,3-*b*) isomer, in low yields (equation 71). However, by treating the



(**153**) (**154**) (71)



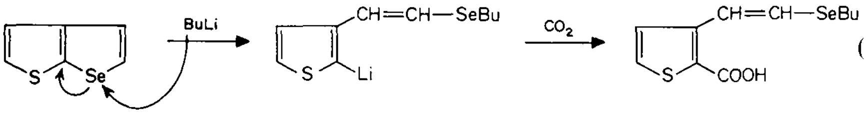
(**155**) (**156a**) or isomer (**156b**) (72) corresponding thienylpropenoic acids with $SeOCl_2$, completely chlorinated cyclized compounds **156** can be obtained. Complete dechlorination can be achieved by copper, to give the parent heterocycles **149** and **150** in 60% yields[371] (equation 72). A 6-methoxy derivative of **150**, i.e. (**159**) could be obtained from 2-acetyl-3-aminothiophene (**157**) (equation 73). This method has also been applied to the corresponding methoxyselenoloselenophene[149].



(73)

(**157**) (**158**) (**159**)

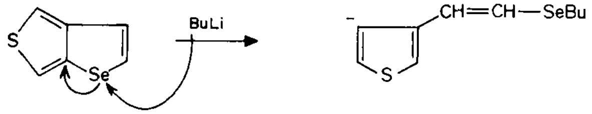
The second methodology, starting from a selenophene ring, and applying the benzothiophene-like synthesis from cyclodehydration of arylthiomethyl ketones, has led recently to the synthesis of derivatives of **149**, substituted on the selenophene ring[372]. Metalation of **150** is realized non-selectively on the two α-positions. However, the (2,3-*b*) isomer **149** gives an interesting ring-opening characteristic of the Se-containing ring, which was identified as a R.O.II selenophilic substitutive type[373,374] (equation 74). The driving force of this ring-opening is the larger polarizability of Se compared with S, combined with the formation of a stabilized α-carbanion on the thiophene ring.



(74)

(**149**) (**160**) (**161**)

The R.O.II reaction has been extended to various '*cis*-fused' tricyclic systems **168** such as selenolo(2,3-*b*)benzothiophene and benzoselenolo(2,3-*b*)thiophene. In all cases, regiospecific ring-opening of the Se ring has been realized, regardless of the nature of its central or lateral position[374]. A ring-opening of the selenophene ring of the more strained isomer selenolo(2,3-*c*)thiophene (**151**) led to the formation of a non-stabilized β-carbanion on the thiophene ring[375] (equation 75).

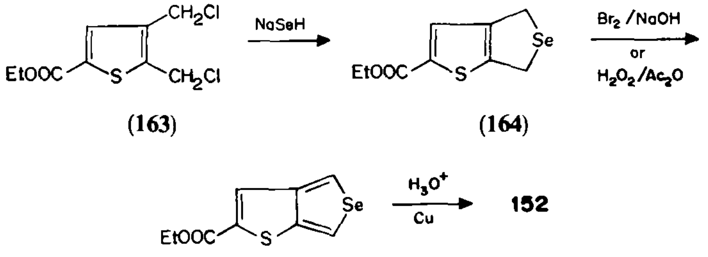


(75)

(**151**) (**162**)

Bromination of **150** by bromine gives 70% of the 5-bromo (α to Se) and 25% of the 2,5-dibromo derivatives, but no 2-bromo derivative. Bromination with *N*-bromosuccinimide gives a 65% yield of a 13:87 mixture of the 2-bromo and 5-bromo derivatives[376]. The Vilsmeier–Haack reagent also reacts preferentially on the selenophene ring, giving a 35:65 ratio of attack at the 2- vs. the 5-position. Acetylation of **150** at position 5 is 1.29 times faster than in the 2-position. The corresponding ratio of 1.89 for reactions at position 5 and at the α-position of the corresponding thieno(3,2-*b*)thiophene[377] demonstrates the larger reactivity of this condensed selenophene ring. The Vilsmeier formylation of **151** gives a mixture of 4- and 6-substitution, in a 60:40 ratio[375]. The transmission of substituent effects in thiophene, selenophene and their condensed analogues[378], and a quantum-mechanical analysis of ^{77}Se chemical shifts of these compounds[379] have been recently studied.

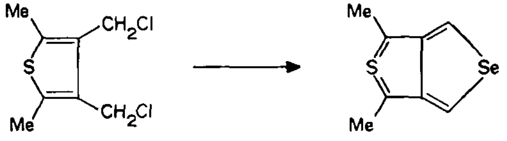
The first derivative of the fourth classical isomer **152**, a selenolo(3,4-*b*)thiophene bearing a 2-thienyl group in position 4 and a diselenide in position 6, has been obtained from a 2-thienyl-substituted phosphorane and $NaHSeO_3$[380]. Unsubstituted **152** was obtained in 1982. The methodology used for the preparation of the corresponding thienothiophene was used (equation 76). The critical steps were the formation of **164**, which was obtained with a 15% yield and gave predominantly the dimer, and the hydrolysis of the ester. A



(163) **(164)** **(165)** (76)

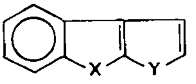
better yield was obtained from 3-formyl-4(methylthio)selenophene, followed by reaction on S with methyl bromoacetate, and cyclization[381].

The non-classical (3,4-*c*) isomer **167** has been prepared by a reaction similar to equation (76) from a 3,4-bis(chloromethyl)thiophene (equation 77). This unstable compound has been trapped by *N*-phenylmaleimide[382].

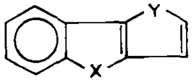


(166) **(167)** (77)

The two benzo-condensed *cis*-fused selenolothiophenes (**168a,b**) and the two corresponding *trans*-fused isomers (**169a,b**) have been synthesized by the classical Perkin-like ring-closure reaction and the process extended to the selenolobenzoselenophene analogues **168c** and **169c**[383–385]. Intermediates of the (3,2-*b*) condensation are obtained more easily by Vilsmeier Haack formylation of indoxyl analogues[384,385].



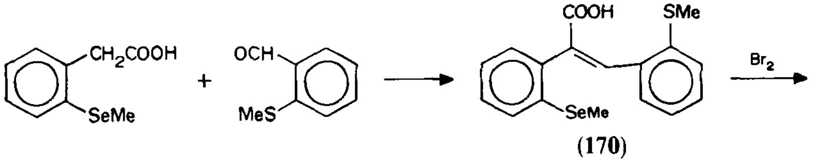
(168)



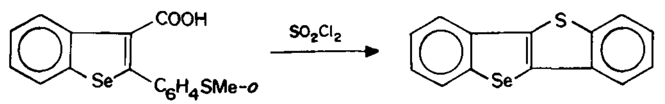
(169)

(a) X = S, Y = Se **(b)** X = Se, Y = S **(c)** X = Y = Se

The electrophilic substitution of **168** and **169** gives substitution only at the 2-position[386]. Tetracyclic (1)benzoselenolo(2,3-*b*)(1)benzothiophene is obtained by cyclo-



(170)



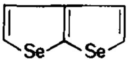
(171) (172)

(78)

dehydration of α-(2-benzoselenienylthio)cyclohexanone followed by aromatization; its (3,2-*b*)-*trans* isomer (**172**) is obtained by applying the new cyclization method of *o*-halochalcogenenyl styrenes (equation 78). The two steps of the cyclization can be easily separated, since Br_2 reacts only on seleno ethers[387].

Thio- and seleno-lactones fused to the heterocycle of benzo(*b*)thiophene and benzo(*b*)selenophene, which can be regarded as oxo derivatives of 1,3-dihydro(3,4-*b*) benzo-condensed selenolothiophenes, are obtained in one step by H_3PO_2 reduction of the *o*-cyanohetaryl chalcogenocyanates[325].

(*iii*) ***Selenoloselenophenes.*** There are four possible isomeric selenoloselenophenes **173**–**176**, including the 'non-classical' isomer **176**. Umezawa was the first to search for selenoloselenophene among the by-products of the reaction of Se with acetylene, and to suggest the possible existence of **173**–**175**[388] but his structural assignment has been shown to be erroneous. It was later shown by NMR and dipole moment measurements, and by independent synthesis that only the (3,2-*b*) isomer **174** was present among 33 other products[248,389]. The syntheses of the isomers **173**–**176** are parallel to those of the selenolothiophene analogues: the isomers (2,3-*b*)-**173** and (3,2-*b*)-**174** were synthesized in 1974 from the suitable selenienyl-1,3 dioxolanes via *o*-formyl selenienylselenoacetates[248]. The third classical (3,4-*b*) isomer **175** was prepared in 1980[390] by a reaction similar to that presented in equation (76).



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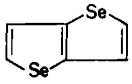

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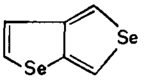

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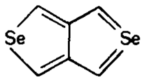
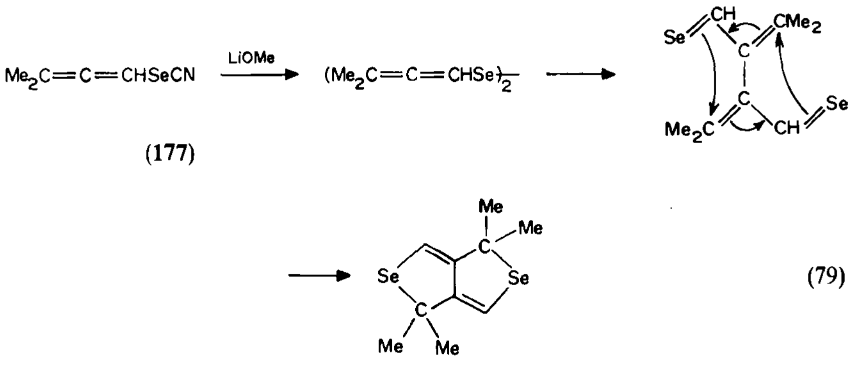


(176)

Evidence has been obtained for the transient existence of the non-classical isomer **176**[182]. A particular synthesis of a dihydro derivative, the 1,1,4,4-tetramethyl-1*H*, 4*H*-selenolo(3,4-*c*)selenophene (**178**) and of its dithio analogue, was realized from an allenic selenocyanate or thiocyanate **177**, via the cyclization of diseleno- or dithio-bridged

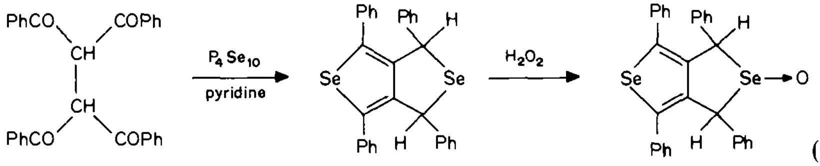


(177)

(178)

(79)

diallenyls[391] (equation 79). Another dihydro derivative, the 1*H*,3*H* system **179**, was obtained by an application of the Paal–Knorr synthesis of monocycles[392] (equation 80). Under the same conditions, P_4S_{10} gives the entirely aromatic ring. The selenoxide **180** has been prepared in order to assign the *cis* or *trans* configuration to **179**.

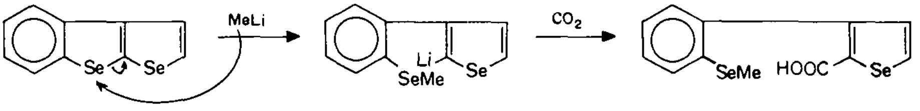


(80)

(179) **(180)**

The electrophilic substitution of **173** and **174** (Vilsmeier formylation, chlorination with *N*-bromosuccinimide, iodination by iodine–iodic acid), gives only 2-substituted products in good yields[369,393]. Acetylation of **174** gives the expected 2-acetyl derivative, while **173** gives only the 2,5-diacetyl derivative. Nitration gives a low yield of the 2-isomer, but it is the only electrophilic substitution that gives detectable 3-substituted isomers[394]. The 3-bromo derivative of **173** has been obtained by successive halogen–lithium exchange of 3,4-dibromoselenophene, reaction with dimethylacetamide, metalation of the intermediate in the 2-position, reaction with Se and methyl bromoacetate and cyclization[395]. Vilsmeier formylation of **175** gives a mixture of the 4- and 6-formyl derivatives in a 55:45, ratio, a parallel reaction as regards the sites of electrophilic attack and the ratios of the derivatives, to those on the corresponding thienothiophenes and selenolothiophenes. These results are also consistent with the quantum-chemical analysis of Litvinov and coworkers[396]. Substitutive selenophilic ring-opening of selenolo(2,3-*b*)- and -(3,4-*b*)-selenophenes are also parallel to similar reactions in selenolothiophenes[394] (equations 74 and 75).

Similarly, tricyclic benzo-condensed '*cis*' selenoloselenophene gives the same type of ring-opening where the less aromatic central selenophene ring is always opened regiospecifically (equation 81)[374]. The tricyclic systems themselves **168c** and **169c**, are obtained as mentioned before[383] and the (3,2-*b*) isomer is also obtained in fewer steps by a Vilsmeier–Haack formylation of selenoindoxyl[354]. Tetra- and poly-condensed (2,3-*b*) systems, such as (1)benzoselenolo(2,3-*b*)(1)benzoselenophene (**183**; R = H) or substituted derivatives or their naphtho analogues were obtained in 28–87% yields by a general method from diarylethylenes and $SeOCl_2$, specific for the Se series[397–399] (equation 82). $SOCl_2$ and $TeCl_4$ react on the same alkenes to give only acyclic thio and telluro derivatives, respectively.

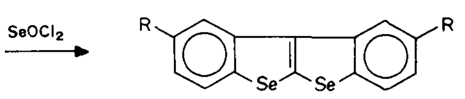


(168c) **(181)** (81)

$(p\text{-}RC_6H_4)_2C{=}CH_2$

(182)

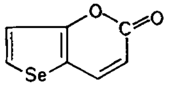
R = H, Me, OMe, Br, Cl



(183) (82)

A heptacyclic system, containing four selenophene rings was obtained by the same methodology from 1,4-di-α-styrylbenzene[399]. The tetracyclic '*trans*' isomer of **183**, (1)benzoselenolo(3,2-*b*)(1)benzoselenophene, was obtained as a by-product from reaction of bromoacetic acid with *o*-methylselenobenzaldehyde, and a mechanism was proposed[267]. Charge-transfer complexes of benzo(*b*)selenophene, selenolo(3,2-*b*)thiophene and selenolo(3,2-*b*)selenophene with tetracyanoethylene have been investigated by UV and IR spectroscopy, and association constants, enthalpies of formation and ionization potentials of the donors determined[400].

b. Selenophenes condensed to six- or seven-membered non-nitrogen heterocycles. A few monocyclic selenophenes condensed to non-nitrogen six-membered or larger rings are known. 2-Oxo-selenolo(3,2-*b*)pyran (**184**), a selenophene analogue of coumarin, has been obtained from 3-hydroxy-2-formylselenophene. The diketo seven-membered oxacycloheptenedione derivative **185**[205] and a selenolopyrylium salt **186** have also been prepared[208,401]. Other selenolopyrylium salts **187**–**189** with isomeric skeletons have been synthesized from disubstituted selenophenes, and transformed, either to hydroxy and dialkylaminobenzoselenophenes or to selenolonitrogen heterocycles[251,402].



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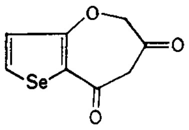

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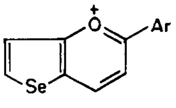

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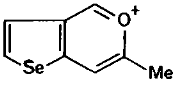

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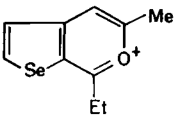

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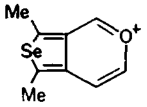

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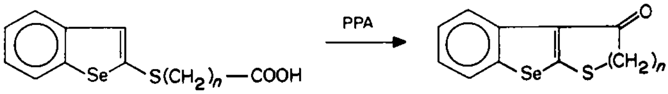
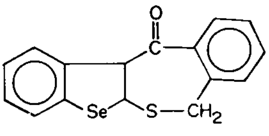
A selenolothiopyranone, 6-methyl-4*H*-selenolo(2,3-*b*)6*H*-benzothiopyran-4-one and several selenoloselenopyranones[403,404] have been obtained by photochemistry of 3-bromo selenophene-2-thio- or -2-selleno carbonic acid -*S*- or -*Se*- aryl esters. 8H-Diselenolo(3,2-*b*:2′,3′-*e*)thiopyran-8-one is obtained by thermolysis of 3*H*-selenolo(2,3-*d*)-1,2-dithiol-3-one, prepared by reaction of 4-mercaptopyridine with 2-chlorocarbonylselenophene[405]. More systematic syntheses are based on benzo(*b*)selenophene and have been realized by the group in Metz. From 2-mercaptobenzo(*b*)selenophene, obtained by sulphurization of the 2-lithio derivative, some benzo(*b*)selenienylmercaptoalkanoic acids **190** are obtained. Cyclization of **190** gives the dihydrothiopyranone **191a** or thiepinone **191b**, and by standard transformation the corresponding very unstable thiopyran analogue is obtained[406] (equation 83). The tetracyclic thiepinone **192** is obtained by a similar reaction[407]. Benzoselenolo(2,3-*c*)condensed thiin and thiepin are obtained by



(83)

(190) (a) $n = 2$ **(191)**

(b) $n = 3$



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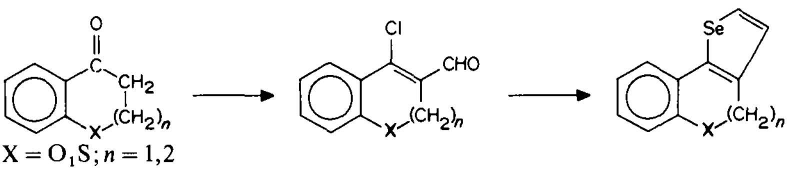
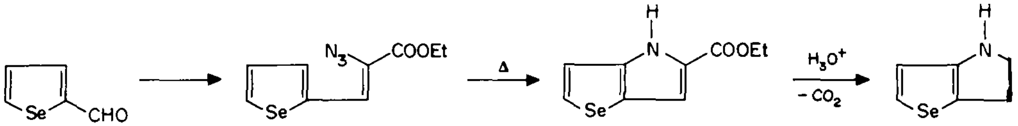


(193) (194) (195) (84)

similar intramolecular Friedel–Crafts ring-closure from 2-benzoselenienylmethylmercapto-acetic and -propionic acids[408]. The (3,2-*b*) isomers and their Wolff–Kishner reduction products are similarly obtained, from 3-carboxyalkylmercaptobenzo(*b*)selenophenes which are obtained in turn from reaction of thioglycolic or β-mercaptopropionic acids with selenoindoxyl[409]. Cagniant and coworkers have applied their selenophene synthesis to the Vilsmeier chloroformylated products obtained from chromanone, thiochromanone and benzothiepinone[355] (equation 84). A similar selenophene-forming condensation gives from dibenzo(*b*, *f*)oxepinone the corresponding selenolo(2,3-*d*) condensed system[410].

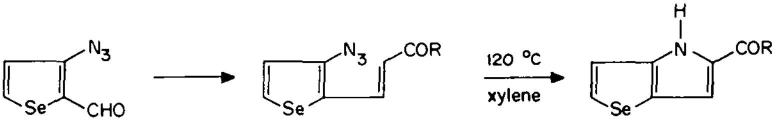
c. Selenophenes condensed to nitrogen heterocycles. The first methodology for the synthesis of selenolo nitrogen heterocycles starts from a suitably substituted selenophene ring. The nitrogen heterocycles are built by the classical methods used for the corresponding benzo-condensed nitrogen systems. The principal difficulties arise from the accessibility of the convenient mono- or di-substituted selenophenes, and from the relative unstability of selenophene derivatives towards some cyclization reagents. Selenolo-(2,3-*b*)- (**199**) and -(3,2-*b*)-pyrroles (**198**) have been obtained by the Hemetsberger cyclization of ethyl azidoaryl acrylates **196** (equation 85)[411,412]. The ester **197** has also been



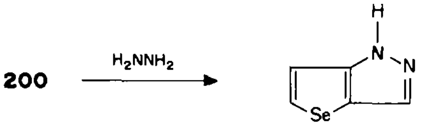
(196) (197) (198)

(85)

obtained by cyclization of a disubstituted selenophene, ethyl 3-(2-formylselenienyl)-*N*-acylaminoacetate[412]. The synthetic utility of the azido group for synthesis of condensed pyrroles is also demonstrated in the thermal cyclization of 2-(3-azidoselenienyl)vinyl alkyl ketones **201** to **202**[413] (equation 86). Compound **200** is also the precursor for obtaining

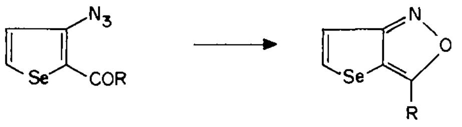


(200) (201) (202) (86)



(203) (87)

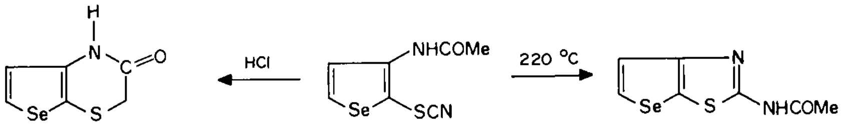
selenolo(3,2-*c*)pyrazole (**203**) (equation 87)[414] by application of the recent Rees synthesis of indazole, for which a mechanism involving a pentazene intermediate has been postulated. This type of heterocycle has been formylated by Vilsmeier–Haack reaction in the position α to Se, a reaction parallel to that for the analogous thio compound[415]. Compound **200** or its acetyl analogue (**204**; R = Me) can also be thermally cyclized to selenolo(3,2-*c*)isoxazoles **205** (R = H, Me)[416,417] (equation 88). This biheterocycle is acylated in a position β to Se[417].



(88)

(204) **(205)**

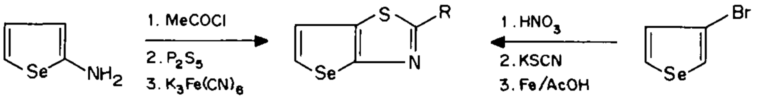
Compound **206** is cyclized by heating at 220 °C to 2-acetylaminoselenolo(3,2-*d*)thiazole (**207**). Contrary to its thiophene analogue, compound **207** cannot be transformed to the parent heterocycle[418,419]. By acidic hydrolysis, compound **206** gives the selenolo-



(89)

(208) **(206)** **(207)**

thiazinone **208**, whose CO group can be reduced to CH_2 by $LiAlH_4$[419]. The isomeric selenolo(2,3-*d*)thiazole systems, **209a** and **209b** have been obtained by two different syntheses, starting from 2-amino- and 3-bromo-selenophene, respectively[420,421] (equa-



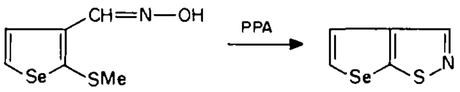
(90)

(209)

(**a**) R = Me

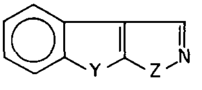
(**b**) R = NH_2

tion 90). Deamination of **209b** has failed. A selenothiazinone isomer of **208** can also be obtained[422]. Selenolo(3,2-*d*)isothiazole (**211**) has been obtained in 16% yield by PPA ring-closure of the 2-(methylthio)aldoxime **210**[423] (equation 91). The corresponding isoselen-



(91)

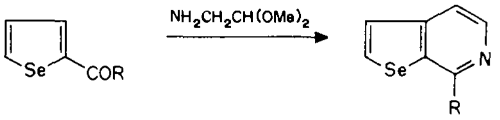
(210) **(211)**



Y = S, Se
Z = S, Se

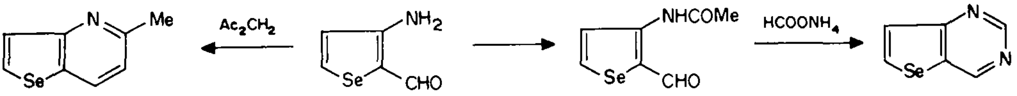
(212)

azole and its (2,3-*d*) isomer are obtained from the suitable methylseleno aldehyde with Br_2/NH_3 under dry ice conditions, with respective yields of 23 and 7%. The method fails for the (3,4-*d*) isomer[424]. Tricyclic benzo-condensed ring systems **212** and isomers are obtained similarly. Ring-opening reactions by methyllithium[425] will be discussed in the section on isoselenazoles. Among the six-membered nitrogen heterocycles, four isomeric selenolopyridines have also been obtained by the methodology starting from selenophene. Ammonolysis of selenolopyrylium salts gives derivatives of selenolo-(2,3-*c*)-[251] and -(3,2-*c*)-pyridines[251,426].



(92)

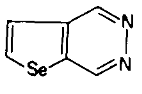
The corresponding parent heterocycles and their Me derivatives are obtained by a Pomeranz–Fritsch cyclization of 2- and 3-formyl- or -acetyl-selenophenes with the dimethyl acetal of aminoacetaldehyde[427,428] (equation 92). They are nitrated and brominated in a position *β* to Se. Their two (*b*)condensed isomers are obtained from the hexachlorostannate of 2- and 3-aminoselenophene and malonaldehyde tetraethyl acetal[148,429]; the (3,2-*b*) system is also prepared by the Friedlander method from 3-amino-2-formylselenophene and acetylacetone (equation 93)[430]. Treating **214** by the excess Vilsmeier reagent gives cyclization to 5-chloro-6-formylselenolo(3,2-*b*)pyridine[431]. Deuteriodeprotonation of the selenolo(3,2-*b*) isomer works preferentially in position 3 as in the furo and thieno analogues. The C_3: C_2 reactivity ratio is 10^3[432]. Compound **214** gives, by reaction with ammonium formate, the selenolo(3,2-*d*)pyrimidine **215**[149,433] (equation 93).



(213) **(214)** **(215)**

(93)

The selenolopyridazine isomeric systems **216** and **217** have been obtained from the 2,3- and 3,4-diformylselenophenes and hydrazine[434]. From 2,3-dicyanoselenophene was obtained the diamino derivative of **216**[189].



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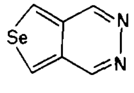
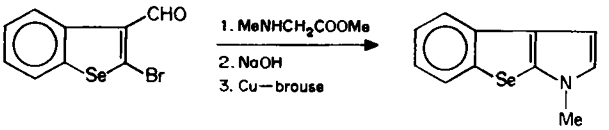


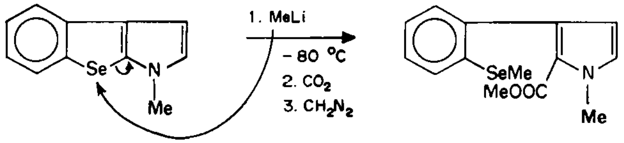
(217)

The general methodology starting from selenophene has also been applied to condensed systems. In this way, starting from selenoindoxyl, were obtained: condensed (1)benzoselenolo(3,2-*b*)indole[435] via a Fischer reaction, 2-nitroso-3-hydroxy-benzo(*b*)selenophene by reaction with nitrous acid, from which upon reduction, *N*-acetylation and thermolysis or thiolysis, the 2-methyl(1)benzoselenolo(2,3-*d*)-oxazole and -thiazole were synthesized[436], and (1)benzoselenolo(3,2-*d*)-1,2,3-selenadiazole, in 8% yield[437] from semicarbazone and SeO_2 oxidation. *N*-Methyl(1)benzoselenolo-(2,3-*b*)-(**218**) and -(3,2-*b*)-pyrrole were prepared by reaction of methyl sarcosinate,



(94)

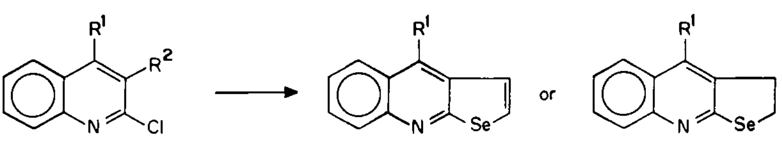
cyclization and decarboxylation on 2-bromo-3-formylbenzo(*b*)selenolophene, and Vilsmeier chloroformylated selenoindoxyl, respectively[438] (equation 94). In contrast to its isomer, the (2,3-*b*) system gives with methyllithium, a typical substitutive R.O.II of the selenophene '*cis*-condensed' on an aromatic five-membered heterocycle[439] (equation 95).



(95)

(218) **(219)**

The second synthetic methodology consists of construction of the selenophene ring by reactions generally used for benzo(*b*)selenophene. For example, from the intramolecular Perkin-like condensation between a formyl group and a selenoacetic derivative, 4-Me-6-substituted selenolo(3,2-*d*)pyrazoles[440], 6-substituted selenolo(3,2-*d*)imidazoles[441] and 5-phenyl-6-methylselenolo(2,3-*b*)pyrrole[442] can be synthesized. By the dehydrohalogenation of 2-selenomercapto-3-bromoacetyl-6-methylpyridine, the 3-hydroxy-6-methylselenolo(2,3-*b*)pyridine can be obtained and reduced to the corresponding 6-methylselenolopyridine[443]. By the bromine–pyridine cyclization of *o*-methylselenostyrenes (equation 50) the first synthesis of the unsubstituted selenolo(2,3-*b*)pyridine was realized[444]. A methyl-substituted (1)benzoselenolo(2,3-*b*)pyridine was synthesized by a Pschorr reaction of the 4-methyl-2-phenylselenopyridine 3-diazonium salt[445]. A Fischer indole synthesis between *o*-(cyanoseleno)benzophenone and phenylhydrazine gives, via dehydrocyanation, the same benzoselenoloindole[446] mentioned previously[435]. Shafiee extended his method of synthesis of selenolo-(3,4)-condensed heterocycles (equation 69) to conveniently substituted *N*-phenyl-indole[358], -thiazole[447] or-1,2,3-thiadiazole[448] precursors. Finally, the synthesis of selenolo(2,3-*b*)quinoline derivatives was achieved in different ways, each starting from a 2-chloroquinoline or its synthetic equivalent. The reactions are summarized in equation (96) ($R^1 = H, Me$). Compounds **221** are obtained,



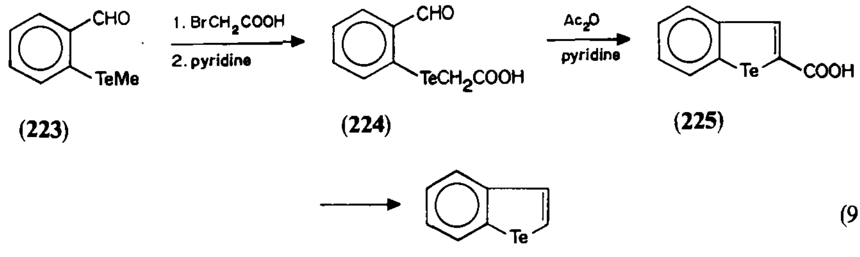
(96)

(220) **(221)** **(222)**

for $R^2 = CH{=}CH_2$ with Na_2Se_2 in ca. 10% yield[449] or for $R^2 = CHBrCH_2Br$, with selenourea/Et_3N[450]. For $R^2 = CH_2CH_2Cl$ with NaSeH[451] or $R^2 = CH_2CH_2OH$, and NaSeH, the necessary 2-chloro compound being prepared in the same pot from the corresponding lactam and $POCl_3$[452], the dihydro system **222** is obtained.

4. Benzo- and dibenzo-tellurophenes

*a. **Benzo(**b**) tellurophene.*** The unsubstituted benzo(*b*) tellurophene (**226**) was the first compound of this system to be prepared and it has been known since 1971[453]. The structure of a previous compound, which was claimed to be telluroindoxyl[454], was later demonstrated to be erroneous[453,455]. **226** is obtained with an overall yield of 75% via a C(2)–C(3) ring-closure, following the very easy quaternization of Te (equation 97).

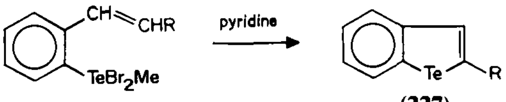


(223) (224) (225)

(226)

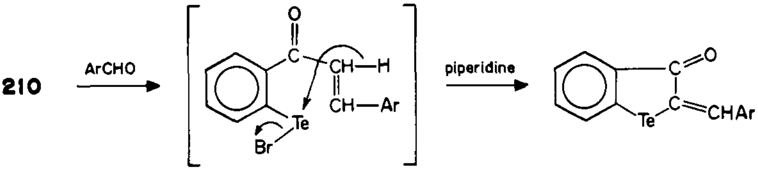
(97)

This method gives directly a very low yield of the 2-acetyl derivative from bromoacetone and is very difficult to apply to *O*-acetyl derivatives from which only 2-carboxy-3-methylbenzo(*b*)tellurophene can be obtained in 10% yield[456]. By standard methods, the acid **225** is transformed to the 2-COCl, 2-$CONH_2$, 2-CONHPh and 2-CH_2OH derivatives[456]. A more general synthesis giving improved yields but generally failing to obtain 3-methyl derivatives (e.g. only 5% yield of 2-carboxy-3-methyl derivative is obtained) uses the intramolecular tellurenyl halide addition–elimination on styrenic compounds, which are obtained in turn by a Wittig reaction (equation 98). Good yields are obtained for R = COMe, COOEt, CN, COPh, but the reaction fails for R = CHO[456]. Telluroaurones **229** are prepared with 80% yield, by a similar reaction on *o*-cinnamoylbenzenetellurenyl bromide (**228**)[457] (equation 99). Selenoaurones are similarly obtained[457]. 2-Substituted benzo(*b*)tellurophenes (2-NO_2, 2-COOEt, 2-COMe) and naphtho(1,2-*b*)tellurophene can also be prepared by DDQ aromatization of the tetrahydro or dihydro derivatives, obtained by the general cyclization methods starting from the Vilsmeier products of cyclohexanone, Na_2Te and ethyl bromoacetate[119]. A key intermediate is the Te analogue of indoxyl (**231**), obtained in low yields by C(2)–C(3) ring-closure of the diacid **230**, but more easily by a dehydrohalogenation of *o*-acetylbenzenetellurenyl halides[458] (equation 100) which is easier with larger Te atom than with Se, and also from *o*-diazoacetyl tellurenyl bromide[275]. Telluroindoxyl (**231**) shows only the ketonic form in all solvents by all spectroscopic techniques, and with no structural variation with time. It does not give 3-methoxy benzo(*b*)tellurophene and gives many



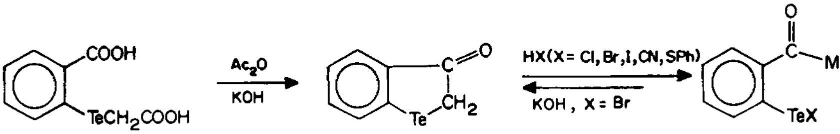
(227)

(98)



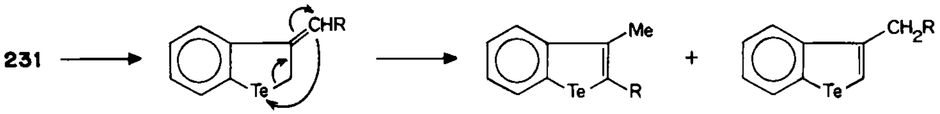
(228) (229)

(99)



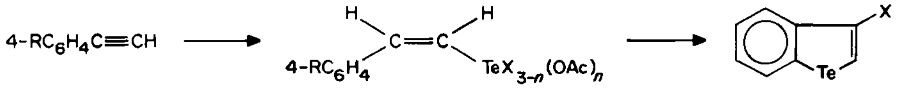
(230) (231) (232) (100)

reactions of the keto form such as formation of oxime, semicarbazone, and phenylhydrazone, followed by Fischer synthesis, reduction to benzo(*b*)tellurophene in low yields[458] and easy oxidation to telluroindigo[458,459], a violet crystalline compound (λ_{max} 637 nm (4.00) compared with λ_{max} 564 nm (4.0) for selenoindigo). It also condenses on the CH_2 group, with aromatic aldehydes to give telluroaurones, with the 3-(C=O) group of isatine, with *p*-nitrosodimethylaniline to give the corresponding anil, and with dimethylacetamide dimethylacetal to give the dimethylaminomethylene derivative[458]. In contrast to selenoindoxyl, **231** is unstable in acidic medium, giving ring-opening reactions by rupture of the Te—C(2) bond (equation 100). The Wittig–Horner reaction gives an interesting rearrangement, characteristic of the Te series, which is the key procedure for obtaining various 3-substituted benzo(*b*)tellurophenes. For example the intermediate **233** has been demonstrated to give a mixture of the prototropic tautomer **235**, and the rearranged product **234**, formed via a ring-opening between Te and C(2) (R = COOEt, CN, COMe)[460] (equation 101).



(233) (234) (235) (101)

A **234** derivative (R = COOH), gives 3-methylbenzo(*b*)tellurophene by decarboxylation. The derivative **235** (R = COOH) is transformed with pyridine-*N*-oxide to 3-formylbenzo(*b*)tellurophene, which can be reduced to the 3-CH_2OH, oxidized to the 3-COOH or transformed to the 3-CN derivative, giving access to the 3-$CONH_2$ derivative. 3-Acetylbenzo(*b*)tellurophene cannot be obtained by these standard transformations. As Lewis acids give complexes with benzo(*b*)tellurophene, direct acetylation has been performed with Ac_2O/trifluoroacetic acid. A mixture of 2- and 3-acetyl isomers is obtained in a 76/24 ratio, from which the pure 3-acetyl isomer can be isolated. The corresponding ratios for a similar acetylation of congeners are: O: 73/27; S: 35/65; Se: 65/35. Formylation by hexamethylenetetramine in the same solvent gives a 10% yield of the 2-formyl derivative only. By the same acetylation method, 3-methyl-, 3-bromo- and 2-methyl-benzo(*b*)tellurophenes can be acetylated on the other free heterocyclic position[460]. Halogenation of benzo(*b*)tellurophene gives a very stable dihalogenated Te derivative from which, by successive halogenation and hydrazinolysis, the 2-chloro and 2-bromo derivatives can be isolated. The 2,3-dibromo analogue is obtained by subsequent bromination and hydrazinolysis of the 1,1,3-tribromo derivative. 3-Methylbenzo(*b*)tellurophene gives in the same manner the 2-chloro-3-methyl and 2-bromo-3-

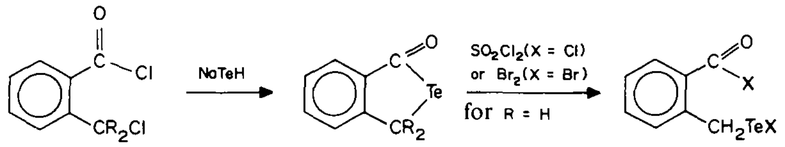


(236) (237) (102)

methyl derivatives. 3-Monohalogeno derivatives can be obtained, either from **231** and CX_4/triphenylphosphine[460] or by reaction of TeO_2 dissolved in HOAc/LiX with arylacetylenes[461,462] (X = Cl, Br) (equation 102). Reaction of TeX_4 with phenylacetylene does not lead to cyclization products[460] but with diphenylacetylene, 3-chloro-2-phenylbenzo(*b*)tellurophene is obtained after reduction of the dichlorotellurium compound[463].

Compound **237** gives **231** by reflux in CF_3COOH. Whereas **237** gives eliminative R.O.I with butyllithium, even at low temperatures, with formation of a 76% yield of *o*-butyltelluroacetylene[462,464] and only a 10% yield of the 3-carboxy derivative by carbonation, benzo(*b*)tellurophene itself is stable towards butyllithium and is easily lithiated on C(2) like its congeners. From this 2-lithio derivative the following 2-substituted benzo-(*b*)tellurophenes can be obtained[464]: 2-CHO (55%); 2-COOH (40%); 2-Me (28%); 2-Cl (26%); 2-MeS (31%); 2-MeSe (31%). The pK_as of the four 2-carboxybenzo congeners have been determined (O:4.21; S:4.67; Se:4.79; Te:5.12)[465] and compared with the corresponding monoheterocyclic acids. The benzo(*b*) fusion lowers the pK_a by a nearly constant value of 0.35 unit, showing the importance of the $-I$ effect of the heteroatom. The pK_a of the 3-carboxy congeners, on the other hand, give very similar values (O:5.54; S:5.67; Se:5.65; Te:5.79)[460]. The solvolysis of 1-(2-benzoheteroaryl)ethyl acetates, shows the reactivity order Te > Se ~ O > S, with a decrease by a factor 10^2 with respect to the corresponding monocycles[466]. Among aromaticity indices, $\delta_{NMR}(\alpha-\beta)$ give lower values (0.71) than for tellurophene (0.937)[465] but with a very good linear correlation relative to monocycles, with a coefficient of ~0.80. On the other hand, the $J_{5,6}/J_{4,5}$ ratio, proposed by Günther as a measure of the delocalization of benzo-condensed rings[467], gives the following values: O:0.92; S:0.90; Se:0.91; Te:0.91; NH:0.90 which should be compared with the values for naphthalene (0.82) and for a completely localized alkene (0.5)[464].

b. Benzo(c)*tellurophene.* Benzo(*c*)tellurophene itself is unknown. However, tellurolo(*c*)-condensed quinones are obtained by the general method of rhodium intermediates (equation 63)[468,469]. 1,3-Dihydrobenzo(*c*)tellurophene is prepared from α,α'-dibromo-*o*-xylene and Na_2Te[470], or Te and NaI, via the 2,2-diiodo compound[471,472]. The naphtho(2,3) analogue is obtained in a similar manner[470]. These dihydro(*c*)condensed compounds easily extrude Te to give condensed benzocyclobutane[471]. A dioxo-1,3 derivative, tellurophthalic anhydride (**239**; $R_2C = C{=}O$) is obtained by a phase- transfer reaction from phthaloyl dichloride[328] (equation 103). Using



(103)

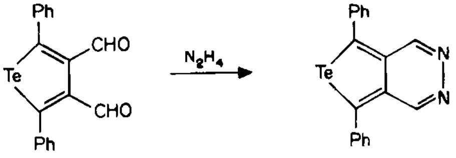
(238) **(239)** **(240)**

the same methodology, 2-tellurophthalid (**239**; R = H), the first example of a five-membered cyclic tellurol ester, is obtained from *o*-bromomethylbenzoyl chloride[473,474]. Its 3-thioxo derivative has been prepared by thionation[474]; 2-tellurophthalid was ring-opened to the first aliphatic *o*-aryl-stabilized tellurenyl halide **240**[474].

c. Dibenzotellurophene. This was obtained for the first time, but with low yield, in 1936 by reaction of TeX_4 with biphenyl[475]. It was also prepared by tellurodesulphonation of dibenzothiophene-*S*,*S*-dioxide[337] or thianthrene-*S*-tetraoxide[476]. Hellwinkel obtained it and its 3,3-dimethyl derivative in good yields from appropriate biphenylyl mercuric tetramers and Te, or from 2,2'-dilithiobiphenyl and $TeCl_4$[477,478]. Dibenzotellurophene was obtained quantitatively by cyclization of o-(trichlorotelluro)biphenyl at 210 °C[479] and nitrated in position 2. It showed a ring-opening by butyllithium to 2,2'-dilithiobiphenyl and dibutyl telluride[480]. Octafluorodibenzotellurophene was also described[340].

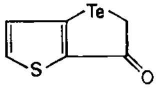
5. *Tellurophene condensed to heterocycles*

Tellurophene has been condensed in some cases to heterocycles. The only monocyclic tellurophene system used as a starting material for fusing another heterocycle is 2,5-diphenyltellurophene. From its 3,4-dichloromethyl derivative and sodium chalcogenide (S,Se) 4,6-diphenyl-1*H*,3*H*-tellurolo(3,4-*c*)-thiophene and -selenophene were obtained[481]. Attempts to prepare the first tellurolotellurophene system for Na_2Te led only to hydrogenolysis of the two dichloromethyl groups, an example of the recently recognized reducing properties of Te^{2-} anions. From 2,5-diphenyl-3,4-diformyltellurophene (**241**) and hydrazine is obtained the tellurolopyridazine **242** (equation 104).

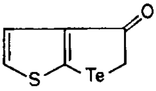


(**241**) (**242**) (104)

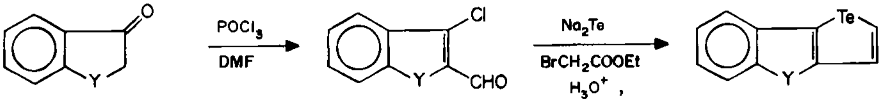
By Hinsberg condensation with di(ethoxycarbonylmethyl) sulphide, **241** gives the corresponding tellurolo(3,4-d)thiepin[482]. All other known hetero-condensed tellurophenes are prepared by constructing the tellurophene ring, e.g., the unsubstituted (2,3-*b*)- and (3,2-*b*)-tellurolothiophenes, are prepared similarly to benzo(*b*)tellurophene[245]. The (3,2-*b*) system, in contrast to its Se analogue which is stable under these conditions, shows a tellurophilic substitutive ring-opening of the tellurophene (R.O.II) by organolithium compounds, with the unusual formation of a carbanion at the *β*-position of the thiophene ring. The two thieno-(3,2-*b*) and -(2,3-*b*) analogues of telluroindoxyl (**243** and **244**) are obtained in good yields by dehydrobromination[464] of the suitable *o*-acetylthiophenetellurenyl bromide[483]. The 5-formyltellurolo(3,2-*b*)thiophene is obtained similary to 2-formyl benzo(*b*)tellurophene by methylene oxidation and ring-contraction of the corresponding 5*H*-thienotellurin[484]. 4,6-Diphenyl-1*H*,3*H*-tellurolo(3,4-*c*)furan is prepared, as its selenophene analogue by the rhodium method[360]. As tricyclic systems, tellurolo(3,2-*b*)-(1)benzofuran and -(1)benzoselenophene are obtained by the general methodology starting from a Vilsmeier–Haack reaction on coumarone and selenoindoxyl[354] (equation 105). 2-Chloro-3-chloroethylquinoline is used as a starting material for tellurolo(2,3-*b*)quinoline[485] or its 2,3-dihydro analogue[486]. A tetracyclic system,



(**243**)



(**244**)



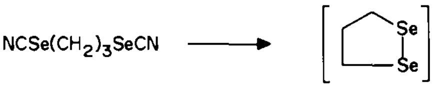
Y = O, Se (105)

(1)benzotellurolo(3,2-*b*)indole is obtained by an appropriate Fischer indole synthesis on telluroindoxyl[458].

B. Two Heteroatoms

1. Se/Te rings without nitrogen

a. Heteroatoms in the 1,2*-position.* (*i*) *Monocyclic systems.* 1,2-Diselenolanes can be considered as cyclic dichalcogenides and can be obtained by oxidative coupling of the intermediate dichalcogenols, prepared by suitable known methods. 1,2-Diselenolane (**246**) has been claimed to be prepared as a yellow powder by hydrolysis of propylene diselenocyanate (**245**)[50,487] (equation 106). Bergson and Claeson[488,489] have suggested that this powder is in fact a dimer or a polymer of **246** the existence of which has been

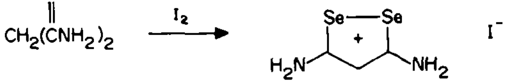


(106)

(245) **(246)**

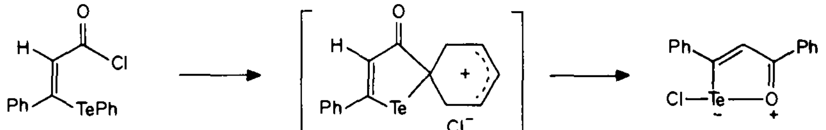
shown only in solution. The more stable 4,4-dimethyl, as well as the 4-methyl-4-phenyl[490a] and the 3,5-diethoxycarbonyl[489] derivatives are obtained by the same method. The 4,4-dimethyl derivative is oxidized by MCPBA at −45 °C to the corresponding mono Se oxide, a cyclic selenolseleninate ester, which gives ring opening at −20 °C[490b]. The 1,2-diselenolane system has also been prepared by sodium diselenide nucleophilic substitution of substituted propylene bromides, which give the 4-carboxy and 4,4-bis(hydroxymethyl) derivatives[489,491] or by debenzylation and oxidation of the corresponding dibenzylseleno ethers. A Se analogue of thioctic acid, i.e. a 3-*ω*-carboxybutyl derivative of **246**, is obtained by these two methods[489,491] and also by using potassium selenite and Se as nucleophiles[492]. The 4-carboxy[493] and 4-aminomethyl mixed 1,2-thiaselenolanes[494] are obtained by the debenzylation method. 3,4-Diphenyl-1,2-diselenol-5-one, recently prepared from diphenylcyclopropenone and selenoamides or NaHSe loses the two Se atoms with hydrazine, giving a corresponding pyrazolinone[495]. Reaction of 2-phenyl-1-diethylaminoethene-1 selenolate salt with CS_2 gives 3-diethylamino-4-phenyl-5-thioxo-1,2-thiaselenole, a ring which loses Se by reaction with dimethyl acetylenedicarboxylate[496]. 4,4-Dimethyl-1,2-oxaselenolane-2-oxide is obtained by H_2O_2 oxidation of 3,3-dimethylselenetane[53].

The first 1,2-diselenolylium system (**248**) was prepared by I_2 oxidation of malonodiselenoamide (**247**)[497] (equation 107). The 3,5-dimethyl analogue of **248** is obtained similarly from diselenoxoacetylacetone and a cobalt(II) salt[498,499]. 1,2-Oxaselenolylium cations are formed by protonation of 1,6-dioxa-6a-selenapentalenes[500]. The first 1,2-oxatel-



(107)

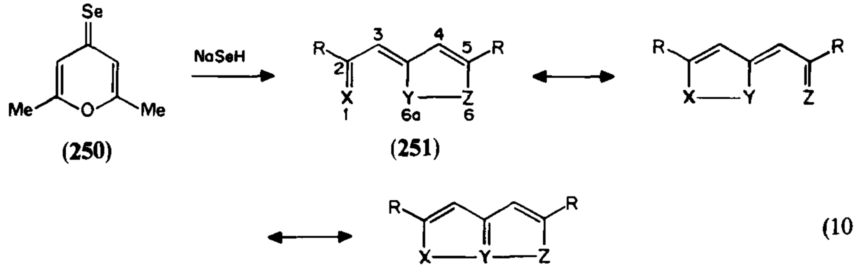
(247) **(248)**



(108)

(249) **(249a)**

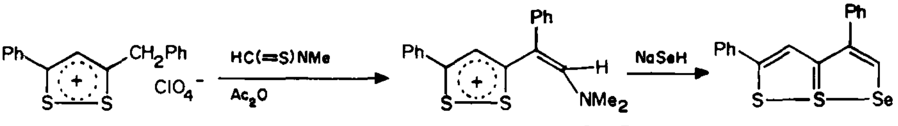
lurolylium system (**249a**) has been obtained by Lewis acid or thermal catalysed rearrangement of β-(phenyltelluro)cinnamoyl chloride (**249**) via *ipso* attack and Te—C aromatic ring-opening. Evidence for this structure has been obtained by X-ray and spectroscopic analysis[501] (equation 108).



(250) **(251)**

(109)

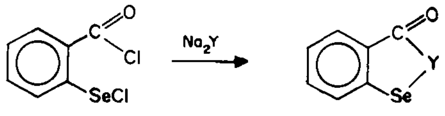
(*ii*) *Chalcogenapentalenes*. The selenapentalene derivatives **251** can be regarded according to their no-bond resonance hydrids, as derivatives of 1,2-oxaselenoles, 1,2-thiaselenoles or 1,2-diselenoles. An oxadiselenapentalene system (**251**; R = Me, Y = Z = Se, X = O) was obtained by reaction of 2,6-dimethylpyran-4-selone (**250**) with $NaHSe$[502] (equation 109); it was first incorrectly formulated, but its correct structure was suggested from X-rays[503] and proved[504]. Its formation was proposed to involve a ring-opening of the pyran system. When treated with P_2S_5, it gives a mixture of the corresponding thiadiselenapentalene (**251**; Y = Z = Se, X = S), and as major product the trans-chalcogen exchange product, the 2,5-dimethyl-1,6a, 6-dithiaselenapentalene (**251**; Y = Z = S, X = Se, R = Me). Similarly, thiopyran-4-selone and its 3,5-dimethyl and 2,6-diphenyl derivatives give with Na_2S and subsequent ferricyanide oxidation, a 1,6,6a-dithiaselenapentalene isomeric system (**251**; X = Z = S, Y = Se, R = H, Ph)[505]. 1,6,6a-Dioxaselenapentalene analogues (X = Y = O, Y = Se), precursors of the previously mentioned 1,2-oxaselenolylium cations, are obtained analogously from **250** and thallium (III) halides via a 4-thallioselenopyrylium salt[506a]. Recently, the 1,6,6a-dioxatellurapentalene was similarly synthesized[506b]. Another general route to selenapentalenes consists of the reaction of NaHSe with the Vilsmeier salt formed from the 1,2-dithiolylium salts **252** (equation 110)[507a]. Compound **253** is also obtained by P_2Se_5 selenation of the corresponding oxadithiapentalene[507b].



(252) **(253)**

(110)

(*iii*) *Condensed systems*. Some oxo derivatives of benzothiaselenole have been studied. 3-Oxo-2,1-benzothiaselenole **255a** and its diselenole analogue **255b** were prepared in 1924

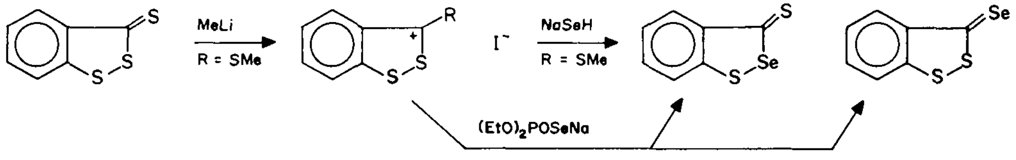


(254) **(255)**

(111)

(a) Y = S
(b) Y = Se

by Lesser's group from *o*-chloroselenobenzoyl chloride (**254**) (equation 111)[508]. The 1,2-benzothiaselenole isomer of **255a** is obtained by P_2Se_5 selenation of dithiosalicylic acid[509]. These systems sometimes give isomerization or chalcogen exchange reactions. Thus, thionation of **255b** gives the anomalous 2,1-benzothiaselenol-3-thione[510]. Its isomer **258** is obtained from **256** following equation (112)[511]; this reaction does not give the attempted selone isomer **259** as previously described[48,49]. However, with diethyl selenophosphate and the 3-chloro analogue of **257**, a mixture of 60% of **259** and 6.5% of **258** is obtained[511]. The 3-oxo analogue of **258** is obtained in 1.2% yield from dithiosalicyloyl dichloride and *p*-tolyl-SeMgBr[512a]. As another rearrangement example, **259** gives 3-diphenylmethylene-1,2-benzothiaselenole with diphenyldiazomethane[512b]. Another example of rearrangement is also given in Ref. 597.



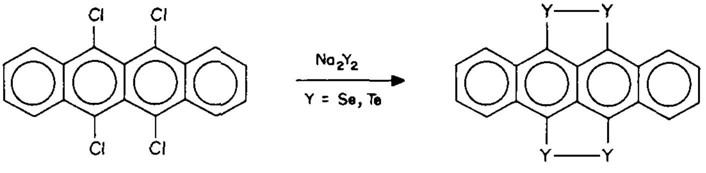
(256) **(257)** **(258)** **(259)**

(112)

1-Hydroxy-1-methyl-2,1-benzoxaselenol-3-one has been demonstrated to be a ring tautomer of *O*-methylselenobenzoic acid Se oxide[512c,d].

From 2-chloro-3-vinylquinoline and NaHSe 3-methyl-1,2-diselenolo(4,5-*b*)quinoline and a derivative with a dihydroselenophene ring were obtained[513,514].

Some *peri*-bridged 1,2-diselenoles or 1,2-ditelluroles have been prepared for use as π donor systems for the design of highly conducting organic metals. These systems may be principally obtained, either by sodium dichalcogenide nucleophilic substitution of the corresponding chloro compounds, or via organolithium reagents. By the first method 5,6:11, 12-bis(diseleno)tetracene (**261a**)[515] and 5,6:11, 12-bis(ditelluro)tetracene (**261b**)[516] were obtained from **260** (equation 113); also obtained were 1,9:4,10-bis(diseleno)anthracene[517] and 1,8:4,5-bis(diseleno)naphthalene[518]. **261a** was prepared

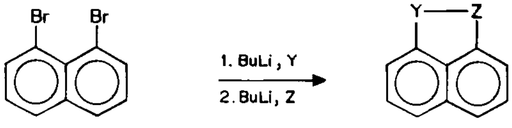


(113)

(260) **(261)**

(**a**) Y = Se
(**b**) Y = Te

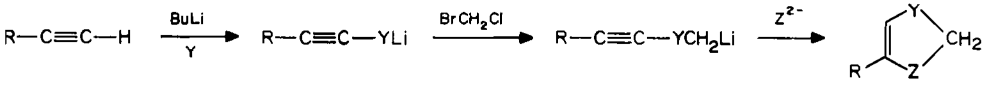
previously in low yield from 5,11-dichlorotetracene which is difficult to obtain[519]. On the other hand, a patented method from tetracene and Se could not be reproduced[515,520]. **261a** is an organoselenium π donor which gives an ion radical with metallic states below 30 K. Electrochemical data suggest that the Te analogue **261b** is more easily oxidized in solution than **216a**, a situation existing also in naphthalene 1,8-dichalcogenides[521]. These dichalcogenonaphthalenes **263**, both symmetrical (Y = Z = S, Se, Te)[521] or unsymmetrical (Y—Z=S—Se, S—Te, Se—Te)[522], and dichalcogenoacenaphthylene analogues[523] are obtained via organolithium compounds (equation 114). The unsymmetrical derivatives, obtained in very low yields together with the symmetrical impurities, are best isolated, when Y = S, from 1-chloro-8-mercaptonaphthalene, via the butyllithium method. One of the Se atoms in **263** (Y = Z = Se) and the two Te atoms in **263** (Y = Z = Te) are easily exchanged



(262) (263) (114)

with organolithium compounds[521]. In this series, S and Se derivatives exhibit similar conducting properties.

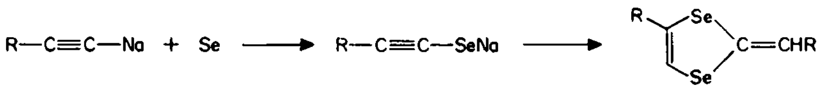
b. Heteroatoms in the 1,3-*position.* (*i*) 1,3-*Dichalcogenoles.* The first 1,3-oxaselenole derivatives were reported in 1978: 2,5-di-*p*-methoxyphenyl-2,4-diphenyl-2*H*-1,3-oxaselenole together with the corresponding 2-oxo derivative, was obtained from *p*-anisoyl α,α-dibromobenzyl ketone and potassium ethyl diselenocarbamate[524]; the 2-acetyliminio-5-cyano-*p*-substituted phenyl derivative[525] was obtained from the 2,2-dicyano-3-aryloxirane and potassium selenocyanate, and a tricyclic derivative was obtained by selenium dioxide oxidation of dimedone[526a]. New 1,3-oxaselenoles were recently obtained in this manner[526b]. A general synthesis of 1,3-dichalcogenoles (**264**) starts from alkynylchalcogenolates and bromochloromethane (equation 115) (R = Ph, *t*-Bu; Y = S; Z = S, Se, Te)[527]. This method has been applied to 1,3-ditelluroles (R = H, Me, *t*-Bu, Ph)[528]. Parent 1,3-ditellurole is lithiated in the 4-position by lithium diethylamide (LDA)[529]. On the other hand the 4-phenyl derivative gives products derived from lithiation in the 2-position, results parallel to those in the sulphur series.



(**264**)

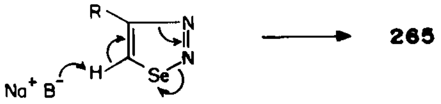
(115)

(*ii*) 1,4-*Dichalcogenafulvenes.* 1,4-Diselenafulvenes (**266**) are obtained by dimerization of alkynylselenols (**265**)[67] (equation 116). The corresponding 2,6-diphenyl -1,4-



(**265**) (**266**) (116)

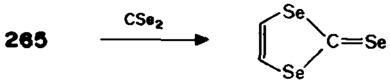
ditellurafulvene was claimed by Russian workers[66] to be obtained by a similar method, but their compound was in fact a ditelluretane system. By careful examination of the reaction Cava and coworkers isolated this 1,4-ditellurafulvene as a by-product among numerous other[64], and transformed it into nitroso and azo derivatives on the lateral carbon. Intermediates **265** have also been obtained by photochemical, thermal[530] or base-catalysed[68,531,532] transformations of monocyclic 1,2,3-selenadiazoles (**267**) (equation 117), and they are also dimerized to the corresponding fulvenes **266**.



(**267**) (117)

6,6-Dicyano- and diethoxycarbonyl-2,3-dihydroselenafulvenes can be obtained from ethylene triselenocarbonate, MeI and malononitrile[533] or diethyl malonate[534]. 1,4-Thiaselenafulvenes are prepared from 1,3-thiaselenole-2-thiones via a phosphonium derivative[535] or by reaction with ethyl diazoacetate[536]. The same thiones give 6-ethoxycarbonyl-6-aza-1,4-thiaselenafulvene with ethyl azidoformate[536]. 6-Phenyl-6-aza-1,4-thiaselenafulvene and 1,4-diselenafulvene are also prepared from **265** and phenylisothiocyanate[537].

(*iii*) 2-*Chalcogenoxo*-1,3-*dichalcogenoles*. 2-Oxo-, 2-thioxo- or 2-selenoxo-1,3-dichalcogenoles have been the subject of many publications, due to the fact that they can lead by coupling reactions to tetrachalcogenafulvalenes, the most popular π donors for designing organic metals. Several types of synthesis have been tested for their preparation. The first one, which leads finally to the parent tetraselenafulvalene (see following section), consists of treating **265** with carbon diselenide and leads to 2-selenoxo-1,3-diselenole

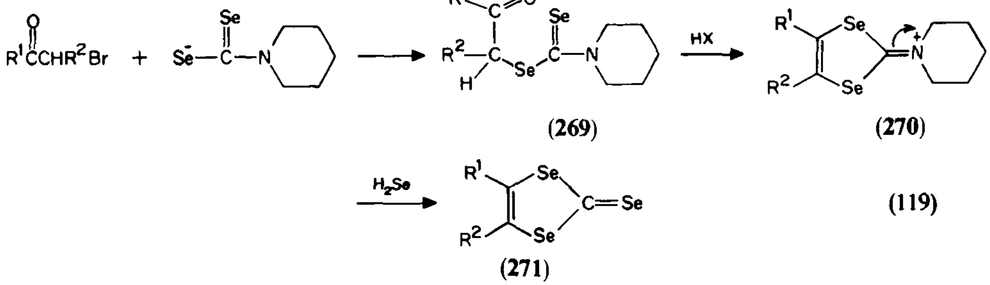


(268)

(118)

(268)[538,539] (equation 118). The reaction has been applied to the 4-phenyl derivative[540], which by P_4S_{10} thionation gives the 2-thioxo and subsequently the 2-oxo analogue. In fact, these reactions are applications of Mayer's synthesis of 4-phenyl-1,3-thiaselenol-3-thione, the first derivative of the series, from phenylacetylene, Se and carbon disulphide[541]. By reaction with mercuric oxide, Mayer obtained the 2-oxo analogue.

A second method for the synthesis of compounds of type **268** consists of the reaction of a diselenocarbamate ion with an α-bromoketone, followed by cyclization and subsequent thionation[542,543] or selenation with H_2Se ($R^1 = Me$, $R^2 = H$[542]; $R^1 = R^2 = Me$; $R^1 = Ph$, $R^2 = H$; $R^1 = R^2 = Ph$[543]; $R^1 = R^2 = CD_3$[544] (equation 119). The cyclization may be effected by H_2SO_4 or best by HBF_4[545]. One of the resonance forms of **270** is a diselenolylium cation. Modifications have been proposed to avoid the use of the very fetid CSe_2 which is a precursor to the diselenocarbamate ion. For example, this anion can be replaced by tetramethylselenourea[546]; when the method is applied to dimethylthiourea and H_2Se it gives trimethylene thiaselenol selone[546]. In another modification the diselenocarbamate ion can also be prepared from *N*,*N*-dimethylphosgeniminium chloride[547–549]. In the last reference the gaseous and toxic H_2Se is replaced by NaHSe obtained from Se and $NaBH_4$ in DMF, and the synthetic conditions are optimized. Since carbon ditelluride and tellurourea are unkown, and NaTeH or H_2Te reduce the phosgeniminium salt, application of this method to the Te series has been tentatively realized by forming vinyltellurothiocarbamate from a vinylmagnesium reagent, Te and a thiocarbamoyl chloride. The tellurothiocarbamate decomposed in the cyclization essays[550].

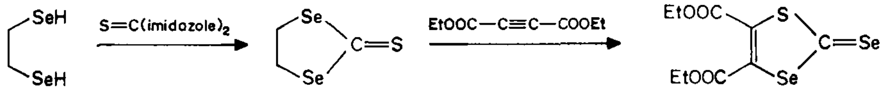


(269) **(270)**

(271)

(119)

A third method for the synthesis of compounds of type **271** consists of the dipolar addition of ethylene triselenocarbonate[551] or thiodiselenocarbonate (**272**) to dimethyl acetylenedicarboxylate[552,553] (equation 120). This reaction requires for a concerted

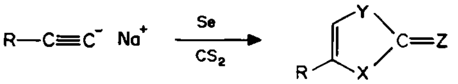


(**272**) (**273**) (120)

mechanism that the selone Se atom of the triselenocarbonate will be incorporated in the ring in the Se analogue of **273**[553]. Substituted **268** may also be formed by electrochemical reduction of CSe_2[554,555] giving after alkylation the 4,5-bis(methylseleno) derivative of **271**[554] and the 4,5-ethylenediseleno derivative[555]. 1,3-Benzothiaselenol-2-thione is obtained by heating 1,2,3-benzoselenadiazole with CS_2[556].

Condensed 2-thioxo-1,3-thiaselenole or diselenole systems can also be obtained from thiocarbonyl diimidazolide and 1,2-benzene diselenolate[557], from thiophosgene and the 2,3- and 3,4-thiophene diselenolate or 3-thiolate 2-selenolate[558]and from thiophosgene and *o*-bis(methylseleno)benzene or *o*-(methylseleno)thioanisole[559]. The last reaction failed for the methyltelluro analogues. The condensed benzo, 5,6-dimethylbenzo-[560] and 4*H*,6*H*-thieno-[561] selenoxo-1,3-selenoles are prepared by heating the corresponding condensed 1,2,3-selenadiazole with CSe_2. 1,3-Ditellurol-2-thione *C*-condensed on the thiophene ring has also been prepared[558b].

Some problems of chalcogen exchange can arise when two different chalcogens, especially S and Se, are used for the synthesis of analogues of **271**. When alkynylselenide anion is reacted with CS_2 five different heterocyclic compounds **274** are obtained, form an unexpected S–Se scrambling process (equation 121). This may arise either from an ambident anion obtained by deprotonation and ring-opening or from a rearrangement of the non-cyclic precursor[562]. After very difficult separations, the required



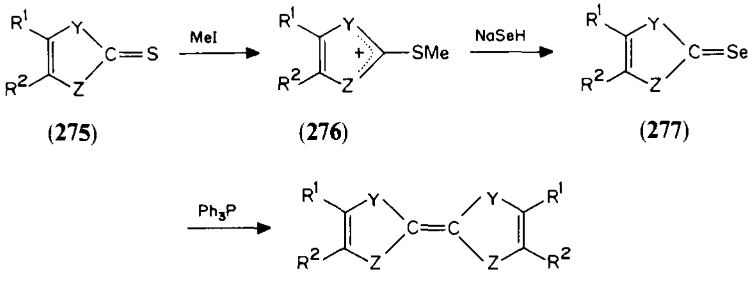
(121)

(**274**)

(**a**) Y = Se; X = Z = S; R = Me, Ph
(**b**) Y = X = S; Z = Se
(**c**) Y = S; X = Z = Se
(**d**) Y = X = Se; Z = S
(**e**) Y = X = Z = Se

274a is obtained in a 0.82% yield. A similar mixture results by using S and CSe_2. Compounds of type **274a** (R = aryl) are also obtained by treatment of the selenolate anion generated by base-catalysed fragmentation of 4-aryl-1,2,3-selenadiazoles with CS_2[563a]. When the reaction is applied to 1,2,3-selenadiazole itself, it gives under the usual conditions a low-yield mixture of the required thione **274a** (R = H) and its isomeric selone **274b**. Non-isomerizing conditions can, however, be found[552]. A fused system, an unstable 2,5-dipiperidinium-1,3,4,6-tetraselenapentalene, has been obtained from piperidinium *N*,*N*-pentamethylene diselenocarbamate and methyl dichloroacetate[563b].

(*iv*) *Tetrachalcogenafulvalenes.* The interest in the chemistry of the tetrachalcogenafulvalenes arose when it was demonstrated in 1972 that charge-transfer complexes of the π donor tetrathiafulvalene (TTF) and the acceptor tetracyanoquinodimethane (TCNQ) possessed remarkable high conducting properties[564,565]. Considerable interest arose in the preparation of a parallel series of tetraselenafulvalene (TSeF) systems. Interesting changes in physical properties were demonstrated by replacing S by Se[566] in TSeF/TCNQ salts. One of these complexes, hexamethylene TSeF/TCNQ, behaves as a semi-metal and becomes an insulator at low temperatures[567,568]. Recently, one salt of these derivatives (tetramethyl-TSeF)$_2$PF$_6$, was the first organic compound found to lose all resistance to



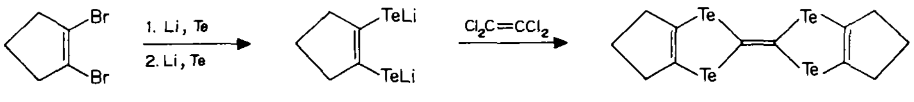
(275) **(276)** **(277)**

(278)

(122)

electric current around 1 K, showing superconductivity[569]. Now at least six $(TMSeF)_2X$ salts have been reported to be superconductors ($X^- = TaF_6^-$, SbF_6^-, AsF_6^-, PF_6^-, ReO_4^- and ClO_4^-), this last salt being the only simple pressure organic superconductor at 1.3 K[570]). The most common synthesis of tetrachalcogenafulvalenes is the coupling of the 1,3-dichalcogenol-2-thiones or -2-selones. Peracid oxidation of 1,3-diselenol-2-thione or -selone, a reaction working well in the dithiole chemistry, failed in the Se series[538,571], perhaps because oxidation on Se atoms took place. Coupling reactions were effected by triphenylphosphine or triethyl phosphite, and they work much better with the 2-selone than with the 2-thione[556]. Consequently, the selone will be preferentially prepared when the method used involves intermediary iminium salts (equation 119). When only the thione is available, it is interesting to transform it to the selone, via *S*-methylation to form a 1,3-dichalcogenolylium salt, and subsequent reaction with NaSeH or H_2Se (equation 122). One of the best methylating reagents is methyl fluorosulphonate[553,556]. The coupling reactions lead to the majority of the known tetraselenafulvalene derivatives **278** ($Y = Z = Se$): $R^1 = R^2 = H$[538]; $R^1 = Me$, $R^2 = H$[543]; $R^1 = R^2 = Me$[542,543,547–549]; $R^1 = Ph$, $R^2 = H$[543]; $R^1 = R^2 = Ph$[543]; $R^1 = R^2 = (CH_2)_3$[542,543,546–548]; $R^1 = R^2 = CD_3$[544]; $R^1 = R^2 = COOMe$[551]; $R^1 = R^2 = SeMe$[554]; $R^1R^2 = CH_2SCH_2$[561]. The method has been applied to dibenzotetraselenafulvalene[560,572a]. Surprisingly, the 4,5-ethylenediseleno derivative of **278** cannot be obtained by triethyl phosphite coupling of the corresponding selone, but it is obtained in 10% yield from the 2-oxo derivative[572b].

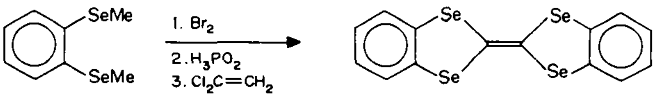
The tetramethoxycarbonyl derivative of **278** can be easily transformed to the parent compound by LiBr[551]. An unsymmetrical non-linear condensed diselenoleselone such as the dihydronaphtho (1,2-*b*) derivative, gives by coupling a mixture of *cis*- and *trans*-condensed TSeF[573]. Mixed thiaselenole derivatives **274** nearly always give unseparable mixtures of thermally stable *cis* (*Z*) and *trans* (*E*) geometrical isomers of coupled derivatives[553,556,574,575]. The parent *E*,*Z*-dithiadiselenafulvalene mixture was obtained by tetradecarboxymethylation. Unexpected S–Se interchanges were discovered by triethylphosphite coupling of 1,3-diselenol-2-thiones. For example **275** ($R^1 = R^2 =$ COOMe, CF_3; $Y = Z = Se$) gives a triselenathiafulvalene, instead of the attempted tetraselenafulvalene. The dimethyl derivative gives the scrambled and unscrambled product[576]. A few other methods were used for the synthesis of tetrachalcogenafulvalenes. So, tetratellurafulvalenes have been recently synthesized. The coupling method was unsuitable for their preparation due to lack of a method for preparing the corresponding



(279) **(280)**

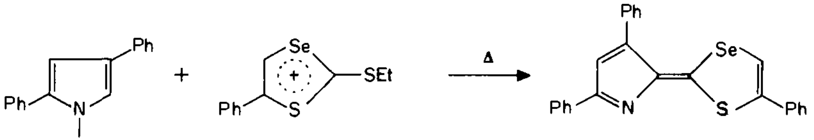
(123)

thiones or selones. The first two known Te derivatives were obtained from a suitable 1,2-ditellurolate ion and tetrachloroethylene (equation 123)[577]. This reaction could also lead to the bis-six-membered ditellurinoditellurin isomer, but structure **280** was proved by X-ray analysis[578]. The method has also been applied to dibenzotetratellurafulvalene[579]. A very easy preparation of dibenzotetraselenafulvalene (**282**) starts from the easily available *o*-bis(methylseleno)benzene (**281**)[559] and gives an overall 48% yield (equation 124).



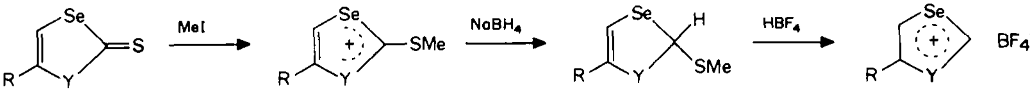
(281) **(282)** (124)

The surprising behaviour of vinylidene chloride is also shown in the preparation of tetra(methylseleno)ethylene from sodium methaneselenolate[559]. It seems that the mechanism involves an elimination step to an alkyne. Monosubstituted TSeF can be obtained from the parent compound via the 2-lithio derivative[580]. Recently, a one-step high-pressure synthesis of TSeF was realized from acetylene and a two-fold excess of carbon diselenide at 4500–5000 atm[581,582]. Some thiaselenafulvenes are also prepared from the thiaselenolylium salt **283** (equation 125)[583]. Some corresponding imidazoles can also be employed for this reaction.



(283) **(284)** (125)

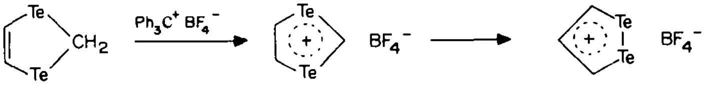
(*v*) 1,3-*Dichalcogenolylium salts.* 1,3-Thiaselenolylium and 1,3-diselenolylium salts are sometimes obtained as intermediates in the transformation of a thione to a selone group. These MeS-substituted cations **286** can be transformed to the relatively unstable parent cations **288** by successive NaBH$_4$ reduction and treatment with HBF$_4$[574] (equation 126). 2-Benzyl-4-phenyl-1,3-dioxolylium, 1,3-dithiolylium and 1,3-diselenolylium cations can also be obtained by trifluoroacetic acid protonation of 2,6-diphenyldichalcogenafulvenes[584]. NMR evidence indicates that the unsubstituted 1,3-ditellurolylium cation is formed by treatment of 1,3-ditellurole with the hydride acceptor triphenylcarbenium tetrafluoroborate. The unsubstituted cation **290** rearranges rapidly to the quite unstable 1,2-ditellurolylium cation, **291** (equation 127), which rapidly deposits Te. Substituted intermediates **290** are not detectable[528].



(285) **(286)** **(287)** **(288)**

R = H, Me
Y = S, Se

(126)



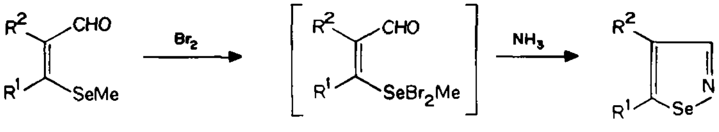
(127)

(289) **(290)** **(291)**

2. Nitrogen Se/Te rings

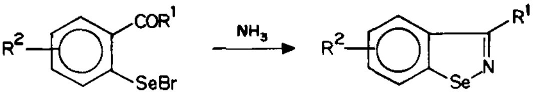
Se–N heterocycles have been reviewed three times in the last decade: twice by Bulka through 1970[585] and 1974[586] and once by Lalezari and Shafiee through 1976[587].

a. Heteroatoms in the 1,2-*position.* (*i*) *Isoselenazoles and condensed analogues.* The first known isoselenazole, 10-oxoanthra(9,1-*c,d*)isoselenazole, was synthesized in 1936 by reaction of NH_3 and Na_2Se with 1-chloroanthraquinone[588,589]. Preparation of isoselenazole itself, and its 3-methyl derivative from selenocyanic acid and acrolein or 3-butyn-2-one were mentioned briefly[590]. The first general synthesis of this ring system which includes the parent compound was achieved by the reaction of Br_2 and NH_3 under dry-ice conditions with *Z*-β-(methylseleno)acrolein derivatives (equation 128)[591]. These precursors are obtained either by reaction of sodium methaneselenolate on the product of Vilsmeier reaction on ketones or for the parent compound by addition of methaneselenol to propargylaldehyde, avoiding in this manner the use of the unstable selenocyanic acid. The following derivatives **294** were obtained: $R^1 = R^2 = H$; $R^1 = Me$, $R^2 = H$; $R^1 = R^2 = Me$; $R^1R^2 = (CH_2)_3$ or $(CH_2)_4$ (equation 128). Probable intermediate selenenyl bromides could never be isolated. The more stable corresponding benzeneselenenyl bromides **295** are in fact good precursors for the synthesis of 1,2-benzisoselenazole by the same methodology[591] (equation 129) (R^1 = H, Me, Ph, CH=CHPh, R^2 = H; R^1 = H, R^2 = 5-NO_2, 7-NO_2).



(292) **(293)** **(294)**

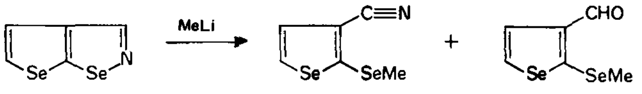
(128)



(295) **(296)**

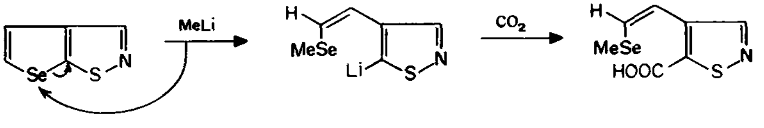
(129)

This method, previously used in the sulphur series for the synthesis of 5-nitrobenzisothiazole, has been extended to a general method of preparation of 1,2-benzisothiazoles. It has also been applied to the synthesis of pyrido(3,2-*d*)isoselenazole, of the three classical bicyclic thieno-condensed 1,2-selenazoles, i.e. the (3,2-*d*), (2,3-*d*) and (3,4-*d*) systems[423,424], of selenolo(3,2-*d*)isoselenazole[424], of its (2,3-*d*) isomer (7% yield) and also of the corresponding benzotricyclic systems: the (1) benzothieno- and (1) benzoselenolo-(3,2-*d*)isoselenazoles[425]. Condensed isoselenazoles can also be obtained by polyphosphoric acid cyclization of 2-(methylseleno)-3-oximinobenzo(*b*)-thiophene or -selenophene[425]. Isoselenazole can be nitrated in position 4, and brominated in positions 4 and 5. Thieno (2,3-*d*)isoselenazole is nitrated or brominated at the β-position of the thiophene ring, whereas its (3,2-*d*) isomer is α-brominated and nitrated to give a mixture of α- and β-derivatives. The parent benzo compound **296** ($R^1 = R^2 = H$) is nitrated and brominated in the homocycle in positions 5 and 7, dibrominated in the 4,5- and 4,7-positions and tribrominated in the 4,5,7-positions. No acylation products can be isolated[591]. Chichibabin reaction leads to the 3-amino derivative, whose structure has been confirmed by independent Curtius reaction on the 3-carboxy derivative. This acid has been prepared from the 3-carboxamide which was directly obtained by reaction of Br_2 and NH_3 with 2,3-dioxo-2,3-dihydrobenzo(*b*)selenophene, or from the 3-styryl derivative via ozonolysis to the corresponding 3-formyl derivative and oxidation[591]. Isoselenazoles behave towards organolithium compounds in the same manner as isothiazoles; they give concomitantly an eliminative R.O.I from the 3-carbanion, forming a *o*-(alkylseleno)nitrile, and a substitutive selenophilic R.O.II, with rupture of the Se—N bond and formation, after hydrolysis, of the corresponding aldehyde[591]. Even in fused bicyclic[423] or tricyclic[425] '*cis*-condensed' selenoloisoselenazoles **297**, the isoselenazole ring is regiospecifically opened (equation 130), giving the nitrile **298**, the aldehyde **299** and products of metal–Se interconversion.

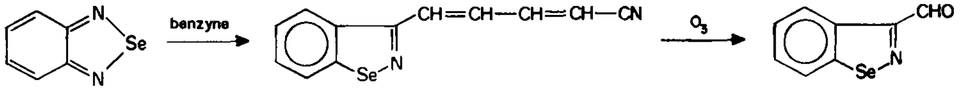


(297) **(298)** **(299)** (130)

Regiospecific ring-opening of the selenophene ring occurs only in selenophenes '*cis*-condensed' to isothiazole (equation 131), as well as in the bicyclic and the tricyclic systems[423,425]. Compound **300** is prepared from the 2-(methylthio)-3-oximinoselenophene[423]. An interesting addition of benzyne across the C=N—Se group of 2,1,3-benzoselenadiazole is accompanied by rearrangement to **304**, whose structure was confirmed by ozonolysis to the known 3-formyl-1,2-benzisoselenazole (**305**)[592] (equation 132).



(300) **(301)** **(302)** (131)



(303) **(304)** **(305)**

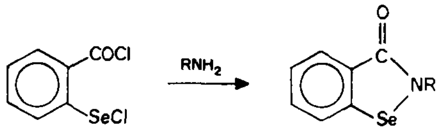
(132)

The 5,6-dimethyl analogue of adduct **304** gives a thermal rearrangement to 4,5-dimethyl-2-(*o*-selenocyanophenyl)pyridine[593]. A corresponding adduct of naphthoselenadiazole with dimethyl acetylenedicarboxylate rearranges similarly to 3-(2',3'-dimethoxycarbonyl-4'-cyano-1'-naphthyl)benzisoselenazole[594]. 2-(Selenocyano)-benzophenone or -acetophenone gives by treatment with $NH_2OH \cdot HCl$ the corresponding 3-phenyl- or 3-methyl-*N*-oxide of benzisoselenazole. With phenylhydrazine and a trace of acetic acid, this acetophenone gives, probably via a Fischer cyclization, the known benzoselenolo(3,2-*b*)indole[446].

An isoselenazolo(4,3-*d*)pyrimidine is obtained by SeO_2 oxidation of 5-amino-6-methyl-3-phenyl-4-(3*H*)-pyrimidine[595].

(*ii*) *Isoselenazolium salts.* Liebscher and Hartmann realized a one-pot synthesis of 5-arylisoselenazolium salts from alkali selenocyanates and *N*,*N*-dimethyl-3-chloro-3-aryl-2-chloropropeniminium salts[596]. 3-Chloro-1,2-benzisoselenazolium salts can be prepared from PCl_5 and *o*-(methylseleno)-substituted benzamides or benzisoselenazolinones[597]. They are hydrolysed to benzisoselenazolin-3-ones, thiolysed by thioacetic acid to 3*H*-*N*-methylimino-2,1-benzothiaselenoles and ammonolysed to 3-substituted amino-1,2-benzisoselenazoles. The 3-methyliminobenzothiaselenole is rearranged in DMSO solution to the 2-methylbenzisoselenazolin-3-thione isomer. The *N*-ethoxycarbonylbenzisoselenazolium salt can be obtained by quaternization of benzisoselenazole with ethyl chloroformate[598].

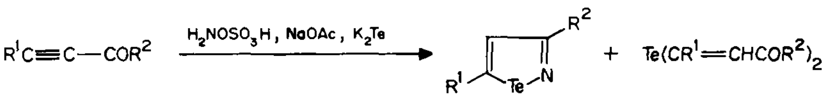
(*iii*) ***Benzisoselenazolinones.*** The first synthesis of benzisoselenazolin-3-ones (**305a**) was achieved in 1924 from *o*-chloroselenobenzoyl chloride[599] and NH_3 or amines RNH_2(R = Me, Et, Ph) (equation 133). They can also be prepared from 3-chlorobenzisoselenazolium salts[597] and by reaction of Br_2 with *o*-methylselenobenzamides. The parent compound is also obtained from *o*-bromoselenobenzamide[597] and by ammonolysis of ethyl *o*-cyanoselenobenzoate[600]. Their modes of preparation, for pharmaceutical purposes, are summarized in a recent patent[601]. The parent compound can be *N*-acetylated by acetic anhydride. Treated by potassium acetate and acetic anhydride this reaction leads to three different types of products: 3-acetylaminobenzo(*b*)selenophene, 3-acetoxybenzo(*b*)selenophene and its transformation products and 2-carbamoyl-3-hydroxybenzo(*b*)selenophene. The last compound is probably formed via the seven-membered ring 2*H*,4*H*-3,5-dioxobenzo(*b*)selenazepine, since its 4-methyl derivative was isolated in a parallel transformation of *N*-methylbenzisoselenazolinone[602]. A Se analogue of saccharin, which can be regarded as a Se-dioxide of benzisoselenazolin-3-one, was claimed to be obtained by $KMnO_4$ oxidation of 2,2′-dicarbamoyldiphenyl diselenide, followed by a crystallization in HCl solution[603]. This compound was in fact *o*-carboxybenzeneseleninic acid, which was also obtained by HCl treatment of an oxidation product of benzisoselenazole. Chemical and X-ray determination of the structure of this oxidation product showed that it is the monohydrate of the ammonium salt of *o*-carboxybenzeneselenonic acid[604]. HCl acts in fact as a reducing agent of the selenonic acid.



(133)

(305a)

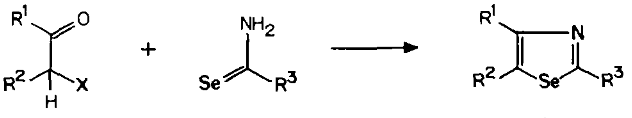
(*iv*) *Isotellurazole and derivatives.* The first known compound having this ring system was 1,2-benzisotellurazole, prepared in 1978 from *o*-bromotellurobenzaldehyde, by a reaction analogous to that described for the Se derivative in equation (129)[605]. It was also obtained by polyphosphoric acid ring-closure of *o*-butyltellurobenzaldoxime. Reaction with MeI gives *N*-methyl-1,2-benzisotellurazolium iodide. Compared with the Se analogue, 1,2-benzisotellurazole presents a higher melting point and a lower solubility. These two anomalies are related to particular crystallographic properties which show very short (2.4 Å) Te...N intermolecular contacts[606]. Thienoisotellurazoles could not be obtained by this method[423]. Monocyclic 3-substituted isotellurazoles **307** were recently obtained in 5–10% yields, from alkynyl ketones **306**, hydroxylamine-*O*-sulphonic acid, sodium acetate and K_2Te together with the by-products telluro-bis-alkenyl ketones (equation 134) (R^1 = H, Me, Ph; R^2 = Me, Et, Pr). The method failed for the corresponding aldehydes (R^2 = H), and it gave instead tellurobis(alkenenitriles) via an elimination reaction of the intermediate *O*-sulphonated oximes[607].



(306) **(307)**

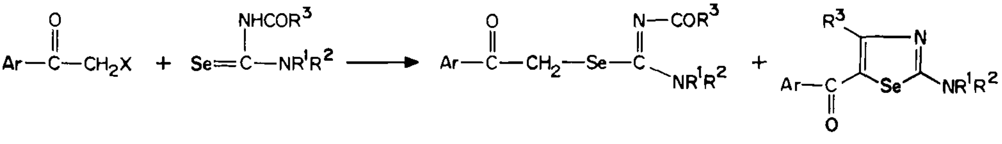
(134)

b. Heteroatoms in the 1,3-*position.* (*i*) *Monocyclic selenazoles.* In addition to other reviews mentioned in the beginning of this chapter, a review covering the state of monocyclic selenazole chemistry was published by Bulka in 1963[608]. Monocyclic selenazoles are almost exclusively obtained by an extension of the Hantzsch synthesis of thiazoles, presented in a general form in equation (135).



(308) **(309)** **(310)** (135)

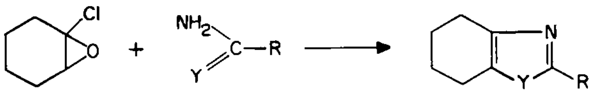
The selenazole ring was reported for the first time in 1889 by Hofmann[609], a student of Hantzsch. All the variants of this reaction are achieved by a convenient choice of the groups R^1, R^2 and R^3. The choice of R^3 determines the substituent in position 2. Starting from primary aliphatic or aromatic selenoamides, 2-substituted, 2,4-disubstituted and 2,4,5-trisubstituted selenazoles (2-Me[609,610], 2,4-di-Me[610,611], 2,4,5-tri-Me[610], 2-Me-4-Ph[610,614], 2-Et-4-Me[610], 2,4-di-Ph[609,614], 2-Ph-4-Me, 2-Ph-4-Me-5-COOEt, 2-Ph-4-Me-5-COOH[609], 2-(-2′ or -3′-furyl, -thienyl and -selenienyl)[188,612,613] and their 4′-chloromethyl and 4′,5′-diethoxycarbonyl derivatives) were obtained. Some recent 2,4-disubstituted selenazoles with $R^3 = CH_2Cl$, Me, Ph and $R^2 = 4\text{-}XC_6H_4$($X = H$, Me, Cl, Br), 3,4-$Me_2C_6H_3$, 2-thienyl[614] were obtained by this method. Since the primary selenoamides are very unstable, a mixture of a nitrile and H_2Se in the presence of condensation catalysts was used[610]. 4-Methylselenazole, one of the sole selenazoles unsubstituted in the 2-position, was obtained from hydrogen cyanide but in a yield of only 2.5%[610]. The parent selenazole still remains unknown. Starting from selenourea ($R^3 = NH_2$), Hantzsch reactions give 2-aminoselenazole derivatives (unsubstituted[609,615,616], 5-Me and 5-Et[615,616], 4-Me[609,616–618], 4-Et, 4,5-di-Me and 4-*t*-Bu[617], 4- and 5-COOEt[619], 4-CH_2Cl, from which was obtained *β*-(2-amino-1,3-selenazol-4-yl)alanine[620] and 4-formylselenazole by Sommelet's reaction[621], 4-Ph[609,616–618,622] and some 4-aryl, 4,5-di-Ph, 4-Ph-5-Me or 4-Me-5-COOEt derivatives[622], 4-aryl-5-carboxymethyl[623]), 2,2′-diamino-4,4′-biselenazolyl[617] and 2′-amino-4-selenazolyl derivatives of cephalosporines[624]. 2-Alkylamino-[625,626] 2-arylamino-[627,628], 2-dialkylamino-[625,626], 2-benzamido- or 2-acylamino-selenazoles[585] can be prepared by using the corresponding *N*-substituted selenoureas. The 2-benzamido derivative can be easily hydrolysed to the 2-aminoselenazole, thus avoiding the use of unsubstituted selenourea and its preparation from the toxic H_2Se. The condensation of *N*′-benzoyl *N*-monosubstituted selenoureas gives the non-tautomerizable 2-(benzoylimino)-3-phenyl selenazolines following Hantzsch reaction, whereas the corresponding *N*-disubstituted selenoureas give selenazoles **312** by ring-closure on the C=O amide, the usual type of ring-closure being hindered by the absence of the necessary hydrogen on the second nitrogen[629] (equation 136). Reaction of α-halonitriles with selenourea leads to 2,4-diaminoselenazoles[630,631]. 2-Hydrazinoselenazoles[632,633] are obtained by the Hantzsch synthesis from acetone or benzaldehyde selenosemicarbazones, after hydrolysis of the 2-



(311) **(312)**

(136)

selenazolylisopropylidene or benzylidene hydrazones[632,633]. Arylidene hydrazones give 2-selenazolyl formazans by coupling with diazonium salts[634]. 2-Hydrazinoselenazoles show the typical properties of arylhydrazines, by being reducing agents and by giving 2-selenazolyl pyrazolones with keto esters[635]. Coupled with *p*-nitrosodimethylaniline, these pyrazolones give a series of azomethines tested as dyes for photography[635]. Similar Hantzsch reactions with 4-phenylselenosemicarbazones and 4-phenyl-1-acylselenosemicarbazides were studied by Polish workers[636–638] and gave substituted 2-imino-Δ^4-selenazolines. Very few other syntheses of the monocyclic selenazole ring have been published. Among them, a recent reaction which formally belongs to the Hantzsch reaction, starts from primary thio- or seleno-amides and 2-chlorooxiranes and gives 4, 5-tetramethylene- (equation 137) and 4-isopropyl-selenazole[639]. Bis-2′-(4′-dimethylcarboxamido-5′-dimethylamino)selenazol, whose structure has been determined by X-rays, is obtained by a specific reaction between carbon diselenide and 2*H*-2-dimethylcarboxamido-3-dimethylaminoazirine[640]. Using other azirines, such as 2*H*-2-phenyl-3-dimethylaminoazirine or the 2,2-dimethyl analogue gives, respectively, 5*H*-5-phenyl-4-dimethylaminoselenoazoline-2-selone and 4,4-dimethyl-2-selenoxo-5-selenazolidinone[640].

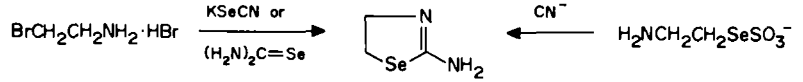


(313) (314)

(137)

Electrophilic nitration[641], nitrosation[642], sulphonation[641] and diazonium coupling[625] of selenazoles are directed to the 5-position. Nitration gives, however, additional complex reactions[586]. Halogenation sometimes gives unstable compounds except with the 2-acylamino derivatives, where the 5-bromo derivative is stable[586]. Acylation and Gattermann formylation failed. Nucleophilic amination failed on 4-methylselenazole, which was the only 2-unsubstituted derivative for a long time. Unsuccessful attempts[616,641] were made to obtain 2-unsubstituted derivatives from 2-aminoselenazoles via a diazotation reaction. Diazotation of 2-amino-4,5-diphenylselenazole, gives coupling to an azo compound, which decomposes on standing to a 2-hydroxy derivative, which gives the 2-chloro derivative with phosphorus oxychloride and the 2-hydrazino derivative with hydrazine hydrate. From the 2-chloro derivative and thiourea the corresponding 2-mercapto analogue is obtained, and this gives 4,5-diphenylselenazole with H_2O_2. This 2-unsubstituted derivative is more easily obtained by oxidation of the 2-hydrazino derivative by use of mercuric oxide, copper(II) salts or silver oxide. The corresponding 2,2′-azoselenazole can also be obtained. Recently, the first successful Sandmeyer–Schiemann reaction on a selenazole ring was realized although in a low yield, when 2-amino-5-acetoxyethyl-4-methylselenazole reacted with nitrosonium tetrafluoroborate, NaF and HBF_4[643]. The reactivity of a 2-Me group on selenazole is higher than that of the 4-Me group. Thus, 2,4-dimethylselenazole gives selectively the 2-styryl derivative and is oxidized by SeO_2 to an unstable 2-carboxy-4-methylselenazole. This acid, as in the thiazole series, decarboxylates easily, giving 4-methylselenazole[585]. Selenazoles are easily quaternized on the nitrogen. The formed selenazolium salts add methoxide ion to the 2-position but they lose Se, forming imidazolium salts, on reaction with anilines[644].

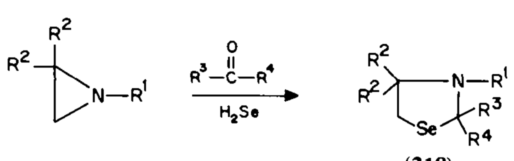
(*ii*) *Selenazolines and selenazolidines.* 2-Methyl-Δ^2-selenazoline has been obtained in several different ways: by phosphorus pentachloride ring-closure of bis-(2-acetylaminoethyl)diselenide[645], by reaction of selenoacetamide with **315**[646] and by treatment of acetamidoethanol with P_2Se_5[647]. Other 2-alkylselenazolines are obtained in a similar manner[648]. 2-Amino-Δ^2-selenazoline (**316**) is prepared from **315** and potassium



(315) (316) (317) (138)

selenocyanate[649] or selenourea[650], or from **317** and cyanide ion[651] (equation 138). **316** ring-opens easily by alkaline or H_2S medium, giving bis-ureo- and thioureo-ethyl diselenide by air oxidation.

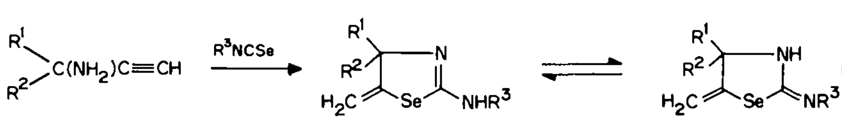
The selenazolidine systems **318**, including the parent compound, are obtained by treating aziridines and aldehydes or ketones with H_2Se (equation 139). In some cases, the intermediary aziridinylmethanols or β-selenomercaptoethylamines ($H_2NCH_2CH_2SeH$) can also be used. In this way various 2-alkyl, dialkyl, aryl and some *N*-substituted derivatives (R^1 = H, Me, Ph) are obtained[652]. Starting from unsymmetrical aziridines, 4-methyl- and 4,4-dimethyl- selenazolidines are prepared[653]; in the same manner 4-carboxy



(139)

(318)

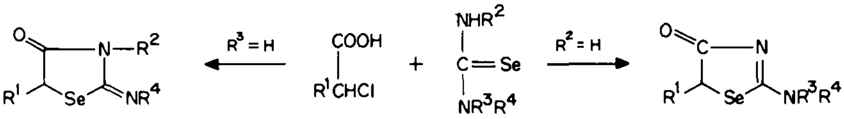
or 4-carboxy-5,5-dimethyl derivatives are obtained from selenocysteine and selenopenicillamine, respectively[654]. By the same method a selenaproline is also obtained[655]. Carbonyl exchange reactions in this selenoaminal system occur easily. Selenazolidines can be *N*-acylated in pyridine solution. Benzoylation in alkali medium gives hydrolysis of this acetal-like system, forming *Se*,*N*-dibenzoylselenoethylamine derivatives. Although 2-phenylthiazolidine gives mainly *N*-methyl-2-phenylthiazolidine by reaction with MeI, 2-phenylselenazolidine gives a product of *Se*-methylation of the chain tautomer[656]. Selenazolidine-2-selones can be obtained by reaction of CSe_2 with aziridine[657]. The corresponding 2-thiones have been prepared from β-chloroethylisothiocyanate and NaHSe[658]. The 2-benzyliminoselenazolidine system **321** ($R^3 = PhCH_2$) is obtained by condensation of benzylisoselenocyanate with the appropriate aminoacetylenes **319**, whereas aryl isoselenocyanate gives the 2-arylaminoselenazoline tautomeric structure **320**[659].



(140)

(319) (320) (321)

A similar tautomerism between aminoselenazoline and iminoselenazolidine exists in the 4-oxo derivatives. These are prepared by an adaptation of the Hantzsch reaction between α-halogeno acids and selenourea[626,660–663]. The tautomerism has been investigated by comparison with systems where only one tautomer can exist. The isomers **323** and **322** are obtained by using *N*,*N*-disubstituted and *N*,*N'*-disubstituted selenoureas,

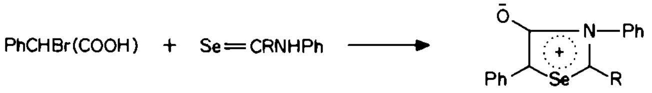


(141)

(322) (323)

respectively (equation 141). The corresponding 2-alkylidene hydrazones are obtained by a similar reaction starting from selenosemicarbazones[664,665]. Generally, the chemistry of the tautomeric compounds is consistent with reactions of the 2-iminoselenazolidine form **322**, which gives easy hydrolysis without ring-opening to the 2,4-dioxoselenazolidine system, *N*-iminobenzoylation, condensation on the 5-CH_2 group with aromatic aldehydes[666] and *N*-iminoureation with isocyanates[667]. However, phenyl isothiocyanate gives reaction on the 3-nitrogen. Similarly, 2,4-selenazolidinediones are also stable and give normal Mannich products on N[667] and *N*-methylation[668–670]. In contrast, the 4-thioxo derivative, obtained by thionation of the 2,4-dione, ring-opens with hydrazine to give a 3-selenomercaptomethyl-5-oxo-2-pyrazolinone. Numerous 2-thioxo-4-oxoselenazolidine isomers are described in the patent literature, from selenomercaptoacetic acid and thiocyanates[585]. Among the selenazolidine selones, 4,4-dimethyl-5-oxo-selenazolidine-2-selone is obtained from CSe_2 and 3,3-dimethyl-2-dimethylaminoazirine, via a ring-opening[640].

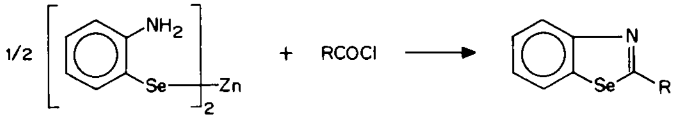
(*iii*) *Mesoionic selenazoles.* Treating α-halo acid derivatives with *N*-substituted selenobenzamides, in a Hantzsch reaction, gives mesoionic selenazoles. The first derivative of this series (**324**) was obtained by Cava and Saris in 1975[671] (equation 142); **324** acts as a dipolarophile towards methylacetylenedicarboxylate and gives a pyridone with a loss of Se. The same reaction has been applied to a number of derivatives of variable stability[672,673]. The derivative with R = SMe gives 3,5-diphenylselenazolidine-2,4-dione easily[672].



(142)

(324)

(*iv*) *Benzoselenazoles.* The most general synthesis of benzoselenazoles uses the reaction of the zinc salt of *o*-aminobenzeneselenolate (**325**) with acid chlorides (equation 143). In this way are obtained 2-alkyl-[672–677], 2-aryl-[676,678,679] (and among them the 2-Ph derivative, the first example of the series in 1913[680]) and 2-hetaryl-benzoselenazoles **326**[679]. Bis(2,2′-benzoselenazolyl) alkanes are formed from acid dichlorides[676] and the parent compound (R = H) is prepared from formic acid[674,676,681].

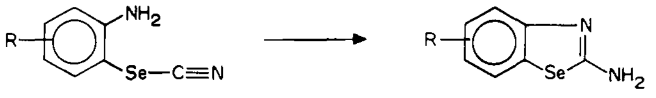


(143)

(325) **(326)**

Cyclic anhydrides react with one equivalent of **325**, and give benzoselenazolyl-alkane arene- or -heteroarene(pyridine)-carboxylic acids[682]. A recent alternative of this method, which uses protected selenide, starts from *o*-methylseleno-acyl- or -aroyl-anilides and phosphorus oxychloride[683] and gives **326** (R = H, Me, Ph, COOEt, COPh). Interestingly, 2-functionalized benzoselenazoles can be obtained in this manner. 2-Substituted benzoselenazoles can also be prepared by rearrangement reactions instead of benzisoselenazole isomers; e.g. 2-methylbenzoselenazole is obtained by polyphosphoric acid cyclization of *o*-methylselenoacetophenone oxime, in a Beckmann rearrangement[605]. From a benzyne addition to 3,4-dimethyl- or 3,4-diphenyl-1,2,5-selenadiazoles, Bryce and coworkers isolated 2-methyl- and 2-phenyl-benzoselenazole, respectively, in yields of

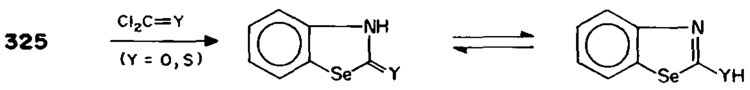
1–2%[684]. 2-Aminobenzoselenazole (**328**; R = H) and substituted derivatives can be obtained by Br_2[685,686] or H_2O_2[687] oxidation of various 1-phenyl-2-selenoureas or from cyclization of *o*-aminoaryl selenocyanates (**327**)[688] (equation 144).



(327) **(328)**

(144)

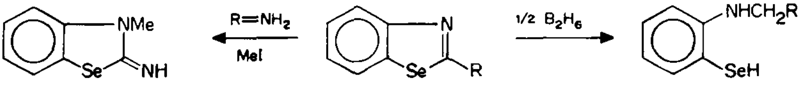
2-Hydroxy- and 2-mercapto-benzoselenazoles **329** (Y = O, S) can be prepared directly from **325** and phosgene or thiophosgene[685] or from bis(*o*-aminophenyl) diselenide, by reaction with ethyl chloroformate or CS_2, respectively[685,689] (equation 145). 2-Mercapto- and 2-selenomercapto-benzoselenazole can also be obtained via a diazotation of the 2-amino group, which behaves typically as an aromatic amine. The 2-chloro derivative, obtained from a Sandmeyer reaction, is easily converted by nucleophilic substitution to the 2-OH[685], 2-SH, 2-SeH[690] and 2-hydrazino groups[691]. The SH and SeH groups can be transformed to the corresponding thio or seleno ethers[690,692,693]. These compounds are described in the patent literature as vulcanization accelerators. Direct attachment of a substituent to the free 2-position is not documented. Nucleophilic amination failed[674,676]. Benzoyl chloride in the presence of KCN gives a ring fission[674], as in benzothiazole. The H/D base-catalysed exchange, measured for the three O, S, Se congeners, gives the relative k_h values of 20:1:4, respectively, a sequence different from that for benzoselenophene and its analogues[316], but similar to that of nucleophilic substitution on furan and its congeners. However, this ratio could not be rationalized by the same arguments.



(329)

(145)

Among the electrophilic reactions, halogenation gives undefined products[676] and although no Friedel–Crafts reactions have been described, mild nitration gives the 6-nitro derivatives[674,678]. Like the 2-chloro group, the 2-Me group is also activated, giving styrenes with aromatic aldehydes[674,676,694], and the 2-formyl derivative by a three-step reaction with chloral[695], by SeO_2 oxidation[696] or by a Kröhnke reaction via the 2-bromomethyl derivative[697]. The 2-carboxylic acid, obtained as a by-product[695] or by further oxidation of the aldehyde, decarboxylates easily upon melting[698]. An interesting ring-contraction with rearrangement was surprisingly demonstrated during the SeO_2 oxidation in pyridine of 3-phenyl-2*H*-1,4-benzothiazine and selenazine, giving 2-benzoylbenzo-thiazole and selenazole[598]. Benzoselenazole gives benzoselenazolium salts easily[699]. The rate of methylation is controlled by the inductive effect of the chalcogen, and the values of logk_{rel} correlate well with the pK_a of azoles. Methylation of the 2-amino derivative **328** (R = H) gives the 2-imino-3-methyl-2,3-dihydrobenzoselenazole (**330**)[685,690]. Its isomer, 2-(methylamino)benzoselenazole, is obtained directly by oxid-

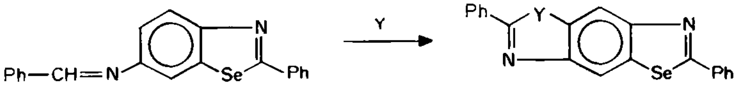


(330) **(331)** **(332)**

(146)

ation of 1-methyl-3-phenylselenourea[685]; **330** is easily hydrolysed to 2-oxo-3-methylbenzoselenazolinone. The easy conversion of benzoselenazolium salts to benzoselenazolines is important, because these last compounds are key substances for the synthesis of cyanine dyes. They cannot be obtained by direct reduction of benzochalcogenazoles. For example, the reaction of diborane with **331** leads to *N*-alkyl-*o*-selenomercaptoanilines (**332**) via a benzoselenazaborole[700] (equation 146). This reduction is similar to those in the oxygen and sulphur series. Benzothiazole, quaternized by a —$(CH_2)_2Cl$ group, leads in basic medium to ring-expansion in 4-formyl-2,3-dihydro-1,4-benzothiazine[701]. Similar ring-expansions are successful with other halide groups. An example of application for a benzoselenazolium derivative will be described in Section VII.A.

(*v*) *Other condensed selenazoles.* Two naphthoselenazole ring systems are known. 2-Acetamidonaphtho(1,2-*d*)selenazole is obtained by cyclization of 4-phenyl-2-amino-5-(carboxyethyl)selenazole with acetic anhydride[623]. The 2-amino derivative of the (2,1-*d*) analogue is prepared by a reaction similar to equation (144), from 1-cyanoseleno-2-aminonaphthalene[685]. Other condensation derivatives on the benzene ring of benzoselenazole have been described. By heating **333** with S or Se, respectively, a thiazole or a second selenazole ring is fused on the (*f*) bond, giving **334a** and **334b**[702] (equation 147).

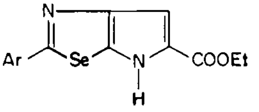


(147)

(333) **(334)**

(**a**) Y = S
(**b**) Y = Se

By a Doebner–Miller reaction on 6-amino-2-methylbenzoselenazole, 2,7,9-trimethylselenazolo(5,4-*f*)quinoline was obtained[703]. The corresponding 6-hydrazino-2-methylbenzoselenazole gives by successive condensation with cyclohexanone and dehydrogenation with chloranil 2-methylcyclohepta(4,5)-pyrrolo(3,2-*f*)benzoselenazole, an aza-azulene derivative[704]. Among heterocondensed systems on the selenazole ring some are condensed on the 4,5-bond. (2′-Thienyl and selenienyl)-2-selenazole analogues of phtalazine have been obtained by reaction of hydrazine on the previously mentioned diester[613]. 2-Aryl-5-(ethoxycarbonyl)pyrrolo(3,2-*d*)selenazole (**335**) has been obtained by constructing the pyrrole ring on the selenazole ring via the corresponding 3-chloromethyl- → 3-formyl- → 3-azidovinyl-selenazole[705].



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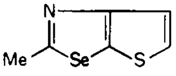
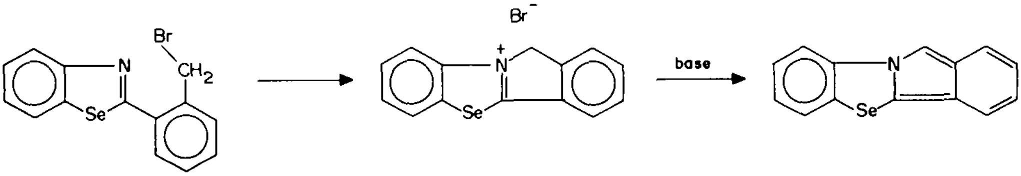


(336)

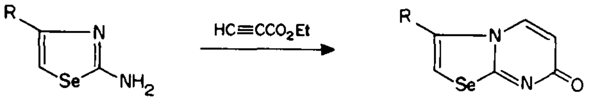
In contrast, the 2-methylthieno(3,2-*d*)selenazole system (**336**) has been synthesized from the thiophene ring, via the ring-closure of 3-acetylamino-2-acetylselenothiophene[419]. However, an attempted cyclization of 2-amino-3-acylselenothiophene failed to give the (2,3-*d*) isomer[412]. On the other hand, some selenazoles are condensed on the 2,3-bond, giving a nitrogen common to two rings. Nearly all these systems are obtained by starting from selenazole derivatives. Some 2-bromoalkyl- or 2-bromomethylaryl-substituted benzoselenazoles (**337**) give intramolecular quaternary salts of type **338**, which lead with bases to isoindolo(1,2-*b*)benzoselenazole (**339**) or its pyridopyrrolo analogue[706] (equation 148).



(337) **(338)** **(339)**

(148)

The selenazolopyrimidine system **340** is obtained by reaction of 2-amino-4-substituted selenazoles with ethyl propiolate[619] (equation 149). The Se in the ring of the levamisole analogue **341** is part of an imidazo(2,1-*b*)selenazole system[192a,707,708]. Selenazolo-*s*-triazine systems **342** (R = Ph, Y = NPh) are prepared by reaction of phenylisothiocyanate with *N*-phenyl-*N*′-(2-selenazolyl)thiourea. Reaction of 2-aminoselenazoline and ethoxycarbonyl isothiocyanate, gives **342** (R = H, Y = O)[709]. Selenazolo(3,2-*b*)-*as*-triazines **343** can be obtained from 6-substituted 2,3,4,5-tetrahydro-*as*-triazin-5-one-3-selone, ethyl bromoacetate and acetic anhydride[710]. Condensation of 2,4-diamino-5-phenylselenazole with ethyl ethoxymethylenecyanoacetate gives tricyclic polyaza systems bearing a selenazole ring[631]. 2-Methylbenzoselenazole can be condensed with malonic ester to give a tetracyclic benzoselenazolo(3,2-*a*)pyridine[711], and with 2 moles of ethyl acetylenedicarboxylate to give a selenazolo(3,2-*a*)azepine derivative[712]. Benzoxepino- and benzothiepino-(3,4-*d*)selenazoles are prepared from 2-aryl-4-(chloromethyl)selenazoles[713].



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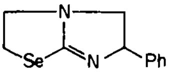

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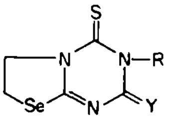

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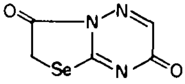
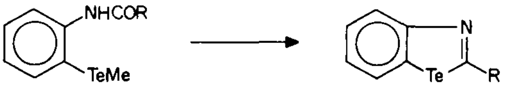


(343)

(*vi*) *Tellurazoles.* No derivative of the tellurazoles ring was known until 1983. The laboratory of Liège succeeded very recently in preparing the first five derivatives of the benzotellurazole ring, including the parent compound itself (**345**; R = H, Me, Ph, COOEt, COPh) (equation 150)[683]. They are obtained in low yields from *o*-(methyltelluro)-anilides **344** by a method which is also applicable to benzoselenazole derivatives.



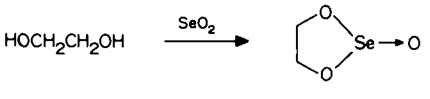
(344) **(345)**

(150)

C. Three Heteroatoms

1. Se/Te rings without nitrogen

1,3,2-Dioxaselenolan-2-oxide (**346**), which is a cyclic organic selenite, is obtained by reaction of selenous acid or SeO_2 with ethylene glycol[714] (equation 151). A similar reaction has been previously applied to erythritol[715]. A 2,2-diphenylselenurane derivative (**348**) is postulated as intermediate in the oxidation of catechols (e.g. **347**) to *o*-quinones by



(151)

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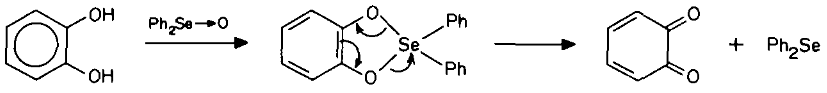
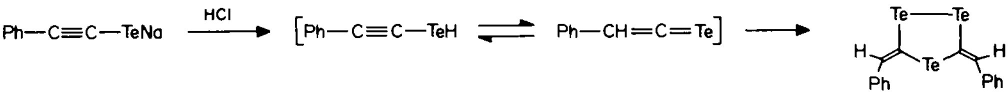


(152)

(347) **(348)**

diphenyl selenoxide[716] (equation 152). A diaryl telluroxide gives the same overall reaction, but the intermediate postulated is acyclic[717]. 2,3-Dimercaptoquinoxaline, gives similarly a dithioselenite, i.e. 1,3,2-dithiaselenolo(4,5-*b*)quinoxaline-2-oxide[718]. Unsubstituted 1,2,3-triselenolane is obtained as a by-product in the hydrolysis of diselenocyanoethane[553]. 2,1,3-Oxadiselenane-1,3-dioxide, which may be regarded as a diseleninic anhydride, is obtained by peracid oxidation of ethylene bis(1,2-diselenide), diselenocyanoethane[719] or 1,4-diselenane[720,721]. 3,5-Dimethylene substituted 1,2,4-triselenoles are obtained as by-products of the decomposition reactions of 1,2,3-selenadiazoles[722], probably via phenylethynyl selenolate. The first tritellurole system, namely E,E-1,3-dibenzylidene-1,2,4-tritellurole (**351**) is obtained as a by-product in the HCl treatment of the corresponding phenylethynyltellurolate (**349**), probably by addition of an intermediate ditelluride anion $Ph\text{-}C\equiv C\text{-}Te\text{-}Te^-$ to the transient telluroketene **350**[723a] (equation 153). The structure of **351** is confirmed by X-ray diffraction. 5,10-Episeleno- and 5,10-epitelluro-5,10-dihydroarsanthrene are prepared from the corresponding 5,10-dichloro derivative[723b].

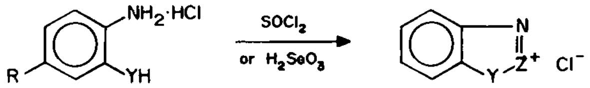


(349) **(350)** **(351)**

(153)

2. Nitrogen Se/Te rings

a. One nitrogen in the ring. Two classes of compounds are included in this group. The first involves 1,2,3-benzodichalcogenazolium cations **353** which are the Se analogues of Herz salts. They are obtained from *o*-aminothiophenol or selenophenol hydrochlorides (**352**; Y = S, Se) and thionyl chloride, giving **353a**[724] or selenous acid, giving **353b**[725] and **353c**[726] (equation 154). It is also possible to transform the dithio analogue to **353b**, by reaction with selenous acid, a reaction which is easier for non-electron-donating substituents and in acidic solution. The *S*-oxide, which reacts vigorously with H_2SeO_3, is a

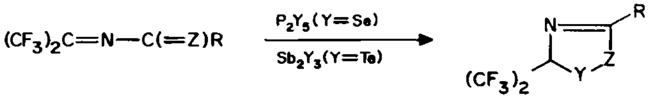


(352) **(353)** (154)

(a) $Y = Se, Z = S$
(b) $Y = S, Z = Se$
(c) $Y = Z = Se$

possible intermediate[727]. The 2-*Se*-oxide is formed by buffered hydrolysis of the salt **353b**[728]. Two stereoisomers are observed, which are interconverted in acidic medium. Hydrolysis of **353a** gives di(*o*-aminophenyl)diselenide[729]. In reaction with amines[730] and especially with *p*-toluidine in acetic acid, **353c** reacts four times faster than its dithio analogue, in agreement with charge densities based on MO calculations[731].

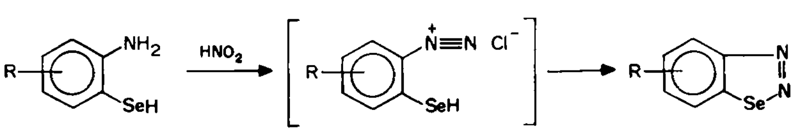
The second class of compounds, obtained by Burger and coworkers according to equation (155), are of the 3*H*-1,2,4-dichalcogenazole type **355** (**a**:Y = Se, Z = S[732]; **b**: Y = Z = Se[733], also obtained from hexafluoroacetone and selenoamides; **c**:Y = Te, Z = S[734]). Some ring transformations, leading to the first cyclic selenophosphorane[735] or using these heterocycles as synthons for heterodienes, have been developed[736a]. Some 1,2,4-diselenazolium salts are obtained by I_2 oxidation of selenoureas[736b].



(354) **(355)** (155)

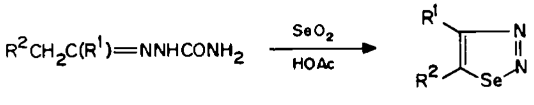
b. Two nitrogens in the ring: chalcogenadiazoles. Derivatives of all four possible isomers of selenadiazoles are known. In the Te series, only 1,2,5-telluradiazoles have been described.

(*i*) 1,2,3-*Selenadiazoles.* 1,2,3-Benzoselenadiazole derivatives (**357**), namely 5-Me, 4-Me and 5,6-di-Me derivatives, have been known since 1935. They are obtained by diazotation of *o*-aminoselenophenols (**356**)[737,738] (equation 156). No further work was



(356) **(357)** (156)

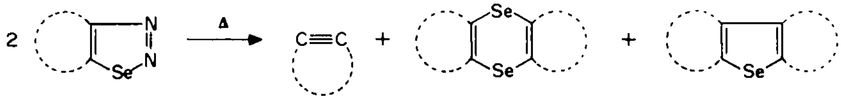
reported until 1975, when the unsubstituted **357** was prepared by the same method[556]. The non-fused system has been known only since 1969, when Lalezari and coworkers obtained 4-phenyl-1,2,3-selenadiazole by SeO_2 oxidation of phenyl ketone semicarbazones[739] (equation 157). The method has been used for the preparation of various 4-substituted[740] and 4,5-disubstituted[741] derivatives.



(358) **(359)** (157)

Starting from aldehyde semicarbazones, the method could be applied to the parent heterocycle, and to various 5-substituted derivatives[741]. The parent compound (**359**;

$R^1 = R^2 = H$) is stable in the dark at 0 °C, but it decomposes slowly under other conditions. The method has been used for obtaining the three 4-pyridyl-[531], 5-cyano-, 5-ethoxycarbonyl-[741], 4,5-cycloocteno-[107,742,743] and other cycloalkeno-selenadiazoles[107]; the 4,4′-alkyl bis-selenadiazolyls[744], 4,5-indeno[745] and other 4,5-benzoalkeno derivatives[746]; the 4-β-naphthyl-, phenanthrenyl- and steroidal[747], 5-(1,3,4-oxadiazolyl)-[748], 4-vinyl- and -butadienyl-[749], 4-aroylmethyl-[750] and 5-arylsulphonyl-selenadiazoles[751]. ^{75}Se-labelled[752] and 5-deuterio-1,2,3-selenadiazoles[753] have been synthesized. SeO_2 is therefore an excellent Se-transfer reagent in these syntheses. Fused phenanthro(*d*)-[754] and benzoselenolo(3,2-*d*)-1,2,3-selenadiazoles[755] are among the rare fused aromatic systems obtained by this method. The regioselectivity of the ring-closure has been studied[756]. 1,2,3-Benzoselenadiazole can be quaternized on the 3-nitrogen[757] but the 1,2,3-selenadiazole ring is generally a rather unstable system, which shows versatile utility in organic synthesis. Unlike the 1,2,3-thiadiazole ring system, the corresponding selenadiazoles are easily pyrolysed with loss of N and Se to give high yields of alkynes[107,531,740,741–743,744,746,747,758]. When the selenadiazole ring is fused to a ring which is lower than eight-membered the acetylene formation is unfavoured and the denitrogenated intermediate can dimerize to diselenin derivatives **361**, which can lose in turn a Se atom to give selenophene derivatives[107,746,747,758] (equation 158). In the other cases, the proportions of compounds **360**–**362** depend on the temperature, concentration and medium of the thermolysis. As seen in a previous section, diselenetane derivatives can also be isolated as by-products[57].

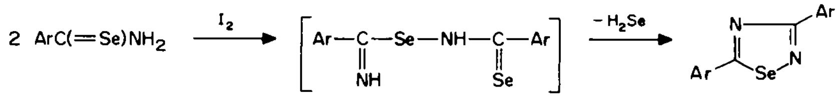


(158)

(360) **(361)** **(362)**

4-Aryl-1,2,3-selenadiazoles can be directly transformed to 2,4- and 2,5-diarylselenophenes without passing through the corresponding selenin, and the mechanism of this reaction has been discussed[108]. The 1,2,3-selenadiazole ring is unstable towards Br_2, and from the bromodediazoniation bis(2-bromovinyl)diselenide was isolated[759]. Reaction with bases (OH^-, EtO^-[563,760,761], BuLi[762]), results initially in proton abstraction from the 5-position (equation 117), and subsequent ring-opening gives an alkyne selenolate **265** which can be dimerized under acid catalysis to diselenafulvenes **266**. It has been demonstrated that selenoketenes are also intermediates in the diselenafulvene formation[532] which involves cycloaddition of alkyne selenolate to the selenoketene species. 1,2,3-Selenadiazoles are also photolysed to alkynes, together with small amounts of diselenafulvenes[763]. Alkyne selenol and selenoketene were identified in these reactions[764]. Intermediate alkyne selenolates can be easily transformed to 1,3-diselenolethiones or -selones by addition of CS_2 or CSe_2, respectively (see above), to selenoamides by addition of secondary amines[761,762] and to seleno esters by reaction with alcohols[741].

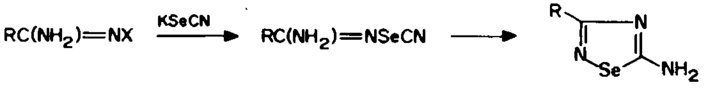
(*ii*) 1,2,4-*Selenadiazoles*. The chemistry of 1,2,4-selenadiazoles is poorly known. This ring system can be obtained by two synthetic methods. The first one, which led to the two first derivatives in 1904[765] and which was developed in 1978 by Cohen[766], consists of the oxidative N–Se coupling of aryl- or hetaryl-selenoamides by I_2



(159)

(363)

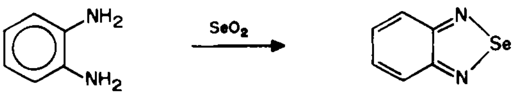
(equation 159). In this way the 3,5-disubstituted derivatives **363** (Ar = Ph, *p*-Tol[765], 2-thienyl) are obtained. The second method, developed by Goerdeler in 1963, is analogous to the preparation of 1,2,4-thiadiazoles and consists of the reaction of KCNSe with *N*-haloamidine **364**. It leads to the 5-amino-3-substituted derivatives (R = Ph, Me) **365**[767] (equation 160). A recent synthesis of 1,2,4-selenadiazolidine-3,5-dione consists of dehydrocyanation of allophanoyl selenocyanate, the first well-documented acyl selenocyanate[768].



(160)

(364) **(365)**

(iii) 1,2,5-*Selenadiazoles.* Fused 1,2,5-selenadiazoles were among the first known Se–N heterocycles. The benzo-condensed system, 2,1,3-benzoselenadiazole (**367**) also called piaselenole or piazselenole, was prepared by Hinsberg in 1889 from phenylenediamine **366** and SeO_2[769] (equation 161).



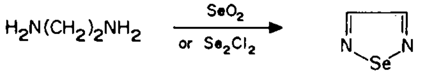
(161)

(366) **(367)**

This very reproducible reaction has been used for absorption or fluorescence spectrophotometric detection of small amount of Se in chemical or natural media, for the detection of *o*-diamines and for the coulometric titration of the Pd^{2+} ion. It is the most widely used route to fused 1,2,5-selenadiazoles. The following fused systems[315] are obtained from SeO_2 or $SeOCl_2$: naphtho(1,2-*c*)-[315,769] and naphtho(2,3-*c*)-phenanthro(9,10-*c*)-[315,770], fluoreno(2,3-*c*)-[771] and pyrazolo(3,4-*c*)-1,2,5-selenadiazoles[772]; (1)benzothieno(2,3-*e*)-[773], (1)benzoselenolo-(2,3-*e*)-[774] and -(3,2-*e*)[775], thiazolo(4,5-*g*)-[776,777] and selenolo(3,2-*e*)-2,1,3-benzoselenadiazoles[315]; 1,2,5-selenadiazolo-5*H*-(3,4-*b*)carbazole[778]; 6*H*-(3,4-*c*)carbazole[778]; (3,4-*b*)- and (3,4-*c*)-pyridine[779,780]; (3,4-*d*)pyrimidine (8-selenapurine)[781–783]; (3,4-*c*)-1,2,5-thiadiazole[784]; (3,4-*b*)quinoxaline[784]; (3,4-*b*)- and (3,4-*h*)-quinoline[785] and the quinonoid systems naphtho(2,3-*c*)-1,2,5-selenadiazole-4,9-dione and 4*H*,8*H*-benzo(1,2-*c*:4,5-*c*′)bis-1,2,5-selenadiazole-4,8-dione[786].

From *N*-methyl-*o*-phenylenediamine are obtained similarly 1-methyl-2,1,3-benzoselenadiazolium salts[787] which can also be prepared by methylation of **367**[788a]. This compound, and the corresponding 1,3-dimethyl-bis-quaternized salt, are easily pyrolysed at 70–110 °C to give, respectively, unsubstituted and 1-methyl-benzimidazole[788b]. The *N*-oxide derivative and some analogues are obtained from *o*-benzoquinone dioxime and Se_2Cl_2[789,790]. The *N*-oxide can be thermolysed to **367** and benzofuroxan[790], and photolysed to benzofuroxan and Se, probably via 2-(selenonitroso)nitrosobenzene[791]. The chemical properties of 2,1,3-benzoselenadiazoles are similar to those of the corresponding thio compounds. Halogenation and sulphonation occur mainly in the 4-position[792]. However, **367** gives many ring-scission reactions including reductions to phenylenediamine under Stephen's conditions[792], and ring-opening by phenyllithium to *N*-phenylethylenediamine and diphenyl selenide via a double selenophilic Se—N rupture. Dienophilic behaviour towards arynes gives the 1,2-benzoselenazole ring system[592–594], and towards ethyl acetylenedicarboxylate gives a quinoxaline diester[592]. The polar nature of 2,1,3-benzochalcogenadiazoles is manifested by their dipole moments (O: 4.04 D; S: 1.79; Se: 1.19). The mesomeric charge transfer, which is not extensive for O, increases in importance for S and Se[793].

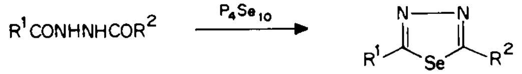
A review on fused 1,2,5-thiadiazoles and 1,2,5-selenadiazoles was published recently[794]. It must be noted that the first description of a monocyclic 1,2,5-selenadiazole is much more recent. In 1967, Shealy described the formation of the 4-amino-3-carboxy derivatives by degradation of the pyrimidine ring of 1,2,5-selenadiazolo(3,4-*d*)pyrimidin-7(6*H*) one[795]. The first general synthesis was reported nearly simultaneously by two other groups and involves a Se transfer from Se_2Cl_2 or SeO_2 to ethylene diamine[796,797] (equation 162). Several 3- and 3,4-substituted derivatives have been obtained by this method[797,798]. The parent system **368** undergoes nucleophilic attack by butyllithium on the Se centre, which is easier than that on 1,2,5-thiadiazole, giving, as for the benzo derivative, a double Se—N cleavage with formation of an α-diketone and dibutyl selenide[799]. The nucleophilic attack of organometallic compounds on chalcogen have been used to prepare 3-vinyl-1,2,5-selenadiazole by a one-pot ring-transformation of 1,2,5-thiadiazole with vinylmagnesium chloride and Se_2Cl_2[800]. The 2-oxide of **368** has been prepared similarly to its benzo analogue[690]. Photolytic cleavage of derivatives of **368** gives a nitrile selenide as the initial product[801,802].



(162)

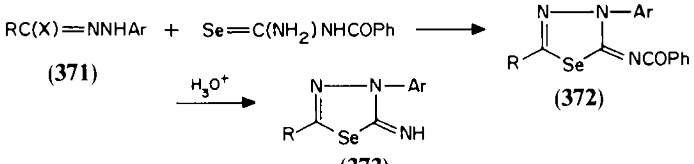
(368)

(*iv*) 1,3,4-*Selenadiazoles*. The first 1,3,4-selenadiazole derivatives (**370**, $R^1 = R^2 =$ Ph, Me) were obtained in low yield by Stollé and Gutmann in 1904, by heating *N*,*N*-dibenzoylhydrazine or its diacetyl analogue with phosphorus pentaselenide[803] (equation 163). Unsubstituted 1,3,4-selenadiazole (**370**, $R^1 = R^2 = H$) is obtained in 25% yield from the azine of DMF, a synthetic equivalent of **369**, and H_2Se[804], together with *N*,*N*-dimethylselenoformamide. Its bond angle, of 81.8°, is the smallest angle known for a planar five-membered ring[805]. Via the diselenoxo derivatives of **369**, obtained by hydrazinolysis of two equivalents of selenoamides, Cohen similarly prepared some derivatives of **370** ($R^1 = R^2 =$ Ar,2-thienyl)[806]. Likewise, starting from 1-acyl-4-benzoylselenosemicarbazide (monoselenoxo derivative of **369**, $R^2 =$ NHCOPh), 2-benzoylamino derivatives of **370** ($R^1 =$ Ar, Me, Pr, 2-furyl) were prepared [807]. These last derivatives give by hydrolysis 2-amino-1,3,4-selenadiazoles (**370**; $R^2 = NH_2$)[807], which were previously obtained by the same method in a one-pot reaction. The precursors, 1-acyl- or -aroyl-selenosemicarbazide, were prepared *in situ* from selenosemicarbazide, an acid and phosphorus oxychloride[808]. 2-Amino-1,3,4-selenadiazoles behave as typical aromatic amines, giving azomethines with aromatic aldehydes, and azo compounds via diazotation. They are alkylated on the 3-nitrogen, giving the tautomeric 2-imino-1,3,4-selenadiazoline form[809]. The 3-aryl derivatives of this imino form **373** are obtained from α-halohydrazones (**371**) and either KSeCN[810,811] or better, aroylselenourea or selenosemicarbazide[809] (equation 164).



(163)

(369) **(370)**

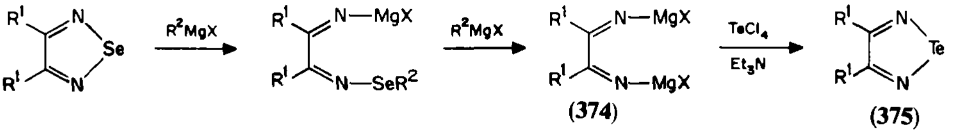


(371) **(372)** **(373)**

(164)

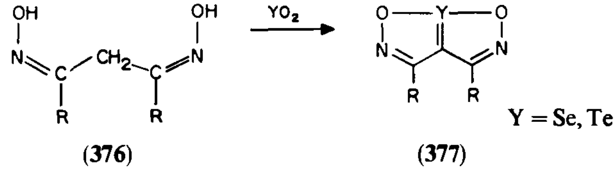
373 gives by nitrosation the 2-nitrosoamino derivatives, which are easily hydrolysed to the corresponding 2-oxo-Δ^4-1,3,4-selenadiazolines[810,811]. A Δ^3-1,3,4-selenadiazoline has been obtained as intermediate in the reaction between di-*t*-butylselenoketone and diphenyldiazomethane, which by thermolysis gives olefins with loss of Se and N[812]. 2-Iminoselenadiazoline derivatives or their 2-aminoselenadiazole tautomers, are starting materials for the synthesis of the following fused 1,3,4-selenadiazoles: imidazo (2,1-*b*)-1,3,4-selenadiazoles[808,809]; 1,3,4-selenadiazolo(3,2-*a*)pyrimidin-7-ones, by reaction with methyl acetylenedicarboxylate[619]; (3,2-*a*)pyrimidium perchlorates, from acetylacetone or diethyl malonate[813], and (2,3-*b*)quinazolines[814].

(*v*) 1,2,5-*Telluradiazoles.* The 1,2,5-telluradiazole ring system was the first known monocyclic ring system with a Te—N bond. It was obtained by Bertini in 1982, from the corresponding 1,2,5-thiadiazole or better selenadiazole, via a R.O.II substitutive chalcogenophilic ring-opening, followed by reaction of the dimetalloimine **374** with $TeCl_4$[815] (equation 165). This new Te system (**375**) is hydrolysed by acids to the α-dione, ammonium cation, Te and tellurous acid. As for benzisotellurazole, the melting point is anomalously high (> 185 °C), and the solubility anomalously low. Te has been trapped by *o*-chloromercuridiazobenzene, giving a compound $C_{12}H_9ClN_2Te$, which was reduced to di-(*o*-aminophenyl) ditelluride and whose X-ray crystallography was in agreement with a quasi-1-chloro-1,2,3-telluradiazole ring system[816].



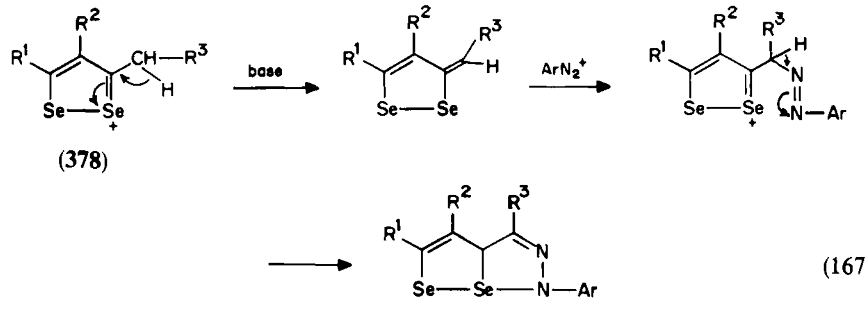
(165)

(*vi*) *Chalcogenaazapentalenes.* The reaction products of SeO_2 with 1,3-cyclohexanedione oximes, previously assigned as monoheterocyclic systems[817], were later proved by NMR[818,819] and X-ray analysis[820,821] to possess a no-bond resonance system of type **377**, as in heterapentalenes. They can be considered as aza analogues of chalcogenapentalenes; 2,5-diaza-1,6-dioxa-6*a*-selena-Se (IV) pentalenes, obtained in this manner have a very short Se—O contact of 2.02 Å. The reaction has been extended to the corresponding Te compounds[822,823] and to various 1,3-dioximes (equation 166) giving the parent compound **377** (R = H)[823] and to the S analogue with the aid of SCl_2[824]. Compounds **377** are sensitive to alkali and to reducing agents, giving, for example, the 1,3-dioxime of 1,2,3-cyclohexanetrione, and with hydroxylamine the corresponding trioxime. They give no electrophilic substitution[823]. By replacing the starting dioxime **376** by an arylhydrazone, a 1,2,5,6-tetraaza analogue is obtained, both in the Se and in the Te series[825].



(166)

The method using the acidity of the 3-methylene group of 1,2-dichalcogenolylium salts can be applied to the reaction of 3-methyl(ene)-1,2-diselenolylium salts (**378**) with arenediazonium fluoroborates, giving 6,6*a*-diselena-1,2-diazapentalenes (**379**)[826a] (equation 167; $R^1 = R^2 = R^3 = H$, Me). A parallel nitrosation gave a 1-oxa-6,6*a*λ^4-diselena-2-aza analogue[826b]. This last compound can be transformed with Hg(II) acetate into the 1,6-dioxa-6*a*-selena-2-aza analogue[827a]. 3,4-Dimethyl- and 3,4-trimethylene-6*a*λ^4-thia-6-selena-1,2-diazapentalenes are obtained from the corresponding 6-oxa derivative, by reaction with the Vilsmeier reagent and potassium selenosulphate[827b].



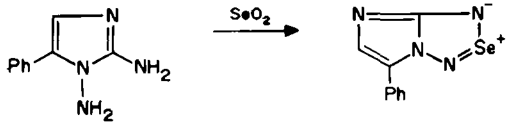
(378)

(379)

(167)

D. Four Heteroatoms

The first selenatriazole ring system has been recently prepared by treating 1,2-diamino-4-phenylimidazole (**380**) and its 4,5-diphenyl analogue with SeO_2, giving 5-phenylimidazolo(1,2-*c*)-1,2,3,5-selenatriazole (**381**)[772] and the corresponding 5,6-diphenyl analogue, following the general reaction of SeO_2 with *o*-diamino derivatives (equation 168). Benzimidazolo(1,2-*c*)selenatriazole was obtained similarly.



(380) (381)

(168)

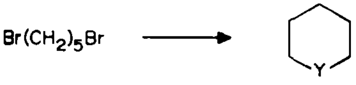
Since then, another ring system, 5-diethylamino-1,2,3,4-selenatriazole, has been prepared from 4,4-diethylselenosemicarbazide and HNO_2. Its half-life time is 180 h in $CHCl_3$ at 20 °C[827c].

V. Se/Te SIX-MEMBERED RINGS

A. One Heteroatom

1. Monocyclic systems

a. Selenanes and telluranes. Selenanes and telluranes **382** are obtained from pentamethylene halides and Na_2Se[828], Se and rongalite in alkaline medium[829], MgTe or Al_2Te_3[830], Te[232] or Na_2Te[831] (equation 169). 2-Methyl-[832] and 2,6-dicarboxyselenanes[833] are obtained similarly. Selenane is also obtained by passing pentamethylene oxide and alumina in a stream of H_2Se and in 57% yield from pentane, SeO_2 and a zeolite catalyst[85].



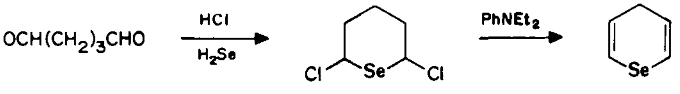
(382)

Y = Se, Te

(169)

The conformations of selenanes and telluranes[834] and their halogen adducts[835] have been studied as a part of a more extended work on the conformational analysis of pentamethylene heterocycles, which has been reviewed[836]. The inversion barrier decreases with the size of the chalcogen (ΔG_{inv}:O: 10.5 kcal mol^{-1}; S: 9.4; Se: 8.3; Te: 7.3). Tellurane-1, 1-diiodide has been submitted to nucleophilic substitution on Te by various nucleophiles (F, CN, NCO, NCS, NCSe, CCl_3)[837].

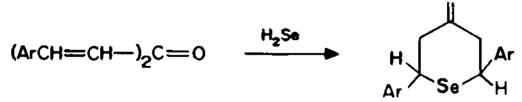
b. Selenopyrans. The parent compound **384** (4*H*-selenin) has been prepared in 16% yield, in the same time as its sulphur analogue, by reaction of H_2Se and HCl on glutaraldehyde[838] (equation 170). The 4-methyl[839], 2,4,6-triphenyl and 3,5-dimethyl-2,6-diphenyl[840a] derivatives are synthesized in a similar way. 6-Phenyl-2-formylmethylene-2*H*-selenopyrans were obtained recently from the selenobenzamide vinylogue and β-chlorocrotonaldehyde[840b]. No monocyclic telluropyrans are so far known.



(170)

(383) **(384)**

c. Chalcogenopyrones and tetrahydro derivatives. 2,6-Diarylselenan-4-ones (**386**) with *trans*-aryl groups[843] are obtained by addition of H_2Se to distyryl ketones **385**[841–844] (equation 171). The reaction also works for the keto derivative obtained in one pot from diethyl acetonedicarboxylate and acetaldehyde, giving 2,6-dimethyl-3,5-diethoxycarbonylselenan-4-one[845]. Conformational studies by NMR, suggest a chair conformation with four equatorial substituents[845]. Conformational studies have also been conducted for **386**, their cyanhydrins[844] and the corresponding selenanols[846]. The same method has been applied to the preparation of 2,6-disubstituted 4*H*-4-selenopyrones and -telluropyrones (**388**), starting from the corresponding dialkynyl ketones (**387**) (equation 172; R = Me, Ph, *t*-Bu)[847,848]. These precursors are prepared directly in one pot from alkynes, ethyl formate and MnO_2[848,849]. Using tellurobis(tri-*t*-butylsilane) as a nucleophile, the reaction gives, in addition to **388**, the isomeric five-membered 5-substituted 2-arylidene-3-oxo-2,3-dihydrotellurophene as a major product[848]. A 2-selenopyrone isomer of **388**, i.e. **390**, has been prepared from a selenoamide vinylogue **389** and arylacetyl chloride[850] (equation 173). 3,5-Dioxo-1,1-dichlorotelluranes, erroneously formulated in the earlier publications, were obtained by the Morgan's group in the twenties from 2,4-pentanedione derivatives and $TeCl_4$[851–853]. These structures have been recently confirmed by X-ray diffraction and NMR spectroscopy[854]. The reaction follows a different route in the Se series, giving 1,3-diselenetane derivatives as previously mentioned[60].



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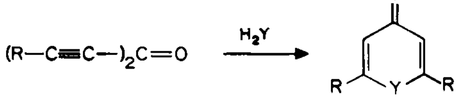
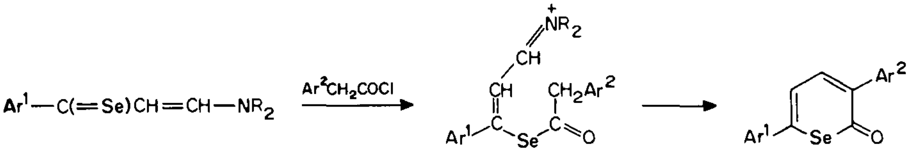
(385) **(386)**



(172)

(387) **(388)**

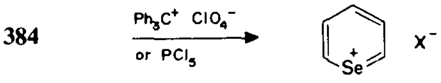
Y = Se, Te



(389) (390)

(173)

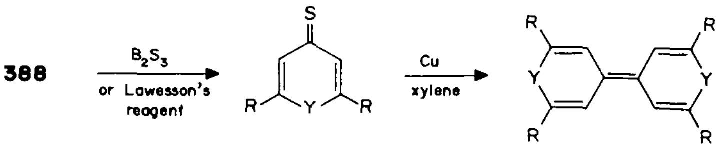
d. Chalcogenopyrylium salts. Selenopyrylium (or seleninium) salts **391**, comprising the parent compound, have been prepared either by hydride abstraction from selenopyrans of type **384**[838,839] (equation 174) or directly from δ-diketones[855]. Their relative stability has been studied and compared with that of the thio analogues[856]. A 2-amino-6-aryl-3-substituted selenopyrylium salt has also been obtained from **389** and derivatives of malononitrile[850]. 2,6-Diphenyltelluropyrylium salts have been recently synthesized, as precursors for the preparation of telluropyrylium dyes[857]. The 4-ethoxy, the 4-*p*-dimethylaminophenyl and the 4-methyl derivatives are obtained from 2,6-diphenyltelluropyrone and ethyl fluorosulphate, *p*-dimethylaminophenylmagnesium bromide and Meldrum's acid respectively, followed by reduction and decarboxylation.



(391)

(174)

e. Bis-4,4′-chalcogenopyranylidenes. Compounds **393** may be good electron-donating heterocycles, since the corresponding cations have an aromatic 6π structure. The O analogue was discovered in 1975 to form electrically conductive complexes with acceptors. The corresponding S[858–860], Se[849] and Te analogues[861] are synthesized by copper coupling of chalcogenopyran-4-thiones (**392**), obtained by thionation of the corresponding pyrones **388** (equation 175; Y = Se, R = Me, Ph; Y = Te, R = Me, Ph, *t*-Bu). Indeed, compounds **393** give with TCNQ complexes of high specific conductivity (~ 0.5 ohm^{-1} cm^{-1}). Their first oxidation potential follows the general trend of increasing with the size of the heteroatom.



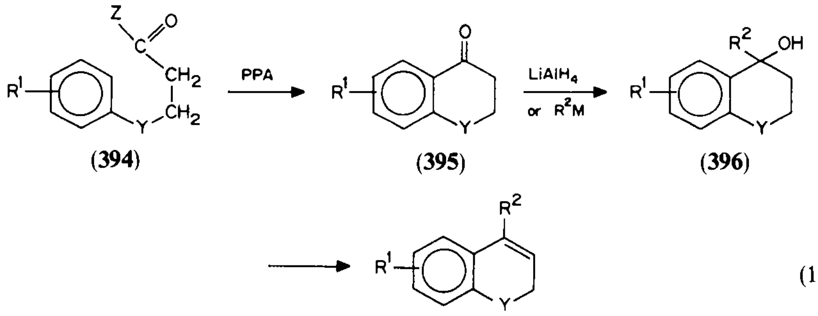
(392) (393)

(175)

2. Benzo-, naphtho- and hetero-condensed systems

a. (b)*Condensed systems: chroman derivatives.* (*i*) *Chalcogeno-chromanones, -chromenes and -chromans.* Benzochalcogenopyrans (chalcogenochromenes) (**397**) are commonly obtained by standard methods from the corresponding chalcogenochromanones **395**. The first known selenochromanone, the parent compound itself (**395a**; R^1 = H) was prepared initially in 1958 in a 23% yield by pyrolysis of the corresponding diacid, β-(*o*-

carboxyphenylseleno)propionic acid[862]. A more general synthetic method described in 1964, consists of an electrophilic cyclization of β-phenylselenopropionic acid **394a** with polyphosphoric acid[863] (equation 176). Sulphuric acid, which is used for preparation of thiochromanone, cleaves the Se—C (aliphatic) bond.



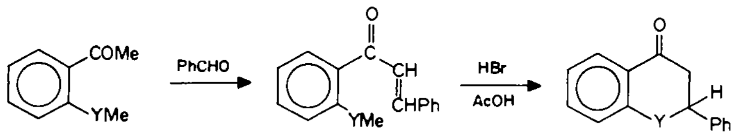
(394) **(395)** **(396)**

(397)

(176)

(**a**) Y = Se
(**b**) Y = Te

The method has been widely applied to acids **394a** (Z = OH) or to their acid chlorides (Z = Cl) for the synthesis of 2-Me, 3-Me, 7-Me, 8-Me[864,874], 6-Me[269,864,874] and 6,7-di-Me[874] selenochromanones **395a**. The corresponding condensed selenopyranones: naphtho-(1,2-*b*)- and -(2,1-*b*)-[865–867], (1)benzothieno-(3,2-*b*)- and -(2,3-*b*)-[868] and (1)benzoselenolo(2,3-*b*)-[869,870] were obtained similarly. It has also been applied to various tellurochromanones **395b**[871] and to the naphtho(2,1-*b*) and thieno(3,2-*b*) analogues, starting from the acid chlorides at dry-ice temperature with aluminium trichloride as catalyst. The 2-phenylchalcogenochromanones (selenoflavanone **399a**[872] and telluroflavanone **399b**[873]) are prepared by a Y—C(2) ring-closure of *o*-cinnamoylchalcogenoanisoles (**398**) and hydrobromic acid, with respective yields of 80 and 20% (equation 177). In the Te series, an important by-product was identified as *o*-cinnamoylbenzenetellurenyl bromide. The same ring-closure has been applied to the synthesis of 4*H*-2,3-dihydro-2-phenyl-4-oxo-(1)-benzothieno- and -(1)benzoselenolo-(2,3-*b*)selenopyrans[869].



(398) **(399)**

(177)

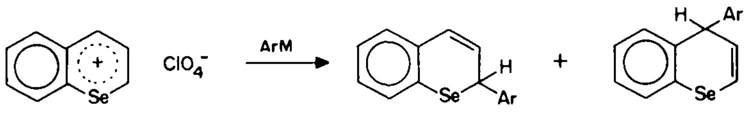
(**a**) Y = Se
(**b**) Y = Te

The chromanols **396**, obtained from **395** by reduction or via addition of organometallic reagents, are easily dehydrated to the corresponding chromenes **397**, or their analogues[863–871]. Selenochromanone leads also, via the Vilsmeier reagent, to 4-chloro-3-formylselenochromene, a starting material for the further condensation of a thiophene[874] or a selenophene[100] ring. The known selenopyrans condensed to a nitrogen heterocycle are obtained by a direct ring-closure of the selenopyran ring: in this manner, 7-methyl-2*H*-

selenino(2,3-*b*)pyridine is prepared, as its O and S analogues, from 2-ethylseleno-6-methyl-3-(1′,3′-dihydroxypropyl)pyridine and HBr[875]. A selenino(3,2-*d*)pyrazole, the 6*H*-3-methyl-1-phenyl-5,6-dicarboxy derivative, is prepared by a Diels–Alder reaction between maleic anhydride and 3-methyl-1-phenyl-4-methylaminomethylene-5-selenoxopyrazole[876].

The reduction of **395a** to the corresponding selenochromans has been performed by the Clemmensen[863] and the Wolff–Kishner reductions[877,878]. Whereas the Clemmensen reaction leads to the required product, sometimes mixed with variable quantities of selenochromenes, the Wolff–Kishner reaction on the parent compound leads partially to the ring-contraction product, 2-methyl-2,3-dihydrobenzo(*b*)selenophene, besides the attempted selenochroman. The reaction differs from that in the sulphur series, where only thiochroman is formed, and from that in the oxygen series where the formation of *o*-cyclopropylphenol is established. The isolation of pure selenochroman has been used as evidence that selenochroman is not formed by thermal rearrangement of phenylallyl selenide as previously described[879]. However, the isolated product is 2-methylbenzo(*b*)selenophene[877]. Pure tellurochroman has been prepared by a diimide reduction of tellurochromene[880].

(*ii*) *Benzochalcogenopyrylium salts* (*chalcogenochromylium salts*). Chalcogenochromylium salts are obtained from selenochromenes **397a** by a reaction parallel to that described in equation (174)[864,867–869,881]. Several 2- or 4-phenylselenochromylium salts are prepared in the same manner[869,882]. 4-Methyl-2-phenyl-[883] and 2,4-diphenyl-selenochromylium[884] salts are also prepared from selenoflavone for the synthesis of polymethine dyes. On the other hand, 4-methoxyselenochromylium salts are obtained by methylation of selenochromone and selenoflavone[885]. The pK_{R^+} value, which characterizes the equilibrium constant between the cation and its pseudobase and hence the stability of the cation, has been determined for the chalcogenopyrylium cation[885] (O: -1.96; S: $+3.15$; Se: $+1.20$), and for the naphtho-(2,1-*b*)- and -(1,2-*b*)-selenopyrylium salts ($pK_{R^+} = +2.7$ and $+1.9$, respectively)[867]. The reaction of selenochromylium salts and analogues with nucleophiles has been shown to occur at the 2- and 4-positions. Whereas the monosubstituted 2-aryl- and 4-aryl-selenochromylium salts react exclusively at the other free activated position with all the nucleophiles studied ($NaBH_4$, PhMgBr, PhSH, PhSeH, $(MeCO)_2CH^-$)[882], the unsubstituted selenochromylium cation **400** gives with aryl organometallic compounds a mixture of addition products at positions 2 (**401**) and 4 (**402**) depending on the nature of the metal and the organic radical (equation 178). The isomer ratio is affected by a secondary oxidation–reduction reaction between 2-arylselenochromenes and the unsubstituted selenochromylium salt[886]. A comparison with the analogues S cation, which gives a 55:45 ratio between positions 2 and 4 (in agreement with the calculated positive charge density), is therefore difficult. On the other hand, other nucleophiles as dimethylaniline, thiophenol and selenophenol react regiospecifically at the 2-position[886]. However, a 2-regiospecificity is demonstrated with all the nucleophiles, including organometallic compounds, for some heterocondensed selenopyrylium cations[887]. The MnO_2 oxidative hydrolysis of the selenochromylium cation differs appreciably from the corresponding reaction of the thiochromylium cation.

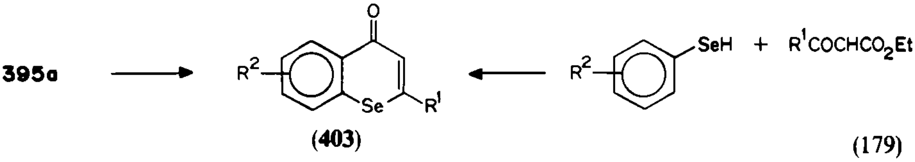


(178)

(**400**) (**401**) (**402**)

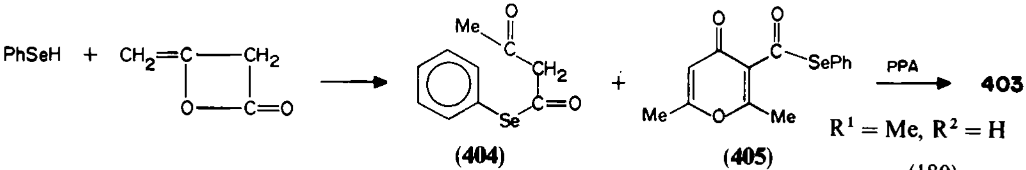
Although the size of the ring of the latter is conserved in the oxidation products, and the thiocoumarin : thiochromone ratio corresponding to respective nucleophilic attack on the 2- and 4-positions, is 90:5, the selenochromylium cation gives exclusively a product of ring-contraction, namely 2-formylbenzo(*b*)selenophene[286,888]. A parallel increase in the extent of ring-contraction with the size of the chalcogen has also been demonstrated in the oxidation of thio-, seleno- and telluro-chromenes. Depending on the oxidant, the reaction can be directed to give selenocoumarines (with chromium trioxide in pyridine, 50% yield) or to ring-contraction products (e.g. 2-acylbenzo(*b*)selenophene)[286,287]. The selenochromones are always minor products. In the Te series, only products of ring-contraction can be obtained[484]. Dichalcogenocinnamaldehydes are intermediates in the ring-contraction reactions.

(*iii*) *Chalcogenochromones.* The parent selenochromone (**403**; $R^1 = R^2 = H$), was obtained in 1964 by dehydrogenation of selenochromanone with chloranil[863] or triphenylmethyl cation[881] (equation 179). Later, a photodehydrogenation of chalcogenochromanones gave a 50% yield of thiochromones, a very low yield of selenochromone (5%) and failed for tellurochromanone[889].



(179)

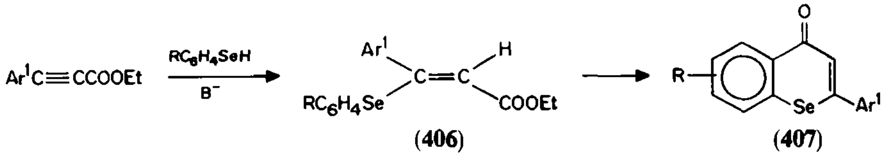
Application of the Simonis synthesis of thiochromones gives from selenophenols and β-oxo esters in polyphosphoric acid (PPA) medium, selenochromones, selenoflavones (**403**; $R^1 = Ph$)[890,891] and isoselenoflavone (3-phenylselenochromone)[890]. The yields are poor (7–30%), due to secondary oxidation of the selenophenols. The following selenochromones are obtained: 2-Me; 3-Et-2-Me; 2,3-, 2,6-, 2,7- and 2,8-di-Me; 2,3,6-, 2,3,7- and 2,3,8-tri-Me; and the 6-Me, 7-Me and 8-Me selenoflavones. The parent selenochromone is obtained by this method in a very low yield from malic acid and selenophenol[890]. 2-Methylselenochromone can also be prepared in the same medium from selenophenol and diketene, or from the isolated intermediate phenyl selenoacetoacetate (**404**)[892]. Compound **404**, which possesses the selenol ester group, does not give the isomeric selenocoumarin and is rearranged to selenochromone. The same selenochromone is also obtained from another isolated intermediate **405**[892] (equation 180).



(180)

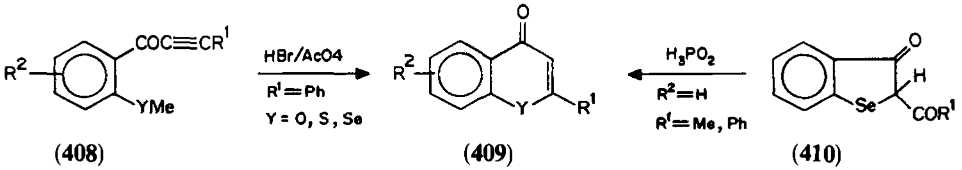
Under the same conditions, malonic esters give with thio- or seleno-phenols 2-(phenylthio)thiochromone and 2-(phenylseleno)selenochromone derivatives, respectively[893]. In the Simonis reaction, β-arylthio- or β-arylseleno- cinnamates (**406**), could also be possible precursors. The isolation of these compounds has been achieved by a regiospecific control of the β-addition of chalcogenophenols across the triple bond of an ethyl arylpropiolate in basic medium[894] (equation 181). In contrast, a regiospecific α-addition is achieved under uncatalysed, probably radical, conditions. *Z*-β-Aryl-thio- and -

seleno-cinnamic acids are cyclized to the corresponding flavones, whereas the α-arylchalcogeno isomers give the corresponding chalcogenoaurones. With cinnamates substituted by activating substituent in the aryl group of **406** the cyclization can be realized on this aryl ring, following the necessary Z–E rearrangement, to give 3-(arylseleno)inden-1-ones.



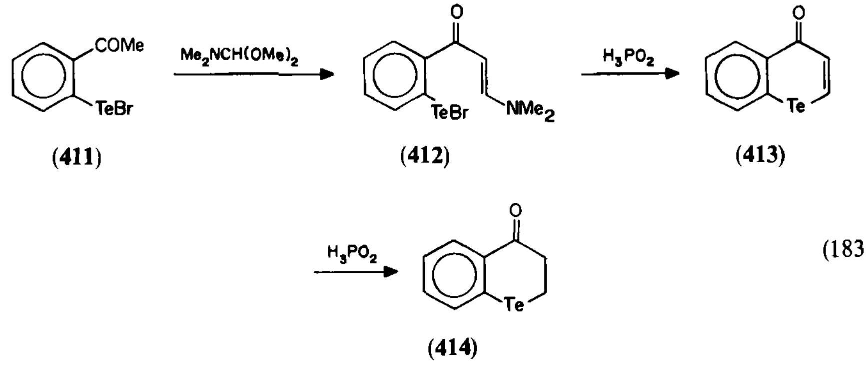
(181)

Selenoflavones (**409**; Y = Se) have also been obtained by another general cyclization method, consisting of a hydrobromic acid ring-closure of *o*-methylchalcogenobenzoyl phenylacetylenes (**408**; R^1 = Ph)[895] (equation 182). An access to 2-methyl- and 2-phenyl-selenochromone, characteristic of the Se series, is the ring-expansion of **410**, which



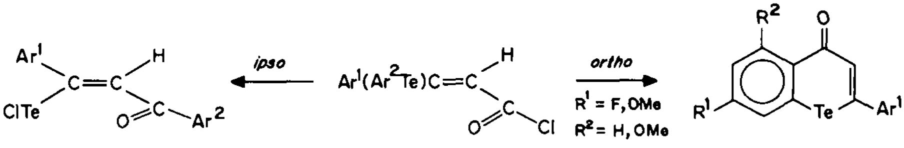
(182)

gives 40–50% yields (equation 182)[245]. The S analogues of **410** give only reduction to benzo(*b*)thiophene derivatives. This ring-expansion reaction has been applied to the synthesis of benzothieno- or benzoselenolo-(2,3-*b*)- or -(3,2-*b*)-selenochromones, where the exocyclic carbonyl group of **410** belongs to thioindoxyl, selenoindoxyl or its 2-oxo isomer[245]. Nearly all of the preceding methods failed in the Te series, so that tellurochromone (**413**) was prepared as late as 1981 by a new method, starting from *o*-acetylbenzenetellurenyl bromide (**411**) and the acetal of DMF. The condensation product **412** has been cyclized by one equivalent of hypophosphorous acid to **413**[896] (equation 183). A second equivalent of H_3PO_2 reduces **413** to tellurochromanone (**414**). This is a typical reduction of the Te series, since selenochromone is not reduced under these conditions.



This synthesis has been extended to the formation of 2-methyltellurochromone, of the thieno-(3,2-*b*)-, -(2,3-*b*)- and -(3,4-*b*)-tellurin analogues and of selenochromone. The major difficulty in the latter case is in the formation of the Se analogue of **412**, since the acidity of the acetyl hydrogen of **411** is lowered[896]. A structural comparison of the four chalcogenochromones (O, S, Se, Te), based on dipole moments, IR, UV and ^{1}H- and ^{13}C-NMR spectra has been conducted[897,898].

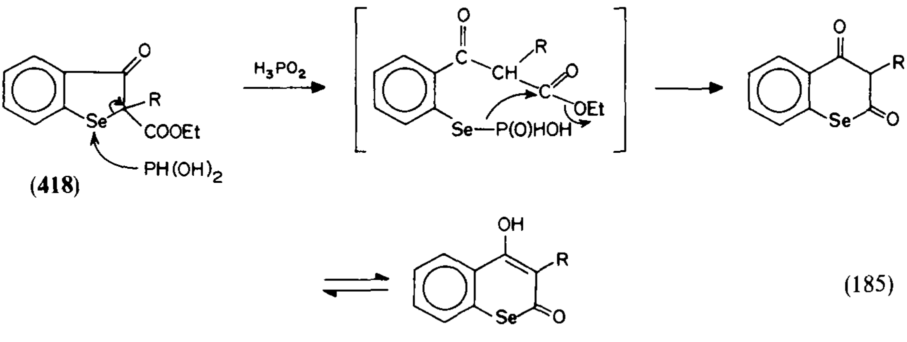
Among the preceding synthetic methods for selenochromones, only the ring-closure analogous to that in equation (181) has led recently to tellurochromone derivatives in particular cases. Generally, the attempted electrophilic ring-closure of the acid chloride of the Te analogue of **406** leads to a tellurenyl chloride (**416**) via an *ipso* acylation,[500] due to the polarizability and electronegativity of Te. The chloride **416** can be considered as a resonance hybrid of the no-bond hybrid 1,2-oxatellurolylium halide. The Te—O distance is effectively low. The *ortho* cyclization to telluroflavones **417** can be controlled in selecting *ipso*-deactivating or *ortho*-activating methoxy or fluoro groups in the *meta* position of the aryltellurocinnamoyl chlorides **415**[899]. In this reaction, the thio compounds give preferentially thiochromones, whereas the seleno compounds show competition between the two reactions. 7-Methoxytelluroflavone (**417**) has been coupled via the corresponding thione in order to obtain a donor molecule for studies in the field of organic metals[900].



(**416**) (**415**) (**417**)

(184)

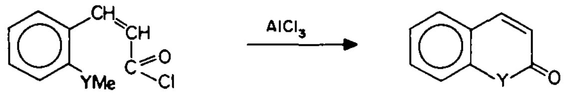
(*iv*) 1-*Chalcogenocoumarins*. 4-Hydroxy-1-selenocoumarins (**419**) are synthesized by cyclization of diphenyl selenomalonate with $AlCl_3$[901], by treatment of substituted malonic acids with selenophenols in PPA[902] (whereas malonate esters give 2-(arylseleno)selenochromones[903]) and, with a very good yield, by ring-expansion of 2-(ethoxycarbonyl)selenoindoxyls (**418**) with hypophosphorous acid. This latter reaction probably involves a ring-opening affected by a selenophilic attack[283] (equation 185). The ring-expansion is much more difficult in the sulphur series, giving only 4-hydroxythiocoumarin with an electron-withdrawing R group at position 3 in a poor yield (25%).



(**418**) (**419**)

(185)

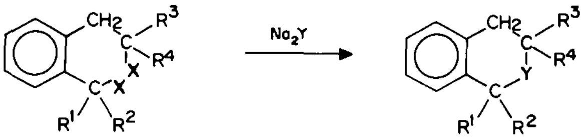
The parent non-hydroxylated 1-seleno-[904] and 1-telluro-coumarins[905] (**421**) are prepared by cyclization of *o*-methylchalcogeno-cinnamoyl chlorides **420** (equation 186). The unsubstituted; 3-Me, 4-Me, 6-Me, 7-Me and 8-Me; 3,4-, 3,6-, 3,7-, 4,6- and 4,7-di-Me; 3-CN-4-Me, 3-CN-4,6-di-Me and 4,7-di-Me; 3-Ph, 4-Ph, 3-Ph-6-Me, 3-Ph-7-Me and 4-Ph-6-Me derivatives were prepared when Y = Se, and the unsubstituted derivative when Y = Te. Some selenocoumarins are also obtained by CrO_3 oxidation of selenochromenes[286,287]. 3,4-Dihydro-1-selenocoumarin has been prepared by a somewhat similar method: treatment of *o*-(methylseleno)dihydrocinnamic acid with Br_2 and H_3PO_2 transforms the seleno ether to the corresponding selenophenol, without cyclization. The selenolactonization is effected by *p*-toluenesulphonic acid[905]. A parallel reaction failed in the Te series.



(186)

(420) **(421)**

b. (c)*Condensed systems: isochroman derivatives* (*i*) *Isoseleno- and isotelluro-chromans.* Isoseleno- and isotelluro-chroman (**423**; R^n = H) were prepared in 1945 with respective yields of 58 and 50% by a nucleophilic substitution of the corresponding dihalo derivative **422** (R^n = H) with the chalcogenide anion[906] (equation 187). They were transformed to quaternarization products, and the Se derivative to the corresponding *Se*-oxide. The 1*H*,3*H*-naphtho(1,8-*cd*) selenin has been obtained by a similar reaction[907].

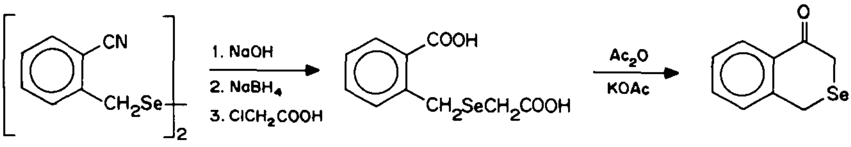


(187)

(422) **(423)**

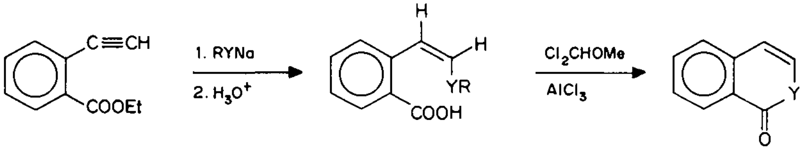
(**a**) Y = Se
(**b**) Y = Te

(*ii*) *Oxo derivatives.* The Se/Te 1-oxo derivatives, i.e. 3,4-dihydro-isoseleno- and -isotelluro-coumarins **423** ($CR^1R^2 = C{=}O$)[473], and the isomeric Se/Te 3-oxo derivatives (**423**; $CR^3R^4 = C{=}O$) are prepared by the same method, starting from the appropriate acid chloride and using phase-transfer catalysis[908]. The isomeric 4-oxo derivative, isoselenochromanone (**426**), could not be obtained by electrophilic cyclization of the corresponding acid, but it was obtained in 31% yield by pyrolysis of the diacid **425** (equation 188)[909]. However, the direct electrophilic cyclization by P_2O_5 leads to the naphtho-(2,1-*c*) and -(1,2-*c*) analogues[867]. The unsaturated heterocycles, isoselenocoumarin and isotellurocoumarin (**428**) are obtained by a method parallel to the synthesis of the chalcogenocoumarin isomers i.e., by intramolecular electrophilic attack of the corresponding acid chloride on an unsaturated seleno or telluro ether (**427**)[910] (equation 189).



(188)

(424) **(425)** **(426)**

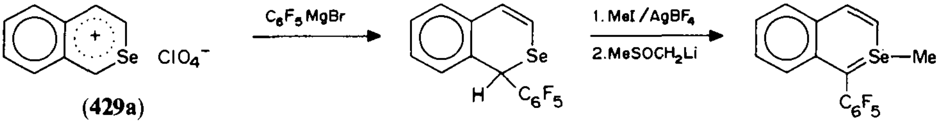


(427) (428) (189)

(a) Y = Se
(b) Y = Te

(*iii*) *Isoselenochromylium salts.* The parent isoselenochromylium salt **429a** (2-selenonianaphthalene cation)[909] and its 2- and 3-selenoniaphenanthrene analogues[867] are prepared by similar reaction paths to those used for the selenochromylium cations. The pK_{R^+} value for the 2-selenonianaphthalene cation (+ 0.2) is lower than that for its 1-selenonia isomer (+ 1.20) and its S analogue 2-thionianaphthalene (+ 2.17).

(*iv*) *Selenabenzene derivatives.* Reaction of **429a** with perfluorophenylmagnesium bromide furnishes 1-perfluorophenyl-2-seleno-Δ^3-chromene (**429b**), which upon methylation leads to the first example of an authentic selenabenzene **429c**[911] (equation 190). Solution **429c** in DMSO shows intense colour (λ_{max} = 500 nm compared with 490 nm for the S analogue). Its stability is lower than that of its S analogue, and it has a half-life of 47 min at 25 °C. The NMR spectra indicate the ylide nature of this selenabenzene. Previously claimed selenaanthracenes have properties which are inconsistent with those expected for selenabenzenes.

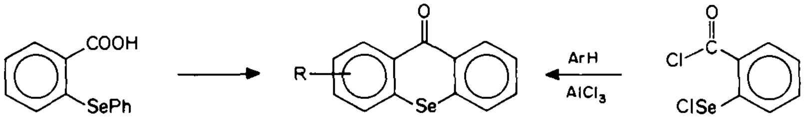


(429a) (429b) (429c)

(190)

3. Dibenzo-condensed systems and analogues

a. *Selenium derivatives.* (*i*) *Selenoxanthones.* The parent selenoxanthone **431** was synthesized in 1914[912]. Its synthesis can be achieved by an electrophilic ring-closure of *o*-phenylselenobenzoic acid (**430**) in sulphuric acid (45[912]–88%[913] yield), or in polyphosphoric acid (82%)[914] (equation 191). By this method 2-chloro-[913] and 2- and 3-methylselenoxanthones have been prepared[914]. Another mode of formation consists of a double electrophilic cyclization of *o*-chloroselenobenzoyl chloride (**432**) with aromatic compounds[914,915]; e.g. reaction with toluene gives the 2-methyl derivative[914]. The parent compound leads to the *Se*-oxide by reaction with chromium trioxide[915]. Praefcke's group synthesized selenoxanthone and some analogues[916,917] photochemically from aromatic *o*-chloro-, *o*-tosyloxy- or *o*-methylsulphinyl-selenol esters, via cleavage of the acyl–Se bond. In this way 7-methyl-cyclopenta(*b*)(1)benzoselenin-9-one[918], 7-methyl-5*H*-

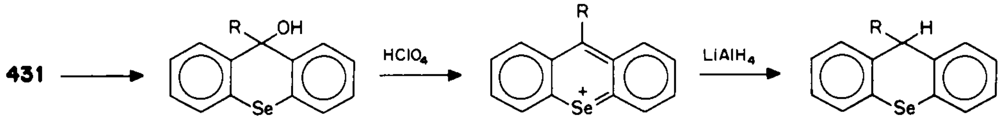


(191)

(430) (431) (432)
R = H

benzoselenino(2,3-*b*)pyridine-5-one[919,920], 7-methyl-9*H*-selenolo(3,2-*b*)(1)benzoselenin-9-one and the isomeric 6-methyl-4*H*-selenolo(2,3-*b*)(1)benzoselenin-4-one[921] were obtained. This cyclization reaction is similar to those in the O and the S series.

(*ii*) *Selenoxanthylium salts.* The selenoxanthen-9-ols, prepared either by reduction or by organometallic treatment of selenoxanthones[913,914,922] are the pseudobases of the selenoxanthylium salts (equation 192). They easily give these salts by treatment with a strong acid. In another method, a 1→8-octahydroselenoxanthylium cation has been prepared by reaction of H_2Se with bis(2-oxocyclohexyl)methane[923]. The stability of the selenoxanthylium cation has been compared by Degani and coworkers with those of the O and S analogues. Their pK_{R^+} values are O: -0.83; S: -0.21; Se: -1.67[885]. These cations react exclusively with nucleophiles at the 9-position. For example, the parent cation is transformed by MnO_2 oxidative hydrolysis to selenoxanthone (**431**), in a nearly quantitative yield[888]. On the other hand, other nucleophiles give 9-monosubstituted or disubstituted selenoxanthenes. Some reports regarding a possible reaction on Se in position 10 of the cation to give selenaanthracenes[924] could not be confirmed[911]. A review on chalcogenoxanthylium salts has appeared recently[925].

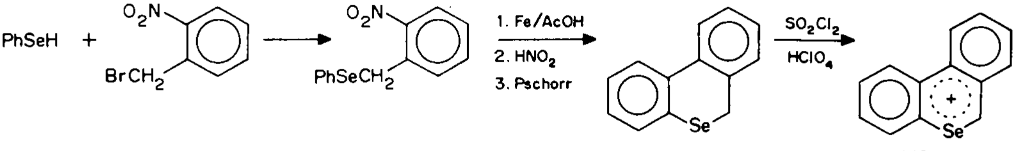


(**433**) (**434**) (**435**)

(192)

(*iii*) *Selenoxanthenes.* The parent selenoxanthene (**435**; R = H), the first derivative of the series, is prepared in a nearly quantitative yield from selenoxanthone, red phosphorus and HI[926]. The other selenoxanthenes are prepared from selenoxanthylium salts. Unsubstituted derivatives in position 9 (e.g. 3,6-dimethylamino-[927] and 3-methyl-selenoxanthenes[914]) are obtained by reduction of the corresponding cation with complex hydrides. 9-Monosubstituted derivatives are prepared by reduction of the 9-substituted cations, or by reaction of organomagnesium compounds with the parent cation (9-Me[914], 9-Ph[914,924]). The last reaction on the chosen cation leads to 9,9-disubstituted derivatives (9,9-di-Me,9-Me-9-Ph[914,924]). 3′-Dimethylaminopropylidene and propylselenoxanthenes have been prepared for pharmaceutical screening by dehydration and HI reduction of the corresponding 9-selenoxanthydrols, respectively[913]. 9-Phenylselenoxanthene is transformed by chloramine T to the corresponding *N*-arylsulphonylselenilimine[928]. Other dipole-stabilized Se-substituted selenoxanthenes including *Se*-oxide were prepared recently and transformed to several 10-selenoxanthenium ylids[929].

(*iv*) *Dibenzo*(b,d)*selenin derivatives.* The angular isomer **437** of selenoxanthene and the corresponding selenoniaphenanthrene (**438**) have been prepared by a Pschorr cyclization[930] (equation 193). Hydride abstraction from **437** by trityl perchlorate is only

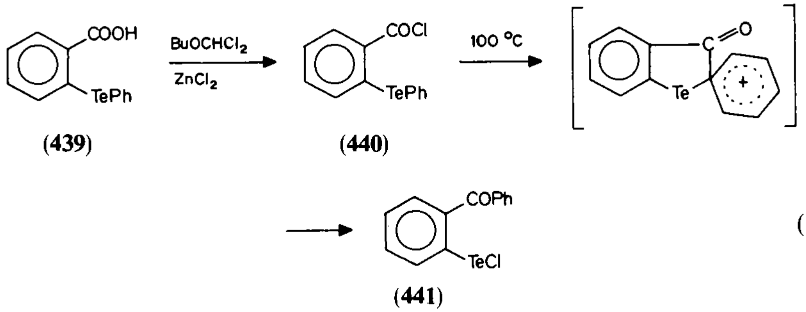


(**436**) (**437**) (**438**)

(193)

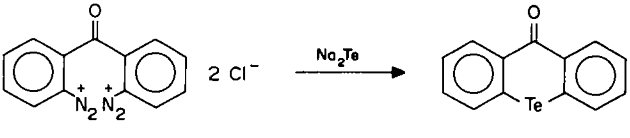
partial. The pK_{R^+} values of **438** and of its O and S analogues (O: -5.96; S: -1.67; Se: -4.28)[855] have been compared with the pK_{R^+} values of other similar cations. Indole analogues of the selenin **437**, namely (1)benzoselenino(3,4-*b*)indoles, have been prepared by constructing the indole ring from the phenylhydrazone of selenochromanone **395a**[931].

b. Tellurium derivatives. The chemistry of telluroxanthone and its derivatives is much more recent. Acidic cyclization of the Te analogue of **430** failed, due to destruction of the precursor. From the acid chloride **440**, a non-cyclized rearrangement isomer, *o*-benzoylbenzenetellurenyl chloride (**441**), is obtained in the presence of Lewis acids; the reaction proceeds via an *ipso* attack on the carbon attached to the Te atom followed by cleavage of the aromatic C—Te bond[932] (equation 194). This isomer **441** cannot be cyclized further[932,933].



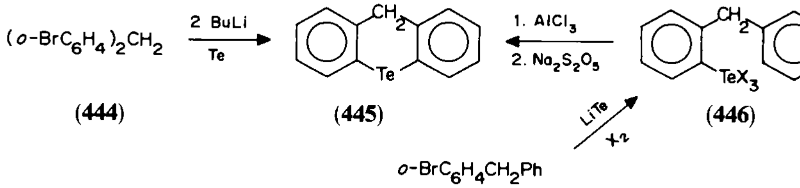
(194)

A similar rearrangement occurs in the thiophene series[932]. Telluroxanthone (**443**) is therefore obtained by more complicated methods. It first preparation was realized in 1979 with a 2% yield by a double nucleophilic ring-closure of 2,2'-benzophenone bis-diazonium salt (**442**) with Na_2Te[934] (equation 195).



(195)

Another method consists of the oxidation of Te-dichlorotelluroxanthene with potassium dichromate[936] or chromium trioxide[933]. The dichloro precursor is prepared by electrophilic cyclization of **446**[935,936]. It can be dechlorinated to telluroxanthene (**445**), which can also be obtained by reaction of Te with 2,2'-dilithiodiphenylmethane[933] (equation 196).



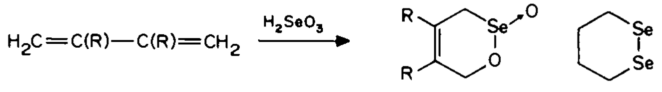
(196)

The characterization of telluroxanthone is troublesome. Its melting point (116 °C) is anomalously low compared with selenoxanthone (191 °C), and the $\nu_{C=O}$ in the IR spectra measured by two research groups are different (1590 and 1640 cm^{-1}). Furthermore, the more logical melting point (202 °C) given in the first publication[934] was later regarded as erroneous by the same authors. Telluroxanthene is characterized by reactions typical of diaryl tellurides such as Te-dihalogenation. Quaternarization by MeI is achieved only with an equimolar amount of silver perchlorate[936]. Telluroxanthone is transformed to 10-telluroniaanthracene perchlorate, the first known telluropyrylium compound, by the standard methods used for the Se analogues (equation 192). These salts also react at position 9 with various nucleophiles[937]. The 9-Ph derivative gives with zinc a stable radical which can be reversibly dimerized[938]. A 1-formyl-2 → 8-heptahydrotelluroxanthene has been surprisingly obtained from bis(2-formylcyclohexen-1-yl) telluride[939].

B. Two Heteroatoms without Nitrogen

1. *Monocyclic systems*

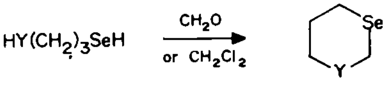
a. Heteroatoms in the 1,2-*position* : 1,2-*dichalcogenanes.* The structure of the reaction products of substituted butadienes with selenous acid (equation 197) at room temperature, previously proposed as selenones of 2*H*,5*H*-selenophene, is actually of a cyclic seleninic ester type, namely 4,5-disubstituted 1-oxa-2-selena-4-cyclohexene-2-oxide (**447**)[940]. However, the structure of the corresponding sulphone was confirmed in a parallel reaction with SO_2. Formation of the 1,2-diselenane **448**[230] leads to a problem similar to that for 1,2-diselenolane. The compound is a low-molecular polymer, present as the monomer only in solution[941]. The 3,6-dicarboxy derivative is prepared by hydrolysis of *rac*-di(selenocyano)adipic acid[942].



(197)

(447) **(448)**

b. Heteroatoms in the 1,3-*position:* 1,3-*dichalcogenanes.* 1,3-Oxaselenanes, 1,3-thiaselenanes and 1,3-diselenanes (**450**) were prepared for conformational studies, from reactions of 1-hydroxy- and 1-mercapto-propaneseleno-3-ols and from 1,3-propanediselenol derivatives (**449**), respectively, with acidic aqueous formaldehyde or dichloromethane[52] (equation 198). 1,3-Diselenane-2-selone (a triselenocarbonate) and 1,3-diselenane-2-dimethoxycarbonylmethylene (a ketene diselenoacetal) have been obtained from the reaction of 1,3-dibromopropane and CSe_2[533] or of CSe_2 and malonate anion[534], respectively. The only 1,3-heteratelluranes known are 1,3-tellurasilane derivatives, obtained from dimethyl(chloromethyl) (γ-chloropropyl)silane[943].

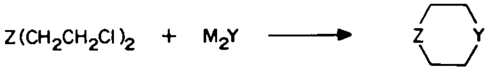


(198)

(449) **(450)**

Y = O, S, Se

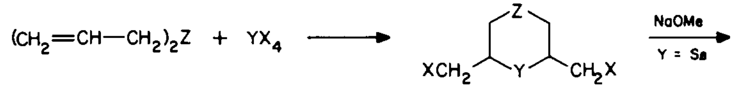
c. Heteroatoms in the 1,4-*position.* (*i*) 1,4-*Dichalcogenanes.* These compounds (**452**) are obtained by two different methods; the more general one consists of a double nucleophilic substitution of *β*,*β*′-dichloroethylchalcogeno ethers (**451**) by the chalcogenide anion (equation 199). 1,4-Oxaselenane (Z = O, Y = Se, 33%)[231,944] 1,4-thiaselenane (Z = S, Y = Se, 44%)[945] (but not Z = Se and Y = S)[946], 1,4-diselenane (0.3% from Li_2Se)[947], 1,4-



(451) **(452)**

(199)

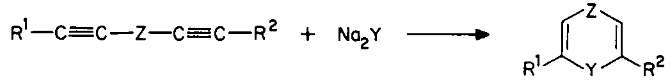
oxatellurane ($Z = O$, $Y = Te$, 46%)[232] and 1,4-thiatellurane ($Z = S$, $Y = Te$, 6%)[948] were obtained by this method. The yield of 1,4-diselenane can be improved to 10% starting from ethylene bromide and aluminium selenide[949]. These heterocycles easily form complexes on Se or Te with halogens. 1,4-Diselenane gives easily the bis-selenoxide, and is quaternarized by MeI[947]. The second method consists of an electrophilic addition of selenium tetrahalide[950] or tellurium tetrahalide[238] to the diallyl ethers or thio ethers **453** (equation 200). A methanolic solution of potassium selenocyanate and cupric chloride gives the same type of derivative **454** ($X = OMe$)[951].



(453) **(454)** **(455)**

(200)

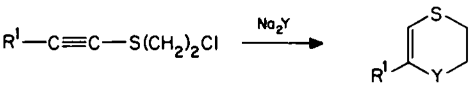
(*ii*) 1,4-*Dichalcogenins*. 3,5-Dimethyl-1,4-thiaselenin (**455**) ($Y = Se$, $Z = S$) and the corresponding 1,4-oxaselenin[950] have been prepared by dehydrohalogenation of **454**; formation of 2,5-diphenyl-1,4-diselenin by basic thermolysis of phenylacetylene with Se has been reported[952a], while tetra(trifluoromethyl)-1,4-selenin is prepared from *cis*-1,2-diiodo-1,2-(trifluoromethyl)ethylene and Se[952b,c]. However, the general method of preparation of 1,4-dichalcogenins (**457**) consists of the bis-nucleophilic addition of chalcogenide anion or hydrogen chalcogenide to the bis-acetylenic system **456** (equation 201) ($R^1 = H$; $R^2 = Me$, Et, *t*-Bu; $Y = S$, Se, Te; $Z = S$[953,954], SO_2[955], or $P(O)R$[956], in the two



(456) **(457)**

(201)

last cases with $R^1 = R^2$). When this method was applied to alkenyl alkynyl sulphoxides and Na_2S or Na_2Se it gave the *S*-oxides of 2,3-dihydro-1,4-dithiin and 1,4-thiaselenin[957]. The 2,3-dihydro derivatives **459** are prepared by a more versatile method: a mixed ring closure from **458** is based on a nucleophilic substitution of the halogen followed by addition to the alkyne (equation 202)[958]. 1,4-Diselenin can also be obtained by thermolysis of 1,2,3-selenadiazoles[758].



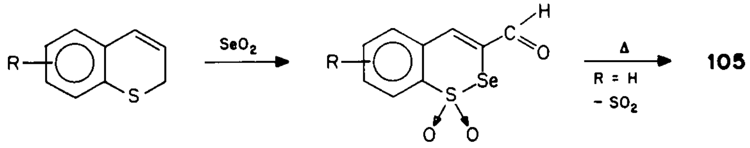
(202)

(458) **(459)**

$Y = Se, Te$

2. Benzo-condensed systems

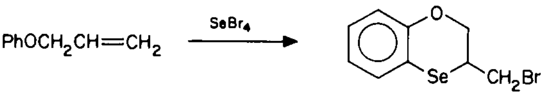
Only two publications have appeared relating to this area. The first one reports the formation of 3-formyl benzo(*e*)-1,2-thiaselenin-1,1-dioxide (**460**), from the oxidation of thiochromenes with four moles of SeO_2 in pyridine (equation 203). The unsubstituted, 6-Me, 7-Me and 8-Me and 5,8-, 6,7- and 6,8-di-Me derivatives were prepared[289] with yields



(203)

(460)

of 35%. The structure of **460**, which is a rare example of a selenosultone, has been proved by X-ray diffraction. Compound **460** loses quantitatively SO_2 by thermolysis and its 3-formyl group can be transformed to the 3-carboxy and the 3-ethoxycarbonyl functionalities. The second report deals with the formation of **462** by a simultaneous addition and electrophilic substitution of $SeBr_4$ on phenyl allyl ether (**461**)[959] (equation 204).

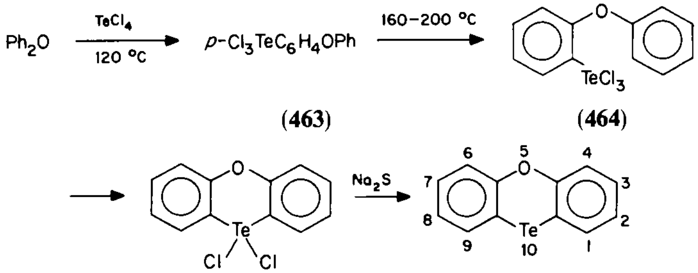


(204)

(461) **(462)**

3. Dibenzo-condensed systems

a. Phenoxaselenins and phenoxatellurins. The main synthesis of phenoxatellurins consists of heating $TeCl_4$ and diphenyl ethers at temperature of ca. 200 °C. In this way the parent compound **466**, which is the first derivative of the series, was prepared in 1926[960,961] (equation 205). Under milder conditions, **463** was initially obtained, but it

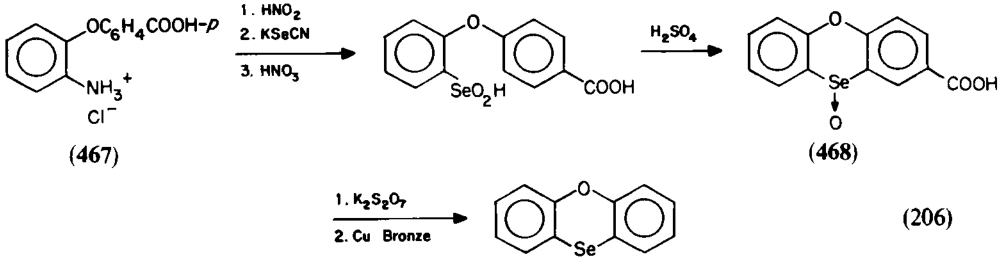


(205)

(463) **(464)**

(465) **(466)**

isomerizes at higher temperatures to **464**. Dechlorination can be affected by sodium sulphite[960] or sulphide[962]. The method has been applied to the preparation of various 2,8-disubstituted derivatives: 2,8-dimethyl[963], 2,8-difluoro[964], 2,8-dichloro[965,966], 2-chloro-8-methyl[968,969] and 2-fluoro-8-methyl[966]. The 2,8-dibromo derivative cannot be prepared by this method. It is obtained in 86% yield by bromination of the dibromo analogue of **465**[967]. The 4′-substituted analogues of **464** can be conveniently obtained from the corresponding 2-chloromercuri salts and $TeCl_4$. By cyclization they give 2-monosubstituted phenoxatellurins (e.g., 2-Me, 2-COOH)[968]. The 2-nitro derivative cannot be prepared by this reaction but it is obtained by nitration of **466**, via the corresponding 2-nitro-10,10-dinitrate[961,968], together with the 4-nitro and the 2,6- and 2,8-dinitro derivatives. It gives by reduction the 2-amino analogue. The reaction described in equation (205) does not work with $SeCl_4$, whose chlorinating power is too high. The phenoxaselenin was obtained for the first time in 1928[970] from **466** and Se and the mixture of the two chalcogenins was separated via their 10,10-dibromides. The parent phenoxase-



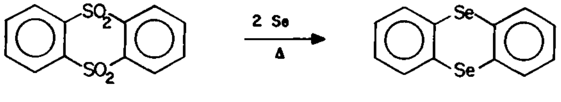
(467) (468) (469)

(206)

lenin **469** was also synthesized ten years later from a suitably substituted aminodiphenyl ether **467**[971] (equation 206). Phenoxatellurin is stable in acidic medium, but extruses Te in basic medium, with formation of diphenyl ether[961]. The Te atom can also be lost by replacement with S[966] or Se. The tellurium dichloride **465** gives dibenzofuran by treatment with degassed Raney Ni and Cu[972]. The strong ability of the Te atom to react with halogens can be used to dehalogenate gem-dihalides[973], such as phenoxaselenin dibromide. Analysis of the dipole moments of phenoxachalcogenins (O: 0.55D; S: 1.18; Se: 0.73; Te: 0.38) leads to the conclusion that these molecules adopt a non-planar conformation in solution, and are folded along the axis of the two heteroatoms. UV and photoelectron spectroscopic data support these conclusions[974]. Phenoxachalcogenins form conductive complexes with TCNQ, and the conductivity, of the order of 10^{-7}–$10^{8}\,\mathrm{ohm^{-1}\,cm^{-1}}$, shows no significant change with the nature of the chalcogen[975].

b. Phenothiatellurin. This has been prepared with a yield of 40% by the method described in equation (205), starting from $TeCl_4$ and diphenyl thioether, at temperatures of ca. 250 °C[976]. The structure has been confirmed by transforming it to thianthrene by means of S[973].

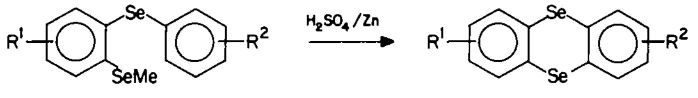
c. Selenanthrene. The first synthesis of selenanthrene (**471**)[977] which was achieved in 1896 and gave later an improved yield of 44%[337] consists of the reaction of Se with thianthrene tetraoxide **470** (equation 207). Selenanthrene was also prepared in 70% yield



(470) (471)

(207)

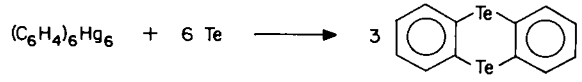
by Japanese workers at the same time as the 1-Me, 2-Me and some polymethyl derivatives (**473**), from 2-(methylseleno)diphenyl selenides **472** and H_2SO_4 in the presence of Zn[738,978] (equation 208). Selenanthrenes were also obtained in high yields by pyrolysis of 1,2,3-benzoselenadiazoles, and this was the first example of a new method which led later to important developments (see Section on condensed 1,2,3-selenadiazoles), for the synthesis of many 1,4-diselenin analogues. Selenanthrene has also been prepared in 8% yield by heating benzeneselenenyl chloride with P_2O_5[737], in 50% yield by reaction of potassium amide with diphenyl selenide in liquid ammonia[979], in 9% yield by pyrolysis of tetraphenyltin with Se at 300 °C[980] and in low yield from 1-aminobenzotriazole and SeO_2[981]. 2,3,7,8-Tetramethoxyselenanthrene, obtained by Se insertion by SeO_2 into *o*-dimethoxybenzene[982], has been studied as a charge-transfer π donor[983,984]. Perfluoroselenanthrene can be produced by heating *o*-diiodotetrafluorobenzene with Se at



(472) (473) (208)

320 °C, whereas loss of a Se atom occurs at higher temperatures[340,985]. Selenanthrene can be easily oxidized to the 5, 10-dioxide with nitric acid via the dihydronitrate[986], as well as with hydrogen peroxide, and the dioxide is also obtained by hydrolysis of the *Se*, *Se*-tetrachloro derivative[987].

d. Telluranthrene. Telluranthrene (**475**), whose production was claimed in 1964 from the reaction between tetraphenyltin and Te metal[988], was actually prepared in 72% yield, and well characterized, in 1981 by Dereu and Zingaro from hexameric *o*-phenylenemercury (**474**) and Te[989] (equation 209). Telluranthrene is convered thermally to dibenzotellurophene. X-ray diffraction confirms the structure and shows a dihedral angle of 124° between phenyl rings[990]. Selenanthrene is also obtained by this method, but in only 5% yield. Perfluorotelluranthrene has been prepared by heating diiodotetrafluorobenzene with Te and Br_2 at 300 °C, and subsequent debromination with Na_2S[991a]

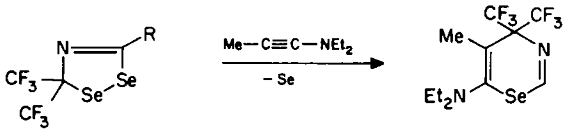


(474) (475) (209)

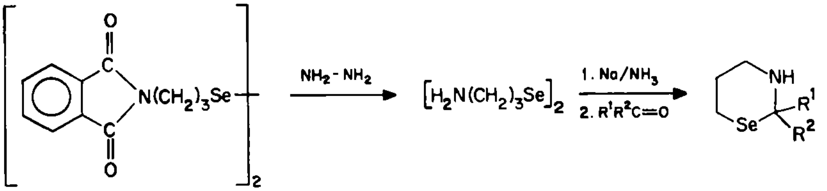
C. Two Heteroatoms with Nitrogen

1. Monocyclic systems

a. 1,3-Selenazines. Only one 1,3-selenazine has actually been described: the 4*H* derivative **477** is obtained from the Se heterocycle **476**, which serves as a potential heterodiene towards an ynamine[733,736] (equation 210). However, some oxo derivatives are known: the 4-oxo compound 2-chloro-4-oxo-1,3-selenazine is produced by hydrochloric acid ring-closure of *Z*-β-(cyanoseleno)acryloyl chloride[991b]. The 4-oxo-5,6-dihydro 2-diphenylamino-5,6-diphenyl derivative is obtained (38% yield) from 1,1-diphenylselenourea and diphenylcyclopropenone. Selenoamides, contrary to thioamides which give normal reaction, lead only to a diselenole system by Se insertion into the small ring[495]. Reaction of *N*,*N*′-dimethyl (or diphenyl)selenourea with methyl acetylenedicarboxylate gives 4-oxo-2-methylimino-(or 2-phenylimino)-3-methyl-(or phenyl)-6-ethoxycarbonyl-3,4-dihydro-selenazine[992], whose ring can be dihydrogenated for confirmation of its structure. Some perhydroselenazines **480** ($R^1 = H$, $R^2 =$ Me, 4-XC_6H_4 (X = H, Cl, Br); $R^1 = R^2 =$ Me) have been prepared by a general method from (di(γ-aminopropyl) diselenide and a carbonyl compound[993] (equation 211). Compounds **480** can be *N*-benzoylated in pyridine, but not in aqueous



(476) (477) (210)



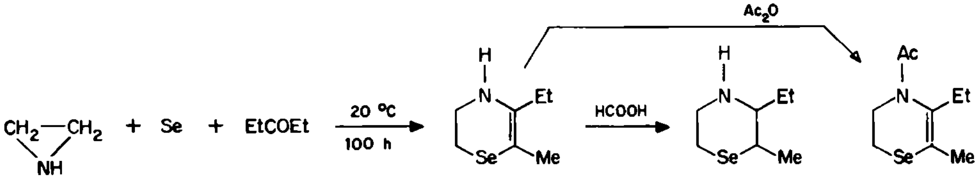
(478) **(479)** **(480)**

$$\xrightarrow[\text{PhCOCl}]{\text{NaOH}} \text{PhCOSe(CH}_2\text{)}_3\text{NHCOPh} \qquad (211)$$

(481)

alkaline medium, where they convert to the *N*,*Se*-dibenzoyl derivative **481**, a reaction parallel to that of the corresponding five-membered ring. The 2-iminoperhydroselenazine, the first derivative of this ring-system, is known since 1890, and obtained by boiling γ-bromopropylamine and potassium selenocyanate in aqueous solution[994]. Some 4-oxo-2-imino and 2,4-dioxo derivatives are prepared from trichloromethylpropiolactone and *Se*-ethylselenopseudourea[995]. Reaction of NaHS with cinnamoyl isoselenocyanate gives the corresponding 6-phenyl-4-oxo-2-thioxo system[996]. 2-Amino-1,3-selenazinium salts are obtained from β-chloropropenylideniminium salts and *N*-substituted selenoureas[997]. Mesoionic derivatives of anhydro-1,3-selenazinium hydroxides are formed from a reaction between a selenoamide and a 1,3-bielectrophile such as chlorocarbonyl phenyl ketene.

b. 1,4-*Selenazines.* The reaction between aziridine, Se and 3-pentanone results in a direct selenization of the acidic CH group, and forms the 5,6-dihydro-4*H*-1,4-selenazine **482**. By reduction of the ring, **482** leads to 2-methyl-3-ethylselenomorpholine[998] (equation 212). **482** can be normally *N*-acetylated to **484**.

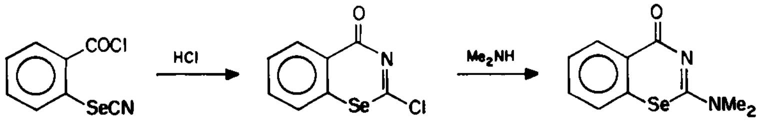


(482) **(483)** **(484)**

(212)

2. Benzoselenazines and hetero analogues

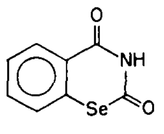
a. 1,3-*Benzoselenazines.* The only described products in this series are 2-chloro-1,3-benzoselenazin-4-one **486**, prepared by cyclization of *o*-(cyanoseleno)benzoyl chloride with HCl, and its 2-dimethylamino derivative**487**[499,1000a] (equation 213). A 4,8-dimethyl-



(213)

(485) **(486)** **(487)**

2-imino-1,3-benzoselenazine-3-oxide has been proposed as the product between 3-methyl-2-cyanoselenoacetophenone and hydroxylamine[595]. Two other derivatives have also been prepared but not reported[598]: the 2,4-dioxo derivative **488** is synthesized by ring-expansion of 2-ethoxycarbonylbenzisoselenazolin-3-one with Fe and acetic acid. It is exclusively methylated on N with diazomethane. 2-Methyl-2,3-dihydrobenzoselenazin-4-one (**489**) can be formed from 2-acetylbenzoselenazolin-3-one and Zn in acetic acid. Hypophosphorous acid gives only a ring-opening in this reaction, but not the subsequent ring-closure. Pyrido-(3,2-*e*) and (3,4-*e*)-1,3-selenazine-4-one-2-thione or -2-selone have been recently obtained[1000b]



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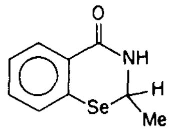
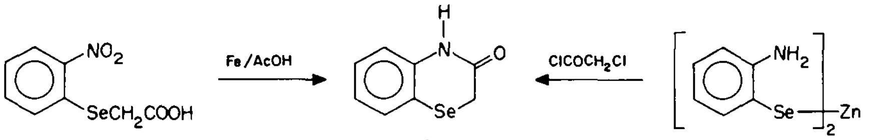


(489)

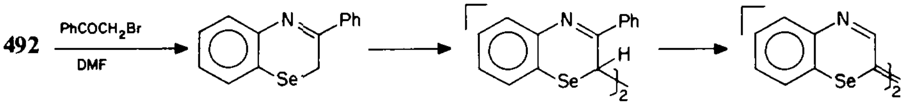
b. 1,4-Benzoselenazines. Behagel and Rollmann[1001] prepared the first derivative of the series (**491**) by reduction of *o*-nitrophenyselenoacetic acid and direct cyclization. It is also obtained from the Zn salt **492** and chloracetyl chloride[1002,1003] (equation 214). By a



(490) **(491)** **(492)**

(214)

similar procedure, reaction of **492** with acetylenedicarboxylic acid results in the 2-carboxymethylene derivative of **491**[1004]. When reated with P_2S_5, **491** is transformed to the corresponding thione[1003] which is further condensed with bromoacetone to give 1-methylthiazolo(2,3-*c*)-1,4-benzoselenazine, a compound used for further synthesis of cyanine dyes. From **492** and ω-bromoacetophenone in DMF a mixture comprising 50% 3-phenyl-2*H*-1,4-benzoselenazine (**493**), 30% 2-phenylbenzoselenazole and 20% benzoselenazole is formed[598]. Like its S analogue, the 2-methylene group of **493** is easily oxidized to give the system **494** and its oxidation derivative **495** (equation 215). By reaction with SeO_2 in pyridine, a product of ring-contraction, 2-benzoylbenzoselenazole has been isolated, besides 2-phenylbenzoselenazole.

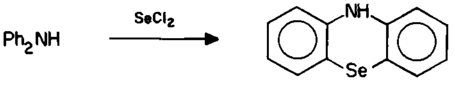


(493) **(494)** **(495)**

(215)

3. *Dibenzochalcogenazines and hetero analogues*

a. Phenoselenazines. Phenoselenazine (**497**) and its 2-chloro derivative have been prepared by the reaction of diarylamines (e.g. **496**) and $SeCl_2$[1005–1008] (equation 216). Bauer has also prepared the 4-nitro and the 2,4-dinitro derivatives[1009] from *o*-

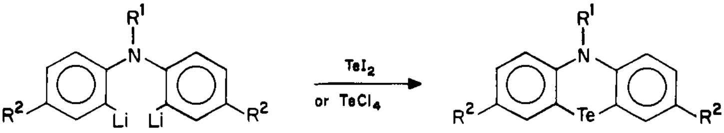


(496) (497)

(216)

aminoselenophenol and picryl chloride. Various reactions on the N of **497** have been performed: methylation[1005,1007], cyanoethylation[1007], attachment of aminoalkyl derivatives for pharmacological screening[1010], alkylation[1011] and aroylation[1008]. Friedel–Crafts has been studied[1012] and the *N*-aroyl derivatives have been oxidized to the corresponding selenoxide with phenyl iodosoacetate[1013]. The dimerization of the cation radicals of phenoselenazine and of its benzo(*c*)derivative, prepared by equation (216), has been studied[1014]. Monopyrazine and monoquinoxaline analogues of **497** have been prepared by reaction of **492** with 2,3-dichloropyrazine[1015] and 2,3-dichloroquinoxaline respectively[595,1015]. Se analogues of methylene blue, in particular 3,6-bis(dimethylamino)phenoselenazinium have also been prepared and studied[1016–1018] as selenazine dyes. They are obtained by the general reaction of equation (216) by using H_2Se, or by bromination of **497**, followed by amination.

b. Phenotellurazines. The chemistry of phenotellurazine is very recent. The first publication deals with the preparation of a monoquinoline analogue, the 1*H*-dibenzo(*b*,*g*)-4-tellura-1,8-naphthyridine[1019], obtained from 2-anilinoquinoline and $TeCl_4$, followed by dechlorination with Na_2SO_3. 2,8-Dimethyl-5-ethylphenotellurazine (**499**: $R^1 = Et$, $R^2 = Me$)[1020] and the 5-methylphenotellurazine (**499**; $R^1 = Me$, $R^2 = H$)[1021] are prepared by reaction of the 2,2′-dilithio derivative **498** with $TeCl_2$ and $TeCl_4$, respectively (equation 217). The direct reaction of $TeCl_4$ on the amine **496**, a reaction working well for the synthesis of phenoxatellurine, failed completely.

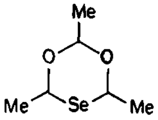


(498) (499)

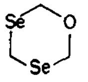
(217)

D. Three Heteroatoms without nitrogen

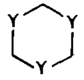
Nearly all the known derivatives of this series are of the 1,3,5-type. Compound **500**, the first known derivative of the 1,3,5-dioxaselenane type, also known as the monoselenium analogue of paraldehyde, is prepared by reaction of H_2Se with acetaldehyde in aqueous acidic solution, near 0 °C[1022]. Similarly, the parent derivative is obtained from formaldehyde, together with 1,3,5-oxadiselenane[1023]. The parent 1,3,5-oxadiselenane (**501**) is also obtained from α,α′-dichlorodimethyl ether and Na_2Se in methanol[1024]. This compound is easily polymerized. The symmetric 1,3,5-triselenane (**502a**), the trimer of selenoformaldehyde, is the best known of these compounds. It was first obtained in 1915[1025] and again in 1938[1026], but it was incorrectly formulated as selenoformaldehyde. It was prepared in 1950 in 11% yield by reaction of H_2Se with acidic formaldehyde, or by hydrolysis of α,α′-dichloromethyl selenide[1027] and identified as the trimer. The by-products of the former reaction are a linear polymer and a tetramer. The structure was confirmed by X-ray crystallography. **502a** was also later obtained from dichloromethane and Na_2Se[1028,1029], and in 1982 by the first method[1030]. It is decomposed by Cl_2 to



(500)



(501)



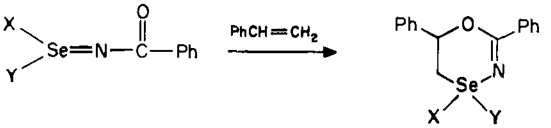
(502)
(a) Y = Se
(b) Y = Te

dichloromethyl selenide, diselenide and chloromethylselenenyl chloride[1027]. The trimethyl homologue of **502a** is prepared similarly from acetaldehyde[1022]. The 1,3,5-tritellurane analogue **502b** is also similarly prepared[1031–1033]. More recently it has been obtained by reaction of Te on the methylene produced by thermolysis of diazomethane[1034]. Its chemistry remains unexplored. Among the other Te derivatives, the 1,3,2-benzodioxatellurane has been prepared according to the general synthesis of dialkoxytellurides by trans-esterification of diols, by using *o*-hydroxybenzyl alcohol as the diol[1035]. A 1,2,6-selenadigermane is also known[1036].

E. Three Heteroatoms with Nitrogen

1. One nitrogen

Three 5,6-dihydro-1,4,3-oxaselenazines were obtained in 1979 1,4-cycloaddition of styrene to the heterodiene Se=N=C=O system of *N*-benzoylselenimides[1037] (equation 218). This was the first six-membered system with Se linked to N. The 5-trichloromethyl-3-imino-3*H*-1,4,2-thiaselenazine-1,1-dioxide, a unique member of this ring system is obtained via the general ring-opening of β-lactones with *Se*-ethyl selenourea, except that the propiolactone is replaced by a propiosultone[1038]. *N*-Methyl-1,3,5-perhydrodiselenazine is obtained by thermolysis of a eight-membered ring-system, a diselenadiazocane[1039] (cf. equation 225).



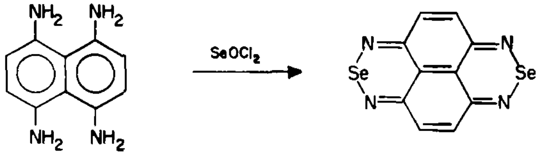
(503) **(504)**

(218)

2. Two nitrogens: selenadiazines

a. 1,2,4-*Selenadiazines.* Reaction of allylthiourea and selenium monochloride leads to 3-thioxo-6-chloromethyl-1,2,4-perhydroselenadiazine[1040a]. 5-Methyl-3,4-diphenyl-1,2,4-benzoselenadiazine has been prepared recently by thermolysis at 180 °C of the ylid form of a diaza analogue of selenabenzene, 5-methyl-1,3-diphenyl-$1\lambda^4$, 2,4-benzoselenadiazine[1040b]. This reaction is parallel to that in the sulphur series.

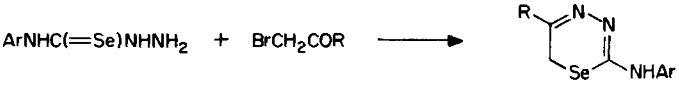
b. 1,2,6-*Selenadiazines.* Se insertion in *o*-diamines by means of SeO_2 has been applied to 1,8-diaminonaphthalene, giving 1*H*,3*H*-naphtho(1,8-*cd*)-1,2,6-selenadiazine[1041]. This reaction could not be reproduced, but with $SeOCl_2$ the corresponding 1*H*,3*H*-2-selenoxide has been isolated in 51% yield. Applied to the tin double salt of 1,4,5,8-tetraaminonaphthalene (**505**), this reaction leads by double Se insertion to naphtho (1,8-*c,d*: 4,5-*c′,d′*) bis-1,2,6-selenadiazine (**506**)[1042] (equation 219).



(505) (506)

(219)

c. 1,3,4-*Selenadiazines.* Reaction of 4-arylselenosemicarbazides with α-haloketones does not give five-membered selenazoline derivatives, but 2-arylamino-5-substituted 6*H*-1,3,4-selenadiazine **507**[637,1043] (equation 220). A structural proof is based on the reaction of the 6-methylene group with *p*-nitrobenzaldehyde. The isolated intermediate eliminates Se easily, as in the sulphur series.



(507)

(220)

d. 1,3,5-*Selenadiazines.* The reaction of primary amines, formaldehyde and CSe_2[1044] or phenyl isoselenocyanate and NaSeH[1045] leads to tetrahydro-1,3,5-selenadiazine-2-selones. By reaction with H_2Se and formaldehyde, benzylamine, contrary to other aliphatic or aromatic amines, gives 3,5-dibenzyl-1,3,5-selenadiazine, a six-membered ring derivative, instead of an eight-membered ring[1039] (see Section VII.A). A tricyclic dibenzoselenadiazinium dibromide, a dipyrido analogue of selenoxanthene, has been synthesized[1046] by a reaction parallel to that in the sulphur series, but which failed in the corresponding oxygen and nitrogen series.

F. Heteroatoms

1-Oxa and 1-thia-4-selena-2,6-disilanes or -digermanes are formed by bis-nucleophilic attack of the appropriate dichlorodisiloxane or digermoxane by Na_2Se[1047,1048]. In the Te series, the 3*H*,6*H*-1,2,4,5-tetratellurin is formed by reaction of K_2SO_3 and methylene bis(tellurium trichloride). The structure has been confirmed by mass spectrometry, NMR and Mössbauer spectroscopies[1049].

VI. SEVEN-MEMBERED RINGS

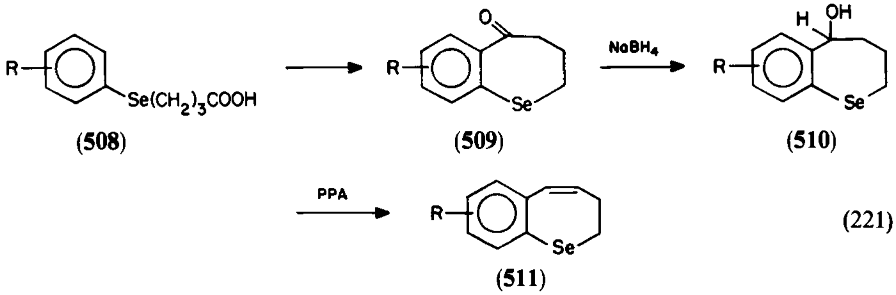
A. One Heteroatom

1. Monocyclic systems

In 1931 Morgan and Burstall[832] prepared selenepane in low yield by the general procedure of ring-closure from Na_2Se and 1,6-dibromohexane. The 1,1,3,6-tetrachloro derivative is obtained by reaction of 1,5-hexadiene with SeO_2 in concentrated HCl[1050]. The 3,6-dimethoxy derivative is also formed in small amounts in the oxyselenation of 1,5-hexadiene with potassium selenocyanate and Cu salts[951].

2. Benzoselenepins and analogues

5-Oxo-2,3,4,5-tetrahydrobenzoselenepins (**509**) (homoselenochromanones) can be synthesized by the electrophilic ring-closure of the corresponding γ-arylselenobutyric acids

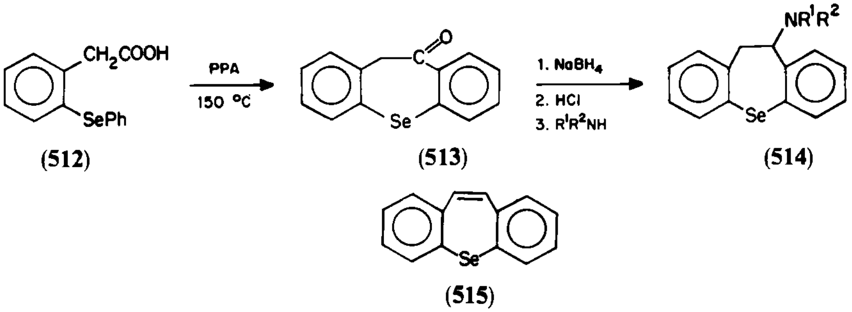


(221)

(**508**) with PPA, or of their chlorides with SnCl$_4$[863,1051]. Compounds **509** have been transformed by standard methods to homoselenochromanols (**510**), the corresponding homochromenes (**511**) and homochromans (equation 221). The method has been applied to various derivatives of **509** (7-Me, 7-t-Bu, 7-Br, 9-Me, 6,9-di-Me and 7,8-di-Me) and to the naphtho[866], benzofuro(2,3-*b*) and benzoselenolo(2,3-*b*)analogues[870].

3. *Dibenzoselenepins*

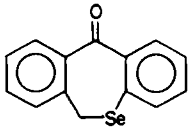
a. Dibenzo(b,f)*selenepins.* The 10,11-dihydro-10-keto compound **513** and its 8-chloro derivative have been prepared in 47% yield by the classical electrophilic ring-closure from **512**. Compound **513** is transformed successively to the corresponding 10-hydroxy, 10-chloro and 10-amino derivatives (**514**) required for the synthesis of analogues of psychotropic benzothiepins[1052] (equation 222). By reaction of *N*-methylpiperazine with the ketone **513**, the parent dibenzoselenepin itself (**515**) has been obtained as a by-product together with the corresponding expected enamine[1053].



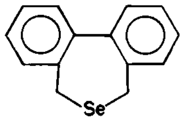
(222)

b. Dibenzo(b,e)*selenepins.* The isomer **516** of **513** has been similarly prepared and transformed to the amino derivatives[1054].

c. Dibenzo(c,e)*selenepins.* A third system, **517**[1055], and its 3,9-diphenyl derivative[1056] have been synthesized from the 2,2′-dibromomethylbiphenyls and Na$_2$Se.



(**516**)



(**517**)

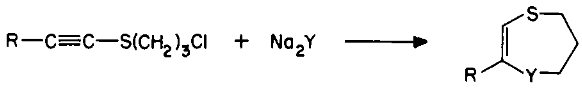
4. Condensed telluracycloheptane

A steroidal telluracycloheptane has been prepared from a steroidal methanesulphonate and Na_2Te[1057].

B. Two Heteroatoms

1. Without nitrogen

Treating 1,5-pentanediselenocyanate with alcoholic KOH gives a compound regarded as 1,2-diselenepane, but which is probably, as are its lower ring homologues, a low-molecular-weight polymer[828]. The intramolecular oxyselenation of diallyl ether gives 3,6-dimethoxy-1,4-oxaselenepane in isomeric mixture with the six-membered ring[951]. By the general reaction of chloroalkylthioalkynes with alkali metal selenide and telluride, Brandsma and coworkers have prepared 5*H*-6,7-dihydro-1,4-thiaselenepin and -thiatellurepin and their 3-Me, 3-Et, 3-*t*-Bu and 3-Ph derivatives (**518**)[958] (equation 223).



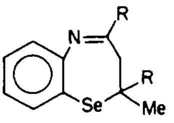
(223)

Y = Se, Te
R = H, Me, Et, *t*-Bu, Ph

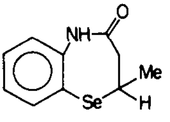
(**518**)

2. With nitrogen: selenazepines

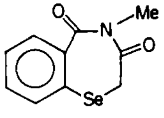
Investigations on the condensation of the Zn salt **492** with mesityl oxide[1058], 3-methylhept-3-en-5-one[1059] and crotonic acid[1060] resulted in the preparation of the 2,3-dihydro-1,5-benzoselenazepines **519** (R = Me, Et), and of the lactam **520**. The dioxo-1,4-benzoselenazepine **521** has been isolated in 74% yield as major product in the reaction of *N*-methylbenzisoselenazolin-3-one with acetic anhydride and sodium acetate[602].



(**519**)



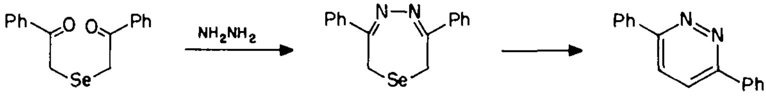
(**520**)



(**521**)

C. Three Heteroatoms

By the general method of trans-esterification of diols a seven-membered dialkoxytelluride is obtained from 2,2′-dihydroxybiphenyl[1034]. A new heterocyclic system, the 2*H*, 7*H*-1,4,5-selenadiazepine ring **523** has been obtained by reaction of equimolecular amounts of hydrazine and selenodiacetophenone **522** (equation 224)[1061a]. This ring undergoes easy thermal ring-contraction to afford the corresponding pyridazine **524**.



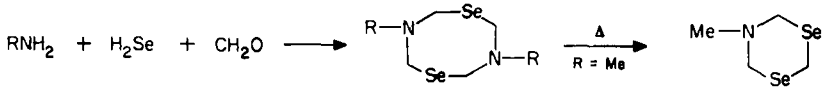
(224)

(**522**) (**523**) (**524**)

VII. LARGER RINGS

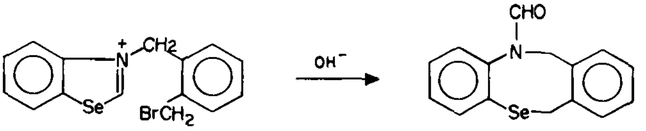
A. Eight-membered Rings

Two tetraselenocane isomer rings are known. The 1,2,5,6-tetraselenocane, a bis-diselenide of diselenoethylene glycol, has been obtained by alkaline hydrolysis of 1,2-ethanediselenocyanate[487,719]. Its dibenzo-condensed system is mentioned as an air oxidation derivative of 1,4-benzenediselenol[1061b]. The 1,3,5,7-tetraselenocane, a cyclic tetramer of selenoformaldehyde, is isolated as a by-product from the reaction of dichloromethane with Na_2Se[1028] and from H_2Se and formaldehyde, which also give the trimer and the pentamer[1023]. The cyclic pentamer, 1,3,5,7,9-pentaselenecane, is also isolated in the former reaction[1029]. 3,7-disubstituted perhydrodiselenadiazocines **525** (R = Me[1039a,b], Et, *n*-Pr, *n*-Bu, Ph, *n*-Hex, PhCHMe[1039b]) are the products generally formed in the reaction of formaldehyde, H_2Se and a primary amine except for benzylamine. These eight-membered rings are thermally unstable and are decomposed to perhydro-1,3,5-diselenazines (**526**)[1039b] (equation 225). The general ring-enlargement of benzoxazolium and benzothiazolium salts has been extended to the benzoselenazolium salt **527**, giving the dibenzo-1,4-selenazocine system **528** (equation 226)[701].



(525) **(526)**

(225)

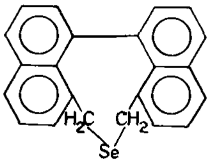


(527) **(528)**

(226)

B. Macrocycles

A few Se-containing peri-bridged naphthalenes are known, including the monoselena 9-membered ring **529**[1062] and the tetraselena 14-membered ring **530**[907]. The latter is obtained by alkaline hydrolysis of 1,8-di(cyanoselenomethyl)naphthalene. A 7-membered cyclic diselenide, the corresponding 'monomer' seems to be the primary product of reaction, and this dimerizes easily to **530**. A dioxaditellura 14-membered ring has been synthesized from sodium orthophthalate and diaryltellurium dichloride[1063]. Among *meta*-substituted benzene macrocycles (metacyclophanes), the 2,11-diselena-(3,3)metacyclophane ring system **531** has been synthesized in 5–10% yield by reaction of *m*-xylylene dibromide with anhydrous Na_2Se[1064a] or KSeCN[1064b]. The corresponding bis-diselenide, namely 2,3,12,13-tetraselena(4,4)metacyclophane (**532**), has been authenti-



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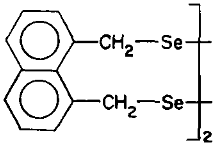
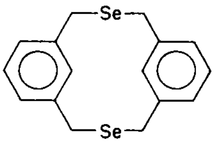
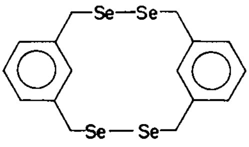


(530)

cally obtained by alkaline hydrolysis of *m*-xylylene diselenocyanate. Its structure has been confirmed by its thermal conversion to **531**[1065], and the dynamic stereochemistry has been studied[1066].



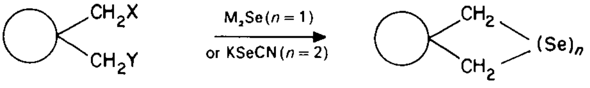
(531)



(532)

VIII. SPIROHETEROCYCLES

The known spiroselenium heterocycles are generally saturated ring systems, where the Se function is a selenide (four-membered ring), a diselenide or a mixed five-membered sulphide and selenide ring system. They are prepared according to equation (227) ($X = Y = Br$). Four-membered ring systems (**534**; $n = 1$), where the first ring may be a cyclohexane (2-selenaspiro(3,5)nonane)[51], an oxetane[1061b] or a second identical selenetane (2,6-diselenaspiro(3,3)heptane)[51], are obtained in this last case by a double ring-closure from sym-tetrabromoneopentane. For the diselenide ring system (reagent KSeCN), the first ring is also either a cyclohexane[1067] or an oxetane[1061b]. The corresponding mixed selenide and sulphide is prepared by reaction of Se with the corresponding four-membered 2-thiaspiro(3,5)nonane[1068a]. The selenone corresponding to the 2-selenaspiro(3,5)nonane is directly obtained by thermal cyclization on the seleninate **533** ($Y = SeO_2Na$) in a sealed tube[51].

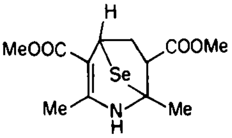


(533) **(534)** (227)

A 1,6-dioxa-5-selena(5-Se^{IV})spiro(4,4)nonane-2,7-dione has been obtained by another method, consisting of oxidation of 3,3′-selenodipropionic acid[1068b].

IX. BRIDGED Se/Te HETEROCYCLES

1-Vinyl-2-selenabicyclo(3.2.0)hepten-3-one is obtained as a by-product of reaction of Se with vinylacetylene[1068c]. 1,3,5-Trimethyl-7-selenabicyclo(2.2.1)heptane-2,3-dione is prepared by SeO_2 oxidation of a cyclic diketone[526b]. A 8-selena-2-azabicyclo(3.2.1)octane **535** is formed through a second ring-closure of dimethyl 4-chloro-2,7-dimethyl-4*H*-azepine-3,6-dicarboxylate by H_2Se, or by ring-enlargement of the corresponding halomethyldihydropyridine[1069], via the same intermediate and with the same Se reagent. Among the bicyclononane analogues the 9-selenabicyclo(3.3.1)nonane **536** is obtained by oxyselenation of *cis,cis*-1,5-cyclooctadiene[951]. The oxathiaselenabicyclo(3.3.1)nonane **537** is also known and is prepared from a tetraiodomethylene cyclobutane[1070]. Based on



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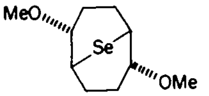

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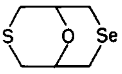

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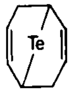

(538)

stereochemical and mechanistic considerations, and episelenonium bridged ion has been suggested as intermediate in the reductive elimination of β-hydroxyselenides of bicyclo(4.2.1)nonatriene in a superacid medium[1071]. A tellura-bridged heterocycle, namely 9-tellurabicyclo(3.3.1)nona-2,6-diene (**538**) has been prepared with 18% yield by reaction of Na_2Te with 3,7-dibromo-1,5-cyclooctadiene. At 175 °C the reaction leads to a bicyclo(5.0.0)octadiene[1072,1073] with bromine elimination induced by telluride anion. A selenatricyclo(2.2.1.1)octane has been obtained by reaction of norbornadiene with $SeBr_4$[1074]. Some selenaadamantanes have also been prepared[1075]. A 2,4,6,8-tetraselenaadamantane and a 2,4,6,8,9,10-hexaselenaadamantane are formed by a route similar to the preparation of the S analogue[60b].

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The Chemistry of Organic
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CHAPTER 14

Tetra- and higher-valent (hypervalent) derivatives of selenium and tellurium

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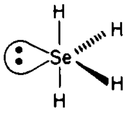
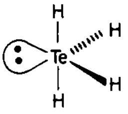
I. INTRODUCTION

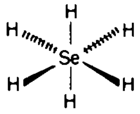
In discussing tetra- and higher-valent Se and Te compounds it is of interest to consider the following hypothetical molecules, which, following Musher[1], are called selenane (**1**), tellurane (**2**), perselenane (**3**) and pertellurane (**4**).



(1)



(2)



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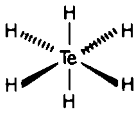
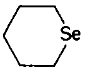


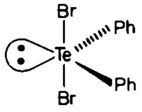
(4)

Simple derivatives of these systems do include $TeCl_4$, SeF_4, SeF_6, TeF_6 and $HOTeF_5$. It should also be noted that the indicated nomenclature is different from that recommended[2,3], but we feel that Musher's system is more suitable for analysis of all the delicate stereochemical problems involved and the system has also been used in a recent comprehensive review[4]. Likewise Martin[5] has recently used this nomenclature when describing a non-dissociative permutational isomerization of a pertellurane. Reich[6] has advocated the name 'selenurane' instead of selenane because the word selenane has been used as a name for selenacyclohexane (**5**). We feel, however, that selenacyclohexane is an excellent name for **5** and 'selenane' a confusing one for that molecule. Hence the name selenane should be reserved for **1**.

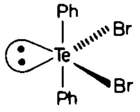


(5)

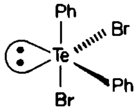
To illustrate Musher's system, consider diphenyldibromotellurane (diphenyltellurium dibromide, by conventional nomenclature) which has been determined[7] by X-ray analysis to be of structure **6a**, i.e. with the halogen atoms in apical positions. The five (still unknown) topomers **6b–f** are also expected to be stable and spectroscopically observable even though it might not be possible to isolate them, due to the likely existence of intra- or inter-molecular equilibration (topomerization).



(6a)



(6b)



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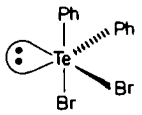

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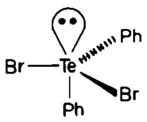

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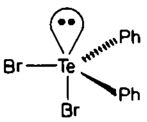
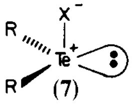


(6f)

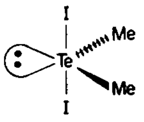
In this connection it is also of interest to note that, in agreement with VSEPR theory[8], all telluranes studied so far[9,10] have their electron pairs in equatorial positions, whereas tetravalent organotellurium compounds of the general structure **7** invariably have a pyramidal arrangement around Te. However, with a suitable choice of substituents or ring constructions other isomers might become favourable (cf. Ref. 11).



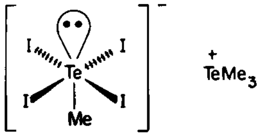
(7)

X = O, NR, CR_2

The classical problem[12] with α- and β-forms of Me_2TeI_2 has been resolved by Einstein[13,14], who found that while the α-form is *e,e*-dimethyl-*a,a*-diiodotellurane (**8**) the β-form has in fact the more complex structure **9**.

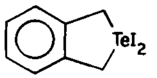


(8)



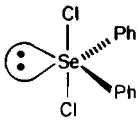
(9)

In this connection the report[15] by Ziolo and Günther about the simultaneous formation of at least two crystalline forms of 1,1-diiodo-3,4-benzo-1-telluracyclopentane (**10**) is of interest. It was concluded that the two forms are polymorphs.

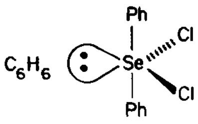


(10)

Although all diorganyldihaloselenanes and diorganyldihalotelluranes studied so far have, in the solid state, the halogen atoms in apical positions the situation might be different in solution. In fact there are indications (dipole moment measurements)[16] that diphenyldichloroselenane, which has the chlorine atoms in apical positions in the solid state (i.e. **11a**), might in solution (e.g. benzene) prefer other arrangement(s) around the central atom (e.g. **11b**). Such topomers, with one or both chlorine atoms in the equatorial position, should be stabilized by solvation as indicated.



(11a)



(11b)

In solution the situation is also complicated by equilibria of the following type (Z = Se, Te; X = halogen):

$$R_2ZX^+ + X^- \rightleftharpoons R_2ZX_2 \rightleftharpoons R_2Z\ldots X_2 \rightleftharpoons R_2Z + X_2 \qquad (1)$$

Problems involved in these equilibria have been studied with various spectroscopic techniques[17] including Se- and Te-NMR. Particularly suitable for such studies is the analysis of magnetic circular dichroism (MCD) data[17a].

II. PREPARATION AND PROPERTIES OF RZX_3, R_2ZX_2 AND R_3ZX

A. General Aspects and Preparation of $ArZX_3$, Ar_2ZX_2 and Ar_3ZX

Many tetravalent organotellurium and organoselenium compounds are readily available via direct methods as indicated by equations (2)–(6). ZCl_4 (or the related combinations TeO_2/HOAc/LiCl and SeO_2/HCl, respectively) are the reagents of choice. If the substrates are insufficiently reactive, addition of $AlCl_3$ or other suitable Lewis acids might be beneficial[18]. Benzene, for instance, will not react with $TeCl_4$ even at reflux temperature but addition of $AlCl_3$ (1 equivalent or more) will cause a vigorous reaction[19] that might even yield Ph_3TeCl. Benzene and a $SeCl_4$–$AlCl_3$ reagent will not similarly[20,32,67–69] yield Ph_3SeCl although Ph_2SeCl_2 can be arylated to Ph_3SeCl by benzene in the presence of $AlCl_3$.

$$AnH + TeCl_4 \xrightarrow[\Delta]{CHCl_3} AnTeCl_3 \xrightarrow[\Delta]{AnH} An_2TeCl_2 \tag{2}$$

$$An = p\text{-}MeOC_6H_4$$

$$AnH + SeCl_4 \xrightarrow[r.t.]{26\,h} An_2SeCl_2 \tag{3}$$

$$PhH \xrightarrow[AlCl_3]{TeCl_4} Ph_3TeCl \tag{4}$$

As indicated above, $TeCl_4$ is acting as a moderate electrophile (a pseudohalogen with a reactivity somewhere between I_2 and Br_2) with an excellent selectivity for telluration and only highly reactive substrates such as undeactivated indoles[21] will be chlorinated. Actually, more than 150 aromatic substrates have been successfully converted into $ArTeCl_3$ or Ar_2TeCl_2 in high yields. For tabulations see Refs. 3 and 4.

The electrophiles ZCl_4 and $ArZCl_3$ do show a strong preference (equations 2 and 3) for attack in the *para* position and the *ortho/para* ratio is unusually low. Thus An_2TeCl_2 is readily isolated as beautiful crystals in 90% yield[22] by reacting $TeCl_4$ with anisole at reflux temperature.

$ArTeX_3$ Ar_2TeX_2 and Ar_3TeX are generally nice crystalline compounds that are easy to store. The aryltellurium trihalides are sensitive to moisture and are hydrolysed[23] to $(ArTe(O))_2O$. The diaryltellurium dihalides are usually quite insensitive to moisture and An_2TeCl_2, for example, can be nicely crystallized[22] from ethanol. Treatment of diaryltellurium dihalides with NaOH will give diaryl telluroxides, Ar_2TeO. Similar exchange reactions[24–26] have been performed with, for example, AcO^-, SCN^- and MeO^- to yield the expected substitution products. Diaryl selenium dihalides behave similarly[27].

Triaryltellurium halides are often distinctly ionic[28,29] (hence they should be written $Ar_3Te^+X^-$) and can often be recrystallized from water or ethanol/water. Needless to say, exchange reactions are easy to perform. Thus addition of a solution of KI in water to a solution of Ar_3TeCl will cause the precipitation of Ar_3TeI. The low solubility of this iodide can be utilized for isolation, e.g. if the compound is prepared according to equation (5), or the variant (6). As indicated, reaction (6) is suitable for the preparation of unsymmetrical compounds.

Preparations according to equations (5) and (6) are relatively complicated and the yields are often unsatisfactory[3].

$$ArMgX + TeCl_4 \rightarrow Ar_3TeX \tag{5}$$

$$Ar_2TeX_2 + RMgX \rightarrow Ar_2RTeX \tag{6}$$

Ziolo and Titus[30] and McWhinnie and coworkers[28,29] have made extensive studies of the structural and solution chemistry of this class of compounds. Solution conductivities and molecular weights show triaryltellurium halides and pseudohalides to be associated non-electrolytes in weakly polar to non-polar solvents such as chloroform and benzene and weak to strong electrolytes in polar solvents.

The triphenyltellurium pseudohalides, Ph_3TeN_3, Ph_3TeNCO, Ph_3TeNCS and $Ph_3TeNCSe$, do all show much more complex IR absorptions in the 1900–2000 cm^{-1} region than one *a priori* should expect. These facts are explained in terms of their oligomeric structures[30].

Ziolo and coworkers[31] have also recently found that Me_2TeCl_2 and Ph_2TeCl_2 undergo direct facile (25 °C in H_2O/CH_3OH) phenylation reactions with $NaBPh_4$ to produce $Me_2TePh^+\ BPh_4^-$ and $Ph_3Te^+\ BPh_4^-$ respectively. Tellurium tetrachloride in benzene similarly undergoes triarylation with excess $NaBPh_4$ to yield $Ph_3Te^+\ BPh_4^-$.

Triarylselenium halides have also ionic character and their chemistry is similar to that of Ar_3TeX, although they are more prone to undergo decomposition in solution according to equation (7).

$$R_3ZX \rightarrow R_2Z + RX \qquad (7)$$

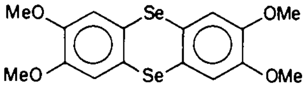
According to Ogawa[32] $Ph_3Se^+\,Br^-$ is not formed when PhMgBr is allowed to react with Ph_2SeBr_2. Instead Ph_2Se and biphenyl are formed, possibly via the unstable tetraphenylselenane (equation 8). The non-formation of $Ph_3Se^+\,Br^-$ thus provides still another difference (cf. equation 6) between organoselenium and organotellurium chemistry. On the other hand Ogawa[32] could prepare $Ph_3Se^+\,Br^-$ in fair yields using equations (9) or (10).

$$Ph_2SeBr_2 + PhMgBr \rightarrow [Ph_4Se] \rightarrow PhSePh + PhPh \qquad (8)$$

$$PhMgBr + SeOCl_2 \rightarrow Ph_3Se^+\,Br^- \qquad (9)$$

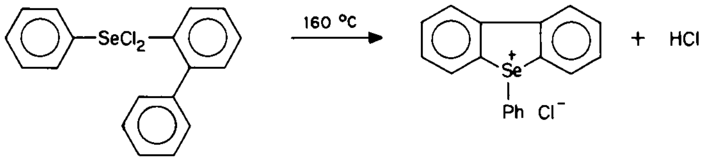
$$Ph_2SeO + PhMgBr \rightarrow Ph_3Se^+\,Br^- \qquad (10)$$

In contrast to the Te series, very few[33] aromatic compounds have been converted into $ArSeCl_3$ or Ar_2SeCl_2 with $SeCl_4$ or $SeOCl_2$ (cf. equations 2 and 3), which are much more reactive than $TeCl_4$. Here chlorination is a much more serious problem. Sometimes dehalogenations occur (cf. equation 1) and selenides are formed, which might react further. Thus 1,2-dimethoxybenzene, when treated[34] with H_2SeO_3 at 130–150 °C, will give **12**.



(**12**)

Electrophilic cyclization reactions of suitable diaryl selenium dichlorides do occur readily[35], as exemplified by equation (11).



(11)

There have been no similar cyclizations reported in the Te series.

$$RSeX_3 \rightarrow RSeX + X_2 \qquad (12a)$$

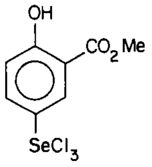
$$RSeX_2R \rightarrow RSeR + X_2 \qquad (12b)$$

$$RSeR \xrightarrow{X_2} RSeX_3 \qquad (12c)$$

$$RSeSeR \xrightarrow[\text{or } SO_2Cl_2]{X_2} RSeX + RSeX_3 \qquad (12d)$$

$$RSeCN \xrightarrow{X_2} RSeX_3 \qquad (12e)$$

Generally speaking, diorganylselenium dihalides and monoorganylselenium trihalides are much less stable than the corresponding Te isologues. The selenium trihalides are generally prepared from[36] diorganyl diselenides or selenocyanates (i.e. by indirect methods) under carefully controlled conditions as indicated by equations (12c–12e). Actually very few organyl selenium trihalides have been isolated using direct procedures and it is tempting to suggest that the often cited stable product **13**[37], obtained by treating methyl salicylate with $SeCl_4$, might in fact be the isomer **14**, which should be stabilized by Se—OH coordination. Certainly this problem should merit a detailed study. In this connection the reported[38] formation of **15** from the reaction of *o*-cresol with SeO_2 in the presence of HCl is of interest, as well as the reported[39] formation of $(4\text{-}HOC_6H_4)_3Se^+\ Cl^-$ together with an unidentified isomer from the reaction of phenol with $SeOCl_2$.



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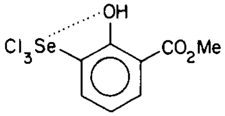

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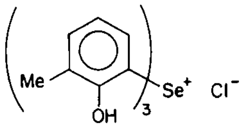


(15)

In addition to the direct methods for the preparation of tetravalent organo-selenium and -tellurium compounds discussed above, other methods, involving, for example, oxidative addition to selenides and tellurides[24,25,40] as well as exchange reactions[24,41–52] of organometallic and organoelemental compounds, are frequently used. The last-mentioned technique is particularly useful for the preparation of unsymmetrical compounds of the type RZX_2R^1.

$$R_2Te + (SCN)_2 \rightarrow R_2Te(SCN)_2 \tag{13}$$

$$R_2TeI_2 + HOSO_2Cl \rightarrow R_2Te(OSO_2Cl)_2 + 2\,HI \tag{14}$$

$$RC_6H_4Si(CH_3)_3 + TeCl_4 \xrightarrow[\text{reflux}]{\text{toluene}} RC_6H_4TeCl_3 \tag{15}$$

$$ArHgCl + Ar^1TeCl_3 \rightarrow ArTeCl_2Ar^1 + HgCl_2 \tag{16}$$

$$AnTeCl_3 + Ph_6Pb_2 \rightarrow AnTeCl_2Ph \tag{17}$$

$$4\text{-}EtOC_6H_4TeCl_3 + 1{,}3\text{-}(HO)_2C_6H_4 \rightarrow 4\text{-}EtOC_6H_4TeCl_2C_6H_4(OH)_2\text{-}1{,}3 \tag{18}$$

$$4\text{-}EtOC_6H_4TeCl_3 + AnH \rightarrow An_2TeCl_2 + PhOEt \tag{19}$$

$$ArHgX + PhH \rightarrow ArH + PhHgX \tag{20}$$

Direct methods for the preparation of unsymmetrical diaryltellurium dihalides can sometimes be used, particularly when the aromatic reactant is readily susceptible to electrophilic aromatic substitution (equation 18)[51]. In other cases (equation 19) exchange reactions[18] might be troublesome. Nothing is known about the mechanism of such exchange reactions in the Te series (they are unknown in the Se series) but related exchange reactions in the Hg and Tl series have been studied[53–57] using kinetic methods (equation 20).

$TeBr_4$ and $SeBr_4$ are less reactive than the corresponding chlorine compounds and should be interesting alternatives when sensitive (notably π-excessive heterocyclic) reactants are involved. TeF_4 and SeF_4 are certainly interesting reagents for introduction of Te and Se into organic substrates, albeit that very limited information is available in the literature. Actually no compounds of the types $ArZF_3$ or Ar_2ZF_2 have been prepared using these reagents. Compounds of the type R_2SeF_2 were prepared for the first time by Wynne and Puckett[58,59] by treating a selenide with AgF_2 (equation 21).

$$ArSeAr \xrightarrow{AgF_2} Ar_2SeF_2 \tag{21}$$

By this reaction also, aliphatic derivatives such as dimethylselenium difluoride and diethylselenium difluoride can be obtained. Later other fluorinating agents[60-66] such as SF_4, XeF_2, F_2 and ClF have been used as examplified by equations (22)–(25).

Other methods for the preparation[28,42] of organic Te and Se compounds containing fluorine depend on exchange reactions (equations 26 and 27).

$$Ph_2Te + Ph_2XF_2(X = S,Se) \rightarrow Ph_2TeF_2 + Ph_2X \tag{22}$$

$$(CF_3)_2Te + ClF \xrightarrow{-78\,^{\circ}C} (CF_3)_2TeClF \tag{23a}$$

$$(CF_3)_2TeClF \rightarrow (CF_3)_2TeF_2 + (CF_3)_2TeCl_2 \tag{23b}$$

$$(CF_3)_2TeX_2 + X_2 \rightarrow CF_3TeX_3 + CF_3X \tag{24}$$

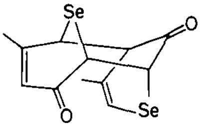
$$ArZAr \xrightarrow{SF_4} ArZF_2Ar \tag{25}$$

$$Ar_2TeO \xrightarrow{HF} Ar_2TeF_2 \tag{26}$$

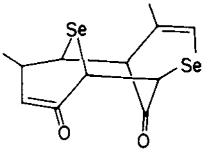
$$Ar_3TeCl \xrightarrow[2.\ HF]{1.\ Ag_2O} Ar_3TeF \tag{27}$$

B. Reactions of ZX_4 and RZX_3 with Carbonyl Compounds

$TeCl_4$ and $SeCl_4$ (and related reagents, e.g. $SeOCl_2$) do readily attack a wide variety of aliphatic and aromatic ketones, as indicated in equations (28)–(34). Early studies in the field were made by Morgan and Elvins[70], Michaelis and Kunckell[71,72] as well as others[73]. Thus, condensation of acetone and of methyl aryl ketones with ZX_4 readily occur in ether or chloroform yielding dichlorides. The products are often unstable and, particularly in the presence of HCl or HBr, α-haloketones as well as other products are formed. Sometimes quite unexpected products are formed (equation 31)[74]. The selenapyrylium salt formed in this reaction undergoes dimerization in the presence of base to give **16**; it is not yet clear which of the two possible isomers (**16a** or **16b**) is formed.



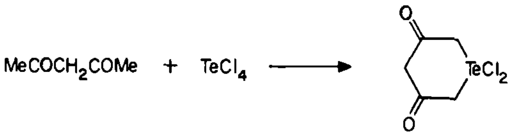
(16a)



(16b)

Silylated carbonyl compounds do react readily with ZX_4 (equations 32 and 33)[75] and might offer advantages when sensitive materials are involved. The reaction according to equation (32) quickly yielded $(PhCOCH_2)_2TeCl_2$ as colourless silky needles. However, so far, very few interactions between electrophilic Te and Se species and silylated reactants have been studied. Much more research in this area is desirable. It should be added that the activation of the ketone indicated in equation (33) is not always necessary. In many cases $RTeX_3$ will give reactions with unactivated ketones[76].

$$PhCOMe + ZCl_4 \rightarrow PhCOCH_2ZCl_3 \xrightarrow{PhCOMe} (PhCOCH_2)_2ZCl_2 \qquad (28)$$



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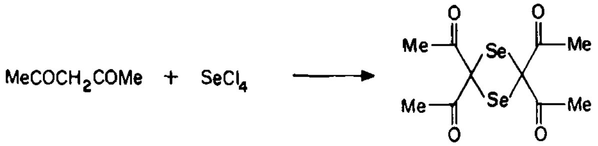

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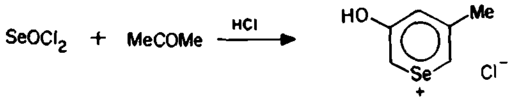
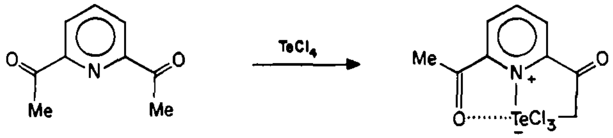


(31)

$$PhC(=CH_2)OSiMe_3 \xrightarrow{TeCl_4} (PhCOCH_2)_2TeCl_2 + ClSiMe_3 \qquad (32)$$

$$PhC(=CH_2)OSiMe_3 + p\text{-}EtOC_6H_4TeCl_3 \rightarrow p\text{-}EtOC_6H_4TeCl_2CH_2COPh + ClSiMe_3 \qquad (33)$$



(34)

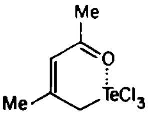
Morgan and Elvins[70] studied the interaction of $TeCl_4$ with several unsymmetrical ketones and claimed, for example, the formation of $(PrCOCH_2)_2TeCl_2$ from 2-pentanone. This regiochemistry is, however, erroneous and O'Brien[77] has recently shown by NMR studies that the correct structure is $(MeCOCHEt)_2TeCl_2$. O'Brien also isolated the compound **17** from the condensation of acetone with $TeCl_4$. The structure of **17** was verified by an X-ray analysis (the C—Te distance is 2.15 Å and the O—Te distance is 2.44 Å) and it was concluded that acetone did first condense to 4-methyl-3-pentene-2-one(mesityl oxide) (**18**), which is subsequently attacked by $TeCl_4$ at one of the γ-methyl groups.

Bis(benzoylmethyl)tellurium dichloride, $(PhCOCH_2)_2TeCl_2$, is sensitive to light and has been considered[78] for imaging purposes in photographic processes. The products from equations (29) and (34)[79] are also of interest in this respect.

The solution photochemistry of $(PhCOCH_2)_2TeCl_2$ has been studied in detail by Marsh and coworkers[80] who found that the compound undergoes facile β-cleavage of the C—Te bonds and an intramolecular Norrish Type II photoelimination reaction as the sole photochemical processes. Te and acetophenone are the two major photoproducts formed during photolysis of $(PhCOCH_2)_2TeCl_2$ at 313 nm in degassed hydrogen atom-donating solvents, while photolysis in degassed solutions of benzene or acetonitrile yields Te and $PhCOCH_2Cl$ as principal photoproducts. In addition smaller amounts of 1,2-dibenzoylethane and acetophenone are produced.

In view of the interesting properties found for $(PhCOCH_2)_2TeCl_2$ and related compounds it is surprising to find that $(PhCOCH_2)_2Te$ is not reported in the literature. Attempts[70] to prepare this divalent Te compound by sulphite reduction failed, due to C—Te bond cleavage. On the other hand Ajello found[81] that the Se isologue,

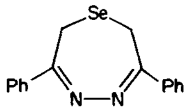
$(PhCOCH_2)_2SeCl_2$, can be successfully reduced by zinc powder in CS_2, a method introduced by Kunckell and Zimmermann[72]. Pyrosulphite reductions are also possible[82]. Ajello also reported that $(PhCOCH_2)_2Se$ with hydrazine yielded the seven-membered compound **19**.



(17)

$Me_2C{=}CHCOMe$

(18)

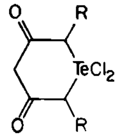


(19)

Very little seems to be known about reactions between aldehydes and tetravalent Se and Te reagents, and defined Se- or Te-containing products have not yet been published in spite of extensive studies[83] of the reactions of SeO_2/HCl with aldehydes in the area of analytical chemistry. However, very recently[218] the formation of 2,6-dialkoxy-3,5-dialkyl-1,4-oxaselanacyclohexane 1,1-dichlorides by reaction of aliphatic aldehydes with SeO_2 in alcohols containing aqueous HCl has been reported.

An interesting distinction between $SeCl_4$ and $TeCl_4$ in their reactions with acetylacetone has already been observed by Morgan and coworkers[84,85]. Thus $SeCl_4$ will attack the CH_2 group to yield what was finally[87] identified as the diselenetane shown in equation (30), while $TeCl_4$ will attack the Me groups yielding the cyclic tellurium dichloride shown in equation (29). The structures given in the original papers for these two products were erroneous and were later corrected (e.g. the diselenetane by NMR studies)[86] and finally verified by X-ray crystallography[87–94].

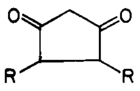
1,5-Substituted acetylacetones will also give products of type **20**. In fact only when the carbon atoms 1 and 5 do not bear any hydrogen atoms will $TeCl_4$ attack the CH_2 group. Thus, dibenzoylmethane yields the unstable compound **21**.



(20)

$PhCOCH(TeCl_3)COPh$

(21)



(22)

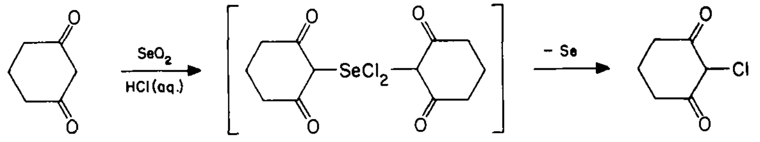
$R^2CH{=}CHCOCH_2COCHR^1$

(23)

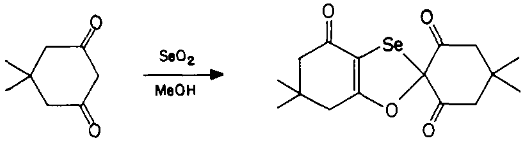
Finally, it might be mentioned that attempts have been made[95] to explore the unique regiochemistry in the product **20b** (from the reactions of derivatives of acetylacetone with $TeCl_4$) for synthetic purposes. However, attempted coupling reactions (e.g. with degassed Raney nickel) gave a disappointingly low yield of the desired cyclopentan-1,3-diones **22** and the major isolated products had the structure **23**. Further experiments in this area, e.g. with silylated reactants, would be of interest.

The outcome of the reactions between Se reagents and 1,3-diketones is strongly dependent on the specific structures as underlined by equations (35) and (36). In none of these reactions were diselenetanes observed[96–98]. The formation of 1-chlorocyclohexan-

1,3-dione probably proceeds via the selenium dichloride indicated in equation (35). This chlorine insertion reaction is closely related to the transformations (RSeR + $Br_2 \rightarrow$ RBr and RSe(O)R + HBr $\rightarrow$ RBr) reported by Krief and coworkers[99].



(35)



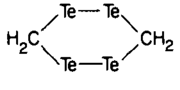
(36)

Acetic anhydride and $TeCl_4$ in a 6:1 molar ratio in chloroform yield bis(carboxymethyl)tellurium dichloride and $CH_2(TeCl_3)_2$ (equation 37), as discovered by Morgan and coworkers[100,101]. The primary condensation products are most likely derivatives of acetic anhydride. Hydrolysis to the acid derivative ($HOOCCH_2TeCl_3$ has also been isolated in some experiments) occurs during isolation of the products.

$$\text{MeCOOCOMe} \xrightarrow[2.\ H_2O]{1.\ TeCl_4} Cl_2Te(CH_2COOH)_2 + CH_2(TeCl_3)_2 \qquad (37)$$

The ability of tellurium tetrachloride to react with homologues of acetic anhydride diminishes rapidly with increasing size of the hydrocarbon chain. Whereas trichlorotelluropropionic acid has been obtained in the reaction with propionic anhydride and identified as the ditelluride, the reaction with butyric and isovaleric anhydrides causes reduction of tellurium tetrachloride and formation of unidentified products[101].

Reduction of $CH_2(TeCl_3)_2$ yields 1,2,4,5-tetratelluracyclohexane (**24**)[100,102]. The structure of **24** is supported[102] by mass spectrometry, NMR data and ^{125}Te Mossbauer spectroscopy. The interesting compound $CH_2(TeCl_3)_2$ has recently been prepared in better yields by Wudl[103,104], who has also used this compound for the preparation of some interesting conducting polymers $(CH_2Te_2)_n$. For further details see the chapter on Se/Te-containing polymers.

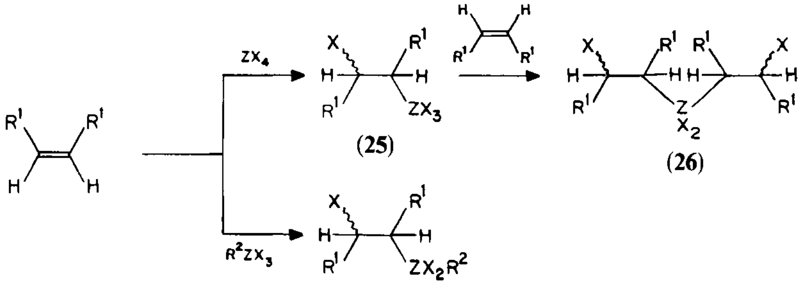


(24)

C. Reactions of ZX_4 and RZX_3 with Alkenes and Acetylenes

1. Reactions with alkenes

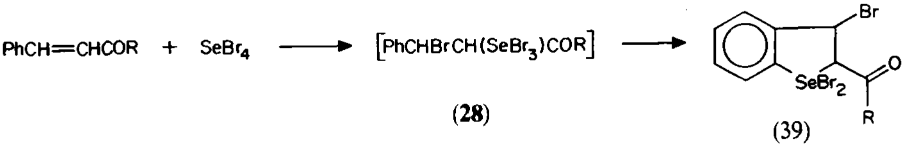
Selenium and tellurium tri- and tetra-halides undergo addition reactions with alkenes to form three principally different addition compounds **25**–**27** as shown in equation (38). The regio- and stereo-chemistry are not indicated in this simplified scheme but will be discussed separately.



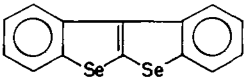
(27)

(38)

In the Se series, no examples of compound **25** seem to be isolable from selenium tetrahalides and olefins. However, these compounds are undoubtedly formed as reactive intermediates during the preparation of compounds **26**. The reaction of $SeBr_4$ with benzalacetone[105] affords products where the unstable 1:1 adduct **28** has undergone a cyclization reaction (equation 39). The formation of benzoselenopheno[2,3-*b*] benzoselenophene (**29**) from $SeOCl_2$ and 1,1-diphenylethylene provides a more complicated example of a similar series of reactions[106–108].

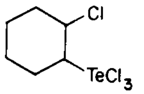


(39)



(**29**)

On the other hand, compounds of the type **25** are quite stable in the Te series. Tellurium tetrachloride and cyclohexene yield the crystalline adduct **30**[109–111]. Similar addition compounds are obtained from ethene[112], propene[113], *E*- and *Z*-2-butene, 1-decene, cyclopentene, cyclooctene[113,114] and 1,5-cyclooctadiene[115]. Tellurium tetrabromide and ethene form[116] the 1:1 adduct $BrCH_2CH_2TeBr_3$ (**31**).



(**30**)

Compounds **26** in the Se series are readily available via several methods.

Diselenium dichloride, Se_2Cl_2, and ethene produce a bis(β-chloroalkyl)selenium dichloride **32** as shown in equation (40)[117,118]. This process does involve several steps, including the formation of $SeCl_2$ (equation 41), which is probably the active selenating agent. Diselenium dichloride is then functioning as a chlorinating agent to give the observed product (equation 42). The described procedure is useful only for a limited number of olefins and often results in formation of bis(β-chloroalkyl)selenides[119,120], or mixtures with the corresponding selenium dichloride[118].

$$2\,CH_2{=}CH_2 + 2\,Se_2Cl_2 \rightarrow \underset{\textbf{(32)}}{(ClCH_2CH_2)_2SeCl_2} + 3\,Se \qquad (40)$$

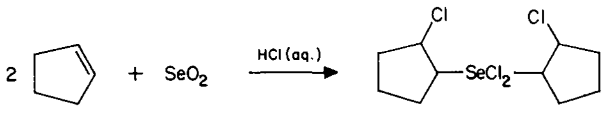
$$Se_2Cl_2 \rightarrow SeCl_2 + Se \qquad (41)$$

$$SeCl_2 + 2\,CH_2{=}CH_2 \rightarrow (ClCH_2CH_2)_2Se \xrightarrow[-2\,Se]{Se_2Cl_2} \textbf{32} \qquad (42)$$

Selenium oxychloride behaves in a similar way to diselenium dichloride towards olefins. Selenium dioxide is a by-product in this process (equation 43)[121].

$$2\,CH_2{=}CH_2 + 2\,SeOCl_2 \rightarrow \textbf{32} + SeO_2 \qquad (43)$$

The most general method for the synthesis of compounds **26** uses selenium dioxide in aqueous hydrochloric or hydrobromic acid, respectively, for the generation of $SeCl_4$ and $SeBr_4$[38,122–124]. The synthesis of bis(2-chlorocyclopentyl)selenium dichloride (**33**), exemplifies this process (equation 44).



(44)

(33)

Ethene, propene, 1-hexene, styrene, allyl chloride, allyl bromide, methallyl chloride, methallyl bromide, vinyl chloride, vinyl acetate, cyclohexene[122–124] as well as methylenecyclobutane, allylbenzene and allyl phenyl ether[125,126] have been treated analogously with $SeCl_4$ and/or $SeBr_4$.

The reaction of $SeCl_4$ and $SeBr_4$, respectively, with olefins under non-aqueous conditions represents another method of obtaining compounds **26**. Thus, styrene and $SeCl_4$ afford compound **34** in high yield (equation 45)[127]. Ethene, propene[128,129], *E*- and *Z*-2-butene[130], 1-hexene, 1-pentene, cyclohexene[127] and vinyl chloride[119] yield similar products with $SeCl_4$. $SeBr_4$ gives addition compounds with ethene[128] and allyl bromide[119].

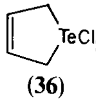
$$2\,PhCH{=}CH_2 + SeCl_4 \rightarrow \underset{\textbf{(34)}}{(PhCHClCH_2)_2SeCl_2} \qquad (45)$$

One problem with these reactions is the halogenating properties of selenium tetrahalides. Uemura[131,132] has observed chlorination of cyclohexene, cyclooctene and norbornene with $SeCl_4$ and Migalina[133] has similarly observed halogenation of a series of styrenes using $SeCl_4$ and $SeBr_4$.

Compounds **26** are not so well represented in the Te series, but a few examples are known. Tellurium tetrachloride can be combined with ethene[112,123], propene[112,134], 1-butene[135] and cyclohexene[111,123] to give normal 1:2-addition compounds. A 1,4-addition is observed for butadiene[112] which yields compound **35**. However, under slightly different reaction conditions[136] (refluxing acetonitrile instead of CCl_4 at 30–60 °C), a 2,5-dihydrotellurophene **36** is obtained as the only product. The latter is probably a cyclization product of the former (loss of 1,4-dichloro-2-butene).

$(ClCH_2CH{=}CHCH_2)_2TeCl_2$

(35)

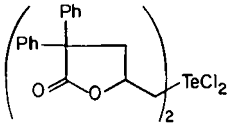


(36)

The unsaturated acid **37** undergoes internal lactonization during the reaction with $TeCl_4$ to give a symmetrical bis-adduct **38**[110].

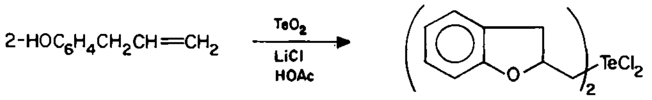
$CH_2{=}CHCH_2CPh_2COOH$

(37)



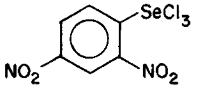
(38)

Similar cyclizations are observed when γ- and δ-hydroxy olefins are treated with tellurium dioxide, TeO_2, in acetic acid containing lithium chloride (this system might be viewed as a source of $TeCl_4$)[137]. The oxidative cyclization of 2-allylphenol is shown in equation (46). These adducts are nice crystalline compounds. The NMR spectra do indicate coordination between O and Te.



(46)

Tellurium tetrabromide forms the symmetrical adduct $(BrCH_2CH_2)_2TeBr_2$ (**39**) with ethene[116].

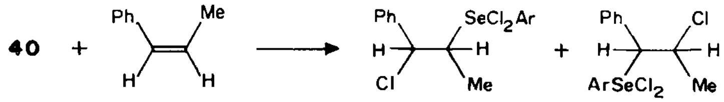


(40)

$MeSeCl_3$

(41)

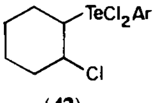
The few known compounds **27** in the selenium series were all prepared by Garratt and coworkers[138–140]. They added 2,4-dinitrophenylselenium trichloride (**40**) and β-methylselenium trichloride (**41**), respectively, to simple olefins like propene, 2-methylpropene, *E*- and *Z*-1-phenyl-1-propene, *E*- and *Z*-2-butene, 3-methyl-1-butene and 3,3-dimethyl-1-butene. Mixtures of compounds resulting from Markownikoff and *anti*-Markownikoff addition were frequently obtained, as shown for the addition of **40** to *Z*-1-phenyl-1-propene (equation 47).



(47)

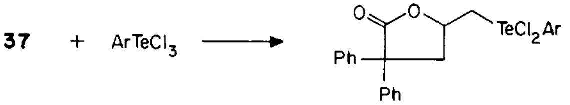
Ar = 2,4-dinitrophenyl

Various aryltellurium trichlorides were added to olefins to obtain compounds **27** in the Te series. Phenyl-, 4-phenoxyphenyl-, 4-ethoxyphenyl- and 1- and 2-naphthyl-tellurium trichloride, respectively, yielded compounds **42** with cyclohexene[109,110].



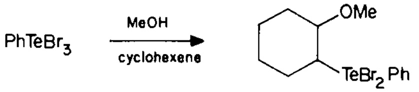
(42)

2-Naphthyltellurium trichloride was similarly allowed to react with propene[141], *E*- and *Z*-2-butene, 1-decene, cyclopentene and cyclohexene[114]. Lactonization was again observed when the unsaturated acid **37** was treated with a series of aryltellurium trichlorides (equation 48)[109,110].



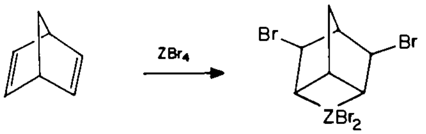
(48)

Uemura[142] allowed aryltellurium tribromides to react with a series of olefins in different alcohols to obtain (β-alkoxyalkyl)aryltellurium dibromides. A typical example is shown in equation (49). When the solvent was changed to aqueous tetrahydrofuran or aqueous *t*-butanol a hydroxy group could be similarly introduced in the β-position.



(49)

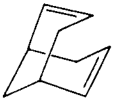
Both selenium and tellurium tetrahalides undergo addition reactions with diolefins to give heterocyclic products. Thus, norbornadiene[143] gives compounds **43** using either $SeBr_4$ or $TeBr_4$ (equation 50). Bicyclo(3,3,1)nona-2,6-diene (**44**) similarly affords compound **45** with $SeCl_4$ and $SeBr_4$[144] and $TeCl_4$ added to 2,2′-bicyclopentene to give compound **46**[145].



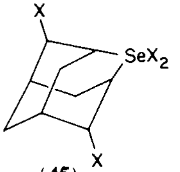
(50)

(43)

Z = Se, Te

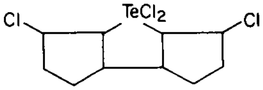


(44)



(45)

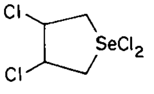
X = Cl, Br



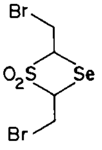
(46)

Selenium tetrachloride generated in aqueous medium gives a selenophene derivative **47** with butadiene[123]. The analogous reaction with $TeCl_4$ (generated from TeO_2 and HCl(aq.)) apparently does not work. As already mentioned, $TeCl_4$ and butadiene form 1,1-dichloro-2,5-dihydrotellurophene (**36**) in acetonitrile[136].

An unusual selenathietan, **48**, has been claimed as the product from divinyl sulphone and $SeBr_4$[146].

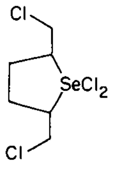


(47)

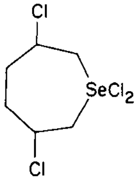


(48)

1,5-Hexadiene forms an addition compound **49** with either diselenium dichloride[120] or selenium tetrachloride[145]. This material was first erroneously formulated as a seven-membered compound **50**[124].

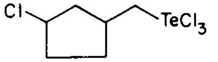


(49)

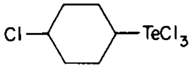


(50)

Migalina and coworkers[148] isolated the Te isologue of compound **49** from the reaction of $TeCl_4$ with 1,5-hexadiene in ethyl ether. However, during a recent reinvestigation of this reaction[149], products **51** and **52** were isolated. This is the first example of a Te-induced

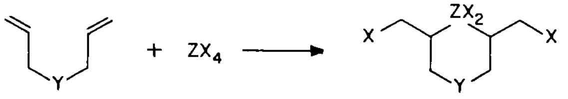


(51)



(52)

carbon–carbon bond formation in reactions with olefins. The 1,6-diolefins **53** undergo addition reactions with selenium and tellurium tetrahalides to form six-membered heterocyclic compounds (equation 51)[147,148,150].



(51)

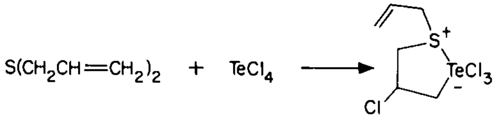
(53)

Y = O, S, NH, NMe

Z = Se, Te

X = Cl, Br

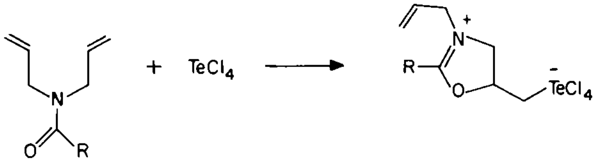
However, when $TeCl_4$ and diallyl sulphide were allowed to interact in acetonitrile, only one double bond was involved in the reaction, yielding the zwitterionic compound **54** (equation 52)[149].



(52)

(54)

A series of *N*-acyldiallylamines behaved similarly[151]. Treatment with $TeCl_4$ and/or $TeBr_4$ afforded a series of zwitterionic oxazolines **55** (equation 53). This is another example of an internal cyclization during the addition of a tellurium tetrahalide to an unsaturated system.

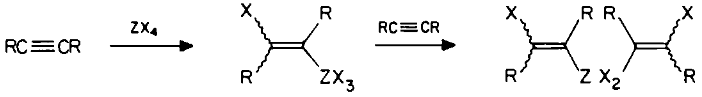


(53)

(55)

2. Reactions with acetylenes

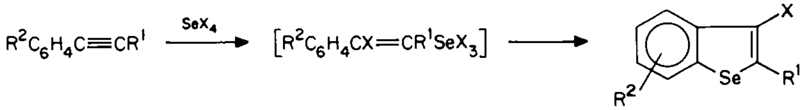
Selenium and tellurium tetrahalides undergo addition reactions with acetylenes to give two different addition compounds **56** and **57** (equation 54); the regio- and stereochemistry of these reactions will be discussed separately.



(56) **(57)**

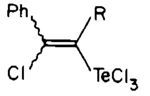
(54)

No compounds of structure **56** seem to have been isolated from the reaction of selenium tetrahalides with acetylenes. However, they were undoubtedly formed as intermediates during the preparation of compounds **57**. They were also postulated as intermediates in the synthesis of benzo(*b*)selenophenes according to equation (55)[152,153].



(55)

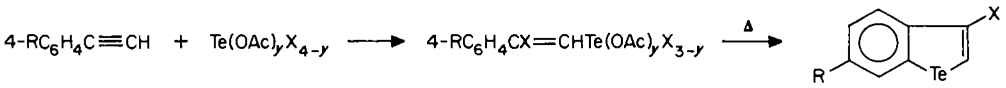
Several examples of compounds **56** have been isolated in the Te series. Phenyl- and diphenyl-acetylene, respectively, yield compounds **58a** and **58b** when treated with $TeCl_4$[154–156]. A series of alkylphenylacetylenes has given similar results[156].



(58)

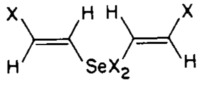
(**a**) R = H
(**b**) R = Ph

Compounds of the principal structure **56** have also been postulated as intermediates in the synthesis of benzo(*b*)tellurophenes from phenylacetylenes and tellurium dioxide in acetic acid containing a lithium halide (equation 56)[157,158].



(56)

Examples of compound **57** can only be found in the Se series. Thus, acetylene was combined with $SeCl_4$ and $SeBr_4$, respectively, to afford compounds **59a** and **59b**[123,124,127]. Phenylacetylene gave an analogous product[127].



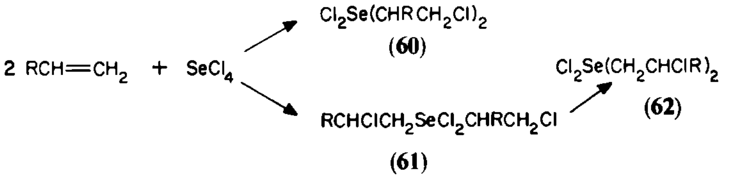
(59)

(**a**) X = Cl
(**b**) X = Br

3. Regio- and stereo-chemistry of the adducts

Although a considerable number of compounds of the different structures **25**–**27** and **56**–**57** have been synthesized, surprisingly little is known about the regio- and stereochemistry of the additions. Consequently, the following conclusions have been arrived at from relatively few experimental observations.

Concerning the regiochemistry of the additions of selenium tetrahalides and alkyl- and aryl-selenium trihalides, both Markownikoff and *anti*-Markownikoff addition has been observed. Equation (47) describes the non-regiospecific addition of 2,4-dinitrophenylselenium trichloride to *Z*-1-phenyl-1-propene[138]. Mixtures of isomers were similarly obtained when selenium tetrahalides were allowed to react with allylic halides[159] and allyl benzene[125]. The addition compounds **27** from selenium tetrahalides and terminal olefins have always been formulated as Markownikoff adducts[119,123], e.g. compound **34**[127]. By the use of modern spectroscopic methods, Garratt has shown that terminal monosubstituted olefins give products **60** and **61** of *anti*-Markownikoff addition under kinetic control as shown in equation (57)[160]. Subsequent rearrangement allows the isolation of the thermodynamically more stable Markownikoff adduct **62**.



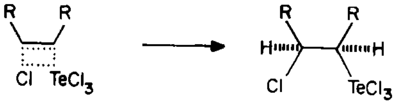
(57)

The stereochemistry of the addition of $SeCl_4$[130] and alkyl-[139] and aryl-selenium[138] trichlorides, respectively, to different olefins has been studied. A stereospecific *anti* addition was observed in all cases.

Tellurium tetrachloride and organyltellurium trihalides always yield products of Markownikoff addition with olefins. However, the few examples of compounds **25**–**27** include only terminal or symmetric 1,2-disubstituted olefins[110,114,134].

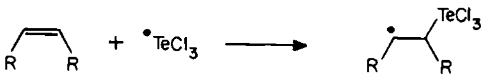
Concerning the stereochemistry Moura Campos and Petragnani[110] have postulated a conventional *anti* addition mechanism as operative for both $TeCl_4$ and aryltellurium trichlorides. This mechanism has recently been confirmed for the addition of 2-naphthyltellurium trichloride to various olefins[114]. The oxytellurations described in equation (49) also occur *anti*-specifically[142].

However, tellurium tetrachloride usually gives mixtures of *syn* and *anti* addition products when the reaction is carried out in chloroform. If a radical inhibitor (*p*-benzoquinone) is added in catalytic amount, the *syn* addition can be highly promoted. A more or less concerted *syn* addition mechanism (equation 58) is therefore postulated for the $TeCl_4$ addition, competing with a non-specific radical process (equations 59–61)[114].

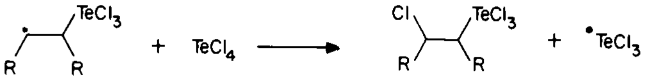


(58)

$$TeCl_4 \longrightarrow {}^{\bullet}TeCl_3 + {}^{\bullet}Cl \qquad (59)$$



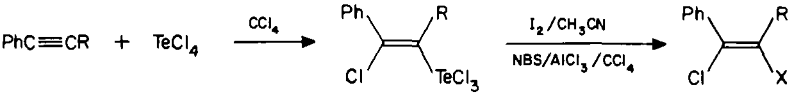
(60)



(61)

The few studies of addition reactions of $SeCl_4$ with acetylenes do not indicate the regio- and stereo-chemistry of the reaction. However, the reaction described in equation (55) has necessarily to involve an *anti* addition to allow cyclization to the benzo(*b*)selenophene system[152,153].

Uemura and coworkers[156] have recently shown that the addition of tellurium tetrachloride to acetylenes is a *syn* process. This conclusion is based on a halodetelluration of the primary addition compound **63** which gives predominantly *Z*-dihaloalkenes **64** (equation 62).

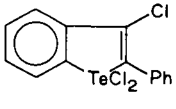


(62)

(63) **(64)**

X = Br, I

On the other hand, equation (56) does indicate that an *anti* addition might also occur under certain reaction conditions, to allow cyclization to a benzo(*b*)tellurophene[157,158]. When Sadekov[155] heated compound **58b** (unknown stereochemistry) in refluxing trichlorobenzene, the benzo(*b*)tellurophene derivative **65** was isolated.



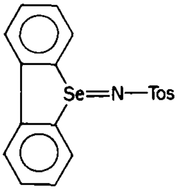
(65)

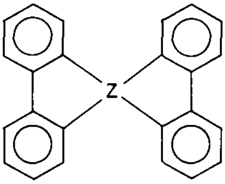
III. PREPARATION AND PROPERTIES OF R_4Z

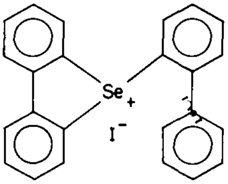
As early as 1888 Marquardt and Michaelis[161] made an unsuccessful attempt to prepare a tetraorganyltellurium compound. They treated $TeCl_4$ with Et_2Zn, which yielded Et_3TeCl. This telluronium salt when heated with Et_2Zn gave Et_2Te and butane.

The first tetraorganyltellurium compound, Ph_4Te, was prepared according to equation (63) by Wittig and Fritz[162] in 1952. Tetraphenyl tellurane could also be prepared from Ph_3TeCl and PhLi. An excess of PhLi is necessary in these reactions, which does indicate the pentacoordinated species, $Ph_5Te^- Li^+$, as an intermediate.

$$Ph_2TeCl_2 + 2\,PhLi \rightarrow Ph_4Te \tag{63}$$





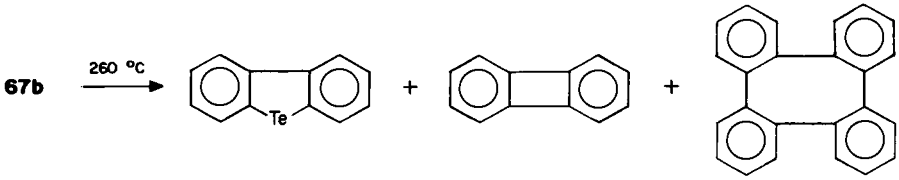


(66) **(67)** **(68)**

(a) Z = Se
(b) Z = Te

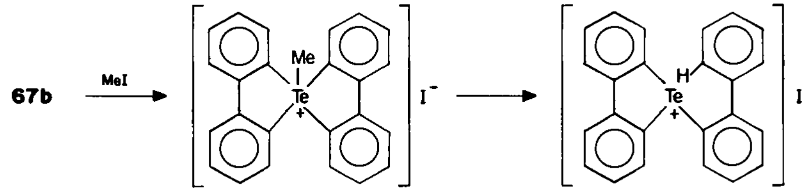
Ph_4Te melts at 104–106 °C with decomposition, but is apparently much more stable than Ph_4Se because treatment of Ph_3SeBr with PhLi gives Ph_2Se and biphenyl. These facts can, however, be explained if Ph_4Se is postulated as an unstable intermediate (cf. also equation 8). This postulate has further been substantiated by subsequent work by Hellwinkel and Fahrbach[163], who prepared, by treating compound **66** with 2,2′-dilithiobiphenyl, compound **67a**, which underwent ring-opening on treatment with water and KI to give 2,2′-biphenylylene-2-biphenylylselenonium iodide (**68**).

Hellwinkel and Fahrbach[163] also prepared compound **67b** by reacting 2,2′-biphenylylene dilithium with $Te(OCH_3)_6$, $Te(OCH_3)_4$ or $TeCl_4$. Compound **67b**, which crystallized as yellow needles and melted at 214 °C is much more stable than tetraphenyltellurium. However, heating to 260 °C for 30 min leads to decomposition yielding dibenzotellurophene, biphenylene and tetraphenylene (equation 64).



(64)

The chemistry of the less stable Se isologue **67a** parallells that of **67b**. Attempts to introduce, with MeI, a fifth group to the spirocyclic Te compound **67b**, resulted in a ring-opening which was interpreted in terms of a pentacoordinated intermediate or transition state (equation 65)[163].



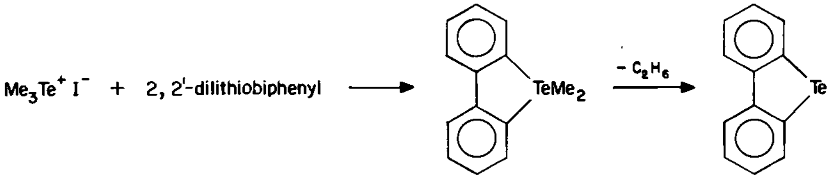
(65)

Another indication of a positively charged pentaorganyltellurium transition state or intermediate was found in the reactions of tetrabutyltellurium with methyl iodide (equation 66). In this reaction a high yield of trimethyltelluronium iodide was obtained and this has been explained by a series of electrophilic exchange processes involving pentacoordination around Te[163].

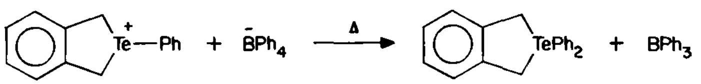
$$\mathrm{Bu_3Te^+\,I^- + BuLi \rightarrow Bu_4Te \xrightarrow{MeI} (Bu_4Te^+Me)I^-}$$

$$\xrightarrow{-\mathrm{Bu\,I}} \mathrm{Bu_3TeMe} \xrightarrow[-3\,\mathrm{BuI}]{3\,\mathrm{MeI}} \mathrm{Me_4Te} \xrightarrow{\mathrm{MeI}} \mathrm{Me_3Te^+\,I^- + C_2H_6} \qquad (66)$$

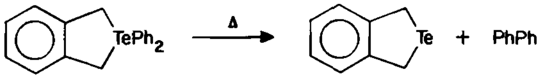
Reactions of related interest are given in equations (67), (68) and (69). The first-



(67)



(68)



(69)

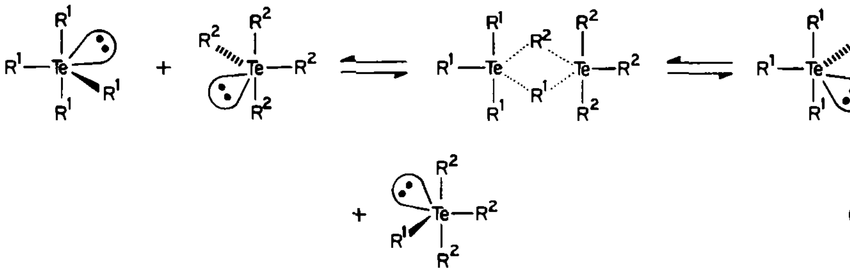
$$\mathrm{Ph_4Te} + t\text{-}\mathrm{BuSH} \xrightarrow{\text{r.t.}} \mathrm{Ph_2Te(SBu\text{-}}t)_2 \longrightarrow \mathrm{Ph_2Te} + t\text{-}\mathrm{BuSSBu\text{-}}t \qquad (70)$$

mentioned is due to Hellwinkel[163] and the others are due to McWhinnie[9]. Mechanistic details of the decomposition of tetraorganyltellurium species have recently been discussed by Glover[164], who also discussed the related reaction (70).

Glover[164] also heated Ar_4Te with known aryl-radical scavengers such as furan and styrene and found that the product pattern did not differ significantly from the neat reaction ($Ar_4Te + \Delta$). It was concluded therefore that the decomposition of R_4Te is a symmetry-allowed concerted process and has an analogy in the reaction of triarylsulphonium salts with optically active alkyllithium reagents (equation 71). This reaction proceeds via the tetravalent Ar_3SR^* intermediate which does decompose with retention of configuration at R.

$$Ar_3S^+ + R^*Li \rightarrow Ar_2S + ArR^* \qquad (71)$$

The results of Glover's radical-scavenging experiments contrast with those from cross-over experiments. Thus, thermal decomposition of mixtures of Ph_4Te and p-Tol_4Te *in vacuo* or in toluene under nitrogen gave, together with the expected symmetrical diaryl tellurides and biphenyls, extensive amounts of 4-methylbiphenyl and phenyl 4-methylphenyl telluride. Since no aryl radicals could be trapped in these experiments it was proposed that the unsymmetrical products arose by a rapid random interchange (equation 72) of aryl ligands prior to decomposition. Analogous non-radical ligand-exchange reactions have been reported for organo-lead and -mercury compounds (cf. also equation 19).



(72)

IV. TETRAVALENT ORGANO-SELENIUM AND -TELLURIUM COMPOUNDS WITH Z—O, Z—S OR Z—N BONDS

Selenoxides (R_2SeO) have been studied intensely due to their importance in synthetic procedures and recent reviews[165,166] are available. This chemistry will therefore not be reproduced here. Some recent interesting entries do include the selective oxidation[167] of

RSH to RSSR and RSR to the corresponding sulphoxides and the introduction of $R_2Se(OCOCF_3)_2$ as an oxidant in organic chemistry by Marino and Larsen[168,169].

Tellurium oxides (R_2TeO), on the other hand, have been relatively neglected. This class of compounds and the closely related compounds, $R_2Te(OR)_2$, can be prepared using methods already established in the Se series as exemplified in equations (73a) and (73b)[65,170,171]. Alcock and Harrison[172] have recently determined the X-ray structure of Ph_2TeO. The compound is monomeric.

$$Ar_2Te \xrightarrow[PhCH_2NEt_3^+, 25°C, H_2O_2]{RCOOH.CHCl_3} Ar_2Te(OCOR)_2 \qquad (73a)$$

$$R_2TeX_2 \quad \overset{OH^-}{} \quad R_2TeO \qquad (73b)$$

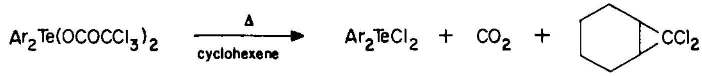
All the known telluroxides, R_2TeO, are white solids. The water-soluble compounds give a basic solution, presumably due to formation of $R_2Te(OH)_2$. In this connection it is interesting to note that the basicity[173] of the oxides increases in the series sulphoxide, selenoxide, telluroxide.

Telluroxides have recently been used for synthetic purposes. Engman and Cava[174] found that bis(*p*-methoxyphenyl)telluroxide did function as a mild catalyst for a variety of aldol condensations.

Lee and Cava[175] and later also Uemura and Fukuzawa[176] studied the elimination of alkenes from telluroxides (equation 74).

$$PhTeBr_2CHMeCH_2R \xrightarrow[H_2O]{OH^-} PhTe(O)CHMeCH_2R \rightarrow RCH_2CH{=}CH_2 + RCH{=}CHMe \qquad (74)$$

Sadekov and coworkers[177] have recently found that Ar_2TeO in *i*-PrOH reacts with formic acid at 60 °C and with trichloroacetic acid at room temperature to give $Ar_2Te(OCOR)_2$ in high yields. The product from trichloroacetic acid, $Ar_2Te(OCOCCl_3)_2$, can be used as a source of dichlorocarbene as indicated in equation (75).



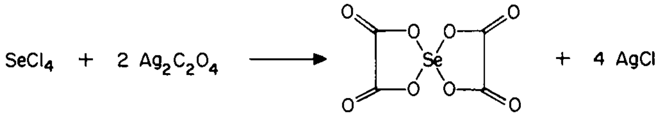
(75)

Telluroxides, notably An_2TeO, have recently been shown to be particularly mild and selective oxidants for a number of substrates[178,179]. Phosphines can be oxidized to their corresponding oxides, while thiols are converted to disulphides. Oxidation of acyl hydrazines produces hydrazides in high yields, whereas aryl hydrazines affords arenes and symmetrical and unsymmetrical tellurides. Of particular significance is the fact that An_2TeO does not react with a number of fairly easily oxidized substrates such as simple phenols, enamines and amines and heterocycles such as pyrrole and indole.

Although a few tetraalkoxytelluranes, e.g. $(MeO)_4Te$, had already been prepared by Meerwein[180] in 1929, their chemistry had not received much attention until the recent work by Denney[181] although Paetzold[182] had studied a number of simple tetraalkoxyselenanes in the early '70s. Generally speaking, $(RO)_4Se$ is much less stable than $(RO)_4Te$ and decomposition according to equation (76) is much more pronounced for the Se compounds. Thus $(EtO)_4Te$ is a distillable colourless liquid, while $(EtO)_4Se$ will readily decompose (above 0 °C) according to equation (76). However, it is well-known that electronegative groups do often stabilize hypervalent molecules and consequently $Se(OCH_2CF_3)_4$ and related compounds are relatively stable distillable liquids[181,183]. Some preparative methods for various $(RO)_4Se$ are given in equations (77)–(80).

$$(RO)_4Z \rightarrow (RO)_2ZO + ROR \qquad (76)$$

$$\mathrm{SeCl_4 + PrOH + 4\,Et_3N \rightarrow Se(OPr)_4 + Et_3NH^+\,Cl^-} \qquad (77)$$



(78)

$$\mathrm{Se(OMe)_4 + 4\,ROH \rightarrow Se(OR)_4 + 4\,MeOH} \qquad (79)$$

$$\mathrm{PhSeBr_3 + 3\,NaOMe \rightarrow PhSe(OMe)_3} \qquad (80)$$

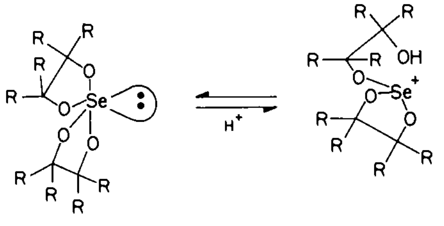
Tetraalkoxyselenanes are stabilized when the central atom is incorporated in a five-membered ring. Thus compound **69a** is a relatively stable crystalline solid[181]. The PMR spectrum of **69a** at room temperature shows[181,184] a single resonance. Upon cooling the spectrum becomes quite complicated and many lines can be observed. Addition of (diethylamino)trimethylsilane, a known acid and water scavenger, led to an extremely complicated but symmetrical ambient spectrum centred at δ 4.07.

Compound **69b** was also prepared as a crystalline solid. The PMR spectrum had resonances at δ 1.20 and 1.25 for hydrogens of non-equivalent pairs of Me groups. The ^{13}C-NMR spectrum of **69b** at room temperature showed two resonances at δ 24.40 and 24.70, assignable to pairs of non-equivalent Me group carbons. A singlet for the quaternary carbons appeared at δ 81.40. At $-112\,°\mathrm{C}$, the ^{13}C-NMR spectrum of compound **69b** exhibited two absorptions separated by 76 Hz at δ 79.0 and 82.8 for non-equivalent quaternary carbons.

The low-temperature ^{13}C-NMR spectrum is consistent with a static trigonal–bipyramidal, TBP, or nearly TBP structure. When the compound is warmed, a reorganization process occurs rapidly on the NMR time-scale which renders the quaternary carbons equivalent but not the pairs of Me group carbons. This process most probably involves axial–equatorial switching of the rings with the lone pair remaining in an equatorial position.

The acid-catalysed process (equation 81) which renders all of the groups equivalent undoubtedly involves **70a** and **70b** in equilibrium with **69a** and **69b**, respectively. Switching of an equatorial position of the rings by ionization, rotation and ring-closure renders *trans* groups equivalent. This process, coupled with intramolecular ligand reorganization, which renders *cis* groups equivalent, leads to all of the various groups becoming equivalent.

The crystal structure of **69b** reveals it to be a distorted TBP with the distortion away from the lone pair. The apical O—Se bond length is 1.871 Å and the equatorial O—Se bond length is 1.77 Å. The angle O—Se—O in the rings is 85.7°, while the O—Se—O angle between the two equatorial oxygens is 109.6°.



(81)

(69)

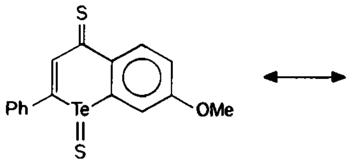
(a) R = H
(b) R = Me

(70)

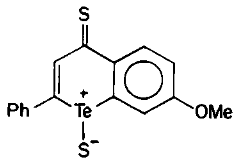
(a) R = H
(b) R = Me

The Te analogues of **69a** and **69b** have also been studied and similar conclusions about ring-switchings and structures have been drawn[181].

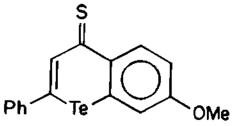
Tetravalent organic selenium and tellurium sulphides have not been greatly studied and part of the field is still controversial. The first compound of the general structure R_2ZS, namely **71**, was reported in 1982 by Detty and Murray[185]. Compound **71** was isolated in low yield when compound **72** was treated with two equivalents of the Lawesson reagent **73** in benzene at room temperature for 17h. The product **71** was a sharp-melting (153.5–155 °C) purple-black solid, whose spectral and analytical data agreed with the formulation **71**. In the transformation **72** → **71** Te has been sulphurated directly by S, presumably from **73**.



(71a)



(71b)



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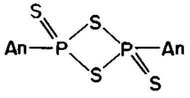
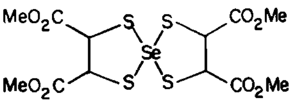


(73)

Compounds of the general structure $Te(SR)_4$ and $Se(SR)_4$ have also been studied[186–188] for some time. Formulae **74–77** are some specific examples claimed in the literature. Compound **74** was obtained by oxidation of *meso*-dimercaptosuccinic acid dimethyl ester with SeO_2 in methanol[187]. Similar reactions were later studied[188] by Czauderna and Samochocka; however, the evidence for the structures is only supported by elemental analytical data. Clearly NMR studies would be of interest in this area.



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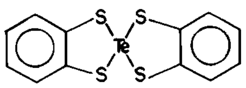
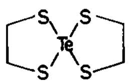


(75)

$Te(SPh)_4$

(76)



(77)

Compounds **75** and **76** were first claimed by Nakhdjavan and Klar[186] who treated the thiols or dithiols with $TeCl_4$ at low temperatures (−8 °C for **76**). The products were relatively unstable and **76** was claimed to decompose around 100 °C. However, very recently Stukalo and coworkers[189] reported that the products described by Klar[186] are in fact equimolar mixtures of diaryl disulphides and bis(arylthio)tellurium. This decomposition (equation 82) took place even at −60 °C. The compound $(PhS)_2Te$ was obtained as low-melting (64–67 °C) orange prisms. The same type of product mixture was obtained with the tetraalkoxytellurane, $(CHF_2CF_2CH_2O)_4Te$, as reactant[189].

$$TeCl_4 + ArSH \rightarrow [(ArS)_4Te] \rightarrow ArSSAr + (ArS)_2Te \qquad (82)$$

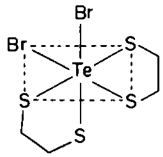
Ready formation of disulphides upon treatment of thiols with tetravalent organotellurium compounds was also reported by Wieber and Kaunziger[171] (equation 83).

$$Ar_2Te(OEt)_2 + HSCH_2CH_2SH \rightarrow Ar_2Te + (SCH_2CH_2S)_n \qquad (83)$$

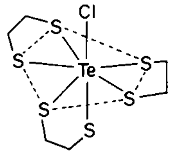
Stukalo and coworkers[189] also reported that treatment of $(ArS)_2Te$ with MeI at room temperature yielded ArSSAr and Me_2TeI_2. This was interpreted in terms of decomposition $(ArS)_2Te$ into ArSSAr and elemental Te, which will then add MeI oxidatively to yield the observed product. However, we think that a reaction pathway as outlined in equation (84) is more likely.

(84)

The interaction of TeX_4 with dithio ligands (dithiocarbamates and xanthates) has been studied by Huseby and Klar[190–196]. In many cases the formation of complexes with interesting structures have been observed. Oxidation–reduction (i.e. formation of disulphides) is common in this area too. Interaction of Et_2NCSSH with $TeBr_4$ and $TeCl_4$ gives $Br_2Te(S_2CNEt_2)_2$ and $ClTe(S_2CNEt_2)_3$, respectively. Simplified structures are represented by **78** and **79**.

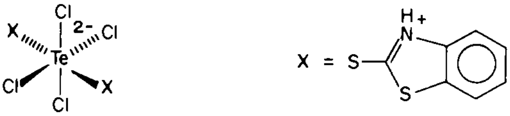


(78)



(79)

2-Mercaptobenzothiazole and $TeCl_4$, yield[116] the interesting complex **80**.



(80)

Organic Te and Se compounds containing Te—N or Se—N bonds had hardly been investigated at all until around 1975. Although the adduct $Me_2TeI_2 . nNH_3$ had been reported in old literature (see Ref. 3, p. 190) the first well-defined compounds with Te—N bonds were reported by Russian workers[197,198], who prepared diaryl tellurimides (equation 85) and tellurium diimide species (equations 86a and 86b, where X = Cl or F).

$$Ar_2TeO + RSO_2NH_2 \rightarrow Ar_2Te{=}NSO_2R \qquad (85)$$

$$TeX_4 + RN(SiMe_3)_2 \rightarrow RN{=}TeX_2 \qquad (86a)$$

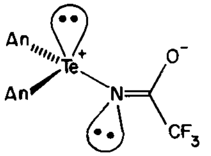
$$RN{=}TeX_2 + RN(SiMe_3)_2 \rightarrow RN{=}Te{=}NR \qquad (86b)$$

The compounds $ArSO_2N{=}TeF_2$ react with *N*-trimethylsilylmorpholine in benzene solution to produce[198] the Te derivative **81**. The Te—N bonds in the compounds $Ar_2Te{=}NSO_2R$ and RN=Te=NR are readily hydrolysed by hot water producing TeO_2 and the amide. Chlorolysis, yielding $TeCl_4$, is also possible.

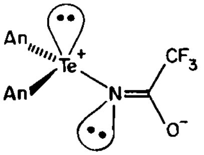
The *N*-trifluoroacetyltellurimides **82** can be isolated in two forms **82a** and **82b** with quite different melting points (80–81 °C for the *syn* form and 168–169 °C for the *anti* form)[199]. An X-ray structure investigation is available for $An_2Te{=}NTos$[200].

$$(\mathrm{Morpholino})_2\mathrm{Te{=}NTos}$$

(81)



(82a)



(82b)

Ogura and coworkers[201] prepared diorganyl tellurimides according to equation (87) and used the product to prepare olefins (equation 88), with yields in the range 66–93%.

$$\mathrm{RCH_2CH_2TePh + TosNClNa \xrightarrow{THF} RCH_2CH_2Te({=}NTos)Ph} \qquad (87)$$

$$\mathrm{RCH_2CH_2Te({=}NTos)Ph \xrightarrow[reflux]{THF} RCH{=}CH_2 + PhTeNHTos} \qquad (88)$$

Only a few organoselenium compounds of the type $Ar_2Se{=}NR$ had been prepared[202] before 1974 (cf. compound **66**), but since then the development has been rapid[203–214]. Of particular importance is probably the discovery that TosN=Se=NTos could effect allylic amination[208] of olefins and 1,2-diamination of 1,3-dienes[207].

Derkach and coworkers[211] have studied the interaction of $PhSO_2N{=}Se{=}NSO_2Ph$ with aromatic aldehydes, dimethylformamide, dimethylsulphoxide, Ph_3PO and PH_2SeO. The reactions are exemplified by equation (89). PhCON=Se=NCOPh was found to be a less active reagent and only dimethyl sulphoxide reacted with it (equation 90).

$$\mathrm{PhSO_2N{=}Se{=}NSO_2Ph + 2\,PhCHO \rightarrow 2\,PhCH{=}NSO_2Ph + SeO_2} \qquad (89)$$

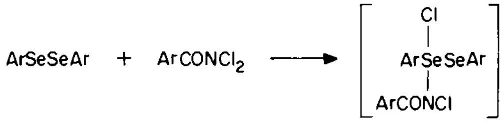
$$\mathrm{PhCON{=}Se{=}NCOPh + 2\,Me_2SO \rightarrow 2\,Me_2S{=}NCOPh + SeO_2} \qquad (90)$$

Treatment of MeCON=Se=NCOMe with aldehydes (ArCHO) resulted in the unexpected formation of $ArCH(NHCOMe)_2$, which seems to require the presence of moisture (equations 91 and 92).

$$\mathrm{MeCON{=}Se{=}NCOMe + ArCHO \rightarrow ArCH{=}NCOMe + SeO_2} \qquad (91)$$

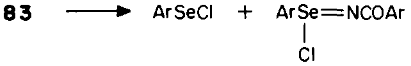
$$\mathrm{ArCH{=}NCOMe \xrightarrow[MeCONH_2]{H_2O} ArCH(NHCOMe)_2} \qquad (92)$$

Treatment of ArSeSeAr with $ArCONCl_2$ will result in a cleavage reaction (equations 93–95) yielding **84**, possibly via the hypervalent intermediate **83**[212]. *N*-Acylareneseleninimidoyl chlorides (**84**) are readily hydrolysed (e.g. by moisture) to the corresponding amides and areneseleninic acids.



$$\mathrm{ArSeSeAr} + \mathrm{ArCONCl_2} \longrightarrow \left[\begin{array}{c}\mathrm{Cl}\\ |\\ \mathrm{ArSeSeAr}\\ |\\ \mathrm{ArCONCl}\end{array}\right] \qquad (93)$$

(83)

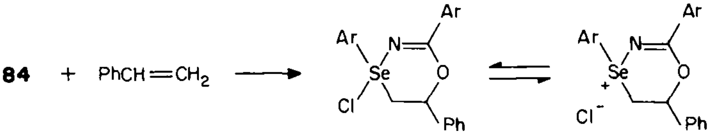


$$\mathbf{83} \longrightarrow \mathrm{ArSeCl} + \underset{\substack{|\\ \mathrm{Cl}}}{\mathrm{ArSe}}{=}\mathrm{NCOAr} \qquad (94)$$

(84)

$$2\,\mathrm{ArSeCl} + \mathrm{ArCONCl_2} \rightarrow \mathbf{84} + \mathrm{ArSeCl_3} \qquad (95)$$

Compound **84** undergoes 1,4-cycloaddition (equation 96) with styrene to yield a new type of Se heterocycle, 5,6-dihydro-4-selena-1,3-oxazine (**85**) as colourless prisms[212a]. Compound **85** shows relatively high conductivity, which indicates that the ionic form **85b** might be preferred. Compounds of the type RN=Se=NCOR give similar adducts with suitable alkenes[212b].



(96)

(85a) **(85b)**

A wide range of arylaminoselenium dichlorides can be prepared[213] by the interaction of ArSeCl with *N*-chloroimides, *N*-chloroimidic esters, *N*-chloroketimines and related compounds (equation 97). The same compounds can also be prepared from $\mathrm{ArSeCl_3}$ and $\mathrm{R_2NSiMe_3}$ (equation 98). $\mathrm{ArTeCl_3}$ can be similarly used as a reactant[214].

$$\mathrm{ArSeCl} + \mathrm{R_2NCl} \rightarrow \mathrm{Ar(R_2N)SeCl_2} \qquad (97)$$

$$\mathrm{ArSeCl_3} + \mathrm{R_2NSiMe_3} \rightarrow \mathrm{Ar(R_2N)SeCl_2} \qquad (98)$$

V. TETRAHALOORGANYLTELLURATES (IV)

Tetrahaloaryltellurates(IV) can be readily obtained[23,215–217] by equation (99). The reactants are simply mixed in, for example, dry $\mathrm{CHCl_3}$ and the crystalline product collected after a reflux period of 4 h in chloroform. A wide range of cations (e.g. $\mathrm{Me_4N^+}$, $\mathrm{Ph_3Te^+}$, $\mathrm{Ph_4As^+}$, $\mathrm{Ph_2I^+}$) have been employed.

$$\mathrm{ArTeX_3} + \mathrm{Y^+X^-} \rightarrow \mathrm{Y^+} + (\mathrm{ArTeX_4})^- \qquad (99)$$

The ionic nature of the tetrahaloaryltellurates is evident from reactions with ion exchange resins and by conductivity measurement[23,215]. The salts are fairly soluble in water albeit not completely stable, as aryltellurium oxohalides start to separate after ca. 20 h (equations 100 and 101). The operation of equation (100) also explains the formation of $\mathrm{PhTeCl_2CH_2COMe}$ on attempted recrystallization of $\mathrm{PyH^+(PhTeCl_4)^-}$ from acetone[23].

$$\mathrm{ArTeX_4}^- \rightleftharpoons \mathrm{ArTeX_3} + \mathrm{X^-} \qquad (100)$$

$$\mathrm{ArTeX_3} + \mathrm{H_2O} \rightarrow \mathrm{ArTe(O)X} + 2\,\mathrm{HX} \qquad (101)$$

As would be expected, exchange reactions, such as (102), can be readily performed.

$$(\mathrm{Ph_3Te})^+(\mathrm{PhTeCl_4})^- \underset{\mathrm{Cl}^-}{\overset{\mathrm{Br}^-}{\rightleftharpoons}} (\mathrm{Ph_3Te})^+(\mathrm{PhTeBr_4})^- \qquad (102)$$

Sometimes tetrahaloaryltellurates(IV) are obtained, due to redox processes, in connection with the preparation of dihaloaryltellurates(II). Thus, addition of bromine to ArTeTeAr in the presence of R_4PBr leads to the formation of $(R_4P)^+(ArTeBr_2)^-$ and $(R_4P)^+(ArTeBr_4)^-$. The results are explained by equations (103)–(106).

$$\mathrm{Br_2 + Ar_2Te_2 \rightarrow 2\,ArTeBr} \qquad (103)$$

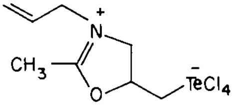
$$\mathrm{ArTeBr + R_4PBr \rightarrow (R_4P)^+(ArTeBr_2)^-} \qquad (104)$$

$$\mathrm{ArTeBr + Br_2 \rightarrow ArTeBr_3} \qquad (105)$$

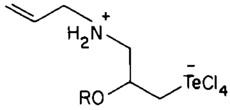
$$\mathrm{ArTeBr_3 + R_4PBr \rightarrow (R_4P)^+(ArTeBr_4)^-} \qquad (106)$$

Whether a pure tellurate(II) or tellurate(IV) or a mixture thereof is obtained apparently depends on a delicate balance involving the relative stability and solubility of the Te(II)- versus the Te(IV)-containing salt in a particular system.

The first aliphatic tetrahalotellurates(IV) were prepared[12] more than 50 years ago, although their true nature was not revealed until 1967 by Einstein[13]. No systematic studies of the chemistry have been reported.



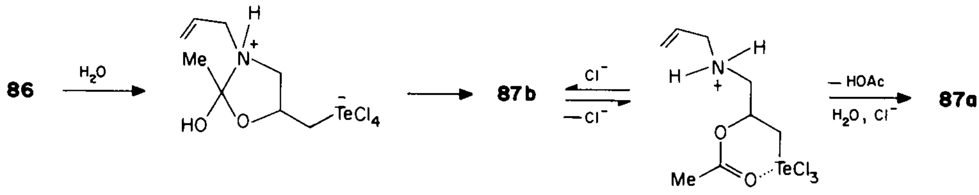
(86)



(87)

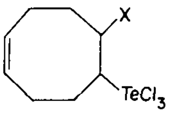
(**a**) R = H
(**b**) R = COMe

Recently Bergman and coworkers[151] have reported a new type of tetrahalotellurate readily formed when, for example, $MeCON(CH_2{-}CH{=}CH_2)_2$ in MeCN is treated with $TeCl_4$ (or $TeBr_4$) at 25 °C. The product **86** is quickly formed in an exothermic reaction. The structure of **86** has been elucidated by X-ray analysis. The four Cl atoms are all equatorial and nearly coplanar, in other words the structure is similar to that of **9**. Compound **86** will readily dissolve in water at 25 °C. Concentration of the solution after 1 h will yield crystals of the ring-opened and hydrolysed product **87a**. The surprisingly facile hydrolysis is explained in terms of an equilibrium between a tetrachlorotellurate(IV) and the corresponding tellurium trichloride followed by intramolecularly catalysed hydrolysis as indicated in equation (107).



(107)

Considering the ready and exothermic formation of **86** from $TeCl_4$ and $MeCON(CH_2CH{=}CH_2)_2$ it is tempting to assume that tetrahalotellurates might also play a role in the reaction of other alkenes with $TeCl_4$. One example is the interaction between $TeCl_4$ and 1,5-cyclooctadiene which yields an unstable adduct, assigned structure **88a** with a highly reactive C—Cl bond[115]. Attempted recrystallization of the adduct from ethanol resulted in the formation of **88b**, whose structure was proven by X-ray analysis[115].



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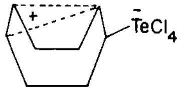
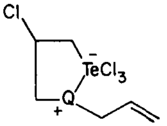


(89)

(**a**) X = Cl
(**b**) X = OEt

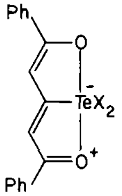
It now appears possible that the formulation **89** of the adduct might better explain its properties. Anyhow, further studies of the problem should be rewarding.

Compounds with zwitterionic (**90**) structures related to **89** can be obtained (as already discussed in Section II.C) by interaction of diallyl ether, diallyl sulphide and diallyl selenide with $TeCl_4$ (equation 52)[219]. In this connection a series of compounds, **91**, recently obtained by Detty, is also of interest[220].



(90)

Q = O, S, Se



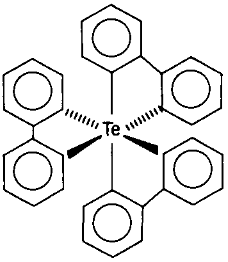
(91)

X = Br, Cl

VI. HEXAVALENT SELENIUM AND TELLURIUM COMPOUNDS

A. General Aspects

Although the pertellurane, $Te(OMe)_6$, readily prepared[221] from $Te(OH)_6$ and diazomethane, has been known since 1916, comparatively little systematic research (except for selenones and tellurones which are treated separately) has been done in the field of hexavalent Se and Te compounds. Attempts[163] to prepare compound **92** by treatment of $Te(OMe)_6$ with 2,2′-dilithiobiphenyl resulted in the tetravalent compound **67b**, and there are no compounds known with six carbon atoms bonded to one Te or Se atom.



(92)

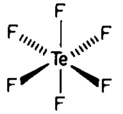
Recently the interesting acids $HOTeF_5$ (available via equation 108 or 109) and $(HO)_2TeF_4$ have been prepared. Esters (e.g. $MeOTeF_5$) are known but no derivatives (such as $MeTeF_5$ or $PhTeF_5$) with C—Te bonds have yet been described[222]. Some interesting derivatives based on $HOTeF_5$ or $HOSeF_5$ do include $Te(OTeF_5)_6$ and $C(OSeF_5)_4$. It is of interest to note that $Te(OTeF_5)_6$ can be sublimed at 110 °C and will melt at 242 °C as a stable molecule with a molecular weight of 1567.

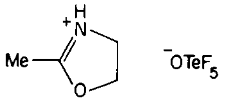
$$Te(OH)_6 + 5\,FSO_3H \rightarrow 5\,H_2SO_4 + HOTeF_5 \qquad (108)$$

$$3\,SeO_2F_2 + 4\,HF \rightarrow 2\,HOSeF_5 + H_2SeO_4 \qquad (109)$$

$$MeOTeF_5 + C_5H_5N \xrightarrow{-40\,^{\circ}C} C_5H_5NMe^+\ {}^-OTeF_5 \qquad (110)$$

The hydrolysis of TeF_6 as well as the solvolysis of $Te(OH)_6$ in HF have been investigated and practically all the intermediate species $(HO)_xTeF_{6-x}$ have been detected[223–227]. As is evident from the structure of **93**, isomerism should be possible for $(HO)_2TeF_4$ and indeed *cis* and *trans* forms of this composition have been isolated. Derivatives, such as *trans*- and *cis*-$(Me_3SiO)_2TeF_4$ are also known[228–230]. Methanolysis[231–236] and aminolysis of TeF_6 have also been studied[237–239]. During this study Fraser and Meikle[236] found that $MeOTeF_5$ is a fairly strong alkylating agent (equation 110). TeF_6 and $MeCONHCH_2CH_2OH$ similarly give the oxazoline salt **94**. Recently Shack has reported[290] that both TeF_5OCl and TeF_5OF react with fluoro olefins to form TeF_5O-containing fluorocarbons.


(93)


(94)

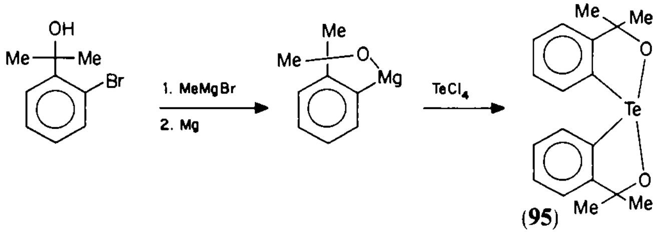
Depending on the conditions, TeF_6 reacts with $(Me_3Si)_2NH$ yielding $Me_3SiNHTeF_5$ or the explosive *cis*-$(Me_3SiNH)_2TeF_4$. The interesting compound $O{=}C{=}NTeF_5$ (m.p. − 95 °C, b.p. 39 °C) has been prepared according to equation (111). Another interesting conversion yielding the orange crystalline $Cl_4W{=}NTeF_5$ is given in equation (112).

$$(Me_3SiNH)TeF_5 + COF_2 \rightarrow O{=}C{=}NTeF_5 + Me_3SiF + HF \qquad (111)$$

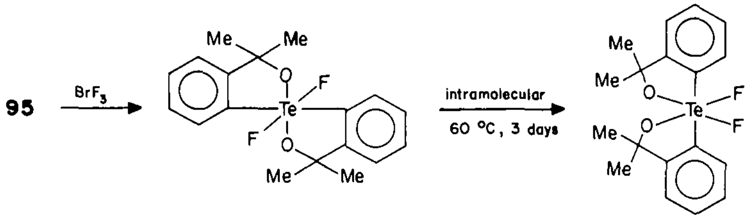
$$(Me_3SiNH)TeF_5 + WCl_6 \rightarrow Cl_4W{=}NTeF_5 + Me_3SiCl + HCl \qquad (112)$$

Compounds of the general structure R_2TeX_4 are scarce in the literature and the first compound of this sort, *trans*-$(C_2F_5)_2TeF_4$, was obtained together with other compounds, $(C_2F_5)_2TeF_2$ and *trans*-$C_2F_5TeClF_4$, upon treatment of $(C_2F_5)_2Te$ with ClF. The compound *trans*-$(C_2F_5)_2TeF_4$ was not isolated but was identified by its ^{19}F-NMR spectrum. *trans*-$C_2F_5TeClF_4$ was isolated as a colourless liquid. The same research group had earlier also described[240] the Se isologue, *trans*-$C_2F_5SeClF_4$.

It is not known if other fluorinating agents, e.g. XeF_2, can be used to convert say Ar_2TeF_2 into Ar_2TeF_4 (cf. Refs. 60–65). Michalak and Martin[5,241] have recently synthesized the pertellurane **96** as outlined in equations (113a) and (113b).



(113a)



(96) (97)

(113b)

The *trans*-pertellurane **96** is converted to the thermodynamically more stable *cis* isomer **97** by an intramolecular twist mechanism, a polytopal rearrangement. The detailed geometry of **97** has been established by a complete X-ray crystallographic study.

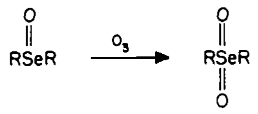
Non-dissociative isomerizations are well established in a few cases for derivatives of transition metals[242,243]. In connection with the now established non-dissociative isomerization **96**→**97**, it is of particular interest to note that the S isologue of **96** will undergo a dissociative, acid-catalysed isomerization to the isologue of **97**. Nothing has yet been published about the Se isologues, although a detailed study[241] of the S isologues is available.

Factors which might lower the activation barrier for non-dissociative isomerizations include the presence of low-lying empty orbitals on the central atom. The Te atom of **96** will provide empty 4 f and 5 d orbitals, not available in the S isologue, which may be low enough in energy to contribute significantly to the bonding, perhaps more in the transition state than in the ground state. Substitution of the much larger Te atom of **96** for S could also lower the energy of activation for the isomerization by introducing ground-state strain resulting from the incorporation of the longer bonds to octahedral Te into the five-membered rings of **96**. The longer bonds to Te may also reduce steric crowding between substituents in the transition state for the transformation **96**→**97** relative to that for a non-dissociative process.

B. Selenones

Diorganyl selenones, R_2SeO_2, have been known for almost 90 years and their chemistry has been reviewed several times[244–246]. Unfortunately, the early literature contains several erroneous structures which have been corrected only recently. Despite this confusion, selenones are, although little studied, a fully respectable class of compounds available via several synthetic routes.

The simple dialkyl selenones **98** are best prepared by ozonation of the corresponding dialkyl selenoxides[247] (equation 114).

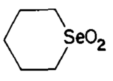


$$\overset{O}{\overset{\|}{RSeR}} \xrightarrow{O_3} \underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{RSeR}}} \qquad (114)$$

(98)

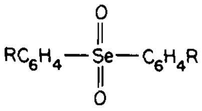
R = Me, Et, Pr, Bu

Attempts to oxidize dimethyl selenide directly to the selenone, using either hydrogen peroxide or potassium permanganate, were unsuccessful[248]. On the other hand, selenacyclohexane-1,1-dioxide (**99**) was obtained by perhydrol treatment of the corresponding selenide[249].



(99)

Diaryl selenones have been obtained by oxidation of the corresponding selenide or selenoxdie with a variety of oxidants. Rebane[250] prepared several substituted diphenyl selenones, **100**, using either peracetic acid[251] or hydrogen peroxide as the oxidant. One noteworthy property of this reaction is the fact that perhydrol is only capable of oxidizing the selenides to selenoxides when R = 3-Cl, 4-Cl or 4-Br.



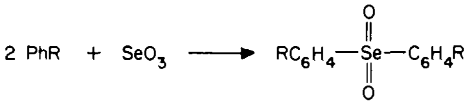
$$RC_6H_4-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Se}}-C_6H_4R$$

(100)

R = H, 4-Me, 4-OMe, 3-Cl, 4-Cl, 4-Br

Potassium permanganate was similarly used for the preparation of 4,4′-dicarboxydiphenyl selenone[252], 3,3′-dicarboxydiphenyl selenone[253], diphenyl selenone[254], 1,1′-dinaphthyl and 2,2′-dinaphthyl selenone[255].

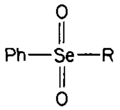
Dostál[256,257] has prepared diaryl selenones in low yield by direct selenonation of aromatic compounds with selenium trioxide, SeO_3, in liquid sulphur dioxide (equation 115). The main products in these reactions were the arylselenonic acids.



$$2\ PhR + SeO_3 \longrightarrow RC_6H_4-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Se}}-C_6H_4R \qquad (115)$$

R = H, Me, Cl, Br

Reich[258] has recently prepared the alkyl aryl selenones **101a** and **101b** by *m*-chloroperbenzoic acid oxidation of the corresponding selenides between 0 °C and room temperature. Yagupolskii[259] has similarly prepared the trifluoromethyl derivative **101c** using trifluoroperacetic acid as the oxidant.



$$Ph-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Se}}-R$$

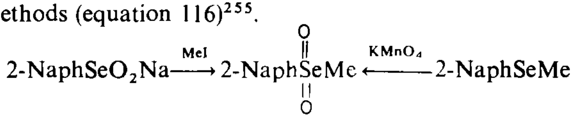
(101)

(a) R = Me

(b) R = *i*-Bu

(c) R = CF_3

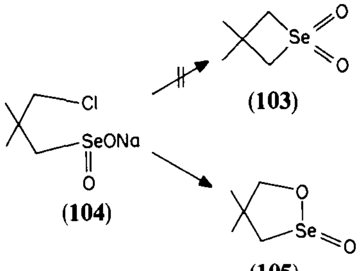
The early literature described the preparation of methyl 2-naphthyl selenone (**102**) by two different methods (equation 116)[255].



$$2\text{-NaphSeO}_2\text{Na} \xrightarrow{\text{MeI}} 2\text{-Naph}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Se}}\text{Me} \xleftarrow{\text{KMnO}_4} 2\text{-NaphSeMe} \qquad (116)$$

(102)

The alkylation of a seleninate represents a rarely used method for the preparation of selenones. It is apparently not always possible to predict if the alkylation is going to occur on Se or on O. Backer and Winter[260] gave a selenone structure **103** for the cyclization product of the sodium seleninate **104**. However, Lindgren[261] has recently shown that alkylation occurs on O instead of Se to give the five-membered compound **105** (equation 117).



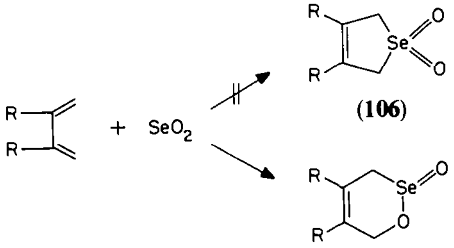
(103)

(104)

(105)

(117)

The addition products formed from selenium dioxide and a series of butadienes were originally formulated as cyclic selenones **106**, by analogy with the well-established sulphur dioxide addition to give sulphones[262]. A reinvestigation by Mock[263] has shown that the products do in fact have a cyclic seleninic ester structure **107** (equation 118).



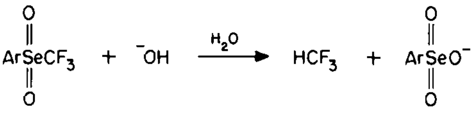
(106)

(107)

(118)

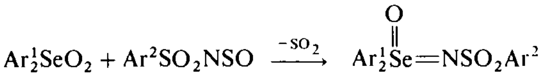
The IR and Raman spectra of selenones have been studied[247,264,265] as well as their mass spectral behaviour[250]. The tendency of selenones to form mixed crystals with sulphones, sulphoxides and selenoxides was early recognized[266,267]. The behaviour of certain selenones in disulphonic[268] and chlorosulphuric acid[269] has also been investigated.

Until recently, very few chemical reactions have been carried out with selenones. Yagupolskii[259] observed a haloform-type decomposition of a series of aryl trifluoromethyl selenones under very mild basic conditions (equation 119).



$$\mathrm{ArSe(=O)_2CF_3} + {}^{-}\mathrm{OH} \xrightarrow{\mathrm{H_2O}} \mathrm{HCF_3} + \mathrm{ArSe(=O)_2O^-} \qquad (119)$$

It has also been found[270,271] that diaryl selenones undergo a reaction with *N*-sulphinylarenesulphonamides to form *Se*,*Se*-diaryl(-*N*-(arylsulphonyl)selenoximines (equation 120).

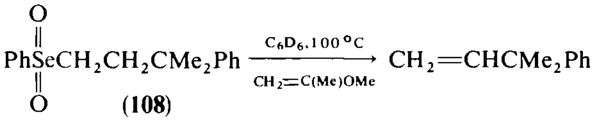


$$\mathrm{Ar^1_2SeO_2 + Ar^2SO_2NSO \xrightarrow{-SO_2} Ar^1_2\overset{O}{\overset{\|}{Se}}{=}NSO_2Ar^2} \qquad (120)$$

Reich[258] has studied the thermal behaviour of simple selenones. Methyl phenyl selenone rearranges at ca. 100 °C to give a methyl seleninate (equation 121).

$$\mathrm{PhMeSeO_2 \xrightarrow[100\,^\circ C,\,CDCl_3]{\Delta} PhSe({=}O)OMe} \qquad (121)$$

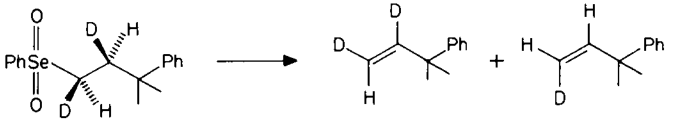
When β-hydrogens are present, as in the selenone **108**, an elimination occurs to give an olefin (equation 122) (2-methoxypropene is required as a trap for electrophilic Se species).



$$\mathrm{Ph\overset{O}{\underset{O}{Se}}CH_2CH_2CMe_2Ph \xrightarrow[CH_2{=}C(Me)OMe]{C_6D_6,\,100\,^\circ C} CH_2{=}CHCMe_2Ph} \qquad (122)$$

(108)

The stereochemistry is shown to be *syn* by the observation that the *threo* deuterium-labelled selenone **109** gives only the *cis*-dideuterio and *cis*-diprotio olefins (equation 123).



(109)

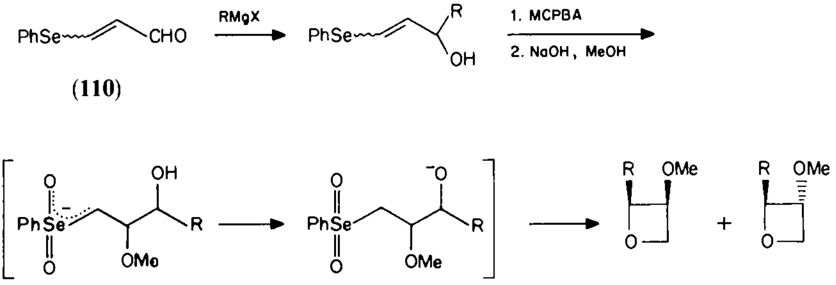
(123)

The excellent leaving-group properties of selenones in S_N2 displacements have recently been used for some synthetic applications. Towards dimethyl sulphide compound **101a** is approximately three times as reactive as methyl iodide[258] (equation 124). The cleavage of dimethyl selenone by HCl was observed early by Paetzold and Bochmann[247].

$$\mathrm{PhMeSeO_2 \xrightarrow[CD_3OD,\,35\,^\circ C]{Me_2S} PhSe({=}O)O^- + Me_3S^+} \qquad (124)$$

$$\mathrm{Me_2SeO_2 \xrightarrow{HCl(aq.)} MeCl + MeSe({=}O)OH}$$

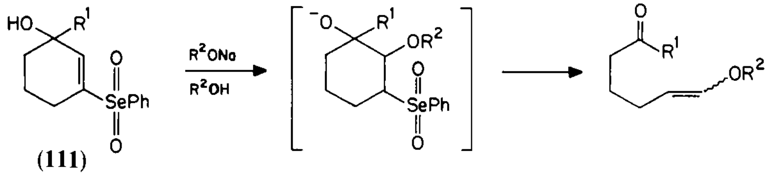
Shimizu and Kuwajima[272] have developed a synthetic sequence for the synthesis of oxetanes, involving a selenone as a leaving group. In this process 3-(phenylseleno)-2-propenal (**110**) is attacked by a Grignard reagent and the resulting alcohol oxidized with two equivalents of *m*-chloroperbenzoic acid (MCPBA) to a selenone. On treatment with sodium hydroxide in aqueous methanol (Michael attack by methoxide), good yields of isomeric oxetanes can be isolated as outlined in equation (125).



(110)

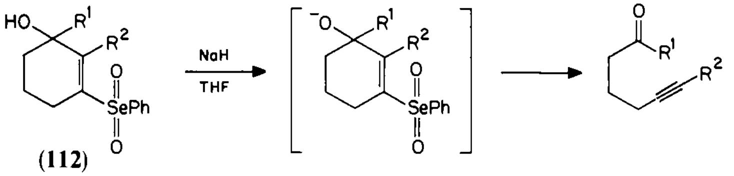
(125)

The vinyl selenones **111** and **112** have been shown to undergo fragmentation on treatment with bases[273]. The former, after Michael attack by alkoxide, gives an ethylenic ketone (equation 126) and the latter (a more hindered tetrasubstituted olefin) directly gives an acetylenic ketone (equation 127).



(111)

(126)



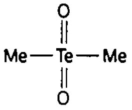
(112)

(127)

C. Tellurones

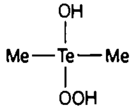
Diorganyl tellurones, R_2TeO_2, the Te analogues of the well-known sulphones and selenones, are ill-defined substances. Although reported in the literature since 1920, their existence has been questioned in two more recent review articles[274,275].

Vernon[276] oxidized dimethyl telluride with hydrogen peroxide and claimed to have isolated dimethyl tellurone (**113**), an insoluble, white, amorphous powder. This compound possessed all the characteristics of a peroxide; thus it had explosive properties and oxidized halogen acids to the corresponding halogen. It is therefore highly probable that Vernon's compound was a 'hydroxyperhydrate' (**114**) instead of the purported tellurone. This type of structure for the hydrogen peroxide oxidation product was first suggested by Balfe and coworkers[277].



$\mathrm{Me{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Te}}{-}Me}$

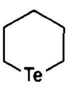
(113)



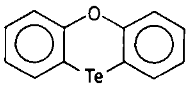
$\mathrm{Me{-}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle OOH}{|}}{Te}}{-}Me}$

(114)

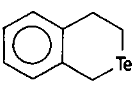
Diethyl telluride[278], telluracyclohexane (**115**)[279], phenoxtellurine (**116**)[280] and telluroisochroman (**117**)[281], respectively, have all been submitted to perhydrol treatment in order to obtain the corresponding tellurones. These products were probably also of the 'hydroxyperhydrate' type.



(115)

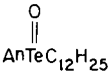


(116)



(117)

The first definitely characterized diorganyl tellurones were prepared only recently by Cava[175,282], using sodium periodate as the oxidant. The telluroxides **118** and **119**, respectively, were oxidized in aqueous methanol to give the corresponding tellurones **120** and **121**.

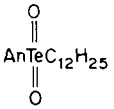


$An\overset{\overset{O}{\|}}{Te}C_{12}H_{25}$

(118)

$An_2Te{=}O$

(119)



$An\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Te}}C_{12}H_{25}$

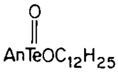
(120)

An_2TeO_2

(121)

An = 4-$MeOC_6H_4$

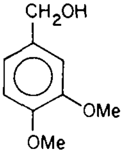
The role of tellurones in organic synthesis has of course been very little explored. However, the tellurone **120**, when thermolysed in refluxing toluene for 40 h, gives a mixture of 1-dodecene (55%) and 1-dodecanol (15%)[175]. These products are probably formed via the rearrangement product **122**.



$An\overset{\overset{O}{\|}}{Te}OC_{12}H_{25}$

(122)

The mild oxidizing properties of tellurone **121** have recently been investigated[282]. Thus, benzenethiol was oxidized to diphenyl disulphide and hydroquinone converted into *p*-benzoquinone. Benzylic alcohols could be converted to the corresponding carbonyl compounds, e.g. veratryl alcohol (**123**) was oxidized to veratraldehyde in 79% yield. On the other hand, hydrobenzoin (**124**) was cleaved by the tellurone to give benzaldehyde in 79% yield.

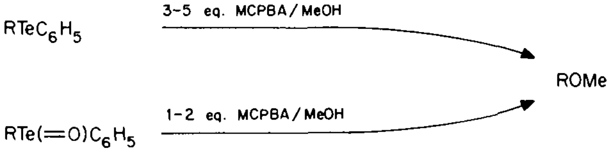


(123)

PhCH(OH)CH(OH)Ph

(124)

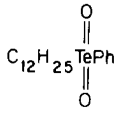
Uemura[283,284] has recently discovered an oxidative procedure for cleavage of C—Te bonds with introduction of a methoxy group (equation 128).



(128)

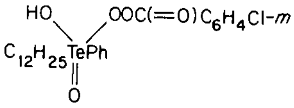
R = $C_{12}H_{25}$

These reactions probably involve the formation of a tellurone **125** and its *m*-chloroperbenzoic acid adduct **126**. A preformed tellurone **125** required treatment with excess *m*-chloroperbenzoic acid to give a good yield of the ether ROMe[285].



$C_{12}H_{25}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Te}}Ph$

(125)



(126)

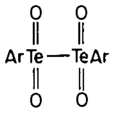
VII. HIGHER-VALENT COMPOUNDS CONTAINING Te—Te OR Se—Se BONDS

Although ditellurides of the type RTeTeR are well known, related hypervalent compounds such as $RTeX_2TeX_2R$ are rare and the only reasonably well-characterized case has been reported by Schulz and Klar[286], who isolated, by treatment of the corresponding ditelluride with iodine, compound **127**, as a lilac-brown diamagnetic powder which decomposed at 145–150 °C.

$$2\text{-}PhC_6H_4TeI_2\text{—}TeI_2C_6H_4Ph\text{-}2$$

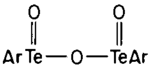
(127)

Recently Zingaro and coworkers[287] have obtained evidence (^{13}C- and ^{125}Te-NMR data) for the formation of the ditellurone **128** together with **129** and ArTeSeTeAr from the oxidation of ArTeTeAr with SeO_2.



$Ar\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Te}}\text{—}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Te}}Ar$

(128)



$Ar\overset{\overset{O}{\|}}{Te}\text{—}O\text{—}\overset{\overset{O}{\|}}{Te}Ar$

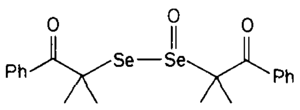
(129)

$Ph_3TeTePh_3$

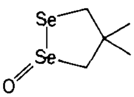
(130)

No published data are available about hexaaryl- or hexaalkyl-ditelluranes, but in connection with studies[288] of the interaction of PhLi and PhMgBr with elemental Te a compound with elemental analytical and mass spectrometric data in agreement with the formulation **130** could be obtained in low and varying yields. Attempts to reductively couple $Ph_3Te^+Cl^-$ to $Ph_3TeTePh_3$ failed.

Reich and coworkers have recently reported[289] the first example of an observable selenolseleninate ester (**131**). The compound is moderately stable at – 50 °C ($t_{1/2} \approx 1$ h). The cyclic selenolseleninate **132** was also prepared by oxidation of the corresponding cyclic diselenide with *m*-chloroperbenzoic acid. The PMR spectrum of **132** is particularly characteristic, showing *AB* quartets for the CH_2 protons and two singlets for the diastereotopic Me groups.



(131)



(132)

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CHAPTER 15

Directing and activating effects involving selenium and tellurium

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I. INTRODUCTION AND GENERAL FEATURES

Over the last decade the chemistry of Se/Te organic compounds has been developed greatly and various books, reviews and advances, have appeared[1–6]. The synthetic, theoretical and physicochemical aspects are the subjects mainly reviewed, with the reactivity of these compounds being insufficiently covered leading one to think that little work has been done in this area. Although the synthetic difficulties and instability of the compounds sometimes limit or preclude obtaining quantitative reactivity data, careful examination of the literature reveals that much work has been done.

The reactivity of organic compounds containing Se and Te discussed in this chapter is mainly confined to those reactions in which Se and Te are not the primary centres of the reaction. Those reactions in which the attack occurs on the heteroatom or in which bonds to the heteroatom are broken, are considered only marginally.

In Section II the electronic, steric and biological effects of groups of atoms containing Se and Te are discussed in terms of the so-called substituent constants. The tangled subject of σ and σ-like substituent constants is introduced to facilitate understanding. All substituent constants of Se and Te-containing groups are, to the authors' knowledge, collected for the first time.

Section III reports the ability of Se and Te to transmit electronic effects from a remote substituent to the reaction centre. The electronic transmission is usually quantified in terms of ρ reaction constant, the physicochemical meaning of which has given rise to controversy[7–9]. The present position in this area is briefly and critically summarized. All relevant ρ reaction constants are, to the authors' knowledge, collected for the first time.

The reactivity of heterocyclic compounds containing Se and Te is discussed in Section IV. Because of the variety of heterocyclic systems, the data are discussed according to reaction type.

Section V reports the directing and activating effects of well-known functional groups containing Se and Te.

In all sections particular emphasis is given to the comparison with O and S analogues. A comparative study is fundamental for evaluating the influence of the basic parameters of the chalcogen atom (mass, electronegativity, polarizability, possibility of utilizing d orbitals, etc.) and the molecule (geometry, resonance energy, etc.) on the chemical reactivity.

This work is not encyclopaedic, but most of the pertinent literature up to March 1983 has been covered.

II. SUBSTITUENT CONSTANTS FOR SELENIUM- AND TELLURIUM-CONTAINING GROUPS

A. The Substituent Constant

A variable substituent S attached to a skeletal group G of a SGW compound affects the chemical or physical phenomena of the molecule measured at the reaction site W. The substituent constant is an empirical parameter of substituent S defined relative to a standard substituent and to a standard property under well-defined conditions. This constant, which is usually denoted by the letter σ, in principle depends only on the nature of the substituent and measures the effect of the substituent in the process concerned.

This approach is very interesting because it should permit correlation of a vast amount of data, calculation of chemical data from those reactions for which experimental data are not available and collection of mechanistic information.

The problems arise when one attempts to investigate the nature of the effect of the substituent (field, inductive, resonance, steric, etc.) and to find compounds and reactions in which only one effect is operative.

The result has been a proliferation of substituent constants denoted by subscripts and superscripts of the letter σ and other symbols. To facilitate the reading of the following sections, the problem is briefly examined. More details can be found in specialist reports[10-12].

The substituent constant on a quantitative basis was first stated by Hammett[13,14] as a measure of the electronic effects of *meta* (σ_m) and *para* substituents (σ_p) on the dissociation of benzoic acids in water at 25 °C. Hydrogen was taken as reference with a zero value. The σ_m value is a measure of polar effects (inductive and/or field) of the substituent and σ_p is a measure of the polar effect including no important resonance interaction between the substituent and the reaction centre. A positive or negative value of the σ constant indicates an electron-withdrawing or an electron-releasing capacity of the substituent, respectively. The difference ($\sigma_p - \sigma_m$) has been used as a measure of conjugative interaction of the substituent.

The Hammett σ values are able to correlate many rate and equilibrium data[10,11,15,16] and many physical measurements[10,11], but deviations are observed by *para* substituents which can enter into direct resonance interactions with the reaction site in the transition state. By using the Hammett procedure, two new sets of substituent constants were defined[10,17] (σ_p^+ and σ_p^-) when the substituent interacts with a positive or a negative charge developed in the transition state. Strong electron-donating groups have high negative values of σ_p^+ (-0.5 to -1.5) and strong electron-withdrawing groups have high positive σ_p^- values (0.4 to 1.3). When there is no important resonance interaction between the substituent and the reaction centre, σ^+ and σ^- should in principle have the same value as the Hammett σ constants. The differences ($\sigma_p^+ - \sigma_p$) and ($\sigma_p^- - \sigma_p$) have been used as a measure for the conjugative ability of the substituent.

By observing that in the ionization of benzoic acids a cross-conjugation effect occurs between an electron-donor substituent and the carboxyl group, Taft defined[18] σ_m° and σ_p° substituent constants based on the ionization of phenylacetic acids, a reaction in which the reaction centre is insulated from the π electrons of the benzene ring. By using a different procedure Van Bekkum and coworkers[19] defined analogous σ_p^n and σ_m^n constants. σ° and σ^n should therefore be free of the mesomeric component and should be a measure for the inductive effect of the substituent depending on its *para* or *meta* position on the benzene ring.

Hammett treatment fails for *ortho* substituents probably because of the interplay of steric, polar and mesomeric effects. A separation of the effects was proposed by Taft[20] who defined a set of σ *ortho* values (σ_o, σ_o^*) as a measure of the polar effect of the substituent.

A σ_I scale based on the reactivity of rigid alicyclic and aliphatic systems and reflecting only inductive effects was defined by Taft[21]. The inductive constant σ_I of the substituent is, in principle, independent of the method of determination and of the position of the substituent with respect to the reaction site. In an attempt to divide the inductive and resonance contribution of the substituent, Taft defined[22] the resonance contribution σ_R by equation (1):

$$\sigma_R = \sigma_p - \sigma_I \qquad (1)$$

Consequently, σ_m can be expressed by equation (2):

$$\sigma_m = \sigma_I + 0.33\,\sigma_R \tag{2}$$

The two fundamental assumptions in the Taft approach are: (*i*) the σ_I, σ_p and σ_m values are on the same scale and (*ii*) the inductive effect of the substituent is the same from both positions. An additional problem is that σ_R depends on the nature of the reaction. In a first attempt to overcome the problem, new mesomeric constants, called σ_R^o, were defined[22] by using σ_p^o constants (equations 3) and the σ_m^o constants were expressed by equation 4.

$$\sigma_R^o = \sigma_p^o - \sigma_I \tag{3}$$

$$\sigma_m^o = \sigma_I + 0.5\,\sigma_R^o \tag{4}$$

Equation (3) was then refined by Exner[23], assuming that σ_I and σ_R^o do not contribute equally to σ_p^o (equation 5).

$$\sigma_R^o = \sigma_p^o - 1.14\,\sigma_I \tag{5}$$

A complete σ_R reaction dependence was then recognized[24] and by using the σ_p^- and σ_p^+ values, σ_R^- and σ_R^+ constants were defined for electron-withdrawing and electron-donating groups which entered into direct resonance interaction with the reaction site in the transition state.

Another attempt to divide the overall electronic contribution of the substituent into inductive and resonance contributions is that by Swain and Lupton[25]. This approach however is not substantially different from Taft's and the symbols $\mathscr{F}$ and $\mathscr{R}$ replace σ_I and σ_R respectively.

Further limitedly successful substituent constants which, like those recorded above, do not take into account the steric effects, are the σ^* constants[26] which have practically the same meaning as σ_I constants and the F (field) and M (mesomeric) quantities derived by Dewar and Grisdale[27] using a semiempirical approach.

Substituent constants which are claimed to measure only the steric effect of the substituent (E_s) were defined by Taft using acid-catalysed hydrolysis of esters in aqueous acetone[28]. The methyl group is taken as reference ($E_s = 0$) and the E_s values approximate the size of the group. Another set of *steric* constants, called E_s^* has been defined[29] by using the hydroboration reaction.

We designate all the above recorded substituent constants as *normal substituent constants* because they refer to a group which replaces the hydrogen atom of benzene or of a heterocyclic ring, and in order to distinguish them from *replacement substituent constants* and *special substituent constants*[30]. The replacement substituent constants denoted as σ_{ar} or σ_a refer to the electronic effects of a heteroaromatic system considered as a substituted benzene[15] or to a substituent fused on to benzene ring[31]. For instance if the selenophene is viewed as an endocyclic substituted benzene, the Se atom is considered as a substituent replacing the —CH=CH— moiety in the benzene ring and $\sigma_{\alpha\text{-selenienyl}}$ and $\sigma_{\beta\text{-selenienyl}}$ are calculated as depending on the site (α or β) of the reaction. The σ_{ar} depends on the reaction and therefore σ_{ar}^-, σ_{ar}^+, σ_{ar}^0, etc. have also been defined.

A new set of σ constants is defined when the concept of the *replacement* is extended to other aromatic rings besides that of benzene. These are known as special substituent constants[30]. Examples are σ_r calculated[32] for the protonation of arenes taking the α-position of naphthalene as reference and σ_{het} calculated[33] for the ionization reaction of *N*-ethyl-2-aminoheteroarenes by using *N*-ethyl-2-aminopyridinium chloride as reference.

Two methods may be employed to evaluate the substituent constant. In the first procedure a single reaction is chosen as a *standard* and the σ constant is determined from the rate (or equilibrium) constant of this reference reaction. Sometimes chemical difficulties preclude this possibility and other reactions or physical methods (^{1}H—, ^{13}C—

and ^{19}F-NMR, IR, UV, $E_{1/2}$) are used. This and the dependence on solvent and temperature[10,11] further complicate the jungle of substituent constants. In the second procedure the substituent constant is derived from a statistical analysis of the available data for that substituent in a wide spectrum of related reactions. The most suitable statistical treatment is that based on the application of the *extended selectivity relationship*[34] in which the σ constant is obtained from the slope of a plot of $\log k_S/k_H$ against the ρ constants for several similar reactions.

A Hammett-like relationship was developed in biology to correlate physical properties of molecules and their ability to penetrate biological membranes[11,35]. The chosen property is the lipid–aqueous partition coefficient P which represents the relative lipophilicity (now called hydrophobicity) of biologically active organic compounds. Most partition coefficients are obtained in an *n*-octanol–water system which is generally accepted as standard for a biological lipid–water system. Other lipid solvent–water systems are sometimes used. By using $\log P$ as a measure for the hydrophobicity of a whole molecule, the hydrophobic (lipophilic) substituent constant π is defined according to equation (6):

$$\pi = \log P_S - \log P_H \tag{6}$$

where P_H and P_S are the partition coefficients of the reference and substituted compounds respectively. Positive and negative π values indicate that the substituent facilitates the penetration of the molecule to the *n*-octanol phase or to water, respectively. A dependence of π value on the reaction system was observed, especially for strongly electron-donating and electron withdrawing substituents.

Only a limited number of substituent constants for Se and Te having organic groups are listed in the specialist reports[1-4]. In the following section the constants available in the literature are reported without discrimination as to their origin and reliability. Where possible, a comparison with analogous O and S substituent constants is made.

B. Bivalent Selenium- and Tellurium-containing Groups

The substituent constants of groups containing bivalent Se and Te are reported in Table 1 with the corresponding data for O and S for comparison. The σ value of the group without heteroatom is also reported to estimate the electronic contribution of the heteroatom.

The SeMe and TeMe groups show $-$I and $+$M effects. The electron-withdrawing inductive effect increases from TeMe to OMe by a factor of two, while the electron-donating resonance effect increases about eight times. ^{13}C-NMR investigations[36-38] confirm the weak electron donor character of TeR and SeR groups and show that the degree of p-π interaction decreases as the size of R (Me, Et, *i*-Pr) increases. The increase of the $+$M effect in the order TeMe < SeMe < SMe < OMe was also observed[39] in the cyanohydrin equilibrium with substituted benzaldehydes, in the UV absorption spectra of substituted benzoic acids and more recently in the calculated[40] mesomeric moments of telluroanisole (0.18 D), selenoanisole (0.25 D), thioanisole (0.5 D) and anisole (1.1 D) and in the ^{13}C-NMR chemical shifts of the *para* carbons of chalcogenoanisoles[41]. A theoretical treatment of the connection between the size of the heteroatom and its mesomeric effect has been published[42]. The σ_p and σ_m values show that the $+$M effect prevails over the $-$I effect. A comparison with the Me group shows that the presence of the chalcogen atom increases the electron-withdrawing power of the group according to the electronegativity of the heteroatom and that the Te atom does not change the releasing mesomeric effect of the group.

The $SeCF_3$ group shows a $-$I effect of the same magnitude as the SCF_3 group but lower than that of OCF_3. In contrast to the OCF_3 group, the $SeCF_3$ and SCF_3 show a $-$M effect owing to the involvement of the d orbitals of S and Se atoms in the conjugation. The

TABLE 1. Substituent constants for groups containing bivalent calcogen atoms

Substituent	σ_p	σ_m	σ_p^-	σ_I	σ_R	σ_R^0	$\mathscr{F}$	$\mathscr{R}$
TeMe	0.04[a]			0.12[a]	−0.08[a]	−0.10[b]		
SeMe	−0.15[c] 0.0[f] 0.07[g] 0.01[d]	0.05[c] 0.09[d] 0.1[f]		0.15[d]	−0.14[d]	−0.15[b]	0.13[e]	−0.12[e]
SMe[h]	0.0	0.15	0.04	0.19	−0.24	−0.24	0.20	−0.18
OMe[h]	−0.27	0.12		0.25	−0.63	−0.41	0.26	−0.51
Me[h]	−0.17	−0.07		−0.05	−0.07	−0.10	−0.04	−0.13
$SeCF_3$	0.38[i] 0.45[k]	0.32[i] 0.44[k]	0.53[j] 0.58[l]	0.28[i] 0.42[k]	0.04[k] 0.10[i]		0.29[e]	0.12[e]
SCF_3[h]	0.50	0.40	0.64	0.44	0.12[d]	0.00	0.35	0.18
OCF_3[h]	0.35	0.40	0.25[j]	0.55	−0.14	0.17	0.38	0.00
CF_3[h]	0.43	0.54	0.65	0.41	0	0.01	0.38	0.19
SeCN	0.66[m]	0.61[n]		0.58[o]				
SCN[h]	0.52	0.41	0.60	0.55[o]		−0.05	0.36	0.19
CN[h]	0.66	0.56	0.88	0.56	0	0.07	0.51	0.19
TePh	0.34[p]			0.38[p]	−0.04[p]			
SePh	0.13[q] 0.42[g]		0.13[q]	0.24[r] 0.37[h]		−0.19[s]		
SPh[h]	0.13	0.17	0.29[t]	0.30		−0.19		
OPh[h]	−0.32	0.25		0.39	−0.31[a]	−0.36[s]	0.34	−0.35
Ph[h]	−0.01	0.06	0.11	0.10	−0.10	−0.10	0.08	−0.08
Se—c-C_6H_{11}				0.38[u]				
S—c-C_6H_{11}				0.31[u]				
O—c-C_6H_{11}				0.26[u]				
c-C_6H_{11}[h]	−0.22	−0.15		0.02			−0.13	−0.10
$SeCH_2CH{=}CH_2$[v]	0.15	0.21						
$SCH_2CH{=}CH_2$[v]	0.12	0.19						
$OCH_2CH{=}CH_2$[v]	−0.25	0.09						
$SeCH{=}CH_2$[v]	0.21	0.26						
$SCH{=}CH_2$[v]	0.20			0.21[h]		0.27[h]		
$CH{=}CH_2$[h]	−0.02	0.00						
$SeCH{=}CHCl$[v]	0.26	0.28						
$SCH{=}CHCl$[v]	0.24	0.31						
$SeC{\equiv}CPh$[w]	0.05 −0.03							
$SC{\equiv}CPh$[w]	0.20							
$C{\equiv}CPh$[h]	0.16	0.14	0.39	0.22		0.00	0.12	0.05
$SeC_6H_4NO_2$			0.41[e]					
$P(Se)(4\text{-}FC_6H_4)_2$				0.42[x]	0.10[x]			
$P(Se)(3\text{-}FC_6H_4)_2$				0.47[x]	0.11[x]			
$P(Se)Ph_2$				0.36[x]	0.09[x]	0.13[y]		
$P(S)Ph_2$[h]	0.47	0.29	0.63	0.40	0.09[x]	0.11		
$P(O)Ph_2$[h]	0.53	0.38	0.68	0.27	0.11[x]	0.12	0.31	0.24
PPh_2[h]	0.19	0.11	0.26	0.17	−0.01[x]	−0.01		
NCSe[aa]	0.31							
NCS[aa]	0.20							
Se^-	−0.98[z]							
S^-	−1.21[z]					−0.33[h]		
O^-	−1.86[z]	−0.71[h]		−0.16[h]		−0.60[h]		

weaker electron-accepting conjugation of the $SeCF_3$ compared to the SCF_3 group has been explained by suggesting[43] that the more diffuse 4d orbitals of Se have a smaller tendency towards (p–d)π conjugation than the 3d orbitals of S. The analysis of values of dipole moments of *p*-SeMe- and *p*-SMe-substituted anilines supports this hypothesis[44]. Indeed when the SeMe group is present the interaction dipole moment ($\mu_{int} = 0.43$ D) is lower than when the substituent SMe ($\mu_{int} = 0.68$ D) is present. A comparison with the CF_3 group shows that the contribution of S and Se atoms is small and therefore it is not surprising that the $SeCF_3$ group does not show an electron-donating effect even when a nitro group is present in the *para* position of the benzene ring[44]. Consequently σ_p and σ_m have the same values.

The behaviour of the SeCN group is the same as that of the $SeCF_3$ group but the – I and – M effects are stronger as a consequence of the electronic effects of the cyano group compared with those of the trifluoromethyl group.

The SePh and TePh groups, like the Ph group, show an electron-withdrawing inductive effect (– I) and a push–pull resonance effect (+ M and – M). Theoreticians[45,46] generally invoke only a polarization effect to explain the stabilization of the incipient carbanion in the transition state by a bivalent S-containing group, but the lower value of σ_p^- of the SePh group with respect to that of the SPh group does not agree with this hypothesis. A larger effect would be expected for the larger and more polarizable Se atom. Therefore a conjugative interaction, in which the d orbitals of the larger Se atom are less effective than those of S in overlapping with the p orbitals of C, must be invoked. From measurements of the hydrolysis rates of aryl vinyl selenides, McClelland and Leung[47] have calculated a σ_p^+ value of -0.47 for the SePh group which is higher in absolute value than that of the Ph group ($\sigma_p^+ = -0.18$)[48] and lower than those of SPh ($\sigma_p^+ = -0.54$)[47] and OPh ($\sigma_p^+ = -0.62$)[47]. The chalcogen atoms stabilize an adjacent carbonium ion centre, but the type of electron donation is supposed to depend on the nature of the heteroatom[47]. Dipole moment data[49] show that when strongly electron-donating or electron-withdrawing substituents are present in the position *para* to SePh and TePh the push–pull resonance effect is markedly exalted.

The cyclohexylseleno group has the expected – I effect but in the series the order is the reverse of that expected on the basis of the inductive effect of methylchalcogen groups.

The allyl-, vinyl- and chlorovinyl-seleno groups have a – I effect and a weak + M effect ($\sigma_p - \sigma_m$, negative).

The Se atom markedly reduces the electron-withdrawing effect of the phenylethynyl

Footnotes to Table 1.

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[a] From ^{19}F-NMR, Ref. 51.

[b] From ^{13}C-NMR, Ref. 52.

[c] From ionization of benzoic acids in 30% EtOH at 25 °C, Ref. 39.

[d] Ref. 53.

[e] Ref. 35.

[f] From ionization of benzoic acids in 50% EtOH at 25 °C, Ref. 54.

[g] From methyl hyperfine splitting of 1-phenyl-1,2-propanesemidones, Ref. 55.

[h] From compilations of Exner (Ref. 10 and 11) and Hansch (Ref. 35).

[i] From ionization of benzoic acids in 50% EtOH, Ref. 53.

[j] From ionization of anilinium ions, Ref. 43.

[k] From ^{19}F-NMR of fluorobenzenes, Ref. 53.

[l] From ^1H-NMR chemical shifts of amino group, Ref. 43.

[m] From the ionization of *p*-substituted *p*′-dimethylaminoazobenzenes in 25% EtOH at 25 °C, Refs. 15, 56.

[n] Ref. 57.

[o] Ref. 58.

[p] From ^{19}F-NMR, Ref. 49.

[q] Ref. 59.

[r] Refs. 60, 61.

[s] From integrated IR intensities, Ref. 62.

[t] From ionization of phenols, Ref. 63.

[u] From dissociation of acetic acids in H_2O at 25 °C, Refs. 58, 64.

[v] From the half-wave reduction potential of nitrobenzenes in DMF, Ref. 65.

[w] From polarographic and spectrophotometric data of *p*-nitrophenyl phenylethynyl chalcogenides. Ref. 50.

[x] Ref. 67; these values were incorrectly[66] labelled σ_R^0.

[y] From ^{13}C-NMR, Ref. 66.

[z] From the half-wave reduction potential of nitrophenyldichalcogenides in DMF, Ref. 68.

[aa] From UV data, Ref. 104.

group, probably as a consequence of a larger conjugative interaction with the benzene ring than with the ethynyl bond[50].

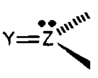
On the other hand, the Se atom greatly increases the negligible Ph–P π interaction and the electron acceptor effect of the PPh_2 group. Examination of the sequence of phosphine chalcogenides indicates that the effect is due to a concordant action of $-$M and $-$I effects of the heteroatom.

The negatively charged Se atom shows a strong electron donor power in the *para* position, which increases in the order $Se^- < S^- < O^-$ as expected on the basis of the + M effects.

C. Tetravalent Selenium- and Tellurium-containing Groups

In compounds containing Se(IV) and Te(IV) (selenuranes and telluranes), the chalcogen atoms have a valence shell of ten electrons. These compounds are usually classified as σ-selenuranes (σ-telluranes) and π-selenuranes (π-telluranes) depending on whether four of the five valence electron pairs of the heteroatom form four σ bonds (**1**) or one electron pair forms a π bond with a neighbouring element of the second period (**2**). Theoretical[72,73]

(1)



(2)

Z = Te, Se, S

Y = O, C, N

TABLE 2. Substituent constants for Se(IV)- and Te(IV)-containing groups

Substituent	σ_p	σ_m	σ_I	σ_R	σ_r^0
$TeCl_3$[a]	0.66		0.55	0.11	
$TeBr_3$[a]	0.62		0.51	0.11	
$TeMeCl_2$[a]	0.56		0.50	0.06	
$TeMeBr_2$[a]	0.59		0.53	0.06	
$TeMeI_2$[a]	0.62		0.58	0.04	
$Te(Ph)Cl_2$[a]	0.59		0.52	0.07	
	0.73[b]		0.66[b]		
$Te(Ph)Br_2$[a]	0.60		0.54	0.06	
	0.59[b]		0.52[b]	0.07	
$SeOCF_3$[c]	0.86	0.81	0.76	0.10	
	0.63[d]				
$SOCF_3$[e]	0.80	0.74	0.67	0.13	
SeO_2CF_3[c]	1.21	1.08	0.96	0.25	
SO_2CF_3[e]	1.04	0.88	0.73	0.31	
$\overset{+}{Te}MeR$[f]					−0.11
$\overset{+}{Se}MeR$[f]					0.13
$\overset{+}{S}Me_2$[f]					0.20

[a] From ^{19}F-NMR data, Ref. 51.
[b] From ^{19}F-NMR data, Ref. 69.
[c] From ^{19}F-NMR data, Ref. 70.
[d] From UV data, Ref. 71.
[e] From ^{19}F-NMR data, Ref. 71.
[f] From ^{13}C-NMR data, $R = C^-{-}(CO)_2C_6H_4$ for Te and $C^-{-}(CO)_2(CH)_2CMe_2$ for Se, Ref. 52.

and experimental data[74–76] show that the configuration of σ-selenuranes and -telluranes is that of a slightly distorted trigonal bipyramid in which the more electronegative ligand occupies the *axial* position. Whereas diorganotellurium dihalides are monomeric in the solid phase and in solution, trihalotelluranes have a dimeric or polymeric structure in the solid state and the Te atom is pentacoordinate[77–79]. π-Selenuranes and -telluranes have the same tetrahedral configuration[80] in oxides (**2**; Y = O) and a trigonal pyramid structure with the heteroatom at the apex in ylides[81] (**2**; Y = C). The σ constants for Se(IV)- and Te(IV)-containing groups are reported in Table 2.

^{19}F-NMR data show[51] that the trihalotelluro groups exhibit a strong $-$I effect in agreement with the strong deshielding effect of the $TeCl_3$ group (almost equal to that of the nitro group) on the ring protons of trichlorophenyltellurium[73]. Dipole moment data of a series of trichlorophenyltelluriums show an absence of mesomeric and interaction moments indicating that the p and d orbitals of Te are not conjugated with the π orbitals of the Ph ring[73]. The calculated value for σ_R should therefore be seen as the result of the arbitrary choice in the separation of inductive and mesomeric effects (equation 1). By using for σ_I a coefficient greater than unity, the σ_R value is reduced. Theoretical calculations[73] explain the electronic properties of the $TeCl_3$ group.

Replacing a halogen atom in the TeX_3 group (X = Cl, Br, I) with Me or Ph, the electron-withdrawing power of the group is reduced by 5–15% and appears to depend on the nature of the halogen.The values $\sigma_p = 0.73$ and $\sigma_I = 0.66$ for the $Te(Ph)Cl_2$ group are probably printing errors because they conflict with the values of 0.59 and 0.52 reported by the same authors using the same technique[51,69]. ^{19}F-NMR data show that $Te(R)X_2$ groups (R = Me, Ph; X = Cl, Br, I) do not exhibit electron-donating mesomeric properties. However, experimental and calculated[69] dipole moments of substituted diaryldihalotelluriums show that when a + M substituent (i.e. NMe_2) is present in the *para* position, the $Te(R)X_2$ group has a $-$M effect probably via d–π conjugation.

The $SeOCF_3$ and SeO_2CF_3 groups exhibit a marked enhancement of the electron-withdrawing inductive effect in respect to the $SeCF_3$ group. The effect is related to the number of O atoms. The SeO_2CF_3 group is one of the most powerful electron acceptors. The presence of O also influences the conjugative effect, indeed the low $\sigma_p - \sigma_m$ value increases on passing from $SeCF_3$ (mean value $\simeq 0.03$) and $SeOCF_3$ (0.05) to SeO_2CF_3 (0.13). $SeOCF_3$ and SeO_2CF_3 exhibit a higher $-$I and lower $-$M effect than the analogous S-containing groups. This has been ascribed to the greater contribution of resonance structures in which a high positive charge is present on the Se atom. The higher values of the group moment[82,83] of $SeOCF_3$ (4.13 D) and SeO_2CF_3 (5.3 D) with respect to $SOCF_3$ (3.88 D) and SO_2CF_3 (4.32 D) and the lower interaction moment of compounds with electron-donating substituents (p-$NH_2C_6H_4SeOCF_3 = 0.97$ D, p-$NH_2C_6H_4SOCF_3 = 1.11$ D; p-$MeC_6H_4SeO_2CF_3 = 0.18$ D, p-$MeC_6H_4SO_2CF_3 = 0.78$ D) support this hypothesis[82,83]

The opposite conjugative electron-withdrawing effect of the selenonium and telluronium groups has been ascribed[52] to the greater difference in energy of the non-occupied Te d orbitals and the benzene 2p orbitals in comparison to Se and S.

The electronic effects of the $TeMeF_2$, $Te(Ph)(NCS)_2$ and $Te(Ph)F_2$ groups have also been investigated[84] by the ^{19}F-NMR technique. These substituents interact with the π system of the benzene ring by an inductive mechanism[84].

D. Heterocyclic Rings as Substituents

Literature data concerning the electronic effects caused by the substitution of a H atom of the benzene ring with a heterocyclic ring having Se or Te are limited to 2-selenienyl and 2-tellurienyl groups[85–87]. The data are reported in Table 3 with the pertinent data of 2-furyl and 2-thienyl for comparison[86,88,89]. The σ^* constants refer to the polar effect of the

TABLE 3. Substituent constants for heterocyclic groups containing a chalcogen atom

Substituent	σ_m	σ_p	σ_m^-	σ_p^-	σ^*	σ_I	σ_R
2-Tellurienyl	0.06[a]	0.03[a]	0.10[b] 0.12[a]	0.25[b] 0.21[a]			
2-Selenienyl	0.06[a] 0.09[c]	0.04[a] 0.01[c,i]	0.16[b] 0.15[a]	0.22[b] 0.20[a]	0.85[d]	0.15[c]	−0.14[c]
2-Thienyl[l]	0.09[e]	0.05[e]	0.11[f]	0.19[f]	0.93[d]	0.12[c]	−0.10[c]
2-Furyl[l]	0.06[g]	0.02[g]	0.11[h]	0.21[h]	1.08[d]	0.09[c]	−0.08[c]
5-Me-(2-selenienyl)		−0.03[i]					
5-Et-(2-selenienyl)		−0.02[i]					
5-Cl-(2-selenienyl)		0.13[i]					
5-Br-(2-selenienyl)		0.12[i]					
5-I-(2-selenienyl)		0.11[i]					
5-Ac-(2-selenienyl)		0.18[i]					
5-NO_2-(2-selenienyl)		0.24[i]					

[a] From ^{1}H-NMR, Ref. 85.
[b] From ionization of phenols in 30% EtOH at 25 °C, Ref. 85.
[c] From ionization of benzoic acids in 50% EtOH, Ref. 86.
[d] From the alkaline and acid hydrolysis of 2-ethoxycarbonyl of five-membered heterocycles in 62% acetone at 25 °C, Ref. 90.
[e] From ionization of benzoic acids in 50% EtOH at 25 °C, Ref. 88.
[f] From ionization of phenols in 30% EtOH at 25 °C, Ref. 88.
[g] From ionization of benzoic acids in 30% EtOH at 25 °C, Ref. 89.
[h] From ionization of phenols in 30% EtOH at 25 °C, Ref. 89.
[i] From ionization of biselenienylcarboxylic acids in 50% buthylcellosolve, Ref. 87.
[l] For additional σ values see Ref. 30.

C_4H_3Z group and were calculated[90] from rate constants of $C_4H_3ZCOOEt$ (Z = Se, S, O) hydrolysis taking ethyl acetate as reference according to the Taft procedure[28].

The 2-selenienyl and 2-tellurienyl groups exhibit an inductive electron-withdrawing effect like 2-furyl and 2-thienyl. The σ^* values reflect the order expected on the basis of the electronegativity of the heteroatoms. The surprising opposite order of σ_I values has been explained[86] by invoking the magnitude and direction of dipole moments and conformational effects. In the absence of important resonance interactions with the reaction site an electron-releasing effect is observed from conjugative positions (negative values of $(\sigma_p - \sigma_m)$ and σ_R). The σ_p^- value and the difference $(\sigma_p^- - \sigma_p)$ show that 2-selenienyl and 2-tellurienyl easily delocalize a negative charge and that the latter appears to show a stronger effect than 2-furyl and 2-thienyl. The electronic behaviour of the selenienyl is markedly influenced by a group at C(5). The ability of heteroaromatic rings containing Se and Te to delocalize both positive (+M effect) and negative (−M effect) charges is ascribable to the polarizability of the heteroatom which can release its p electrons or accept electrons into its free d orbitals. The degree of effect is probably related to the resonance energy of the heteroaromatic ring.

E. Replacement Substituent Constants

The so-called replacement substituent constants have been calculated for a large number of heterocyclic groups[11]. However, their use is questionable both from the point of view of nomenclature and the concept of the constant.

The terms $\sigma_{\alpha\text{-selenienyl}}$, $\sigma_{\alpha\text{-tellurienyl}}$ etc. should be used [89] to indicate the effect caused by the substitution of a hydrogen atom of the benzene ring with C_4H_3Se or C_4H_3Te groups (see Section II.D) and not used to measure the effect caused by the replacement of the CH=CH moiety of the benzene ring with Se or Te atoms.

TABLE 4. Replacement substituent constants for chalcogenaryl groups

Substituent[a]	Heterocyclic group[b]	σ_{ar}	
Te	Tellurophene	σ_α	0.23[c]
		σ_α^+	-0.92[d]
Se	Selenophene	σ_α	0.62[e] 0.60[c] 0.55[d] 0.28[f] -0.4[g] -0.22[h] -0.24[i] -1.16[h]
		σ_α^+	-1.28[c] -1.25[j] -0.95[k] -0.88[l] -0.43[i]
		σ_β^+	> -0.53[k]
S	Thiophene	σ_α	0.71[q] 0.67[c] 0.36[f] 0.05[f] -0.28[h] -0.21[i] -0.92[h]
		σ_α^+	-1.15[j] -0.79[l] -0.38[i]
O	Furan	σ_α	1.04[c] 0.61[f] 0.28[f] 0.10[m] -0.29[h,g] -0.79[h]
		σ_α^+	-1.26[j] -0.93[l] -0.51[i]
—N=CH—Se—	Benzoselenazole	σ_α^o	1.9[n] 1.2[o]
		σ_α^-	1.8[p]
—N=CH—S—	Benzothiazole	α_α^o	1.6[n] 1.3[o]
		σ_α^-	1.6[p]
—N=ĊH—O—	Benzoxazole	σ_α^o	1.4[o] 1.2[n]
		σ_α^-	1.7[p]

[a] Substituent which replaces the CH=CH moiety of the benzene ring or which is fused on the benzene ring.
[b] From which the substituent constant is derived.
[c] From the ionization of α-carboxylic acids in H_2O at 25 °C, Ref. 91.
[d] From statistical analysis, Ref. 92.
[e] Ref. 31.
[f] Ref. 99.
[g] Ref. 100, the value has been calculated erroneously[87].
[h] From the ionization of *E*- and *Z*-α,β-diarylacrylic acids in 80% 2-methoxyethanol at 25 °C, Ref. 93.
[i] From the ionization of *para*-substituted chalcones in $AcOH-H_2SO_4$, Ref. 94.
[j] From a protodemercuriation reaction, Ref. 95.
[k] From acid protodedeuteriation, Ref. 98.
[l] By an extended selectivity relationship, Ref. 96.
[m] Ref. 101.
[n] From ^{1}H-NMR, Ref. 97.
[o] From IR data, Ref. 97.
[p] From alkaline deuteriodeprotonation reaction, Ref. 97.
[q] Ref. 30.

The σ_{ar} values reported in Table 4 question the concept of the constant and its electronic meaning. The polar constant σ_{ar} sometimes has a high degree of variation for the same substituent and appears to exhibit both an electron-releasing and an electron-withdrawing inductive effect. The effect is also strongly dependent on minor changes in polarity of the solvent. Significant examples are the $\sigma_{\alpha\,\mathrm{selenienyl}}$ values of -0.22 and -1.16 calculated[93] from the ionization of *E*- and *Z*-α-phenyl-β-(2-selenienyl)acrylic acids. However, it has been observed[93] that the greater electron-donating effect of the Se in the *Z*-isomer conflicts with stereochemical data indicating that the carboxyl group is twisted out of plane and therefore a minor conjugation is possible.

The σ_{ar}^+ values obtained by the extended selectivity relationship[96] are more reliable, but deviations are observed in this case also.

In the authors' opinion the replacement substituent constants are the result of an incorrect application of the Hammett equation and should be viewed with caution.

F. Special Substituent Constants

The σ_{het} constants for chalcogenazidinium salts are reported in Table 5. Their use is very limited and discrepancies in values are observed[33,102]. In the authors' opinion these

TABLE 5. Special substituent constants for chalcogen heteroarenes

Compound	σ_{het}
2-Amino-3-ethylbenzoselenazolium–BF_4	4.98[a–c]
2-Amino-3-ethylbenzothiazolium–BF_4	4.92[a] 4.89[b,c]
2-Amino-3-ethylbenzoxazolium–BF_4	5.73[a] 4.33[b]

[a] From ionization of azidinium salts in water at 25 °C, Ref. 33.

[b] From the reaction rates of azidinium salts with 1-(*p*-sulphophenyl)-3-methylpyrazolin-5-one in water at 25 °C, Ref. 102.

[c] From the reaction rates of azidinium salts with 1-(*m*-sulphophenyl)-3-methyl-5-aminopyrazole in water at 40 °C, Ref. 102.

values are also the result of an arbitrary extension of the Hammett equation and therefore their physicochemical meaning is questionable.

G. Hydrophobic Substituent Constants

Substituent constants of chalcogen atoms containing groups for structure–activity correlations are reported in Table 6. The hydrophobic substituent constant π of the SeMe group is slightly higher than that of SMe but opposite in sign to that of the OMe group. This indicates that when going from O to Se the molecule's movement into the organic phase is facilitated. A comparison with the Me group shows that the Se atom increases the hydrophobic character. This is also evident from the π constant of the $SeCH_2COOH$ group when compared with that of the S and O analogues. As the chain is lengthened (Me, Et, Pr) the hydrophobic character increases.

TABLE 6. Hydrophobic substituent constants for chalcogen-containing groups[a]

Substituent	π	Substituent	π
SeMe	0.74	SePr	1.82
SMe	0.61	SPr	1.61
OMe	− 0.02	OPr	1.05
Me	0.56	Pr	1.55
SeEt	1.28	$SeCH_2COOH$	− 0.08[b]
SEt	1.07	SCH_2COOH	− 0.25[b]
OEt	0.38	OCH_2COOH	− 0.87
Et	1.02	CH_2COOH	− 0.72

[a] Values taken from Ref. 35 and 103.

[b] Calculated from the partition coefficient[35].

III. SUBSTITUENT EFFECTS INVOLVING SELENIUM AND TELLURIUM

A. The Reaction Constant

Structure–reactivity relationships are usually expressed by single- or dual-parameter equations. The most popular treatment of the first type is that proposed by Hammett[13] (equation 7) for side-chain equilibria (K) or rate (k) reactions of *para* and *meta*-substituted benzenes. K_0 or k_0 refer to the unsubstituted parent compound and σ is the substituent constant defined by ionization of *para*- and *meta*-substituted benzoic acids in water at

25 °C (σ_p, σ_m) assuming the reaction constants $\rho = 1$ (see Section II.A).

$$\log K/K_o = \rho\sigma \quad \text{or} \quad \log k/k_o = \rho\sigma \tag{7}$$

The Hammett equation has been extended[10,11] to physical data (^{1}H-, ^{19}F- and ^{13}C-NMR, $E_{1/2}$, IR, UV etc.), to other substrates besides that of benzene and to other reactions determining new types of σ constants (σ^+, σ^-, etc., see Section II.A). A more general Hammett-like equation (equation 8) can be written, where ΔQ is the substituent effect on equilibria, kinetic or physical data and σ is any type of substituent constant (σ_m, σ_p, σ^+, σ^-, etc.) which correlates ΔQ. The ρ constant is the reaction constant which is independent of the substituent, depending only on the reaction or physical measurement and experimental conditions (solvent, catalyst, temperature).

$$\Delta Q = \rho\sigma \tag{8}$$

The ρ constant is a measure of the sensitivity of the reaction to the substituent effects and of the transmission of the electronic effects from the substituent to the reaction centre.

In equilibrium processes ρ is the result of the difference between the ρ values of the direct and inverse reaction and therefore its value is positive or negative depending on the considered direction of the reaction. If in the ionization equilibria the acid is on the left, the ρ value is positive.

For side-chain solvolytic reactions of aromatic substrates in which a positive delocalizable charge is developed in the rate-determining step and in electrophilic aromatic substitutions, the sign of ρ is negative. The value of ρ is positive in aromatic nucleophilic substitution and in other rate processes in which a delocalizable negative charge is developed in the rate-determining step.

The best known dual-parameter equations used for correlating equilibrium, kinetic and other physical data of aromatic substrates are those proposed by Taft[21], Swain–Lupton[25] and Yukawa–Tsuno[104]. The first two (equations 9 and 10) are those almost exclusively used in Se and Te organic compounds. The regression parameters ρ_I and f, ρ_R and r should respectively be a measure of the relative importance of polar and mesomeric effects transmitted from the substituent to the reaction centre.

$$\Delta Q = \rho_I\sigma_I + \rho_R\sigma_R \tag{9}$$

$$\Delta Q = f\mathcal{F} + r\mathcal{R} + i \tag{10}$$

Two serious criticisms have been made about the use of these equations. The first is statistical in nature[105]. The significance of regression parameters of a multiple linear regression depends strongly on the number of points and on the width of the range covered. Therefore when a limited number of substituents are used, or there is multicollinearity between the two substituent constants, the regression parameters ρ_I, f, ρ_R and r have no meaning. This was made clear by Taft himself[24] who suggested a minimal set of substituents; nevertheless many of the correlations reported in literature commit this error.

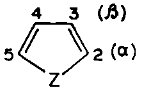
The second criticism is one of concept[7,9]. Supporting statistics show that within a given type of reaction the regression parameters of the dual parameter equations (9) and (10) are not significantly different from those expected on the basis of the Hammett ρ constant and of the correlation between the proper set of σ constants. Equations (9) and (10) cannot therefore distinguish between a different blend of polar and resonance contributions even when the aromatic system is changed but the reaction remains the same.

The use of both single- and dual-parameter equations in ^{1}H-NMR spectroscopy has been criticised[106–110] because there is no clear theoretical relationship between the shielding mechanism and the chemical reactivity parameters and other effects, in addition to electronic effects, influence the chemical shifts. Wiley and Miller[106] have stated: '^{1}H-NMR correlations which depend solely on the reactivity constants ($\sigma, \mathscr{F}, \mathscr{R}$) are theoretically deficient and we would discourage their use. The introduction of additional terms, e.g. to correct for substituent magnetic anisotropy, appears to be essential, but the merits of such a hybrid approach are doubtful.' This criticism can be extended to other spectroscopic parameters.

Finally it must be recalled that the goodness of a correlation, and therefore of the regression parameters ρ, ρ_I, f, ρ_R and r, cannot be established solely on the basis of the value of the correlation coefficient. The use of appropriate statistic tests is absolutely necessary[105].

B. Electronic Transmission Through Heterocyclic Systems

Transmission of the substituent electronic effects through selenophene (3; Z = Se) and tellurophene (3; Z = Te) rings has been determined[4,91,111] for the ionization reaction in water at 25 °C of 4- and 5-substituted selenophen-2-carboxylic acids (4; Z = Se) and 5-substituted tellurophen-2-carboxylic acids (4; Z = Te). By plotting the pK_a values against the Hammett σ constants excellent linear correlations are obtained. The ρ values are reported in Table 7 with those for the ionization of substituted thiophen-2-carboxylic acids[4,112] (4; Z = S) and furan-2-carboxylic acids[4,113] (4; Z = O). A comparison shows that the furan ring is the most sensitive to structural change and that selenophene, tellurophene and thiophene behave similarly. Analogous results are obtained[87] in the ionization reaction of 2,2′-biselenienyl and 2,2′-bithienyl-5′-substituted 5-carboxylic acids (5; Z = Se, S) in water–butylcellosolve. The ρ values (Table 7) show that



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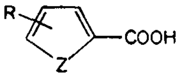

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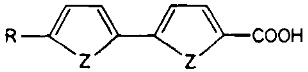

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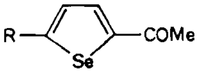


(6)

TABLE 7. Transmission of substituent effects in the ionization of α-carboxylic acids of chalcogenic heterocycles

α-Carboxylic acids	ρ^a	Solvent	T(°C)	Ref.
Tellurophen-	1.20	H_2O	25	4, 91
Selenophen-	1.23	H_2O	25	111
	1.76	H_2O/BC^b	20	87
Thiophen-	1.23	H_2O	25	4, 112
	1.71	H_2O/BC	20	87
Furan-	1.40	H_2O	25	4, 113
2,2′-Biselenienyl-	0.50	H_2O/BC	20	87
2,2′-Bithienyl-	0.56	H_2O/BC	20	87

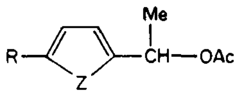
[a] Calculated by using the Hammett σ constants and pK_a values determined potentiometrically.

[b] Butylcellosolve in 1:1 v/v mixture.

the transmission through the biselenienyl and bithienyl systems is the same ($\rho = 0.50$ and 0.56) and very similar to that of the biphenyl system[114] (0.59), but markedly lower than that through the corresponding monocyclic compounds **4** ($\rho = 1.76$ and 1.71).

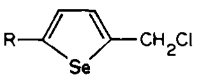
Quantitative information on the ability of the selenophene ring to transmit the substituent electronic effects was obtained through a study[115] of the protonation of 5-substituted 2-acetylselenophenes (**6**) in an aqueous solution of H_2SO_4 by ^{1}H-NMR spectroscopy and by IR investigation[116] of the proton acceptor power of compounds **6** in the incomplete acid–base interaction with phenol in tetrachloroethylene. In the first study the correlation between the values of p$K = H_0$ (half-protonation) and the electrophilic σ^+ constants gives a ρ value of 3.35 which compared with those of 5-substituted 2-acetylthiophenes[115] ($\rho = 3.34$) and substituted acetophenones[115] ($\rho = 2.49$) indicates that the two heterocyclic rings once again exhibit the same sensitivity to structural changes but transmit the substituent effects more efficiently than the benzene ring. The d orbitals of Se and S are invoked[115] to justify the higher transmission ability. In the second study the association constants K_{as} and the shifts $\Delta\nu$(OH) of the stretching vibrations of the hydroxy group of phenol occurring in the hydrogen bond formation, were correlated with the σ_p and σ_p^+ constants. Although the statistical analysis does not give clear information[116], the correlation with σ_p^+ constants was preferred because it seems to take better account of the conjugative interactions of the substituent and the carbonyl group. The values of -0.64 (K_{as} vs. σ_p^+) and -0.08 ($\Delta\nu$ vs. σ_p^+) compared with those calculated for the substituted acetophenones under the same experimental conditions (-0.36 and -0.09) seem to confirm the higher sensitivity of the selenophene compared to the benzene ring to the electronic effects of the substituent. However, these results[115,116] should be regarded with suspicion because of the type and limited number of substituents used in the correlations.

The transmission ability of selenophene and tellurophene rings has also been determined[117] in the side-chain solvolyses of 1(2-heteroaryl)ethyl acetates (**7**; Z = Se, Te and **8**; Z = Se, Te) in 30% ethanol by the k(Me)/k(H) reactivity ratios. The values of the ratios are 23 and 12 for the derivatives of selenophene and tellurophene, respectively. If the k(Me)/k(H) ratios are considered an estimate of the transmission through the individual ring system, it may be concluded that the selenophene transmits the electronic effects of the substituent better than the tellurophene. A comparison[117] with the k(Me)/k(H) ratios of the analogous derivatives of furan and thiophene (160 and 70, respectively) shows that the transmission ability decreases in the order furan > thiophene > selenophene > tellurophene. The transmission across the selenophene ring has also been determined[118] in the solvolyses of 5-substituted 2-chloromethylselenophenes (**9**). A ρ value of -6.42 can be calculated from the regression analysis between the log of the reaction rate constants and σ^+ values.



(7) R = H

(8) R = Me



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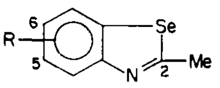


(10)

The sensitivity of the benzoselenazole system to structural changes has been evaluated[119] by ^{1}H-NMR spectroscopy. The chemical shifts of the 2-Me protons of a number of 5- and 6-substituted 1,3-benzoselenazoles (**10**) have been correlated with Hammett's σ constants using σ_m values for the substituents bonded at C(5) and σ_p values for those bonded at C(6). The value of the ρ constant is 6.72 and is very similar to those obtained[119] for 5- and 6-substituted 2-methyl-1,3-benzoxazoles ($\rho = 6.82$) and benzothiazoles

($\rho = 7.31$). The chemical shifts of the 2-Me protons are strongly dependent[119] on the nature of the chalcogen atom, but the ρ values for the three benzoazoles show that the heteroatom does not play an important role in the transmission of electronic effects, most of which are therefore transmitted across the N atom.

C. Electronic Transmission Through Selenium and Tellurium Atoms

The transmission of electronic effects of the substituents through the —Te— and —TeX_2—(X = Cl, Br) bridges has been investigated by Sadekov and coworkers[120–122] by measuring the thermodynamic basicity constants of *p*- and *m*-aryl [*p*-(dimethylamino)phenyl]tellurides (**11**) and corresponding dihalotelluranes (**13**, **14**) and the ^{19}F-NMR chemical shifts of *p*-aryl [*p*-fluorophenyl]tellurides (**15**) and corresponding dichlorotelluranes (**16**). The results of single-parameter correlations using σ, σ^0 and σ^+ constants indicate that the Hammett σ constants generally give the best correlation. Examination of the ρ constants reported in Table 8 show that the Te in tellurides is able to transmit the electronic effect better than the Te in the telluranes by a factor of 2.3–4 and that ^{19}F chemical shifts are more sensitive than pK_a values.

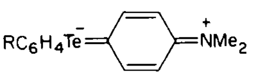
m- or *p*-RC_6H_4—Z—$C_6H_4NMe_2$-*p*
(**11**) Z = Te
(**12**) Z = Se

m- or *p*-$RC_6H_4TeX_2C_6H_4NMe_2$-*p*
(**13**) X = Cl
(**14**) X = Br

p-$RC_6H_4TeC_6H_4F$-*p*
(**15**)

p-$RC_6H_4TeCl_2C_6H_4F$-*p*
(**16**)

Transmission through a —TeX_2— bridge is mainly of the inductive type, but through the —Te— bridge a contribution of polar resonance structures **17** and **18**, with the participation of the vacant d orbitals of Te, is possible. Dipole moment data seem to support this hypothesis[49,69]. The ^{19}F chemical shifts of **15** and **16** were also elaborated by


(**17**)

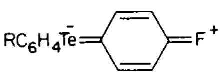

(**18**)

TABLE 8. Hammett ρ constants for the transmission of substituent effects through Se and Te bridges

Compound	Bridge	ρ^a	Ref.
11	—Te—	0.776	120
15		3.83	122
28		− 19.3	136
13	—$TeCl_2$—	0.335	121
16		0.984	122
14	—$TeBr_2$—	0.251	121
19	—Se—	1.47	127
20		0.35	60
21		− 1.55	47
22		-1.05×10^{-4}	133
27		− 18.7	136

[a] Hammett σ constants were used except for **20** and **22** (see text).

TABLE 9. Taft ρ_I and ρ_R constants for the transmission of substituent effects through chalcogenic bridges[a]

Constant[b]	Bridge				Ref.
	—Te—	—TeCl$_2$—	—O—	—S—	
ρ_I	3.18	1.14	3.84	4.77	122, 123, 124
ρ_R	3.06	1.11	5.07	5.90	122, 123, 124

[a] From ^{19}F-NMR data of **15**, **16** and O and S analogues.

[b] σ_I and σ_R were used in the dual-parameter equation.

the Taft equation and comparison of ρ_I and ρ_R values (see Table 9) with those obtained from *p*-fluorodiphenyloxides[123] and *p*-fluorodiphenylsulphides[124] seems to indicate that Te is less able to transmit the electronic effects of the substituents than O and S.

The transmission through the —Se— bridge has been investigated in a variety of compounds and reactions (Table 8). The first studies were by Litvinenko and coworkers[59,125] who measured the k(H)/k(NO$_2$) reactivity ratios of selenides (**12**; R = *p*-NO$_2$, H) in the reactions with picryl chloride and *p*-nitrobenzyl chloride. At 25 °C the k(H)/k(NO$_2$) ratios for the two reactions are 22.2 and 17, respectively and are higher than those for O (16 and 12.1) and lower than those for S (30.6 and 23.8) analogues. Further studies[126] extended to other bridging groups have pointed out the following decreasing order of transmissivity: NMe > NH > S > Se > O > CH$_2$.

The log of the rate constants for alkaline hydrolysis of aryl selenoesters (**19**) in 70% aqueous acetone gives a good linear correlation with the Hammett σ constants[127,128]. The value of the reaction constant ($\rho = 1.47$) is the same as that found[127] for O ($\rho = 1.46$) and S ($\rho = 1.46$) analogues. Although the selenoesters (**19**) are more reactive than the analogous esters and thioesters, the Se atom exhibits the same power for transmitting electronic interaction as O and S. Parallel lines are also obtained in the correlations of carbonyl frequencies of **19** and O and S analogues with σ values confirming the previous results[127]. Analogous results are obtained in the ionization reaction of *para*- and *meta*-substituted aryl chalcogenacetic acids (**20**). The pK_a values correlate[60] with Bekkum's σ^n substituent constants[19], where possible, and otherwise with the Hammett σ values, and give a ρ value of 0.35 for substituted phenylselenoacetic acids (**20**; Z = Se) which is similar to that calculated for phenoxyacetic acids[129] (**20**; Z = O) (0.30) and phenylthioacetic acids[60] (**20**; Z = S) (0.32), but lower than that for phenylacetic acids[130,131] (0.49), and higher than that of β- arylpropionic acids[132] (**20**; Z = CH$_2$) (0.21). Chalcogen atoms have therefore a lower insulating effect than that of a methylene group. The similarity of transmission of electronic effects of chalcogen atoms is probably the result of an interplay between the increase in the polarizability of the heteroatom and the increased distance of the substituent from the reaction centre going from O to Se[60].

p-RC$_6$H$_4$SeC(=O)CH$_2$CH$_2$Ph **(19)**

m- or *p*-RC$_6$H$_4$—Z—CH$_2$COOH **(20)**

Differences in the electronic transmission through —Se—, —S— and —O— bridges are also observed in the acid-catalysed hydrolysis of aryl vinyl chalcogenides. The mechanism of the reaction of aryl vinyl selenides (**21**) has been studied by McClelland and Leung[47]. The rate-determining step of the reaction is the proton transfer to the olefinic bond (equation 11) and the reaction products are acetaldehyde and benzoselenols which quickly convert to diselenides under the reaction conditions. The Hammett ρ constant of selenides (-1.55) is smaller than those of sulphides (-1.84) and ethers (-2.00). The ability to transmit the substituent effects to an adjacent positive reaction centre therefore appears to be largely determined by the degree of the electron-donating character of the chalcogen atom.

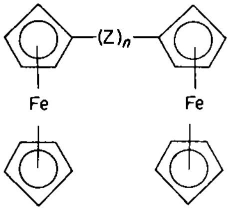
$$\underset{\textbf{(21)}}{\mathrm{ArSeCH{=}CH_2}} \xrightarrow[\text{slow}]{H^+} \mathrm{ArS\overset{+}{e}CHMe} \rightarrow \rightarrow \mathrm{ArSH + MeCHO} \qquad (11)$$

In aryl allyl chalcogenides (**22**; Z = O, S, Se) and aryl cyanoselenides a linear dependence between the $\bar{\nu}_{max}$ (cm^{-1}) of the K-band in UV spectra and σ_n^- has been found[133]. One-parameter regression analysis shows that the power of transmission of a chalcogenic bridge in allyl compounds decreases in the order —Se—($\rho = -1.05 \times 10^{-4}$) > —O—($\rho = -1.03 \times 10^{-4}$) > —S—($\rho = -0.83 \times 10^{-4}$) and is higher than in the cyanoselenides ($\rho = -0.71 \times 10^{-4}$).

$$p\text{-}RC_6H_4\text{—}Z\text{—}CH_2CH{=}CH_2$$

(22)

The transmissivity of the —Se— bridge has been evaluated[134] and compared with those of —Se—Se—, —CH_2— and —CH_2—CH_2— bridges by measurements of half-potential of diferrocenyl compounds **23**–**26**. The values $E'_{1/2}$ and $E''_{1/2}$ of the first and second half-wave potentials and their differences $\Delta E_{1/2}$ are reported in Table 10.



(23) Z = Se, $n = 1$
(24) Z = Se, $n = 2$
(25) Z = CH_2, $n = 1$
(26) Z = CH_2, $n = 2$

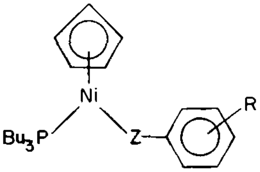
Assuming[135] the $\Delta E_{1/2}$ value as a quantitative estimate of the electronic interaction between the two ferrocene moieties, the order of decreasing power of transmission is: —Se— > —Se—Se > —CH_2— > —CH_2—CH_2—. A field effect should not be important since the C—Se and Se—Se bonds are much longer than the C—C bond and therefore the increased interaction between the ferrocene moieties in **23** and **24** is probably due to an inductive effect which is transmitted more efficiently from the more polarizable Se atom.

The ability of transmission of —Se— and —Te— bridges has been compared[136] by ^{1}H-NMR investigation of the complexes **27** and **28** of π-cyclopentadienylnickel tri-*n*-butylphosphine with *meta*- and *para*-substituted phenyl selenides and phenyl tellurides. Good linear correlations are observed between the cyclopentadienyl proton chemical

TABLE 10. First and second half-wave potentials of bridged diferrocenes[a]

Compound	$E'_{1/2}$	$E''_{1/2}$	$\Delta E_{1/2}$
23	0.46	0.68	0.22
24	0.53	0.67	0.14
25	0.39	0.56	0.17
26	0.37	0.37	0.00

[a] In acetonitrile except for **25** for which MeCN (90% EtOH) was used. For references see text.

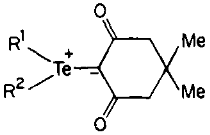


(27) Z = Se
(28) Z = Te

shifts and the Hammett σ constants. The ρ values for Se and Te ligands are -18.7 and -19.3, respectively, and the comparison with the ρ value of -17.9 for the S ligand[137] shows that the order of transmission of the substituent electronic effects through the heteroatom–Ni bond increases in the order —S— < —Se— < —Te—.

The electronic transmission in π-tellurane system has been evaluated[138] by single- and multi-parameter correlations between the thermodynamic basicity constants of telluronium ylides (**29**) and $\Sigma\sigma$, $\Sigma\sigma^0$, $\Sigma\sigma^+$, $\Sigma\sigma_I$, $\Sigma\sigma_R$, etc.

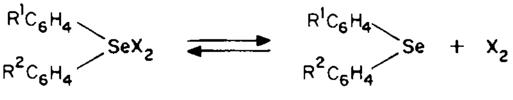
The $\Sigma\sigma^0$ constants seem to give the best one-parameter correlation ($\rho = 0.958$) but the results should be used cautiously.



(29)

Hammett-like correlation between the basicity constants of *para*-substituted diphenylselenoxides and $\Sigma\sigma^*$ has been used[142] to evaluate the transmission in π-selenuranes. The ρ constant (-0.89) is very similar to that calculated for analogous sulphoxides (-0.92), indicating that the two heteroatoms have the same transmission ability.

The sensitivity of the Se–halogen bond to electronic effects has been evaluated[139–141] by determining the dissociation constants of symmetrically and unsymmetrically disubstituted diphenylselenium dibromides (**30**; X = Br) and symmetrically disubstituted diphenylselenium diiodides (**30**; X = I, $R^1 = R^2$). These compounds dissociate in CCl_4 solution to give diphenyl selenides (**31**) and halogen (equation 12). The pK values of the dissociation constants plotted against the Hammett σ constants give ρ values of 2.1 and 0.7 for dibromides and diiodides, respectively, indicating a higher sensitivity of the Se—Br bond as compared with the Se—I bond to electron density.



(12)

(30) (31)

D. Substituent Effects in Electrophilic and Nucleophilic Aromatic Reactions

The k(Me)/k(H) reactivity ratios for all chalcogen heterocycles (3; Z = Te, Se, S, O) and their 2-Me derivatives have been determined in our laboratories[117,143] by kinetic and competitive procedures in two electrophilic substitution reactions (see Section IV.A), i.e. formylation and trifluoroacetylation. The values are summarized in Table 11. If the k(Me)/k(H) ratios are considered as estimates of the sensitivity of the heterocyclic ring to

TABLE 11. k(Me)/k(H) reactivity ratios for electrophilic substitution of five-membered chalcogen heterocycles

Ring	Formylation[a]	Trifluoroacetylation[b]
Tellurophene	620	500
Selenophene	300	280
Thiophene	290	380
Furan	880	1700

[a] By $COCl_2$-DMF in $CHCl_3$ at 20 C.

[b] By trifluoroacetic anhydride in dichloroethane at 75 °C. For references see text.

substituent electronic effects the following order is observed: furan > tellurophene > thiophene > selenophene. The order is different from that observed[117] in side-chain reactions in which a delocalizable positive charge is developed in the intermediate carbocation (see Section III.B) indicating that parallelism between the two classes of reactions is not always possible (see Section IV.A). The different order may be the result of concomitant factors such as the charge distribution, the position of transition state along the reaction coordinate and the interaction between the substituent and heteroatom[117].

The sensitivity of selenophene (**3**; Z = Se) to substituent electronic effects in electrophilic and nucleophilic reactions has been determined by mercuriation[144] of 2-substituted selenophenes and by piperidino-debromination[145] of 2-bromo-3-nitro-5-substituted selenophenes, respectively. The reaction constants ρ are reported in Table 12 together with those calculated for the analogous thiophenes[144,146]. The sensitivity of the selenophene ring to structural changes is high (high ρ values) and is the same as that of the thiophene ring.

A theoretical study of the sensitivity of selenophene, selenopheno[2,3-*b*]selenophene and selenopheno[3,2-*b*]selenophene rings to the electronic effect of substituents bonded at C(2) has been reported by Konar and coworkers[147]. Localization energies were chosen as reactivity indices and calculations were performed for the aromatic compounds and their *C*-protonated form (σ complex). The theoretical values correlated with Swain–Lupton $\mathcal{F}$ and $\mathcal{R}$ constants seem to indicate a dominant resonance effect for the α-position of five-membered rings and a more efficient transmission of resonance effect at C(5) through the [3,2-*b*] system than through the [2,3-*b*] system.

TABLE 12. Reaction ρ constants for electrophilic and nucleophilic substitutions at selenophene and thiophene rings

Ring	Mercuriation[a]	Piperidino-debromination[b]
Selenophene	− 5.77 (25 °C) − 5.80 (35 °C) − 5.14 (50 °C)	3.15 (20 °C)
Thiophene	− 5.86 (35 °C) − 5.60 (50 °C)	3.21 (20 °C)

[a] Log of rate constants vs. σ^+, Ref. 144.

[b] Log of rate constants vs. σ^-, Refs. 145, 146.

E. Substituent Effects on Ring Protons and Carbons of Heterocyclic Systems by NMR Spectroscopy

The proton and carbon chemical shifts of substituted compounds relative to parent unsubstituted ones ($\Delta\delta = \Delta H_i^j$ or ΔC_i^j where i indicates the position of proton and carbon and j that of the substituent) are frequently related to the electronic effects of the substituents by σ or σ-like constants[10,11]. In Se/Te organic compounds $\mathcal{F}$ and $\mathcal{R}$ Swain–Lupton constants[25] are the most used. The regression constants f and r (equation 10) have been calculated for 2- and 3-substituted selenophenes[148,149], 2-substituted tellurophenes[150], 2- and 3-substituted benzo[*b*]selenophenes[150], benzo[*b*]tellurophenes[150], 2-substituted selenopheno[3,2-*b*]selenophenes[151], 2-substituted selenopheno[2,3-*b*]selenophenes[147] and *para*-substituted 4-aryl-1,2,3-selenadiazoles[152]. Some examples are summarized in Table 13. One-parameter regressions between $\Delta\delta$ and σ_p^+ have been calculated for 2-substituted selenopheno[3,2-*b*]selenophenes[151]. Theoretical considerations discourage the use of reactivity constants in ^{1}H-NMR correlations and supporting statistics question the meaning of dual-parameter equations (see Section III.A).

Another approach is to correlate the relative chemical shifts of a substrate $S_1[\Delta\delta(S_1)]$, against those of another substrate S_2, $[\Delta\delta(S_2)]$, by equation (13). The straight line of the regression should pass through the origin, but deviations are observed. The regression constant A can be viewed (B should be zero) as the ratio of the transmissions of the substituent effect of the two substrates. The constant A has been determined for the couples selenophene–thiophene[153,154], selenophene–tellurophene[153,154], tellurophene–thiophene[153,154], selenophene–benzo[*b*]selenophene[150], tellurophene–

TABLE 13. Regression constants (f and r) and intercept (i) of the Swain–Lupton equation for substituted heterocyclic rings containing Se and Te[a]

$\Delta\delta$ (Compound)[b]	f	r	i	Ref.
ΔH_3^2 (Te)	0.51	2.97	−0.07	150
ΔH_3^2 (Se)	0.34	2.67	0.00	148, 149
ΔH_3^2 (BTe)	0.33	2.49	0.04	150
ΔH_3^2 (BSe)	0.28	2.13	0.12	150
ΔH_2^3 (Se)	0.57	3.23	0.02	148, 149
ΔH_2^3 (BTe)	0.17	4.20	0.33	150
ΔH_2^3 (BSe)	0.49	3.28	0.22	150
ΔC_3^2 (Se)	−5.7	46.6	4.0	148, 149
ΔC_2^3 (Se)	−3.7	61.7	2.3	148, 149
ΔC_5^2 (2,3-SeSe)	2.0	4.9	−0.3	147
ΔC_5^2 (3,2-SeSe)	7.5	15.2	0.86	147, 151

[a] Data for other positions of proton, carbon and substituent are reported in the cited references.

[b] Te = tellurophene, Se = selenophene, BTe = benzo[*b*]tellurophene, BSe = benzo[*b*]selenophene, 2,3-SeSe = selenopheno[2,3-*b*]selenophene, 3,2-SeSe = selenopheno[3,2-*b*]selenophene.

TABLE 14. Relative shifts of 2-substituted tellurophenes, selenophenes and furans vs. those of 2-substituted thiophenes[a]

Relative proton chemical shift				Relative carbon chemical shift			
$\Delta\delta(S_1)$	$\Delta\delta(S_2)$	*A*	*B*	$\Delta\delta(S_1)$	$\Delta\delta(S_2)$	*A*	*B*
				ΔC_2^2(Te)	ΔC_2^2(S)	1.18	1.73
				ΔC_2^2(Se)	ΔC_2^2(S)	1.11	−0.62
				ΔC_2^2(O)	ΔC_2^2(S)	0.81	−5.05
ΔH_3^2(Te)	ΔH_3^2(S)	1.23	−0.16	ΔC_3^2(Te)	ΔC_3^2(S)	1.10	−0.99
ΔH_3^2(Se)	ΔH_3^2(S)	1.11	−0.08	ΔC_3^2(Se)	ΔC_3^2(S)	1.17	−1.57
ΔH_3^2(O)	ΔH_3^2(S)	1.16	0.16	ΔC_3^2(O)	ΔC_3^2(S)	1.22	−0.11
ΔH_4^2(Te)	ΔH_4^2(S)	1.64	0.04	ΔC_4^2(Te)	ΔC_4^2(S)	1.04	−0.86
ΔH_4^2(Se)	ΔH_4^2(S)	1.06	0.01	ΔC_4^2(Se)	ΔC_4^2(S)	1.18	−0.43
ΔH_4^2(O)	ΔH_4^2(S)	1.07	0.19	ΔC_4^2(O)	ΔC_4^2(S)	1.28	−0.75
ΔH_5^2(Te)	ΔH_5^2(S)	1.16	−0.02	ΔC_5^2(Te)	ΔC_5^2(S)	1.25	−0.45
ΔH_5^2(Se)	ΔH_5^2(S)	1.02	0.00	ΔC_5^2(Se)	ΔC_5^2(S)	1.14	−0.50
ΔH_5^2(O)	ΔH_5^2(S)	0.68	0.10	ΔC_5^2(O)	ΔC_5^2(S)	0.58	0.28

[a] Te = tellurophene, Se = selenophene, S = thiophene, O = furan; *A* and *B* are the regression constant and the intercept, respectively, of equation (13); data taken from Refs. 153 and 154.

benzo[*b*]tellurophene[150], selenopheno[3,2-*b*]selenophene–thieno[3,2-*b*]thiophene[151] and dibenzylchalcogenides–dibenzyldichalcogenides[155]. The data relative to 2-substituted five-membered heterocycles are summarized in Table 14. Except for a few cases no significant differences are observed in the slopes with values near to unity. Therefore the four rings transmit the substituent effects by the same mechanism and with practically the same intensity.

$$\Delta\delta(S_1) = A \cdot \Delta\delta(S_2) + B \qquad (13)$$

The coupling constants *J*(H–H) and *J*(Se–H) of 2- and 3-substituted selenophenes have also been correlated with Swain–Lupton $\mathcal{F}$ and $\mathcal{R}$ constants[156], but generally poor correlations are obtained.

F. Miscellaneous

The sensitivity of the seleninic group (—SeO_2H) to substituent effects has been evaluated by the correlation[157,158] between the ionization constants[157–160] of *p*- and *m*-benzeneseleninic acids determined in water at 25 °C and the Hammett σ constants. The ρ value ($\rho = 1.0$) indicates that in aromatic systems the seleninic group has the same sensitivity as the carboxylic group.

Kristian and Suchar[161] found a linear correlation between the vibration frequencies of the isoselenocyano group (—NCSe) of *p*- and *m*-substituted phenyl isoselenocyanates and Hammett's σ constants. The reaction constant ($\rho = -16.14$ in chloroform) is solvent-dependent and is markedly lower than that for the isothiocyanates ($\rho = -36.60$ in chloroform). The result agrees with the greater mesomeric interaction of the isothiocyano group with the aryl ring.

Correlations with σ constants were also found in the base-catalysed decomposition of 4-aryl-1,2,3-selenadiazoles[162] ($\rho = 2.4$) and in the ionization reaction of 5,6-substituted 2,1,3-benzoselenadiazoles[163].

IV. REACTIVITY AND DIRECTING EFFECTS IN HETEROCYCLIC SYSTEMS

Organic compounds of Se and more particularly Te are sometimes unstable in mineral acids and sensitive to light. They give complexes at the heteroatom and undergo carbon–heteroatom fission with nucleophilic reagents. Hence the study of their reactivity is difficult, and most of the available reactivity data are qualitative. Quantitative data refer mainly to five-membered rings and will be discussed first. When necessary, a comparison with analogous compounds of O and S is made.

A. Electrophilic Aromatic Substitutions

The behaviour of selenophene (**3**; Z = Se) and tellurophene (**3**; Z = Te) in electrophilic substitutions is similar to that of other aromatic systems. The electrophile is directed mainly or exclusively to the 2-position (α-position) as in furan (**3**; Z = O) and thiophene (**3**; Z = S). The α:β ratio of selenophene in the acid-catalysed protodedeuteriation reaction[98] ($MeOH-H_2O$, 20 °C) is $> 5 \times 10^3$ and only the α-isomer is observed in sulphonation[168], halogenation[164,169], mercuriation[170], trifluoroacetylation[166], acetylation[164], formylation[165], chloromethylation[144] and aminomethylation[171]. Nitration[172] gives 15% of the 3-nitro derivative (β-isomer) so that the α:β ratio is similar to that found for thiophene[173]. Tellurophene is acetylated[143,165], formylated[143,165] and trifluoroacetylated[143,165] exclusively in the α-position. Bromination gives 1,1-dibromotellurophene[174].

An electron-donating or -withdrawing substituent present at the 2- or 3-position does not change the orientation and the electrophilic substitution still proceeds mainly or exclusively at the free α-position[181]. An exception is nitration with fuming HNO_3 and concentrated H_2SO_4 of 2-substituted selenophenes containing strong electron-withdrawing groups (i.e. CHO, COOH, CN, COMe, SO_2Cl). In this case the reaction occurs[175,181] mainly at the 4-position (60–80%). The preference for the α-position may be

TABLE 15. Rates of tellurophene, selenophene and furan relative to thiophene

Electrophilic substitution[a]	k(Te)/k(S)	k(Se)/k(S)	k(O)/k(S)
Bromination, Br_2, AcOH, 25 °C		47.5[b]	120[c]
Chlorination, Cl_2, AcOH, 25 °		6.5[b]	48.7[c]
Bromination, Br^+		4.5[b]	
Trifluoroacetylation, TAA, DCE, 75 °C	46.4[d]	7.33[d]	140[e]
Acetylation, Ac_2O, $SnCl_4$, DCE, 25 °C	7.55[d]	2.28[d]	11.9[b]
Protodemercuriation, HCl, EtOH, 70 °C		2.2[f,i]	2.3[f,i]
Protodedeuteriation, $MeOH-H_2O$, H^+, 20 °C		10[g,h]	1.8[g,j]
Formylation, $COCl_2$, $HCONMe_2$, 30 °C	36.8[d]	3.64[d]	107[d]

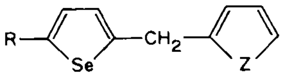
[a] Te = tellurophene, Se = selenophene, S = thiophene, O = furan, TAA = trifluoroacetic anhydride, DCE = 1,2-dichloroethane.
[b] Ref. 164. [c] Ref. 96. [d] Ref. 165. [e] Ref. 166.
[f] Ref. 95. [g] Ref. 98.
[h] $k(Se)/k(S) = 6–10$, Ref. 167, p. 24.
[i] It has been assumed[96] that the reaction proceeds via preliminary coordination of Hg with the heteroatom.
[j] Partial cleavage of the furan ring occurs, Ref. 96, p. 267.

rationalized in terms of the relative stabilities of Wheland intermediates as models for the transition states[96].

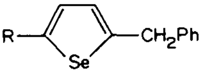
The α-reactivity data for selenophene and tellurophene relative to thiophene are reported in Table 15. Both compounds are more reactive than thiophene. A comparison with furan was made[165] in three electrophilic reactions: trifluoroacetylation, acetylation and formylation. In all three reactions the reactivity sequence is: furan > tellurophene > selenophene > thiophene. This order is the reverse of that of ground-state aromaticities[176] and suggests that the relative differences of ground-state energies play a more important role than the relative stabilities of intermediate carbocations in determining the reactivity scale. The activation parameters of the formylation of compounds **3** support this observation[165]. The activation entropy has the same value in all four reactions and the activation enthalpies are linearly correlated both with localization energies and empirical values of resonance. The constancy of entropy suggests that the transition states of all chalcogenides **3** lie in a similar position along the reaction coordinate.

Recent[177] theoretical calculations of electron density distribution of the intermediate carbocations show that the π charge on the heteroatom decreases in the sequence selenophene > thiophene > furan both for α- and β-substitution and is greater for β- than for α-substitution (Table 16). This supports the previous hypothesis[165] that in electrophilic substitutions the α:β ratio can be explained by the relative stabilities of carbocation intermediates, and that the relative rates of chalcogenides **3** are not determined only by the relative stabilities of the intermediates.

Reactivity and substituent effects of the 2-selenienyl group in electrophilic substitution reactions have also been studied[87,178] in compounds **32**, **34** and **36**. In all cases α-substitution at the selenienyl group was the prevalent reaction for giving the corresponding **33**, **35** and **37** compounds.

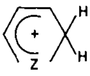
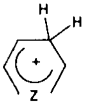


(32) R = H ; Z = S
(33) R = CHO, OMe ; Z = S
(34) R = H ; Z = Se
(35) R = Cl, Br, I, NO$_2$, COMe ; Z = Se



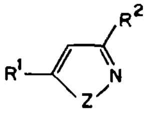
(36) R = H
(37) R = COMe

TABLE 16. π Charge distribution of Wheland intermediates of electrophilic substitution reactions[a]

Carbocation				Atom		
	Z	Z	C(2)	C(3)	C(4)	C(5)
	O	0.248	−0.007	0.368	−0.093	0.297
	S	0.277	0.010	0.374	−0.038	0.260
	Se	0.312	0.019	0.345	−0.027	0.250
	O	0.394	0.399	0.008	−0.017	−0.044
	S	0.600	0.288	0.019	0.146	−0.073
	Se	0.638	0.249	0.024	0.141	−0.058

[a] Data from Ref. 177.

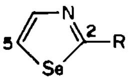
A N atom in the five-membered ring markedly reduces the reactivity of the ring. When it is in the α-position, as for example in 1,2-chalcogenazoles (usually called isochalcogenazoles) (**38**; Z = O, S, Se, Te), the directing effect of the aza group appears to prevail over that of the chalcogen atom and the electrophile attacks in the 4-position[179]. Protodedeuteriation of 3,5-dimethylisotellurazole (**39**; Z = Te) and 3,5-dimethylisoselenazole (**39**; Z = Se) occurs at the free position and the former is more reactive than the latter[179]. Attacks at the 4-position have also been observed in nitration, bromination and chlorosulphonation reactions[179]. The nitration of 3-methyl-5-phenylisoselenazole (**40**; Z = Se) also gives 3-methyl-5(*p*-nitrophenyl)isoselenazole indicating that the α-isoselenazolyl is a *para*-directing group[179]. The attack of the electrophile in 1,3-selenazoles (**41**) occurs in the 5-position as in the O and S analogues as a consequence of convergence of the directing effects of the aza group and the chalcogen atom[204]. The reactivity of the 5-position has been compared[204] to that of the *para* and *meta* positions of the benzene ring in the nitration of 2-benzamido-4-phenylselenazole (**42**), which is first nitrated in the 5-position and then a second NO_2 group enters in the *meta* position of the phenyl ring of the benzoyl group under more drastic conditions. A third NO_2 group is directed to the *para* position of the Ph ring bonded at C(4). The high reactivity of the 5-position in selenazoles has also been observed in bromination and azo-coupling reactions[204].



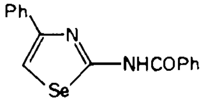
(**38**) $R^1 = R^2 = H$

(**39**) $R^1 = R^2 = Me$

(**40**) $R^1 = C_6H_5$, $R^2 = Me$

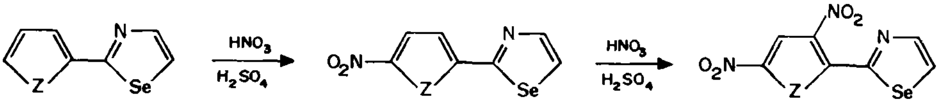


(**41**)

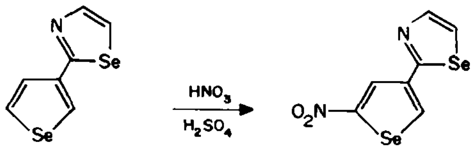


(**42**)

The reaction products **44**, **45** and **47** of nitration of 2-selenienyl-2-selenazole (**43**; Z = Se), 2-thienyl-2-selenazole (**43**; Z = S) and 3-selenienyl-2-selenazole (**46**) indicate

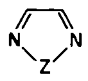


(**43**) (**44**) (**45**)

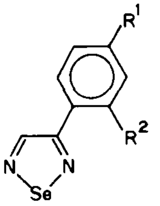


(**46**) (**47**)

that the reactivity of 2-selenazole is even less than that of thiophene[180]. When two N atoms are present, as in 1,2,5-selenadiazole (**48**; Z = Se), the compound is unreactive to hot fuming nitric acid and the 1,2,5-selenadiazolyl group is *ortho–para* directing[182]. Bromination with Br_2 and nitration using 99% HNO_3 of **49** gives **50** and **51**, respectively.

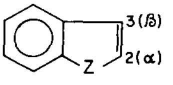


(49)



(49) $R^1 = R^2 = H$
(50) $R^1 = Br$, $R^2 = H$
(51) $R^1 = NO_2$, $R^2 = H$
(52) $R^1 = R^2 = NO_2$

By using a 1:2 v/v mixture of concentrated HNO_3 (99%) and H_2SO_4 (94%), **52** is obtained[182]. Competitive nitration (99% HNO_3) and bromination reactions show that **49** is less reactive than S and O analogues [k(S/Se) = 3.5 and k(O/Se) = 1.5 for nitration and k(S/Se) = 7 for bromination]. The higher reactivity of 3-phenyl-1,2,5-thiadiazole has been related to the higher delocalization of π electrons[182]. 1,2,5-Telluradiazole (**48**; Z = Te) has recently been synthesized[206], but easy decomposition by aqueous acid obstructs the study of its electrophilic substitution.



(53)

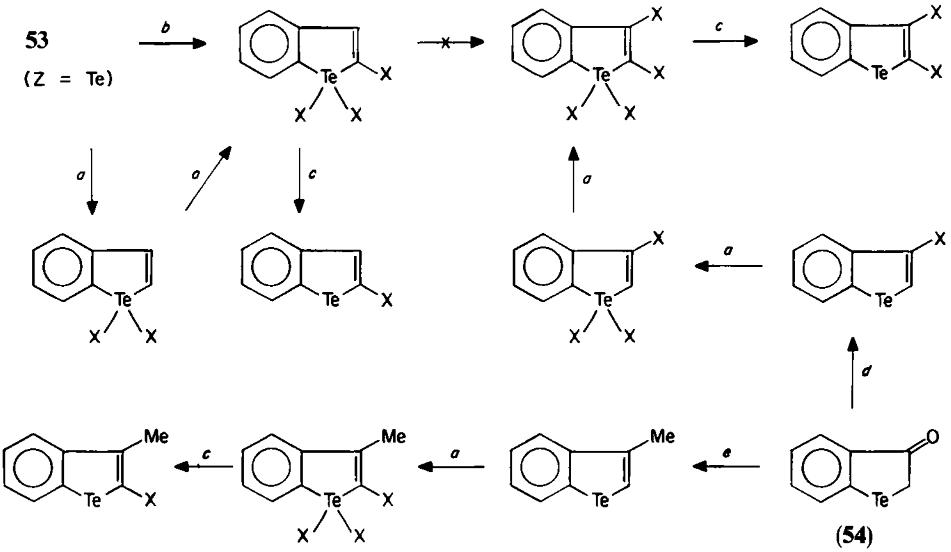
Benzo[*b*]selenophene (**53**; Z = Se) and benzo[*b*]tellurophene (**53**; Z = Te) are less reactive than the parent compounds and undergo preferential electrophilic substitution on the heterocyclic ring[183–186]. The α:β ratio depends on the nature of the electrophile and the experimental conditions. The isomer distributions in the acetylation and trifluoroacetylation reactions of **53**(Z = Te, Se, S, O) are reported in Table 17. Nitration of benzo[*b*]selenophene with concentrated HNO_3 in AcOH at 20 °C gives a mixture of α- and β-mononitro adducts with a ratio of 1:7. At 70 °C only 2,3-dinitrobenzo[*b*]selenophene is obtained[205]. The monobromination of benzo[*b*]selenophene occurs[185] preferentially in the β-position with a α:β ratio of 25:75. The reaction goes through a tribromide intermediate and an isotopic effect is observed[185]. Further bromination gives 2,3-dibromobenzo[*b*]selenophene. A third Br atom is directed in the benzene ring at C(6). The bromination[185,186] of benzo[*b*]tellurophene (Scheme 1) gives a 1,1-adduct which is then brominated exclusively in the α-position. Bromination in the β-

TABLE 17. Isomer distributions in the acetylation and trifluoroacetylation of benzo[*b*]-fused five-membered chalcogen heterocycles.

Compound	Electrophilic reagent			
	$MeCOCl/AlCl_3$[a]		Ac_2O/CF_3COOH[b]	
	α	β	α	β
Benzo[*b*]tellurophene	100	0	76	24
Benzo[*b*]selenophene	90	10	65	35
Benzo[*b*]thiophene		Predominant	35	65
Benzo[*b*]furan	Predominant		73	27

[a] Refs 96 and 185.
[b] Ref. 186.

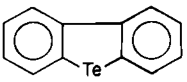
position occurs neither in halogenation of **53** (Z = Te) nor of its 2-bromo derivative. 3-Halobenzo[*b*]tellurophenes are obtained[186] by the reaction of telluroindoxyl (**54**) with CCl_4 or CBr_4 in the presence of triphenylphosphine (Scheme 1), and by refluxing phenylacetylene with TeO_2 in acetic acid in the presence of lithium halide[187].



a: X_2(X = Cl, Br); *b*: X_2 in excess or SO_2Cl_2; *c*: N_2H_4; *d*: CX_4/Ph_3P; *e*: $Ph_3PCHCO_2Et/KOH/\Delta$

SCHEME 1

When a substituent is present in the α- or β-position of benzo[*b*]selenophene (**53**; Z = Se) the electrophile is directed to the adjacent free position independently of the electronic nature of the substituent[183,188]. If both the α- and β-positions are substituted, electrophilic substitution occurs[185,189] in the benzene ring prevalently at C(6). It is useful to observe that the nitration of dibenzotellurophene (**55**) occurs mainly in the *para* position with respect to the heteroatom[207].

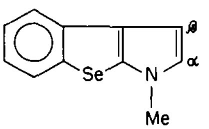


(55)

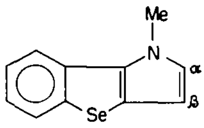
The isosters of phenanthrene **56**–**58** are more reactive than the parent benzo[*b*] compounds and electrophilic substitution occurs in the α-position[190]. The

(**56**) $Z^1 = S$, $Z^2 = Se$
(**57**) $Z^1 = Se$, $Z^2 = S$
(**58**) $Z^1 = Se$, $Z^2 = Se$
$R = NO_2$, COMe, Br, CHO

benzo[*b*]seleno system affects the $\alpha:\beta$ reactivity of the fused *N*-methylpyrrole ring in **59** and **60**. The $\alpha:\beta$ ratios of the acetylation reactions of **59** and **60** are 66:34 and 42:58, respectively[191].

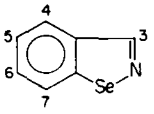


(59)



(60)

The benzo fusion further decreases the reactivity of the selenazole and selenadiazole rings and electrophilic substitutions occur on the Ph ring. The 3- and 2-positions of 1,2-benzisoselenazole (**61**) and benzoselenazole (**62**), respectively, are unreactive to electrophilic substitutions. The nitration (H_2SO_4–KNO_3) of **61** occurs at C(5) or C(7) and two mononitro derivatives are obtained[208]. The same orientation is observed in the bromination reaction (Br_2–H_2SO_4–Ag_2SO_4) but the 4,5- and 4,7-dibromides and the 4,5,7-tribromide are also isolated[208]. By nitration of **62** under mild conditions substitution at C(6) occurs[209,210] while under more drastic conditions a 4,6-dinitro derivative is obtained. In the detritiation reaction[192,204] the reactivity order of **62** and its O and S analogues decreases in the order O > S > Se. In the sulphonation[211,212] and halogenation[212–214] of 2,1,3-benzoselenadiazole (**63**) the electrophile is first directed to C(4) and 4,5- or 4,7-disubstituted products are obtained under more drastic conditions.



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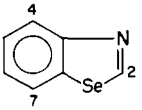
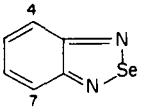
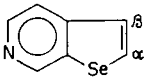


(62)

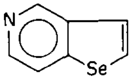


(63)

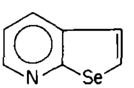
Pyridine fusion also decreases the reactivity of the selenophene ring towards the electrophiles and the directing effect is opposite to that of benzo fusion and does not depend on the relative position of the N and Se atoms. Nitration and bromination of selenopheno[2,3-*c*]-, [3,2-*c*]-, [2,3-*b*]- and [3,2-*b*]-pyridines **64**–**67** give β-nitro and β-bromo derivatives[193,194]*. The $\alpha:\beta$ ratio of deuteriodeprotonation[195] of **67** is ca. 10^{-3} as in the S analogue and higher than that for furo [3,2-*b*]pyridine ($\alpha:\beta = 10^{-5}$).



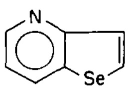
(64) [2,3-*c*]



(65) [3,2-*c*]



(66) [2,3-*b*]



(67) [3,2-*b*]

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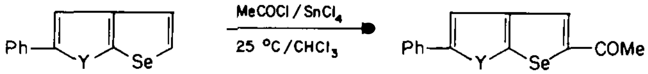
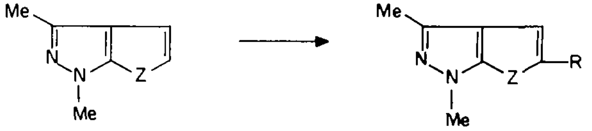
*Most of the literature uses the prefix 'selenopheno'. *IUPAC Rules of Nomenclature* and *Chemical Abstracts* prefer the prefix 'selenolo'.

The fusion with α-phenyl-*N*-methylpyrrole increases[196] the electrophilic reactivity of the selenophene ring and substitution occurs in the α-position. The rate constants of acetylation of selenopheno[2,3-*b*] compounds **68**–**70** relative to selenophene are 8.1, 4.3 and 0.89, respectively. Compounds **68**–**70** are more reactive than analogous thieno compounds and the heterocyclic fusion increases the reactivity of thiophene more than that of selenophene.



(**68**) Y = NMe
(**69**) Y = O
(**70**) Y = S

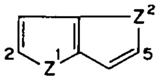
The reactivity of selenophene decreases when fused with the pyrazole ring but the directing effect does not change[197]. Vilsmeier formylation and bromination of selenopheno[3,2-*b*]pyrazole (**71**) gives only α-substituted derivatives and the reactivity of **71** is higher than that of **72**.



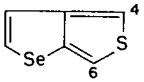
(**71**) Z = Se
(**72**) Z = S

R = COMe, Br

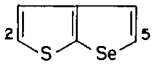
A recent quantitative study on the electrophilic substitution reactions of selenopheno[3,2-*b*]thiophene (**74**), selenopheno[3,2-*b*]selenophene (**75**), selenopheno[2,3-*c*]thiophene (**76**) and selenopheno[2,3-*b*]thiophene (**77**) has been re-



(**73**) Z¹ = Z² = S
(**74**) Z¹ = S, Z² = Se
(**75**) Z¹ = Z² = Se



(**76**)



(**77**)

TABLE 18. Isomer distributions (%) in electrophilic substitutions of selenophenothiophenes 74, 76 and 77[a]

	Compound					
	74		76[c]		77	
Reaction	C(2)	C(5)	C(4)	C(6)	C(2)	C(5)
Formylation	27	73	60	40	45	55
Acetylation	44	56				
Chlorination	0	100				
Bromination[b]	0	100			13	87

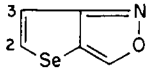
[a] Ref. 198 and references cited therein.

[b] 20% of the 2,5-dibromo derivative is present.

[c] Ref. 199.

ported by Gronowitz and coworkers[198–200]. The isomer distributions for **74**, **76** and **77** are reported in Table 18. Compounds **74** and **77** give predominant substitution in the selenophene ring while in **76** the formylation occurs exclusively on the thiophene ring. The high selectivity of the halogenation is probably ascribable to a primary attack of the halogen at the Se ring atom. The reactivity of **74** and **75** relative to **73** and to thiophene and selenophene has been studied in three electrophilic substitution reactions, namely acetylation, formylation and chlorination, by means of competitive experiments. The overall reactivity (Table 19) follows the order **75** > **74** > **73** > thiophene and the ratios increase in the series acetylation < chlorination < formylation. Positions 2 and 5 (Table 20) of **74** are more reactive than the α-positions of **73** and the parent five-membered compounds. Quantum-mechanical calculations substantially agree with the experimental data[198–200].

Isoxazole fusion increases the reactivity of the β-position of the selenophene ring[201]. Nitration with KNO_3–H_2SO_4 (conc.) and H–D exchange of **78** occur preferentially at C(3) as in the thieno analogues.



(78)

Hori and coworkers[202], in the course of their studies on the chemistry of selenoxanthylium salts, reported the nitration of 9-phenylselenoxanthylium perchlorate (**79**; Z = Se).

TABLE 19. Relative reactivities of **74** and **75** in electrophilic substitutions[a]

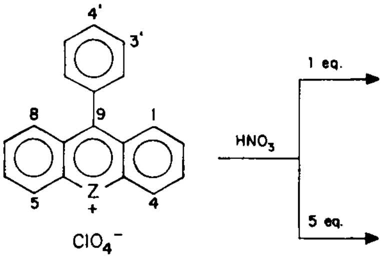
Relative reactivity	Acetylation[b]	Formylation[c]	Chlorination[d]
k(SSe)/*k*(SS)	1.69	4.59	4.19
k(SeSe)/*k*(SS)	2.81	14.3	10.5
k(SeSe)/*k*(SSe)	1.66	3.12	2.50
k(SSe)/*k*(S)	5.02	204	139
k(SeSe)/*k*(S)	8.35	635	347
k(SSe)/*k*(Se)	2.20	39.4	
k(SeSe)/*k*(Se)	3.66	123	

[a] Ref. 198; S = thiophene, Se = selenophene; SS = **73**, SSe = **74**, SeSe = **75**.
[b] $SnCl_4/Ac_2O$ in dichloroethane at 20 °C.
[c] $DMF/POCl_3$ at 20 °C.
[d] *N*-Chlorosuccinimide in acetic acid at 20 °C.

TABLE 20. Partial reactivities of the 2- and 5-positions of **74** in electrophilic substitutions[a]

Partial reactivity	Acetylation[b]	Formylation[c]
k(SSe-2)/*k*(SS-2)	1.46	2.41
k(SSe-5)/*k*(SS-2)	1.89	6.70
k(SSe-5)/*k*(SSe-2)	1.29	2.78
k(SSe-2)/*k*(S-2)	4.34	107
k(SSe-5)/*k*(Se-2)	2.46	57.5

[a–c] See Table 19.



(79)

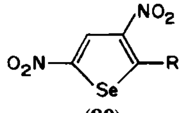
	Z		
	Se	S	O
4'	40	55.5	18.2
3'	60	44.5	81.8
4',4	44.5	54.5	-
3',4	55.5	45.5	-

SCHEME 2

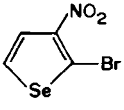
With HNO_3–H_2SO_4 (1 eq. HNO_3) the electrophile is directed exclusively on the phenyl ring giving a mixture of 4'- and 3'-derivatives in the ratio 1:1.5 (Scheme 2). By using 5 eq. HNO_3, 4',4- and 3',4-dinitro compounds are obtained in the ratio 1:1.25. The S analogue (**79**; Z = S) gives similar results but the O analogue (**79**; Z = O) behaves differently. The reactivity decreases in the order $—S^+= > —Se^+= > —O^+=$. The reaction indices calculated from SCF-MO computation agree with experimental data[203].

B. Nucleophilic Aromatic Substitutions

Quantitative data on nucleophilic substitutions in selenophenes were first reported by Italian workers[216,217]. The kinetic constants of the reactions of compounds **80**



(80)



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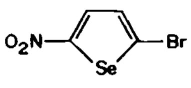
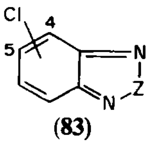


(82)

R = Cl, Br, I, SO_2Ph, $OC_6H_4NO_2$

with piperidine follow the order expected on the basis of the leaving-group type. The relative reactivities of **81** and **82** depend on the nucleophile and solvent. With piperidine **81** is more reactive than **82** [*k*(**81**)/*k*(**82**) = 7.5 in dioxane–water and 620 in benzene], but with sodium thiophenoxide in methanol a reverse reactivity is observed [*k*(**81**)/*k*(**82**) = 0.89]. Comparison with S analogues shows that selenophenes are about 1.2–10 times more reactive both with piperidine and sodium thiophenoxide[146,218]. The greater reactivity of selenophene compared to thiophene, both in nucleophilic and electrophilic reactions, may be explained by the lower aromatic character and greater ability of the selenophene ring to delocalize both negative and positive charges of intermediate[165,176,216] carbon ions.

The second-order rate constants for the reaction at 130 °C between 4- and 5-chloro-2,1,3-benzoselenadiazoles (**83**; Z = Se) and MeONa have been determined and com-



(83)

pared[219] with those of S and O analogues. Compound **83** (5-Cl, Z = Se) is more reactive than **83** (4-Cl, Z = Se) and both are more reactive than chlorobenzene. The activation effect depends on the chalcogen atom and decreases in the order Se(13.7) > S(5.2) > O(3.46). The relative reactivities [$k(\text{Z})/k(\text{S})$; Z = O,S,Se] of 4- and 5-chloro derivatives decrease in the order O > Se ≥ S and O > Se > S, respectively.

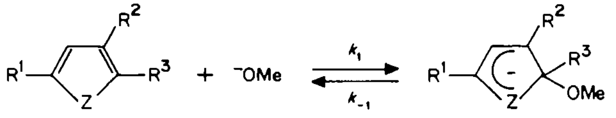
The reactivities of the 2-position of benzoselenazole (**62**) and the 3-position of 1,2-benzisoselenazole (**61**) towards nucleophilic attacks are very different. While **62** does not give Cicibabin amination[209,215] with $NaNH_2$, **61** reacts[208] with KNH_2 in liquid NH_3 to give the corresponding 3-amino derivative in fair yield. A Me group at C(2) in **62** is on the other hand activated and reacts with aromatic aldehydes to give styrene derivatives[209,215].

Nucleophilic substitution data on heteroaromatic compounds having Te atoms are not abundant. An example[187] is the reaction of 2-aryl-3-chlorobenzo[*b*]tellurophenes with EtONa in refluxing EtOH to give the corresponding ethoxy derivatives.

C. Meisenheimer Complexes

Selenophenes, 2-methoxyselenophenes, thiophenes and 2-methoxythiophenes 3,5-disubstituted with NO_2 and CN groups (**84**) give stable Meisenheimer complexes[220–224] (equation 14). The equilibrium and rate constants for the formation and decomposition of complexes **85**–**92** are reported in Table 21.

The complexes **85**, **87** and **89** are thermodynamically more stable than the analogous



$$k_1 / k_{-1} = K_1 \qquad (14)$$

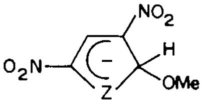
(**84**) Z = Se, S

(**a**) $R^1 = R^2 = NO_2$, $R^3 = H$

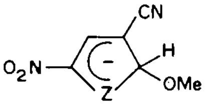
(**b**) $R^1 = NO_2$, $R^2 = CN$, $R^3 = H$

(**c**) $R^1 = CN$, $R^2 = NO_2$, $R^3 = H$

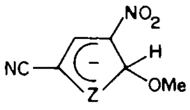
(**d**) $R^1 = R^2 = NO_2$, $R^3 = OMe$



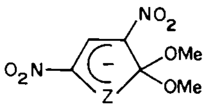
(**85**) Z = Se
(**86**) Z = S



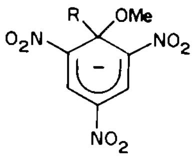
(**87**) Z = Se
(**88**) Z = S



(**89**) Z = Se
(**90**) Z = S



(**91**) Z = Se
(**92**) Z = S



(**93**) R = H
(**94**) R = MeO

TABLE 21. Ratios of equilibrium constants and rates for the formation and decomposition of selenophene and thiophene Meisenheimer complexes with methoxide ion in methanolic solution at 25 °C (equation 14)

Compounds[a] A	B	Equilibrium $K_1(A)/K_1(B)$	Decomposition $k_{-1}(A)/k_{-1}(B)$	Formation $k_1(A)/k_1(B)$
85	**86**	68	2.8×10^{-2}	1.8
87	**88**	113	1.9×10^{-2}	2.1
89	**90**	72	1.5×10^{-2}	1.1
86	**88**	6.7	3.5	20
86	**90**	125	5×10^{-2}	6.2
85	**87**	4	5	20
85	**89**	118	9×10^{-2}	10
91	**92**	20	13.3×10^{-2}	2.5
91	**85**	100	3.6×10^{-b}	3.7
92	**86**	400	0.6×10^{-2b}	2.7

[a] Data from Ref. 224 and 225; A and B indicate the complexes listed on p. 590; k_{-1} in s^{-1}, k_1 in $M^{-1}s^{-1}$, K_1 in M^{-1}.
[b] At 20 °C.

adducts of thiophene, **86**, **88** and **90**, and can be isolated as stable potassium salts. The presence of two methoxy groups has a stabilizing influence[222,225] and therefore **91** and **92** are more stable than **85** and **86** respectively. The complexes **85** and **91** are about 2500- and 300-times more stable than the benzene adducts **93** and **94**, respectively, and the reason has been discussed in terms of geometrical differences[222]. The stability also depends on the electron-withdrawing power of substituents and on their position in the five-membered ring[225].

The rates of formation of selenophene complexes are only a little higher[225] than those of the corresponding thiophene adducts, confirming the higher reactivity of selenophenes towards nucleophilic reagents[145,216,217]. The presence of a NO_2 group in the *β-ortho*-like position influences the rate of methoxide ion attack more than when the NO_2 group is in the *α-para*-like position[225]. This is in agreement with Spinelli's suggestion that the structure of the transition state coming from an attack at C(2) is affected more by a change in the *ortho*-like position than in the *para*-like position to the reaction centre[226,227].

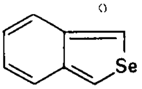
The rates of decomposition of **85**, **87** and **89** are lower than those of **86**, **88** and **90**, respectively[225]. Surprisingly[225] the decomposition rates of **87** and **88** are lower than those of the corresponding **85** and **86**.

D. Addition Reactions

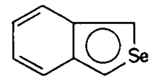
The Diels–Alder reaction has sometimes been used to estimate the aromaticity of heterocyclic compounds on the assumption that the less the ring is aromatic, the easier is the formation of the Diels–Alder adduct[167].

Selenophene, thiophene and furan give 1 : 1 adducts with maleic anhydride but the first two compounds require more drastic reaction conditions than the third in agreement with their greater aromatic character[167]. Quantitative data on the rate of cycloaddition of tetracyanoethylene oxide to selenophene, thiophene and furan have been reported by Gronowitz and Uppstrom[228]. The order of reactivity (furan > selenophene > thiophene) is the opposite of the order of ground-state aromaticity[176] and is the same as that observed in the electrophilic substitution reactions[165,228].

Benzo[*c*]selenophene (**95**,**96**) gives Diels–Alder adducts more easily than selenophene. With tetracyanoethylene the reaction occurs in the heterocyclic ring and is very fast[229] in



(95)

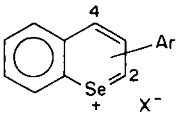


(96)

agreement with the poor aromatic character[230] of the compound. ^{1}H-NMR data and theoretical analysis[230] indicate that the structure **96**, in which 6 π electrons are delocalized on the heterocyclic ring, is more representative than the *ortho* quinoidal one (**95**).

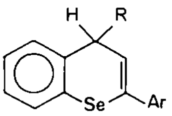
The rates of quaternarization of benzoselenazole (**62**) and 2,1,3-benzoselenadiazole (**63**) have been determined[231,232] by means of a competitive method using Me_2SO_4 in sulpholane and have been compared with those of S and O analogues. Benzo fusion decreases the reactivity of parent five-membered compounds and the order of activation by the chalcogen atom in **62** and **63** is Se = S > O and Se > S > O, respectively.

The 2- and 4-aryl-substituted selenochromylium salts **97** and **98** direct the nucleophile R^- (H^-, Ph^-, PhS^-, Ac_2CH^-, etc.) into *para* and *ortho* positions of the heterocyclic ring like their O and S analogues and give **99** and **100** respectively[233]. The orientation does not depend either on the electronic nature of the aryl substituent or the type of nucleophile[233].

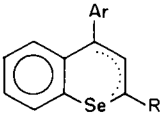


(**97**) X = ClO_4 , BF_4 ; 2-Ar

(**98**) X = ClO_4 , BF_4 ; 4-Ar

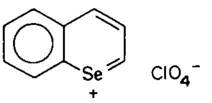


(**99**)

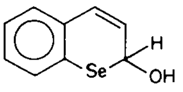


(**100**)

The unsubstituted selenochromylium cation[101] behaves in a more complex manner. The preferential site of addition seems to be the 2-position, but addition at C(4) and substitution also occur[234].



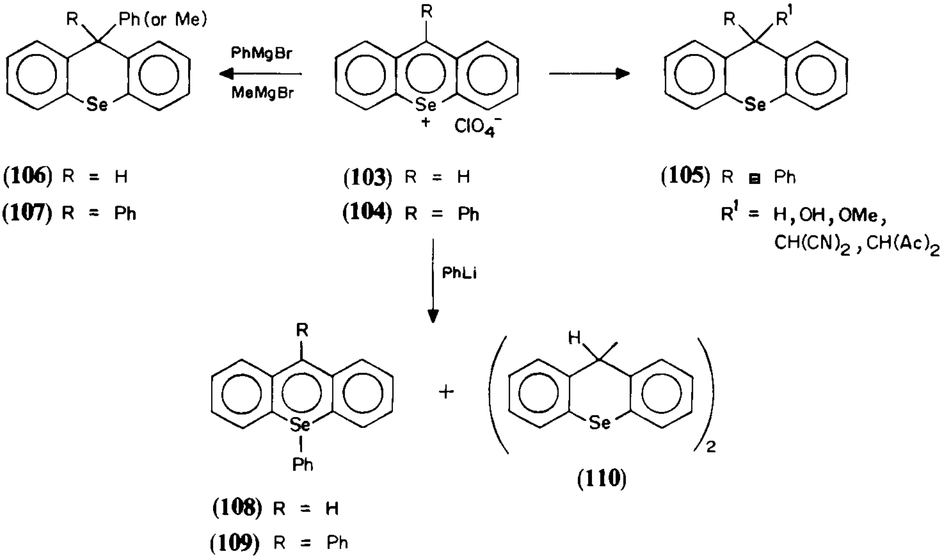
(**101**)



(**102**)

When the nucleophile is OH^- the first reaction product of **101** is the α-pseudobase **102** which is converted in the opened desmotropic form in the medium of the reaction[238].

Selenoxanthylium salts **103** and **104** react with several nucleophiles[203,235,236]. 9-Phenylselenoxanthylium perchlorate (**104**) reacts with various nucleophiles [NaOH, $LiAlH_4$, MeOH, $CH_2(CN)_2$, CH_2Ac_2] to give the addition products **105**. Compounds **103** and **104** react in the same way with Grignard reagents to give 9-Me and 9-Ph derivatives **106** and **107**, but with PhLi the reaction takes place exclusively or predominantly at the Se atom. The compound **104** gives only[236] **109**, and the compound **103** gives a mixture of **108** (87%) and **110** (13%). The reaction of **104** with organometallic reagents (PhLi, PhMgBr,



(106) R = H
(107) R = Ph

(103) R = H
(104) R = Ph

(105) R = Ph
R^1 = H, OH, OMe, CH(CN)$_2$, CH(Ac)$_2$

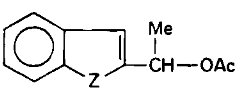
(108) R = H
(109) R = Ph

(110)

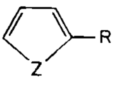
MeMgBr) has been investigated by ESR spectroscopy and a radical mechanism has been proposed[203,235,236]. Stackhouse and coworkers[237] report that **108** and **109** are not selenoanthracenes but oligomers of undetermined composition.

E. Side-chain Reactions

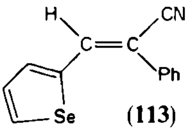
It is usual to consider complete parallelism between aromatic electrophilic substitutions and side-chain reactions in which the formation of a carbocation is the rate-determining step[96,239]. The first-order rate constants for the solvolysis of 1-(2-tellurienyl)- and 1-(2-selenienyl)-ethylacetates (7; Z = Se, Te) and their S and O analogues 7 (Z = S, O) in 30% ethanol (Table 22) show[117] a reactivity order (Te > O > Se > S) which is different from that (Table 15) found[117] in electrophilic substitutions (O > Te > Se > S).



(111)



(112)



(113)

A different order of sensitivity to the substituent effect is also observed[117] (see Section III.B.D). Tellurophene behaves in a different way in the two types of reaction and the reason has been discussed in terms of solvation effects, charge distribution in the transition state and the position of the transition state along the reaction coordinate in the two types of reactions[117].

Solvolysis of **112** (Z = Se, R = CH_2Cl) and of 3-chloromethyl-2,5-dimethylselenophene proceeds by a S_N1 mechanism and comparison[118] with S and O analogues gives the same reactivity order found in the solvolysis of acetates 7.

Benzo fusion decreases the reactivity of the esters 7 and the reactivity order of compounds **111** (Table 22) is similar to that observed for the monocyclic compounds. The

TABLE 22. Rate constants and relative rates for the solvolysis of 1-(2-heteroaryl)ethyl acetates **7** and **111** in 30% ethanol at 60 °C[a]

Heteroaryl group	$k \times 10^5(s^{-1})$	$k(Z)/k(S)$[b]	$[k(B)/k(M)] \times 10^3$[c]
2-Tellurienyl	341	5.2	
2-Selenienyl	109	1.7	
2-Thienyl	65	1	
2-Furyl	205	3.1	
2-Benzo[*b*]tellurienyl	3.26	5.2	8.9
2-Benzo[*b*]selenienyl	1.04	1.7	9.5
2-Benzo[*b*]thienyl	0.63	1	9.7
2-Benzo[*b*]furyl	0.95	1.5	4.8

[a] Data from Ref. 117.

[b] Ratios relative to thienyl(S) for five-membered compounds and to benzo[*b*]thienyl for benzo-fused ones; Z = Te,Se,S,O.

[c] Reactivity ratios between bicyclic (B) and monocyclic (M) systems.

annelation effect $k(B)/k(M)$ is larger for **7** (Z = O) whereas it is the same for the other systems[117].

Arcoria and coworkers[90] reported kinetic data for the nucleophilic side-chain reactions of 2-selenophene derivatives **112**. The reactions and the reactivity sequences are reported in Table 23. The reactivities of corresponding Ph derivatives do not occupy the same position in the six sequences. The variability of the reactivity order has been interpreted in terms of different mechanisms of the reactions.

Maccarone and coworkers[240] found that the base-catalysed isomerization of *cis*-1-(2-selenienyl)-2-phenylacrylonitrile (**113**) is faster than that of the acid-catalysed one and the reactivity order is: 2-thienyl > 2-selenienyl > 2-furyl. In the acid-catalysed isomerization the reverse order is found: 2-furyl > 2-selenienyl > 2-thienyl. A mechanism is suggested and the results are discussed in terms of inductive, mesomeric and steric effects of the heterocyclic ring.

TABLE 23. Reactivity of 2-selenienyl, 2-thienyl and 2-furyl derivatives in nucleophilic side-chain reactions[a]

Reaction	Compound **112**	Reactivity order[b]
Acid-catalysed hydrolysis	R = COOEt; Z = Se, S, O	O > Se > S
Base-catalysed hydrolysis	R = COOEt; Z = Se, S, O	O > S > Se
Substitution with aniline	$R = SO_2Cl$; Z = Se, S, O	Se > O > S
Substitution with aniline	$R = CH_2Cl$: Z = Se, S, O	O > S > Se
Condensation with aniline	R = CHO; Z = Se, S	S > Se
Condensation with BMTF[c]	R = CHO: Z = Se, S, O	O > S > Se

[a] Data from Ref. 90.

[b] Se = selenienyl, S = thienyl, O = furyl.

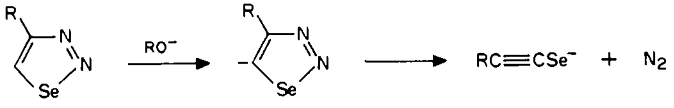
[c] BMTF = benzoylmethylenetriphenylphosphorane.

F. Protophilic Reactions

Hydrogen exchange reactions in strong alkaline media (*t*-BuOK in DMSO, KNH_2 in liquid NH_3, alkoxides in alcoholic solutions) are called 'protophilic reactions' and proceed via a carbanion intermediate[241,242].

Selenophene in the presence of *t*-BuOLi in Me_2SO at 25 °C exchange[167] a D atom in the α-position faster than thiophene (1.5 times) and furan (700 times) and the estimated α:β ratio is 2.5 × 10^5. Me groups at C(3) or C(5) reduce the rate of the reaction[167].

The 1,2,5-selenadiazole (**48**) in opposition to 1,2,5-thiadiazole does not give H–D exchange in strong basic conditions[243]. On the contrary 4-aryl-substituted 1,2,3-selenadiazoles (**114**), give easily H exchange at C(5), but the intermediate anion quickly decomposes to give an arylethynylselenolate ion[162].

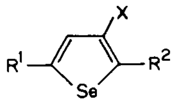


(114)

G. Metalation Reactions

Organolithium compounds give two main reactions with heterocyclic compounds of Se and Te: hydrogen– (or halogen–) metal exchange and nucleophilic attack at the heteroatom. The organolithium reagent, type of heteroatom, electronic nature of the substituent, experimental procedure and solvent influence either of the two reactions[244]. Organolithium intermediates from hydrogen– and halogen–metal exchange are used as nucleophiles[3] or converted to electrophilic reagents[245,246] to prepare substituted heterocyclic compounds[245,246]. Sometimes an eliminative ring-fission or a substitutional ring-opening occurs giving organolithium intermediates of synthetic utility[3,244].

Tellurophene[174], selenophene[167,244], 2-iodoselenophene[169], 2-bromoselenophene[247], benzo[*b*]tellurophene[185] and benzo[*b*]selenophene[185] are readily metalated in the α-position with BuLi or PhLi at 25–35 °C. The preferred α-orientation has been related[258] to ^{13}C–H one-bond coupling constants. The most reactive position is that with the greater $J(^{13}\text{C–H})$. 3-Bromoselenophene[247] is metalated by PhLi in the 2-position at 36 °C whereas BuLi at −50 °C gives Br–Li exchange. On the contrary 2,5-disubstituted 3-bromo or 3-iodo-selenophenes (**115**) undergo a partial or total ring-opening reaction[248,250]. 2,5-Dichloroselenophene gives a stable 3-lithium derivative with diisopropylaminolithium[250]. Contrary to 2,5-dimethoxythiophene (**116**; Z = S, R = OMe), 2,5-dimethoxyselenophene (**116**; Z = Se, R = OMe) is not metalated in the 3-position by BuLi and PhLi, but a substitutional ring-opening occurs[256] giving dienes. The 2,5-diphenylselenophene (**116**; Z = Se, R = Ph) and 2,5-diphenyltellurophene (**116**; Z = Te, R = Ph) behave differently[255,256] when metalated with the complex BuLi-tetramethylethylenediamine (TMEDA). Both of these give ring-cleavage, but the first gives 5,8-diphenyl-5,7-dodecadiene (**117**) probably via β-lithiation of **116** (Z = Se, R = Ph) followed by eliminative ring-fission and addition of BuLi to 1,4-diphenylbutadiyne and



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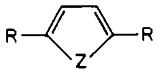
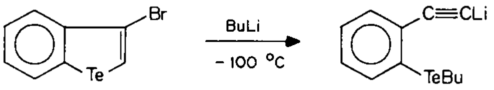


(116)

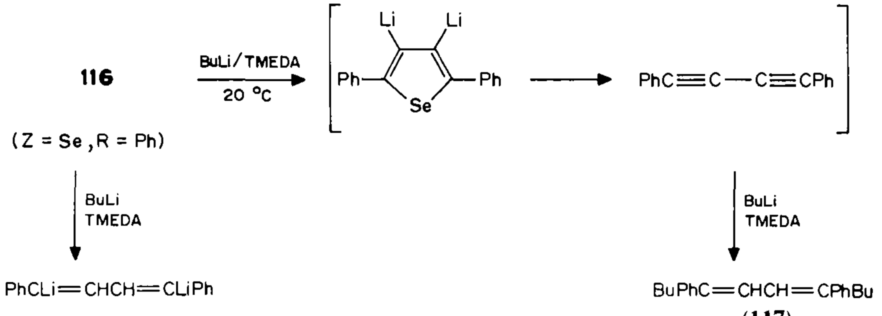
BuPhC=CHCH=CPhBu

(117)

R¹ = R² = Cl
R¹ = Me, R² = SMe
R¹ = SMe, R² = Me
X = Br, I

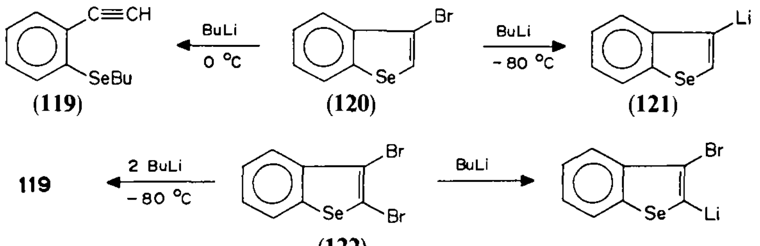


(118)



(117)

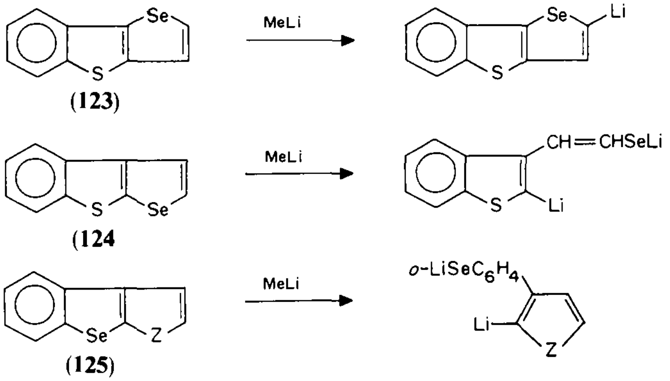
the second gives 1,4-diphenyl-1,4-dilithiumbutadiene which is trapped by various electrophiles. 3-Bromobenzo[*b*]tellurophene (**118**) undergoes[147] a ring-opening reaction even at − 100 °C, whereas the Se analogue **120** gives[185] the expected 3-lithium derivative **121** at low temperature. The behaviour of 2,3-dibromobenzo[*b*]selenophene (**122**) when is treated with two equivalents of BuLi is interesting[185]. At room temperature halogen–metal exchange at C(2) occurs, but at − 80 °C both Br atoms are exchanged and the intermediate 2,3-dilithiumbenzo[*b*]selenophene undergoes a ring-opening reaction giving **119**.



(119) (120) (121)

(122)

The metalation of **123**, **124** and **125** allows evaluation of both the relative sensitivity of selenophene and thiophene rings to the lithium reagent and the importance of the type of ring-fusion[185,187,248–251]. The tendency to ring-opening is greater in the selenophene than in the thiophene series.



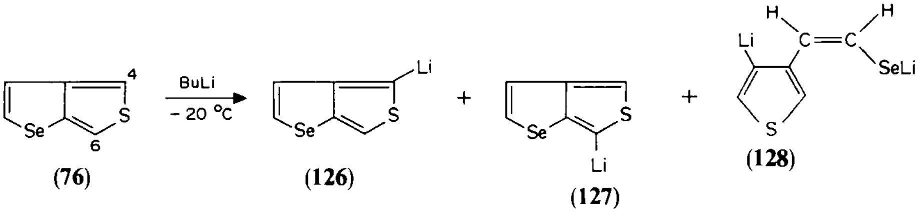
(123)

(124

(125)

Z = Se, S

Gronowitz's[199] recent report on the metalation of selenopheno[2,3-*c*]thiophene (**76**) confirms that the Se atom is more sensitive than the S to nucleophilic attack and shows that there is a parallelism between the reactivity of α- and β-protons in hydrogen–metal exchange and the attack sites in electrophilic substitution reactions. Only the H atoms at C(4) and C(6) (as in the formylation reaction[199]) were exchanged giving **126** and **127** in the ratio 18:82. The main reaction product **128** was the only one obtained by the ring-opening reaction.



(76) **(126)** **(127)** **(128)**

The behaviour of selenopheno[2,3-*b*]thiophene (**77**) is similar to **76** when treated with MeLi[251,257]. Through the reaction of 1,2-benzisoselenazole (**61**) with BuLi under different experimental conditions, both the hydrogen–metal exchange and nucleophilic attack at the heteroatom are observed[208].

Nucleophilic cleavages of 1,2,5-selenadiazoles, 1,2,5-telluradiazoles and isotellurazoles by organolithium and Grignard reagents have recently been reported[252–254].

TABLE 24. pK_a values of carboxy-, hydroxy- and amino-heterocyclic compounds having one chalcogen atom

Compound	pK_a H_2O, 25 °C	 H_2O–EtOH, 25 °C
2-Tellurophenecarboxylic acid	3.97[a]	5.48[e]
2-Selenophenecarboxylic acid	3.60[b]	5.14[e]
2-Thiophenecarboxylic acid	3.53[c]	5.05[e]
2-Furancarboxylic acid	3.16[d]	4.54[e]
2-Benzo[*b*]tellurophenecarboxylic acid		5.13[e]
2-Benzo[*b*]selenophenecarboxylic acid		4.79[e]
2-Benzo[*b*]thiophenecarboxylic acid		4.67[e]
2-Benzo[*b*]furancarboxylic acid		4.20[e]
4-Hydroxy-2,1,3-benzoselenadiazole	8.16[f]	9.06[g]
4-Hydroxy-2,1,3-benzothiadiazole	7.86[f]	8.80[g]
4-Hydroxy-2,1,3-benzoxadiazole	6.83[f]	7.58[g]
5-Hydroxy-2,1,3-benzoselenadiazole	8.06[f]	8.73[g]
5-Hydroxy-2,1,3-benzothiadiazole	8.16[f]	8.82[g]
5-Hydroxy-2,1,3-benzoxadiazole	7.28[f]	7.84[g]
4-Amino-2,1,3-benzoselenadiazole	2.18[h]	
4-Amino-2,1,3-benzothiadiazole	2.02[h]	
4-Amino-2,1,3-benzoxadiazole	0.78[h]	

[a] Ref. 91.
[b] Ref. 11, in H_2O-butylcellosolve 1:1 at 20 °C, pK_a = 5.00 (Ref. 87).
[c] Ref. 112.
[d] Ref. 259
[e] H_2O–EtOH 1:1, Ref. 260.
[f] Ref. 261.
[g] 47.5% EtOH, Ref. 261.
[h] Ref. 262.

H. Equilibrium Reactions

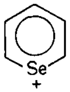
Ionization constants of carboxy-, hydroxy- and amino-heterocyclic compounds having one chalcogen atom are reported in Table 24. The main conclusion that may be drawn is that the order of acidity appears to be a function of the inductive effect of the heteroatom: $O > S > Se > Te$. The difference in pK_a values of 5-hydroxybenzothia- and benzoselenadiazole falls within the experimental error and therefore the observed reverse order is probably not significant. Monoprotonation of 4-amino-2,1,3-benzoselenadiazole and its chalcogenic analogues occurs at the amino group but 5-amino-2,1,3-benzoselenadiazole gives protonation mainly at the aza group[262]. Protonation of two N atoms of 2,1,3-benzoselenadiazole (p$K_{a1} = -1.41$; p$K_{a2} = -8.10$) and 2,1,3-naphthoselenadiazole (p$K_{a1} = -1.30$; p$K_{a2} = -7.78$) occurs in conc. H_2SO_4 and the ionization constants have been calculated using the Hammett H_0 acidity scale[163,263].

Equilibrium constants pK_{R^+} for cation–pseudobase (equation 15) for 1- (**101**) and 2-selenachromylium (**130**), selenaxanthylium (**103**) and dibenzo[*b*,*d*]selenapyrilium (**131**) cations are 1.20, 0.20, -1.67 and -4.28, respectively[264,265]. The benzo fusion decreases the stability of the cation and the benzo[*b*] cation **101** is more stable than its isomer **130**. These results coupled with those from the equilibrium reaction of H exchange (equation 16) show that the selenapyrilium cation **129** is more stable than the corresponding benzo-fused cations and that S-containing cations are more stable than O- and Se-containing cations[266].

$$R^+ + H_2O \rightleftharpoons ROH + H^+ \tag{15}$$

$$RH + R^{1+} \rightleftharpoons R^+ + R^1H \tag{16}$$

There is a close structural relationship between the conjugate acid **134** (equation 17) of selenachromone (**132**; Z = Se) and selenaxanthone (**133**; Z = Se) and the oxy derivatives of selenachromylium (**101**) and selenaxanthylium (**103**) salts.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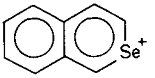
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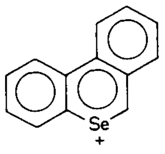
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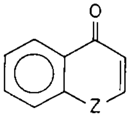
The pK_{BH^+} values of selenachromone (**132**; Z = Se) and selenaxanthone (**133**; Z = Se) have been determined (Table 25) and compared with those of O and S analogues[267]. The basicity decreases with benzo fusion in the order $S > Se > O$ and $S > O > Se$ in the chromone and xanthone series, respectively.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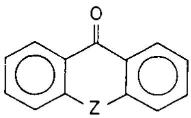
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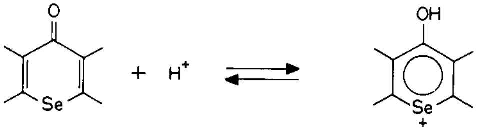
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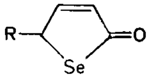
(17)

TABLE 25. pK_{BH^+} of selenachromone, selenaxanthone and their S and O analogues at 25 °C in H_2SO_4 solution[a]

Compound	pK_{BH^+}
Selenachromone	− 1.46
Thiachromone	− 1.20
Chromone	− 2.05
Selenaxanthone	− 4.36
Thiaxanthone	− 3.95
Xanthone	− 4.12

[a] By UV spectrophotometric method, Ref. 267.

2-Hydroxyselenophene and its 5-Me derivative exist in an equilibrium in which the α, β-unsaturated selenalactone (**135**; R = H, Me) is the main isomer. Alkylation using an ion-pair extraction method mainly gives C- or O-alkylation with the 'soft' MeI and 'hard' Me_2SO_4, respectively. 2,5-Dimethyl-3-hydroxyselenophene (**136**) exists in oxo–enol equilibrium and selectively gives *C*- and *O*-alkylation depending on the nucleophilic reagent[268–271]



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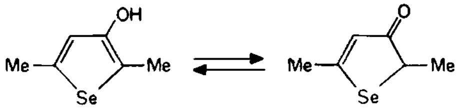


(136)

V. SYSTEMS WITH EXOCYCLIC FUNCTIONAL GROUPS

In recent years the chemistry of functional groups containing Te and, more so Se has been developed[6,272] and new reagents and new reactions have been introduced in the organic synthesis. The present discussion is mainly confined to directing effects of typical functional groups and how they affect the remaining part of the molecule.

A. Selenium Acids and Selenols

Selenenic acids (RSeOH) are supposed intermediates in a number of reactions and except for the antraquinone-1,4-diselenenic acid, no selenenic acid is stable in the pure form[273], but they easily disproportionate to diselenides and seleninic acids. Selenonic acids ($RSeO_3H$) are strong oxidizing substances, unstable in heat and light[274]. A limited number of selenonic acids, with proven structures, are known[274]. Quantitative data on the oxidizing power of aromatic selenonic and seleninic acids have recently been reported[275].

Seleninic acids ($RSeO_2H$) represent the most stable class of oxyselenium acids and are more stable than the corresponding sulphinic acids[159]. Alkyl- and aryl-seleninic acids (Table 26) are weaker than the corresponding carboxylic and sulphinic acids. The acidity decreases in the order S > C > Se. Theoretical calculations[159] indicate that conjugation between the Ph ring and the sulphinic group is prevented. The greater acidity of benzenesulphinic acid ($pK_a = 2.76$)[159] has been explained by invoking the solvent effects in the dissociation reaction. To explain the weaker acidity of benzeneseleninic acid a π(d–p) conjugation has been invoked[159]. This is supported by the fact that *p*-methoxybenzenesulphinic acid is stronger than the unsubstituted one ($\Delta pK_a = 0.04$) but

TABLE 26. Dissociation constants of seleninic acids in water at 25 °C

Compound	pK_a	pK_{a1}	pK_{a2}	Ref.
$\mathrm{MeSeO_2H}$	5.19			279
$\mathrm{EtSeO_2H}$	5.27			279
$\mathrm{PrSeO_2H}$	5.25			279
$\mathrm{BuSeO_2H}$	5.29			279
$\mathrm{PhSeO_2H}$[a]	4.70–4.90			157, 159
$\mathrm{HO_2CCH_2SeO_2H}$		2.60	5.43	280
$\mathrm{HO_2CCH(Me)SeO_2H}$		2.47	5.48	280
$\mathrm{HO_2CCH(Et)SeO_2H}$		2.53	5.48	280
$\mathrm{HO_2CCH(Pr)SeO_2H}$		2.56	5.48	280
$\mathrm{HO_2C(CH_2)_2SeO_2H}$		3.47	5.99	280

[a] For dissociation constants of substituted benzeneseleninic acids see Refs 157 and 159 and Section III.F.

the *p*-methoxybenzeneseleninic acid is weaker than the corresponding unsubstituted (Δp$K_a = -0.26$) acid.

To evaluate the substituent effect of a negatively charged Se atom on the acidity of the carboxyl group the microscopic dissociation constants for the SeH and COOH groups of selenoglycolic acid were determined[276] (Scheme 3) by spectrophotometry at 25 °C. The effect of a negatively charged Se atom in $\mathrm{^-SeCH_2COOH}$ is 0.8 pK_a units larger than that produced by a charged N or O atom. A similar effect (0.6 pK units) is observed for a charged S atom. This effect is explained by decrease of the effective dielectric constant as a consequence of the increase of the atomic radius in the series O, S, Se.

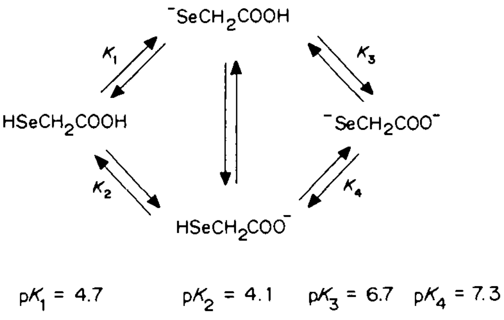
The selenols have a relatively high acidity and Table 27 shows that the increased acidity of selenols over thiols is almost constant 3–3.2 pK units); the pK_a of PhSeH is probably not corrected[277]. A consequence is that selenols are able to protonate the amines in organic solvents, whereas thiols do not[277]. The same difference of pK_a is observed[278] between HSH (pK_a = 7.0) and HSeH (pK_a = 3.74). The pK_a value of HTeH[278] is 3.64 and therefore the tellurols are probably stronger acids than the selenols. The order of acidity of the —ZH groups (Z = O, S, Se, Te) is therefore reversed with respect to the acidity order of the —$\mathrm{ZO_2H}$ and —$\mathrm{ZCH_2COOH}$ (see Section V.D) groups when going from O to Te.

TABLE 27. Dissociation constants of selenols and thiols in water at 25 °C

Compound	pK_a		Ref.
	Z = Se	Z = S	
PhZH	5.9[a]	6.5	281
$\mathrm{HOOCCH_2ZH}$	4.7	8.1	276
$\mathrm{^-OOCCH_2ZH}$	7.3	10.58	276
$\mathrm{MeOOCCH_2ZH}$	4.70	8.08	276
$\mathrm{HOOCCH(NH_2)CH_2ZH}$	5.24	8.25	283
$\mathrm{H_3\overset{+}{N}CH_2CH_2ZH}$	5.0	8.3	284
$\mathrm{C_9H_6NZH}$[b]	4.94	7.68	285
$\mathrm{H_2NCH_2CH_2ZH}$	6.47	10.21	286

[a] Ref. 282; doubts on this value have been reported[277].

[b] $\mathrm{C_9H_6N}$ = 8-quinoline.



SCHEME 3

B. Onium Salts

Gilov and coworkers[287–289] have investigated the reactivity and orientation of selenonium ions[137–140] in electrophilic substitutions. The isomer distribution in nitration, chlorination and bromination of **137** and **138** is reported in Table 28. These ions exhibit —I, —M and *meta*-directing effects. Bromination of **137** in acetic acid without Ag^+ ions surprisingly gives a *para* derivative. The *meta* substitution decreases and the *para* substitution increases as the positive pole s insulated from the ring by a methylene group. By changing the counterion no significant differences were observed in isomer distribution. The sulphonium ion behaves similarly to the selenonium ion but the oxonium group exhibits a different directing effect. Nitration of triphenyloxonium tetrafluoroborate results in 100% *meta* substitution[290]. Selenonium ions are more reactive than sulphonium ions and bromination is faster than chlorination. Reactivity data of **137**, **139**

$[Ph\overset{+}{Se}Me_2]MeSO_4^-$
(137)

$[Ar\overset{+}{Se}Me_2]A^-$
(138) $Ar = PhCH_2$, A = picrate
(139) $Ar = PhCH_2$, $A = ClO_4$
(140) $Ar = PhCH_2CH_2$, $A = ClO_4$

TABLE 28. Isomer distribution in nitration, chlorination and bromination of selenonium salts[a]

Compound[b]	Reaction conditions[c]	*ortho*(%)	*meta*(%)	*para*(%)
	Nitration			
$PhSeMe_2MS$	HNO_3–H_2SO_4 conc.	2.6	91.3	6.1
$PhCH_2SeMe_2PI$	HNO_3–H_2SO_4 conc.	18.8	11.9	69.1
$PhCH_2SeMe_2PI$	HNO_3 fuming	12.5	18.0	69.5
	Chlorination			
$PhSeMe_2MS$	Cl_2/Ag_2SO_4; H_2SO_4	17.4	74.9	7.7
$PhSeMe_2MS$	Cl_2/AgO_2CCF_3; CF_3COOH	24.5	71.1	4.4
	Bromination			
$PhSeMe_2MS$	Br_2/Ag_2SO_4; H_2SO_4	6.4	88.1	5.5
$PhSeMe_2MS$	Br_2/AgO_2CCF_3; CF_3COOH	6.4	89.3	4.2
$PhSeMe_2MS$	Br_2; MeCOOH	9.4	0	90.6

[a] Data from Refs 287–290.
[b] MS = methyl sulphate, PI = picrate.
[c] At room temperature except for picrates (0 °C).

TABLE 29. Rate constants for nitration of selenonium and sulphonium salts in aqueous H_2SO_4 at 25 °C[a]

Compound[b]	% H_2SO_4	10^2k_2(l $M^{-1}s^{-1}$)
$PhSeMe_2MS$	98.1	2.56
$PhSMe_2MS$	98.1	0.113
$PhCH_2SeMe_2PC$	75.5	1.62
$PhCH_2SMe_2PC$	75.5	0.558
$PhCH_2CH_2SeMe_2PC$	70.1	3.52
$PhCH_2CH_2SMe_2PC$	70.1	3.44

[a] Data from Refs 287–290.

[b] MS = methyl sulphate, PC = perchlorate.

TABLE 30. Relative rates and partial factors for nitration at 25 °C of selenonium and sulphonium ions in aqueous H_2SO_4[a]

Compound	10^8 relative reactivity	$10^8 f_o$	$10^8 f_m$	$10^8 f_p$
$Ph\overset{+}{Se}Me_2$	9.22	0.719	25.3	3.37
$Ph\overset{+}{S}Me_2$	0.407	0.044	1.10	0.147
$PhCH_2\overset{+}{Se}Me_2$	100,000	56,400	35,000	415,000
$PhCH_2\overset{+}{S}Me_2$	80,000	38,400	93,800	210,000

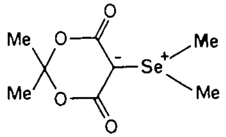
[a] Data from Ref. 288.

and **140** and those of S analogues for the nitration reaction are reported in Tables 29 and 30. The selenonium ion **137** is 22.7 times more reactive than the S analogue and an insulating methylene group increases the reactivity by about 10^4 times. The results have been explained [228] in terms of π(d–p) overlap for the positive pole bonded to the Ph ring and invoking a hyperconjugative effect when the insulating group is present.

C. Selenonium and Telluronium Ylides

In the recent years selenonium and telluronium ylides have received much attention especially from the synthetic point of view[291–293].

The stability of these ylides is related to the delocalization of the negative charge. Ylides in which the carbanionic centre is part of a delocalized system (i.e. cyclopentadienyl) or is bonded to two electron-withdrawing substituents are stable and can be isolated. However, as the stability increases, the reactivity towards electrophilic reagents decreases. The reactivity also depends on the nature of the electrophilic reagent. Stabilized ylides **141**, **142** and **143** (Z = Se, Te) do not react[294,295] with *p*-nitrobenzaldehyde. Stable ylides **144** do not react[296] with *o*-nitrobenzaldehyde, acrylonitrile, diethyl methylenemalonate and dimethyl fumarate, but react with dimethyl acetylenedicarboxylate to give intermediates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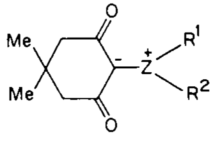
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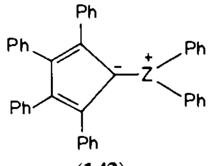
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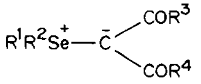

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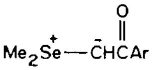

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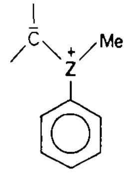
$Me_2\overset{+}{S}e—\overset{-}{C}HCAr$ (with O double-bonded above the C of CAr)



(146)

which then evolve to tetrasubstituted furans. The unstable ylides **145**, prepared *in situ* by deprotonation of the corresponding selenonium salts, give electrophilic additions with benzaldehyde, *p*-nitrobenzaldehyde, diethyl diacetylenedicarboxylate, salicylaldehyde, 2-formylfuran, 2-formylthiophene and 2-formylselenophene at 0 °C. The intermediate addition products cannot be isolated but evolve to trisubstituted furans, epoxides or benzo[*b*]furans according to the electrophiles used[291,292]. Sulphur ylides analogous to **145** show a lower reactivity[297–299].

The thermodynamic basicity constants of ylides **142** ($Z = Se$, Te) in anhydrous acetonitrile have been determined[138]. Telluronium ylides of this type are fairly strong bases ($Z = Te$, $R^1 = R^2 = Ph$, $pK_a = 10.59$; $Z = Se$, $R^1 = R^2 = Ph$, $pK_a = 9.59$; pK_a of aniline under the same conditions[138] is 10.57) and the basicity decreases in the order $Te > Se > S$. The substituents bonded to the Te atom of **142** interact with the positive pole mainly by an inductive mechanism[138].

A recent spectroscopic study[52] of stabilized ylides **146** ($Z = S$, Se, Te) reports that sulphonium and selenonium groups show an electron-withdrawing effect on the Ph ring whereas the telluronium group exhibits a π-donating effect; in our opinion these results should be used with caution.

Selenium ylide salts with two onium centres have recently been synthesized[293] and their reactivity towards electrophilic and nucleophilic reagents has been investigated.

D. Selenides and Tellurides

Selenides are important sources of organoselenium reagents and their chemical behaviour is related to the ability of alkyl- and aryl-seleno groups to stabilize both carbanions and carbocations. PhSe and MeSe groups increase the acidity of the hydrogens bonded to the adjacent C atom so that selenides are α-deprotonated by strong bases. Alkyllithium reagents are generally used for the deprotonation of the Me group[300] since in absence of the latter an attack of the lithium reagent on the Se atom occurs[301–303].

The deprotonation of phenyl selenides (**147**) can be conveniently carried out by using lithium amides which have a low tendency to attack the soft electrophilic Se atom.

$$\underset{\textbf{(147)}}{PhSeCH_2R} \rightarrow \underset{\textbf{(148)}}{PhSeCHLiR}$$

$$R = Ph, SiMe_3, CO_2Et, COPh, CH{=}CR_2,$$
$$CH_2, C{\equiv}CH, SePh$$

Lithium diisopropylamide (LDA) and lithium 2,2,6,6-tetramethylpiperidide (LTMP) have been found to be the most useful reagents and their choice depends on the nature of the group R[304–308]. Lithium diisobutylamide and $LiNEt_2$ have sometimes[300,309,310] been used. Phenylselenomethane (**147**; $R = H$) is not satisfactorily deprotonated by lithium amide bases. A CF_3 group in the *meta* position on the phenylseleno group greatly increases the acid-strengthening effect and LTMP easily gives deprotonation[304,311]. The α-alkyl substitution of selenide decreases the acidity of the C—H bond and the deprotonation can be carried out only if a strong electron-withdrawing substituent is present[312] as in **149**.

$$\text{PhSeCH(CN)(CH}_2)_5\text{Me} \xrightarrow[-78^\circ\text{C}]{\text{LDA/THF}} \text{PhSeCLi(CN)(CH}_2)_5\text{Me}$$

(149) **(150)**

The relative acidity increasing effect of Se and S on adjacent C—H hydrogens is a problem debated on theoretical[45,46,313,314] and experimental grounds[61,315]. A compendium of experimental data (Table 31) shows that carbanions with the negative charge in p or sp^3 orbitals are stabilized by S (probably by conjugative interaction) better than by Se and hence S compounds are more acid[315]. In carbanions coming from vinyl systems the conjugation with the heteroatoms is precluded, nevertheless the Se stabilizes more effectively than S because of its higher polarizability; therefore a higher acid-strengthening effect of Se is observed[315].

The anions **148** coming from the deprotonation reaction are powerful nucleophiles of great interest in organic synthesis[305]. Allyl selenide anions **152** give prevalently α-alkylation[310,319], but sometimes a remarkable amount of γ-alkylation is observed (Table 32). These results are similar to those observed in S systems[320,321].

$$\text{PhSeCH}_2\text{CH}{=}\text{CR}^1 \xrightarrow[-78\,^\circ\text{C}]{\text{LDA}} \text{PhSeCHLiCH}{=}\text{CR}^2$$

(151) **(152)**

R^1, R^2 = H, H; Me, Cl; Me, H; Ph, H

In principle, selenoketone enolates can direct alkylating reagents to Se, O and C atoms. Treatment[322] of the α-(phenylseleno)acetophenone enolate (**154**) with prenyl halides (Scheme 4) gives only *C*- and *Se*-alkylation, the preferred site of attack depending on the reaction conditions. *Se*-Alkylation is followed by a 2,3-sigmatropic rearrangement to give compound **158**.

TABLE 31. Relative acid-strengthening effect of S and Se on hydrogens bonded to the adjacent C atom

Reaction (Z = S, Se)	Ratio of constants[c]	Ref.
1. Deprotonation of $(PhZ)_2CH_2$	K(S/Se) ~ 100	300, 309
2. Deprotonation of $PhCOCH_2ZPh$	K(S/Se) = 32	61
3. Isotopic exchange of PhZMe[a]	k(S/Se) = 10	316
4. Deprotonation of $PhZCH_2CH{=}CH_2$	k(S/Se) = 75	310
5. Base-catalysed isomerization of $PhZCH_2C{\equiv}CH$ to $PhZCH{=}C{=}CH_2$	k(S/Se) = 6.14	317, 318
6. Base-catalysed isomerization of $PhZCH{=}C{=}CH_2$ to $PhZC{\equiv}CMe$	k(S/Se) = 4.8	317, 318
7. Deprotonation of *m*-$CF_3C_6H_4ZMe$	k(S/Se) = 3.8	304
8. Isotopic exchange of C_4H_4Z[b]	k(S/Se) = 0.67	167
9. Deprotonation of *m*-$CF_3C_6H_4ZCH{=}CH_2$	k(S/Se) = 0.42 K(S/Se) = 0.3	315 315
10. Deprotonation of $PhZCH{=}CH_2$	k(S/Se) = 0.37 K(S/Se) = 0.21	315 315

[a] In KNH_2/NH_3.

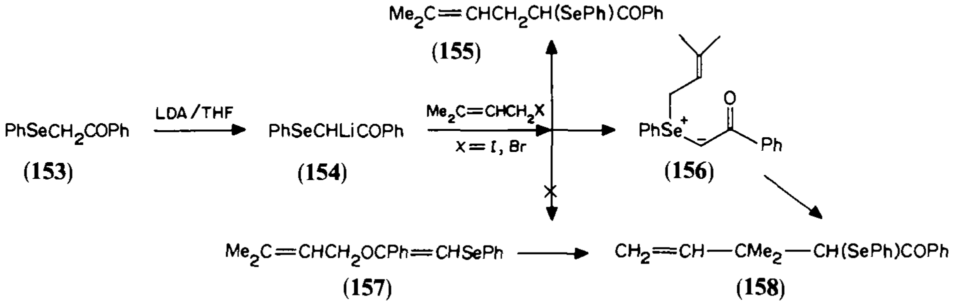
[b] Thiophene and selenophene in *t*-BuOLi/DMSO, see Section IV.F.

[c] *K* and *k* refer to equilibrium and rate processes, respectively.

TABLE 32. α:γ Ratio in alkylation[a] of allyl selenide anions **152**[b]

Anion (R^1,R^2)	Electrophile	α:γ
H,H	$PhCH_2CH_2CH_2Br$	~80:20
H,H	Me_3SiCl	82:18
H,H	$Me_2PhSiCl$	41:59
H,H	PhCOMe	15:85
Me,H	$PhCH_2CH_2Br$	>90:10
Me,Me	$Me_2PhSiCl$	>90:10
Ph,H	MeCOMe	~50:50

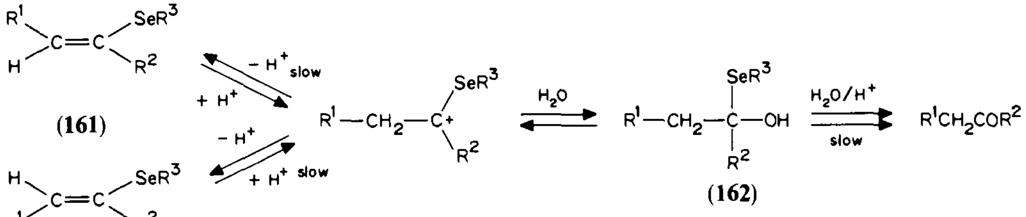
[a] The γ-alkylation products are a 1:1 mixture of *E*- and *Z*-isomers. [b] Data from Ref. 310.



Under proper reaction conditions, alkyllithium reagents can be added to vinyl selenide **159** to give α-lithiumalkyl phenyl selenides (**160**) which can then be trapped by electrophiles[323]. The directing effect of the phenylseleno group is that of an electron-withdrawing substituent.

$$\underset{(\mathbf{159})}{\mathrm{PhSeCH{=}CH_2}} \xrightarrow[\mathrm{R\,=\,Bu,i\text{-}Pr}]{\mathrm{RLi}} \underset{(\mathbf{160})}{\mathrm{PhSeCHLiCH_2R}}$$

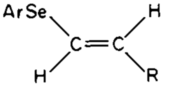
The ability of the phenylseleno group to stabilize carbocations has recently been pointed out by measuring the acid-catalysed hydrolysis rate of vinyl selenides[324,325]. Vinyl selenides **161** bearing an alkyl or aryl substituent at the α-position of the vinyl moiety hydrolyse by an A2-type mechanism in which (Scheme 5) the initial protonation is a slow reversible step and the decomposition of the intermediate hemiselenoacetal **162** is also slow[324]. Unsubstituted aryl vinyl selenides (**161**; $R^1 = R^2 = H$, $R^3 = Ar$) hydrolyse



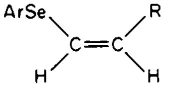
SCHEME 5

according to the classical A2 mechanism[47,325] in analogy with vinyl ethers and vinyl sulphides. The nature of the *para* substituent present in the aryl group of vinyl selenides (**161**; $R^1 = R^2 = H$, $R^3 = Ar$) and in the aryl group of α-(methylseleno)styrenes (**161**; $R^1 = H$, $R^2 = Ar$, $R^3 = Me$) does not affect the reaction mechanism. This is an indication that the ability of the Se moiety to stabilize the carbocation is fundamental in determining the mechanism. Hydrolysis rate ratios show that a methylseleno group stabilizes a positive charge better than a phenylseleno group (MeSe: PhSe = 15) and this effect increases in S (MeS: PhS = 41) and O (MeO: PhO = 133) analogues.

Aryl vinyl selenides involved in addition and elimination reactions have been reported by Chierici and Montanari[326]. *Trans-* and *cis-β*-arylselenoacrylic acids **163** and **165** add Br_2 very easily giving stereoisomers of 1-arylseleno-2,3-dibromopropionic acid which in water easily eliminate CO_2 and HBr giving *trans-* and *cis*-1-bromo-2-arylselenoethylenes **164** and **166**. The *cis* compound **166** always prevails (80%) over the *trans* one (**164**).

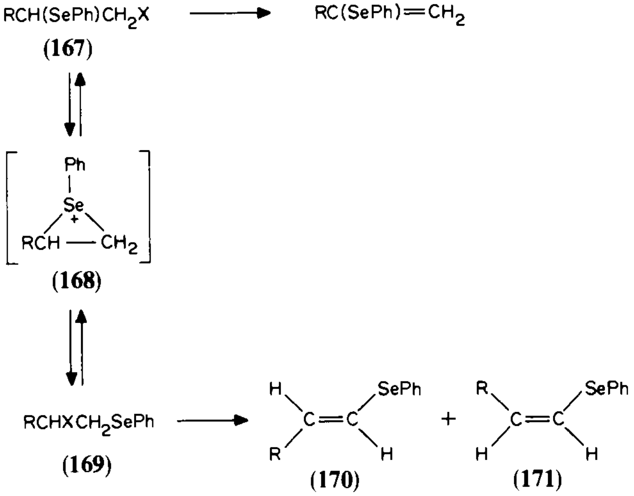


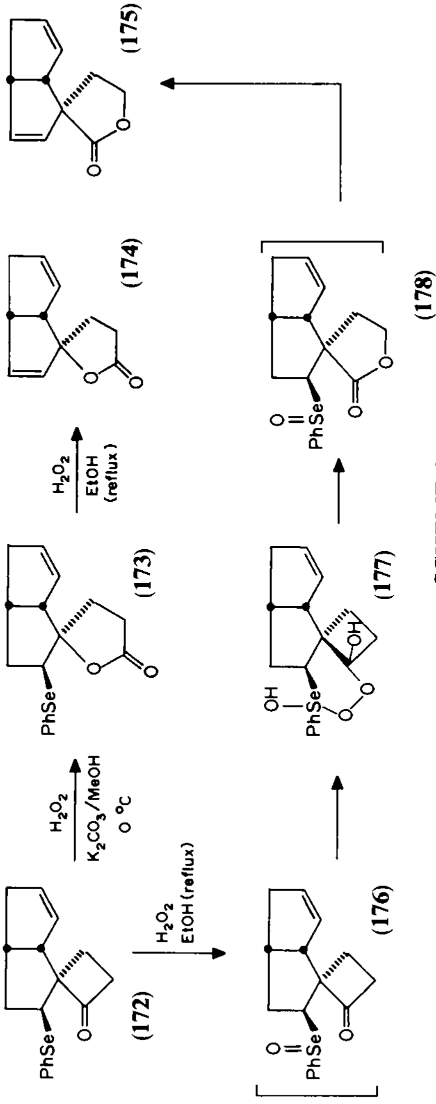
(**163**) R = COOH
(**164**) R = Br



(**165**) R = COOH
(**166**) R = Br

The phenylseleno group affects the stability, dehydrohalogenation and solvolysis of phenylselenoalkyl halides. *β*-Bromoalkyl phenyl selenides (**167**; X = Br) isomerize[327] to the thermodynamically more stable **169** presumably via the seleniranium ion **168**. The rate of isomerization depends on the leaving group (X = Br, Cl, $OCOCF_3$, OAc) and the solvent[327]. Dehydrobromination[328] of **169** (X = Br) in LDA–Et_2O at 0 °C gives a prevalence of the *E*-isomer **170**. The stereoselectivity of the reaction depends on the reaction conditions and nature of the R group. The first-order rate constant of solvolysis of phenylselenoethyl chloride (**167**; R = H, X = Cl) in MeOH is five times higher than that of the S analogue but in 80% EtOH it is 200 times higher[329]. This extraordinary phenylseleno effect is explained supposing that the reaction is anchimerically assisted and that the solvent could nucleophilically assist the PhSe neighbouring group[329].




PhSe
(172)
H_2O_2
K_2CO_3/MeOH
0 °C
PhSe
(173)
H_2O_2
EtOH
(reflux)
(174)
(175)
H_2O_2
EtOH (reflux)
PhSe=O
(176)
PhSe—OH
OH
(177)
PhSe=O
(178)

SCHEME 6

TABLE 33. Constants for substituted benzaldehyde–cyanohydrin equilibria and for dissociation of benzoic acids[a]

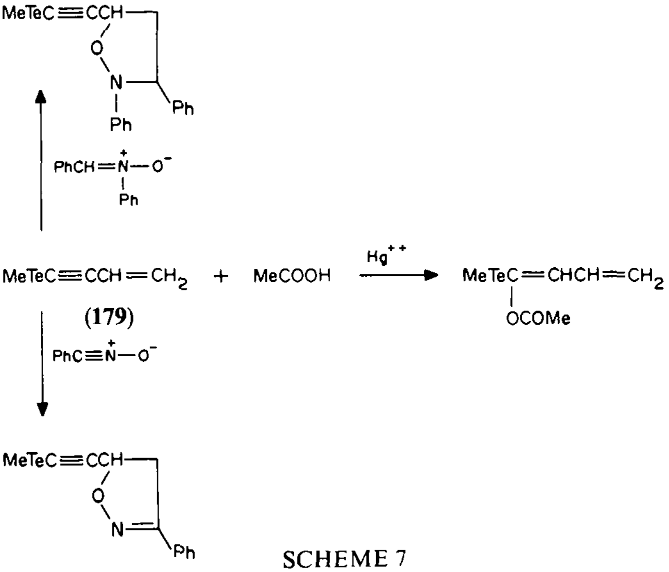
Substituent	Benzaldehydes[b] $10^3 K$	Benzoic acids[c] pK_a
p-SeMe	35.5	5.00
m-SeMe	3.95	4.74
p-SMe	38.1	5.02
m-SMe	4.07	4.75
p-OMe	42.9	5.11
m-OMe	4.27	4.71
H	4.40	4.81

[a] Data from Ref. 39.
[b] In EtOH at 20 °C.
[c] In 30% EtOH at 25 °C.

The phenylseleno group also increases the acidity of the carboxy group insulated by a methylene group[60]. Phenylselenoacetic acid is stronger ($pK_a = 3.75$) than acetic acid but weaker than S ($pK_a = 3.38$) and O ($pK_a = 3.15$) analogues[60]. The inductive electron-withdrawing effect of the PhZ group (Z = Se, S, O) decreases in the order O > S > Se.

The equilibrium constant of the addition of CN^- ion to benzaldehyde is increased[39] by a methylseleno group in the *para* position and decreased if the group is in the *meta* position (Table 33). Similar electron-releasing and -withdrawing effects are observed in the dissociation of *p*- and *m*-methylselenobenzoic acids[39]. A comparison with S and O analogues (Table 33) shows that the + M effect of the MeZ (Z = Se, S, O) group decreases in the order O > S > Se and it is also operative from the *meta* position.

An example of a regiochemical effect of a selenide group is the influence of the phenylseleno group on the Baeyer–Villiger rearrangement[330]. Through oxidation of



SCHEME 7

selenide **172** (Scheme 6) with H_2O_2 under basic conditions at 0 °C the expected compound **173** is obtained which gives **174** by treating with H_2O_2 in refluxing EtOH. When **172** is treated in absence of the base, **175** is obtained. The different outcome of the rearrangement has been interpreted in terms of different rates in selenide oxidation and in the Baeyer–Villiger reaction. In the presence of the base, selenide oxidation is slower than Baeyer–Villiger oxidation and the migration of quaternary carbon occurs giving the expected **173** which is converted to **174** by selenoxide elimination. In the absence of the base, H_2O_2 reacts with the selenoxide as well as with the carbonyl group of the cyclobutanone system of intermediate **176** giving **177** which in turn gives **175** via migration of the cyclobutanone methylene group and selenoxide elimination from **178**.

Information on the reactivity and directing effects of methyl- and phenyl-telluro groups is very limited. Radchenko and coworkers[331,332] report that the methyltelluro group of methyltellurovinylacetylene (**179**) directs the addition of the acetoxyl part of acetic acid to the triple bond in the α-position and the addition of benzonitrile oxide and α,*N*-diphenylnitrone to the double bond (Scheme 7).

E. Selenoxides and Selenones

Phenylseleninyl (PhSeO—) and phenylselenonyl ($PhSeO_2$—) are strong electronegative groups which increase the acidity of a H atom bonded to an adjacent C atom and activate an olefinic bond in the vinylic position. These characteristics, coupled with the fact that they are good leaving groups, have recently been utilized to develop new syntheses of olefins[304], allyl alcohols[304], dienes[304], cyclopropyl ketones[333], oxetanes[334], ethylenic and acetylenic ketones[335].

Selenoxides are not generally very stable at room temperature. They are hygroscopic substances and exhibit a greater basicity than the analogous sulphoxides[142].

Selenoxides are deprotonated better than selenides and the reaction proceeds quickly at −78 °C with lithium diisopropylamide (LDA)[304]. Alkyllithium reagents (i.e. butyllithium) give partial or total cleavage rather than deprotonation[304]. Lithium selenoxides **181** react with a variety of electrophiles (aldehydes, ketones, acyl and alkyl halides) to give α-substituted selenoxides which are directly converted to olefins by selenoxide *syn* elimination or to selenides by reduction reaction[304].

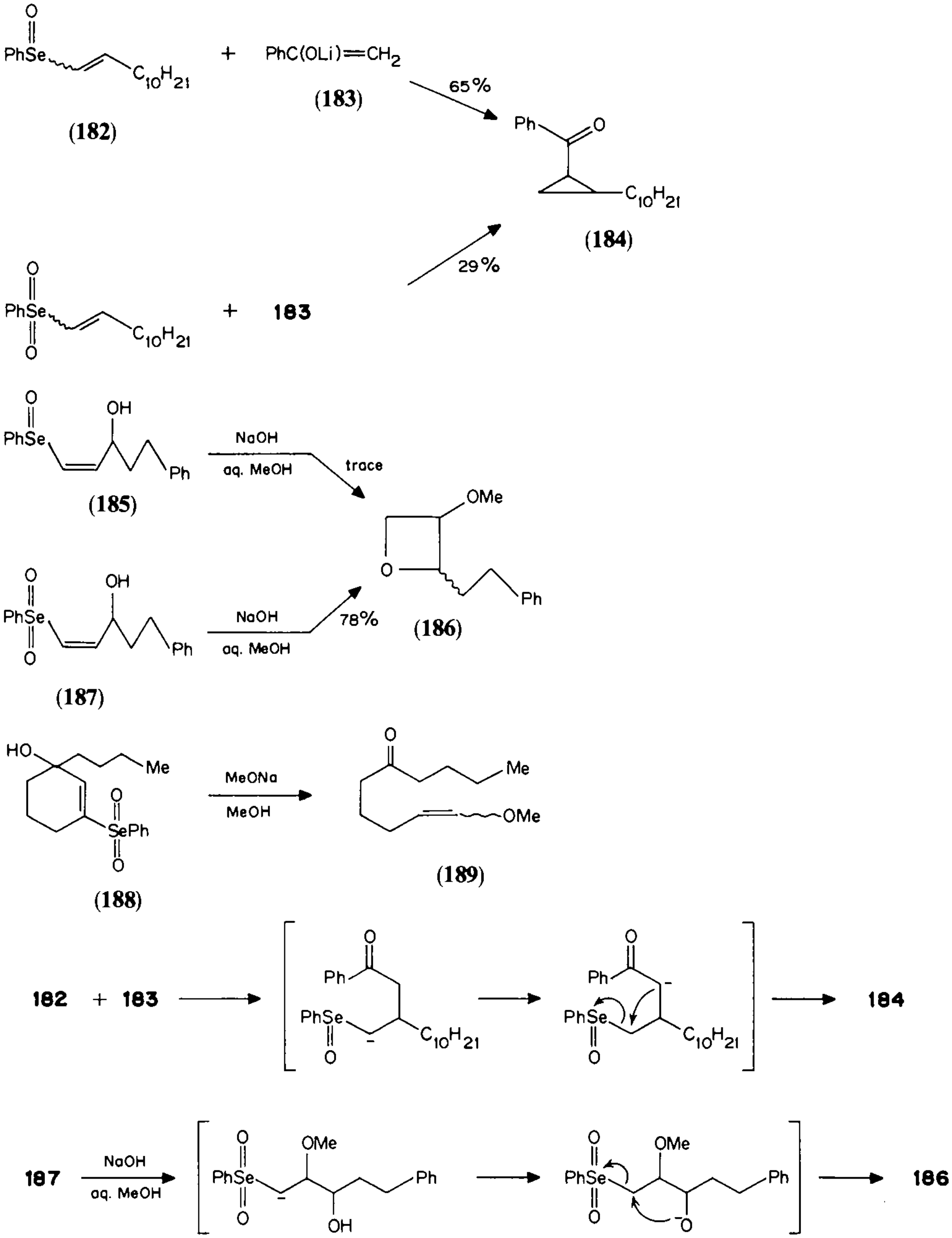
$$\begin{tikzcd}
\underset{\mathbf{(180)}}{\mathrm{PhSeCHRMe}} \arrow[r, "\mathrm{LDA}", "-78\,^\circ\mathrm{C}"'] & \underset{\mathbf{(181)}}{\mathrm{PhS({=}O)CLiRMe}} \arrow[r, "\mathrm{Me_2CO}"] & {} \\
\mathrm{PhS({=}O)CRMeCMe_2OH} \arrow[r, "\Delta"] \arrow[d, "\mathrm{red.}"] & \mathrm{H_2C{=}CRCMe_2OH} \\
\mathrm{PhSeCRMeCMe_2OH}
\end{tikzcd}$$

Vinyl selenoxides and vinyl selenones give conjugative nucleophilic addition with ketones, ester enolates and alkoxides, followed by displacement of the seleno group. Examples are given in Scheme 8 which also outlines the difference in reactivity between the PhSeO and $PhSeO_2$ groups[333–335].

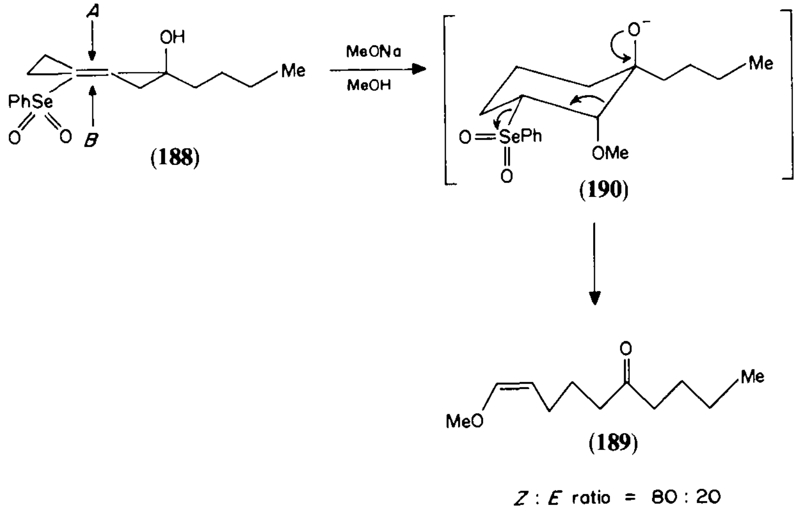
The proposed mechanism for the formation of cyclopropyl ketone (**184**) and oxetane (**186**) involves three steps: nucleophilic addition, proton transfer and nucleophilic substitution[333,334].

The oxetane formation is not a stereospecific reaction but a prevalence of *cis*-oxetane is observed[334].

The synthesis of ketones **189** shows good stereoselectivity because the attack of methoxide from the *B* side is energetically favoured and the phenylselenonyl group in the intermediate **190** is in a favourable position for 1,4-fragmentation.


PhSe(O)–CH=CH–C10H21
(182)
PhC(OLi)=CH2
(183)
65%
29%
(184)
+ 183
NaOH
aq. MeOH
trace
(185)
OMe
Ph
(186)
78%
(187)
HO
Me
SePh
MeONa
MeOH
OMe
(188)
(189)
182 + 183
184
187
NaOH
aq. MeOH
186

(*Contd.*)



SCHEME 8

Vinyl selenones containing a tetrasubstituted double bond have a very low reactivity towards nucleophilic addition[304] of alkoxide and the fragmentation process which gives an acetylenic ketone, is predominant.

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*When quoting Russian journals, E.E. means the corresponding English translation, followed by the page number.

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The Chemistry of Organic
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CHAPTER **16**

Functional groups containing selenium and tellurium in various oxidation states

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I. INTRODUCTION

There have been many reports of organic molecules having functional groups containing Se and Te in various oxidation states involving higher valencies. The main purpose of this chapter is to describe the chemistry of organic compounds containing Se or Te in various oxidation states such as selenols (RSeH), selenenic acids, seleninic acids, selenonic acids and their derivatives and Te analogues. Attention has been mainly focused on their preparative methods and their characteristic reactions. Since Klayman's excellent review[1] has covered the main literature on Se chemistry up to 1972, we shall deal with the subject mainly on the basis of references published in the last decade.

II. SELENOLS

Selenols (RSeH) are acidic and air-susceptible compounds having an intolerable odour. They are soluble in alkaline aqueous solution due to their acidic nature, but are usually insoluble in water. In general, selenols have greater acidities than those of the corresponding S analogues. For example, the pK_a values of H_2Se and benzeneselenol are 3.7 and 5.9, respectively[2–5], whereas H_2S and benzenethiol show 7.0 and 6.5. Selenols are generally more sensitive to air than thiols, and are oxidized to the corresponding diselenides. Selenolate ions (RSe^-), formed in alkaline solution of selenols, are generally more sensitive to molecular oxygen and are rapidly converted to diselenides (equation 1).

$$RSeH \xrightarrow{[O]} RSeSeR \qquad (1)$$

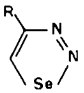
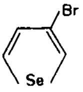
A. Synthesis

In general, alkaneselenols and aromatic selenols can be synthesized by the reaction of Grignard reagents and organolithium compounds with controlled quantities of elemental Se (equation 2)[1,6–9].

$$RLi(MgX) \xrightarrow{Se} RSeLi(MgX) \xrightarrow{H_2O} RSeH \qquad (2)$$

The other readily available and convenient starting materials for preparation of selenols

TABLE 1. Preparation of selenols and selenolates

Starting Material	Reagents	Products	Ref.
Se	$RMgX/H_2O/H^+$	RSeH	1
	$ArMgX/H_2O/H^+$	ArSeH	1
	ArLi	ArSeLi	1
	RLi	RSeLi	1, 6–8
	$RC{\equiv}CNa$	$RC{\equiv}CSeNa$	9
	1. Na 2. ArX/$h\nu$,e^-	ArSeNa	12
H_2Se	RX	RSeH	1
	$RCH{=}CH_2$	RCH_2CH_2SeH	1
		$HOCH_2CH_2SeH$	1
RSeSeR	Na/liq. NH_3	RSeNa	1
	$NaBH_4$	RSeNa	1
	H_3PO_2/H_2O	RSeH	13, 14
$(H_2NCH_2CH_2Se)_2$	Na_2S/KCN	$H_2NCH_2CH_2SeH$	15
ArSeSeAr	Na/THF	ArSeNa	10
	$NaBH_4$	ArSeNa	1, 11
	NaOH/phase-transfer catal.	ArSeNa	16
	$Zn/HCl/H_2O$	ArSeH	17
RSeCN	H^+/H_2O	RSeH	1
ArSeCN	H^+/Zn	ArSeH	1, 17
	H_3PO_2	ArSeH	1
	$NaBH_4$	ArSeH	18
ArSe(O)OH	$NaBH_4$	ArSeH	1
$ArSeO_2OH$	$H_2S/SO_2/Zn/HCl$	ArSeH	1
$ArSeSiMe_3$	$MeOH/H^+$	ArSeH	19, 20
	KF/18-crown-6	ArSeK	22
	KOH/EtOH/dioxane	$RC{\equiv}CSeK$	23–26
	EtLi	$Z\text{-}LiSeCH{=}CHC{\equiv}CLi$	27, 28
$t\text{-}Bu_2C{=}Se$	$LiAlH_4$	$t\text{-}Bu_2CHSeH$	29

are alkyl or aryl diselenides which are stable in air, and some of them are commercially available. They are easily reduced to the corresponding selenols by appropriate reducing reagents such as Na[10] or $NaBH_4$[11].

A number of other methods involving the use of other Se compounds have been devised. Table 1 shows a variety of methods for the synthesis of selenols or selenolates[1-29].

B. Reactions

1. Reactions with alkylating reagents

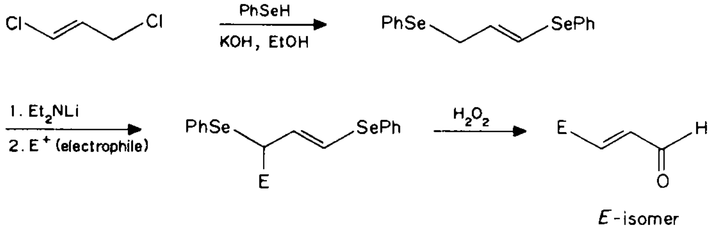
a. Reaction with various halides. Alkylation of alkylselenols and aromatic selenols with alkyl halides in the presence of base gives the corresponding dialkyl selenides in satisfactory yields (equation 3)[16,30-39]. Various types of selenides are synthesized by this method. For example, acetylenic selenols and selenolates are converted to the acetylenic selenides (equations 4 and 5)[9,28,40,41].

$$\mathrm{RSeH} + \mathrm{R^1X} \xrightarrow{\text{base}} \mathrm{RSeR^1} \tag{3}$$

$$\mathrm{RC{\equiv}CSeH} \xrightarrow{\mathrm{R^1X}} \mathrm{RC{\equiv}CSeR^1} \tag{4}$$

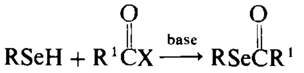
$$\mathrm{RC{\equiv}CSeLi(Na)} \xrightarrow{\mathrm{R^1X}} \mathrm{RC{\equiv}CSeR^1} \tag{5}$$

Reich and coworkers have prepared an *E,Z*-mixture of 1,3-bis(phenylseleno)propene by the alkylation of benzeneselenolate with 1,3-dichloropropene. This product is converted to α,β-unsaturated aldehydes as shown in equation (6)[42].



(6)

Alkylation of selenols with acyl or aroyl halides in the presence of base produces seleno esters of the corresponding carboxylic acids (equation 7)[7,43-45].



$$\mathrm{RSeH} + \mathrm{R^1\overset{O}{\overset{\|}{C}}X} \xrightarrow{\text{base}} \mathrm{RSe\overset{O}{\overset{\|}{C}}R^1} \tag{7}$$

b. Reaction with aromatic halides. Phenylselenolate has been known to participate in $S_{RN}1$-type reaction with aryl halides under irradiation, giving rise to aryl phenyl selenides[12,46,47]. The reaction mechanism is depicted in equation (8).

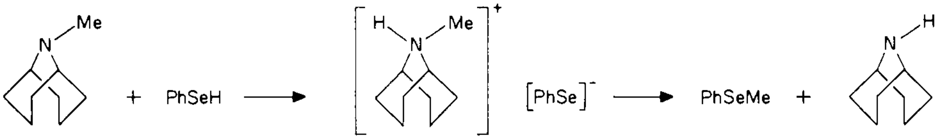
$$\begin{gathered}\mathrm{ArX} + \mathrm{PhSe^-} \xrightarrow{h\nu} (\mathrm{ArX})^{\cdot-} + \mathrm{PhSe}\\ (\mathrm{ArX})^{\cdot-} \longrightarrow \mathrm{Ar}^{\cdot} + \mathrm{X^-}\\ \mathrm{Ar}^{\cdot} + \mathrm{PhSe^-} \rightarrow (\mathrm{ArSePh})^{\cdot-} \xrightarrow{\mathrm{ArX}} \mathrm{ArSePh} + (\mathrm{ArX})^{\cdot-}\end{gathered} \tag{8}$$

It has been shown that the reaction of arylselenolate ion with aryl iodides is catalysed efficiently by cuprous iodide in HMPA solution (equation 9)[48,49].

$$\mathrm{ArI} + \mathrm{Ar^1Se^-} \xrightarrow[\mathrm{HMPA}]{\mathrm{CuI}} \mathrm{ArSeAr^1} \tag{9}$$

c. Reaction with alkylamines. In general, selenols form quarternary ammonium salts of the selenolate ion with various amines by ionization of the acidic proton. Ammonium salts of benzeneselenols usually decompose on heating to produce the alkyl phenyl selenide[2]. This pyrolytic reaction offers a method for alkyl group migration from the N atom of amine to the Se atom. The salts formed from tosylated amines[50] or from tertiary alkylamines[2] give alkyl phenyl selenides as shown in equations (10) and (11).

$$\mathrm{RCH_2NH_2} \xrightarrow{\mathrm{TsCl}} \mathrm{RCH_2NHTs} \xrightarrow{\mathrm{PhSeH}} [\mathrm{RCH_2NH_2Ts}]^+ [\mathrm{PhSe}]^- \longrightarrow \mathrm{RCH_2SePh} + \mathrm{TsNH_2} \tag{10}$$



(11)

It has been shown that an alkyl shift from tertiary amines to benzeneselenolates to give alkyl phenyl selenides can be achieved by use of a Ru catalyst (equation 12)[51].

$$\mathrm{PhSeNa} + \mathrm{R^1R^2R^3N} \xrightarrow[2.\ \mathrm{H_2O}]{1.\ \mathrm{Ru\ catalyst}} \mathrm{PhSeR^1} + \mathrm{R^2R^3NH} \tag{12}$$

2. Reduction by selenols

It has been known that selenols are good reducing agents for various classes of organic compounds. Functional groups such as nitroso (—N=O), azo (—N=N) and imino (> C=N—) are readily reduced to give amino, hydrazo and amino groups, respectively[52,53]. Organic sulphoxides are generally reduced to the corresponding sulphides[54].

Methylselenol reacts reductively with ketones[55,56] or benzyl halides[57] as shown in equations (13) and (14).

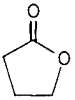
$$\mathrm{R^1R^2C{=}O} + \mathrm{MeSeH} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{ZnCl_2}} \mathrm{R^1R^2CHSeMe} + \mathrm{R^1R^2C(SeMe)_2} \tag{13}$$

$$\mathrm{PhCH_2X} + \mathrm{MeSeH} \rightarrow \mathrm{PhCH_2SeMe} + \mathrm{PhMe} \tag{14}$$

3. Ring-opening reactions

Treatment of epoxides[58–63,70], lactones [6,10,64–69] and cyclopropanes[68,71] with selenols results in ring-opening to selenenylated derivatives. These reactions are due to the high nucleophilicity of the Se atom in the selenols. Examples are given in equations (15)–(17).

$$+ \mathrm{RSeH} \rightarrow \mathrm{HOCH_2CH_2SeR} \tag{15}$$



$$+ \text{RSeH} \rightarrow \text{HOOC(CH}_2\text{)}_3\text{SeR} \qquad (16)$$

$$+ \text{RSeH} \rightarrow \text{MeCH}_2\text{CH}_2\text{SeR} \qquad (17)$$

4. Addition reactions

Reaction of selenols with conjugated ketones and aldehydes having the C=C—C=O bond system, gives products of addition to the C=C bonds (equation 18)[19,21,72–74].

(18)

Addition of benzeneselenol to mono- and di-substituted acetylenes at room temperature gives vinylic selenides (equation 19)[75–85].

$$\text{RC}{\equiv}\text{CH} + \text{PhSeH} \rightarrow \text{RCH}{=}\text{CHSePh} \qquad (19)$$

Some other studies concerning Section II.B, i.e. on selenols and their derivatives have been reported[86–111].

III. SELENENIC ACIDS AND THEIR DERIVATIVES

The generalized structure of selenenyl compounds can be represented by R—Se—X, in which R is an alkyl, aryl or heterocyclic moiety. Selenenyl compounds are classified into five general groups: (*i*) selenenic acid (X = OH), (*ii*) selenenic esters ($X = OR^1$) and selenocarboxylates ($X = OC(O)R^1$), (*iii*) selenenamides ($X = NR^1_2$), (*iv*) selenocyanates (X = CN) and (*v*) selenenyl halides (X = halogen). All of these types of selenenyl compounds share a common feature, i.e. polarization of the $\text{Se}^{\delta+}$—$\text{X}^{\delta-}$ bond, resulting in reactions involving positively charged Se species (equation 20).

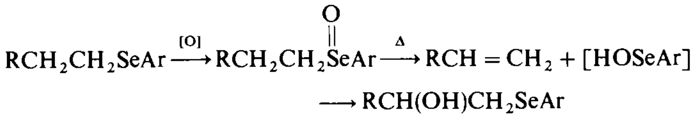
$$\text{R}-\text{Se}-\text{X} \rightarrow \text{R}-\text{Se}^{+} + \text{X}^{-} \qquad (20)$$

A. Selenenic Acids and Their Anhydrides

Selenenic acids and their anhydrides are usually generated *in situ* and used without isolation, because of their instability. There are several reactions in which selenenic acids and their anhydrides play important roles as transient intermediates.

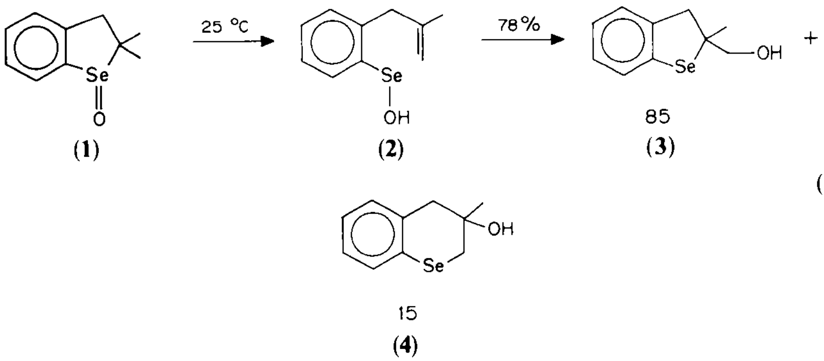
1. Generation

a. β-Elimination of alkyl aryl selenoxides. β-Elimination of alkyl aryl selenoxides proceeds under mild conditions with high selectivity and has been used as a facile and convenient method for synthesis of olefins[11,112–115]. β-Hydroxyselenides, which may be derived by addition of the eliminated arylselenenic acid (ArSeOH) to the olefinic products, are incidentally formed as by-products (equation 21)[117,131,148].



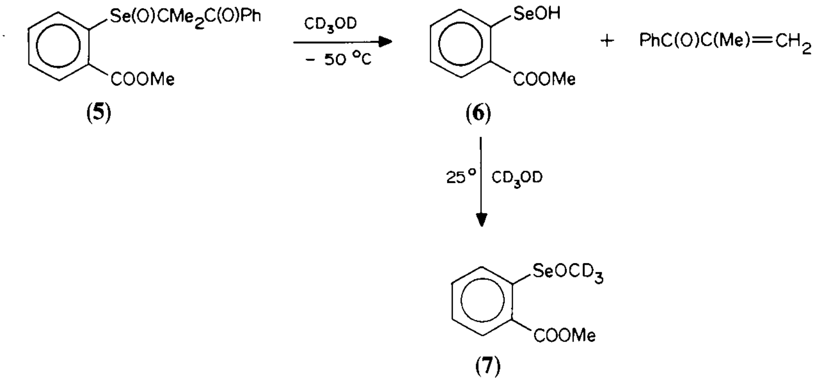
$$\text{RCH}_2\text{CH}_2\text{SeAr} \xrightarrow{[\text{O}]} \text{RCH}_2\text{CH}_2\overset{\overset{\text{O}}{\|}}{\text{Se}}\text{Ar} \xrightarrow{\Delta} \text{RCH}=\text{CH}_2 + [\text{HOSeAr}] \longrightarrow \text{RCH(OH)CH}_2\text{SeAr} \qquad (21)$$

Decomposition of 3,3-dimethyldihydrobenzoselenophene oxide (**1**) leads to generation of an unstable intermediate selenenic acid (**2**), which is trapped intramolecularly to give the isomeric hydroxyselenides **3** and **4** (equation 22)[116,117].



(22)

A ^{77}Se-NMR signal assignable to the selenenic acid **6** has been observed during the *syn* elimination of selenoxide **5** in CD_3OD (equation 23)[118]. The formation of the seleninic ester **7** serves as a chemical evidence supporting the intermediacy of the selenenic acid in this reaction.



(23)

b. Oxidation of selenols and diselenides. Selenenic acids are known to disproportionate into the corresponding diselenides and seleninic acids (going right to left in equation 24[11,131]. The reverse processes were sometimes termed 'comproportionation' in the literature[117,131] and benzeneselenenic acid can be generated *in situ* by this comproportionation.

$$\mathrm{PhSeSePh} + \mathrm{PhSeO_2H} + \mathrm{H_2O} \rightleftharpoons 3\,[\mathrm{PhSeOH}] \qquad (24)$$

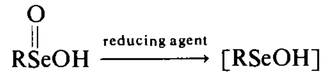
Similar comproportionation between diphenyl diselenide and benzeneseleninic anhydride (2:1 molar ratio) has been also reported to give benzeneselenenic anhydride (equation 25)[125–127,129].

$$2\,\mathrm{PhSeSePh} + (\mathrm{PhSeO})_2\mathrm{O} \rightleftharpoons 3\,[\mathrm{PhSeOSePh}] \qquad (25)$$

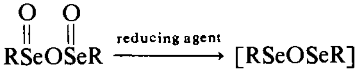
t-Butyl hydroperoxide is employed as an oxidizing agent for the oxidation of diphenyl diselenide to benzeneselenenic anhydride (equation 26)[125,126,128,129]. However, it seems likely that the anhydride is not present in high concentration during the reaction[130].

$$\mathrm{PhSeSePh} + t\text{-}\mathrm{BuOOH} \rightarrow [\mathrm{PhSeOSePh}] + t\text{-}\mathrm{BuOH} \qquad (26)$$

c. Reduction of seleninic acids and their anhydrides. Several reducing reagents, such as hypophosphorous acid (H_3PO_2)[132,137], hydrazines (NH_2NH_2[134], $RNHNH_2$[138,139]) and thiols (RSH)[133], have been used for reducing seleninic acids and their anhydrides to seleninic acids and their anhydrides, respectively (equations 27 and 28).

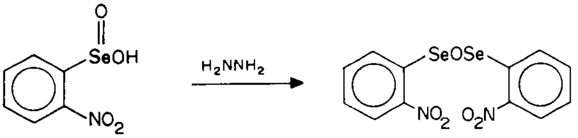


$$\mathrm{R\overset{O}{\overset{\|}{Se}}OH} \xrightarrow{\text{reducing agent}} [\mathrm{RSeOH}] \qquad (27)$$

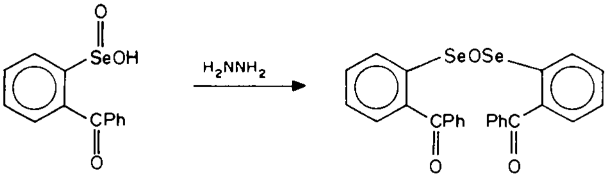


$$\mathrm{R\overset{O}{\overset{\|}{Se}}O\overset{O}{\overset{\|}{Se}}R} \xrightarrow{\text{reducing agent}} [\mathrm{RSeOSeR}] \qquad (28)$$

Recent reinvestigations[135,136] of the reduction products of *ortho*-substituted benzeneseleninic acids, which were initially reported[132–134,151,152] to be sufficiently stable for isolation, have shown that the products are not the selenenic acids but the corresponding selenenic anhydrides (equations 29 and 30).



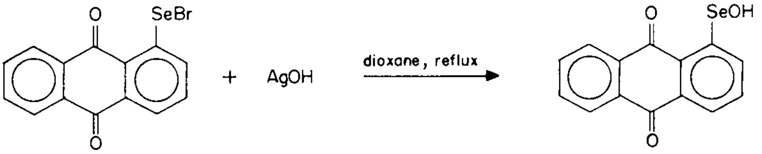
(29)



(30)

d. Hydrolysis of selenenyl halides. Hydrolysis of selenenyl halides has been reported to give the corresponding selenenic acids (equation 31)[44]. Anthraquinone-1-seleninic acid is prepared by the reaction of the corresponding selenenyl bromide with moist silver oxide in dioxane (equation 32)[145].

$$o\text{-}\mathrm{O_2NC_6H_4SeBr} + \mathrm{H_2O} \rightarrow o\text{-}\mathrm{O_2NC_6H_4SeOH} + \mathrm{HBr} \qquad (31)$$



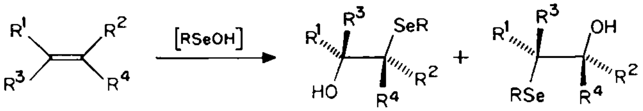
(32)

2. Reactions

In general selenenic acids are unstable and rapidly disproportionate to diselenides and seleninic acids (equation 33)[115].

$$3\,\mathrm{RSeOH} \rightleftharpoons \mathrm{RSeSeR} + \mathrm{RSeO_2H} + \mathrm{H_2O} \qquad (33)$$

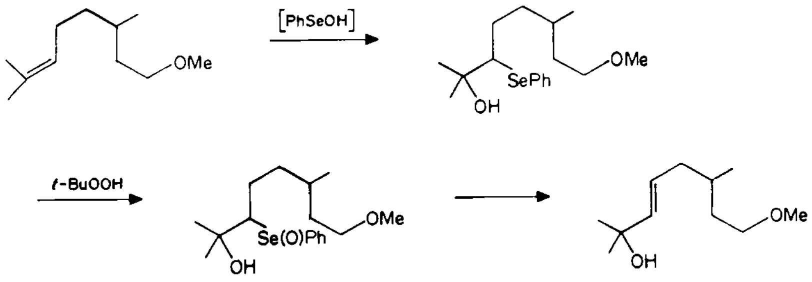
Selenenic acid is a good electrophilic reagent and often used for *in situ* oxyselenation of olefins (equation 34)[137]. The resulting β-hydroxyselenides can be easily converted to the



(34)

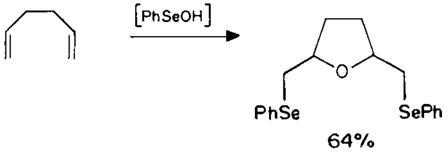
corresponding allylic alcohols or epoxides, in a one-pot reaction, via oxidation to selenoxides by appropriate oxidizing reagents.

The disproportionation (equation 33) is a reversible reaction, and the reverse process can be used for the *in situ* formation of selenenic acid (equation 24)[117,131]. Hori and



(35)

Sharpless[131] have reported the conversion of olefins to allylic alcohols using this reverse reaction system (equation 35). This method can be applied to the synthesis of various cyclic ether derivatives from dienes (equations 36 and 37)[150].



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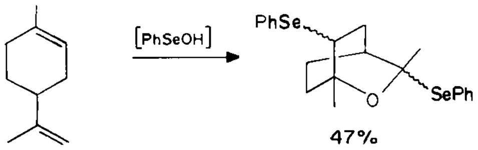
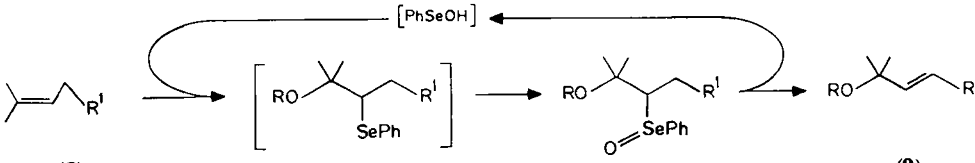


(37)

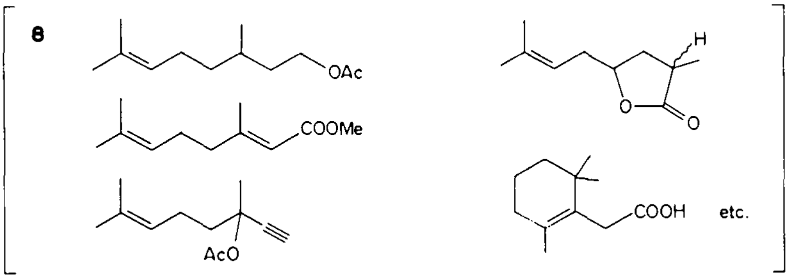
Electrochemical *in situ* generation of phenylselenenic acids has been undertaken by Torii[149] (equation 38), and this method was used for a one-step synthesis of allylic derivatives (**9**) from isoprenoids (**8**). In this case the selenenylation reagents can be recycled by using a catalytic amount of diphenyl diselenide (equation 38)[149].

$$(\mathrm{PhSe})_2 \xrightarrow[2\,\mathrm{ROH}]{-2\,e} 2\,\mathrm{PhSeOR} + 2\,\mathrm{H}^+ \ (\mathrm{R} = \mathrm{Me, H}) \qquad (38)$$

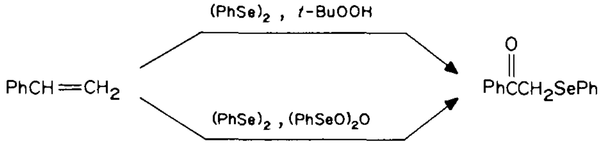


(**8**) (**9**)

8



Recently, Kuwajima and coworkers reported a regioselective oxidation of olefins to α-phenylseleno ketones by using $(PhSe)_2$–*t*-BuOOH or $(PhSe)_2$–$(PhSeO)_2O$ systems (equation 39)[126]. The nature of the reactive species in this reaction has not yet been confirmed. However, benzeneselenenic anhydride (PhSeOSePh) is assumed to be a plausible one as shown in equations (25) and (26). *anti*-Markownikoff-type oxidation is observed with allylic alcohols, while the oxidation of terminal olefins proceeds in Markownikoff manner (equation 40)[125–127,129].



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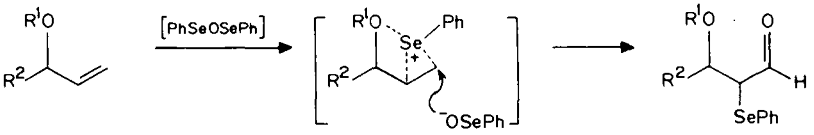
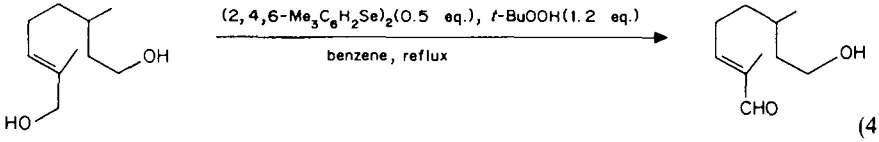


(40)

In connection with this reaction system, oxidation of allylic alcohols to the corresponding aldehydes or ketones by the combined use of *t*-butyl hydroperoxide and diaryl diselenide (equation 26) was reported (equations 41 and 42)[128].



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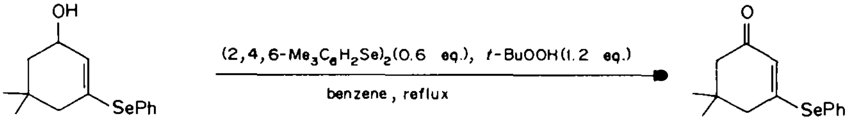


(42)

B. Selenenyl Halides

In this section, general methods for the synthesis of selenenyl halides, and some of their characteristic reactions will be described.

1. Synthesis

The most general preparative method of selenenyl halides is direct halogenation of corresponding diselenides (equation 43)[114,151,154–161].

$$\text{RSeSeR} + \text{Cl}_2\,(\text{or Br}_2) \rightarrow 2\,\text{RSeCl}\,(\text{or } 2\,\text{RSeBr}) \qquad (43)$$

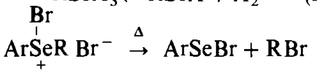
Benzeneselenenyl chloride has been prepared from bromobenzene as shown in equation (44) and is commercially available[162].

$$\text{PhBr} \xrightarrow[\text{2. Se}]{\text{1. Mg}} \text{PhSeMgBr} \xrightarrow[64-70\%]{\text{Br}_2} \text{PhSeSePh} \xrightarrow[88-93\%]{\text{Cl}_2} \text{PhSeCl} \qquad (44)$$

Alternative methods for the synthesis of selenenyl halides are shown in equations (45)–(47), and their details have been described in Klayman's review[1].

$$\text{ArSeCN} + \text{Cl}_2\,(\text{or Br}_2) \rightarrow \text{ArSeCl}\,(\text{or ArSeBr}) \quad \text{(Refs. 134, 157, 163, 164)} \qquad (45)$$

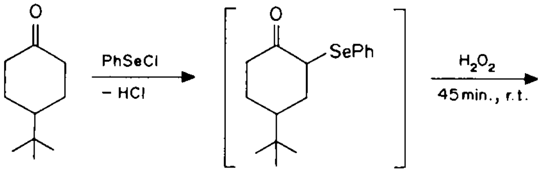
$$\text{RSeX}_3 \rightleftharpoons \text{RSeX} + \text{X}_2 \quad \text{(Refs. 153, 154)} \qquad (46)$$



$$\text{Ar}\underset{+}{\overset{\text{Br}}{\text{Se}}}\text{R Br}^- \xrightarrow{\Delta} \text{ArSeBr} + \text{RBr} \quad \text{(Ref. 165)} \qquad (47)$$

2. Reactions

a. With carbonyl compounds. Sharpless and coworkers have reported that benzeneselenenyl chloride reacts with various ketones and aldehydes to give α-phenylselenenyl carbonyl compounds, which on treatment with H_2O_2 or $NaIO_4$ at room temperature yield the corresponding α,β-unsaturated ketones or aldehydes (equations 48 and 49)[114,154].



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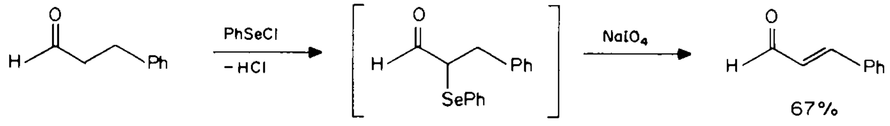
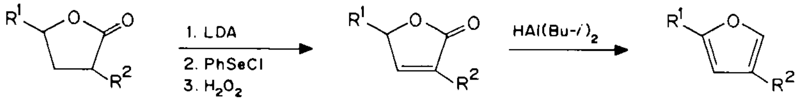


(49)

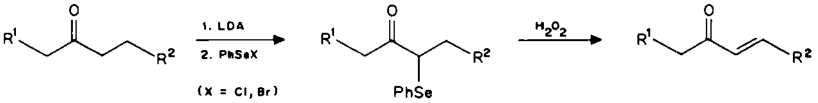
Reich and coworkers have reported a higher yield method in which benzeneselenenyl halides are allowed to react with lithium enolates prepared *in situ* from lithium diisopropylamide (LDA) and ketones (Table 2, entries 1–4)[115,168]. Similarly, α,β-unsaturated esters[115] and lactones[154] are synthesized from the corresponding saturated compounds as shown in Table 2 (entries 5–7).

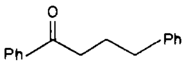
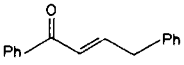
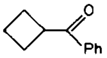
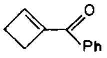
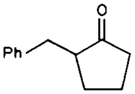
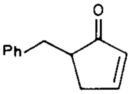
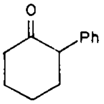
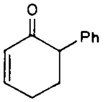
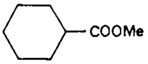
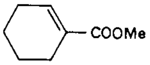
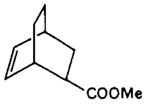
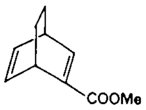
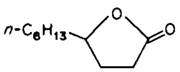
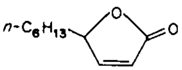
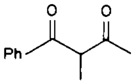
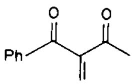
A similar method can be applied for the preparation of substituted furans (equation 50)[171].



(50)

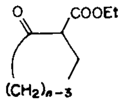
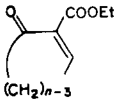
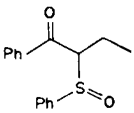
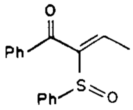
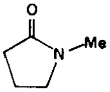
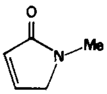
TABLE 2. Synthesis of α,β-unsaturated carbonyl compounds by reaction of phenylselenenyl halides with lithium enolates[114,115,154,166–170]



Entry	Starting material	Product	Yield (%)	Ref.
1			84	115, 168
2			83	115, 168
3			66	115, 168
4			60	115, 168
5			96	115
6			68	115
7			56[a]	154
8			80[b]	115

(*Contd.*)

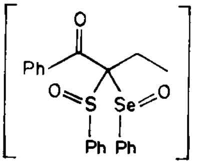
TABLE 2. (*Contd.*)

Entry	Starting material	Product	Yield (%)	Ref.
9	 	 	$n = 8$ 93[b] $n = 7$ 93[b] $n = 6$ 89[b] $n = 5$ 81[b]	115
10	 	 	71	115
11	 	 	55	170, 113

[a] $MeCO_3H$ is used as the oxidizing agent.
[b] NaH is used instead of LDA.

In the case of 1,3-dicarbonyl compounds, sodium hydride is used as a base, and α,β-unsaturated 1,3-dicarbonyl compounds are obtained regioselectively (Table 2, entries 8–9)[115].

The reaction with a β-ketosulphoxide proceeds through intermediate **10**, and gives only a sulphinoenone by *syn* elimination of a benzeneseleninyl group and a β-hydrogen. Elimination of a benzenesulphinyl group does not take place (Table 2, entry 10)[115].

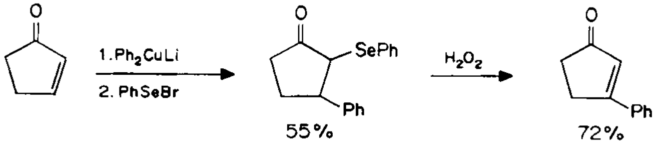


(10)

Two equivalents of LDA are employed for the preparation of α,β-unsaturated lactams (Table 2, entry 11)[170].

Other examples of α,β-unsaturated carbonyl compounds prepared by selenenylation followed by selenoxide β-elimination are summarized in Reich's review[113].

Benzeneselenenyl halides also react similarly with copper enolates[167], aluminium enolates[172] and zirconium enolates[172] (equations 51 and 52).



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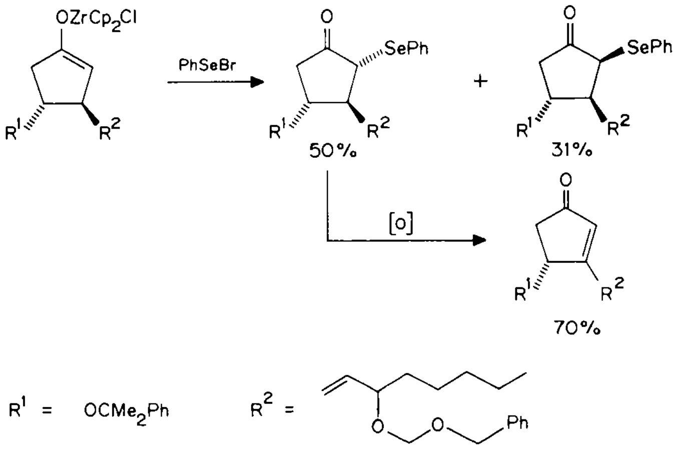
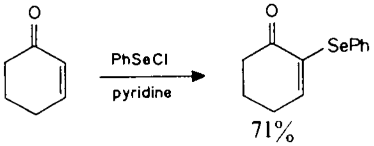
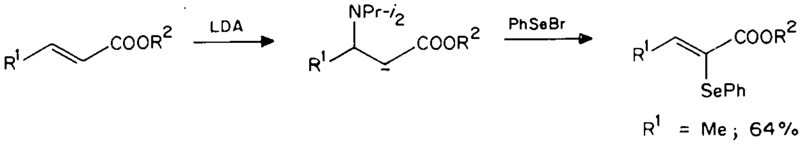


(52)

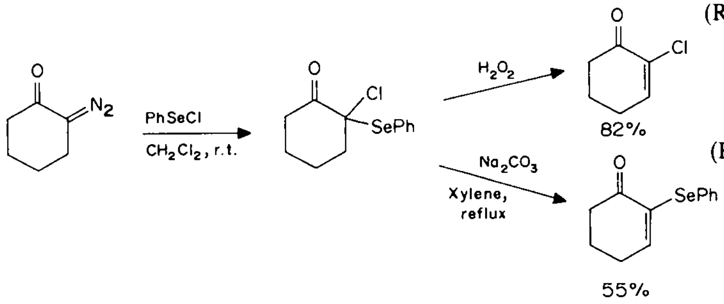
The reactions of selenenyl halides with α,β-unsaturated carbonyl compounds or α-diazoketones are found to give α-selenenyl α,β-unsaturated carbonyl compounds (equations 53–55).



(Ref. 173) (53)

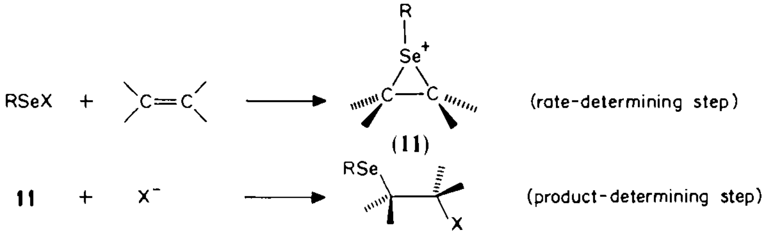


(Ref. 174) (54)



(Ref. 175) (55)

b. With unsaturated compounds. (*i*) *With alkenes.* Electrophilic *anti* addition of selenenyl halides to olefinic double bonds has been found to proceed stereospecifically[114,160,176–191]. The rate law of the reaction is overall second order—first order in both alkenes and selenenyl halides[181]. From these observations, the mechanism shown in equation (56), involving a seleniranium ion (**11**), is postulated[180].

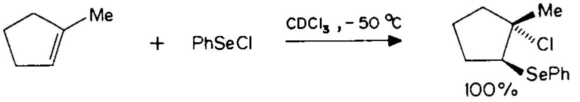


With respect to the regiochemistry of the addition, Raucher[178,179] has shown that the reaction of benzeneselenenyl bromide with terminal olefins gives predominantly *anti*-Markownikoff adducts under kinetically controlled conditions (CCl_4, −20 °C). The adducts isomerize to give predominantly Markownikoff adducts in 48 h at 25 °C in CCl_4 (equation 57).

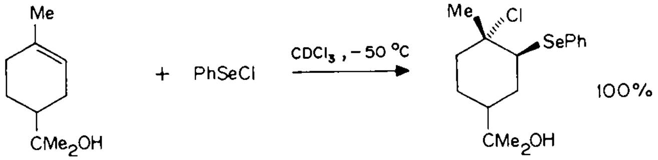
$$\mathrm{Me(CH_2)_3CH{=}CH_2} \xrightarrow[\mathrm{CCl_4},\,-20\,^{\circ}\mathrm{C}]{\mathrm{PhSeBr}} \mathrm{Me(CH_2)_3CH(SePh)CH_2Br}$$

$$\xrightarrow{\mathrm{CCl_4},\,-25\,^{\circ}\mathrm{C}} \mathrm{Me(CH_2)_3CH(Br)CH_2SePh} \tag{57}$$

On the other hand the reaction with internal olefins usually gives a mixture of Markownikoff and *anti*-Markownikoff adducts. Their ratio is influenced by both electronic and steric effects of the substituents[180,181]. Liotta and Zima have synthesized adducts isomerize to give predominantly Markownikoff adducts in 48 h at 25 °C in CCl_4 (equation 57).

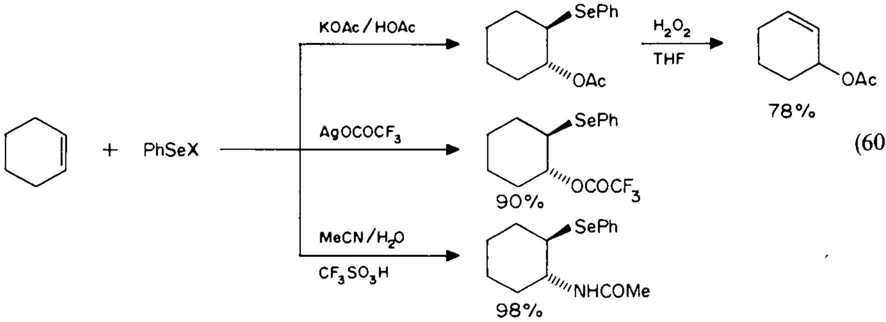


(58)



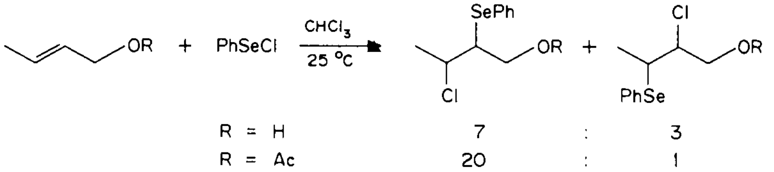
(59)

The adducts of selenenyl halides and olefins are generally unstable both thermally and solvolytically. However, when the reactions are carried out in the presence of various nucleophiles such $KOAc$[114], $AgOCOCF_3$[185,186], H_2O[187,191], ROH[188], $MeCN$[189] and $AgNO_2$[190], thermodynamically stable adducts can be isolated in high yields (equation 60).

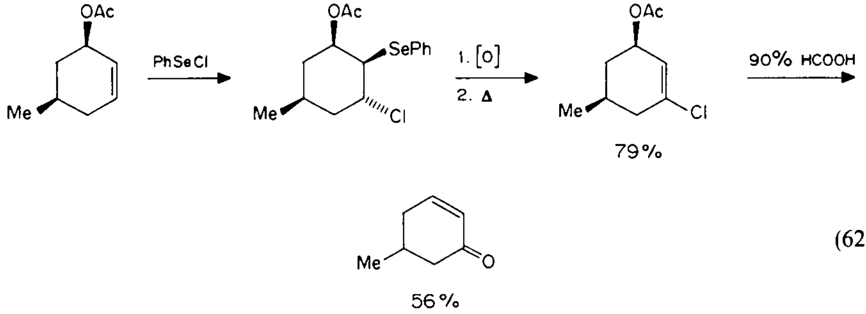


(60)

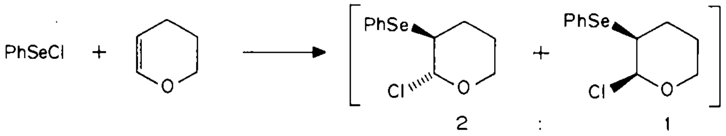
Benzeneselenenyl chloride adds to allylic alcohols and acetates in a highly regio- and stereo-selective fashion (equation 61) and this type of addition can be used as the key step of a simple 1,3-enone transposition sequence (equation 62)[192,193]. However, the addition to 3,4-dihydro-2*H*-pyran is known to be exceptionally non-stereospecific (equation 63)[177].



(61)



(62)

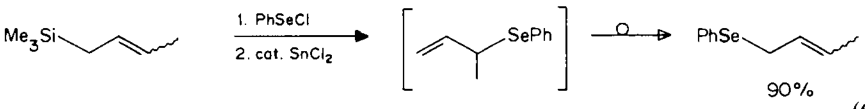


(63)

The reaction of benzeneselenenyl halides with enol ethers gives the corresponding α-phenylseleno ketones in good yields (equation 64)[194–197].

(64)

Benzeneselenenyl chloride reacts regioselectively with allylsilanes to give allyl selenides, through a 1,3-shift of the phenylselenenyl group (equation 65). On the other hand, such 1,3-rearrangement does not take place in the reaction with benzenesulphenyl chloride (equation 66)[198,199].



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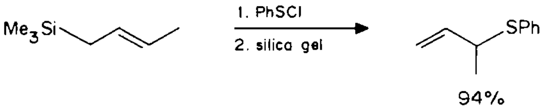
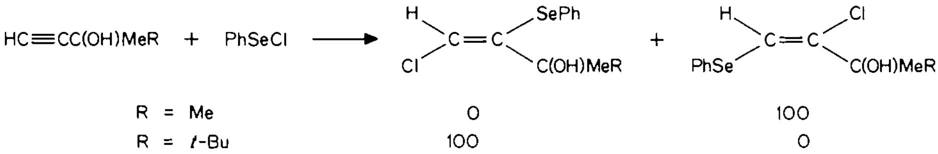


(66)

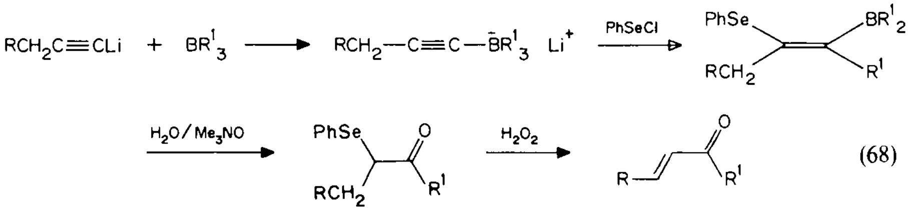
In addition, the reaction of fluoroalkenes with benzeneselenenyl halides has been also reported[183,184].

(*ii*) *With alkynes.* Little is known about the reaction of selenenyl halides with simple alkynes[200]. The reaction of propargyl alcohols with benzeneselenenyl chloride gives regioselectively the corresponding vinyl selenides (equation 67)[201].



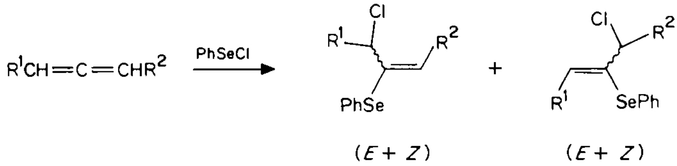
(67)

The reaction of lithium trialkylalkynylborate with benzeneselenenyl chloride, followed by selective oxidation, provides a new synthetic pathway from acetylenes to acyclic *trans*-α,β-unsaturated ketones (equation 68)[202].



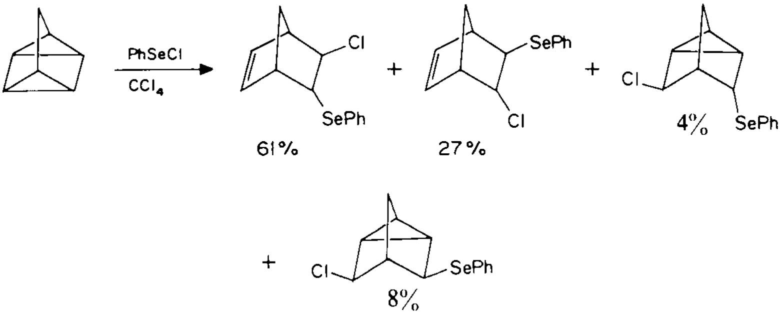
(68)

(*iii*) *With allenes.* Benzeneselenenyl halides also add to allenes, giving 1 : 1 adducts[203–205] in which the phenylselenenyl group is predominantly located at the central carbon of allenes (equation 69).



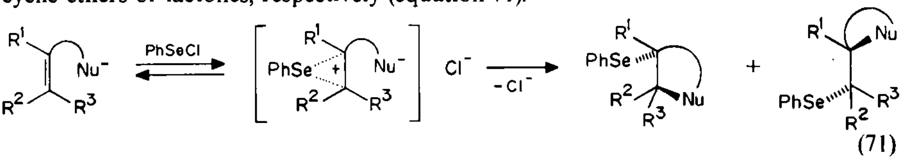
(69)

(*iv*) *With quadricyclene.* The reaction of benzeneselenenyl chloride with tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (quadricyclene) yields adducts of both 1,3- and conjugative 1,6-addition (equation 70)[206].



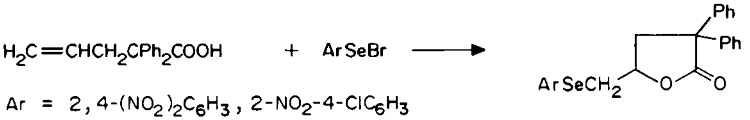
(70)

(*v*) *Cyclofunctionalization.* Electrophilic addition of the phenylselenenyl group to olefins possessing nucleophilic moieties (Nu^-), such as hydroxyl or carboxyl groups, followed by intramolecular ring-closure gives stereospecifically cyclized products, such as cyclic ethers or lactones, respectively (equation 71).



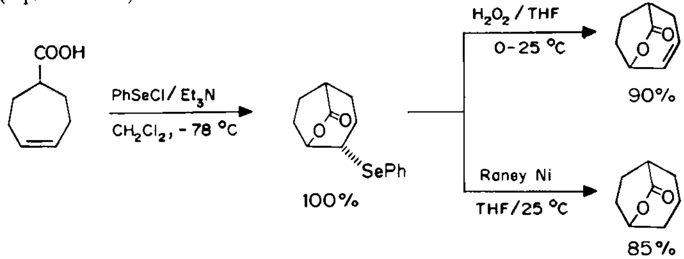
(71)

This type of synthetic reaction is well characterized by the term cyclofunctionalization introduced by Clive and coworkers[207,209]. Another example of cyclofunctionalization in Se chemistry is the reaction of γ,δ-unsaturated carboxylic acids with arylselenenyl bromides (equation 72)[208].

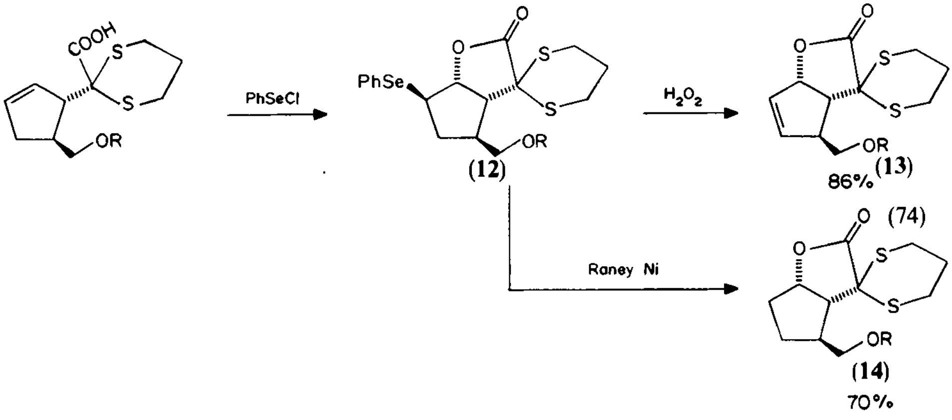


(72)

Recently this type of cyclization has been studied extensively and a wide variety of cyclic compounds have been synthesized with a high degree of regio- and stereo-selectivity. Some examples are shown in Table 3. Many kinds of internal nucleophiles have been examined for the cyclofunctionalization:—COOH (entries 1–6)[207–212],—COOR (entry 7)[213,217], $>$C=O (entry 8)[214],—OH (entries 9–11)[215–217,222],—NHCOOEt (entries 12, 13)[218,219,228],—SH (entry 14)[220] and $>$C=C$<$ (entry 15)[221,229]. The resulting benzeneselenenyl lactones (entry 4) can be treated with H_2O_2 or some reducing agents such as Raney Ni or tri-*n*-butyltin hydride to give unsaturated or saturated lactones (equation 73)[210,211].



(73)



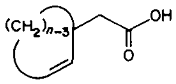
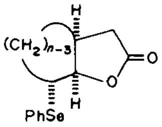
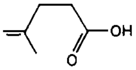
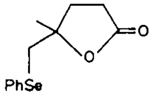
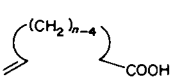
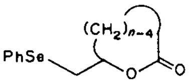
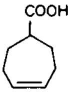
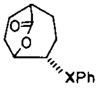
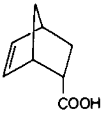
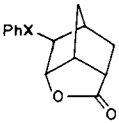
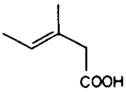
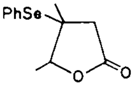
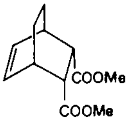
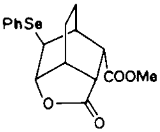
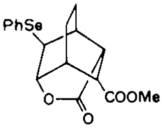
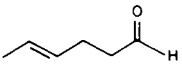
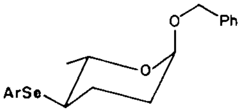
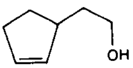
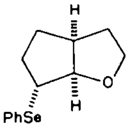
(12)

(13)

(74)

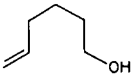
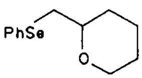
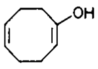
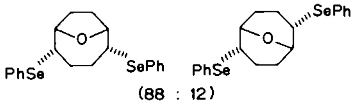
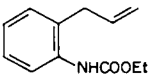
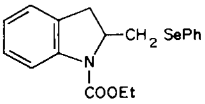
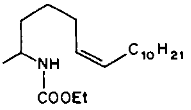
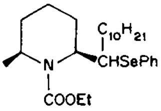
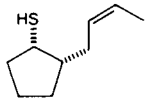
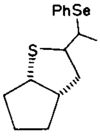
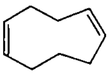
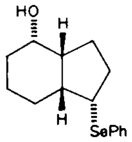
(14)

TABLE 3. Cyclofunctionalization of unsaturated compounds with benzeneselenenyl chloride

Entry	Substrate	Product	Yield (%)		Ref.
1			$n = 5$ $n = 6$ $n = 7$	73 82 97	207, 209
2				85	209
3			$n = 5$ $n = 6$ $n = 7$	80 74 70	210
4			X = Se X = S	100 (82)[a]	210, 211
5			X = Se X = S	95 (95)[a]	210, 211
6				86	212
7		 		68:25	213
8				67[b]	214
9				84	215

(*Contd.*)

TABLE 3. (*Contd.*)

Entry	Substrate	Product	Yield (%)	Ref.
10			90	216
11		 (88 : 12)	92[c]	217
12			73	218
13			72	219
14			80	220
15			68[d]	221

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[a] PhSCl was used instead of PhSeCl.

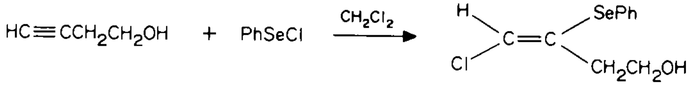
[b] p-$ClC_6H_4SeBr/PhCH_2OH$.

[c] PhSeCl/aq. MeCN.

[d] $PhSeCl/AcOH/AcONa$ and then $MeOH/H_2O/K_2CO_3$.

Applications to the synthesis of complex biologically active molecules have also been reported[224–227]. For example, lactones **12**, **13** and **14** are important synthetic intermediates for the construction of prostaglandin A2 and blefeldin A (equation 74)[210,211].

On the other hand, the reaction of benzeneselenenyl chloride with alkynyl alcohols gives only 1,2-adducts (equation 75)[223].



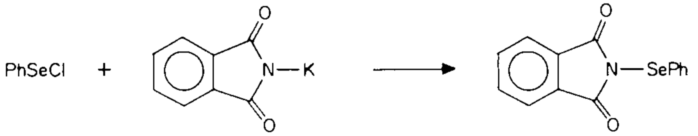
89%

(75)

c. With nucleophiles. A variety of selenenic acid derivatives RSeX (X = OH[144,187], OR[114,185,186], NR_2[216,230], CN[231,236]) have been synthesized by nucleophilic displacement on the Se atom of selenenyl halides. Some examples are shown in equations (76)–(79). SCN^-[232,233] and RSO_2^-[234] have also been used as nucleophiles.

$$2\text{-}O_2NC_6H_4SeX + H_2O \rightarrow 2\text{-}O_2NC_6H_4SeOH \qquad (76)$$

$$RSeX + KOAc \xrightarrow{AcOH} RSeOAc \qquad (77)$$

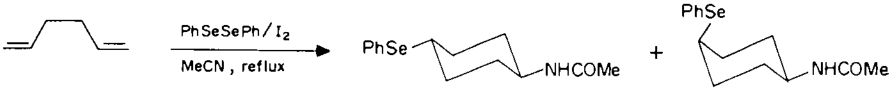


(78)

$$PhSeCl + Me_3SiCN \rightarrow PhSeCN + Me_3SiCl \qquad (79)$$

3. *Selenenyl iodides and fluorides*

Recently the reaction of diphenyl diselenide with I_2 and 1,5-hexadiene has been reported to give a 68:32 mixture of **15** and **16** in 62% yield (equation 80)[235]. It is assumed that benzeneselenenyl iodide is formed *in situ* and plays an important role as the active reagent.



(15) **(16)** (80)

No successful synthesis of selenenyl fluoride has been reported so far.

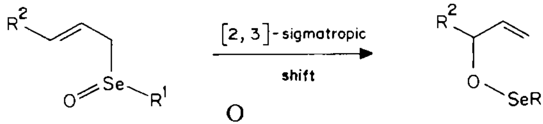
C. Miscellaneous

1. *Selenenic esters and selenocarboxylates*

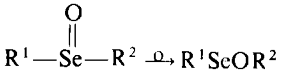
a. Synthesis. Selenenic esters (R^1SeOR^2) are usually prepared by a alcoholysis of selenenyl halides or selenocyanides (equations 81 and 82)[151,237–240]. The simple esterification of selenenic acids has not been reported. It is likely that selenenic esters are formed *in situ* in the rearrangement of selenoxides (equations 83 and 84)[119–124,142]. Selenocarboxylates ($R^1SeOCOR^2$) are produced by the reaction of selenenyl halides with some metal carboxylates (equation 85)[114,166].

$$R^1SeBr \xrightarrow{R^2OH} R^1SeOR^2 \qquad (81)$$

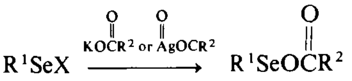
$$R^1SeCN \xrightarrow{R^2OH} R^1SeOR^2 \qquad (82)$$



(83)

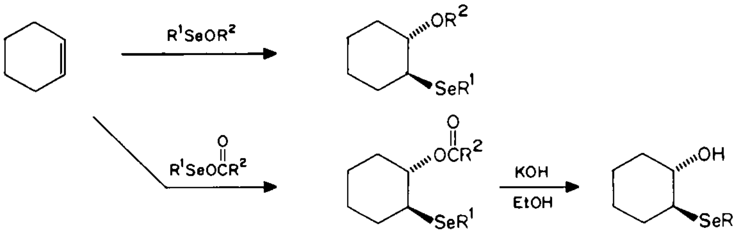


$$R^1—\overset{\overset{\displaystyle O}{\|}}{Se}—R^2 \xrightarrow{\Omega} R^1SeOR^2 \qquad (84)$$



$$R^1SeX \xrightarrow{K\text{O}\overset{\text{O}}{\overset{\|}{C}}R^2 \text{ or } AgO\overset{\text{O}}{\overset{\|}{C}}R^2} R^1SeO\overset{\text{O}}{\overset{\|}{C}}R^2 \tag{85}$$

b. Reactions. Selenenic esters and selenocarboxylates are hydrolysed with water to the selenenic acids. The selenenyl group of selenenic esters and selenocarboxylates is electrophilic and can be introduced into organic molecules via oxyselenenylation of various olefins (equation 86)[140,143,166,186].



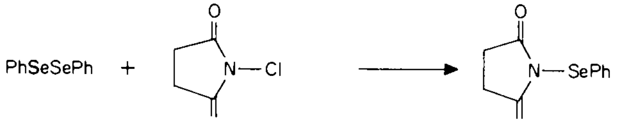
(86)

2. Selenenamides

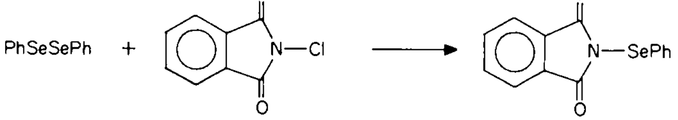
a. Synthesis. Selenenamides are synthesized by the reaction of selenenyl halides or selenenic acids with amines (equation 87)[232,237,245,248,249]. *N*-Phenylselenosuccinimide and *N*-phenylselenophthalimide are prepared by the reaction of diphenyl diselenide with *N*-chlorosuccinimide or *N*-chlorophthalimide (equations 88 and 89)[216,257,283].

$$R^1SeX \text{ or } R^1SeOH \xrightarrow{R_2^2NH} R^1SeNR_2^2 \tag{87}$$

$$X = Cl, Br$$

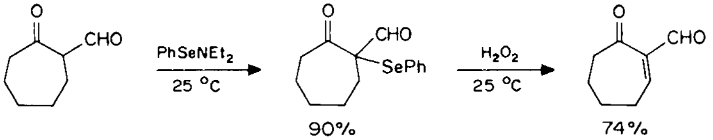


(88)

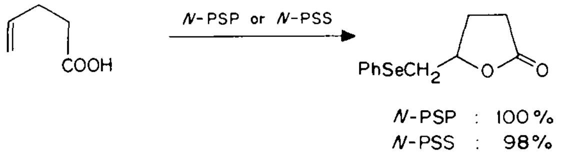


(89)

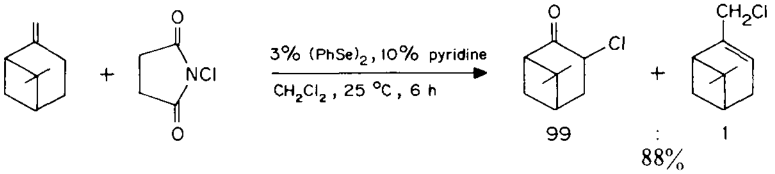
b. Reactions. Selenenamides react with some carbonyl compounds to afford α-selenenyl carbonyl compounds, which can be converted to α,β-unsaturated carbonyl compounds by oxidative elimination (equation 90)[254]. Selenenamides are used for oxyselenenylation of olefins. Especially *N*-phenylselenosuccinimide (*N*-PSS) and *N*-phenylselenophthalimide (*N*-PSP) are reported to be excellent reagents for this purpose (equation 91)[216,257,283]. *N*-



(90)



(91)



(92)

PSS, formed *in situ* also acts as a catalyst for the allylic chlorination by *N*-chlorosuccinimide (NCS) (equation 92)[257].

3. Selenocyanides

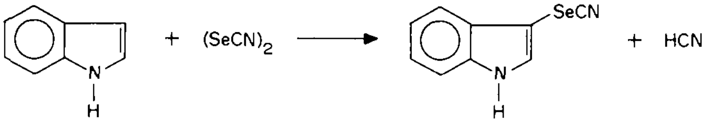
a. Synthesis. Selenocyanides are generally prepared by the reaction of aryl or alkylselenenyl halides (or sulphonates) with cyanide ion (equation 93)[269,270]. Aliphatic selenocyanides can also be produced by the reaction between alkyl halide and $SeCN^-$ (equation 94)[260–268,275,276,295–299]. The use of selenocyanogen as a substitution reagent gives 3-cyanoindole from indole (equation 95)[134,271–274,292,294,300,301].

$$RSeX + CN^- \rightarrow RSeCN + X^- \qquad (93)$$

$$X = \text{halogen}, \text{—}SO_2R^1$$

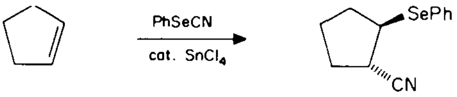
$$RX + KSeCN \rightarrow RSeCN + KX \qquad (94)$$

$$X = \text{halogen}, \text{—}OSO_2R^1, \text{—}HgBr$$



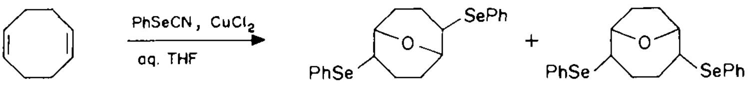
(95)

b. Reactions. Phenyl selenocyanides add to olefinic double bonds in the presence of tetrachlorostannane as catalyst to give 2-phenylselenocyanide (equation 96)[284–287].



(96)

On the other hand, phenyl selenocyanide causes electrophilic selenenylation in the presence of cupric chloride. An application of this reaction is a facile preparation of cyclic ethers by oxyselenation of diolefins using phenyl selenocyanide. For example, 1,5-cyclooctadiene gives a mixture of cyclic ethers in aqueous tetrahydrofuran solution (equation 97)[296,302,306–308,311].



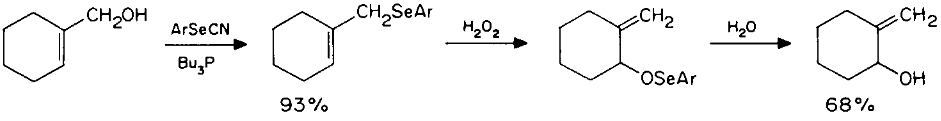
(97)

Hydroxyl groups can be easily converted to arylselenenyl groups using selenocyanides and phosphines. Treatment of alcohols with aryl selenocyanide in the presence of tri-*n*-butylphosphine affords alkyl aryl selenides (equation 98)[312].

$$CH_3(CH_2)_{10}CH_2OH \xrightarrow[Bu_3P,\ THF]{o\text{-}NO_2C_6H_4SeCN} CH_3(CH_2)_{10}CH_2SeC_6H_4NO_2\text{-}o \qquad (98)$$

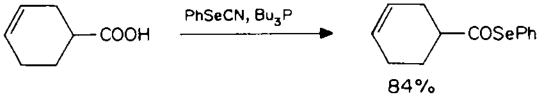
$$94\%$$

In connection with this reaction, a 1,3-rearrangement of primary allylic alcohols can take place as shown in equation (99)[288].

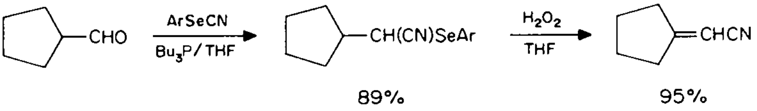


Ar = p-$O_2NC_6H_4$

Aryl selenocyanides also react with carboxylic acids and aldehydes, giving rise to seleno esters and cyanoselenides in excellent yields (equations 100 and 101)[289,290].



(100)



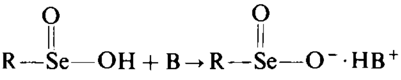
(101)

Ar = o-$O_2NC_6H_4$

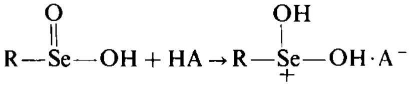
Some other studies concerning Section III, i.e. on selenenic esters, selenocarboxylates[146,147,241–247], selenenamides[250–253,255,256,258,259] and selenocyanides[153,277–282,288,291,293,303–305,309,310] have been reported.

IV. SELENINIC ACIDS AND THEIR ANHYDRIDES

The generalized structures of seleninic acids and their anhydrides can be described as RSe(O)OH and RSe(O)OSe(O)R, respectively. Seleninic acids are less acidic than the corresponding carboxylic acids RCOOH, and are known to be amphoteric: both base and acid react with seleninic acids to give the corresponding salts (equations 102 and 103). Arylseleninic acids and their anhydrides have been used as versatile and specific oxidizing reagents for various organic compounds.



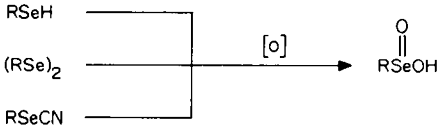
$$R{-}\overset{\overset{\displaystyle O}{\|}}{Se}{-}OH + B \rightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{Se}{-}O^-\cdot HB^+ \qquad (102)$$



$$R{-}\overset{\overset{\displaystyle O}{\|}}{Se}{-}OH + HA \rightarrow R{-}\underset{+}{\overset{\overset{\displaystyle OH}{|}}{Se}}{-}OH\cdot A^- \qquad (103)$$

A. Synthesis

In general, seleninic acids are prepared by oxidation of the corresponding selenols, diselenides and selenocyanides with various oxidizing agents such as HNO_3[264,269,355–357,360], H_2O_2[279,357–359] and AcOOH[279] (equation 104).



(104)

Benzeneseleninic acid is commercially available. Alternative methods for preparation of seleninic acids are shown in equations (105) and (106).

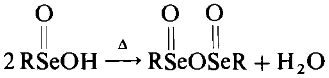
$$RMgBr + SeO_2 \rightarrow RSeO_2MgBr \xrightarrow[H_2O]{H^+} RSeO_2H \qquad \text{(Ref. 1)} \quad (105)$$

$$R = \text{alkyl}$$

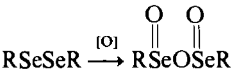
$$3\,RSeX + 2\,H_2O \rightarrow RSeO_2H + RSeSeR + 3\,HX \qquad \text{(Refs. 1,269)} \quad (106)$$

$$X = Cl, Br; R = \text{alkyl, aryl}$$

Seleninic anhydrides are synthesized by dehydration of seleninic acids[246,360] or by oxidation of diselenides with oxidizing reagents such as ozone[246,361] (equations 107 and 108). Benzeneseleninic anhydride is commercially available and can be prepared by the oxidation of diphenyl diselenide with nitric acid or ozone[315].



$$2\,R\overset{O}{\overset{\|}{Se}}OH \xrightarrow{\Delta} R\overset{O}{\overset{\|}{Se}}O\overset{O}{\overset{\|}{Se}}R + H_2O \qquad (107)$$



$$RSeSeR \xrightarrow{[O]} R\overset{O}{\overset{\|}{Se}}O\overset{O}{\overset{\|}{Se}}R \qquad (108)$$

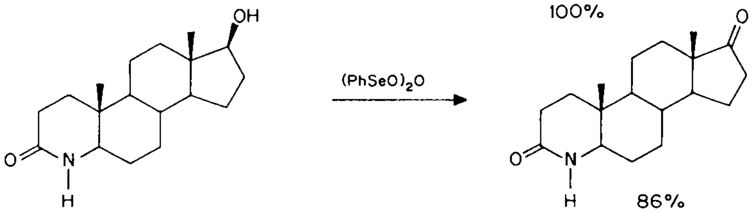
B. Reactions

1. Oxidation of alcohols

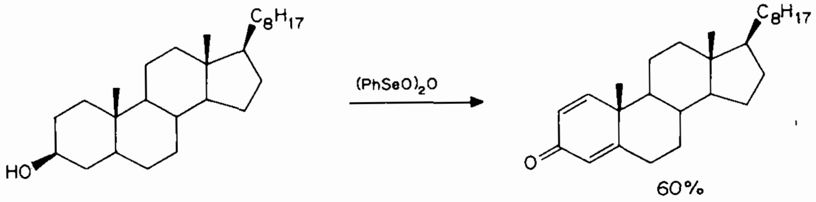
Benzeneseleninic anhydride is a mild oxidizing agent for a variety of alcohols, giving high yields of the corresponding carbonyl compounds (equations 109 and 110)[314]. In some cases, the corresponding α,β-unsaturated compounds are obtained by further dehydrogenation (equation 111)[314]. Benzeneseleninic anhydride can be also used to oxidize

$$PhCH_2OH \xrightarrow{(PhSeO)_2O} PhCHO \qquad (109)$$

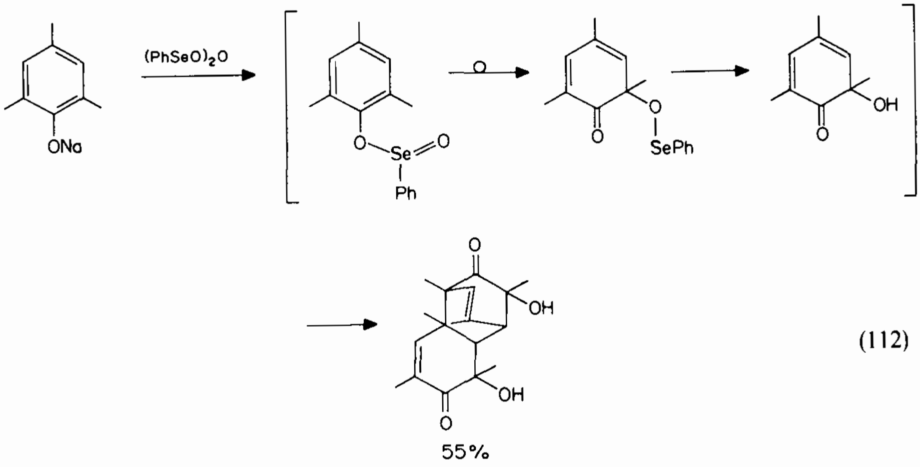
100%



(110)

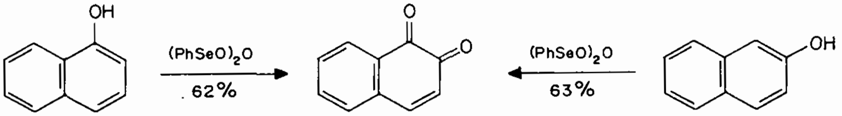


(111)



(112)

simple alkylphenols to hydroxydienones (equation 112)[315], and to convert phenols to *o*-quinones[313,316] (equation 113). The oxidation of phenols in the presence of hexamethyldisilazane gives the corresponding phenylselenoimines, which in turn can be readily reduced to aminophenols (equation 114)[317,318].



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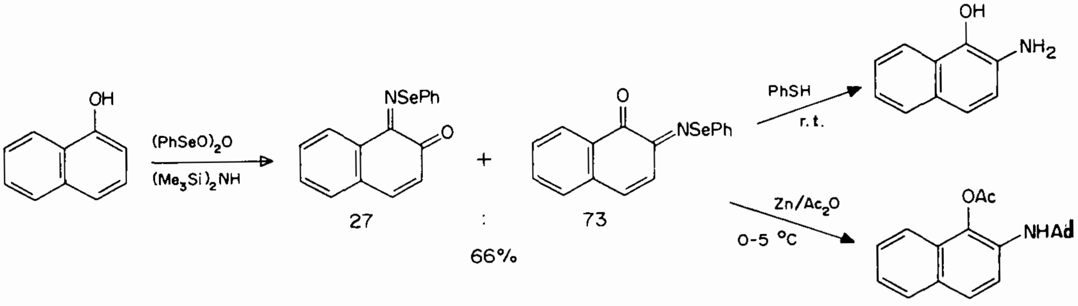
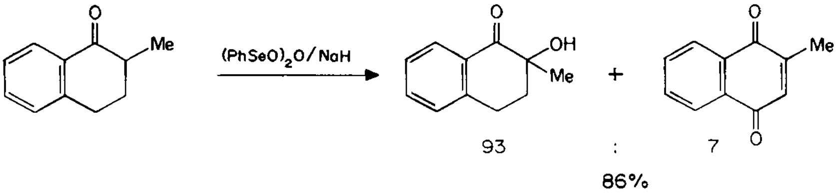


(114)

2. α-Hydroxylation of ketones

Introduction of a hydroxyl group to the α-tertiary carbon of ketones by using benzeneseleninic anhydride has been reported (equations 115 and 116)[323,324,340].



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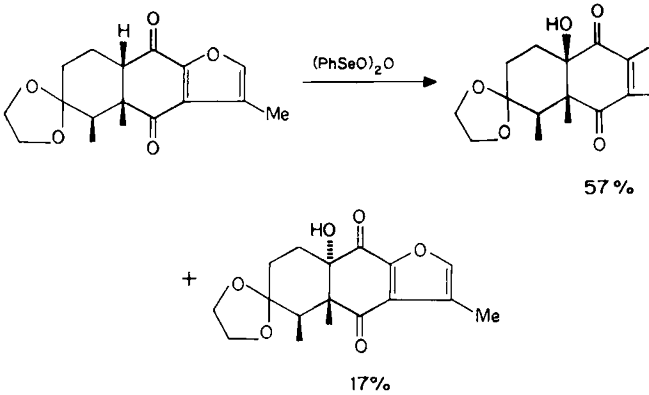
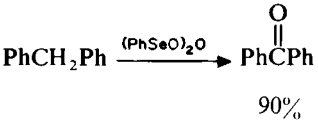


(116)

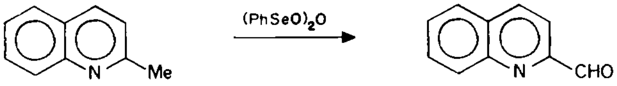
3. Oxidation of benzylic hydrocarbons

A methyl or methylene group adjacent to an aromatic ring is converted to a carbonyl group by benzeneseleninic anhydride (equations 117 and 118)[319,320].



$$PhCH_2Ph \xrightarrow{(PhSeO)_2O} Ph\overset{\overset{\displaystyle O}{\|}}{C}Ph \qquad (117)$$

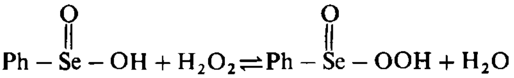
90%



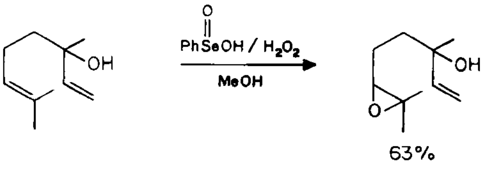
(118)

4. Epoxidation of olefins

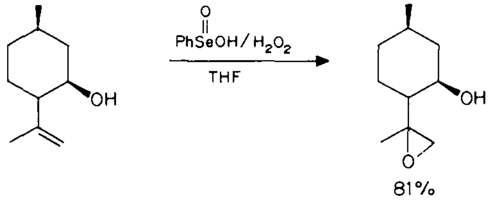
Reaction of benzeneseleninic acid with H_2O_2 generates *in situ* benzeneperoxyseleninic acid (equation 119) which epoxidizes olefinic double bonds (equations 120 and 121)[328,329]. Indeed seleninic acids are found to catalyse epoxidations with H_2O_2 (equation 122)[330].



$$Ph-\overset{\overset{\displaystyle O}{\|}}{Se}-OH + H_2O_2 \rightleftharpoons Ph-\overset{\overset{\displaystyle O}{\|}}{Se}-OOH + H_2O \qquad (119)$$



(120)



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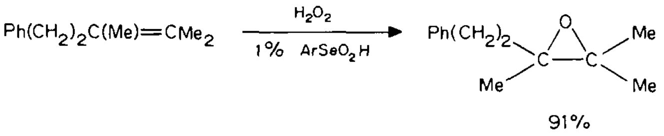
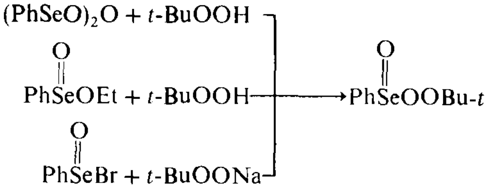


(122)

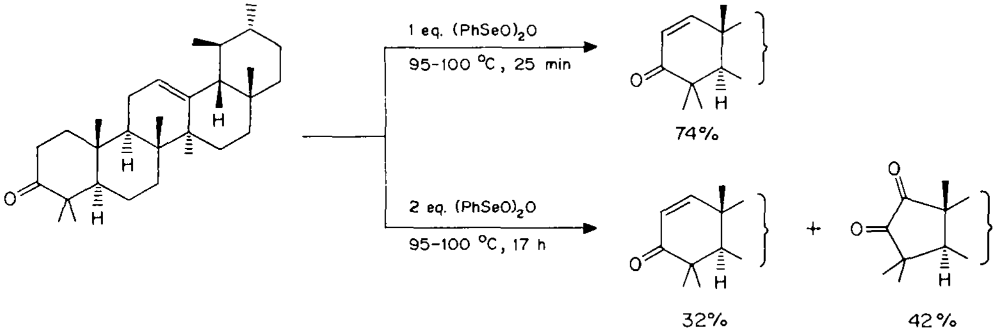
The *t*-butyl ester of benzeneperoxyseleninic acid is synthesized by reacting several seleninic acid derivatives with *t*-butyl hydroperoxide or its sodium salt (equation 123)[331].



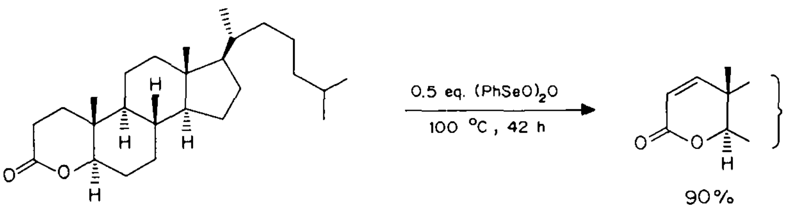
$$\left.\begin{array}{l}(PhSeO)_2O + t\text{-BuOOH}\\ Ph\overset{O}{\overset{\|}{Se}}OEt + t\text{-BuOOH}\\ Ph\overset{O}{\overset{\|}{Se}}Br + t\text{-BuOONa}\end{array}\right] \longrightarrow Ph\overset{O}{\overset{\|}{Se}}OOBu\text{-}t \qquad (123)$$

5. Dehydrogenation

A number of steroidal ketones are dehydrogenated to α,β-unsaturated ketones in excellent yields under mild conditions using benzeneseleninic anhydride. When the

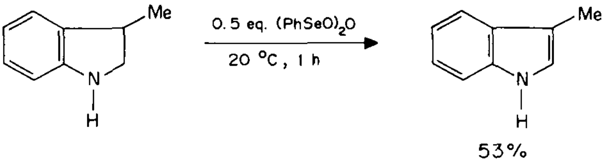


(124)



(125)

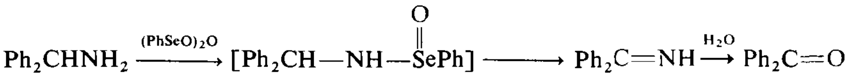
reaction is conducted with excess anhydride for a prolonged reaction time, ring-*A*-contracted diketones are produced in moderate yields (equation 124)[325,339]. Similarly, δ-lactones[338] and lactams[345] undergo smooth dehydrogenation (equation 125). Transformation of indolines to indoles by dehydrogenation with benzene seleninic anhydride is also possible (equation 126)[337].



(126)

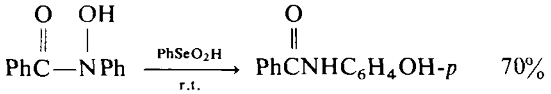
6. Oxidation of nitrogen compounds

Primary amines are oxidized in high yields to carbonyl compounds through the corresponding imines by benzeneseleninic anhydride (equation 127)[326,327]. Hydroxylamines can be converted into nitroso compounds using benzeneseleninic anhydride (equation 128)[347]. In the case of *N*-arylhydroxamic acids, rearrangement to *p*-hydroxybenzanilides has been reported (equation 129)[332].



$$Ph_2CHNH_2 \xrightarrow{(PhSeO)_2O} [Ph_2CH{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{Se}Ph] \xrightarrow[-PhSeOH]{} Ph_2C{=}NH \xrightarrow{H_2O} Ph_2C{=}O \qquad (127)$$

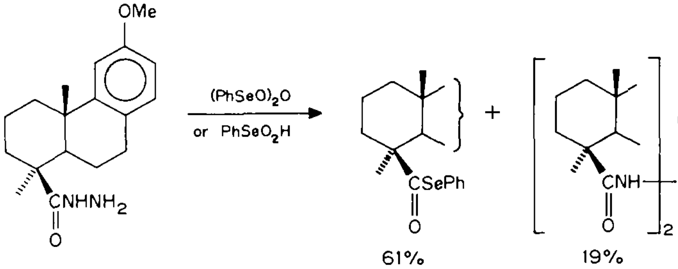
$$Me_3CNHOH \xrightarrow[1\ min]{1\,eq.(PhSeO)_2O} Me_3CN{=}O \quad 96\% \qquad (128)$$



$$Ph\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle OH}{|}}{N}Ph \xrightarrow[r.t.]{PhSeO_2H} Ph\overset{\overset{\displaystyle O}{\|}}{C}NHC_6H_4OH\text{-}p \quad 70\% \qquad (129)$$

Back has reported the reaction of a variety of hydrazines with benzeneseleninic acid and anhydride, in which aryl, acyl or sulphonhydrazides are converted to phenyl selenides as shown in equations (130–132). Hydrazones from aldehydes and hydrazo compounds can

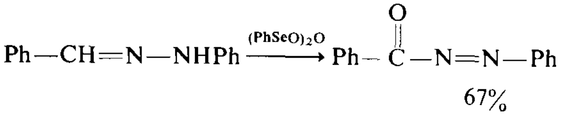
$$p\text{-}O_2NC_6H_4NHNH_2 \xrightarrow[\text{or } PhSeO_2H]{(PhSeO)_2O} \underset{60\%}{p\text{-}O_2NC_6H_4SePh} + \underset{20\%}{PhNO_2} \qquad \text{(Ref. 336) (130)}$$



(Refs. 138, 139, 336) (131)

$$PhSO_2NHNH_2 \xrightarrow[\text{or } PhSeO_2H]{(PhSeO)_2O} \underset{88\%}{PhSO_2SePh} \qquad \text{(Ref. 333) (132)}$$

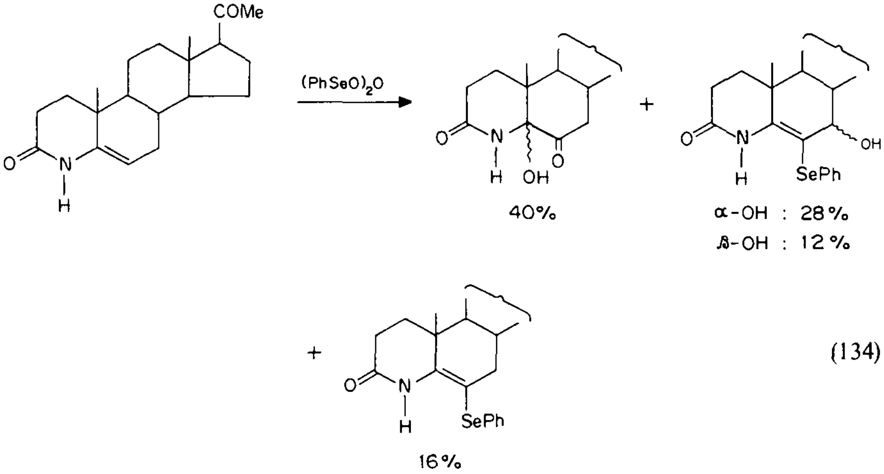
be readily oxidized with benzeneseleninic anhydride to afford high yields of azo compounds (equation 133)[347].



$$\mathrm{Ph{-}CH{=}N{-}NHPh} \xrightarrow{(\mathrm{PhSeO})_2\mathrm{O}} \mathrm{Ph{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}N{=}N{-}Ph} \quad (133)$$

67%

Enamides react with benzeneseleninic anhydride to give Pummerer-type products (equation 134)[344,354].

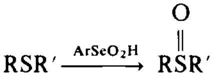


(134)

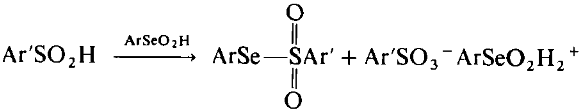
7. Reaction with sulphur and phosphorus compounds

Seleninic acids react with thiols[349,350], sulphides[351], sulphinic acids[352] and phosphines[351] to give the corresponding oxidized products (equation 135–138). The kinetics of these reactions have been studied in detail[349–352].

$$\mathrm{RSH} \xrightarrow{\mathrm{ArSeO_2H}} \mathrm{RSSR} \qquad (135)$$



$$\mathrm{RSR'} \xrightarrow{\mathrm{ArSeO_2H}} \mathrm{R\overset{\overset{\displaystyle O}{\|}}{S}R'} \qquad (136)$$

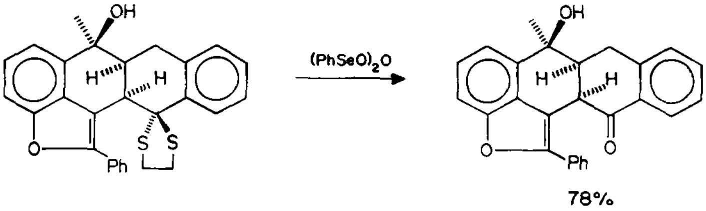


$$\mathrm{Ar'SO_2H} \xrightarrow{\mathrm{ArSeO_2H}} \mathrm{ArSe{-}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}Ar'} + \mathrm{Ar'SO_3^-ArSeO_2H_2^+} \qquad (137)$$

$$\mathrm{Ph_3P} \xrightarrow{\mathrm{ArSeO_2H}} \mathrm{Ph_3P{=}O} \qquad (138)$$

8. Deprotection

Benzeneseleninic anhydride smoothly regenerates parent ketones and aldehydes from their thioacetals in high yields under mild conditions (equation 139)[341–343]. Similarly ketone hydrazones, oximes and semicarbazones are converted to the parent carbonyl compounds by treatment with benzeneseleninic anhydride (equation 140)[346,348]. Conversion of thiocarbonyl compounds to their corresponding oxo derivatives has been performed successfully by using benzeneseleninic anhydrides (equation 141)[321,322].



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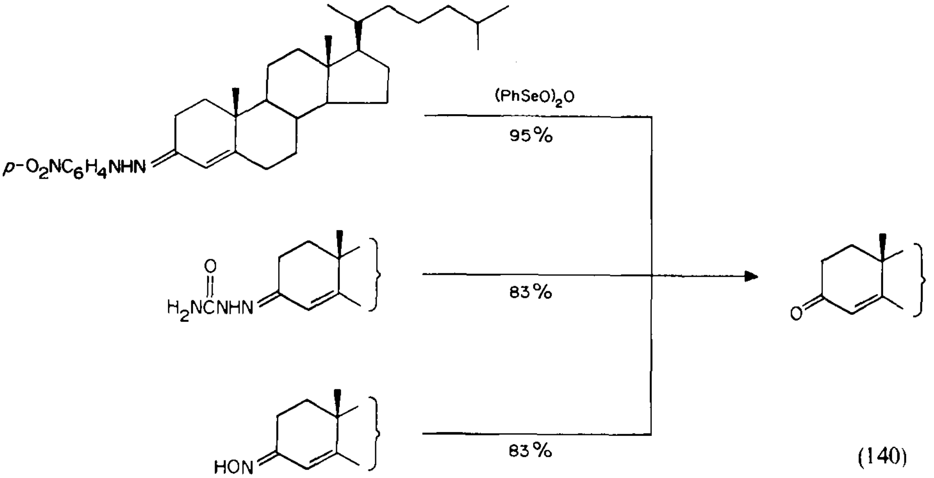

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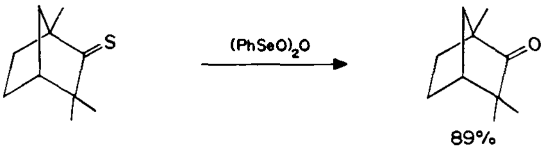


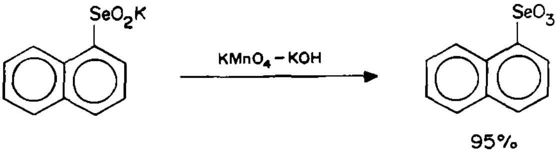
(141)

Some other studies, concerning Section IV, i.e. on seleninic acids and their anhydrides have been reported[281,334,335,353].

V. SELENONIC ACIDS AND THEIR DERIVATIVES

A. Synthesis

Little is known about the chemistry of selenonic acids ($RSeO_3H$) and their derivatives compared with the chemistry of selenenic and seleninic compounds, because of their lower thermal stability.



(Ref. 370) (142)

In general, selenonic acids have been prepared by oxidation of the seleninic acids with $KMnO_4$ in alkaline aqueous solution (equation 142)[370]. Several alternative methods for the preparation of selenonic acids and their derivatives are also known[1,141,262,358,362-370]. Examples are given in equations (143) and (144).

$$(H_2NCH_2CH_2Se)_2 \xrightarrow{Cl_2,H_2O} H_2NCH_2CH_2SeO_3H \quad \text{(Ref. 262)} \qquad (143)$$

$$SeO_3 + RSH \rightarrow RSSeO_3H \quad \text{(Ref. 363)} \qquad (144)$$

B. Reactions[362,351,371,372]

Selenonic acids are used as oxidizing reagents in the oxidation of alkyl sulphides and triphenylphosphine to give alkyl sulphoxides and triphenylphosphine oxide, respectively[351]. The reaction between a selenonic acid and HI gives rise to I_2 and diselenide[262]. Aminolysis of methyl benzeneselenonate provides the corresponding selenonamides (equation 145)[371].

$$PhSeO_3Me + HNR^1R^2 \rightarrow PhSeO_2NR^1R^2 \qquad (145)$$

VI. TELLURIUM ANALOGUES

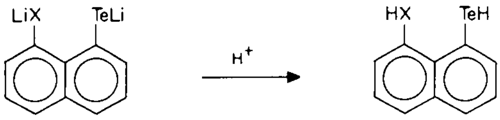
A. Tellurols

Tellurols are much more sensitive to oxygen than selenols, and are readily oxidized to ditellurides. Simple aliphatic tellurides are water-insoluble liquids. However, tellurols are soluble in aqueous alkali because of their acidic character. Aliphatic tellurols have been synthesized by the reduction of ditellurides with Na in liquid NH_3 or by the reaction of aluminium telluride with alcohols (equations 146 and 147). Aromatic tellurols cannot be isolated in a pure form. They are usually generated *in situ* and used for successive reactions (equations 148 and 149).

$$R_2Te_2 \xrightarrow{Na/liq.NH_3} [RTeNa] \xrightarrow{dil.H_2SO_4} RTeH \quad \text{(Ref. 381)} \qquad (146)$$

$$Al_2Te_3 + ROH \xrightarrow[\text{under } H_2]{240-350\,^{\circ}C} RTeH \quad \text{(Refs. 382–384)} \qquad (147)$$

$$\begin{tikzcd}[column sep=small] (RTe)_2 + R^1MgX \arrow[r] & RTeMgX \arrow[d, "H_2O"] + RTeR^1 \quad \text{(Ref. 385)} \qquad (148) \\ & RTeH + MgX(OH) \end{tikzcd}$$



(Refs. 386, 387) (149)

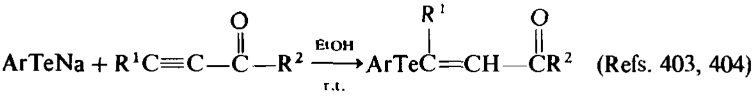
X = S, Se, Te

Metal tellurolates, which are generated from the reaction of elemental Te with organometallic compounds RM (equation 150), are often employed for the synthesis of asymmetric diorganyl tellurides (equations 151 and 152). Aromatic tellurols or tellurolates are also prepared *in situ* by reduction of ditellurides with $NaBH_4$[421,422]. The tellurols formed in this way are employed directly in an addition reaction to alkynes or in a substitution reaction with alkyl halides (equation 153)[421–425].

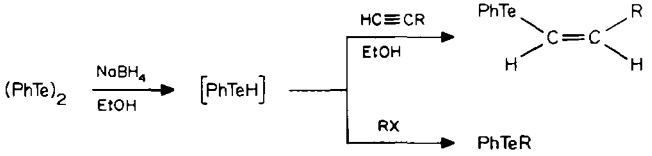
$$\mathrm{RM + Te \rightarrow RTeM} \qquad (150)$$

$$\mathrm{M = MgX^{388-390}, Li^{390-393}, Na^{394-396}}$$

$$\mathrm{PhLi + Te \rightarrow PhTeLi \xrightarrow{RX} PhTeR} \qquad \text{(Refs. 40, 397–402)} \qquad (151)$$

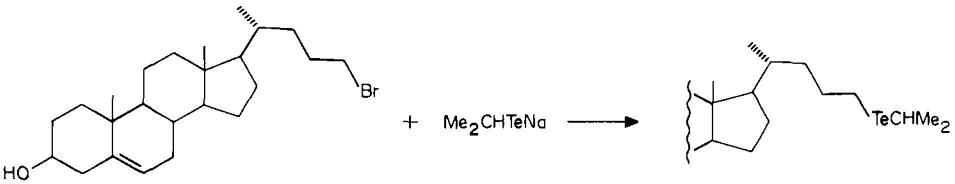


$$\mathrm{ArTeNa + R^1C{\equiv}C{-}\overset{\overset{O}{\|}}{C}{-}R^2 \xrightarrow[\text{r.t.}]{\text{EtOH}} ArTe\overset{\overset{R^1}{|}}{C}{=}CH{-}\overset{\overset{O}{\|}}{C}R^2} \qquad \text{(Refs. 403, 404)} \qquad (152)$$

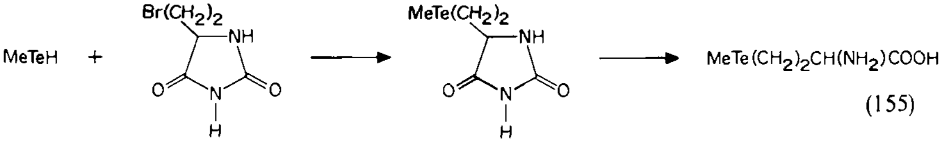


(153)

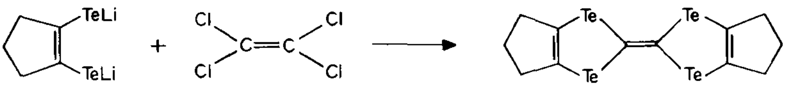
Recently, biologically important compounds[405–414] such as telluro steroids[405–410] and telluroamino acids[411] and superconductive materials such as tetratellurofulvalenes[415–417] have been synthesized from tellurols or tellurolates which were prepared by these methods (equations 154–156).



(154)



(155)



(156)

Lithium and sodium tellurolates are used for the reductive dehalogenation of α-halocarbonyl compounds (equation 157)[418–420].

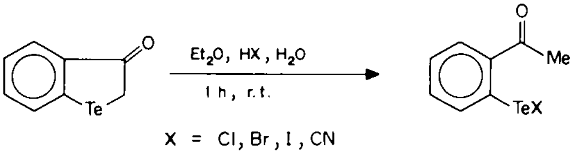
$$\mathrm{RCOCH_2X + ArTe^- \rightarrow [RCOCH_2TeAr] \xrightarrow{ArTe^-/H^+} RCOMe + (ArTe)_2} \qquad (157)$$

B. Tellurenyl Compounds

In general tellurenyl derivatives are unstable. Therefore they have been isolated as complexes with donor molecules such as thioureas or selenoureas. An alkyltellurenyl chloride–thiourea complex has been prepared from tellurinyl trichloride and thiourea[426–429] (equation 158).

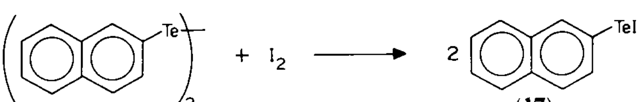
$$\mathrm{RTeCl_3 + 3\,S{=}C(NH_2)_2 \rightarrow RTeCl{\cdot}S{=}C(NH_2)_2} \qquad (158)$$

The isolation of aryltellurenyl halides having an electron-withdrawing group in the position *ortho* to the Te atom has been successfully achieved (equation 159)[430–433]



(159)

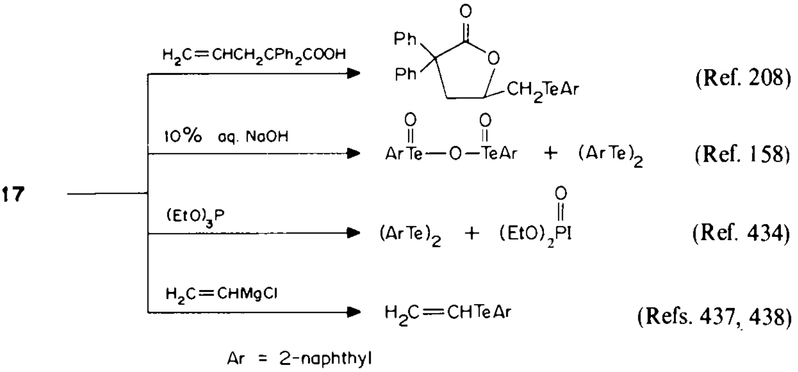
Vicentini and coworkers have reported that 2-naphthyltellurenyl iodide **17** can be isolated in a pure form by reaction of the ditelluride with I_2 (equation 160)[158].



(17)

(160)

Similarly, several aryltellurenyl halides (ArTeX: Ar = Ph, 4-$MeOC_6H_4$, 3,4-$(MeO)_2C_6H_3$, 4-PhC_6H_4, 2-PhC_6H_4; X = Br, I) have been isolated from the reaction of diaryl ditellurides with halogens[435,436]. 2-Naphthyltellurenyl iodide undergoes various types of reactions as shown in equation (161).



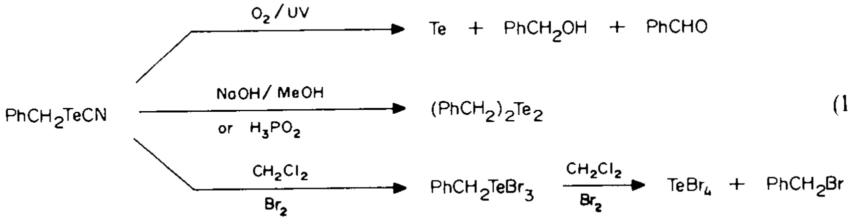
(161)

Several tellurocyanides have been prepared as shown in equations (162) and (163).

$$(PhTe)_2 \xrightarrow[\circledcirc\text{-EtOH}]{NaBH_4} PhTeNa \xrightarrow[EtOH]{BrCN} PhTeCN \qquad \text{(Ref. 439)} \qquad (162)$$

$$KCN + Te \xrightarrow{Me_2SO} KTeCN \xrightarrow{PhCH_2Cl} PhCH_2TeCN \qquad \text{(Ref 440)} \qquad (163)$$

Benzyl tellurocyanide is reactive towards both oxidizing and reducing reagents (equation 164)[441–444].



(164)

C. Tellurinyl Compounds

Tellurinyl compounds are classified into four groups ($RTeX_3$, R_2TeX_2, R_3TeX, and $RTe(O)X$) with respect to their structures.

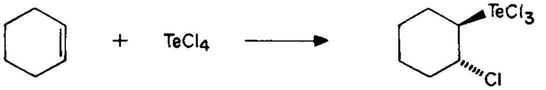
1. $RTeX_3$ (X = halogen, OH, etc.)

Organotellurinyl trihalides have been prepared by the four methods given in equations (165)–(168).

(*i*) ***Reaction of ditellurides with halogens***

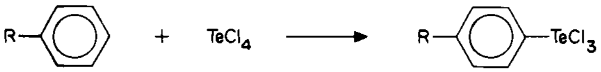
$$R_2Te_2 + X_2 \rightarrow RTeX_3 \qquad \text{(Refs. 158, 454, 455)} \qquad (165)$$

(*ii*) ***Addition to olefins***



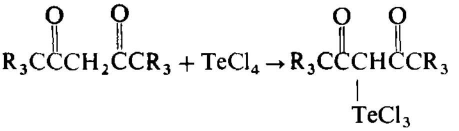
(Refs. 445–451) (166)

(*iii*) ***Aromatic substitution***



(Refs. 452, 453) (167)

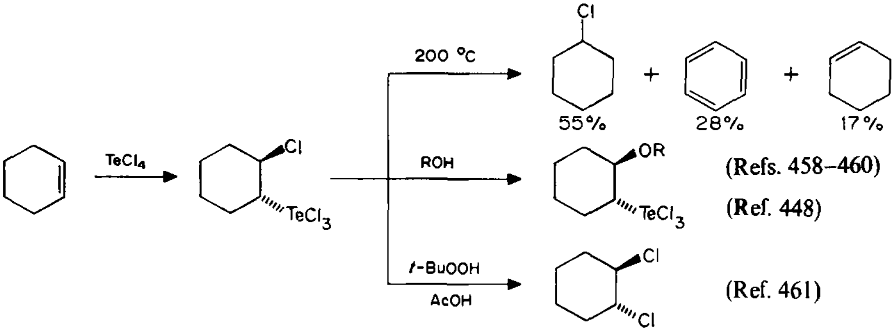
(*iv*) ***Reaction of tellurium tetrachloride with active methylene groups***



$$R_3C\overset{\displaystyle O}{\overset{\|}{C}}CH_2\overset{\displaystyle O}{\overset{\|}{C}}CR_3 + TeCl_4 \rightarrow R_3C\overset{\displaystyle O}{\overset{\|}{C}}\underset{\displaystyle TeCl_3}{\underset{|}{C}H}\overset{\displaystyle O}{\overset{\|}{C}}CR_3$$

(Refs. 454, 456, 457) (168)

vic-Dihalides can be derived from the adducts of $TeCl_4$ to olefins as shown in equations (169) and (170). Combined application of the addition reaction of $TeCl_4$ to olefins and a subsequent reduction of the adducts with Na_2S provides a new method for the conversion of *trans*-olefins into *cis* isomers (equation 171)[449].

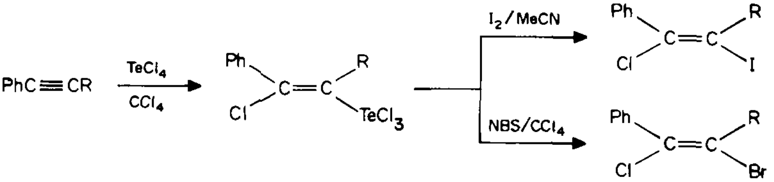


(Refs. 458–460)

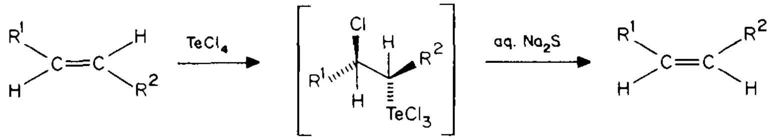
(Ref. 448)

(Ref. 461)

(169)

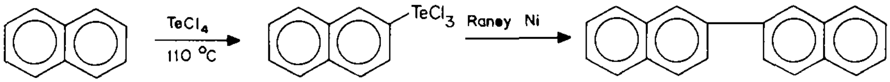


(Ref. 451) (170)



(171)

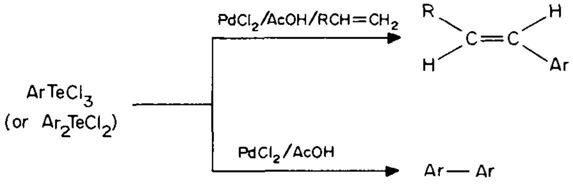
The C—C bond formations shown in equations (172)–(174) have been successfully achieved with the aid of transition metal derivatives.



(Ref. 462) (172)

$$\mathrm{ArTeCl_3} \xrightarrow[2.\ \mathrm{H_2O/H^+}]{1.\ \mathrm{Ni(CO)_4}} \mathrm{ArCOOH}$$

(Ref. 463) (173)



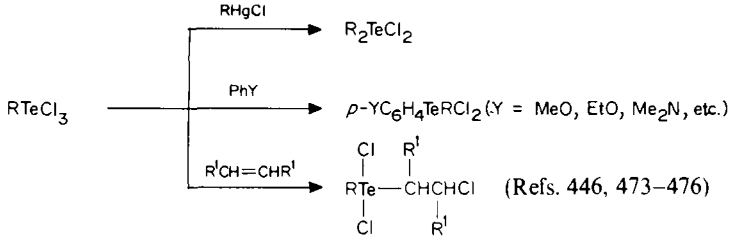
(Refs. 464, 465) (174)

2. R_2TeX_2

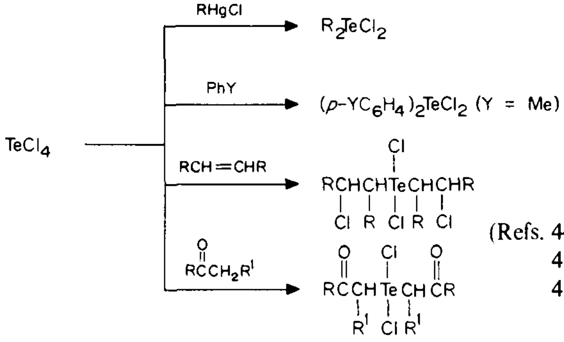
Several methods for the preparation of R_2TeX_2 have been reported (equations 175–178).

$$\mathrm{Te} \xrightarrow{\mathrm{RI\ or\ RN_2{}^+Cl^-\ or\ R_2I^+Cl^-}} \mathrm{R_2TeX_2} \quad \text{(Refs. 466–470)} \quad \mathrm{X = Cl, I} \qquad (175)$$

$$\mathrm{RTeR} \xrightarrow{\mathrm{X_2\ or\ SO_2X_2}} \mathrm{R_2TeX_2} \quad \text{(Refs. 471–473)} \qquad (176)$$



(Refs. 446, 473–476) (177)

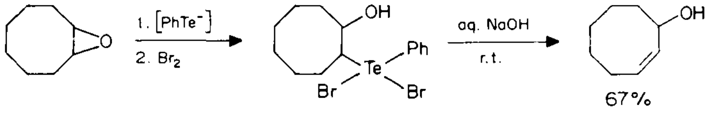


(Refs. 445, 452, 455, 456, 458, 460, 466, 474–477) (178)

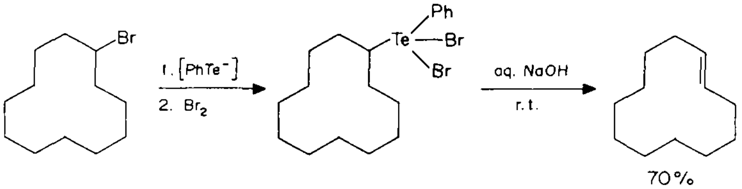
Diaryltellurium dichlorides are reduced with Raney Ni to give aromatic coupling products (equation 179)[462,463,478,479]

$$(p\text{-XC}_6\text{H}_4)_2\text{TeCl}_2 \xrightarrow{\text{Raney Ni}} p\text{-XC}_6\text{H}_4\text{—C}_6\text{H}_4\text{X-}p \qquad (179)$$

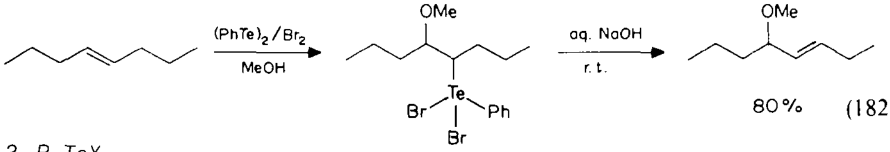
Recently, Uemura and Fukuzawa have reported that olefins, allylic alcohols and/or allylic ethers are obtained in high yields by treatment of *s*-alkyl(phenyl)tellurium dibromides with aqueous NaOH (equations 180–182)[480].



(180)



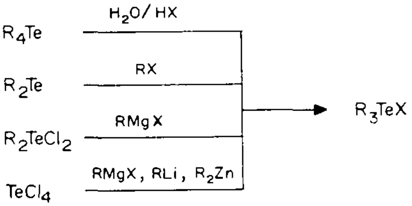
(181)



(182)

3. R_3TeX

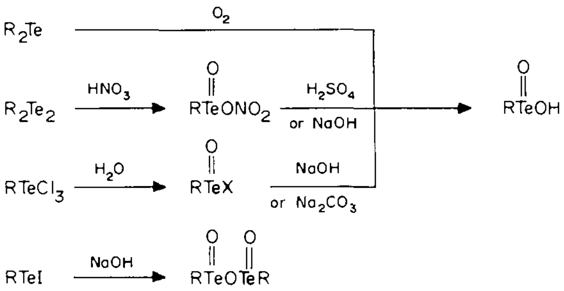
Triorganyltellurium compounds have been synthesized by the methods shown in equation (183).



(Refs. 481, 482)
(Refs. 391, 392, 483–485)
(Refs. 481, 486)
(Refs. 481, 487)
(183)

4. RTe(O)X

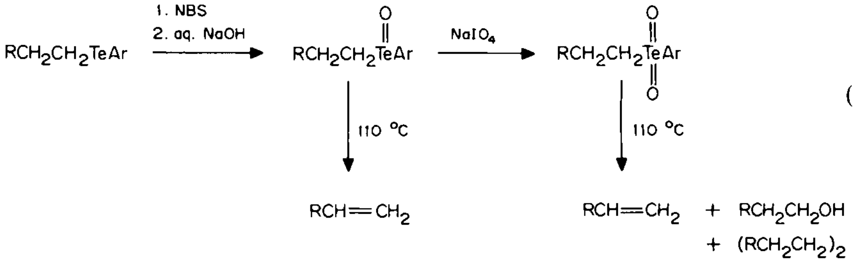
Several synthetic routes for tellurinic acids (RTe(O)OH) and their derivatives (RTe(O)X; X = halogen, NO_3, OTe(O)R) have been reported, and examples are given in equations (184)–(187).



(Refs. 488, 489) (184)
(Ref. 490) (185)
(Refs. 392, 491) (186)
(Ref. 158) (187)

D. Telluronyl Compounds

Little is known about telluronyl compounds, probably because of their instability. Lee and Cava have reported that alkyl aryl telluroxide is oxidized by $NaIO_4$ to the corresponding telluron (or its hydrate) which is then pyrolysed to give a mixture of the olefin, the alcohol and the coupling product. Pyrolysis of the telluroxide gives only the olefinic product (equation 188)[492].



(188)

More details on organotellurium chemistry are summarized in several of Irgolic's books[373,374] and reviews[375–380].

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The Chemistry of Organic
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CHAPTER 17

Stereochemistry and chiroptical properties of organic selenium and tellurium compounds

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I. GENERAL CONSIDERATIONS

Optical activity, as optical rotation or its dispersion with wavelengths (ORD), circular dichroism (CD) and the development of ellipticity, requires the presence of at least one element of chirality in its molecules[1]. Such may involve the Se or Te atom itself in cases where this is either a centre of chirality (selenonium and telluronium salts, selenoxides), or part of an axis of chirality (diselenides, ditellurides). When this chiral moiety also gives observable Cotton effects, a correlation may be possible between the (local) absolute configuration and the signs of these effects. For the diselenides and ditellurides a 'helicity rule', similar to the one known for disulphides[2], is expected, and for all other cases 'sector rules' may hold.

In order to estimate whether a sector rule may be valid at all, Ruch's[3] general algebraic treatment of chirality has first to be consulted. To this end the number n of ligand places in a transitivity area has to be determined, as well as the chirality order o. The first is the number of ligand places which are equivalent under the symmetry operations of the molecule, the second is the maximal number of alike ligands which can be present in a transitivity area without making this molecule achiral. Only if the difference $(n - o)$ equals 1 is a sector rule possible.

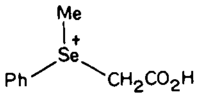
In the onium compounds $n = 3$ and for the selenoxides $n = 2$. As in both cases the chirality order $o = 1$, only for the latter is the difference $(n - o) = 1$ and a general sector rule possible; according to Schellman[4] the simplest one is a hemisphere rule. For the onium compounds, at most a 'local' hemisphere rule may be envisaged if one keeps one ligand constant and thus reduces the C_{3v} to C_s symmetry around the positive ion.

A comprehensive review of the chiroptical properties of Se and Te compounds (at that time mainly optical rotations and ORD data) appeared in 1973[5]; a shorter comparison between UV, CD and MCD (Magneto-CD) data was published more recently[6]. This present review summarizes mainly papers describing Cotton effects (anomalous ORD or CD).

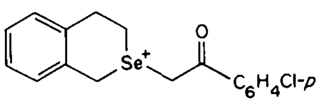
II. SELENIUM OR TELLURIUM AS PART OF THE CHIRALITY ELEMENT

A. Selenonium and Telluronium Compounds

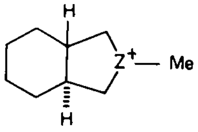
In analogy to the corresponding sulphonium salts a pyramidal arrangement can be assumed, and although crystal structure determinations have shown that selenonium[7] and telluronium[8] compounds contain a five-coordinate central atom, the R_3X moiety (X = Se or Te) has trigonal pyramidal geometry (average bond angles: C—Se—C 101 °, C—Te—C 94 °). NMR measurements have proved that this pyramid is fairly stable[6], so that optical activity can be expected with three different ligands. Indeed compounds **1** and **2** have been resolved[9,10] and both enantiomers prepared, although the absolute configuration has not been determined and only the rotation at the Na_D line recorded[9,10]. No Cotton effect in the accessible range has been observed for either type of compound (e.g. for **3**, Z = Se or Te), even with more modern equipment[6], with the exception of a telluronium iodide; the very weak Cotton effect for this compound around 270–290 nm has therefore been associated with some charge transfer between Te and I[6]. The MCD bands come only from the iodine anion[6].



(1)



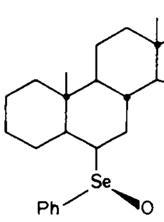
(2)



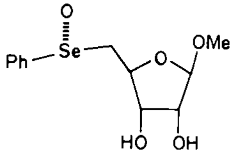
(3)

B. Selenoxides

In general selenoxides are rather unstable, but a few optically active ones have been prepared and their chiroptical properties could be studied. Jones and coworkers[11] have succeeded in obtaining a few selenoxides in the steroid series (e.g. **4** and its diastereomer at Se) and their stereochemistry has been determined from their different rates in pyrolyses.



(4)



(5)

The (*S*) isomer showed a negative Cotton effect (by ORD) around 260–270 nm and this is in full agreement with the correlation between sign and stereochemistry in the case of the corresponding sulphoxides[11]. Most probably this is not actually a Se transition but one from the chirally perturbed benzene ring (α-band).

Several such chiral selenoxides which are surprisingly thermally stable have been prepared by Zylber and coworkers[12] in the nucleoside series. X-ray analysis has proved the (*S*) configuration of one of the compounds which give a positive CD band around 250 nm. As, however, nucleosides alone give Cotton effects in the same range, the assignment of the CD band is not unambiguous. Hence, for investigation of the chiroptical properties, the simple methyl glycoside **5**, whose chemical and NMR properties suggest the same configuration at the chiral Se atom, was prepared[12]. Its CD spectrum is given in Figure 1. Three Cotton effects around 250, 220 and 200 nm are clearly visible, but the long-wavelength tail of the first CD band is very broad, so that an additional (positive) Cotton effect could still be present around 270 nm. Of course, the older ORD curves did not show such subtleties[11], but the positive sign of the 250 nm CD band agrees with the results found

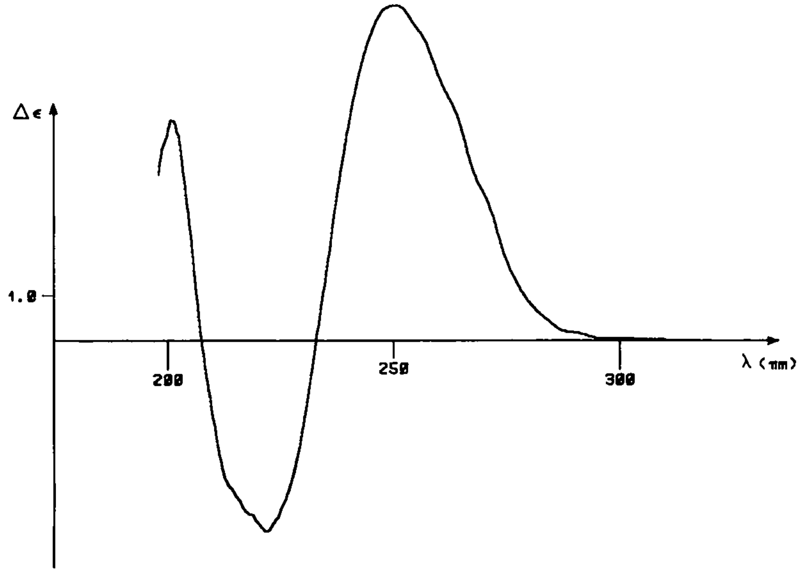
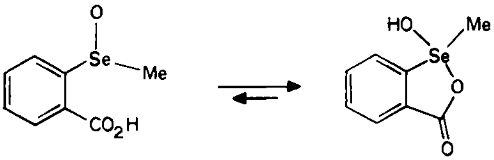


FIGURE 1. CD spectrum of **5** in acetonitrile solution.

for 4, if indeed 5 and its adenosine analogue have the same absolute configuration at the Se centre.

The existence of two diastereomeric selenoxides which give Cotton effects of opposite signs shows clearly that the stereochemistry around the Se atom must be similar to that around S in the corresponding sulphoxides; X-ray diffraction of 6, which could have proved this and which was done side-by-side with the corresponding S compound revealed, however, that this compound is present exclusively in the crystal as the ring-closed isomer[13].



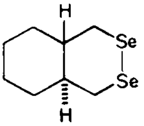
(6)

C. Diselenides and Ditellurides

As in the isologous O and S compounds, the torsional angle (C—)X—X(—C) in diselenides and ditellurides is approximately 90° (e.g., 87.5° for dimethyl diselenide in the gas phase[14] and 87.7° for di-*p*-tolyl telluride in the crystalline phase[15]). The barrier to rotation is, however, smalller than for disulphides[6,16], so that in the absence of chiral ligands the racemates cannot be resolved.

In the presence of a chiral ligand diastereomers are possible, but the deviation from a 1 : 1 ratio for the P- and M-helical forms is nevertheless expected to be quite small. Any CD measurement for such compounds will thus mirror the chiral perturbation of the diselenide chromophore (and should then follow a sector rule) rather than be due to its inherent helicity. Furthermore, in analogy to the corresponding disulphides, degeneracy of the first two absorption bands is expected for a torsional angle of around 90° and as the two Cotton effects have opposite signs they will approximately cancel each other.

The chiroptical properties of the inherently chiral isologous disulphides have been predicted by theoretical calculations at different levels of sophistication[2,17]; the first two bands at longest wavelengths are associated with the excitations from the n^- and n^+ combination, respectively, of the two energetically highest lying n orbitals on the two S atoms into the σ^* MO of the S—S bond, and a positive torsional angle (ranging approximately from 15° to 75°) leads to a positive first, and negative second, Cotton effect. These same results can also easily be rationalized by using qualitative MO theory[1b]. The same correlation has been found for diselenides[18], but all bands are shifted bathochromically. In addition, two other Cotton effects have been detected at shorter wavelengths, and the data for, e.g., 7 are as follows: 364 (−3.0), 275 (+4.2), 237sh (−2.0) and 220 nm ($\Delta\varepsilon = -17.1$)[6]. It has been proposed that the 237 nm CD corresponds to the $n^- \rightarrow \sigma^*$ (C—Se) transition and the band at shortest wavelengths to the $\sigma \rightarrow \sigma^*$ transition of the Se—Se



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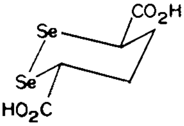
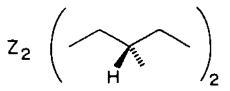


(8)

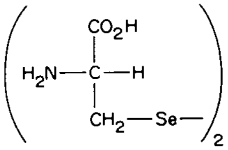
moiety. Since the rotational strength of the 220 nm band is, however, one order of magnitude larger than that of the 237 nm shoulder, and the excitation from n^- into the energetically lower lying combination with A-symmetry of the two σ^* (C—Se) moieties is associated with the stronger magnetic transition moment, we believe that the assignment of these two bands should be exchanged.

The torsional (C—)Se—Se(—C) angle of the preferred conformation of the diselenane **8** is + 57°, since the two carboxylic groups adopt equatorial position[19]; in agreement with this the first two Cotton effects are positive and negative, respectively: 351 (+ 1.43), 277 (− 2.39) and 249 nm ($\Delta\varepsilon = +4.90$)[18b]. As the band positions and magnitudes of these Cotton effects do not drastically deviate from those of **7** the carboxylic groups in the position α to the Se_2 grouping do not strongly influence the CD.

The chiroptical data of open-chain diselenides are much smaller: for the dialkyl diselenide **9** Cotton effects at 342 (+ 0.10), 286 (− 0.12), 233sh (+ 0.85) and 218 nm ($\Delta\varepsilon = +18$) have been reported[6], whereas the isologous ditelluride **10** gives the following data[6]: 442 (+ 0.032), 350 (− 0.022), 279 (+ 0.35) and 236 nm ($\Delta\varepsilon = +0.74$). Again, strong bathochromicity is found on going from the Se_2 to the Te_2 compound, but all the corresponding Cotton effects have the same sign for these homochirally analogous compounds. When the torsional angle of the (C—)Z—Z(—C) (Z = S, Se or Te) unit is fixed around 60° the UV and CD maxima at long wavelengths coincide approximately. In case of open-chain compounds such as **9** and **10** (and their S isologues) the first UV maximum lies, on the contrary, between two (small) Cotton effects of opposite signs[6], as predicted from theory[20] for an almost perpendicular geometry of the two halves. The position of the first band follows in the Se_2 compounds the easily explained trend[2,17] that the longer is λ_{max} the closer the torsional angle (C—)Se—Se(—C) approaches to 0°.

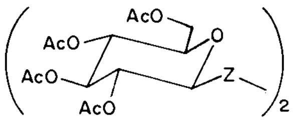


(**9**) Z = Se
(**10**) Z = Te

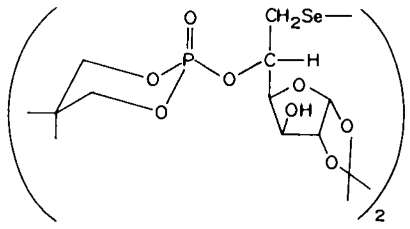


(**11**)

The CD of the Se isologue **11** of L-cystine and of its enantiomer have been investigated in more detail[21]. In the protonated form (pH = 0.5) the CD bands are at 306 (− 0.24), 241 (− 0.88), 225 (+ 1.10) and 207 nm ($\Delta\varepsilon = -6.1$). Instead of two Cotton effects at longest wavelengths as found for **9**, only one such CD band is observed. Furthermore, the 225 nm Cotton effect is most probably due to the carboxylic acid chromophore, because it is very similar to that found for other L-amino acids. At pH 5.5 the zwitterion is present in solution, and the positions of its Cotton effects resemble more those of the simple reference compound **9**: 320 (− 0.46), 272 (+ 0.32), 232 (− 2.53), 211 (− 3.1) and 200 nm ($\Delta\varepsilon = +3.6$). Preference of M-helicity of the C—Se—Se—C moiety has be inferred from these values[21].



(**12**) Z = Se
(**13**) Z = Te



(**14**)

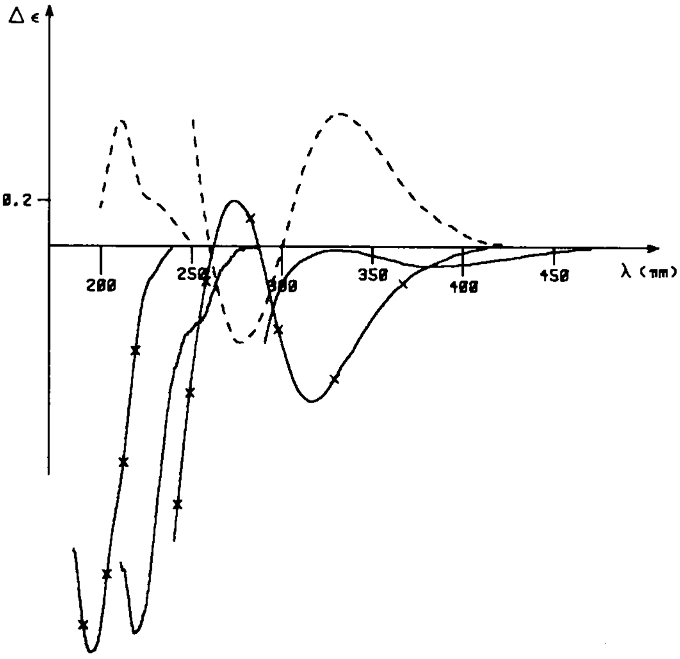


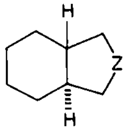
FIGURE 2. CD spectra of **12** (-×-×-), **13** (——) and **14** (----) in acetonitrile solution. Curves at shorter wavelengths were reduced by a factor of 10 for **13** and **14** and by a factor of 25 for **12**.

Many other diselenides have been prepared, but only their rotations at the Na_D line have been reported[22]. We have measured the full CD curve for two diselenides **12** and **14** in the sugar series[23] as well as that of **13**, the Te_2 isologue of **12**[23] (Figure 2). Three Cotton effects have been observed: e.g., **12** gives CD maxima at 314 (−0.66), 273 (+0.22) and 194 nm ($\Delta\varepsilon = -45$). These band positions differ somewhat from those in the CD spectrum of **9**, but resemble more those of **11** in the zwitterion form. The long-wavelength tail of the first Cotton effect extends out to more than 400 nm; it cannot be excluded, therefore, that another weak Cotton effect of same sign as the 315 nm effect is still hidden around 370 to 380 nm although the shape of the CD curve matches perfectly that of a Gaussian curve of half-band width 6170 cm^{-1}. Moreover, for these sugar derivatives the Cotton effects of the Te_2 compound are smaller than those of the Se_2 isologue.

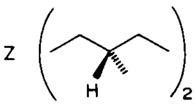
III. SELENIUM OR TELLURIUM NOT PART OF THE CHIRALITY ELEMENT

A. Selenides and Tellurides

For isologous dialkyl sulphides the first three Cotton effects appear around 240, 220 and 200 nm, and theoretical considerations lead to the assignment that the first two correspond to $n \rightarrow \sigma^*$ (C—S) transitions and in the third one a Rydberg transition may be involved[24]. The CD spectrum of the (−)-(*S*,*S*)-*trans*-selenahydrindane **15** also shows three Cotton effects at 273 (−1.7), 218 (+2.9) and 200 nm ($\Delta\varepsilon = +4.4$)[6], and they even have the same signs as their counterparts in the spectrum of its homochirally analogous S isologue for which, for technical reasons, only first and second Cotton effects have been measured[6].



(**15**) Z = Se
(**16**) Z = Te



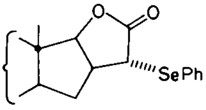
(**17**) Z = Se
(**18**) Z = Te

The corresponding data for the Te compound **16** are 350 (− 1.38), 260 (− 0.35), 240 (+ 4.4) and 200 nm ($\Delta\varepsilon = +2.9$)[6]. The same parentage for the first three transitions as for the sulphides seems therefore probable at least for the selenides but the MCD spectra are somewhat more complex[6]. It is, therefore, tentatively assumed that for the absorptions at longest wavelengths excited triplet states may be involved[6].

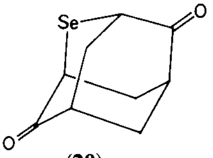
Even less clear is the situation with open-chain compounds, because several conformers may be present; the CD spectrum of the selenide **17** contains three bands at 274 (− 0.027), 251 (+ 0.125) and 220 nm ($\Delta\varepsilon = +1.1$) in the accessible range[6], but the corresponding telluride **18** shows five bands: 378 (+ 0.002), 355 (− 0.0055), 312 (+ 0.13), 239 (− 0.48) and 223 nm ($\Delta\varepsilon = -0.28$)[6]. Since at lower temperatures this latter CD spectrum simplifies and the Cotton effects become larger, conformational equilibria may (at least to a great extent) be the reason for the complexity of these CD spectra.

The CD spectra of a few selenoamino acids, such as the Se isologue of lanthionine, have been published[25]; with one exception only a single Cotton effect can be recognized, and all CD maxima are at wavelenths not longer than 220 nm, as for any amino acid. These Cotton effects might, therefore, be mainly due to $n \rightarrow \pi^*$ transitions within the COOR chromophore.

Many optical rotations at the Na_D line but only a very few Cotton effects have been published for sugar and amino acid derivatives (see Ref. 22) in which Se replaces O or S. Selenophenyl esters of amino acids give a Cotton effect around 284 nm, and selenonaphthyl esters at ca. 291 nm[26]. Acetylation at the amino group leads to sign inversion and bathochromicity of this Cotton effect; thus it has been ascribed to an $n \rightarrow \pi^*$ transition mainly within the seleno ester moiety[26]. For the β-phenylselenolacetone **19** small but distinct Cotton effects have been found[27] at 305 (+ 0.19), 278 (+ 0.20), 251 (+ 0.95), 242 (− 0.41) and 223 nm ($\Delta\varepsilon = +3.66$), of which only the last one should come from the lactone chromophore; the others involve both the aromatic π system and the Se atom. It is, therefore, more probable that the 284 nm Cotton effect of the phenylseleno esters also has a large contribution from a $\pi \rightarrow \pi^*$ transition of the benzene ring.

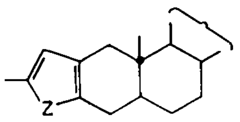


(**19**)

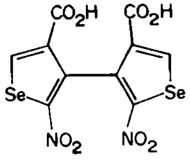


(**20**)

A strong interaction between the Se atom and the two carbonyls of the selenaadamantanedione **20** can be inferred from its CD spectrum[28]: in this case Se acts (similarly to S) in the same way as an axial halogen in a position α to a carbonyl, and therefore the CD is extremely strong for the carbonyl $n \rightarrow \pi^*$ band ($\Delta\varepsilon = +33.20$ at 308 nm); in addition, however, bands are also found at 336 (− 7.70), 322sh (app. + 12), 253 (− 8.00) and 212 nm (+ 8.10). Similar, though slightly smaller, large values are found for the S isologue[28,29].



(21) Z = Se
(22) Z = S



(23)

Analogy between the spectra is expected in the series furan, thiophene, selenophene, as overlap between the 2p AOs of the butadiene system and the chalcogen AOs with main quantum number 3 or 4 is not very good. Yet the usual bathochromic shift is found, as seen by comparison of the CD spectra of 21 and its S isologue 22 (Figure 3)[30]. A strong positive Cotton effect (determined by ORD measurements) has been published for the bis-

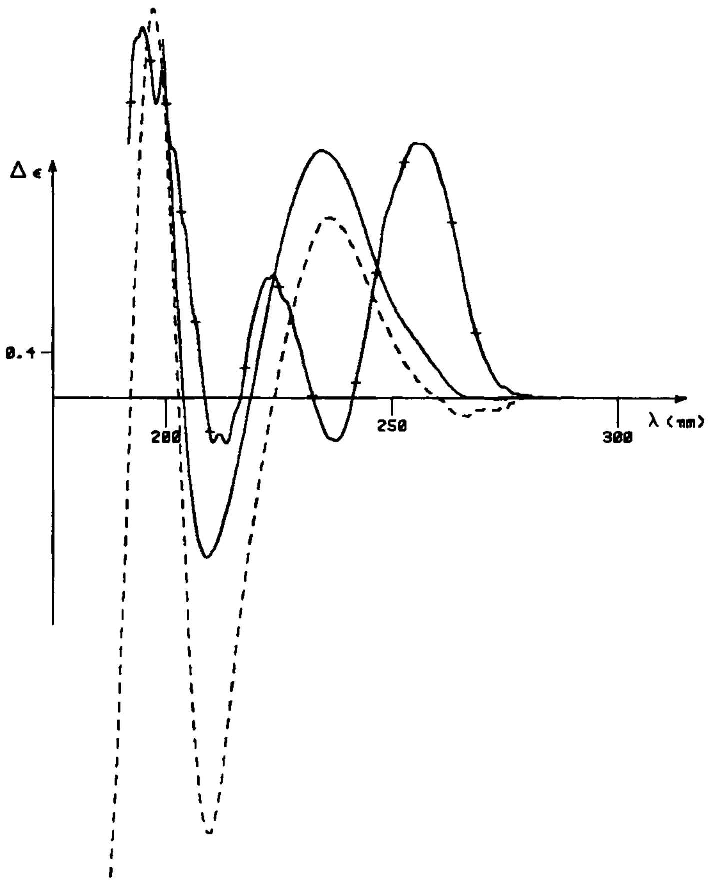
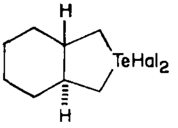


FIGURE 3. CD spectra of 21 in isooctane (—++—) and of 22 in isooctane (----) and in ethanol (———) solution.

selenophene derivative **23** with *R*-axial chirality[31]. Here also the homochirally analogous S isologue gives a very similar Cotton effect[32].

Addition of Br_2 or I_2 to **16** leads to the corresponding dihalogeno adducts. The CD data for the dibromo compound **24** are 285 (−6.3), 265 (−6.2) and 233 nm ($\Delta\varepsilon = +22.4$)[6]. Hence, the Cotton effect at longest wavelengths is strongly blue-shifted as compared to that of its halogen-free parent compound, and all CD values are intensified. The CD spectrum of the iodo product is, however, completely different[6].



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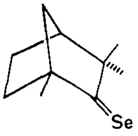

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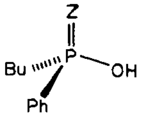

(26) Z = S
(27) Z = Se

B. Selenoketones

The CD of selenofenchone (**25**) derived from (−)-fenchone was recently published[33], together with that of fenchone and its thioketone derivative, but no Cotton effect was given for the absorption band found at 626 nm in the UV/visible spectrum. Obviously this was for instrumental reasons, and remeasurement of a new sample[34] gave the CD spectrum shown in Figure 4. The missing CD band was at 638 nm ($\Delta\varepsilon = +0.033$, cyclohexane solution). In the same stereochemical series the main bands at longest wavelengths have for all 3 compounds the same signs, which, at least for the ketone and its thio derivative, is in agreement with recent calculations[35]. It is possible that the 638 nm Cotton effect comes from an excitation into a triplet state, but it is also not uncommon that $n \to \pi^*$ CD bands are bisignate for one single electronic transition.

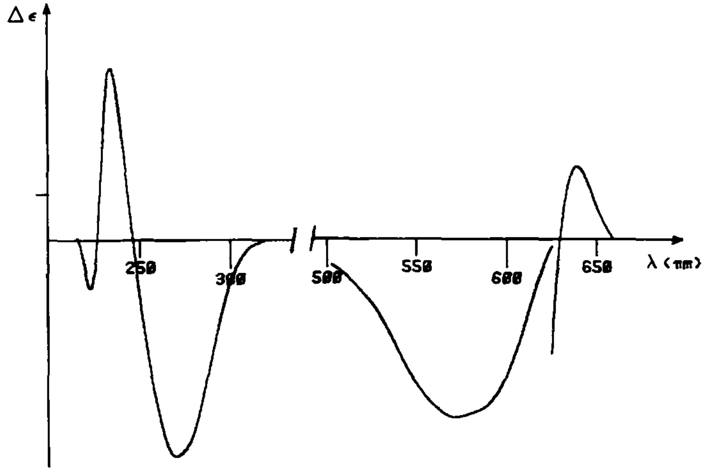

FIGURE 4. CD spectrum of **25** in isooctane solution. Δε scales: 0.02 from 660 to 625 nm, 0.2 from 625 to 500 nm and 0.5 from 330 to 215 nm.

C. Biopolymers Containing Selenium

In diaminooxytocin the S_2 bridge has been replaced by Se_2 and both possible SeS combinations[36]. The identification of the corresponding CD bands is, however, complicated by the presence of tyrosine in the peptide. The labile S atom of natural parsley ferredoxin has also been replaced by Se (approximately 1 Se per atom Fe)[37], and the CD spectra of the fully oxidized, the 50% reduced and the fully reduced forms have been compared in both series. A slight bathochromic shift is observed by this exchange, but the bands are most probably associated with d–d transitions of the Fe.

D. Raman Optical Activity

Data for Raman optical activity have been published in two spectral ranges for **15**, but no interpretation has been tried[6].

E. Selenophosphinic Acid Derivatives

Alkyl(phenyl)thiophosphinic acids (like **26**) complex *in situ* with dimolybdenum tetraacetate in trifluoracetic acid solution and give CD bands around 480 and 400 nm (and eventually around 540 nm)[38]. The isologous Se compound **27** also forms such a complex and gives (besides the 540 nm CD band) practically the same CD curve as **26** of the same absolute configuration[38].

IV. ACKNOWLEDGEMENT

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CHAPTER 18

Ligand properties of organic selenium and tellurium compounds

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I. INTRODUCTION

Selenium and tellurium ligands have, until recently, been rather neglected in the renaissance of transition-metal coordination and organometallic chemistry[1,2] beginning in the late 1950s. Although selenourea[3] was first described as a ligand in 1886, and dialkyl selenide[4-7] and telluride complexes[6,8] of Pd(II) and Pt(II) were first reported near the beginning of this century, the ligand chemistry of these two elements has been relatively unexplored compared to the lighter Group 5a (N[1,9], P[1,10]) and 6a (O[1,11], S[1,12]) elements. This situation is probably, to a considerable extent, the result of the commonly held assumption that the organometallic derivatives of Se and Te are generally toxic, foul-smelling, air-sensitive materials. Indeed, a review by Murray and Hartley[13] in 1981 of transition-metal cordination complexes of thio, seleno and telluro ethers includes the statement: 'It is difficult to prepare all but the simplest organotellurium ligands, and at the present time only monodentate tellurium ligands are known.'

This general misconception is no doubt based on the fact that the early work in this area did indeed involve rather unstable and foul-smelling Se and Te ligands (e.g. selenourea and low-molecular-weight dialkyl selenides and tellurides). Current methodology, however, allows the synthesis of a wide variety of stable Se[14] and Te[15] ligands.

For example, increasing the chain length of the simple dialkyl derivatives can give air-stable solids (e.g. $Te(C_{16}H_{33}\text{-}n)_2$[16], m.p. 45 °C), and the aromatic derivatives are generally air-stable solids. Ironically, the structural diversity of Se and Te ligands is considerably greater than that of the most widely used ligand class in modern coordination chemistry, triorganophosphines[1,10]. Recent work in Se[17] and Te[15,18] ligand chemistry has centred on the synthesis of new ligand types rather than on the synthesis and detailed studies of the properties of metal complexes with the most common ligands of these elements (e.g. ER_2[13] and ER^-[19], E = Se, Te).

Only a few descriptions of applications-oriented work have appeared. A few examples have been reported of metal selenide electroless plating solutions that contain Se ligands in combination with main-group metal halides (PbSe[20], Sb_2Se_3[21], TlSe[22], CdSe[23]).

A few examples have been reported of the use of Ag(I)[24] and Cu(I)[25] complexes with organotellurium ligands in thermally processed imaging elements. The use of $PtCl_2(SePh_2)_2/SnCl_2$ as a homogeneous catalyst for the hydrogenation of non-aromatic olefins has also been reported[26].

Recently, metal complexes with 1,2-diseleno ligands have been prepared and their conductivities measured[27]. The current interest in 'organic metals'[28] suggests that this chemistry will be the subject of future extensions with both Se ligands and their Te analogues.

A variety of chemical vapour deposition processes for thin-film fabrication (e.g. CdTe, ZnTe, PbTe, SnTe) have been described in which TeR_2 (R = Me, Et)[29] is codeposited on a hot substrate with an appropriate metal alkyl (in corresponding processes for metal selenide deposition, H_2Se is generally used as the chalcogen source[29,30]).

With the recent increased interest in Se[13,14,31] and Te[15a,18,31] ligands, as evidenced by publications describing such complexes, more fundamental studies of such complexes can be expected. Of particular interest are comparative studies of the Se and Te ligand analogues of the many well-established transition-metal phosphine complexes that have applications as homogeneous catalysts[32]. As this ligand chemistry is developed, it can be expected to produce new transition-metal coordination complexes with a variety of applications. The diverse scope of Se and Te ligands should allow for considerable flexibility in fine-tuning the electronic and steric properties of coordination complexes with these types of ligands.

This chapter will summarize the various types of Se and Te ligands that have been reported. Since the emphasis of this volume is on the organic chemistry of these elements, the classification used is based on the number and type of donor atoms incorporated in the ligands. To avoid repetition of structures as well as to define the various bonding modes either established by single-crystal X-ray diffraction or proposed on the basis of spectral data, tables in each section summarize this structural information.

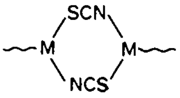
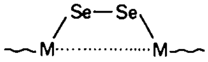
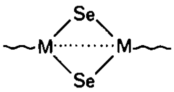
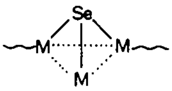
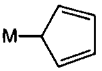
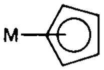
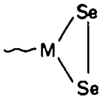
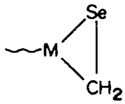
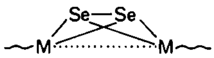
Finally, since comprehensive monographs and reviews have summarized the synthetic methodology associated with many of the Se[14] and Te[15] ligands described here, discussions of this aspect will be limited to recent work.

Table 1 summarizes the notations used to indicate the ligand bonding modes in chelates, dimers and clusters.

A. Abbreviations

acac = acetylacetonato
bipyr = 2,2′-bipyridine
COD = 1,5-cyclooctadiene
Cp = η^5-cyclopentadienyl
Cp′ = η^5-pentamethylcyclopentadienyl
Cp″ = η^5-methylcyclopentadienyl
detc = *N,N*-diethyldithiocarbamato; $Et_2NCS_2^-$
DME = 1,2-dimethoxyethane
DMF = *N,N*-dimethylformamide
dmgH = dimethylglyoxime

TABLE 1. Notations for ligand bonding modes

Prefix	Bonding mode
μ_n	Ligand bridges *n* metal centres in the complex $\sim M(\mu_2\text{-SCN})_2M\sim$ =  $\sim M(\mu_2\text{-Se}_2)M\sim$ =  $\sim M(\mu_2\text{-Se})_2M\sim$ =  $\sim M_3(\mu_3\text{-Se})\sim$ =  (M···M; a metal–metal bond may or may not be present)
η^n	Ligand bonds to a single metal atom through *n* sites of the ligand $(\eta^1\text{-}C_5H_5)M$ = $(\eta^1\text{-Cp})M$ ≡  $(\eta^5\text{-}C_5H_5)M$ = $(\eta^5\text{-Cp})M$ ≡  $(\eta^2\text{-Se}_2)M\sim$ =  $(\eta^2\text{-SeCH}_2)M\sim$ = 
μ_n, η^m	The ligand both bridges *n* metal centres and chelates to a metal centre via *m* sites on the ligand $(\mu_2, \eta^2\text{-Se}_2)M_2\sim$ = 

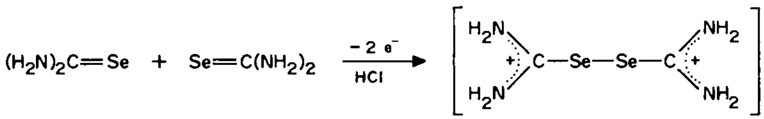
en = ethylenediamine
esu = ethyleneselenourea
F_6acac = hexafluoroacetylacetonato
HMPA = hexamethylphosphoramide
i-Am = isoamyl
dppe = $Ph_2PCH_2CH_2PPh_2$
NBD = norbornadiene
np_3 = $N(CH_2CH_2PPh_2)_3$
phen = 1,10-phenanthroline
PPN = $[(Ph_3P)_2N]^+$
su = selenourea
THF = tetrahydrofuran
triphos = $CH_3C(CH_2PPh_2)_3$
XPS = X-ray photoelectron spectroscopy

II. ORGANOSELENIUM LIGANDS

A. Neutral Monodentate Ligands

1. Selenourea

Although the first reported complexes with a Se ligand involved selenourea (i.e. the poorly characterized complexes $Ag(su)_2Cl$, $Hg(su)_2Cl$ and $Hg(su)Cl)^3$, the oxidative instability of this ligand and its *N*-alkyl-substituted derivatives has limited the study of its coordination chemistry. Indeed, the isolation of these complexes was apparently fortuitous (e.g. the use of acid solutions of su and correct su/metal stoichiometries), since a subsequent paper[33] describing the reaction of AgCl with a concentrated aqueous su solution reported the deposition of elemental Ag and Se and yellow crystals of α,α'-diselenobisformamidinium dichloride via a redox process. The same su oxidation product was obtained by oxidation of a cooled HCl–ethanol solution of su with H_2O_2[33]; it was characterized by a single-crystal X-ray diffraction study (equation 1). In the first detailed study[34] of the ligand properties of su, it was reported to form the yellow $[Bi(su)_9]^{3+}$ and red $[Bi(su)_{12}]^{3+}$ complexes in 0.1M HNO_3 solution. Although the solid complexes were not isolated, the stability constants of the two species were estimated to be 10^{-2} and $10^{-2.5}$, respectively. The stability and intense colour of these complexes suggested their use for qualitative and quantitative detection of this element (e.g. sensitivity limit of 1 μg/ml for the yellow complex and 2.5 μg/ml for the red complex). Qualitative observations of the reactions of su solutions with various metal salts were also reported by these authors[34]; Cu(II), Hg(II), Ag(I), Sn(II), Au(III) and Pd(II) all gave precipitates that dissolved in excess su, and Pb(II) gave a yellow precipitate that was insoluble in excess su.



(1)

A spectrophotometric investigation[35] of the aqueous OsO_4/su system established that su initially reduces Os(VIII) to Os(IV) with the subsequent formation of an intense blue-green 8:1 Os(III) complex (equation 2).

$$\begin{array}{l} \mathrm{OsO_4 + 4\,H_2NC(Se)NH_2 \xrightarrow{1\,M\ HCl} OsO_2 + 2[\{(H_2N)_2CSe\}_2]^{2+} + 2\,H_2O} \\ \qquad\qquad\qquad\qquad\qquad \downarrow \mathrm{9\,H_2NC(Se)NH_2} \\ \qquad\qquad\qquad \mathrm{[Os(Se{=}C(NH_2)_2)_8]^{3+} + \tfrac{1}{2}[\{(H_2N)_2CSe\}_2]^{2+}} \\ \qquad\qquad\qquad\qquad\qquad\qquad \mathrm{+ 2\,H_2O} \end{array} \qquad (2)$$

Thiourea gives a similar five-electron initial reduction but forms a final 6:1 complex, $[\mathrm{Os(thiourea)_6}]^{3+}$.

A variety of complexes of selenourea with transition metals and Te(II) have been isolated and characterized (Table 2).

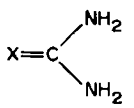
TABLE 2. Data for some typical selenourea complexes

Complex	Reported data[a]	Reference
$[\mathrm{Pd(su)_4}]\mathrm{Cl_2}$	Wine-red crystals	36
	M.p. 179 °C dec.	
	$\nu_{\mathrm{Pd—Se}}$	
	aq. soln., R: 178(P)	
	powder, R: 182s, 176sh	
	IR: 253m, 235s	
$[\mathrm{Pt(su)_4}]\mathrm{Br_2}$	Yellow crystals	36
	M.p. 160 °C dec.	
	$\nu_{\mathrm{Pt—Se}}$	
	powder, R: 202s, 182s	
	IR: 227s, 215w	
$[\mathrm{Co(su)_4}](\mathrm{ClO_4})_2$	Air-sensitive, deep olive-green, platelike crystals	
	M.p. 142 °C dec.	
	Strong su IR bands: 1625, 1400, 575, 500, 380	37
	$\nu_{\mathrm{Co—Se}}$ = 245s, 218m, sh	38
	Visible absorptions	38
$[\mathrm{Co(su)_2Cl_2}]$	Air-sensitive, blue-green solid	38, 39
	$\nu_{\mathrm{Co—Se}}$ = 213s, 189w(sh)	38
	Visible absorptions	38, 39
$[\mathrm{Zn(su)_4}](\mathrm{ClO_4})_2$	$\nu_{\mathrm{Zn—Se}}$ = 208s, 196s	38
$[\mathrm{Zn(su)_2Cl_2}]$	$\nu_{\mathrm{Zn—Se}}$ = 205s, 180m (sh)	38
$[\mathrm{Cd(su)_2Cl_2}]$	$\nu_{\mathrm{Cd—Se}}$ = 188s, 165s(br)	38
	X-Ray powder pattern	40
$[\mathrm{Hg(su)_2Cl_2}]$	Moderately air-sensitive, white microcrystalline solid	37, 38
	$\nu_{\mathrm{Hg—Se}}$ = 176	
	$\nu_{\mathrm{Hg—Cl}}$ = 204, 200	
$[\mathrm{HgCl_2(su)}]_2$	Moderately air-sensitive, white microcrystalline solid	37, 38
	$\nu_{\mathrm{Hg—Cl}}$ = 276s	37, 38
	$\nu_{\mathrm{Hg—Cl—Hg}}$ = 200s	38
	$\nu_{\mathrm{Hg—Se}}$ = 183s(br)	38
$[\mathrm{Te(su)_4}]\mathrm{Cl_2}$	Yellow crystals	41
	Single-crystal X-ray diffraction analysis	
	Te—Se bond lengths = 2.814(3) Å, 2.809(3) Å	
	Se—Te—Se angles = 90°	
$[\mathrm{PhTe(su)Cl}]$	Orange-red monoclinic prisms	42

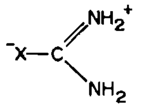
[a] Infrared (IR) and Raman (R) data in cm^{-1}; recorded as Nujol mulls unless otherwise indicated; s = strong, m = medium, w = weak, sp = sharp, sh = shoulder, br = broad, P = polarized band.

In both su complexes that have been unequivocally characterized structurally by single-crystal X-ray diffraction, Se bonding was found ($[Te(su)_4]Cl_2$[41], $Te(su)_2(Ph)Cl$[43]). A similar Se bonding mode has been established from the X-ray powder pattern of $CdCl_2(su)_2$, which shows it to be isostructural with the analogous thiourea complex, for which a single-crystal X-ray diffraction study has established a $CdCl_2S_2$ tetrahedral coordination sphere[40]. For the other complexes, infrared spectroscopy[36–39,44] has been most generally used to determine the bonding mode of the potentially ambidentate su ligand, and Se bonding has been assigned in all cases.

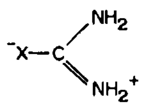
In contrast, urea and thiourea coordinate through both N and O or S in their coordination complexes[44]. The tendency of su to coordinate via its Se atom is supported by force-constant calculations[38], which support the increasing importance of canonical forms **B** and **C** in the series $X = Se > S > O$:



A



B



C

Although metal–Se vibrations have been measured for several M–su complexes ($M = Pd$[36], Pt[36], Co[38], Zn[38], Cd[38], Hg[38]; Table 2), these low-energy bands are often weak and difficult to assign, and careful measurements of infrared shifts of ligand-localized absorptions upon coordination are generally more useful in establishing coordination sites of such potentially ambidentate ligands.

Although there is considerable mixing in the normal modes of su, those bands with a strong CN stretching contribution ($\nu_4 = 1400\,cm^{-1}$, s; $\nu_5 = 1085\,cm^{-1}$, w; $\nu_{16} = 1480\,cm^{-1}$, m) generally increase upon coordination (to 1400–1410, 1090–1120 and 1500–1520 cm^{-1}, respectively), and those with a strong C—Se stretching contribution ($\nu_6 = 640$ and $\nu_7 = 390\,cm^{-1}$) generally decrease 10–20 cm^{-1} upon coordination[38]. The ν_{N-H} vibrations of free su (3320 and 3250 cm^{-1}) also generally sharpen and increase up to 100 cm^{-1} [31] on coordination, owing to the destruction of the weakly hydrogen-bonded structure of the free ligand[45].

The selenourea complexes (Table 2) are readily prepared by reaction of an appropriate metal salt (in aqueous solution) with the stoichiometric amount of selenourea. In aqueous systems a relatively low pH (ca. 3) is used to prevent decomposition of su[34–36]. Non-aqueous solvents include MeOH[42], EtOH[39], n-BuOH[37–39] and acetone[37,38]. The syntheses are generally carried out in an inert atmosphere with minimum exposure to light[37]. As with thiourea, reactions of selenourea with reducible metal species (e.g. Te(IV)[41] and Cu(II)[3]) can give complexes in a lower oxidation state (e.g. Te(II) and Cu(I), respectively), the su functioning as both a reducing agent and a stabilizing ligand for the lower oxidation state. With Te, the complex isolated depends on the stoichiometry of su used (equations 3–5).

$$\begin{array}{l}TeO_2 \xrightarrow{HCl} TeCl_6^{2-} \xrightarrow{4\,su} TeCl_2(su)_2\downarrow + [(H_2N)_2C{-}Se]_2^{+2} \qquad \text{(Ref. 41)} \qquad (3)\\ \qquad\qquad\qquad\qquad\qquad \Big\downarrow{\scriptstyle 2su}\\ \qquad\qquad\qquad\qquad\quad [Te(su)_4]Cl_2\end{array}$$

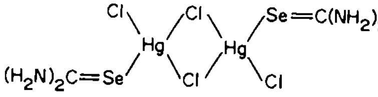
$$PhTeTePh + Cl_2 + 2\,su \rightarrow 2\,[PhTeCl(su)] \qquad \text{(Ref. 42)} \qquad (4)$$

$$PhTeTePh + Cl_2 + 4\,su \rightarrow 2\,[PhTe(su)_2]Cl \qquad \text{(Ref. 42)} \qquad (5)$$

The crystal structure of $[Te(su)_4]Cl_2$[41] has established that the Te(II) is surrounded by four Se atoms in a square planar configuration and the bond lengths and angles in the selenourea ligands are similar to those of free selenourea[45].

The complex $PhTe(su)_2Cl$ contains essentially planar three-coordinate Te(II) (i.e. $[PhTe(su)_2]^+Cl^-$) with a nearly linear three-centre Se—Te—Se system perpendicular to the bonded phenyl C atom[43]. In contrast, the thiourea analogue, $PhTe(tu)_2Cl$, while having a similar structure, has a weak but observable Te···Cl interaction to give a distorted square planar configuration[43]. Such secondary bonding has been observed in a number of Te(II) and Te(IV) complexes[46].

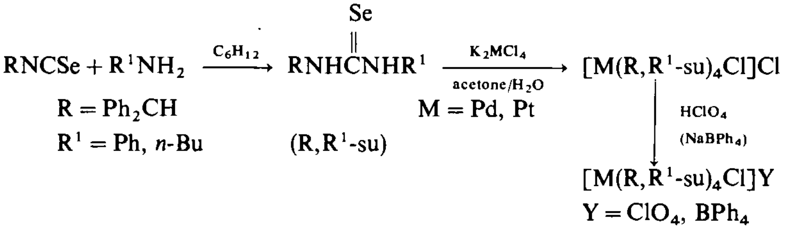
The complex $HgCl_2(su)$ has been formulated as a chloro-bridged dimer (**1**) on the basis of the presence of both terminal Hg—Cl and bridging Hg—Cl—Hg vibrations in the far-infrared region[37,38].



(**1**)

Several electroless plating solutions containing selenourea or *N*,*N*-dimethylselenourea, which are useful for the deposition of thin films of CdSe[23] and PbSe[20], have been reported. These solutions generally incorporate an additional chelating agent for Cd(II) and are used under alkaline conditions. Such plating processes presumably involve the formation of unstable $M—Se{=}C(NR_2)_2$-type complexes.

In addition to selenourea[3,34–43] itself, several *N*,*N*′-disubstituted selenoureas[47–49] have been reported to form coordination complexes (Table 3). These substituted derivatives, prepared from the corresponding isoselenocyanates and primary amines[51], form unusual square pyramidal five-coordinate Pd(II) and Pt(II) complexes[47,48] (equation 6). The infrared data support Se bonding in all cases (Table 3). The formulation of the apparently square planar $M(R,R^1\text{-su})_4Cl_2$ complexes (i.e. $[M(R,R^1\text{-su})_4]Cl_2$) as pentacoordinate species (i.e. $[M(R,R^1\text{-su})_4Cl]Cl$)[47,48] is based on their electronic spectra, 1:1 electrolyte behaviour in non-polar organic solvents (Table 3) and the isolation of $[M(R,R^1\text{-su})_4Cl]Y$ ($Y = ClO_4$, BPh_4) complexes on reaction of solutions of the dichloro complexes with excess of the poorly coordinating ClO_4^- or BPh_4^- anions[52] (equation 6). Although they are relatively rare, five-coordinate Pd(II) and Pt(II) complexes have been characterized crystallographically (e.g. $[M(F_6acac)_2(PR_3)]$; M = Pd, R = *o*-Tol; M = Pt, R = *c*-Hex)[53].



$$RNCSe + R^1NH_2 \xrightarrow{C_6H_{12}} RNH\overset{\overset{Se}{\|}}{C}NHR^1 \xrightarrow[\text{acetone}/H_2O]{K_2MCl_4} [M(R,R^1\text{-su})_4Cl]Cl \qquad (6)$$

$R = Ph_2CH$ $\qquad$ $M = Pd, Pt$ $\qquad$ $\Big\downarrow{\scriptstyle HClO_4\ (NaBPh_4)}$

$R^1 = Ph, n\text{-}Bu$ $\qquad$ $(R,R^1\text{-su})$

$[M(R,R^1\text{-su})_4Cl]Y$

$Y = ClO_4, BPh_4$

Several Ni(II) complexes with *N*,*N*′-disubstituted selenoureas have been prepared: tetrahedral $[NiL_2X_2]$, square planar, diamagnetic $[NiL_4](ClO_4)_2$ and the unique tetrahedral $[Ni(N\text{-}Ph_2CH, N'\text{-}Bu\text{-su})_3Br]Br$[49] (Table 3). The stereochemistries of these complexes have been established by electronic spectroscopy and magnetic susceptibility measurements (Table 3).

The solution and reflectance spectra of the NiL_2X_2 derivatives are identical, indicating that the tetrahedral coordination is retained in solution. The monomeric formulations of these complexes are confirmed by molecular weight measurements, and conductivity measurements show non-electrolyte behaviour.

TABLE 3. Data for some complexes with *N,N'*-disubstituted selenoureas, $RHN\overset{\overset{Se}{\|}}{C}NHR^1$ (L)

Complex	Reported data[a]	Complex	Reported data[a]
R = Ph₂CH, R¹ = Ph		*R = R¹ = Ph*	
$[PdL_4Cl]Cl^{47,48}$	Red solid M.p. 136–138 °C $\nu_{C-N} = 1565^b$ $\nu_{C=Se} = 788^c$ $\Lambda_M(MeOH) = 105$ (acetone) = 75 $(CH_2Cl_2) = 48$	$NiL_2Cl_2{}^{49}$	Green solid M.p. 131–134 °C $\mu_{eff} = 3.34$
		$[NiL_4](ClO_4)_2{}^{49}$	Green solid M.p. 126–128 °C Diamagnetic
$[PdL_4Cl]ClO_4{}^{47,48}$	Red–yellow solid M.p. 122–124 °C $\Lambda_M(MeOH) = 125$ $(CH_2Cl_2) = 56$ (acetone) = 170	*R = Ph, R¹ = allyl*	
		$NiL_2Br_2{}^{49}$	Green solid M.p. 118–122 °C $\mu_{eff} = 3.30$
		$[NiL_4](ClO_4)_2{}^{49}$	Green solid M.p. 135–137 °C Diamagnetic
$[PtL_4Cl]Cl^{47,48}$	Yellow solid M.p. 147–149 °C $\nu_{C-N} = 1560^b$ $\nu_{C=Se} = 785^c$ $\Lambda_M(MeOH) = 91$ (acetone) = 80 $(CH_2Cl_2) = 59$	*R = Ph₃C, R¹ = Bu*	
		$NiL_2Br_2{}^{49}$	Green solid M.p. 160–163 °C $\mu_{eff} = 3.57$
$[RhL_4Cl_2]Cl^{47}$	Dark-red solid M.p. 160–163 °C $\nu_{C-N} = 1552^b$ $\nu_{C=Se} = 788^c$ $\Lambda_M(MeOH) = 85$	$NiL_2I_2{}^{49}$	Brown solid M.p. 128–130 °C $\mu_{eff} = 3.28$
		R = Ph₃C, R¹ = Ph₂CH	
		$NiL_2Br_2{}^{49}$	Green solid M.p. 178–180 °C $\mu_{eff} = 3.33$
R = Ph₂CH, R¹ = n-*Bu*			
$[PdL_4Cl]Cl^{48}$	Red-brown solid M.p. 120–127 °C	$NiL_2I_2{}^{49}$	Yellow-brown solid M.p. 134–136 °C $\mu_{eff} = 3.26$
$[PtL_4Cl]Cl^{48}$	Light yellow solid M.p. 118–121 °C		
$[NiL_3Br]Br^{49}$	Yellow-brown solid M.p. 140–142 °C $\mu_{eff} = 3.40$		

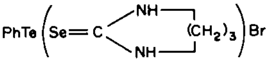
[a] Λ_M = molar conductance ($ohm^{-1} cm^2 mol^{-1}$) of 5×10^{-4} M solution (typical values for 1:1 electrolytes are 80–115 (MeOH)[50], 100–400 (acetone)[50]); μ_{eff} = magnetic moment in Bohr magnetons (B.M.) measured at 293 K.
[b] Corresponding band for free *N*-Ph₂CH,*N'*-Ph-su is at 1535 cm⁻¹.
[c] Corresponding band for free *N*-Ph₂CH,*N'*-Ph-su is at 788 cm⁻¹.

Although the $[NiL_4](ClO_4)_2$ complexes (Table 3) have been formulated as square planar complexes in the solid state on the basis of their electronic spectra and magnetic susceptibilities, their instability in solution, even in the presence of excess L, precludes solution studies.

The unique Ni(*N*-Ph_2CH, *N'*-Bu-su)$_3Br_2$ complex has been formulated on the basis of electronic spectroscopy and magnetic susceptibility as the tetrahedral species $[NiL_3Br]^+Br^-$ in the solid state. However, in acetone solution, its conductivity is about zero, and its molecular weight is about half the theoretical value, supporting the dissociation shown in equation (7).

$$[NiL_3Br]Br \rightarrow NiL_2Br_2 + L \qquad (7)$$

TABLE 4. Complexes with cyclic selenourea derivatives

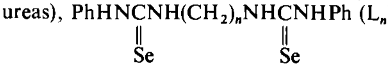
Complex	Reported data[a]	Reference
PhTe(esu)$_2$Cl	Orange–red orthorhombic prisms	54
	M.p. 190–191 °C dec.	
	Crystallographic data	
PhTe(esu)Br	Orange–red monoclinic crystals	54
	M.p. 163–164 °C	
	Single-crystal X-ray diffraction study	56
	Te—Se = 2.6160(16) Å	
	Te—Br = 3.0537(16) Å	
	Te—C = 2.118(7) Å	
	∠Se—Te—C = 89.94(19)°	
	∠Br—Te—C = 86.67(19)°	
	∠Se—Te—Br = 175.62(3)°	
	Te···Br (intermolecular) = 3.8490(16) Å	
	$\nu_{\text{Se—Te—Br,sym}}$ = 170s,	
	130w (IR)	59
	169m (R)	
	$\nu_{\text{Se—Te—Br,asym}}$ < 190m (IR).	
	192w (R)	
PhTe(esu)I	M.p. 137–139 °C	55
	Single-crystal X-ray diffraction study	
	Te—Se = 2.6791(18) Å	
	Te—I = 3.0951(14) Å	
	Te—C = 2.112(7) Å	
	∠Se—Te—C = 89.92(17)°	
	∠I—Te—C = 88.15(17)°	
	∠Se—Te—I = 177.31(2)°	
	$\nu_{\text{Se—Te—I,sym}}$ = 150s, 133w (IR)	59
	152vs (R)	
	$\nu_{\text{Se—Te—I,asym}}$ = 180m (IR),	
	178w (R)	
Trimethyleneselenourea		
	Yellow monoclinic prisms and plates	54
	M.p. 152–153 °C	
	Crystallographic data	

[a] Units as in Table 3.

The only reported complexes with a tetrasubstituted selenourea (tetramethylselenourea, tmsu) were prepared by the route described in equation (4) (i.e. PhTeX (tmsu); X = Cl (m.p. 151–152 °C), X = Br (m.p. 162–163 °C)[54].

Attempted formation of Ni(II)-ethyleneselenourea (esu) complexes resulted in immediate decomposition with deposition of elemental Se. In contrast, ethylenethiourea gave stable NiL$_4$X$_2$ complexes[49]. Esu complexes of Te(II), however, have been isolated (PhTe(esu)X; X = Cl[54], Br[54], I[55]; PhTe(esu)$_2$Cl[54]) and characterized by far-infrared spectroscopy and, for X = Br and I, by single-crystal X-ray diffraction (Table 4). The chloro and bromo complexes were prepared[54] by halogen cleavage of Ph$_2$Te$_2$ in the presence of esu in methanol solution, as described for the corresponding su complexes (equation 4). The iodo complex was prepared via a metathetical reaction of the bromo analogue and 2 equiv. of NaI in methanol[55]. The formation of these complexes of PhTeX illustrates the stabilizing influence of selenourea ligands, since the parent phenyl tellurenyl halides, although useful as synthetic reagents[57], are unstable[58].

TABLE 5. Ni(II) complexes with polymethylenebis(phenylselenoureas),



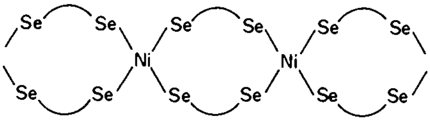
$\mathrm{PhHN}\underset{\underset{\mathrm{Se}}{\|}}{\mathrm{C}}\mathrm{NH(CH_2)_nNH}\underset{\underset{\mathrm{Se}}{\|}}{\mathrm{C}}\mathrm{NHPh}\ (\mathrm{L}_n)$[60]

Complex	Reported data[a]
$Ni(L_4)_2X_2$	
X = Cl	Green solid, m.p. 161–164 °C
X = Br	Green solid, m.p. 154–156 °C
X = I	Brown-yellow solid, m.p. 132–135 °C
$Ni(L_5)_2X_2$	
X = Cl	Green-yellow solid, m.p. 120–125 °C
X = Br	Green-yellow solid, m.p. 130–135 °C
X = I	Yellow-green solid, m.p. 115–118 °C
$Ni(L_7)_2Cl_2$	Green solid, m.p. 111–114 °C
$Ni(L_7)_2Br_2$	Green solid, m.p. 126–129 °C
$Ni(L_7)_2I_2$	Green solid, m.p. 133–136 °C
$Ni(L_8)_2Cl_2$	Green-yellow solid, m.p. 110–112 °C
$Ni(L_8)_2Br_2$	Green solid, m.p. 115–118 °C
$Ni(L_8)_2I_2$	Green-brown solid, m.p. 125–128 °C

Single-crystal X-ray diffraction studies of PhTe(esu)X (X = Br[56], I[55]) were carried out as part of a study[46a] of the stereochemistry of Te(II) complexes and the *trans* influence of various thio- and seleno-urea ligands (i.e. variation of Te—X_{trans} bond distances in three-coordinate PhTeLX-type complexes). The infrared and Raman spectra of these two complexes have also been recorded[59] in the solid state in the 50–500 cm^{-1} region, and bands due to the asymmetric and symmetric stretching frequencies of the linear Se—Te—X have been assigned (Table 4).

Polymethylenebis(phenylselenourea), $PhNHC(Se)NH(CH_2)_nNHC(Se)NHPh$ ($n = 2$–5, 7, 8) (prepared from the corresponding diamines, $H_2N(CH_2)_nNH_2$ and PhNCSe), gives a variety of complexes with Ni(II), the structures being determined by the Ni(II) salt used in the reaction as well as the reaction temperature[60] (Table 5).

With $n = 2$ or 3, and with acetone or ethanol as the reaction solvent, unstable monomeric tetrahedral complexes of the type $[NiLX_2]$ containing (Se, Se) chelating selenourea ligands are formed[60] (see Section II.C.3). Use of BuOH as the reaction solvent with L_3 or any of the above solvents with the higher homologues gives complexes of the composition $Ni(L_n)_2X_2$ (Table 5). On the basis of their low solubility, electronic spectra and magnetic susceptibilities, these complexes have been formulated as polymeric, square planar species (2) with $NiSe_4$ coordination spheres formed by bridging selenourea ligands with ionic halide.



(2)

If the reaction temperature is not kept low during the synthesis, the magnetic susceptibility of the products tends to be higher (up to 1.5 B.M.) than the limiting zero value expected for the square-planar diamagnetic products.

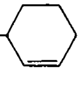
Chelating (Se, O) and (Se, S) selenoureas have also been reported (see Section II.D.2).

2. *Diorganoselenides (SeR_2; R = alkyl, aryl)*

Dialkyl selenides can be synthesized by a variety of standard routes[14]. Recently, Superhydride™, $LiBEt_3H$, has been used as a convenient reagent in such syntheses in non-aqueous solvents (equation 8).

$$\mathrm{Se + LiBEt_3H \xrightarrow{THF} Li_2Se \xrightarrow{2\,RX} SeR_2} \qquad (8)$$

R = n-C_5H_{11}[61], $C_6H_5CH_2$[61], p-$ClC_6H_4CH_2$[61], $PhCH_2CH_2$[61], —$SiMe_3$[62],



[63],

(analogous reactions of allylic halides with Te^{2-} give coupled 1,5-dienes)[63]

Unsymmetrical diorganoselenides have also been prepared according to equation (9).

$$\begin{tikzcd} \mathrm{RSeSeR + 2\,LiBEt_3H} \arrow[r] & \mathrm{2\,RSeLi + 2\,Et_3B + H_2} \arrow[d, "2R^1X"] & \text{(Ref. 61)} \qquad (9) \\ & \mathrm{RSeR^1} & \end{tikzcd}$$

$$\mathrm{R = Ph,\ R^1 = PhCH_2}$$
$$\mathrm{R = PhCH_2,\ R^1 = Me}$$

Complexes of several metals with various dialkyl selenides have been reported (Pd[6,7,64–79], Pt[4,5,7,67,68,71,76,77,79–92], Ag[89,93,94], Ga[93], W[95], Re[96,97], Rh[98–100], Ru[101–104], Hg[89,105], Ir[106], Au[107], Cr[108]), and the few reported complexes with diaryl selenides involve $SePh_2$[5,6,69,73,96,101,109–111]. A few examples of metal complexes with alkyl aryl selenides (EtSePh[102,103,105], $(Me_3SiCH_2)SePh$[112]) have also been prepared.

The $MX_2(Se(alkyl)_2)_2$ (M = Pd, Pt; X = Cl, Br, I) complexes have been the subject of the most investigation. The solid-state and solution geometries (*cis/trans*) of these square-planar complexes have been studied by infrared[67,68,71,74,78], Raman[67,68,78] and dipole-moment measurements[78,80]. In a number of studies, variable-temperature ^{1}H-NMR spectroscopy was used to investigate inversion about the Se atom in solutions of such species, e.g. $MX_2(SeEt_2)_2$ (X = Cl, Br, I; M = Pd, Pt[76,77]), $MCl_2(Se(CH_2SiMe_3)_2)_2$ (M = Pd, Pt[79]), $RuX_3(NO)(SeEt_2)_2$ (X = Cl, Br[103]), $RuCl_3(NO)(PhSeEt)_2$[103], $MX_2\{PhSe(CH_2SiMe_3)\}_2$ (M = Pd, X = Cl; M = Pt, X = Br[112]), $PdCl_2(EtSePh)_2$[105]. Such spectra are often complicated by simultaneous intramolecular *cis–trans* isomerization and intermolecular ligand exchange processes[77].

The earliest reports involved the dialkyl selenide complexes of Pt and Pd halides, which readily precipitate upon addition of 2 equiv. of the selenide to an aqueous solution of potassium tetrachlorometallate. The corresponding bromo and iodo complexes are generally prepared by metathetical reactions, although bromo complexes have also been prepared directly (equation 10).

$$\mathrm{K_2MCl_4 + 2\,SeR_2 \xrightarrow{H_2O} [MCl_2(SeR_2)_2]\downarrow \xrightarrow{2\ NaX/acetone} [MX_2(SeR_2)_2]} \qquad (10)$$

$$\mathrm{X = Br,\ I}$$

$$\mathrm{M = Pd,\ Pt}$$
$$\mathrm{R = Me,\ Et,\ }i\text{-Am}$$

The $PtX_2(SeR_2)_2$ complexes generally precipitate as mixtures of the *cis* and *trans* isomers, which can be separated by their solubility differences in $CHCl_3$ (the *cis* isomers are considerably more soluble than the *trans*).

Hieber and coworkers first prepared transition-metal carbonyl complexes with diorganoselenide ligands (equations 11–14). Similar substitution reactions have been used to prepare several other diorganoselenide complexes of transition-metal carbonyls (e.g.

$Mo(CO)_3(phen)(SePh_2)$[110], *trans*-$Rh(CO)(SeEt_2)_2Cl$[98], $Re(CO)_{5-n}(SeEt_2)_nCl$ ($n = 1,2$)[97], $[Ir(CO)_2(SeEt_2)Cl]_n$[106]).

$$Re(CO)_5X + 2\,SeEt_2 \xrightarrow[\Delta]{EtOH} Re(CO)_3X(SeEt_2)_2 \qquad \text{(Ref. 96)} \qquad (11)$$

$$X = Br, I$$

$$2\,Re(CO)_5X + 2\,SeR_2 \xrightarrow[\Delta]{EtOH} (OC)_3(R_2Se)Re(\mu\text{-}X)_2Re(CO)_3(SeR_2) \qquad \text{(Ref. 96)} \qquad (12)$$

$$X = Cl;\ R = Et$$
$$X = Cl, Br, I;\ R = Ph$$

$$Mn(CO)_5Br + 2\,SePh_2 \xrightarrow[\Delta]{C_6H_6} Mn(CO)_3Br(SePh_2)_2 \qquad \text{(Ref. 111)} \qquad (13)$$

$$[Ru(CO)_2I_2]_n + SeR_2 \rightarrow Ru(CO)_2(SeR_2)_2I_2 \qquad \text{(Ref. 101)} \qquad (14)$$
$$R = Et, Ph$$

The only metal complex with a diorganoselenide ligand that has been characterized by single-crystal X-ray diffraction is *trans*-$PdCl_2(SeEt_2)_2$[70]. The small decrease in the observed Pd—Se distance (2.424(7) Å) compared to the sum of the covalent radii (2.45 Å) indicates little or no Pd→Se π back-donation.

A novel route to a diorganoselenide ligand involving alkylation of coordinated Se has been reported recently (equation 15).

$$\begin{tikzcd}
Cr(CO)_6 \arrow[r, "h\nu", "THF"'] & Cr(CO)_5THF \arrow[r, "Li_2Se", "EtOH"'] & {[Cr(CO)_5SeH]^-} \arrow[d, "{[Et_3O][BF_4]}"] & \text{(Ref. 108)} \quad (15) \\
 & & Cr(CO)_5SeEt_2 &
\end{tikzcd}$$

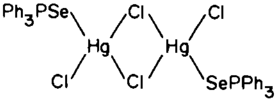
A more complete discussion of the chemistry and spectroscopic properties of complexes with seleno ethers is given by Murray and Hartley[13].

3. *Triorganophosphine selenides ($Se{=}PR_3$)*

Triorganophosphine selenides are most commonly prepared by the reaction of the phosphine with red Se[113].

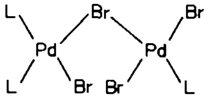
The first coordination complexes with a triorganophosphine selenides ligand were reported by Bannister and Cotton in 1960 ($PdCl_2(SePPh_3)_2$, $SnCl_4(SePPh_3)_2$)[114]. These complexes, which were isolated by reaction of the phosphine selenide with metal chloride complexes (H_2PdCl_4/aqueous ethanol reaction solvent; $SnCl_4(Et_2O)_2$/ether reaction solvent), were not characterized by these authors, but subsequent work has established the utility of infrared spectroscopy as a convenient probe for coordination of such ligands[115]. Upon coordination, the $\nu_{P=Se}$ vibration generally shifts 10–40 cm^{-1} to lower energy vs. the free ligand. Such shifts are smaller than those observed for analogous EPR_3 (E = O, S) complexes ($\Delta\nu_{P=O} = -(38\text{–}70)\,cm^{-1}$; $\Delta\nu_{P=S} = -(40\text{–}50)$), and it has been suggested[116] that these shifts indicate that P—Se π bonding is weaker than in the lighter phosphine chalcogens, although this effect is probably at least partly due to the lower sensitivity of the heavier Se atom to coordination.

A number of complexes with triaryl- and trialkyl-phosphine selenides have been reported, and one such complex, $[HgCl_2(SePPh_3)]_2$ (3), has been characterized by single-crystal X-ray diffraction, which established a chloro-bridged dimeric structure with distorted tetrahedral coordination about Hg[117].



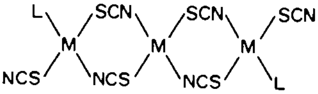
(3)

Pd, Pt and Cd complexes of unusual stoichiometries have been reported, the proposed structures (4–7) assigned primarily on the basis of infrared spectral data.



(4)[118]

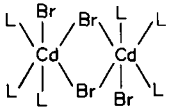
L = $SePPh_3$



(5) M = Pd[119]

(6) M = Pt[119]

L = $SePPh_3$



(7)[120]

L = $SeP(C_6H_4Me\text{-}p)_3$

TABLE 6. Complexes with triorganophosphine selenides

Complex	Reported data[a]	Reference
$PdCl_2(SePPh_3)_2$	Orange-brown solid	114
	M.p. 206 °C	116
	$\nu_{P=Se} = 543$[b]	116
$(PdBr_2)_2(SePPh_3)_3$ (4)	Red-brown solid	118
	M.p. 220 °C dec.	
	$\Lambda_M(PhNO_2) = 2.55$	
	$\nu_{P=Se} = 538s$	
$PdCl_2(SeP(C_6H_4Me\text{-}m)_3)_2$	Pale orange solid	119
	$\nu_{P=Se} = 558$[c]	
	$\Lambda_M(MeCN) = 3.2$	
$[Pd(SCN)_2]_3(SePPh_3)_2$ (5)	$\nu_{P=Se} = 540ms$	119
	$\nu_{C\equiv N} = 2155ms$ (Pd—SCN—Pd bridge) 2122mw (terminal Pd—SCN)	

TABLE 6. (*Continued*)

Complex	Reported data[a]	Reference
$[Pd(SCN)_2(SePPh_3)]_2$ **(8)**	$\nu_{P=Se} = 540$ms $\nu_{C\equiv N} = 2154$m, 2122m	121
$PtCl_2(SePPh_3)_2$	Light tan solid $\nu_{P=Se} = 544$	119
	M.p. 201 °C Formulated as *cis* isomer on basis of colour and insolubility	116
$[Pt(SCN)_2]_3(SePPh_3)_2$ **(6)**	$\nu_{C\equiv N} = 2160$m, 2105mw $\nu_{P=Se} = 537$ms	121
$[Ni(SePMe_3)_4](ClO_4)_2$	Red-brown solid $\nu_{P=Se} = 408s^{d}$ $\nu_{Ni-Se} = 250$m $\mu = 3.41$ B.M.	122
$[Cu(SePPh_3)_3]BF_4$	$\nu_{P=Se} = 546$vs $\Lambda_M(MeNO_2) = 69$	123
$[Ag(SePPh_3)_2]ClO_4$	Colourless solid $\Lambda_M(MeCN) = 132$ $\nu_{P=Se} = 551, 542$	119
$[Au(SePPh_3)Cl]$	Colourless solid M.p. 145 °C	116
$[ZnI_2(SePPh_3)_2]$	M.p. 240 °C $\Lambda_M(PhNO_2) = 17.70$ $\nu_{P=Se} = 532$s	120
$[ZnI_2(SeP(C_6H_4Me\text{-}p)_3)_2]$	M.p. 278 °C dec. $\Lambda_M = 15.88$ $\nu_{P=Se} = 520s^{e}$ $\nu_{Se-Zn} = 345$w	120
$[Zn(SePMe_3)_4](ClO_4)_2$	White solid $\nu_{P=Se} = 414$s $\nu_{Zn-Se} = 202$ms	122
$[Zn(SePMe_3)_2Cl_2]$	White solid $\nu_{P=Se} = 419$s $\nu_{Zn-Cl} = 297$s, 285s $\nu_{Zn-Se} = 225$m	122
$CdBr_2(SePBu_3)_2$	M.p. 68–69 °C ^{31}P-NMR[f] (CH_2Cl_2-$CHCl_3$) 33 °C: $\delta = 42.3$ ($^1J_{PSe} = 569$) -62 °C: ($^1J_{PSe} = 543)^{g}$ -72 °C: ($^1J_{PSe} = 542$, $J_{PCd} = 40)^{g}$	124
$CdCl_2(SePBu_3)_2$	M.p. 76–77 °C ^{31}P-NMR (CH_2Cl_2-$CHCl_3$) 33 °C: $\delta = 42.5$ ($^1J_{PSe} = 564$) -59 °C: ($^1J_{PSe} = 544)^{g}$ -85 °C: ($^1J_{PSe} = 530)^{g}$	124
$CdBr_2(SePPh_3)_2$	^{31}P-NMR (CH_2Cl_2-$CHCl_3$) 33 °C: $\delta = 34.6$ ($^1J_{PSe} = 696)^{h}$	124
$CdI_2(SePPhBu_2)_2$	^{31}P-NMR 33 °C: $\delta = 40.8$ ($^1J_{PSe} = 591)^{i}$	124

TABLE 6. (*Continued*)

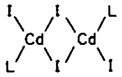
Complex	Reported data[a]	Reference
$[CdBr_2(SeP(C_6H_4Me\text{-}p)_3)_3]_2$ (7)	White crystalline solid M.p. 234 °C $\Lambda_M(PhNO_2) = 6.20$ $\nu_{P=Se} = 525s$	120
 L = $SeP(C_6H_4Me\text{-}p)_3$	$\Lambda_M(PhNO_2) = 3.85$ $\nu_{P=Se} = 520s$ Tetrahedral coordination	120
$HgI_2(SePPh_3)$	Light yellow solid $\nu_{P=Se} = 542$	119
	M.p. 221 °C	116
	P 2p binding energy (XPS) = 132.4 ± 0.3 eV (value for $SePPh_3$ = 133.0 ± 0.2)	125
$HgBr_2(SePPh_3)$	Colourless solid M.p. 260 °C (sublimes) $\nu_{P=Se} = 542$	116
$HgCl_2(SePPh_3)$	Colourless solid M.p. 231 °C $\nu_{P=Se} = 543$	116
	Molecular structure **3**	117
$HgCl_2(SePBu_3)_2$	M.p. 91–92 °C ^{31}P-NMR $(CH_2Cl_2\text{–}CHCl_3)^{f}$ 33 °C: $\delta = 45.1$ $(^1J_{PSe} = 551)$ -12 °C: $\delta = 45.4$ $(^1J_{PSe} = 539)$ -45 °C: $\delta = 45.5$ $(^1J_{PSe} = 535)$ -55 °C: $(^1J_{PSe} = 526,$ $^2J_{PHg} = 157)$ -65 °C: $(^1J_{PSe} = 525$ $^2J_{PHg} = 157)$ -96 °C: $(^1J_{PSe} = 524,$ $^2J_{PHg} = 159)$	124
	$\delta(^{77}Se) = 1535d\ (J_{SeP} = 518)$ $\delta(^{199}Hg) = 325s$	126
$Hg_2Cl_4(SePBu_3)_2$	$\delta(^{31}P) = 45.1\ (J_{PSe} = 527)$ $\delta(^{77}Se) = 1555d\ (J_{PSe} = 505)$ $\delta(^{199}Hg) = -335s$	126
$HgCl_2(SePPhBu_2)_2$	^{31}P-NMR $(CH_2Cl_2\text{–}CHCl_3)$ 33 °C: $\delta = 43.5$ $(J_{PSe} = 555)^{j}$	124
$HgBr_2(SePPhBu_2)_2$	^{31}P-NMR $(CH_2Cl_2\text{–}CHCl_3)$ 33 °C: $\delta = 42.5$ $(^1J_{PSe} = 575)$ -29 °C: $\delta = 43.2$ $(^1J_{PSe} = 563)$	124
$Hg_2I_4(SePPh_2Bu)_2)$	$\delta(^{31}P) = 37.4\ (J_{PSe} = 586)^{k}$, 33 °C	124
$[HgCl_2(SeP(C_6H_4Me\text{-}p)_3)]_2$	M.p. 205–220 °C dec. $\Lambda_M(PhNO_2) = 3.56$ $\nu_{P=Se} = 520s$	120

TABLE 6. (*Continued*)

Complex	Reported data[a]	Reference
$[Co(SePMe_3)_4](ClO_4)_2$	Green solid $\nu_{P=Se} = 409s$ $\nu_{Co-Se} = 273m$ $\mu = 4.40$ B.M.	122
$[Co(SePMe_3)_2Cl_2]$	Blue solid $\nu_{P=Se} = 414s$ $\nu_{Co-Cl} = 321s, 301s$ $\nu_{Co-Se} = 227m$ $\mu = 4.38$ B.M.	122
$[Co(NO)_2(CN)(SePPh_3)]$	M.p. 117 °C $\nu_{C\equiv N} = 2099$ $\nu_{N=O} = 1849, 1791$	127
$[(COD)RhCl(SePPhMe_2)]$	Yellow crystals M.p. 128–130 °C $\nu_{P=Se} = 484$[l] $\nu_{Rh-Cl} = 275$	128
$[Fe(NO)_2(CN)(SePPh_3)]$	M.p. 102 °C $\nu_{C\equiv N} = 2081$ $\nu_{N=O} = 1820, 1729$	127
$Ru(CO)_2(SePPh_3)_2I_2$	Brown–yellow solid	98
$Cr(CO)_5(SePPhMe_2)$	Moderately air-stable yellow crystals M.p. 95 °C $\nu_{P=Se} = 483$ $\nu_{C\equiv O} = 2058, 1980, 1941, 1927, 1912$	129
$W(CO)_5(SePPhMe_2)$	Moderately air-stable yellow crystals M.p. 121 °C $\nu_{P=Se} = 482$ $\nu_{C\equiv O} = 2064, 1975, 1924, 1935, 1907$	129
$WCl_5(SePPh_3)$	Air-sensitive yellow–green powder $\nu_{P=Se} = 532$	130
$[W_2Cl_8(SePPh_3)_2]Cl_2$ (9)	$\nu_{W-Cl} = 331sh, 329sh, 320vs$ $\Lambda_M(PhNO_2) = 42.2$ $MW(PhNO_2) = 475 \pm 15$ (theor. = 468)	130
$WCl_4(PPh_3)(SePPh_3)$	Yellow solid $\mu = 1.98$ B.M. (W(IV))	131
$SnCl_4(SePPh_3)_2$	Yellow air-sensitive solid M.p. 168 °C	114
	$\Lambda_M(DMF) = 5.8$	132

[a] NMR chemical shift values in ppm and *J* values in Hz. ^{31}P: 85% aqueous H_3PO_4 external reference; ^{77}Se: 1 M aqueous selenous acid external reference; ^{199}Hg: 1 M PhHgOAc in DMSO as external reference. Other data are in units given in Table 3. The stretching frequencies for the carbonyl and nitrosyl ligands are given as $\nu_{C\equiv O}$ and $\nu_{N=O}$, respectively, although the actual bond orders in these ligands depend on the specific properties of a given complex (e.g. metal oxidation state, the donor properties of the other ligands present in the coordination sphere etc.; see Ref. 1).

[b] The corresponding value for free $SePPh_3$ is 562 cm^{-1}[117].

[c] The corresponding value for free $SeP(C_6H_4Me\text{-}m)_3$ is 574 cm^{-1}.

[d] The corresponding value for free $SePMe_3$ is 436 cm^{-1}[122].

[e] The corresponding value for free $SeP(C_6H_4Me\text{-}p)_3$ is 535 cm^{-1}[120].

[f] The corresponding values for free $SePBu_3$ are $\delta = 37.0$ ppm, $J_{PSe} = 693$ Hz.

[g] The reference (85% H_3PO_4) freezes, so that accurate chemical shift values were not recorded.

[h] The corresponding value for free $SePPh_3$ is 693 Hz.

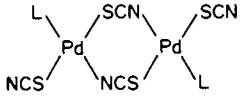
[i] The corresponding value for free $SePPhBu_2$ is 693 Hz.

[j] The corresponding value for free $SePPhBu_2$ is 715 Hz.

[k] The corresponding value for free $SePPh_2Bu$ is 730 Hz[124].

[l] The corresponding value for free $SePPhMe_2$ is 495 cm^{-1}[126].

The complex $Pd(SCN)_2(SePPh_3)$ (8) has a dimeric structure with both S-bonded terminal and bridging thiocyanate (see infrared data, Table 6).



(8)[121]

L = Ph_3PSe

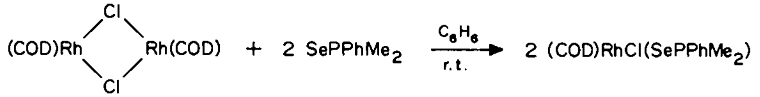
These complexes are readily prepared by reaction of the phosphine selenide in a non-aqueous solvent such as ethanol or acetone with an appropriate aqueous or non-aqueous solution of the metal salt. The Cu(I) complex[123] (Table 6), however, was prepared by adding an ethanol solution containing 3 equiv. of the phosphine selenide to an ethanol solution of $Cu(BF_4)_2 \cdot 6H_2O$ saturated with SO_2 to effect the Cu(II)→Cu(I) reduction. Triorganophosphines[133] and phosphine sulphides[123,134] are well known to effect this reduction without a supplementary reducing agent. Although the bidentate phosphine selenide, $Ph_2P(Se)CH_2P(Se)Ph_2$, reduces $Cu(ClO_4)_2 \cdot 6H_2O$ with the formation of $[Cu(Se,Se)_2]ClO_4$[134], no example of the use of a monodentate R_3PSe derivative as a reductant has been reported.

A trigonal planar three-coordinate Cu(I) complex has been formulated for $[Cu(SePPh_3)_3]BF_4$[123] on the basis of the ionic characterization of the tetrafluoroborate anion by infrared spectroscopy and analogy with the X-ray structure of $[Cu(SPMe_3)_3]ClO_4$, for which this structure has been unequivocally established.

The solution lability of Hg(II) and Cd(II) complexes with $SePR_3$ ligands has been studied by variable-temperature ^{31}P[124], ^{77}Se[126] and ^{199}Hg[126] NMR spectroscopy (see Table 6). In the cases of the $CdX_2(SePBu_3)_2$ complexes, the crystallization of the chloro and iodo complexes at low temperatures prevented freezing out the static tetrahedral structure, but the exchange in the bromo complex was stopped at ca. $-70\,°C$[124]. The complexes $HgX_2(SePBu_3)_n$ ($X = Cl, Br, I$; $n = 1, 2$) have been studied by multinuclear NMR (^{31}P, ^{77}Se, ^{199}Hg)[126]. In all cases the selenide ligand is labile and exchanges rapidly on the NMR time-scale at room temperature, but the exchange can be slowed down at ca. $-100\,°C$, as evidenced by the appearance of ^{31}P–^{199}Hg coupling. Halogen exchange is also fast at room temperature in these complexes[126].

The Co(II) complexes (Table 6) were precipitated from concentrated ethanol solutions containing $SePMe_3$ and the appropriate salt by addition of ether (ethyl orthoformate was used for *in situ* chemical dehydration of the metal salts)[122]. Tetrahedral geometries were assigned to these complexes on the basis of their electronic spectra and magnetic susceptibilities. Electronic spectroscopy also showed that the ligand field strength of $EPMe_3$ ($E = O, S, Se$) were comparable in the ionic complexes $[Co(EPMe_3)_4](ClO_4)_2$[122].

The moderately air-stable complex $(COD)RhCl(SePPhMe_2)$ was prepared by a bridge-cleavage reaction (equation 16).



(16)

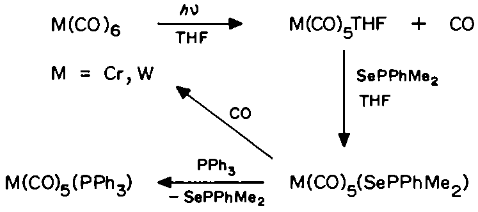
The only reported Ru complex with a phosphine selenide, $Ru(CO)_2(SePPh_3)_2I_2$[101], undergoes solvent-induced polymerization in DMF (equation 17).

$$\begin{tikzcd} \mathrm{Ru(CO)_2(SePPh_3)_2I_2} \arrow[r, "\mathrm{DMF}"] & {[\mathrm{Ru_2(CO)(SePPh_3)_2I_4(Me_2NCHO)}]} \\ {[\mathrm{Ru(CO)_2I_2}]_n} \arrow[u, "\mathrm{C_6H_6}", "\mathrm{SePPh_3/100\,°C/25\,h}"'] & \end{tikzcd} \qquad (17)$$

$$\nu_{C\equiv O} = 1931\ \mathrm{vs\,cm^{-1}}$$

$$\nu_{C=O}\ (\mathrm{DMF}) = 1647\mathrm{s\,cm^{-1}}$$

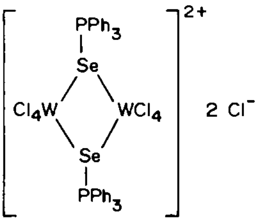
The decrease in the DMF carbonyl stretching frequency ($-31\ \mathrm{cm}^{-1}$ vs. free DMF) is characteristic of the coordination of this solvent[135]. Phosphine selenide complexes of a few transition-metal nitrosyls (Co[127], Fe[127]) and carbonyls (Ru[101], Cr[129]) have also been described briefly. The weak coordination of $SePPhMe_2$ in $Cr(CO)_5(SePPhMe_2)$ is evidenced by its facile replacement by CO or PPh_3 (equation 18). Attempts to prepare $Cr(CO)_5(SePPhMe_2)$ directly by a thermal reaction with $Cr(CO)_6$, rather than the thermally labile THF complex, gave decomposition. This problem of metal-promoted Se extrusion from phosphine selenides has been observed in a number of cases[116,134]. Se transfer between $SePR_3$ and PR_3 in solution is rapid on the NMR time-scale, and a bimolecular process has been proposed[136].



(18)

The problem of Se extrusion from selenocyanate complexes containing organophosphine ligands (i.e. with formation of $SePR_3$ and a cyanide complex) has been discussed in several papers[137–139], and the syntheses of complexes incorporating these two types of ligands must generally be carried out under mild conditions. Indeed, the reaction of KSeCN with PR_3 is a standard preparative route to phosphine selenides[140] (the other route being reaction with red Se[113,122,141]).

The tungsten complex $WCl_5(SePPh_3)$ (**9**) has been formulated, on the bases of infrared spectroscopy, molecular weight and solution conductivity measurements[130] (Table 6), as an ionic dimer with bridging phosphine selenide ligands.



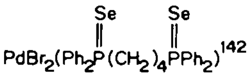
(9)

The corresponding $SPPh_3$ complex shows an especially large decrease in its $\nu_{P=S}$ vibration ($\Delta = -96\ \mathrm{cm}^{-1}$ vs. ~ -30 for the $SePPh_3$ complex)[130].

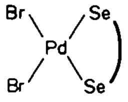
The complex $WCl_4(PPh_3)(SePPh_3)$ was formed by an unusual reaction of a coordinated Se atom[131] (equation 19). The evidence for this formulation includes[131]: (*a*) a $\nu_{W=Se}$ vibration was absent in the infrared spectrum of the product, (*b*) hydrolysis of the product gave a 1:1 mixture of PPh_3 and $OPPh_3$, (*c*) the $\nu_{P=S}$ of the coordinated $SPPh_3$ ligand in the S analogue was observed, although the $\nu_{P=Se}$ band was obscured in the infrared spectrum of the $SePPh_3$ complex.

$$WCl_4Se + \text{excess } PPh_3 \xrightarrow[\substack{\text{sealed}\\ \text{ampoule}\\ \text{1 week}}]{C_6H_6} WCl_4(PPh_3)(SePPh_3) \qquad (19)$$

Although several examples of metal complexes with bidentate bis phosphine selenides ($R_2P(Se)(CH_2)_n(Se)PR_2$, $n = 1$–4) have been reported (see Section II.C.3), in a few cases bridging monodentate coordination modes (**10**–**15**) have been proposed on the basis of spectroscopic evidence.

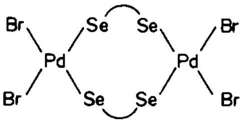


$PdBr_2(Ph_2\overset{Se}{\overset{\|}{P}}(CH_2)_4\overset{Se}{\overset{\|}{P}}Ph_2)^{142}$



(10)

or



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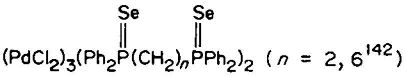
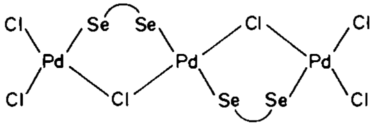
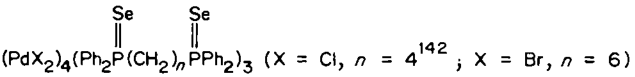


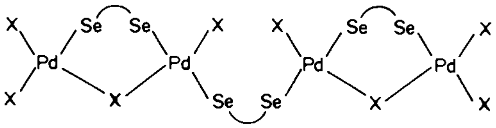
$(PdCl_2)_3(Ph_2\overset{Se}{\overset{\|}{P}}(CH_2)_n\overset{Se}{\overset{\|}{P}}Ph_2)_2$ $(n = 2, 6^{142})$



(12)

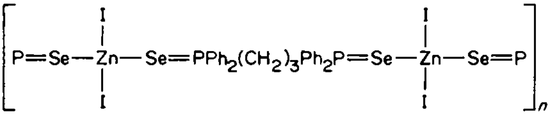


$(PdX_2)_4(Ph_2\overset{Se}{\overset{\|}{P}}(CH_2)_n\overset{Se}{\overset{\|}{P}}Ph_2)_3$ $(X = Cl, n = 4^{142};\ X = Br, n = 6)$



(13)

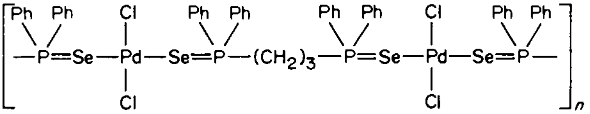
$ZnI_2(Ph_2P(Se)(CH_2)_3(Se)PPh_2)$ (polymeric[120])



$\left[P{=}Se{-}\underset{I}{\overset{I}{Zn}}{-}Se{=}PPh_2(CH_2)_3Ph_2P{=}Se{-}\underset{I}{\overset{I}{Zn}}{-}Se{=}P\right]_n$

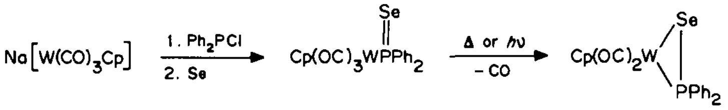
(14)

$[PdCl_2(Ph_2P(Se)(CH_2)_3(Se)PPh_2)]_n{}^{118}$



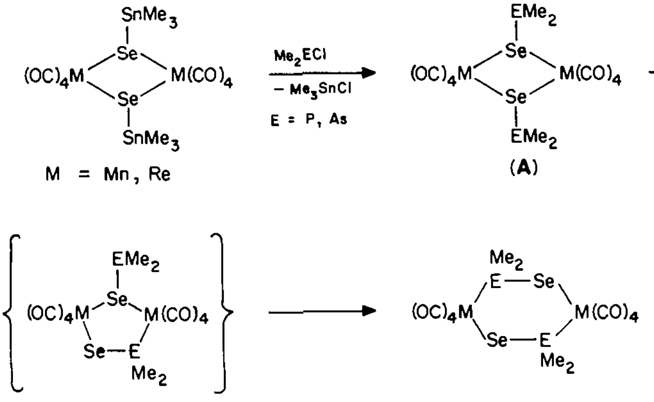
(15)

An interesting reaction sequence involving selenation of a coordinated phosphido ligand and thermally or photochemically induced chelation of the phosphido selenide ligand has been described[143] (equation 20).



(20)

Bridging phosphido- and arsenido-selenide ligands have also been reported[144] (equation 21). The phosphido selenide complexes **A** are very reactive and readily give the six-membered heterocycles **C**. In the arsenidoselenide systems, both the four-membered ring intermediates (**A**: M = Mn, Re; E = As) and the six-membered ring products (**C**) were isolated.

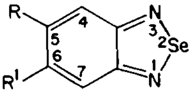


(21)

(**B**) (**C**)

4. Selenium heterocycles

Several Se heterocycles have been shown to function as ligands for transition metals. Metal complexes with 2,1,3-benzoselenadiazole (**16**) and some substituted derivatives (**17**–**19**) have been prepared (Table 7). The 2,1,3-benzoselenadiazole (bsd) complex with palladium, $PdCl_2(bsd)_2$, has been used for the spectrophotometric determination of the metal[145], in which the excess bsd is determined after removal of the insoluble precipitate of the yellow $PdCl_2(bsd)_2$ by centrifugation. This application, which was also the emphasis of much of the early coordination chemistry of various Se ligands, is no longer of interest because of the developments in modern analytical chemistry (e.g. atomic absorption[151] and neutron activation analysis[152]).



(**16**) R = R^1 = H (bsd)
(**17**) R = R^1 = Me (5,6-Me_2-bsd)
(**18**) R = Me; R^1 = H (5-Me-bsd)
(**19**) R = Cl; R^1 = H (5-Cl-bsd)

TABLE 7. Metal complexes with 2,1,3-benzoselenadiazoles

Ligand	Metal complexes/properties[a]
bsd (**16**)[b]	$[PdCl_2(bsd)_2]$[145]
	$[CdCl_2(bsd)]$[148] yellow solid no terminal $\nu_{Cd-Cl} > 250$
	$[CdCl_2(bsd)_2]$[148] white solid no terminal $\nu_{Cd-Cl} > 250$
	$[HgCl_2(bsd)]_2$[148] yellow solid $\nu_{Hg-Cl} = 305\,cm^{-1}$ (terminal)
	$[HgCl_2(bsd)_2]$ white solid $\nu_{Hg-Cl} = 304, 326$ (terminal)
	$CuCl_2(bsd)$[148] brown solid $\nu_{Cu-Cl} = 306$
	$CuCl_2(bsd)_2$[148] green solid $\nu_{Cu-Cl} = 316$
	$CoCl_2(bsd)$[149] no terminal $\nu_{Co-Cl} > 250$ $\mu = 4.86$ B.M. (O_h)
	$NiCl_2(bsd)$[149] no terminal $\nu_{Ni-Cl} > 250$ $\mu = 3.05$ B.M. (O_h)
	$W(CO)_5(bsd)$[150] purple crystals $\nu_{C\equiv O}$ (hexane): 2078, 1947, 1927 ^1H-NMR $\delta(C_7D_8, 27\,°C)$[c] 6.51 (1H, dd), 6.64 (1H, dd), 7.14 (1H, d), 7.24 (1H, d) $^3J(4,5) \approx {}^3J(6,7) = 9.2$ $^3J(5,6) = 6.5$
5-Me-bsd (**18**)	$CuCl_2(5\text{-Me-bsd})$[148] yellow–brown solid $\nu_{Cu-Cl-Cu} = 318$
	$CdCl_2(5\text{-Me-bsd})$[148] $\nu_{Cd-Cl} = 270$
5-Cl-bsd (**19**)	$CuCl_2(5\text{-Cl-bsd})$[148] yellow–brown solid $\nu_{Cu-Cl-Cu} = 275, 290$
	$CdCl_2(5\text{-Cl-bsd})$[148] $\nu_{Cd-Cl} = 310$
5,6-Me_2-bsd (**17**)	$CdCl_2(5,6\text{-}Me_2\text{-bsd})$[148] $\nu_{Cd-Cl} = 270$

[a] Data are in the units given in Table 3. O_h = octahedral.

[b] This ring is also called 1,2,5-selenadiazole[146,147].

[c] The spectrum at 100 °C had four broad signals at about the same δ values.

A number of Cd(II), Cu(II), Hg(II), Ag(I), Ni(II) and Fe(III) complexes of 2,1,3-benzoselenadiazole (**16**) and some substituted derivatives (**17**–**19**) have been prepared and characterized by elemental analyses and infrared spectroscopy, and their thermal stability has been studied by thermogravimetric and differential thermal analyses under a nitrogen atmosphere[148,149] (Table 7).

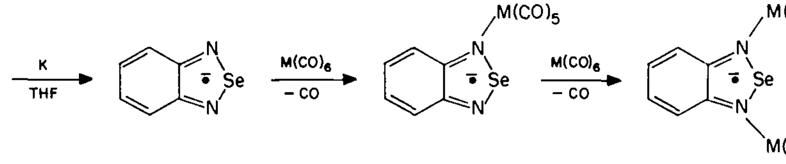
These complexes, MCl_2L_n ($n = 1,2$), which are readily precipitated by the addition of an appropriate amount of the selenadiazole to the metal chloride in aqueous ethanol (anhydrous ethanol for Ni and Co), were formulated as dimeric or polymeric species with bridging chloro and/or selenadiazole ligands, except for the monomeric tetrahedral $HgCl_2(bsd)_2$[148,149]. The structural characterization of these complexes is tentative; indeed, the bonding sites of the selenadiazole ligands were not clearly established, although nitrogen bonding was inferred by the trend of the thermal stabilities of the complexes as a function of the substituent in the 5-position of the heterocyclic system. Most likely, the bonding sites of such heterocycles vary according to the nature of the metal ion and other ligands present in the coordination sphere of the complex, as has been well established for other ambidentate ligands[153].

In an ESR study[154] of the complexes $Cu(bsd)_2X_2$ (X = F, Cl, Br) Cu—Se bonding (and Cu—S bonding in the benzothiadiazole (btd) analogues) was proposed. A subsequent investigation[155] of the btd complexes by ESR and infrared spectroscopy and magnetic susceptibility measurements led to the conclusion that these complexes are mononuclear and contain N-bonded btd. Bonding via N(1) has been established by a single-crystal X-ray diffraction analysis[156] of $CdBr_2$ $(4\text{-}NH_2\text{-btd})_2$, which has octahedral geometry around the Cd(II) with bridging bromo ligands that form infinite chains and two $4\text{-}NH_2$-btd ligands coordinated to each Cd in *trans* positions.

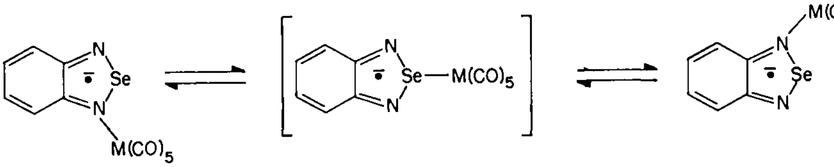
This work all illustrates the importance of caution in assigning the structures of complexes containing such ambidentate ligands. Ideally, it is possible to make such assignments on the basis of high-resolution infrared spectroscopy if the appropriate model compounds have been characterized by single-crystal X-ray diffraction. Thiocyanate and selenocyanate complexes, which have the added advantage of having strong $\nu_{C\equiv N}$ bands in a rather isolated infrared spectral region (2000–2200 cm^{-1}), are examples for which this is a fairly safe procedure[153]. More recently, XPS[157] and solid-state NMR[158] have been used to 'fingerprint' bonding sites of ambidentate ligands and should prove more generally useful for such studies.

The observation that the polarographic reduction waves of the 2,1,3-benzo-*X*-diazoles (X = O, S, Se) are shifted only for the S and Se compounds upon addition of Cu(II) and Cd(II) was explained by coordination of only these two ambidentate heterocycles to the metals via the S or Se atoms[159]. In a related study[160], 2,1,3-benzoselenadiazole was shown to function as a catalytically active ligand for the reduction of Ni(II) at a dropping-mercury electrode. A prewave of Ni(II) observed here was assigned to a polarographically active complex formed between the metal ion and the adsorbed ligand.

The radical anion of 2,1,3-benzoselenadiazole (**16**), observed in the two-step polarographic reduction of these heterocycles in DMF[154], has been shown by ESR spectroscopy to form 1:1 and 2:1 complexes with $M(CO)_6$ (M = Cr, Mo, W)[150] (equation 22).

16  (22)

The formation of the monosubstituted product is rapid, with the formation of the disubstituted product decreasing in the order Cr > Mo > W; $[W(CO)_5]_2(bsd^{\cdot-})$ forms only after several months at room temperature. These reactions were run in ESR tubes with ca. 5:1 molar ratios of $M(CO)_6$ to bsd. These paramagnetic species are stable in THF for several months at room temperature. The spectra of the Cr and Mo complexes indicated static M—N bonding, whereas the spectrum of $W(CO)_5(bsd^{\cdot-})$ suggested rapid fluctuation of the $W(CO)_5$ fragment between the two N sites (equation 23). Attempts to freeze out a static structure were hampered by typical anisotropic line-broadening effects below 0 °C.

 (23)

The ^1H-NMR spectrum of the neutral complex $W(CO)_5(bsd)$, prepared from $W(CO)_5(THF)$ and bsd in THF, gave a resolved spectrum at room temperature (Table 7), and at 120 °C the four resonances were still resolved but slightly broadened with loss of the ^3J coupling.

Complexes with terminal and bridging N-bonded cycloalkenyl-1,2,3-selenadiazoles (**20a–d**) have been obtained with Cr, Mo and W carbonyls[161,162] (Table 8; equations 24–26).

TABLE 8. Metal complexes with cycloalkenyl-1,2,3-selenadiazoles (**20**)

Metal complexes/ properties[a] [162]	Metal complexes/ properties[a] [162]	Metal complexes/ properties[a] [162]
21b: m.p. 111 °C dec. $\nu_{C\equiv O}{}^{b}$ = 2070w, 1989w, 1944s, 1920m	**23b**: m.p. 115 °C dec. $\nu_{C\equiv O}{}^{b}$ = 2070w, 1980w, 1940s, 1920m $\delta(^1H)^c$: 3.2m and 3.0m (αH); 1.85m (βH) $\delta(^{13}C)^c$: sp^{2}C, 162.5, 159.5; sp^{3}C, 25.2, 25.1, 22.6, 21.7; *trans*-CO, 202.7; *cis*-CO, 200.4	**24**: m.p. 90 °C dec. $\nu_{C\equiv O}{}^{d}$ = 2020w, 1907s, 1840s
22b: m.p. 112 °C dec. $\nu_{C\equiv O}{}^{b}$ = 2070w, 1980w, 1935s, 1915m		**25**: m.p. 176 °C dec. $\nu_{C\equiv O}{}^{e}$ = 1905s, 1818s

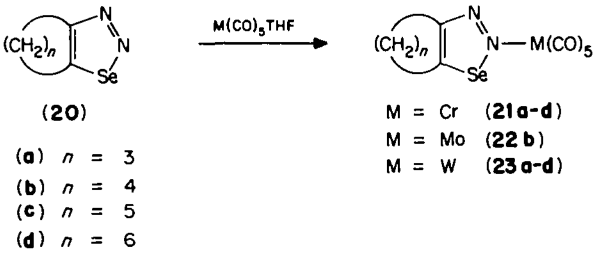
[a] Data are in the units given in Table 3. SP = square planar.

[b] In hexane solution.

[c] In $CDCl_3$, internal TMS.

[d] In CH_2Cl_2.

[e] In THF.



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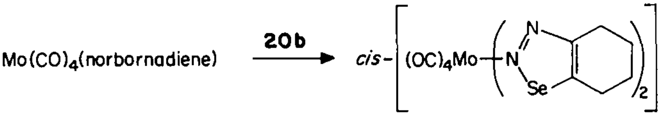

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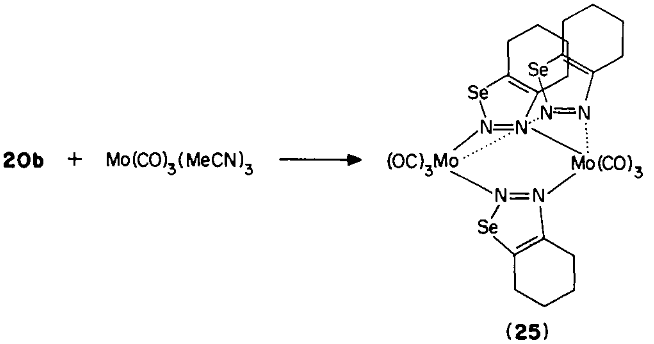
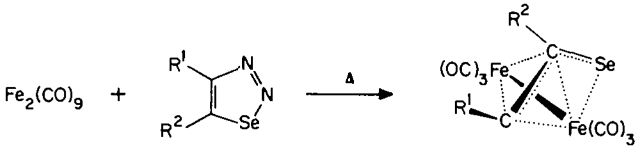


(25)

(26)

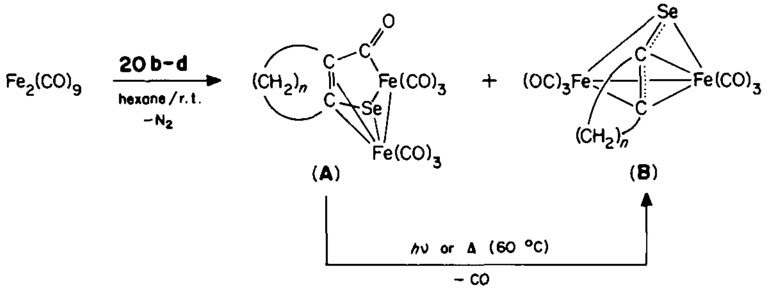
Reactions of 1,2,3-selenadiazoles with $Fe_2(CO)_9$, however, result in facile extrusion of N_2 from the heterocyclic ring system and formation of iron dimers containing bridging selenoketocarbene ligands[161–164] (equation 27). The isomeric ratios of products obtained from the latter two unsymmetrically substituted derivatives were obtained by ^1H-NMR spectroscopy of the crude reaction product obtained after one preparative TLC separation, the major isomer then being isolated by further chromatography and recrystallization[163]. The by-products, $Fe_3(\mu_3\text{-}Se)_2(CO)_9$ and $PhC{\equiv}C\text{-}p,\text{-}t\text{-}BuC_6H_4$, were obtained only in small amounts in these reactions, although in the reaction with the unsubstituted 1,2,3-selenadiazole, the only iron complex formed was the known cluster $Fe_3(\mu_3\text{-}Se)_2(CO)_9$[163].



(27)

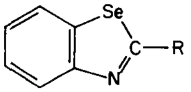
$R^1 = R^2 = Ph$	6%[163] 21%[164]
$R^1 = Ph$, $R^2 = p\text{-}t\text{-}BuC_6H_4$	$R^1 = Ph$, $R^2 = p\text{-}t\text{-}BuC_6H_4$: 26%[163] $R^1 = p\text{-}t\text{-}BuC_6H_4$, $R^2 = Ph$: 8%
$R^1 = p\text{-}t\text{-}BuC_6H_4$, $R^2 = Ph$	$R^1 = p\text{-}t\text{-}BuC_6H_4$, $R^2 = Ph$: 26%[163] $R^1 = Ph$, $R^2 = p\text{-}t\text{-}BuC_6H_4$: 8%

In subsequent work[161], such reactions at room temperature gave intermediate selenaferrole complexes that could be isolated by chromatography (equation 28). The selenaferrole complexes (**A**) readily gave the selenoketocarbene complexes (**B**) upon UV irradiation or thermolysis. Examples of both products have been unequivocally characterized by single-crystal X-ray diffraction (**A**, $n = 4$[165]; **B**, $n = 6$[166]).



(28)

Beck and coworkers have reported complexes of benzoselenazole (**26a**)[167] and its 2-methyl derivative (**26b**)[168] with Cr, Mo and W carbonyls (Table 9). These complexes were prepared by typical substitution reactions (equations 29 and 30).



bs, (**26a**) R = H
mbs, (**26b**) R = Me

$$M(CO)_6 + L \xrightarrow[h\nu]{THF} M(CO)_5L \tag{29}$$

$$L = bs^{167}, \quad mbs^{168}$$

$$Mo(CO)_4(C_7H_8) + bs \xrightarrow[-C_7H_8]{THF} Mo(CO)_4(bs)_2 \tag{30}$$

$$C_7H_8 = \text{cycloheptadiene}$$

Characterization by ^{14}N- and ^{1}H-NMR spectroscopy has indicated that in the bs

TABLE 9. Complexes with benzoselenazoles **26a** (bs) and **26b** (mbs)

Metal complexes/properties[a]
$Cr(CO)_5(bs)^{167}$ yellow solid m.p. 153 °C dec. $\nu_{C\equiv O}{}^{b} = 2071, 1938, 1895$ $\delta(^{14}N)^{b,c}$: $+118$ ($\Delta = +64$) $\delta(^{1}H)^{d}$: -10.70 ($\Delta = -0.59$)
$Mo(CO)_5(bs)^{167}$ yellow solid m.p. 145 °C $\nu_{C\equiv O}{}^{b} = 2078, 1944, 1894$ $\delta(^{14}N)^{b,c}$: $+117$ ($\Delta = +63$) $\delta(^{1}H)^{d}$: -10.78 ($\Delta = -0.67$)
$W(CO)_5bs^{167}$ yellow solid m.p. 167 °C $\nu_{C\equiv O}{}^{b} = 2078, 1934, 1896$ $\delta(^{1}H)^{d}$: -10.94 ($\Delta = -0.83$)
$Mo(CO)_4(bs)_2{}^{167}$ yellow solid m.p. 141 °C $\nu_{C\equiv O}{}^{e} = 2019, 1898, 1859, 1804$
$Cr(CO)_5(mbs)^{168}$ green-yellow solid m.p. 110 °C $\nu_{C\equiv O}{}^{b} = 2073, 1939, 1887$ $\delta(^{14}N)^{b,c}$: $+49$ ($\Delta = -10$) $\delta(^{1}H)^{d}$: -2.82 ($\Delta = -0.11$)
$W(CO)_5(mbs)^{168}$ yellow crystals m.p. 168 °C $\nu_{C\equiv O}{}^{b} = 2071, 1930, 1886$ linkage isomers in acetone solution W—Se $\delta(^{14}N)^{b,c}$: $+45$ ($\Delta = -14$) $\delta(^{1}H)^{d}$: N—Me, -2.83 ($\Delta = -0.12$) W—N $\delta(^{14}N)^{b,c}$: $+180$ ($\Delta = +121$) $\delta(^{1}H)^{d}$: -3.28 ($\Delta = -0.57$)
$NiCl_2(mbs)^{169}$ red crystals m.p. 216 °C dec.
$Ni(NO_3)_2(mbs)_2{}^{169}$ pale green crystals m.p. 222 °C dec. $\mu = 3.71$ B.M.
$NiBr_2(mbs)_2{}^{169}$ pale blue crystals m.p. 170–171 ° dec.
$NiI_2(mbs)_2{}^{169}$ dark green solid m.p. 234–235 °C dec.
$Ni(NCS)_2(mbs)_2{}^{169}$ red solid m.p. 199 °C (colour change to green at 132 °C) μ(20–130 °C) = 1.05 B.M. μ(135 °C) = 3.6 B.M.

[a] Data are in the units given in Table 3.

[b] In acetone solution.

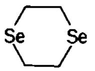
[c] Vs. external aqueous $NaNO_3$; $\Delta =$ shift vs. free ligand.

[d] Resonance in acetone-d_6 solution (internal TMS) of R in **26**; $\Delta =$ shift vs. free ligand.

[e] In Nujol.

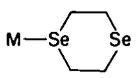
complexes the heterocycles coordinate via the nitrogen, whereas W(CO)$_5$mbs contains about equal amounts of the W—N and W—Se linkage isomers, and the Mo analogue, primarily N-bonded, forms a small amount of the Se-bonded isomer on standing in acetone solution (Table 9). The structure of W(CO)$_5$mbs in the solid state has not been established but would be a problem amenable to solid-state Se-NMR[158] or X-ray photoelectron spectroscopy[157].

Several Ni(II) complexes of **26b** have been isolated and characterized by infrared and electronic spectroscopy as well as magnetic susceptibility measurements (Table 9)[169]. Electronic spectroscopy and conductivity measurements indicated significant dissociation of the heterocyclic ligand in methanol. The complex Ni(NCS)$_2$(mbs)$_2$ exhibited an unusual transition from an equilibrium mixture of paramagnetic tetrahedral–diamagnetic square planar to pure tetrahedral stereochemistry at ~ 132 °C, a change accompanied by a colour change from red to green. A broad $\nu_{C\equiv N}$ band in the bridging region (2125–2175 cm^{-1}) indicated a dimeric or polymeric formulation for this complex.

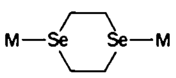


dse, (**27**)

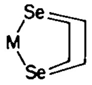
1,4-Diselenan (dse) (**27**), prepared in 10% yield from Al$_2$Se$_3$ and BrCH$_2$CH$_2$Br[170], forms complexes with a variety of transition metals[170,171] (Table 10). This heterocycle can, in principle, function as a monodentate (terminal, **A**, or bridging, **B**) or bidentate ligand



(A)

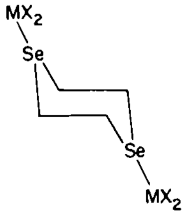


(B)



(C)

C). Since no definitive single-crystal X-ray diffraction analysis has been reported for such complexes, the proposed bonding modes, in some cases tentative, are based on the stoichiometries as well as infrared[171] and NMR[172] spectroscopy. The complexes of the stoichiometry (MX$_2$)$_2$(dse) (M = Cd, Hg; X = Cl, Br; Table 10) were formulated as dimers with a bridging dse ligand[171]:



The ν_{M-Cl} bands in these complexes all occur in the terminal region[171].

A centrosymmetric chair configuration of the bridging ligand has been proposed on the basis of the similarity of its infrared spectrum[171] to that of free dse, for which this conformation has been established by X-ray crystallography[173]. The cuprous chloride complex, CuCl(dse), also gave an infrared spectrum similar to that of the free ligand, but its insolubility suggested a polymeric formulation with dse in a chair conformation. Either bridging chloro or dse ligands (or both) may be present in this complex[171].

TABLE 10. Complexes with 1,4-diselenan (dse) (**27**)

Complex	Properties[a]	Complex	Properties
$[PdCl_2(dse)]$	Bright yellow solid[170]	$(HgBr_2)_2dse$	White solid[171]
	$\nu_{Pd-Cl} = 303, 318$[171]	$(CdCl_2)_2dse$	White solid[171]
$[PdBr_2(dse)]$	Orange yellow solid[171]	$(CuCl_2)dse$	Dark violet crystals[171]
	$\nu_{Pd-Br} = 253, 268$	$(CuBr_2)_2dse$	Brown powder[171]
$[PtCl_2(dse)]$	Pale yellow powder[171]	$AgNO_3(dse)$	White powder[171]
	$\nu_{Pt-Cl} = 314, 324$	$CuCl(dse)$	White powder[171]
$(HgCl_2)_2dse$	White solid[171]	$AuCl_3(dse)$	Pale yellow solid[171]
	$\nu_{Hg-Cl} = 310$	$AuBr_3(dse)$	Dark brown solid[171]

[a] Data are in the units given in Table 3.

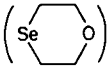
The infrared spectra of the complexes $MX_2(dse)$ (Table 10) are markedly different from the above complexes and have been interpreted in terms of either a monomeric formulation with chelating dse in a boat conformation (C) or dimers with two bridging dse ligands in boat conformations. The stoichiometries and infrared spectra of the $AuX_3(dse)$ ($X = Cl$, Br) complexes suggest monomeric, four-coordinate complexes containing monodentate dse in the chair configuration[171].

The ambidentate 1,4-oxaselenan (ose) (**28**) coordinates through its Se atom as a terminal ligand or via both O and Se atoms as a bridge ligand[174] (Table 11), but no well-established examples of terminal oxygen or chelating (O, Se) coordination have been reported. The essentially unchanged values of the symmetric and unsymmetric C—O—C

TABLE 11. Complexes with 1,4-oxaselenan (ose) (**28**)

Complex	Properties[a]	Complex	Properties[a]
$SnCl_4(ose)_2$[174]	$\nu_{C-O-C,asym} = 1100$vs[b]	$NbCl_5(ose)$[174]	$\nu_{C-O-C,asym} = 1100$vsb
	$\nu_{C-O-C,sym} = 818$m[c]		$\nu_{C-O-C,sym} = 819$s[c]
	δ: $OCH_2 = 4.13$ ($\Delta = 0.08$)[d]		δ: $OCH_2 = 4.20$ ($\delta = 0.15$)[d]
	$SeCH_2 = 2.91$ ($\Delta = 0.25$)[d]		$SeCH_2 = 3.66$ ($\Delta = 1.00$)[d]
$SnBr_4(ose)_2$[174]	$\nu_{C-O-C,asym} = 1100$vs[b]	$TiCl_4(ose)$[174]	Orange-red solid
	$\nu_{C-O-C,sym} = 891$m[c]		$\nu_{C-O-C,asym} = 1043$vs[b]
	δ: $OCH_2 = 4.10$ ($\Delta = 0.05$)[d]	$MX_2(ose)_2$[175]	$\nu_{C-O-C,sym}$ 790s[c]
	$SeCH_2 = 2.71$ ($\Delta = 0.05$)[d]	M = Pd, Pt; X	
$TiCl_4(ose)_2$[174]	Orange solid	= Cl, Br	
	$\nu_{C-O-C,asym} = 1102$vs[b]		Variable-temperature ^1H-NMR
	$\nu_{C-O-C,sym} = 812$m[c]		
	δ: $OCH_2 = 4.13$ ($\Delta = 0.08$)[d]	*trans*-	
	$SeCH_2 = 2.91$ ($\Delta = 0.25$)[d]	$PtBr_2(ose)_2$[176]	Molecular structure Pt—Se: 2.430 Å Pt—Br: 2.442 Å < Se—Pt—Br: 93.3°

[a] Data are in the units given in Table 3.
[b] The corresponding value in the free ligand is 1102vs.
[c] The corresponding value in the free ligand is 812s.
[d] Shifts downfield vs. free ose.



ose, (**28**)

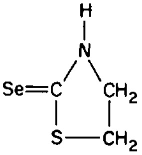
stretching modes of the heterocycle in the complexes $SnX_4(ose)_2$ (X = Cl, Br), $TiCl_4(ose)_2$ and $NbCl_5(ose)$ vs. the free ligand support Se bonding in these complexes[174]. The decrease in the shifts of these bands to lower values for $TiCl_4(ose)$ vs. the free heterocycle (Table 11) and the stoichiometry of this complex support a polymeric formulation with octahedral coordination of the Ti and bridging ose ligands[174].

The weakness of the corresponding CSeC modes precludes direct verification of the proposed Se bonding in these complexes. The larger shift of the methylene protons adjacent to the Se vs. those adjacent to the O in the ^{1}H-NMR of these complexes relative to the free heterocycle (e.g. $\Delta\delta_{SeCH_2} \simeq 1.0$ vs. $\Delta\delta_{OCH_2} \simeq 0.1$) further supports monodentate Se bonding in the above monomeric complexes (Table 11). These results indicate that these halides (Cl, Br) exhibit class B Lewis acid behaviour; the fluorides however, exhibit the class A behaviour expected of such elements in their highest common oxidation states (e.g. $BF_3{\cdot}O(CH_2CH_2)_2S$ exhibits O coordination; the corresponding selenan complex was not reported)[174].

A variable-temperature ^{1}H-NMR study[175] of the complexes $MX_2(ose)_2$ (M = Pt, Pd; X = Cl, Br) showed that the observed coalescence phenomena are caused by site inversion about the Se atom rather than by ring inversion of the heterocyclic ligand.

A single-crystal X-ray diffraction study of the monomeric square-planar complex *trans*-$PtBr_2(ose)_2$ confirmed a monodentate Se bonding mode of the 1,4-oxaselenan ligand with an axial orientation of the Pt—Se bond relative to the ring (the analogous oxathian complex has this bond equatorial to the ring)[176].

Thiazolidine-2-selenone (tzse) (**29**), prepared by the reaction of NaHSe and 1,3-thiazolidine-2-methylthiol, also exhibits ambidentate ligand behaviour[177]. The electronic spectra and magnetic susceptibilities of its Co(II) and Ni(II) complexes (Table 12) indicate tetrahedral geometries in all cases, and infrared spectroscopy supports N bonding in the Co(II) complexes and Se bonding in the Ni(II) complexes. The ν_{N-H} bands for the Co(II) complexes exhibit large negative shifts of ~270 cm^{-1} vs. the free ligand; but the bands associated with the S(ν_{C-S}) and Se ($\nu_{C=Se} + \delta_{N-C-Se}$) are essentially unchanged or show slight positive shifts. More direct evidence for N bonding is found in the far-infrared region, where ν_{Co-N} bands for the three complexes are observed at ~250 cm^{-1}; ν_{Co-S} bands would be expected to appear at ~230 cm^{-1}. The electronic spectra of the complexes also support CoN_2X_2 (X = Cl, Br, I) tetrahedral coordination spheres.



tzse, (**29**)

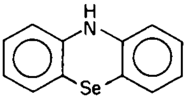
The ν_{N-H} vibrations of the Ni(II) complexes appear as broad bands in the region 3350–3400 cm^{-1}, near that of the free ligand, and bands in the FIR region, at 170–180 cm^{-1}, are assigned to ν_{Ni-Se} vibrations (ν_{Ni-N} bands would be expected at 220–230 cm^{-1}). The proposed Se bonding mode is further supported by the essentially unchanged position of the NH resonance vs. the free ligand in the ^{1}H-NMR spectra of the Ni(II) complexes, whereas shifts of ~1.5 ppm to lower field are observed for the Co(II) complexes.

TABLE 12. Complexes with thiazolidine-2-selenone (tzse) (**29**)[177]

Complex	Properties[a]	Complex	Properties[a]
$[Co(tzse)_2Cl_2]\cdot 2H_2O$	Turquoise solid M.p. > 350 °C $\mu = 5.1$ B.M. $\nu_{N-H} = 3130$vs[b] $\nu_{C-N} = 1530$vs[c] $\nu_{C=Se} + \delta_{N-N-Se} = 1310$vs[d] $\nu_{C-S,asym} = 715$[e] $\nu_{C-S,sym} = 660$ms[f] $\nu_{Co-Cl} = 321$m, 305m $\nu_{Co-Se} = 252$m	$[NiCl_2(tzse)]$	Olive green solid M.p. > 350 °C $\mu = 3.6$ B.M. $\nu_{N-H} = 3400$vs[b] $\nu_{C-N} = 1560$m[c] $\nu_{C=Se} + \delta_{N-C-Se} = 1310$m[d] $\nu_{C-S,asym} = 710$w[e] $\nu_{Ni-Cl-Ni} = 204$m, 154m $\nu_{Ni-Cl} = 268$m, 240s $\nu_{Ni-N} = 180$ms
$[Co(tzse)_2Br_2]\cdot 2H_2O$	Dark green solid M.p. 300 °C dec. $\mu = 4.6$ B.M. $\nu_{N-H} = 3140$s[b] $\nu_{C-N} = 1520$vs[c] $\nu_{C=Se} + \delta_{N-C-Se} = 1300$vs[d] $\nu_{C-S,asym} = 695$m[e] $\nu_{C-S,sym} = 660$ms[f] $\nu_{Co-Br} = 283$m, 215m $\nu_{Co-Se} = 250$m	$[NiBr_2(tzse)]$	Dark brown solid M.p. > 350 °C $\mu = 3.7$ B.M. $\nu_{N-H} = 3350$vs[b] $\nu_{C-N} = 1510$m[c] $\nu_{C=Se} + \delta_{N-C-Se} = 1295$ms[d] $\nu_{C-S,asym} = 700$w[e] $\nu_{C-S,sym} = 660$w[f] $\nu_{Ni-Br-Ni} = 158$m, 148m $\nu_{Ni-Br} = 200$m $\nu_{Ni-N} = 171$ms
$[Co(tzse)_2I_2]\cdot 2H_2O$	Dark green solid M.p. 224 °C dec. $\mu = 4.6$ B.M. $\nu_{N-H} = 3230$m[b] $\nu_{C-N} = 1505$vs[c] $\nu_{C=Se} + \delta_{N-C-Se} = 1290$vs[d] $\nu_{C-S,asym} = 695$w[e] $\nu_{C-S,sym} = 665$w[f] $\nu_{Co-I} = 206$ms $\nu_{Co-Se} = 255$s	$[NiI_2(tzse)_2]$	Black solid M.p. > 350 °C $\mu = 3.9$ B.M. $\nu_{N-H} = 3130$vs[b] $\nu_{C-N} = 1550$m[c] $\nu_{C-Se} + \delta_{N-C-Se} = 1310$w[d] $\nu_{C-S,asym} = 690$w[e] $\nu_{C-S,sym} = 660$[f] $\nu_{Ni-I} = 210$m $\nu_{Ni-N} = 176$ms

[a] Data are in the units given in Table 3.
[b] Corresponding band in free tzse = 3100vs (solid) and 3400vs ($CHCl_3$ solution).
[c] 1515vs in free tzse.
[d] 1285vs in free tzse.
[e] 705ms in free tzse.
[f] 655m in free tzse.

Reaction of $Pd(F_6acac)_2$ with 1 or 2 equiv. of phenoselenazine (psz) (**30**) in acetone/toluene gives, on concentration of the reaction solution, blue microcrystals of the composition $Pd(F_6acac)_2(psz)_2$[178] (Table 13). An ionic structure, $[Pd(F_6acac)(psz)_2](F_6acac)$, is supported by the presence of a $\nu_{C=O}$ band at 1670 cm^{-1} (vs.



psz , (**30**)

TABLE 13. Complexes with phenoselenazine (psz) (**30**)

Complex	Properties[a]
$[Pd(psz)_2(F_6acac)](F_6acac)$[178]	Deep blue solid λ_{max} (Nujol) = 610, 735 nm
trans-$PtCl_2(psz)_2$[179]	Orange crystals $\nu_{Pt-Cl} = 325$
cis-$[PtCl_2(psz)_2]\cdot MeCN$[179]	Orange needles $\nu_{Pt-Cl} = 310, 285$ $\nu_{C\equiv N} = 2260$ (lattice MeCN) Molecular structure Pt—Se: 2.376(2), 2.400(2) Å
trans-$PdCl_2(psz)_2$[179]	$\nu_{Pd-Cl} = 335$

[a] Data are in the units given in Table 3.

1603 cm^{-1} in $Pd(F_6acac)_2$). The proposed structure was unequivocally established by a single-crystal X-ray diffraction analysis for the bipy complex ($[Pd(F_6acac)bipy]^+(F_6acac)^-$)[178]. The visible absorption bands of this complex (Table 13) were assigned to ligand → metal charge-transfer processes, since free psz is readily oxidized to a stable radical cation. Dilute acetone solutions of the complex are readily bleached in air[178]. Nucleophilic attack by excess psz at Pd is not observed in this complex although in the cases of L = pyr, Ph_3As and *i*-$PrNH_2$, further substitution to give ultimately $[PdL_4](F_6acac)_2$ has been reported[180].

Reaction of psz with $K[PtCl_3(C_2H_4)]$ in acetonitrile gives an initial orange precipitate of *trans*-$PtCl_2(psz)_2$; after filtration and concentration of the solution, large orange crystals of *cis*-$PtCl_2(psz)_2\cdot MeCN$ are isolated[179]. The *cis* isomer is apparently the thermodynamically stable form, since recrystallization of the *trans* isomer from hot acetonitrile gives the *cis* isomer along with some decomposition products, as evidenced by infrared spectroscopy. Exposure of the *cis* and *trans* complexes to iodine vapour gives the partially oxidized non-crystalline compounds *cis*-$PtCl_2(psz)_2I_{3.9}$ and *trans*-$PtCl_2(psz)_2I_{3.5}$, respectively[179]. These latter complexes have significantly greater electrical conductivity than the insulating precursors. Resonance Raman and XPS indicate that the hole sites are localized on the psz ligand and that the iodine is present predominantly as I_5^- [179].

Tetraphenylselenophene has been obtained in 60% yield by heating a mixture of powered amorphous Se and $Fe_2(CO)_6(C_2Ph_2)_2$ at 200 °C[181]. An ESR study of the interaction of tetrahydroselenophene with the planar Co(II) complex *N*,*N'*-bis(salicyliden)-*o*-phenylenediaminocobalt(II) (Co(saphen)) has indicated the formation of a 2:1 adduct[182].

5. Diorganodiselenides (RSeSeR) and related ligands (RSeER'$_2$; E = P, As)

Although the most characteristic reaction of these derivatives in transition-metal chemistry involves the cleavage of the Se—Se bond with formal oxidation of the metal centre and formation of terminal or bridging SeR^- ligands (see Section II.B.2), several examples of coordination of intact RSeSeR ligands have been reported (Table 14).

The Pt(IV) dimers were prepared according to equation (31)[183]. The yellow products were isolated by addition of light petroleum after concentration of the reaction solutions. The crystal structural determination[184,185] of the bromo analogue established it as the first example of a complex containing a bridging diorganodiselenide ligand. A similar structure was subsequently established for the iodo analogue[186]. A variable-temperature

TABLE 14. Metal complexes with RSeSeR and RSeER$^1_2$ (E = P, As) ligands

Complex	Reported data	Reference
μ_2-(Alkyl)SeSe(alkyl)		
31a	Yellow solid	183
	M.p. 144–146 °C dec.	
	^{1}H-NMR	183–185
	Molecular structure	184
	Pt—Pt: 3.740(3) Å	
	Pt—Br: 2.629 Å	
	Se—Se: 2.36(1) Å	
31b	Yellow solid	183
	M.p. 150–151 °C dec.	
	MW = 730^a (calc. 739)	
	^{1}H-NMR	183, 185
31c	Yellow solid	183
	M.p. 120–125 °C dec.	
	MW = 929^a (calc. 921)	
	^{1}H-NMR	183, 185
	Molecular structure	186
	Pt—Pt: 3.901(2) Å	
	Pt—I: 2.798(2) Å, 2.778(2) Å	
	Se—Se: 2.358(4) Å	
32a	Pale yellow crystals	187
	M.p. 158–159 °C dec.	
	$\nu_{C\equiv O}{}^b$ = 2054, 2038, 1950, 1926	
	Variable-temperature ^{1}H-NMR	
	Molecular structure	
	Re—Re: 3.883 Å	
	Re—Br: 2.644 Å	
	Se—Se: 2.375(4) Å	
32b	Red–orange solid	187
	M.p. 181–182 °C dec.	
	$\nu_{C\equiv O}{}^c$ = 2040, 2027, 1956, 1925	
Terminal (alkyl) SeSe(alkyl)		
$W(CO)_5(R_2Se_2)$	Variable-temperature ^{1}H-NMR	188
$R = CH_2SiMe_3$	E_a (kJ mol^{-1})	
	inversion: 59.8 ± 0.8	
	1,2-shift: 82.6 ± 1.6	
μ_2-*(Aryl)SeSe(aryl)*		
32c	Orange–red solid	189
	$\nu_{C\equiv O}{}^d$ = 2057m, 2041s, 1963s, 1960sh, 1936s	
	Molecular structure	
	Re—Re: 3.899(43) Å	
	Re—Br: 2.656(20) Å	
	Se—Se: 2.411(23) Å	
	Re—Se: 2.604(4) Å	
32d	$\nu_{C\equiv O}{}^d$ = 2051m, 2035s, 2022w, 1961s	190
32e	$\nu_{C\equiv O}{}^d$ = 2053m, 2036s, 2023w, 1977s,	
	1973sh, 1946s	191
	Molecular structure	
	Mn—Se : 2.478(3) Å	
	Mn—Mn: 3.680(5) Å	
	Se—Se : 2.401(3) Å	
	Mn—Br : 2.542(4), 2.541(3)	
$[Ag_2(Se_2Ph_2)_4](AsF_6)_2$	Molecular structure (Figure 1)	191a

TABLE 14. (*Continued*)

Complex	Reported data	Reference
R_2PSeR^1		
$Cr(CO)_5(Me_2PSeMe)$	Dark yellow air-sensitive crystals $\nu_{C\equiv O}{}^e = 2071m, 1987w, 1960s, 1949vs$ $\delta(^1H) = 1.28\ (\Delta^f = -0.03)$ $1.38\ (\Delta^f = -0.44)$ $\delta(^{31}P) = 38.5\ (\Delta^f = 37.7)$	192, 193
$Cr(CO)_5\{(CF_3)_2PSeMe\}$	Yellow-brown oil $\nu_{C\equiv O}{}^e = 2094m, 2016vw, 1989s, 1984vs$ $\delta(^1H) = 1.80\ (\Delta^f = -0.04)$ $\delta(^{19}F) = -56.6\ (\Delta^f = -2.5)$ $\delta(^{31}P)^g = 99.0\ (\Delta^f = 74.1)$	192
$Mo(CO)_5(Me_2PSeMe)$	$\nu_{C\equiv O} = 2080m, 1994w, 1962s, sh, 1955vs$ $\delta(^1H) = 1.29\ (\Delta^f = 0.04)$ $\delta(^{31}P) = 12.3\ (\Delta^f = 11.5)$	194
$Mo(CO)_5\{(CF_3)_2PSeMe\}$	$\nu_{C\equiv O} = 2095m, 1992s, 1987vs$ $\delta(^1H) = 1.82\ (\Delta^f = 0.06)$ $\delta(^{19}F)^h = -52.0\ (\Delta^f = -2.0)$ $\delta(^{31}P)^g = 72.2\ (\Delta^f = 44.3)$	194
$Mo(CO)_5\{(CF_3)_2PSeCF_3\}$	$\nu_{C\equiv O} = 2096m, 2022w, 1996s, 1986vs$ $\delta(^{19}F)^h = -68.4\ (P(CF_3)_2)$ $(\Delta^f = -14.6)$ $-33.0\ (SeCF_3)$ $(\Delta^f = 1.8)$ $\delta(^{31}P)^g = 129.7\ (\Delta^f = 115.2)$	194
$W(CO)_5(Me_2PSeMe)$	Prepared in quantitative yield via equation (36)	193
R_2AsSeR_1		
$Cr(CO)_5(Me_2AsSeMe)$	Colourless air-sensitive crystals $\nu_{C\equiv O}{}^e = 2073w, 1988vw, 1959s, 1952vs$ $\delta(^1H) = 1.24\ (\Delta^f = 0.04)$ $1.63\ (\Delta^f = -0.27)$	192,193
$Cr(CO)_5\{(CF_3)_2AsSeMe\}$	Brown air-sensitive oil $\nu_{C\equiv O}{}^e = 2077w, 1961s, 1954vs$ $\delta(^1H) = 0.23\ (\Delta^f = 1.52)$ $\Delta(^{19}F)^h = -52.4\ (\Delta^f = -2.4)$	192
$Cr(CO)_5(Me_2AsSeCF_3)$	Red-brown air-sensitive oil $\nu_{C\equiv O}{}^e = 2076m, 1997vw, 1966s, 1956vs$ $\delta^1H) = 1.55\ (\Delta^f = -0.1)$ $\delta(^{19}F)^h = -25.2\ (\Delta^f = 0.6)$	192
$Mo(CO)_5(Me_2AsSeMe)$	$\delta(^1H) = 1.25\ (\Delta^f = 0.02),$ $1.68\ (\Delta^f = -0.22)$	193, 194
$Mo(CO)_5\{CF_3)_2AsSeMe\}$	$\delta(^1H) = 0.23\ (\Delta^f = -1.52)$ $\delta(^{19}F)^h = -52.0\ (\Delta = -2.0)$	194
$Mo(CO)_5(Me_2AsSeCF_3)$	$\delta(^1H) = 1.67\ (\Delta^f = 0.02)$ $\delta(^{19}F)^h = -24.8\ (\Delta^f = 1.0)$	194
$W(CO)_5(Me_2AsSeMe)^i$		193

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[a] Determined osmometrically in $CHCl_3$ at 37 °C.

[b] Measured in toluene.

[c] Measured in $CHCl_3$.

[d] Measured in CCl_4.

[e] In cyclohexane solution.

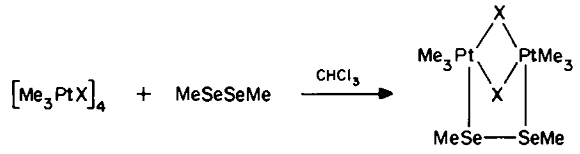
[f] $\Delta = \delta_{complex} - \delta_{free\ ligand}$.

[g] Vs. external 85% H_3PO_4.

[h] Vs. internal CCl_3F.

[i] Prepared in quantitative yield via equation (36).

^{1}H-NMR study[185] gave the barrier energies for pyramidal inversion of Se atoms, Se atom switching between Pt atoms and scrambling of PtMe groups in these three complexes.



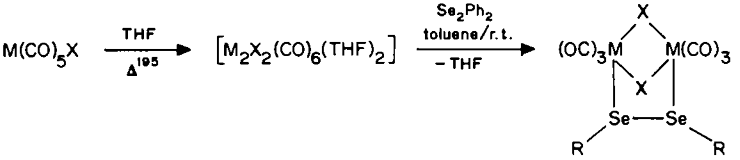
(31)

(31a) X = Br

(31b) X = Cl

(31c) X = I

Re[187,189,190] and Mn[191] carbonyl dimers with similar bridging structures (**32**) have been prepared according to equations (32) and (33). The diselenide bridged dimers **32a**, **32c** and **32d** were also obtained when Se_2R_2 ($R = PhCH_2$, Ph) reacted with $Re_2(CO)_8Br_2$/toluene[187], $Re(CO)_5Br/C_6H_6$[189] or $Re(CO)_5I$/toluene[190] under reflux conditions, which suggests that these dimers are thermodynamically, not kinetically, controlled products.



(32)

(**32a**) $M = Re$, $R = CH_2Ph$, $X = Br$

(**32b**) $M = Re$, $R = CH_2SiMe_3$, $X = Br$

(**32c**) $M = Re$, $R = Ph$, $X = Br$

(**32d**) $M = Re$, $R = Ph$, $X = I$

(**32e**) $M = Mn$, $R = Ph$, $X = Br$

$$Mn(CO)_5Br + Se_2Ph_2 \xrightarrow[\Delta]{Et_2O} \mathbf{32e} \quad \text{(Ref. 191)} \tag{33}$$

Refluxing a solution of **32e** in diisopropyl ether gave a precipitate of $MnBr_2$ and $(OC)_4Mn(\mu_2\text{-}SePh)_2Mn(CO)_4$ was isolated from the solution[191].

The structures with bridging diorganodiselenide ligands have been unequivocally established by single-crystal X-ray diffraction for **32a**[187], **32c**[189] and **32e**[191] (Table 14).

The reaction of Ph_2Se_2 with $AgAsF_6$ in liquid SO_2 gave a product, $[Ag_2(Se_2Ph_2)_4](AsF_6)_2$, which has been characterized by single-crystal X-ray diffraction[191a]. The structure (Figure 1) contains centrosymmetric 6-membered rings with two Ph_2Se_2 ligands bridging pairs of Ag atoms and three coordination about the Ag atoms being completed by 'intermolecular' Ph_2Se_2 bridges. The Se—Se distances in these bridging ligands are longer than in the free diselenide as generally observed[184,186,187,189,191], but the Se—Se distance in the 6-membered ring (2.344(2) Å) is significantly shorter than that for the other type of bridging ligand (2.360(2) Å).

A single report[188] briefly describes three examples of a terminally bonded diorganodiselenide ligand (equation 34). Variable-temperature ^{1}H-NMR has demonstrated the occurrence of two distinct fluxional processes in these complexes: pyramidal inversion about the coordinated Se atom and, at higher temperature, a novel 1,2-metal shift between

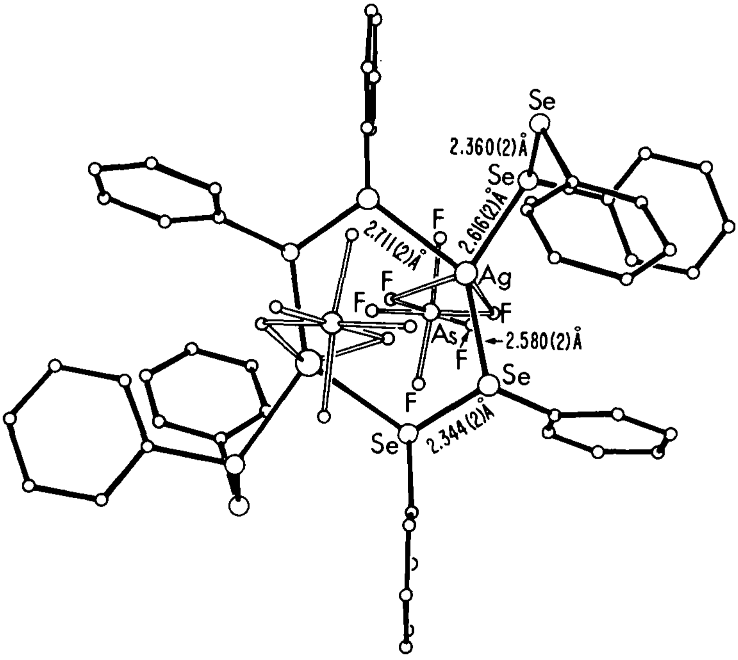


FIGURE 1. Molecular structure of $[Ag_2(Se_2Ph_2)_4](AsF_6)_2$. Reproduced with permission from Ref. 191a

the two chalcogenide atoms of the diselenide[188]. Activation parameters have been reported for the W complex (Table 14).

$$M(CO)_5THF + Me_3SiCH_2SeSeCH_2SiMe_3 \rightarrow (OC)_5M(Me_3SiCH_2SeSeCH_2SiMe_3)$$
$$M = Cr, Mo, W \qquad (34)$$

Grobe and LeVan[192-194] have studied the coordination chemistry of a wide variety of ambidentate ligands of the type $R_nEE^1R_m$ ($E,E^1 = P$, As; $n = m = 2$. $E = P$, As; $n = 2$; $E^1 = S$, Se, Te; $m = 1$). Included in this work are the synthesis and bonding characterization of some of the R^2ESeR^1 ($E = P$, As) complexes of Cr, Mo and W (Table 14). These complexes were prepared as shown in equations (35) and (36).

$$M(CO)_5THF + R_2ESeR^1 \rightarrow M(CO)_5(ER_2SeR^1) \qquad (35)$$
$$\begin{array}{ll} M = Cr & E = P;\ R = Me, CF_3;\ R^1 = Me \\ & E = As;\ R = Me, CF_3;\ R^1 = Me, CF_3 \\ M = Mo & E = P;\ R = Me, CF_3;\ R^1 = Me, CF_3 \\ & E = As;\ R = Me, CF_3;\ R^1 = Me \\ & R = Me;\ R^1 = CF_3 \end{array}$$

$$M(CO)_5(R_2EER_2) + Se_2R_2^1 \rightarrow M(CO)_5(R_2ESeR^1) + R_2ESeR^1 \qquad (36)$$
$$\begin{array}{l} M = Cr, Mo, W;\ E = P, As;\ R = R^1 = Me \\ M = Mo;\ E = P, As;\ R = Me;\ R^1 = CF_3 \end{array}$$

For the complexes described in equation (35), preparative-scale reactions were run, and products were isolated and characterized spectroscopically (infrared, ^{1}H-, ^{19}F- and ^{31}P-NMR; Table 14). Dismutation reactions (equation 36) were run in NMR tubes, and products were characterized *in situ* by ^{1}H- and/or ^{19}F-NMR.

In the initial work[192], NMR was shown to be useful for assigning the bonding mode of these ambidentate ligands. In the ^{1}H-NMR spectra methyl signals of groups bonded to the metal are shifted to lower fields vs. the free ligand (the absolute values of the PH coupling constants change little (e.g. ca. 12 Hz) but the sign changes). Methyl signals of non-coordinated groups generally shift ~0.4 ppm to higher fields, and the shift is larger for $(CF_3)_2AsSeMe$ than for $(CF_3)_2PSeMe$ complexes. The changes in PH coupling constants for the Me groups of non-coordinated groups vs. the free ligands fall in the range 1.5–5 Hz.

In the ^{19}F-NMR spectra the $\delta(CF_3)$ of coordinated groups shifts ~2–4 ppm to higher field, and the effect is larger for $(CF_3)_2As$— than for $(CF_3)_2P$— ligands. The $\delta(CF_3)$ of non-coordinated groups exhibits only a slight shift to lower field. In general, the coupling constants in both cases change by 2–6 Hz vs. the free ligand.

In the ^{31}P-NMR spectra coordinated R_2P—sites show a strong shift to low field (e.g. ~40 ppm for Me_2P— and ~70 ppm for $(CF_3)_2P$— ligands). Non-coordinated R_2P— groups exhibit only a small shift.

The spectroscopic data (Table 14) indicate that, except for $Cr(CO)_5\{SeMeAs(CF_3)_2\}$, the ambidentate ligands coordinate via the P or As site.

6. *$Se(EMe_3)_2$ (E = Ge, Sn, Pb)*

The octahedral complexes $M(CO)_5\{Se(EMe_3)_2\}$ (M = Cr, Mo, W; E = Ge, Sn, Pb) have been prepared by reaction (37)[196,197]. The Sn derivatives have also been prepared by direct photochemical substitution reactions (equation 38). All nine of these complexes are yellow solids that are sensitive to atmospheric oxygen and water and decompose in the range 82–105 °C with the thermal stability within each series increasing in the order W > Mo > Cr. They have been characterized by infrared, Raman and ^{1}H-NMR spectroscopy[197]; since they are isostructural, representative data for only one complex, $W(CO)_5\{Se(SnMe_3)_2\}$, are given below:

$$M(CO)_6 \xrightarrow[THF]{h\nu} M(CO)_5THF \xrightarrow{Se(EMe_3)_2} M(CO)_5\{Se(EMe_3)_2\} \qquad \text{(Ref. 197)} \qquad (37)$$

$$M(CO)_6 + Se(SnMe_3)_2 \xrightarrow[h\nu]{THF/r.t.} M(CO)_5\{Se(SnMe_3)_2\} \qquad \text{(Ref. 196)} \qquad (38)$$

$$M = Cr, Mo, W$$

For M = W: M.p. 105 °C

$\nu_{C{\equiv}O}$ (IR, pentane soln.): 2068, 1973, 1935, 1928, 1917m, 1892 cm^{-1}

Raman, solid (rel. int.): 2067(8), 1974(10), 1940(1), 1924(1), 1918(3), 1883(8) cm^{-1}

$\nu_{Sn_2Se,asym}$ = 228 (IR); 230(1) (Raman) cm^{-1}

$\nu_{Sn_2Se,sym}$ = 220(IR); 224(2) (Raman) cm^{-1}

$\delta(^{1}H) = +409.2$ Hz vs. internal C_6H_6

$J(^{1}HC^{117}Sn) = 52.8$ Hz

$J(^{1}HC^{119}Sn) = 55.0$ Hz

$J(^{1}HCSn^{77}Se) = 2.4$ Hz

This complex has also been structurally characterized by single-crystal X-ray diffraction[198]. Consideration of the W—Se and Se—Sn distances and the Sn—Se—W angles

TABLE 15. Selenocarbonyl complexes

Complex/properties[a]

$RuX_2(CO)(CSe)(PPh_3)_2$ (X = Cl (Figure 2), Br)[214]
Colourless air-stable solids
$\nu_{C=Se} = 1125$; $\nu_{C\equiv O} = 2030$
$RuI(OH)(CO)(CSe)(PPh_3)_2$[214]
$\nu_{C=Se} = 1137$; $\nu_{C\equiv O} = 2070$
$RuCl_2(CSe)(p\text{-}MeC_6H_4CN)(PPh_3)_2$[215]
$\nu_{C\equiv N} = 2175$; $\nu_{C=Se} = 1134$
$[RuCl(CO)(CSe)(p\text{-}MeC_6H_4CN)(PPh_3)_2]ClO_4$[215]
$\nu_{C\equiv N} = 2201$; $\nu_{C\equiv O} = 2070$; $\nu_{C=Se} = 1135$
$OsCl_2(CSe)(CO)(PPh_3)_2$ (35)[216]
colourless air-stable solid
$\nu_{C=Se} = 1156$vs; $\nu_{C\equiv O} = 2036, 2018$
$IrCl(CSe)(PPh_3)_2$[217]
orange needles
m.p. 247–249 °C
$\nu_{C=Se} = 1198$
$IrHCl_2(CSe)(PPh_3)_2$[217]
$\nu_{C=Se} = 1200$; $\nu_{Ir-H} = 2240$
$IrCl_3(PPh_3)_2(CSe)$[217]
$\nu_{C=Se} = 1201$
$[Ir(NCMe)(PPh_3)_2(CSe)]ClO_4$[217]
$\nu_{C=Se} = 1184$; $\nu_{C\equiv N} = 2320$
$[Ir(CSe)(CO)_2(PPh_3)_2]ClO_4$[217]
$\nu_{C=Se} = 1145$; $\nu_{C\equiv O} = 2060, 2000$
$IrCl(PPh_3)_2(CSe)(O_2)$[217]
$\nu_{C=Se} = 1165$; $\nu_{O-O} = 848$
Fe(TPP)(CSe)(EtOH)[218]
purple crystals
$\nu_{C=Se} = 1140$s
$\delta(^1H, CDCl_3, TMS)$: 8.88 (s, 8H), 8.15 (m, 8H), 7.75 (m, 12H)
TPP = 5, 10, 15, 20-tetraphenylporphinato
EtOH: 1.25 (t, $J = 6.5$, 3H), 3.78 (q, $J = 6.5$, 2H)
$\delta(^{13}C, CDCl_3, TMS)$
TPP: 145.8, 141.6, 133.6, 132.5, 127.8, 126.9, 122.1
EtOH:58.4, 18.2
CSe: 320.1
$CpMn(CO)_2(CSe)$[212,219,220]
yellow air-stable crystals (moderately light-sensitive)
m.p. 67–68 °C
$\nu_{C\equiv O}$ (hexane) = 2015s, 1965s
$\nu_{C=Se} = 1113$vs
δ(Mn—C—Se) = 515s, 508s;
$\nu_{Mn-C(Se)} = 363$m (R)
$\delta(^{13}C, CS_2, TMS) = 85.8$ (s, Cp), 205.5 (s, $(CO)_2$), 358.0 (s, CSe)
mass spectrum: $[M]^{+\cdot}$, $[M-2CO]^+$, $[M-2CO-CSe]^+$[212,219–221]

Complex/properties[a]

$Cp''Mn(CO)_2(CSe)$[220]
golden oil (b.p. 30–60 °C/0.001 Torr)
$\nu_{C\equiv O} = 2003, 1953$; $\nu_{C=Se} = 1106$
mass spectrum: $[M]^{+\cdot}$, $[M-2CO]^{+\cdot}$, $[MnCSe]^+$[220,221]
$CpRe(CO)_2(CSe)$[220]
pale yellow air-stable crystals
m.p. 97–100 °C
$\nu_{C\equiv O} = 2005, 1946$; $\nu_{C=Se} = 1124$
mass spectrum: $[M]^{+\cdot}$, $[M-2CO]^{+\cdot}$, $[ReCSe]^+$[220,221]
$(\pi\text{-}C_6H_5CO_2Me)Cr(CO)_2(CSe)$[219,220]
orange-red air-stable solid
m.p. 185 °C dec.
$\nu_{C\equiv O} = 1986, 1946$; $\nu_{C=Se} = 1063$
$(\pi\text{-}C_6H_6)Cr(CO)_2(CSe)$[213,220]
air-stable orange-yellow crystal (moderately light-sensitive)
m.p. 99 °C
$\nu_{C\equiv O}(CS_2) = 1976$s, 1932s; $\nu_{C=Se} = 1061$
$\delta(^{13}C, CH_2Cl_2, TMS) = 100.9$ (s, C_6H_6), 229.0 (s, $(CO)_2$), 363.7 (s, CSe)
$Cr(CO)_5(CSe)$[213,222]
volatile, deep yellow air-stable crystals
sublimes before melting
moderately light-sensitive
$\nu_{C\equiv O}$(hexane) = 2093m, 2031m, 2000 vs; $\nu_{C=Se} = 1077$s
$\delta(^{13}C, CH_2Cl_2, TMS) = 208.1$ (s, *trans*-CO), 211.7 (s, *cis*-CO), 360.7 (s, CSe)
$\delta(^{17}O, CH_2Cl_2, {}^{17}OH_2) = 373.4$ (s, *cis*-CO), 385.3 (s, *trans*-CO)
mass spectrum: $[M]^{+\cdot}$, $[M-nCO]^+$ ($n = 2$–5), Cr^+
$Me_4N[L(OC)_2Mo(CSe)]$[223]
L = 37
moderately air-stable solid
$\nu_{C\equiv O} = 1913$, 1824vs; $\nu_{C=Se} = 1005$s
$CpCo(CSe)PMe_3$[224]
$\nu_{C=Se} = 1128$
$\delta(^1H, C_6D_6) = 4.70$ (d, Cp) ($J_{PH} = 1.0$); 1.14 (d, Me) ($J_{PH} = 9.9$)
m.p. 58 °C dec.
$CpCo(CSe)PPh_3$[224]
$\nu_{C=Se} = 1130$
$\delta(^1H, C_6D_6) = 4.58$ (d, Cp) ($J_{PH} = 0.8$); 7.24 (m, 3H(Ph)); 7.84 (m, 2H(Ph))

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[a] Data are in the units given in Table 3.

indicates that the W—Se bonds are single bonds without a significant π-bond contribution.

The ligands, $Se(EMe_3)_2$ ($E = Ge$, Sn, Pb), used to prepare these complexes were prepared according to equations (39) and (40)

$$(Me_2ESe)_3 + 3\,LiMe \rightarrow 3\,Me_3ESeLi \xrightarrow[-LiCl]{Me_3ECl} (Me_3E)_2Se \qquad \text{(Ref. 199)} \qquad (39)$$

$$E = Ge, Sn$$

$$2\,Me_3PbCl + Na_2Se \xrightarrow{C_6H_6} (Me_3Pb)_2Se \qquad \text{(Ref. 197)} \qquad (40)$$

More recently, several derivatives of this type were prepared by simplified routes[200] (Equations 41 and 42).

$$E \xrightarrow[E = Se, Te]{NaBH_4/H_2O/EtOH} Na^+EH^- \xrightarrow[C_6H_6]{Ph_3SnCl} E(SnPh_3)_2 \qquad (41)$$

$$E \xrightarrow[THF]{LiBEt_3H} Li_2E \xrightarrow{2\,Me_3SnCl} E(SnMe_3)_2 \qquad (42)$$

The derivatives $E(SiR_3)_2$ ($E = Se$, Te; $R = H$[201], Me[62], Et[202]) and $EtESiMe_3$[202] have also been prepared, but their ligand properties have not been evaluated.

7. Selenocarbonyl complexes (M—CSe)

Although a vast literature of transition-metal carbonyl complexes[1] exists, considerably less ligand chemistry of thiocarbonyl[203-211] and selenocarbonyl[203,204] has been described. Although the diatomic molecules CO and CS can be readily synthesized, free CSe has never been isolated. It can, however, be stabilized when coordinated in transition-metal complexes[212,213] (Table 15). The instability of free CSe requires that indirect routes

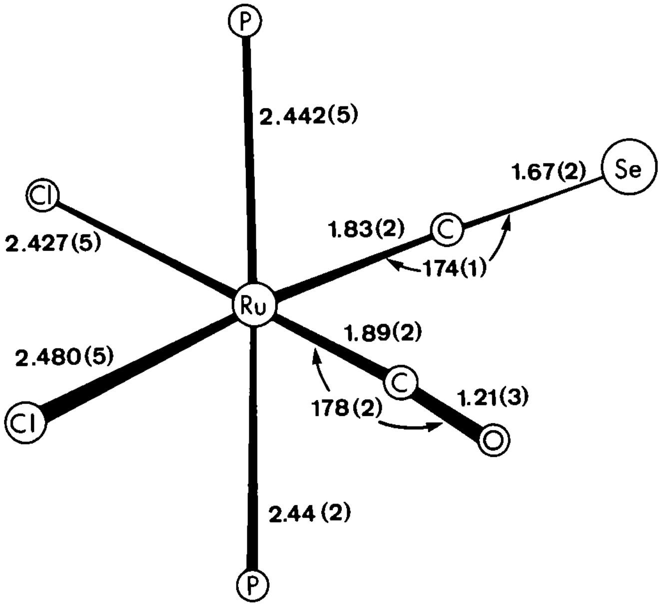


FIGURE 2. Molecular structure of $RuCl_2(CO)(PPh_3)_2(CSe)$. Reproduced with permission from Ref. 214.

be used to prepare selenocarbonyl complexes, two such preparative methods having been used: (1) extrusion of Se from coordinated CSe_2 (η^2-CSe_2, see Section II.C.1.a)[212–214,219,220,224] and (2) substitution reactions of $M{=}CCl_2$[216,219] or $M{\equiv}CCl$[223] complexes.

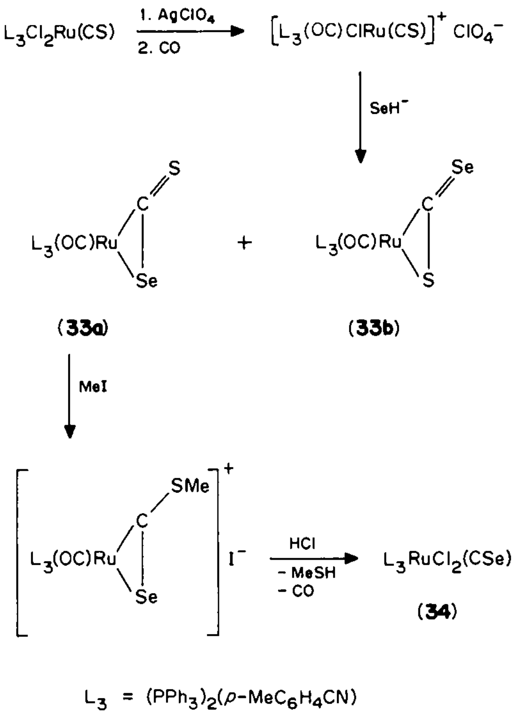
The first selenocarbonyl complexes were prepared by conversion of a CSe_2 complex by alkylation followed by acidification (equation 43). The crystal structure of the chloro complex (Figure 2) has verified a carbon bonding mode of the potentially ambidentate selenocarbonyl ligand. The rather long Ru—Cl distance *trans* to the CSe ligand (e.g. compared to typical values of 2.29–2.39 Å) indicates a strong *trans* influence of this ligand. The conversion of $RuI_2(CO)(CSe)(PPh_3)_2$ to $RuI(OH)(CO)(CSe)(PPh_3)_2$ on attempted chromatography on alumina is a chemical manifestation of this structural feature[214].

$$\mathrm{Ru(CO)_2(PPh_3)_2} \xrightarrow[\mathrm{CO}]{\mathrm{CSe_2}} \mathrm{Ru(CO)_2(PPh_3)_2(CSe_2)} \xrightarrow[-\mathrm{CO}]{\mathrm{MeI}} \qquad \text{(Ref. 214)} \qquad (43)$$

$$\mathrm{Ru(CO)(PPh_3)_2(CSe_2Me)I} \xrightarrow[(-\mathrm{MeSeH})]{\mathrm{HX}} \mathrm{RuX_2(CO)(PPh_3)_2(CSe)}$$

$$X = \mathrm{Cl, Br}$$

A four-step conversion of a coordinated thiocarbonyl ligand to a selenocarbonyl ligand has been described[215] (equation 44).



(44)

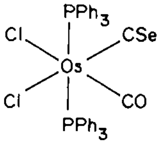
The linkage-isomeric intermediates **33a** and **33b** were separated by chromatography on silica gel prior to the *S*-methylation and final conversion to the selenocarbonyl complex by treatment with aqueous HCl in refluxing toluene/ethanol solution.

The analogous reaction with $L_3Cl_2Os(CS)$ gave a very slow reaction in the final acidification step with formation of only traces of the selenocarbonyl complex, as evidenced by infrared spectroscopy.

The selenocarbonyl complex (**34**) was converted to the cationic complex $[RuL_3Cl(CO)(CSe)]^+ClO_4^-$ by treatment with $AgClO_4$ followed by CO.

Synthesis of a selenocarbonyl complex via a dichlorocarbene precursor is illustrated by equation (45). The proposed stereochemistry of this complex, confirmed for the CS analogue by single-crystal X-ray diffraction[225] is shown in formula **35**.

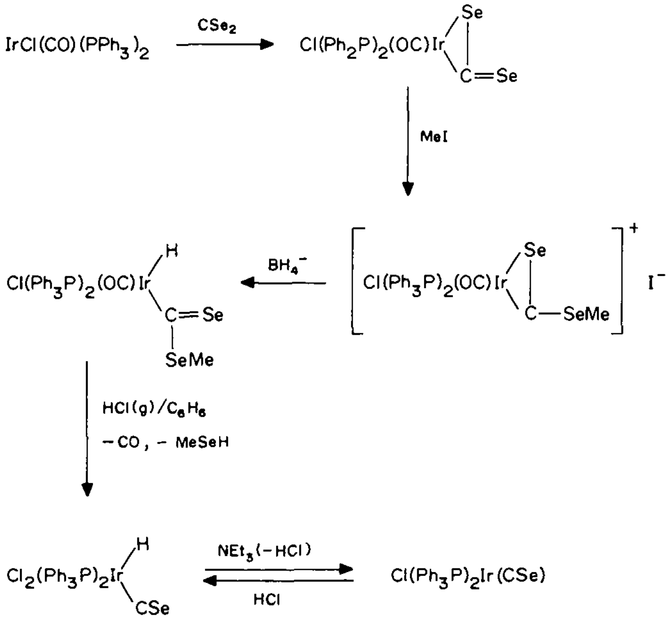
$$Cl_2(Ph_3P)_2(OC)OsCCl_2 \xrightarrow{SeH^-} Cl_2(Ph_3P)_2(OC)Os(CSe) \quad \text{(Ref. 216)} \qquad (45)$$



(35)

The Ru analogue, $Cl_2(Ph_3P)_2(OC)RuCCl_2$, was reported to react with SeH_2 to give the corresponding $Cl_2(Ph_3P)_2(OC)Ru(CSe)$, although characterization of this product was not reported[226].

A five-step conversion of Vaska's complex, $IrCl(CO)(PPh_3)_2$[227], to its CSe analogue has been described[217] (equation 46). This complex undergoes oxidative addition and chloride substitution reactions typical of the parent Vaska's compound[227] (equation 47).



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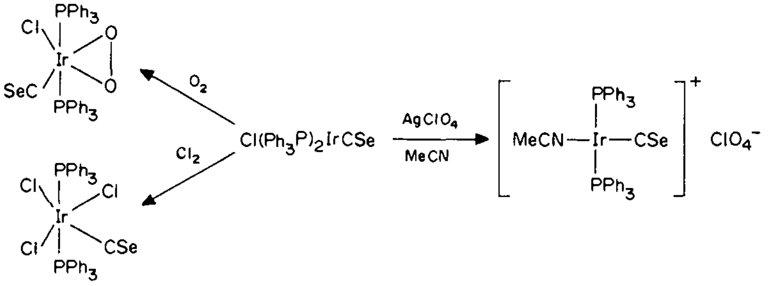
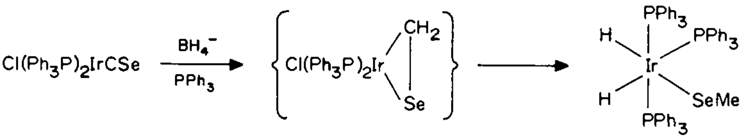


(Ref. 217)

(47)

The $\nu_{C=Se}$ bands in these adducts (Table 15) do not reflect the metal electron density as for the carbonyl analogues[1,227] e.g. in the O_2 adduct $\nu_{C=Se}$ is lowered by 33 cm^{-1} vs. the parent selenocarbonyl complex rather than increased to reflect decreased metal-to-CSe ligand back-donation upon effective metal oxidation. This observation has been attributed to extensive mixing of the $\nu_{C=Se}$ modes with lower energy modes (e.g. $\nu_{Ir-(CSe)}$)[217].

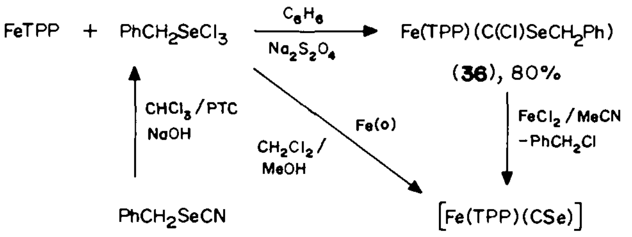
Reaction of the parent selenocarbonyl complex with $NaBH_4$ in the presence of excess PPh_3 gives complete reduction of the CSe ligand rather than the simple hydride formed from the CO and CS analogues (equation 48). Stable complexes containing the proposed selenoformaldehyde reduction intermediate have been isolated recently (see Section II.C.1.c).



(Ref. 217)

(48)

The complex Fe(TPP)(CSe) (TPP = 5,10,15,20-tetraphenylporphinato) has been prepared from a selenocarbene precursor[218] (equation 49). Addition of a catalytic amount of $FeCl_2$ in acetonitrile to a solution of the carbene complex **36** gave ca. 50% yield of the Fe(TPP)(CSe) product, on the basis of ^{1}H-NMR spectroscopy. The reaction used to isolate this complex, however, was the Fe-powder reduction of $PhCH_2SeCCl_3$ in the presence of Fe(TPP). This reaction produced a product containing ca. equimolar amounts of the carbene complex **36** and the selenocarbonyl complex, which was purified by silica gel thin-layer chromatography and recrystallization from CH_2Cl_2/EtOH to give the octahedral ethanol complex, [Fe(TPP)(CSe)(EtOH)], in 40% yield (Table 15).

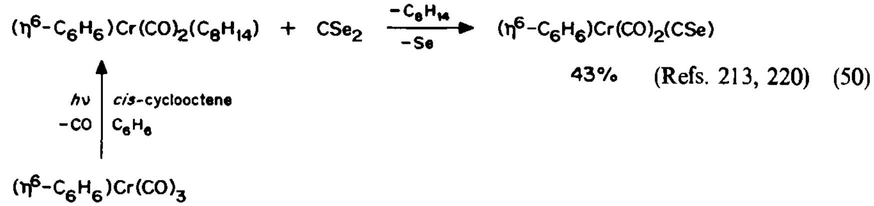


(49)

Electronic spectroscopy showed that the ethanol complex was in equilibrium with the pentacoordinate [Fe(TPP)(CSe)] complex and that more basic ligands (*N*-methylimidazole, pyridine) gave hexacoordinate adducts with enhanced stability[218]. The Fe—CSe bond in these complexes is considerably stronger than in the corresponding

Fe—CO species, as evidenced by the integrity of the former complex in high dilution (2×10^{-8} M) as well as by the fact that the above purification can be done under atmospheric conditions[218]. An EXAFS study of this complex showed linear Fe—C—Se bonding with Se—C = 1.64 Å and Fe—Se = 3.37 Å[228].

Butler and coworkers[212,213,220] have used the reaction of CSe_2 with labile transition-metal complexes (equation 50), in some cases with the addition of PPh_3 as a Se extrusion reagent (equation 51), to synthesize selenocarbonyl complexes.



$$(\eta^6\text{-}C_6H_6)Cr(CO)_3 \xrightarrow[h\nu,\ -CO]{cis\text{-cyclooctene},\ C_6H_6} (\eta^6\text{-}C_6H_6)Cr(CO)_2(C_8H_{14}) + CSe_2 \xrightarrow[-Se]{-C_8H_{14}} (\eta^6\text{-}C_6H_6)Cr(CO)_2(CSe)$$

43% (Refs. 213, 220) (50)

$$(R\text{—}Cp)M(CO)_3 \xrightarrow[h\nu]{THF} (R\text{—}Cp)M(CO)_2(THF) \xrightarrow[PPh_3\ (-SePPh_3)]{CSe_2} (R\text{—}Cp)M(CO)_2(CSe)$$

(Refs. 212, 220) (51)

R = H, Me; M = Mn, Re

These complexes are air-stable in the solid state, although they darken slowly on exposure to light (rapidly in solution). Their mass spectra[221] are characterized by their tendency to lose CO and organic radicals before the CSe ligand, indicating that the latter is bonded rather strongly to the metal. These complexes have been characterized by infrared and NMR spectroscopy (Table 15).

In a recently reported application of this PPh_3-induced Se extrusion reaction a selenocarbonyl complex incorporating PPh_3 as a ligand was obtained along with the expected product (e.g. $CpCo(\eta^2\text{-}CSe_2)(PMe_3)$ gave a mixture of $CpCo(CSe)(PMe_3)$ and $CpCo(CSe)(PPh_3)$, which was separated by column chromatography)[224].

A unique example of a selenocarbonyl complex containing CO as the only other ligand has been prepared (equation 52).

$$(\eta^6\text{-}C_6H_6)Cr(CO)_2(CSe) + 3\,CO \xrightarrow[20\ \text{atm. CO}]{50\ ^\circ C} Cr(CO)_5(CSe) + C_6H_6 \quad \text{(Refs. 213, 222)} \quad (52)$$

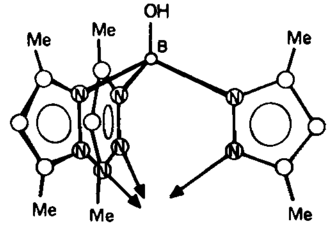
A detailed study of the vibrational spectra of the complexes $M(CO)_5CE$ (M = Cr, Mo, W; E = S, Se) has also appeared[221].

Nucleophilic displacement by Se^{2-} at the carbon atom of a terminal methylidyne ligand has recently[223] provided a new route (equation 53) to a selenocarbonyl complex (the CS and CTe derivatives were also prepared by this route). This selenocarbonyl complex was isolated in ~60% yield as its Me_4N^+ salt (Table 15).

$$Li_2Se + L(OC)_2Mo{\equiv}CCl \rightarrow L(OC)_2Mo{\equiv}C\text{—}Se^- \leftrightarrow L(OC)_2Mo^-\text{—}C{\equiv}Se$$

(Ref. 223) (53)

L =



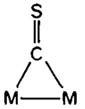
(37)

(hydrotris(3,5-dimethylpyrazol-1-yl)borato)

Although at present only terminally bonded M—CSe complexes are known, the recent development of synthetic methodology for selenocarbonyl complexes should allow further investigations of this ligand chemistry. The carbonyl ligand can coordinate to transition metals in a variety of bonding modes[1,2], and three bonding modes have been found for the thiocarbonyl ligand (**A** and **B** have been characterized by X-ray diffraction)[227]:

$M—CS$

(A)



(B)

$M—C{=}S—M$

(C)

8. Diorganoselenoxides (R_2SeO)

The coordination chemistry of sulphoxides has received considerable attention[229–235], and the ambidentate character of such ligands has been well established (including the crystal structure determination of both O-bonded (e.g. $[Rh_2(O_2CCF_3)_4(O\text{-}Me_2SO)_2]$[231], $[Th(NO_3)_4(O\text{-}Me_2SO)_3]$[232]) and S-bonded (e.g. $[Rh_2(O_2CEt)_4(S\text{-}Me_2SO)_2]$[231], $[Ru(NH_3)_5(S\text{-}Me_2SO)](PF_6)_2$[233]) complexes, as well as complexes containing both O- and S-bonded Me_2SO (e.g. *cis*-$[RuCl_2(S\text{-}Me_2SO)_3(O\text{-}Me_2SO)]$[234]). In contrast, only a few papers[236–241] have described coordination complexes with diorganoselenoxides, and whenever spectroscopic data were presented, M—O bonding was proposed. The sole exception to this is the first report[236] of metal complexes with diorganoselenoxides, e.g. $HgX_2 \cdot (p\text{-}ROC_6H_4)_2SeO$ (R = Me, Et) and HgX_2 (dibenzoselenophene oxide) (X = Cl, Br), where Hg—Se bonding was proposed. These complexes precipitated on cooling hot solutions of ca. equimolar amounts of the reagents in 95% ethanol. Attempts to isolate complexes with $CuCl_2$, $CdCl_2$, $FeCl_3$, $NiCl_2$, $CrCl_3$ and $ZnCl_2$ using water or 95% ethanol gave only the starting materials[236]. Since the ligand field strength of O-bonded selenoxides[242] is less than that of the aquo ligand, this result could be expected.

In a subsequent study using rigorously anhydrous halides of Mn(II), Co(II), Ni(II), Cu(II), Sn(IV) and Zr(IV), diphenyl selenoxide (DPSeO) complexes were isolated[237]. In this work the hydrated halides were thermally dehydrated, although chemical dehydrating agents (e.g. 2,2-dimethoxypropane, ethyl orthoformate) are widely used to form anhydrous metal salts *in situ* in reactions with weak ligands[52,243]. The more basic dimethyl selenoxide (DMSeO) ligand forms complexes with a variety of transition metals, with either the hydrated chloride[238] or perchlorate salt[239]. In the former case the isolated complexes contain dimethyl selenoxide ligands with the chloride still coordinated ($HgCl_2 \cdot (DMSeO)$; $MCl_2(DMSeO)_2$, M = Cd, Cu, Co; $PdCl_4(DMSeO)_2$; $FeCl_3(DMSeO)_2$)[238]. In the latter case, however, the weakly coordinating perchlorate anion, as well as the water, is eliminated from the coordination sphere, the complexes formed having the stoichiometry $[M(Me_2SeO)_n]^{m+}(ClO_4^-)_m$ (M = Mn, Co, Ni, Zn, Cd, Mg; $n = 6$, $m = 2$. M = Cr, Fe; $n = 5$, $m = 3$. M = Ag; $n = 2$, $m = 1$. M = Cu; $n = m = 2$).

In all of these cases, the lowering of the Se—O stretching frequency ($10–110\,cm^{-1}$; Table 16) is the basis of the assignment of M—O bonding with these potentially ambidentate ligands, no definitive single-crystal X-ray diffraction study having been reported. The decrease in the $\nu_{Se—O}$ vibration vs. the free ligand is a measure of the M—O bond strength, and this value increases, as expected, as the charge on the metal ion increases (e.g. Pd(IV), Sn(IV) and Zr(IV) show the largest decreases). In analogous dimethyl sulphoxide complexes, the $\nu_{S=O}$ decreases on O coordination but increases on S coordination[229–235].

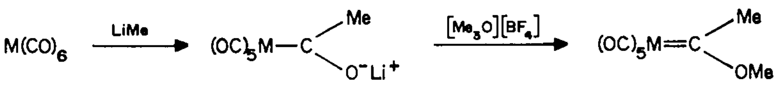
TABLE 16. Infrared data (cm^{-1}) for some metal diorganoselenoxide complexes[a]

Complex[b]	$\nu_{Se=O}$	ν_{C-Se}	ν_{M-O}	Ref.
DMSeO	800vs	585vw		238
$HgCl_2(DMSeO)$	770vs	580vw		238
$CdCl_2(DMSeO)_2$	775vs, 735vs	585w		238
$PdCl_4(DMSeO)_2$	698vs, 690vs	610w	520w, br	238
$CuCl_2(DMSeO)_2$	760vs, 720vs	595w, 580w	515m, 475m	238
$CoCl_2(DMSeO)_2$	760vs, 705s	590w	410s	238
$FeCl_3(DMSeO)_2$	760vs	580w	440s	238
$[Cr(DMSeO)_6](ClO_4)_3$	765vs		440s	239
$[Fe(DMSeO)_6](ClO_4)_3$	772vs	602m, 590m	444s	239
$[Mn(DMSeO)_6](ClO_4)_2$	787vs	593m, 580m	400m	239
$[Co(DMSeO)_6](ClO_4)_2$	787vs, 775vs	595m, 581m	400s	239
$[Ni(DMSeO)_6](ClO_4)_2$	790vs	595s	400s	239
$[Cu(DMSeO)_4](ClO_4)_2$	770vs	610m, 493m	498m, 484m	239
$[Ag(DMSeO)_2]ClO_4$	779vs	593m, 585m	405m	239
$[SnCl_4(DMSeO)_2]$	756vs, 740s	598w, 583w	466s, 445s	241
$[Me_2SnCl_2(DMSeO)_2]$	737vs	594m, 583m	387s	241
$[Et_2SnCl_2(DMSeO)_2]$	744vs	595m, 584m	407s, 200sh	241
DPSeO	831			237
$MnCl_2(DPSeO)_2$	798, 809			237
$CoCl_2(DPSeO)_2$	767, 782			237
$NiCl_2(DPSeO)_4$	795, 800			237
$[Ni(DPSeO)_6]Cl_2$	797, 801			237
$CuCl_2(DPSeO)_2$	790			237
$HgCl_2(DPSeO)$	800			237
$ZrCl_4(DPSeO)_2$	770			237
$SnCl_4(DPSeO)_2$	789			237

[a] Ionic ClO_4^- is confirmed in all cases by strong bands at ~ 1100 and 625 cm^{-1} [52].
[b] DMSeO = Me_2SeO; DPSeO = Ph_2SeO.

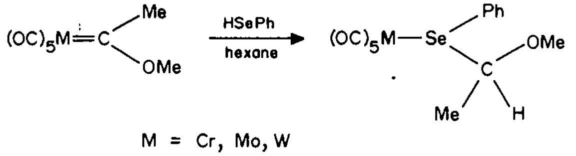
9. *Selenium-functionalized carbene complexes (M=C(SeR)(R'))*

Since Fischer's original discovery of transition-metal carbene complexes[244] (equation 54), this area has been one of the most actively investigated in organometallic chemistry[245], the main impetus being its mechanistic implications in Fischer–Tropsch and olefin metathesis processes.



(54)

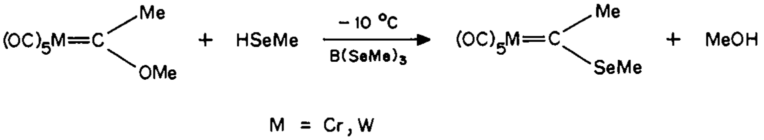
Included in Fischer's extensive investigations of metal carbene chemistry, and more recently metal carbyne chemistry, have been several papers[246–250] dealing with Se-functionalized derivatives of these two classes of organometallics. The first attempt to prepare selenocarbene complexes by the route successful for thiocarbenes gave products containing M—Se bonds, presumably by nucleophilic replacement of the carbene carbon atom and proton migration (equation 55).



(55)

The three complexes, which had similar properties, were characterized by infrared and ^{1}H-NMR spectroscopy (Table 17). The Se ligand was readily displaced by pyridine, with the formation of $M(CO)_5pyr$.

Successful synthesis of the first selenocarbene complexes involved selenolysis with anhydrous, highly purified methylselenol at low temperature in the dark[247] (equation 56). The triselenoboric acid ester was added to the reaction to scavenge the water and



(56)

TABLE 17. Selenium-functionalized carbene complexes

Complex	Complex
$(OC)_5CrSe(Ph)(CH(Me)(OMe))$[246] brown–yellow solid m.p. 74 °C $\nu_{C\equiv O}$[a] = 2070, 1990, 1948, 1934 $\delta(^1H)$[b]: Me, 1.6d; OMe, 3.55s; CH, 5.20q; Ph, 7.63m	$(OC)_5WC(SeMe)(PMe_3)(Me)$[247] yellow crystals $\delta(^1H)$[d]: CMe, 2.37d; SeMe, 1.87s; PMe_3, 1.82d $\nu_{C\equiv O}$[f]: 2055w, 1960w, 1903vs, 1878s, sh
$(OC)_5WC(SeMe)(Me)$[247] black crystals m.p. 35 °C $\nu_{C\equiv O}$[a] = 2069m, 1956vs $\delta(^1H)$[c]: SeMe, 1.66s; Me, 2.80s $\delta(^{13}C)$[d,e]: W=C, 355.5; *trans*-CO, 205.0; *cis*-CO, 197.86; Se*Me*, 21.79; C*Me*, 54.27	$(OC)_5CrC(SePh)(NEt_2)$[248] pale yellow crystals m.p. 74 °C dec. $\nu_{C\equiv O}$[g] = 2057, 1977, 1942, 1933 $\nu_{C\equiv N}$ = 1518 $\delta(^1H)$[h]: NEt_2, 1.00t, 1.44t, 3.73q, 4.35q Ph, 7.60m
	$(OC)_5CrSePhEt$[250] yellow needles m.p. 17 °C $\nu_{C\equiv O}$[a] = 2075w, 1951vs, 1944s sh, 1938m $\delta(^1H)$[i]: Ph, 7.7m; Et, 3.3q, 1.35t

[a] In hexane, measured in cm^{-1}.

[b] In $CDCl_3$, internal TMS.

[c] In toluene-d_6.

[d] In acetone-d_6.

[e] The corresponding values for the C(Me) (OMe) complex are: 332.9, 203.62, 197.60, 69.69 and 51.51.

[f] In CH_2Cl_2; cm^{-1}.

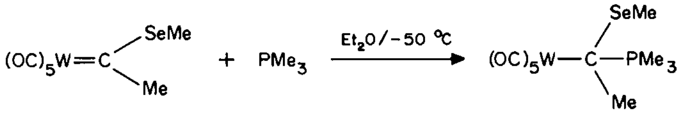
[g] In methylcyclohexane; cm^{-1}.

[h] In CCl_4, internal TMS.

[i] δ values relative to acetone-d_6 = 2.1 ppm.

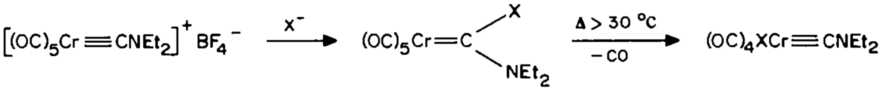
methanol released in the reaction. The air, light and thermal sensitivity of these complexes required careful purification by low-temperature chromatography (SiO_2/hexane/ – 10 °C) followed by sublimation at 0 °C. The two complexes had similar chemical and spectroscopic properties (Table 17).

Hindered rotation about the carbene C—Se bond and inversion at the Se atom were indicated by the reversible broadening of the C—Me and Se—Me NMR singlets as the temperature was decreased. The acidic character of the C—Me protons was reflected in the ^{13}C chemical shift of the Me group as well as its uncatalysed deuteriation above 40 °C by acetone-d_6 (the OMe derivative requires OMe^- catalysis for this reaction). The strong *trans* influence of the carbene ligand was reflected in the ^{13}C chemical shift of the CO *trans* to this ligand (e.g. more deshielded than the *cis*-CO ligands). The low-field shift of the carbene C resonance vs. the OMe analogue (Table 17) indicated enhanced Lewis acidity, and this was reflected in the facile formation of an ylid complex with PMe_3[247] (equation 57).



$$(OC)_5W{=}C(SeMe)(Me) + PMe_3 \xrightarrow{Et_2O/-50\,^\circ C} (OC)_5W{-}C(SeMe)(Me){-}PMe_3 \qquad (57)$$

The synthetically useful transformation carbyne→carbene→carbyne complex in equation (58) has been applied to organoselenium-functionalized derivatives[248], and the kinetics of the rearrangement to the final product have been studied in detail[249].

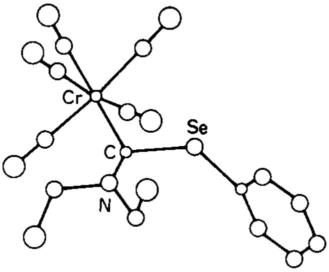


$$[(OC)_5Cr{\equiv}CNEt_2]^+ BF_4^- \xrightarrow{X^-} (OC)_5Cr{=}C(X)(NEt_2) \xrightarrow[-CO]{\Delta > 30\,^\circ C} (OC)_4XCr{\equiv}CNEt_2 \qquad (58)$$

X = Cl, Br, I, $SnPh_3$, $Se(C_6H_4R\text{-}p)$

R = H, F, Br, Me, OMe, CF_3

The selenocarbene intermediates in this series were isolated by carrying out the initial conversion step and chromatographic purification of the products at low temperature (ca. – 25 °C)[248]. These carbenes, which upon warming readily eliminate CO with migration of the SeR^- group from the carbene carbon to the Cr, were characterized spectroscopically (Table 17). An unusual feature of their infrared spectra was the high intensity of the formally infrared-forbidden B_1 bands (~ 1977 cm^{-1}) in the CO stretching region. This suggested that the ideal C_{4v} symmetry of the $M(CO)_5L$-type complexes was lowered by some distortion. Such a distortion was confirmed for $(OC)_5CrC(SePh)(NEt_2)$ by single-crystal X-ray diffraction[248]. The four equatorial carbonyl ligands are bent back away from



(38)

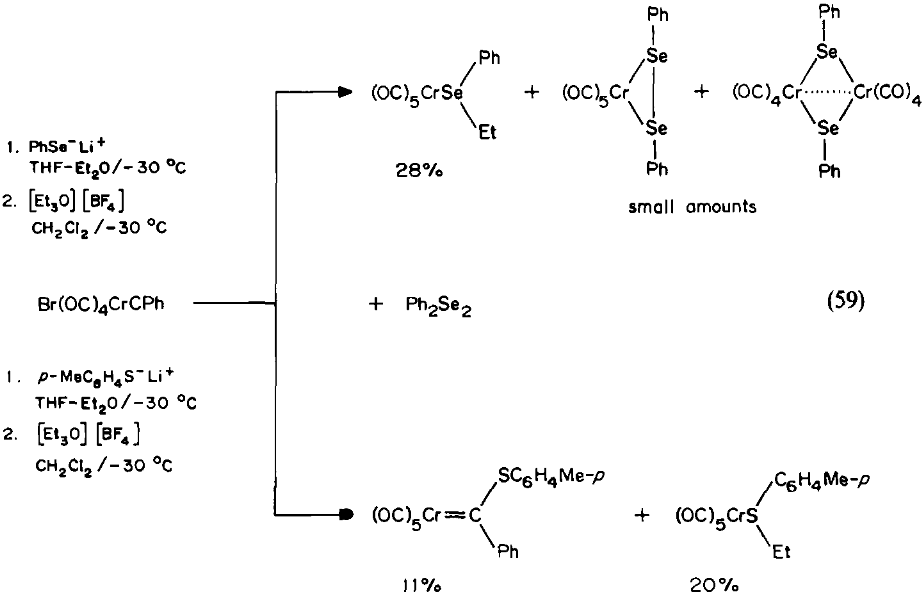
the carbene ligand with the Cr atom thereby shifted 0.113 Å from the plane of these four ligands (**38**). This complex also has the longest Cr—C (carbene) distance found for such derivatives (2.171 Å).

The double-bond character of the C—N bond, indicated by the value of the $\nu_{C\cdots N}$, is further supported by the appearance of two triplets and quartets for the non-equivalent N—Et groups (Table 17).

Warming CH_2Cl_2 or 1,1,2-trichloroethylene solutions of the selenocarbenes (room temperature to 30 °C) under 10 atm CO gave readily the thermally sensitive carbyne complexes. These were assigned a *trans* configuration on the basis of the observed four $\nu_{C\equiv O}$ bonds[248]. As with the parent selenocarbenes, the intensity ratios of these bands indicated a significant perturbation of the coplanar arrangement of the four carbonyls in solution. Derivatives with considerably enhanced thermal stability can be obtained by carrying out the thermolysis of the carbenes in the presence of PPh_3. The resulting products, $(OC)_3(Ph_3P)(SeAr)CrCNEt_2$, were assigned meridional geometries (i.e. two CO ligands are *trans* and the third is *cis* to the other two) on the basis of the three observed $\nu_{C\equiv O}$ bands[249].

The selenocarbene→carbyne rearrangement followed first-order kinetics and was independent of free-CO concentration and only slightly dependent on solvent polarity and type of substituent R (equation 58). The activation parameters determined are: $\Delta H^{\neq} = 101\text{–}104\,\mathrm{kJ\,mol^{-1}}$, $\Delta S^{\neq} = 27\text{–}33\,\mathrm{J\,mol^{-1}\,K^{-1}}$.

The reactivity of the carbyne complex *trans*-bromotetracarbonyl(phenylcarbyne)chromium varied according to the chalcogen base used, a modest yield of the carbene complex being obtained only with the thiolate[250] (equation 59).



(59)

10. Miscellaneous ligands

A few other metal complexes containing monodentate neutral Se ligands have been reported (Table 18).

TABLE 18. Complexes with miscellaneous monodentate neutral ligands

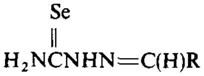
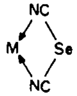
Complex of	Reported data	Reference
Selenosemicarbazones		
 $H_2NC(=Se)NHN{=}C(H)R$ R-ssc	$[Co(dmg)_2(Ph\text{-}ssc)Cl]\cdot H_2O$ pale-brown microcrystals, sparingly water-soluble	251
	$[Co(dmg)_2((C_6H_4OH\text{-}o)\text{-}ssc)_2]Cl$ pale brown solid, sparingly soluble in water $\Lambda_M(10^{-3}M$ aq. sol.$) = 65.3$	251
$Se(CN)_2$ 	$TiCl_4\{Se(CN)_2\}$ yellow-orange hygroscopic solid m.p. 105 °C dec. $\nu_{C\equiv N}{}^{a,b} = 2270w, 2245s$ (R: 2198m, 2145w) $\nu_{C-Se}{}^{c} = 648vs, 638s, sh, 318sh$ (R: 657w, 309m, br) $\nu_{Ti-Cl} = 385vs, 370sh$ (R: 392vs) $\delta_{Se-C\equiv N} = 345$ $\nu_{Ti-N} = 298w, 268w$ (R: 272w, br)	252
	$ZrCl_4\{Se(CN)_2\}$ bright yellow hygroscopic solid m.p. 125 °C dec. $\nu_{C\equiv N} = 2198m, 2145w$ $\nu_{C-Se} = 618w, 570s$ $\nu_{Zr-Cl} = 345vs, 315sh$ $\nu_{Zr-N} = 290sh, 270sh$	252
$M{-}Se(CN)_2$	*trans*-$VCl_4\{Se(CN)_2\}_2$ yellow hygroscopic solid m.p. 196 °C dec. $\nu_{C\equiv N}{}^{a,b} = 2210s, 2160m$ $\nu_{C-Se}{}^{c} = 585s, 510m$ $\nu_{V-Se} = 302sh$ $\delta_{V-SeCN} = 280vw$	253
	$MoCl_5\{Se(CN)_2\}$ dark brown hygroscopic solid m.p. 130 °C dec. $\nu_{C\equiv N}{}^{a,b} = 2260s, 2185m$ $\nu_{C-Se} = 580w, 510m$ $\nu_{Mo-Cl} = 380sh, 350vs, 300w, sh$ $\nu_{Mo-Se} = 280vw, sh$	253
$Se{=}C(SeEt)_2$	$(OC)_5Cr{-}Se{=}C(SeEt)_2$ red-purple plates m.p. 51 °C	254
$Se(Ph)(SPh)$	$(OC)_5Cr\{SePh(SPh)\}$ molecular structure Cr—Se: 2.531(4) Å Se—S: 2.226(6) Å	255
Selenoketones		
$Se{=}CAr_2$	$(OC)_5Cr{-}Se{=}CPh_2$ m.p. 58–59 °C $\nu_{C\equiv O}{}^{d} = 2060, 1991, 1956, 1943$ $\delta(^{13}C)^{e}$: C=Se, 243.1; CO(*trans*), 223.0; CO(*cis*), 214.6	256

TABLE 18. (*Continued*)

Complex of	Reported data	Reference
	$(OC)_5W{-}Se{=}CPh_2$ black crystals m.p. 45–46 °C $\nu_{C\equiv O}{}^{d} = 2069, 1987, 1953, 1937$ $\delta(^{13}C)^{e}$: C=Se, 240.0; CO(*trans*), 200.6; CO(*cis*), 196.9	256
	$(OC)_5W{-}Se{=}C(Ph)C_6H_4CF_3$-*p* m.p. 70–71 °C $\nu_{C\equiv O}{}^{d} = 2070, 1991, 1959, 1944$ $\delta(^{13}C)^{e}$: C=Se, 236.7; CO(*trans*), 200.4; CO(*cis*), 196.4	256
$RSeCH_2SR$	$Me_3Pt(\mu\text{-}Cl)_2(\mu\text{-}MeSeCH_2SMe)PtMe_3$ white air-stable crystals m.p. 210–212 °C variable-temperature NMR study	257
$\eta^1\text{-}P_4Se_3$	$(np_3)Ni(P_4Se_3)\cdot 2\,C_6H_6$ air-stable solid insoluble in common organic solvents crystal structure	258 259
$\eta^3\text{-}P_3Se_3$	[triphos $Rh(P_3Se_3)$] orange air-stable crystals	260
$\eta^3\text{-}P_2Se$	$[Co(triphos)(P_2Se)]BF_4\cdot C_6H_6$ orange, moderately air-stable crystals $\Lambda_M(10^{-3}M, EtNO_2) = 84$ $\delta(^{31}P)^{f} = 32.70(3)br;\ -145.50(2)q;$ $^2J_{PP} = 12$ crystal structure	261

[a] The infrared spectra were recorded as Nujol mulls.

[b] The corresponding bands in free $Se(CN)_2 = 2183, 2175$.

[c] The corresponding bands in free $Se(CN)_2 = 608, 516$.

[d] In hexane.

[e] In acetone-d_6 at −20 °C; δ values relative to acetone-d_6, $\delta = 205.1$ ppm.

[f] In CD_2Cl_2; chemical shifts relative to 85% H_3PO_4. The spectra are the same at 301 and 203 K.

Selenosemicarbazone complexes of Co(III) have been prepared according to equation (60)[251].

$$trans\text{-}[CoX(dmg)_2(H_2O)] + n\text{-}\underset{\text{Ph-ssc}}{PhCH{=}NNHC(Se)NH_2} \rightarrow Co(dmg)_2(Ph\text{-}ssc)_nX \qquad (60)$$

$$X = Cl, Br; \qquad n = 1, 2$$

The Co(III) in these complexes is octahedrally coordinated so that for $n = 1$, the product is a neutral complex, but for $n = 2$, ionic complexes (e.g. $[Co(dmg)_2(Ph\text{-}ssc)_2]X$) are obtained. These complexes were prepared by this substitution reaction to avoid the acidic reaction conditions usually used to prepare dmg complexes of this general type [i.e. aerial oxidation of hot aqueous solutions of the corresponding Co(II) salt, dmg-H and the other ligand to be incorporated into the coordination sphere (e.g. $Co(dmg)_2L_nX$, L = thiosemicarbazones[262], thiourea[263])]. Analogous complexes with the selenosemicarbazones of acetone, cyclohexanone, vanillin and salicylaldehyde were also prepared[251].

A remarkable feature of these complexes is the significantly enhanced acid stability of the selenosemicarbazones upon coordination. The complex $[Co(dmg)_2(Ph\text{-}ssc)_2]^+$, for example, was reported to be stable in boiling 1:1 aqueous HCl, whereas free selenosemicarbazones readily deposit elemental Se in even weakly acid solutions[251]. This property was cited as evidence for Se bonding of the ambidentate selenosemicarbazone ligands in these complexes. No spectroscopic characterization of the complexes was reported.

Coordination of $Se(CN)_2$, prepared by disproportionation of selenocyanogen[264–266], as an (N,N) bidentate ligand ($MCl_4\{(NC)_2Se\}$; M = Ti, Zr)[252] or a monodentate Se donor (e.g. *trans*-$VCl_4\{Se(CN)_2\}_2$, $MoCl_5\{Se(CN)_2\}$)[253] has been proposed on the basis of infrared and Raman spectroscopy (Table 18). The spectra of $MCl_4\{(NC)_2Se\}$ (M = Ti, Zr) indicate C_{2v} symmetry with bidentate (N,N) coordination of $Se(CN)_2$[252]. For the Ti complex, both infrared and Raman spectra were recorded, but the facile decomposition of the Zr complex in the laser beam precluded the measurement of its Raman spectrum. In both cases, the increases in the $\nu_{C\equiv N}$ and ν_{C-Se} bands vs. the free ligand, the expected number of ν_{M-Cl} bands and the assignments of ν_{M-N} bands all support the $[MCl_4(N,N)]$ C_{2v} structure. Similar reactions with $S(CN)_2$ gave the octahedral complexes $MCl_4\{S(CN)_2\}_2$ containing two S-bonded ligands in *trans* positions[252]. The larger CEC (E = Se, S) angle in $Se(CN)_2$ (99°) vs. $S(CN)_2$ (95.6°) and the larger size of Se vs. S both provide less steric strain for (N,N) bidentate coordination in the former case.

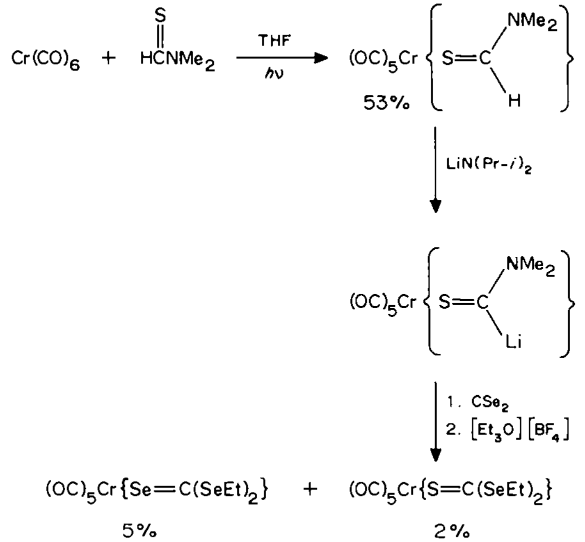
Reactions of $MoCl_5$ and VCl_4 with $Se(CN)_2$, however, gave octahedral complexes with monodentate Se bonding of this ligand ($MoCl_5\{Se(CN)_2\}$, $VCl_4\{Se(CN)_2\}_2$)[253]. The infrared spectra of these complexes show increases in the $\nu_{C\equiv N}$ bands but decreases in the ν_{C-Se} bands vs. the free ligand (Table 18). The *trans* (D_{4h}) symmetry indicated by infrared data for $VCl_4\{Se(CN)_2\}_2$ is supported by the ESR spectrum (V(IV), d^1) in acetone at −160 °C.

Reactions of $Se(CN)_2$ with some main-group organometallics gave cyano rather than selenocyanato complexes (equations 61 and 62).

$$HgPh_2 + Se(CN)_2 \rightarrow PhHgCN + PhSeCN \qquad \text{(Ref. 264)} \qquad (61)$$

$$PbPh_4 + Se(CN)_2 \rightarrow Ph_3PbCN + PhSeCN \qquad \text{(Ref. 265)} \qquad (62)$$

The first examples of diselenothiocarbonate and triselenocarbonate ligands were prepared according to equation (63)[254]. Other products were obtained in lower yields, and the mechanism of this complex reaction is not understood.



(63)

Coordination of the ambidentate ligand PhSSePh by its Se atom in $(OC)_5Cr(PhSeSPh)$ was established by single-crystal X-ray diffraction[255]. This complex was formed in very low yield by the reaction of the carbyne complex $Br(OC)_4CrCPh$ with $PhSe^-Li^+$ (equation 59) due to the presence ($< 1\%$) of PhSH as an impurity in the PhSeH used to form the lithium reagent. Diffraction-quality crystals of this complex were manually separated from $(OC)_5Cr(Se_2Ph_2)$, with which they crystallized.

Diarylselenoketone complexes of Cr and W carbonyls have been prepared in good yields from the corresponding carbene complexes by use of phenyl isoselenocyanate or potassium selenocyanate as Se insertion reagents[256] (equation 64).

$$(OC)_5M{=}C(Ph)(C_6H_4X\text{-}p) + PhNCSe \xrightarrow[-30\ C]{Et_2O} (OC)_5M{-}Se{=}C(Ph)(C_6H_4X\text{-}p)$$

$$M = Cr;\ R = H$$

$$M = W;\ R = H, Br, CF_3, Me, OMe, NMe_2 \qquad (64)$$

The dimeric complexes incorporating bridging halo and the hybrid (Se, S) ligand, $Me_3Pt(\mu\text{-}X)_2(\mu\text{-}MeSeCH_2SMe)PtMe_3$ ($X = Cl, Br, I$), have been prepared[257] by reaction of the (Se, S) ligand with $[Me_3PtX]_4$, as previously described for analogous complexes with bridging RSeSeR ligands (equation 31). Variable-temperature ^1H-NMR studies have demonstrated configurational non-rigidity in these complexes (i.e. ligand ring inversion, pyramidal inversion of both S and Se atoms, ligand switching between Pt atom pairs and scrambling of the Pt methyl environments[257]). The energy barriers for these non-dissociative dynamic processes have been determined.

The P_4E_3 ($E = S, Se$) cage molecule (Figure 3a) has an unusual coordination chemistry, coordinating as an intact molecule (monodentate coordination through the apical P atom[258,259]; Figure 3b), or undergoing fragmentation to give complexes containing η^3-P_3[267], η^3-P_2E[261,268] (Figure 3c) or η^3-P_3E_3[260] (Figure 3d) ligands.

The type of ligand that is incorporated in a metal complex upon reaction with P_4E_3 depends on the particular transition metal, its oxidation state and the other types of ligands in the coordination sphere. Work to date with the P_4Se_3 system has involved complexes with the tridentate ligands triphos ($MeC(CH_2PPh_2)_3$) and np_3 (equations 65–67).

$$M(np_3) + P_4Se_3 \xrightarrow[35-40\,^{\circ}C]{C_6H_6/THF} M(np_3)(\eta^1(P)\text{-}P_4Se_3) \qquad (\text{Ref. } 258) \qquad (65)$$

$$M = Ni, Pd$$

$$[RhCl(COD)]_2 + triphos + P_4Se_3 \xrightarrow[BuOH/\Delta]{C_6H_6/THF} [Rh(triphos)(\eta^3(P,P,Se)\text{-}P_3Se_3)]\cdot C_6H_6$$

$$(\text{Ref. } 260) \qquad (66)$$

$$Co(BF_4)_2{\cdot}6\,H_2O + triphos + P_4Se_3 \xrightarrow[\Delta]{C_6H_6/EtOH} [Co(triphos)(\eta^3\text{-}P_2Se)]BF_4\cdot C_6H_6$$

$$(\text{Ref. } 261) \qquad (67)$$

The proposed structures have been confirmed by single-crystal X-ray diffraction for $[Ni(np_3)(\eta^1(P)\text{-}P_4Se_3]\cdot 2\,C_6H_6$[259], $[Rh(triphos)(\eta^3(P,P,S)\text{-}P_3S_3)]\cdot C_6H_6$[260], $[Co(triphos)(\eta^3\text{-}P_2Se)]BF_4\cdot C_6H_6$[261] and $[Co(triphos)(\eta^3\text{-}P_2S)]BF_4\cdot C_6H_6$[268]. Because of the novel structures of these complexes, characterization was limited to elemental analysis, mass spectroscopy and single-crystal X-ray diffraction of typical complexes, and no spectroscopic data have been reported except for the ^{31}P-NMR data for $[Co(triphos)(\eta^3\text{-}P_2Se)]BF_4$[261] (Table 18).

An interesting feature of this spectrum is the resolution of the ^{31}P resonance of the P_2Se

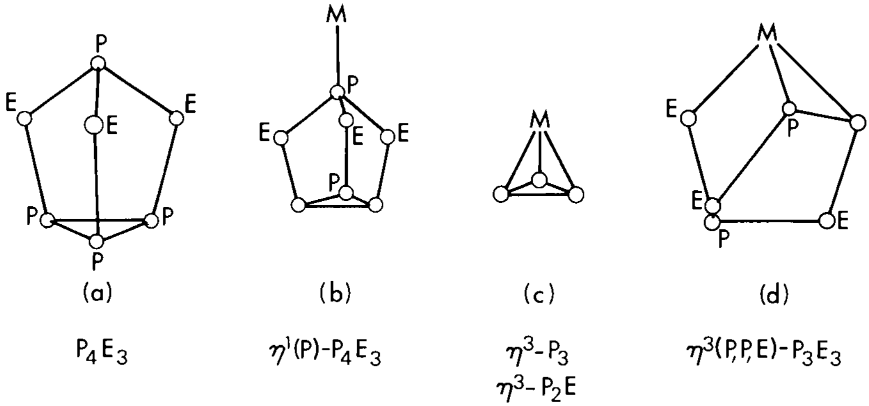


FIGURE 3. Bonding modes of P_4E_3 (E = S, Se) and its fragments

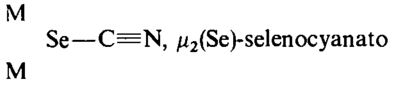
ring into a quartet at room temperature, while the triphos resonance is more affected by the cobalt quadrupole moment and remains broad down to − 70 °C. The resonance of the ring system in [Co(triphos)(η^3-P_2S)]BF_4, in contrast, is broad at room temperature but is resolved into a quartet (^2J = 12 Hz) at − 70 °C, while the P_3 resonance of [Co(triphos)(η^3-P_3)] is unresolved even at − 80 °C[261]. The larger quadrupolar effect on the triphos resonance vs. the η^3-P_2E (E = S, Se) resonances has been attributed to the involvement of the former ligand in lower-energy molecular orbitals than the latter cyclic ligands[261].

B. Anionic Monodentate Ligands

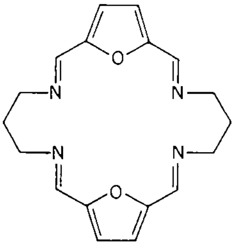
1. Selenocyanates

The coordination chemistry of this ligand has been the most studied of any Se or Te ligand, several hundred papers describing its complexes having appeared[269]. Much of the interest in this ligand is related to its ambidentate character[153]. The following bonding modes (*a*)–(*d*) have been unequivocally established by single-crystal X-ray diffraction, and the one-atom bridging mode (*e*) is strongly suggested by the spectroscopic similarity of the complex with the thiocyanate analogue, whose structure has been confirmed by crystallography.

(*a*) M—SeCN, selenocyanato ligand
  $NH_4[trans\text{-}Co(dmg)_2(SeCN)_2]\cdot 3\,H_2O$[270]
  $Me_4N[PhTe(SeCN)_2]$[271]
(*b*) M—NCSe, isoselenocyanato ligand
  $[Ni(DMF)_4(NCSe)_2]$[272]
(*c*) M—SeCN—M, μ_2-selenocyanato
  $HgCo(NCSe)_4$[273]

(*d*)

$$\begin{array}{l} M \\ \quad Se{-}C{\equiv}N,\ \mu_2(Se)\text{-selenocyanato} \\ M \end{array}$$
  $[Cu(H_2O)(en)_2][Cu_2(CN)_3(SeCN)]$[274]

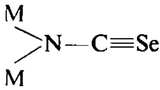
$[Cu_2L(ECN)_2]$; L =



= **(39)**

E = S (crystal structure)[275], Se[276]

(*e*)



$$\begin{matrix}M\\ \quad\rangle N{-}C{\equiv}Se\\ M\end{matrix}$$

μ_2(N)-selenocyanate.)

$[Co_2L(OEt)(NCE)_3]$[277]; L = **39**
E = S (crystal structure), Se
(M(CNSe) indicates an undefined bonding mode of selenocyanate.)

Several main-group organometallic complexes with selenocyanate have been prepared[278] (equations 68 and 69). These complexes can also be prepared by metathetical reactions (equations 70 and 71). All of these complexes except Ph_3MNCSe (M = Si, Sn) were formulated as selenocyanato complexes on the basis of infrared spectroscopy (Table 19).

$$Se(SeCN)_2 \begin{array}{l} \xrightarrow{BiPh_3{}^{279}} Ph_2BiSeCN + PhSeCN + Se \\ \xrightarrow{HgR_2\ (R\,=\,Me,\ Ph)^{264}} RHgSeCN + RSeCN + Se \\ \xrightarrow{PbPh_4{}^{265}} Ph_3PbSeCN + PhSeCN + Se \\ \xrightarrow{Pb_2Ph_6{}^{265}} 2\,Ph_3PbNCSe + Se \\ \xrightarrow{TlPh_3{}^{265}} Ph_2TlSeCN + PhSeCN + Se \end{array} \qquad (68)$$

$$HgR_2 + Hg(SeCN)_2 \rightarrow 2\,RHgSeCN \qquad \text{(Ref. 264)} \qquad (69)$$
$$R = Me, Ph$$

$$(p\text{-}MeC_6H_4)_2TlCl + KSeCN \xrightarrow{MeCN/pyr} (p\text{-}MeC_6H_4)_2TlSeCN \qquad \text{(Ref. 280)} \qquad (70)$$

$$Me_3SiCl + AgSeCN \xrightarrow{acetone} Me_3SiNCSe + AgCl \qquad \text{(Ref. 281)} \qquad (71)$$

Recent studies have examined the bonding mode of the selenocyanate ligand in $Ph_3PbSeCN$ as a function of adduct formation with O and N donors[294] as well as solvent[295]. The solid-state infrared spectrum of the parent compound has been reinterpreted, a polymeric structure with strong Pb—Se and weak Pb—N bonds being proposed[294]. In benzene or CH_2Cl_2 solutions the spectra in the $\nu_{C\equiv N}$ region indicates monomeric Se-bonded selenocyanate (Table 20). A more detailed study[295] of the infrared spectrum ($\nu_{C\equiv N}$) of $Ph_3PbSeCN$ in a variety of solvents showed that N-bonded, Se-bonded and ionic pentacoordinate species were formed, depending on the dielectric constant and donor properties of the solvent. These results (Table 20) were interpreted by the following equilibria.

$$\begin{tikzcd} & Ph_3PbNCSe\cdot L \arrow[d, shift left] & \\ Ph_3PbSeCN \arrow[r, shift left, "L"] & Ph_3PbSeCN\cdot L \arrow[u, shift left] \arrow[l, shift left] \arrow[r, shift left, "L"] & {[Ph_3PbL_2]^+\ SeCN^-} \arrow[l, shift left] \end{tikzcd} \qquad (72)$$

TABLE 19. Selenocyanate complexes (M—SeCN)

Complex	Reported data			Reference
PhHgSeCN	White photosensitive crystals $\nu_{C\equiv N} = 2129s$ $\nu_{C-Se} = 542w$ $\delta_{Se-C\equiv N} = 373s, 398m$ $\nu_{Hg-Se} = 246s$			264
$(p\text{-}MeC_6H_4)_2Tl(SeCN)$	Air-stable white solid M.p. 212–214 °C dec. $\nu_{C\equiv N} = 2090vs$ $\nu_{C-Se} = 571vw$ $\delta_{N-C\equiv Se} = 402vw$			280
$[Ph_3PbSeCN]_n$	White crystals M.p. 192 °C $\nu_{C\equiv N} = 2100$			265
	Solid state: $\nu_{C\equiv N} = 2107vs, 2063w$ $\nu_{C-Se} = 566m$ $2\delta_{N-C\equiv Se} = 759vw, 798vw$			294
$(Me_4N)_2[Pt(SeCN)_6]$	$\nu_{C\equiv N} = 2123s$, sp $\nu_{C-Se} = 528m$ $\delta_{Se\equiv C-N} = 398vw, 373m$ $\nu_{Pt-Se} = 218w, 210w$			282
$[n\text{-}Bu_4N]_2[Pt(SeCN)_4]$	$\nu_{C\equiv N} = 2105s$, sp, 2060 acetone soln.: 2117s, sp ($A = 0.59 \times 10^4$)[a] $\nu_{C-Se} = 516w$			283
$[Pt(bipy)(SeCN)_2]$	$\nu_{C\equiv N} = 2135s, 2135s$ $\nu_{C-Se} = 532w, 527w$			284
$PdL_2(SeCN)_2$	$\nu_{C\equiv N}$ (mull)	$\nu_{C\equiv N}$ ($A \times 10^{-4}$)[a,b]	ν_{C-Se}	285
L = PPh_3	2127	2122 (0.61)	[c]	
4-acetylpyridine	2132	2115 (1.0)	531	
4-methylpyridine	2119	2112 (1.0)	[c]	
pyr	2116	2109 (1.0)	[c]	
NH_3	2126	2111 (0.93)	528	
L_2 = phen	2123, 2110	[d]	530	
bipyr	2134, 2119	[e]	528	
en	2126, 2108	2112 (0.65)	[c]	
$[Ni\{P(OPh)_3\}_2(SeCN)_2]$	red–brown solid $\nu_{C\equiv N}$(mull) = 2128vs (0.5)[f] (CH_2Cl_2) soln.: 2125 $\nu_{C-Se} = 520w$ $\delta_{Se-C\equiv N} = 412w$ $\nu_{Ni-Se} = 255$			286
$K_2[Hg(SeCN)_4]$	$\nu_{C\equiv N} = 2098s$ $\nu_{C-Se} = 543w$			287
	$\delta(^{77}Se)$[g]; (D_2O) = − 191; − 471 (rel. int. = 10:1)			288
$NH_4[trans\text{-}Co(dmg)_2(SeCN)_2] \cdot 3\,H_2O$	$\nu_{C\equiv N} = 2136$ $\nu_{C-Se} = 550$			289, 290
	Crystal structure:			270
	Co—Se = 2.4 Å			246

TABLE 19. (*Continued*)

Complex	Reported data	Reference
trans-[Co(dmg)$_2$(PPh$_3$)(SeCN)]	$\nu_{C\equiv N} = 2125\ (2.4)^h$ PhNO$_2$ soln: 2120 $(A = 0.68 \times 10^4)^a$	291
[(Ph$_3$P)AuSeCN]	$\nu_{C\equiv N}(CH_2Cl_2) = 2135s$ $(A = 0.70 \times 10^4)^a$ $\nu_{C-Se} = 529$ $\delta_{N\equiv C-Se} = 372$	292
trans-Pd(PPh$_3$)$_2$(SeCN)$_2$	$\nu_{C\equiv N} = 2134s$, sp CH$_2$Cl$_2$: 2131m, sp $(A = 0.42 \times 10^4)^a$	293
trans-Pt(PPh$_3$)$_2$(SeCN)$_2$	$\nu_{C\equiv N} = 2130s$, sp CH$_2$Cl$_2$: 2131s, sp (Pt—SeCN) 2100s, br (Pt—NCSe) DMF: 2129s, sp (Pt—SeCN) 2096s, br (Pt—NCSe) 2053w, br (free SeCN$^-$)	293

[a] Solution $\nu_{C\equiv N}$ integrated absorption intensity (see Table 23) in units of $M^{-1}\,cm^{-2}$.
[b] In DMF.
[c] Obscured by other vibrations.
[d] Complex insoluble in DMF.
[e] Selenocyanate ligand completely dissociates in DMF.
[f] $\nu_{C\equiv N}$ intensity relative to internal salicyclic acid in the solid state (see Table 23).
[g] Vs. external 1M SeMe$_2$ in CHCl$_3$.
[h] $\nu_{C\equiv N}$ intensity relative to internal 1,4-dicyanobenzene in the solid state (see Table 23).

In non-coordinating non-polar solvents (C_6H_6, CH_2Cl_2) the solution species is exclusively monomeric Ph$_3$PbSeCN. Strong donors (e.g. DMF, OP(OMe)$_3$) and the highly polar but weak donor solvent MeCN cause complete ionization, as reflected in the appearance of only the 'ionic' value of $\nu_{C\equiv N}$ for the selenocyanate. In acetone only partial ionization occurs, with the coordinated selenocyanate being N-bonded, but in THF, a stronger donor but less polar than acetone, an isomeric mixture of N- and Se-bonded monomers is observed. In pyridine partial ionization occurs, and the molecular species is an isomeric mixture.

TABLE 20. Solution infrared spectra in the $\nu_{C\equiv N}$ region of Ph$_3$PbSeCN[295]

			$\nu_{C\equiv N}$ (cm^{-1})			
				Ph$_3$Pb(CNSe)·L		
Solvent	DN[a]	ε	Ph$_3$PbSeCN	Pb—NCSe	Pb—SeCN	SeCN$^-$
C_6H_6	0.1		2139			
CH_2Cl_2	0.1	9.1	2136			
DMF	26.6	36.1				2066
OP(OMe)$_3$	23.0	20.6				2068
Acetone	17.0	20.7		2056		2066sh
MeCN	14.1	38.0		2066		
THF	20.0	7.6		2036m	2129s	
pyr	33.1	12.3		2117m	2049vs	2064s

[a] Donor number as described by Gutmann[296].

TABLE 21. Infrared spectral data (cm^{-1}) for $Ph_3Pb(CNS)L$ adducts[294]

L	Reported data $\nu_{C\equiv N}$ (solid)	(C_6H_6 soln.)	ν_{C-Se} (solid)
$OPPh_3$	2119s, sp 2055w	2139vs, sp[a] 2125m, sp[b] 2037m, br[c]	[d]
4-picO	2105s, sp 2061vw	2138m, sp[a] 2123vs, sp[b] 2038m, br[c]	547w
pyrO	2106s, sp 2061vw	2138vs, sp[a] 2125m, sp[b] 2031m, br[c]	[d]
HMPA	2053vs, br 2010w	2139s, sp[a] 2123s, sp[b] 2037vs, br[c]	609m

[a] Band of $Ph_3PbSeCN$ formed by dissociation of the neutral ligand.
[b] Pb—SeCN.
[c] Pb—NCSe.
[d] Obscured by other vibrations.

A series of 1:1 adducts, $Ph_3Pb(CNSe)\cdot L$ (L = HMPA, pyridine-*N*-oxide (pyrO), 4-picoline-*N*-oxide (4-picO) and $OPPh_3$), have been prepared and the selenocyanate bonding modes in the solid state and solution (C_6H_6 and CH_2Cl_2) have been determined by infrared spectroscopy[294] (Table 21). In the solid state all the complexes are monomeric with the HMPA adduct containing N-bonded selenocyanate, and the other three oxygen donors give Se-bonded selenocyanate. In solution (C_6H_6 and CH_2Cl_2) all four complexes partially dissociate with the intact soluble adduct being present as both N- and Se-linkage isomers (Table 21).

The derivatives $R_3SiNCSe$ (R = Me, Et, Ph) were formulated as isoselenocyanates (Table 22)[281]. Unlike the heavier main-group organometallic selenocyanates, these compounds readily decompose thermally or hydrolytically, depositing elemental Se[281] (equations 73 and 74). As described for other systems[137–139], Se extrusion can also be effected by PPh_3[281] (equation 75).

$$2\,R_3SiNCSe \xrightarrow{H_2O} (R_3Si)_2O + HCN + Se \qquad (73)$$

$$R_3SiNCSe \xrightarrow{\Delta} R_3SiCN + Se \qquad (74)$$

$$Me_3SiNCSe + PPh_3 \xrightarrow{-SePPh_3} Me_3SiCN \qquad (75)$$

The structure of $Ph_3SnNCSe$, originally proposed to be monomeric with N-bonded selenocyanate[265], has recently been reformulated as polymeric with strong Sn—N bonds and weak Sn—Se bonds (a similar structure has been established by X-ray diffraction for Ph_3SnNCS[301]).

The general approach in structural ambidentate ligand chemistry has been to unequivocally establish the various bonding modes by single-crystal X-ray diffraction and then assign bonding modes in other complexes on the basis of some spectroscopic

TABLE 22. Isoselenocyanate complexes (M—NCSe)

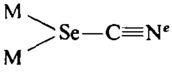
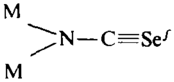
Complex	Reported data		Reference
$R_3SiNCSe$	$\nu_{C\equiv N}$	ν_{C-Se}	281
R = Me	2055vs	625m	
Et	2065vs, 2090sh	600w	
Ph	2070vs	620w	
$Ph_3SnNCSe$	white powder $\nu_{C\equiv N} = 2108$br $\nu_{C-Se} = 594$m		265
$[(n\text{-}Bu)_4N]_3[Y(NCSe)_6]$	$\nu_{C\equiv N} = 2067$s, br; 2030sh acetone soln.: 2068s, br $(A = 5.1 \times 10^4)^a$ $\nu_{C-Se} = 634$m $\delta_{N\equiv C-Se} = 429$m		283
$(AsPh_4)_2[Co(NCSe)_4]$	$\nu_{C\equiv N} = 2060$s, br		287, 297
$CpCo(CO)(NCSe)_2$	$\nu_{C\equiv N} = 2136$vs $(1.7)^b$; 2096vs $(2.0)^b$ $\nu_{C\equiv O} = 2060$s $\nu_{C-Se} = 575$m $\delta_{N\equiv C-Se} = 540$w		298
$Ru(CO)_2(PPh_3)_2(NCSe)_2$	$\nu_{C\equiv N} = 2085$ms (*trans*-$Ru(NCSe)_2$) $\nu_{C\equiv O} = 2015$vs; 2068vs (*cis*-$Ru(CO)_2$) $\nu_{C-Se} = 595$m		299
$Cp_2Ti(NCSe)_2$	$\nu_{C\equiv N} = 2050\ (2.4)^b$; 2015 $(2.3)^b$ CH_2Cl_2 soln.: 2050, 2015 $\nu_{C-Se} = 600, 593$ $\nu_{N\equiv C-Se} = 457, 448$		300
$Cp_2V(NCSe)_2$	$\nu_{C\equiv N} = 2083\ (1.8)^b$; 2065 $(1.9)^b$ CH_2Cl_2 soln.: 2080, 2063 $\nu_{C-Se} = 620, 596$ $\delta_{N\equiv C-Se} = 472, 450$		300
$Cp_2Cr(NCSe)(SeCN)$	$\nu_{C\equiv N} = 2120\ (0.4)^b$; Cr—SeCN 2042 $(1.8)^b$; Cr—NCSe CH_2Cl_2 soln.: 2122, 2038 $\nu_{C-Se} = 590$ (Cr—NCSe); 540 (Cr—SeCN) $\delta_{N\equiv C-Se} = 435, 425$		300
$CpCo(CO)(CN)(NCSe)$	$\nu_{C\equiv N} = 2148$vs $(1.8)^b$; Co—CN $\nu_{C\equiv N} = 2100$vs $(1.9)^b$; Co—NCSe $\nu_{C\equiv O}$ masked by other bands $\nu_{C-Se} = 575$m CH_2Cl_2 solution: $\nu_{C\equiv N} = 2143$vs (Co—CN) $\nu_{C\equiv N} = 2100$vs (Co—NCSe) $\nu_{C\equiv O} = 2043$vs (Co—CO)		298

[a] Solution $\nu_{C\equiv N}$ integrated absorption intensity (see Table 23) in units of $M^{-1}\ cm^{-2}$.

[b] $\nu_{C\equiv N}$ intensity relative to internal salicylic acid in the solid state (see Table 23).

technique, most commonly infrared spectroscopy. This approach has been most developed for thiocyanate complexes. Structural probes include infrared, Raman, electronic, NMR (^{1}H, ^{13}C, ^{14}N), NQR (^{14}N) and X-ray photoelectron spectroscopy (see Ref. 302 for a review of this work). Recent work in this area includes solid-state quantitative infrared[303] (using an internal reference compound for measuring the relative intensity of the $\nu_{C\equiv N}$), ^{14}N-NQR[304], XPS[157c], and solution[305] and solid-state[158a] ^{13}C-NMR and solution ^{77}Se-NMR[288] spectroscopy. All of these techniques should be applicable to selenocyanate ligand chemistry, although considerably less work has been

TABLE 23. Infrared spectroscopic characterization of the selenocyanate ligand

Bonding mode	$\nu_{C\equiv N}$	$A \times 10^{-4}$[b]	ISR[c]	ISR[d]	ν_{C-Se}[a]	$\delta_{N\equiv C-Se}$[a]
M—NCSe	2050–2100 (broad)	5–12	1.5–3	20–30	600–650	410–460
M—SeCN	2070–2130 (sharp)	0.5–1.5	0.3–0.6	2–13	520–550	370–410
M—SeCN—M	2100–2175				550–640	390–410
[e]	2105sp				700m	443w, 462w
[f]	1995					
Ionic SeCN⁻ [g]	2068s, sp	1.8			558	416, 424

[a] In cm^{-1}.

[b] Solution $\nu_{C\equiv N}$ integrated absorption intensity in units of M^{-1} cm^{-1}. The concentration is based on selenocyanate.

[c] Internal standard ratio: the ratio of the intensity of the $\nu_{C\equiv N}$ vs. salicyclic acid as an internal standard in the solid state[306].

[d] Internal standard ratio using 1,2-dicyanobenzene as an internal reference for $\nu_{C\equiv N}$ in the solid state[303].

[e] The data listed are for the only complex with this bonding mode which has been reported ($Cu_2L(SeCN)_2$; L = 39)[276].

[f] Only one complex with this bonding mode has been reported: $Co_2L(OEt)(NCSe)_3$ (L = 39)[277]. The crystal structure of the thiocyanate analogue was reported[277] and showed a structure involving a terminal isothiocyanate ligand on each Co, a bridging ethoxide ligand, and a N-bridged thiocyanate ligand. Two other N-bridging thiocyanate complexes have been structurally characterized by single-crystal X-ray diffraction ($[(n\text{-}Bu)_4N]_3Re_2(NCS)_{10}$[307] and $[Cd_2(NCS)_4(butrz)_3]_n$ (butrz = 4-*t*-butyl-1,2,4-triazole)[308]).

[g] KSeCN in acetone[283].

TABLE 24. NMR spectroscopic characterization of selenocyanate bonding modes

^{13}*C-NMR* (*δ, ppm*[a])[304]		
M—SeCN	SeCN⁻	M—NCSe
105–114	116–121	120–130
^{77}*Se-NMR* (*δ, ppm*[b])[288]		
$K_2Hg(SeCN)_4$	KSeCN	$ZnL_2(NCSe)_2$[c]
−191	−273	−318
		$CdL_2(NCSe)_2$
		−305
		$CdL_2(NCSe)_2$
		−282

[a] Vs. internal TMS. Only three selenocyanate complexes and one isoselenocyanate complex were studied in this work but the SeCN⁻ resonance tends to shift to high (M—NCSe) or low (M—SeCN) field vs. free SeCN⁻ upon coordination.

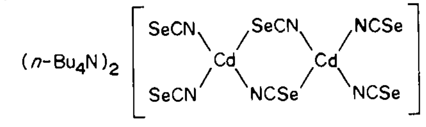
[b] Vs. external 1 M Me_2Se in $CHCl_3$. Only four complexes have been studied, but again there seems to be a high field/low field shift vs. ionic SeCN⁻ upon coordination.

[c] 4-*t*-Butylpyridine.

done in this area, infrared spectroscopy being the most generally used spectroscopic technique. Infrared and NMR parameters for the assignment of selenocyanate bonding modes are summarized in Tables 23 and 24.

Most of the reported coordination chemistry with this ligand involves transition-metal complexes, and the simple complexes, containing only selenocyanate ligands, follow the bonding pattern expected on the basis of Pearson's hard–soft acid–base theory[309]. This generalization refers to simple complexes containing only selenocyanate ligands (e.g. $[Co(NCSe)_4]^{2-}$ vs. $[Pt(SeCN)_4]^{2-}$), and a variety of factors such as metal oxidation state, steric and electronic effects of other ligands in the coordination sphere, and crystal-packing effects can influence the bonding mode of the ambidentate selenocyanate ligand[153]. Two examples of isolated linkage isomeric pairs with this ligand have been reported: $[Pd(Et_4dien)(SeCN/NCSe)]BPh_4$[310] ($Et_4dien = Et_2NCH_2CH_2NHCH_2CH_2NEt_2$) and $CpFe(CO)(PPh_3)(SeCN/NCSe)$[311]. The limited number of such isomeric pairs compared to the thiocyanate ligand indicates a significantly lower susceptibility of the selenocyanate ligand to the above steric and electronic influences on bonding mode.

Selenocyanate can also form dimeric and polymeric complexes with bridging selenocyanate[312] (Table 25). This bonding mode is most easily detected by an unusually high value of $\nu_{C\equiv N}$ (e.g. 2140–2175 cm^{-1}). The trend from Class A to Class B metal ions is well reflected in the bonding of the selenocyanate ion in the complexes of Group IIb, Zn(II) and Hg(II) giving tetrahedral $Zn(NCSe)_4{}^{2-}$ and $Hg(SeCN)_4{}^{2-}$ complexes with the expected Zn—NCSe (hard acid/hard N site) and Hg—SeCN (soft acid/soft Se site), whereas Cd(II) gives a dimeric complex with N-bonded terminal selenocyanate and bridging selenocyanate[283]:



(40)

TABLE 25. Complexes with bridging selenocyanate (M—SeCN—M)

Complex	Reported data	Ref.
$\{AgSeCN\}_n$	$\nu_{C\equiv N} = 2141$s, 2098sh $\nu_{C-Se} = 580$w	287
$HgCo(NCSe)_4$ (Co—NCSe—Hg)	$\nu_{C\equiv N} = 2146$ $\nu_{C-Se} = 639$	273, 287
$(n\text{-}Bu_4N)_2[Cd_2(SeCN)_6]$ **(40)**	$\nu_{C\equiv N} = 2109$s, br (Cd—NCSe) 2125sh (Cd—NCSe—Cd) acetone soln.: 2120s, br ($A = 3.2 \times 10^4$)[a] 2076s, br ($A = 2.6 \times 10^4$)[a] $\nu_{C-Se} = 589$sh, 582m $\delta_{N\equiv C-Se} = 417$w, 408m	283
$\{Co[Ag(SeCN)_2]_2\}_n$ (Co—NCSe—Ag)	$\nu_{C\equiv N} = 2125$s, 2150s $\nu_{C-Se} = 580$, 598sh $\delta_{N\equiv C-Se} = 395$, 405sh $\nu_{Co-N} = 278$s	313
$(SCN)_2Co(NCSeHg(Pr\text{-}n))_2$	$\nu_{C\equiv N} = 2170$s, 2120s (Co—NCSe—Hg) 2090m (Co—NCS) $\nu_{C-S} = 820$m $\nu_{C-Se} = 540$s	314

[a] Solution $\nu_{C\equiv C}$ integrated absorption intensity (see Table 23) in units of M^{-1} cm^{-2}.

The heterometallic complex $HgCo(NCSe)_4$ is polymeric with bridging selenocyanate, the hard N site bonding to the hard Co(II) Lewis acid and the soft Se site coordinating to the soft Hg(II) acid (Table 25).

The general routes to selenocyanate complexes include metathetical reactions (equations 76–78) and oxidative addition reactions, $(SeCN)_2$ (equations 79–85), $Se(SeCN)_2$ (equations 86–88) and $Se(CN)_2$ (equations 89–91) all having been used as reagents in such reactions.

Metathetical reactions

$$Y(NO_3)_3 \cdot 6\,H_2O + 6\,Bu_4N[SeCN] \xrightarrow{EtOH} (Bu_4N)_3[Y(NCSe)_6] \qquad \text{(Ref. 283)} \qquad (76)$$

$$\begin{tikzcd} CpCr(NO)_2Cl \arrow[r, "AgNO_3", "H_2O/MeOH"'] & \{CpCr(NO)_2NO_3\} + AgCl \arrow[d, "KSeCN"] \\ & CpCr(NO)_2NCSe \end{tikzcd} \qquad \text{(Ref. 311)} \qquad (77)$$

$$trans\text{-}[Co(dmg)_2Cl(H_2O)] + 2\,KSeCN \xrightarrow{H_2O/EtOH} K[trans\text{-}Co(dmg)_2(SeCN)_2]$$

(Ref. 289) (78)

Oxidative addition reactions
$(SeCN)_2$

$$\begin{tikzcd} Pd(PPh_3)_4 \arrow[r, "(SeCN)_2"] & trans\text{-}Pd(PPh_3)_2(SeCN)_2 \\ (AgSeCN)_x \arrow[u, "I_2/Et_2O"'] & \end{tikzcd} \qquad \text{(Ref. 293)} \qquad (79)$$

$$CpCo(CO)_2 \xrightarrow{(SeCN)_2} CpCo(CO)(NCSe)_2 \qquad \text{(Ref. 298)} \qquad (80)$$

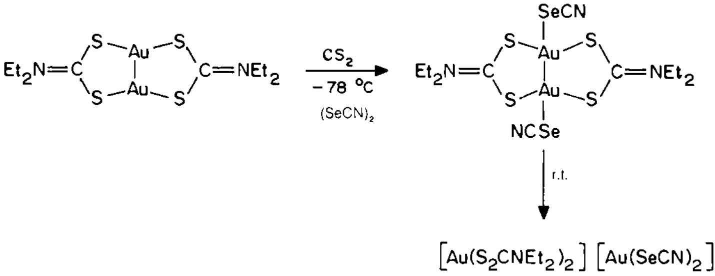
$$Ru(CO)_3(PPh_3)_2 \xrightarrow{(SeCN)_2} Ru(CO)_2(PPh_3)_2(NCSe)_2 \qquad \text{(Ref. 299)} \qquad (81)$$

$$Cp_2M \xrightarrow{(SeCN)_2} Cp_2V(NCSe)_2 \text{ or } Cp_2Cr(NCSe)(SeCN) \qquad \text{(Ref. 300)} \qquad (82)$$

$M = V, Cr$

$$Cp_2Ti(CO)_2 \xrightarrow{(SeCN)_2} Cp_2Ti(NCSe)_2 \qquad \text{(Ref. 300)} \qquad (83)$$

$$Ni\{P(OPh)_3\}_4 \xrightarrow{(SeCN)_2} \{P(OPh)_3\}_2Ni(SeCN)_2 \qquad \text{(Ref. 286)} \qquad (84)$$



(Ref. 315) (85)

Se(SeCN)₂

$$\mathrm{Cp(OC)(Ph_3P)FeCH_2Ph} \xrightarrow{\mathrm{Se(SeCN)_2}} \mathrm{Cp(OC)(Ph_3P)FeNCSe} \quad \text{(Ref. 137)} \qquad (86)$$

$$48\%$$
$$\nu_{\mathrm{C\equiv N}}(\mathrm{CHCl_3}) = 2120$$
$$A = 5.3 \times 10^4$$
$$\nu_{\mathrm{C-Se}} = 663\,\mathrm{m}$$

$$+\ \mathrm{Cp(OC)(Ph_3P)FeSeCN} + \mathrm{CpFe(CO)(PPh_3)CN} + \mathrm{Se} + \mathrm{PhCH_2SeCN}$$

$$17\% \qquad\qquad 7\%$$
$$\nu_{\mathrm{C\equiv N}}(\mathrm{CHCl_3}) = 2117$$
$$A = 1.7 \times 10^4$$
$$\nu_{\mathrm{C-Se}} = 523\mathrm{w}$$

$$\mathrm{CpFe(CO)_2CH_2Ph} \xrightarrow[\mathrm{C_6H_6/\Delta}]{\mathrm{Se(SeCN)_2}} \mathrm{CpFe(CO)_2(SeCN)} \quad \text{(Ref. 311)} \qquad (87)$$

$$\mathrm{CpM(CO)_3H} \xrightarrow[\mathrm{C_6H_6}]{\mathrm{Se(SeCN)_2}} \mathrm{CpM(CO)_3SeCN} \quad \text{(Ref. 311)} \qquad (88)$$
$$\mathrm{M = Mo, W}$$

Se(CN)₂

$$\begin{tikzcd} \mathrm{CpCo(CO)_2} \arrow[rr, "\mathrm{Se(CN)_2}"] & {} & \mathrm{CpCo(CO)(CN)(NCSe)} \quad \text{(Ref. 298)} \qquad (89) \\ & \mathrm{KSeCN} \arrow[u, "\mathrm{BrCN/Et_2O}"'] & \end{tikzcd}$$

$$\mathrm{Cp_2Ti(CO)_2} \xrightarrow[\mathrm{Et_2O}]{\mathrm{Se(CN)_2}} \mathrm{Cp_2Ti(CN)(NCSe)} \quad \text{(Ref. 300)} \qquad (90)$$

$$\mathrm{Cp_2M} \xrightarrow[\mathrm{Et_2O}]{\mathrm{Se(CN)_2}} \mathrm{Cp_2M(CN)(NCSe)} \quad \text{(Ref. 300)} \qquad (91)$$
$$\mathrm{M = V, Cr}$$

The complex K[*trans*-Co(dmg)$_2$(SeCN)$_2$] (equation 78) is an example of significant stabilization of a reagent upon coordination. Addition of concentrated HCl to a hot aqueous solution of this complex causes no deposition of elemental Se. Cooling the resulting solution results in the deposition of crystalline H[Co(dmg)$_2$(SeCN)$_2$][289]. A similar coordination stabilization of selenosemicarbazones has been reported for Co(III) complexes of this type[251]. A considerable amount of work has been reported dealing with complexes of the type *trans*-[Co(dmg)$_2$L(SeCN)] (L = neutral ligands, e.g. PR_3, AsR_3). In such complexes the steric environment of the ambidentate $SeCN^-$ ligand can be held constant while the electronic properties of the ligands in the *trans* position across the Co(dmg)$_2$ plane can be systematically modified to study electronic effects on the $SeCN^-$ bonding[291,316–319].

The first example of isolated linkage isomers of the selenocyanate ligand took advantage of the increased steric requirements of the bent M—SeCN vs. linear M—NCSe linkages, the initially isolated Se-bonded isomer being formed when the substitution reaction was run at low temperature (equation 92).

$$\begin{tikzcd}
\mathrm{K_2Pd(SeCN)_4 + Et_4dien} \arrow[r, "-150\,^{\circ}\mathrm{C}"] & {\mathrm{[Pd(SeCN)(Et_4dien)]^+}} \arrow[d, "\mathrm{NaBPh_4}"] \\
\mathrm{Et_4dien = (Et_2NCH_2CH_2)_2NH} & {\mathrm{[Pd(SeCN)(Et_4dien)]BPh_4}} \arrow[d, "\mathrm{DMF/r.t.}"] \\
 & {\mathrm{[Pd(NCSe)(Et_4dien)]BPh_4}}
\end{tikzcd}$$ (92)

The N-bonded isomer was precipitated from DMF solution by addition of ether[320], but it reisomerized in the solid state at room temperature to the Se-bonded isomer, an unusual example of the influence of a non-coordinated ion on the bonding mode of an ambidentate ligand[310]. The influence of steric effects is demonstrated in this system by the stability of the initially isolated Se-bonded isomer when diethylenetriamine is used in the above reaction in place of the Et_4dien[310]. The linkage isomers $CpFe(CO)(PPh_3)(NCSe/SeCN)$ were prepared with the reagent $Se(SeCN)_2$ (equation 86), and the isomeric products were purified by column chromatography[137]. The two isomers were stable at room temperature, and attempts to cause isomerization by heating resulted in deselenation, this reaction being much faster for the Fe—NCSe isomer (equation 93).

$$\mathrm{CpFe(CO)(PPh_3)(CNSe)} \xrightarrow[\Delta]{C_6H_6} \mathrm{CpFe(CO)(PPh_3)CN + Ph_3PSe} \qquad (93)$$

The formulation of the linkage isomers involving the isomeric $CpFe(CO)(SePPh_3)CN$ was ruled out by ^1H-NMR (the J_{PH} of both isomers and the independently prepared $CpFe(CO)(PPh_3)(CN)$ was 1.3 Hz, indicating the presence of the $Fe—PPh_3$ moiety)[137].

The infrared data for these two linkage isomers (equation 86) illustrate the ambiguity with bonding assignments based on $\nu_{C\equiv N}$. The values for the two isomers are close, and both could reasonably be assigned to Fe—SeCN bonding. Even the solution-integrated intensities for these bands are at the high and low ends of the ranges for M—SeCN and M—NCSe, respectively. The $\nu_{C—Se}$ bands, generally the most unequivocal vibrations for bonding assignment, clearly indicate, however, the presence of linkage isomers. Unfortunately, the spectral region in which the $\nu_{C—Se}$ bands are found is often obscured by other ligand vibrations (e.g. Table 19).

Both M—SeCN and M—NCSe products were obtained in the other oxidative addition reactions (equations 79–90), as well as a unique example of a complex containing both bonding modes (equation 82; Table 22). The oxidative addition reaction with the dimeric Au(I) diethyldithiocarbamate complex gave an isolable complex of gold in the unusual +2 oxidation state[291].

The reaction of Mo_2Cl_{10}, a chloro-bridged dimer with a weak Mo—Mo bond, gives a product, $MoCl_5(NCSe)_2$, in which an intact N-bonded $(NCSe)_2$ ligand is proposed on the basis of infrared and ESR spectroscopy[321].

Several metal complexes of organic selenocyanates have also been isolated ($M(CO)_5NCSeR$: M = Cr, R = Me, Et, Ph; M = W, R = Me, Et)[322]. These complexes, which were assigned M—NCSeR bonding modes on the basis of infrared and NMR data, were prepared by substitution reactions (equation 94a) or by alkylation of coordinated isoselenocyanato ligand (equation 94b).

$$\begin{tikzcd}
\mathrm{Et_4N[M(CO)_5I]} \arrow[r, "\mathrm{AgBF_4/acetone}", "-\mathrm{AgI/Et_4NBF_4}"'] & {\mathrm{[M(CO)_5(acetone)]}} \arrow[d, "\mathrm{RSeCN}"] & (94a) \\
\mathrm{(Et_4N)[M(CO)_5NCSe]} \arrow[r, "\mathrm{alkylation}", "(\mathrm{e.g.\ [Et_3O][BF_4]})"'] & {\mathrm{[M(CO)_5NCSeR]}} & (94b)
\end{tikzcd}$$

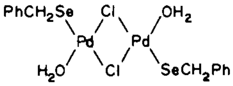
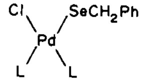
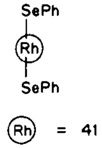
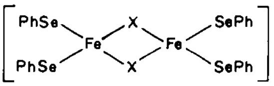
2. *Selenols (RSe^-)*

Since the first transition-metal complex with an organoselenol ligand, the dimeric doubly selenol-bridged complex $(OC)_3Fe(\mu_2\text{-}SeEt)_2Fe(CO)_3$, was reported in 1960 by Hieber and Beck[323], a number of complexes incorporating terminal (M—SeR) and bridging (—$M(\mu_2\text{-}SeR)_2M$—) have been described. Crystal structures of two monomeric

TABLE 26. Metal complexes with terminal selenol ligands

Complex[a]	Reported data	Reference
$Cp_2Ti(SePh)_2$	blue-violet crystals	
	M.p. 120–122 °C dec.	324, 325
	153–155 °C	326
	$\delta = 5.99$ (Cp), 7.45 (Ph)	
	MW = 463[b] (calc. 490.2)	
$CpMo(CO)_3SePh$	Red solid	327
	M.p. 92–94 °C	
	$\nu_{C\equiv O}(CS_2) = 2026$vs, sp; 1948vs	
$Ti(SePh)_4$	Black solid	328
$Ti(SeNp)_4$	Black solid	328
$Zr(SePh)_4$	Turquoise solid	328
$Nb(SePh)_3$	Brown microcrystals	328
	MW = 551[b] (calc. 561.1)	
$Nb(SeNp)_3$	Brown-black solid	328
$Ta(SePh)_3$	Brown microcrystals	328
$W(SePh)_4$	Brown solid	328
$(Bu_3P)_2Ni(SePh)_2$	MW = 747[b] (calc. 775.5)	328
$CpFe(CO)_2SePh$	Dark crystals	329
	M.p. 50–52 °C	
	MW = 372[c], 333[d] (calc. 333)	
	$\nu_{C\equiv O}(C_6H_{12}) = 2026$s, 1984s	
	$\delta(CS_2) = 5.21$ (Cp)	
$CpNi(PBu_3)SePh$	Green crystals	330
	M.p. 51–52 °C	
	$\delta(CS_2) = 5.06$ (s, Cp), 7.50–7.41, 6.98–6.71 (m, Ph)	
$Cp_2Ti(SeMe)_2$	Green solid	326
	M.p. 210–211 °C	
	$\delta(CS_2) = 5.97$ (s, Cp), 2.64 (s, Me)	
$Cp_2Zr(SePh)_2$	Yellow solid	326
	M.p. 134–136 °C; 156 °C	326,331
	$\delta(CS_2) = 5.83$ (s, Cp), 7.60–7.46, 7.22–7.07 (m, Ph)	
	MW = 512[b] (calc. 533)	
$Cp_2V(SePh)_2$	Green solid	332
	M.p. 126–130 °C	
$Cp_2Nb(SePh)_2$	Dark green solid	332
	M.p. 101–105 °C	
$Cp_2Mo(SeMe)_2$	Brown crystals	332
	M.p. 197–198 °C	
	$\delta[(CD_3)_2SO] = 5.20$ (s, Cp), 1.55 (s, Me)	
$Cp_2Mo(SePh)_2$	M.p. 230–231 °C	332
	$\delta[(CD_3)_2SO] = 5.22$ (s, Cp), 7.37–6.97 (m, Ph)	

TABLE 26. (*Continued*)

Complex[a]	Reported data	Reference
$Cp_2W(SeMe)_2$	M.p. 207 °C $\delta(CDCl_3) = 5.31$ (s, Cp), 2.53 (s, Me)	332
$Cp_2W(SePh)_2$	M.p. 231–232 °C $\delta(CDCl_3) = 5.36$ (s, Cp), 7.70–6.92 (m, Ph)	332
	Orange–brown solid M.p. 220 °C dec.	333
 L = p-$H_2NC_6H_4Me$	Yellow crystals M.p. 220 °C $\nu_{Pd-Se} = 300$ $\nu_{Pd-Cl} = 345$ $\nu_{Pd-N} = 475, 510$	333
	Red crystals Infrared spectrum ^{1}H-NMR Crystal structure Rh—Se = 2.510(1), 2.544(1)Å	334, 335 334
$(\eta^7\text{-}C_7H_7)W(CO)_2SePh$	Green crystals M.p. 132 °C $\nu_{C\equiv O} = 1985$vs, 1930vs $\delta(^1H) = 5.11$ (s, C_7H_7), 7.16 (m, Ph) Crystal structure	336 337
$Cp_2Hf(SeMe)_2$	M.p. 208 °C $\delta(^1H, CS_2) = 2.35$ (s, Me), 5.95 (s, Cp)	331
$Cp_2Hf(SePh)_2$	M.p. 160 °C $\delta(^1H, CS_2) = 5.70$ (s, Cp), 7.15m, 7.40m	331
$Cp_2Zr(SePh)Me$	$\delta(^1H) = 0.02$ (s, Me), 5.60 (s, Cp), 7.03 (m), 7.60 (m, Ph)	 338
$dppe(OC)_2ReSePh$	Yellow crystals $\nu_{C\equiv O}(CHCl_3) = 2020$s, 1945m, 1899m	339
$(OC)_4(PhSe)CrCNEt_2$	Orange solid $\nu_{C\equiv O} = 2078$vw, 2022m, sh; 2007vs, 1976vs $\nu_{C\equiv N} = 1575$	250
$(OC)_3(Ph_3P)(PhSe)CrCNEt_2$	$\nu_{C\equiv O} = 2023$m, 1965s, 1933vs $\nu_{C\equiv N} = 1553$	250
 X = S, Se	ESR spectrum	340
$(Ph_4P)[Hg(SePh)_3]$	Yellow solid M.p. 102 °C dec.	341
$(Ph_4P)_2[Hg(SePh)_4]$	Yellow solid	341

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[a] Units are as described in Table 3.

[b] Determined cryoscopically in benzene.

[c] Determined by osmometry in $CHCl_3$.

[d] Mass spectroscopy.

TABLE 27. Metal complexes with bridging selenol ligands

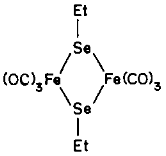
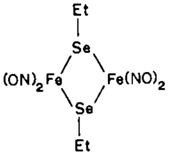
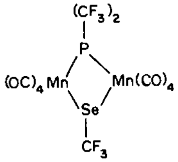
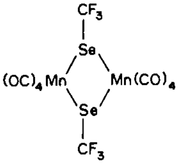
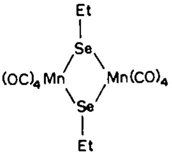
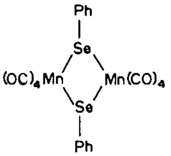
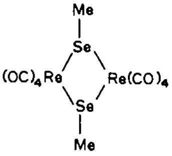
Complex	Reported data	Reference
	Red crystals M.p. 34 °C M W = 501^a (calc. 495.8) $\mu = 2.20$ $\nu_{C\equiv O} = 2056s, 2027vs, 1985vs$	323
	M.p. 97 °C dec. $\mu(C_6H_6) = 0.92$	342
	Orange solid $\nu_{C\equiv O}(CCl_4) = 2089m, 2082w, 2036s, sh; 2029vs, 2003s$ $\delta(^{19}F)^b = 50.8, 51.3; J_{PF} = 53.8^c\ (-P(CF_3)_2), 29.3\ (-SeCF_3)$	343
	Air-stable orange–brown solid M.p. 96–97 °C $\nu_{C\equiv O} = 2100vs, 2060vs, 2020vs, 1955vs$	344
	Air-stable red–brown solid M.p. 135 °C dec. $\nu_{C\equiv O}(KBr) = 2065vs, 2002vs, 1980vs, 1932vs$ $\delta(CCl_4) = 2.82\ (q, J = 7.5), 1.22\ (t, J = 7.5)$	344
	Orange crystals M.p. 77 °C $\nu_{C\equiv O}(C_6H_{12}) = 2056m, 2002sh, 1999vs, 1988s, 1957vs$	345
	Orange–brown crystals M.p. 135 °C dec. MW = 686 (calc. 646) $\nu_{C\equiv O}(C_6H_{12}) = 2065s, 2010vs, 1994s, 1962vs$	346 345, 347
	Orange crystals M.p. 172 °C dec. $\nu_{C\equiv O}(C_6H_{12}) = 2082m, 2002vs, 1990m, 1952vs$ $\delta(CCl_4) = 2.4$	345

TABLE 27. (*Continued*)

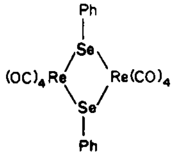
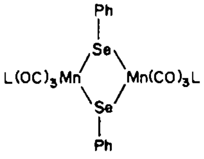
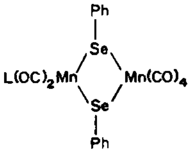
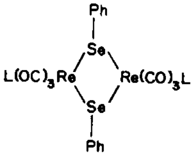
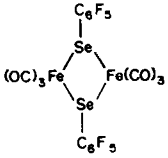
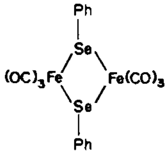
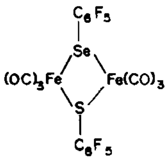
Complex	Reported data	Reference
	Bright orange crystals M.p. 175 °C dec. $\nu_{C\equiv O}(C_6H_{12}) = 2088m, 2012vs, 1988m, 1952s$	345–347
 L = PPh_3	$\nu_{C\equiv O}(CHCl_3) = 1988m, 1949s, 1906s$	339
 L = dppe	$\nu_{C\equiv O}(CHCl_3) = 2048w, 2022s, 2002s, 1946sh, 1935s, 1908s$	339
 L = PPh_3	$\nu_{C\equiv O}(CHCl_3) = 2028s, 2009s, 1937m, 1917s, 1905s$	339
	Air-stable solid M.p. 158–159 °C $\nu_{C\equiv O}(CS_2) = 2080, 2051, 2016, 2004$	348
	Air-stable red crystals M.p. 94–96 °C $MW = 572^d$ (calc. 548) $\nu_{C\equiv O}(CS_2) = 2066, 2029, 2000, 1988$ $\nu_{C\equiv O}(C_6H_{12}) = 2061, 2031, 1998, 1991$	348 349
	Air-stable solid Mössbauer spectrum^e: $\delta = 0.36$ $\Delta = 1.35$	348

TABLE 27. (*Continued*)

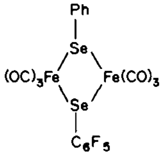
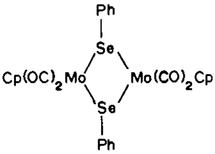
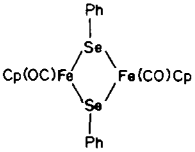
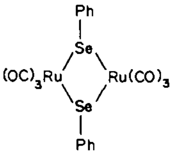
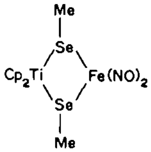
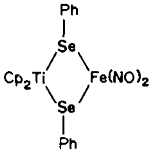
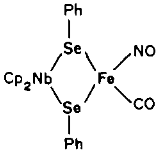
Complex	Reported data	Reference
	$\nu_{C\equiv O}(CS_2) = 2072, 2038, 2000$	348
	Yellow solid $\nu_{C\equiv O} = 1865, 1874$	327
	*Isomer A* gold needles m.p. 170–172 °C dec. $\nu_{C\equiv O}(C_6H_{12}) = 1975s$ MW = 601[d] (calc. 610)	329
	Isomer B dark brown crystals m.p. 170–172 °C $\nu_{C\equiv O}(C_6H_{12}) = 1947s, 1931s$ MW = 589[d]	329
	Yellow solid MW = 644[d] (calc. 682) $\nu_{C\equiv O}(CHCl_3) = 2081, 2052, 2006$	349
	Blue solid M.p. 217–218 °C $\nu_{N=O} = 1670s, 1715s$	350
	Blue solid M.p. 182–183 °C $\nu_{C\equiv O} = 1688s, 1706s$	350
	Brown solid M.p. 156–157 °C $\nu_{N=O} = 1610s$ $\nu_{C\equiv O} = 1845s$	350

TABLE 27. (*Continued*)

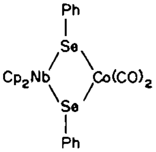
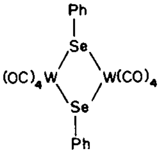
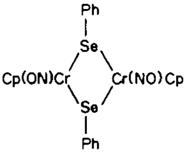
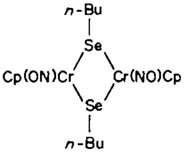
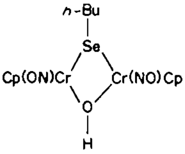
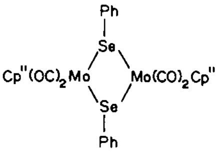
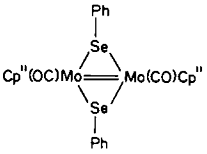
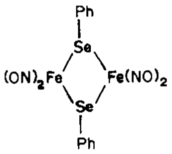
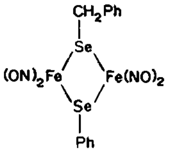
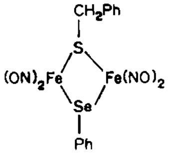
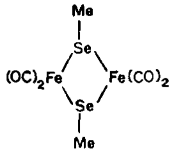
Complex	Reported data	Reference
	Brown solid M.p. 136–138 °C $\nu_{C\equiv O}$ = 1909s, 1850s	348
	Dark green crystals M.p. 130 °C dec. $\nu_{C\equiv O}$ = 2015s, 1965s	336
	Red–brown solid M.p. 202 °C $\nu_{N=O}$ = 1646 Crystal structure	351
	Brown crystals M.p. 134 °C $\nu_{N=O}$ = 1635vs	351
	Brown crystals M.p. 125 °C $\nu_{N=O}$ = 1645s, 1612vs ν_{O-H} = 3506m Crystal structure	351
	Dark brown solid	352
	Grey–brown solid M.p. 140 °C dec. $\nu_{C\equiv O}$ = 1878s, 1850m	352

TABLE 27. (*Continued*)

Complex	Reported data	Reference
	Brown crystals $\nu_{N=O}(CH_2Cl_2) = 1775, 1750$ MW = 546 (EIMS) ^{1}H-NMR	353
	Brown crystals $\nu_{N=O}(CH_2Cl_2) = 1775, 1750$ MW = 574 (EIMS) ^{1}H-NMR	353
	Brown crystals $\nu_{N=O}(CH_2Cl_2) = 1780, 1745$ MW = 482 (EIMS) ^{1}H-NMR	353
	Red air-stable crystals M.p. 134–135 °C $\nu_{C\equiv O}(CHCl_3) = 2066s, 2032vs, 1990vs$ $\delta(^1H, CDCl_3) = 2.10$	354
$[Hg(SeMe)_2]_n$	Yellow crystals Crystal structure	355 356
$[HgClpyr(\mu\text{-}SeEt)]_4$	Crystal structure	356
$Hg(SePh)_2$	Pale yellow solid	357
$Hg(SeC_6F_5)_2$	M.p. 171–173 °C	348
$[Ph_4P]_3[Hg_2(SePh)_7]$	Yellow–green air-stable crystals $\nu_{Hg-Se-Hg} = 132, 140$	341
$Os_3(CO)_{10}(\mu_2\text{-}SePh)_2$ (**45**)	Yellow crystals MW = 1168 (EIMS; ^{192}Os, ^{79}Se) $\nu_{C\equiv O}(C_6H_{12}) = 2104m, 2064s, 2055s, 2050w, 2019vs, 2000w, 1988m, 1980w$	358
$[Mn(CO)_3(\mu_3\text{-}SePh)]_4$ (**42**)	Brown solid $\nu_{C\equiv O}(C_5H_{12}) = 2022vs, 1951s$ MW = 1180 (EIMS)	359

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[a] Determined cryoscopically in benzene.

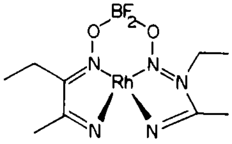
[b] Chemical shift values relative to internal CCl_3F.

[c] *The corresponding values for free* $(CF_3)_2PSeCF_3$ *are:* $(CF_3)_2P$—, $\delta = 53.7$ ($J_{PF} = 77.2$).

[d] Determined by osmometry in $CHCl_3$.

[e] Data in mm s^{-1}. Isomer shift relative to sodium nitroprusside.

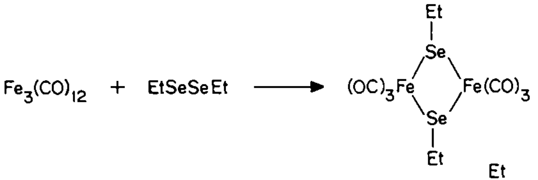
complexes with terminal M—SeR bonds have been reported (i.e. $(\eta^7\text{-}C_7H_7)W(CO)_2SePh$, *trans*-[(Rh)(SePh)$_2$], (Rh) = **41**; Table 26).



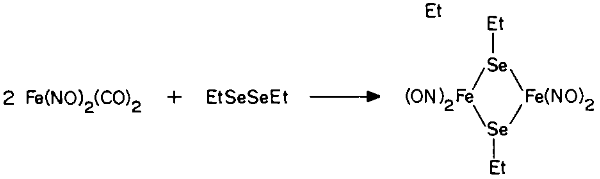
(**41**)

A number of homo- and hetero-nuclear dimeric complexes with bridging selenol ligands have been prepared and characterized by various spectroscopic techniques (Table 27).

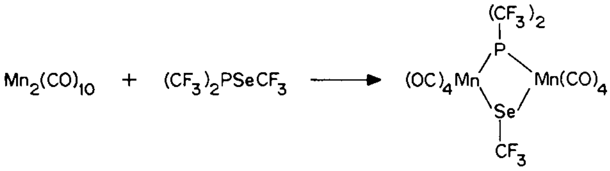
A variety of routes have been used to synthesize complexes incorporating these ligands. The most generally used routes involve diorganodiselenides, either directly with a metal substrate in an oxidative addition (equations 95–101) or elimination (equations 102–104) reaction or via an initial reductive cleavage of the Se—Se bond and subsequent metathetical reaction (equations 105 and 106).



(Ref. 323) (95)



(Ref. 339) (96)



(Ref. 340) (97)

$$Mn_2(CO)_{10} + Se_2(CF_3)_2 \xrightarrow[h\nu]{CH_2Cl_2/C_6H_{14}} (OC)_4Mn(\mu\text{-}SeCF_3)_2Mn(CO)_4$$

(Ref. 360) (98)

$$Fe(CO)_5 + Se_2(CF_3)_2 \xrightarrow{CH_2Cl_2/C_6H_{12}} (OC)_3Fe(\mu\text{-}SeCF_3)_2Fe(CO)_3$$

(Ref. 360) (99)

$$Ru_3(CO)_{12} + Ph_2Se_2 \xrightarrow[60^\circ C]{C_6H_6} (OC)_3Ru(\mu\text{-}SePh)_2Ru(CO)_3 \qquad \text{(Ref. 349)} \qquad (100)$$

$$Hg + Ar_2Se_2 \xrightarrow[\text{(b) PhMe/r.t.}]{\text{(a) 180 °C/sealed tube}} Hg(SeAr)_2 \qquad (101)$$

(a) $Ar = C_6F_5$[348]

(b) $Ar = Ph$[357]

$$2\,Mn(CO)_5H + R_2Se_2 \xrightarrow[\text{tube}]{\text{sealed}} (OC)_4Mn(\mu\text{-}SeR)_2Mn(CO)_4 + H_2 + 2\,CO \qquad \text{(Ref. 344)} \quad (102)$$

$$R = Me, Et, Pr, CF_3, C_2F_5, C_3F_7$$

$$\begin{tikzcd} Cp_2ZrMe_2 + PhSeSePh \arrow[r, "\text{heptane}"] & Cp_2Zr(SePh)Me + PhSeMe \arrow[d, "\text{PhSeSePh}"] & \text{(Ref. 338)} \quad (103) \\ & Cp_2Zr(SePh)_2 + PhSeMe & \end{tikzcd}$$

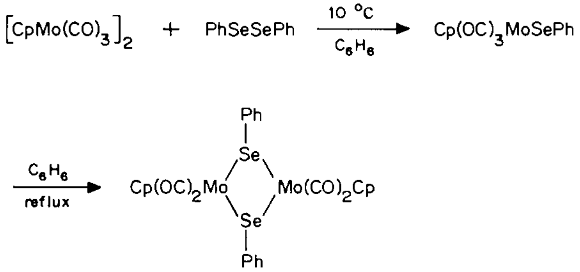
$$Cp_2ZrPh_2 + PhSeSePh \xrightarrow[\text{irradiation}]{\text{heptane/UV}} Cp_2Zr(SePh)_2 + PhPh \qquad \text{(Ref. 338)} \quad (104)$$

$$[CpNi(P(Bu\text{-}n)_3)_2]^+Cl^- \xrightarrow{\text{NaSePh}} CpNi(P(Bu\text{-}n)_3)SePh \qquad \text{(Ref. 330)} \quad (105)$$

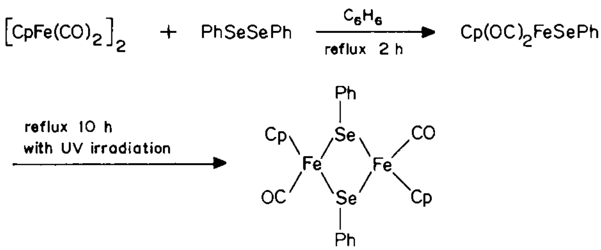
$$Cp_2MCl_2 + 2\,Li^+SeR^- \rightarrow Cp_2M(SeR)_2 + 2\,LiCl \qquad \text{(Ref. 331)} \quad (106)$$

$$M = Zr, Hf;\ R = Me, Ph$$

By careful control of reaction conditions, Baddley and coworkers[327,329] demonstrated that monomeric intermediates with terminally bonded selenolate ligands could be isolated (equations 107 and 108). Two isomers of the dimeric iron compound were isolated by column chromatography, differing in the relative orientations of the phenyl groups with respect to the carbonyl ligands (*cis* and *trans*).

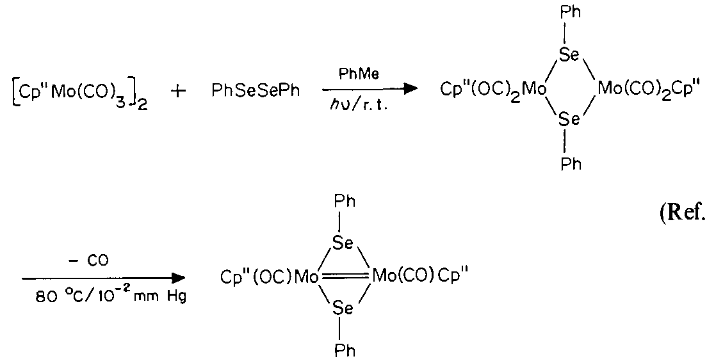


(Ref. 327) (107)



(Ref. 329) (108)

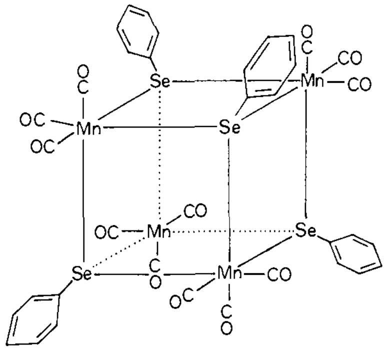
Photolysis of a toluene solution of methylcyclopentadienylmolybdenum tricarbonyl dimer and Ph_2Se_2 gave an isolable dimeric tetracarbonyl, which was further decarbonylated thermally in the solid state to give a formally double-bonded Mo=Mo complex (equation 109).



(Ref. 352) (109)

The crystal structure of the analogous complex, $[CpMo(CO)(\mu\text{-}SR)]_2$, showed that the Mo—Mo distance was shorter by ca. 1.3 Å vs. the dicarbonyl precursor, which had no Mo—Mo interaction (Mo—Mo bond distances = 2.616 Å vs. 3.940 Å)[361].

A cubane-type structure (**42**) was proposed for the product obtained by photolysis of a mixture of $Mn_2(CO)_{10}$ and Se_2Ph_2 in pentane[359].



(42)

Oxidative addition of PhSeSePh to the Rh(I) complex **41** gave the octahedral Rh(III) complex *trans*-(Rh)$(SePh)_2$[334] ((Rh) = **41**). The planar macrocyclic ligand in this system precludes the formation of a selenium-bridged dimer more characteristic of such reactions (e.g. equations 95–102 and 107–109).

Elimination reactions with $RSeSnR^1_3$ reagents (equations 110 and 111) have also been used to form M—SeR bonds.

$$2\,M(CO)_5Cl + 2\,RSeSnMe_3 \xrightarrow{-2\,ClSnMe_3} (OC)_4M(\mu\text{-}SeR)_2M(CO)_4 \quad \text{(Ref. 345)} \quad (110)$$

$$M = Mn,\ Re;\ R = Me,\ Et,\ Ph$$

$$2(Ph_3P)_2M(CO)_3Cl + RSeSnMe_3 \xrightarrow[-2\,PPh_3]{-2\,Me_3SnCl} Ph_3P(OC)_3M(\mu\text{-}SeR)_2M(CO)_3PPh_3$$

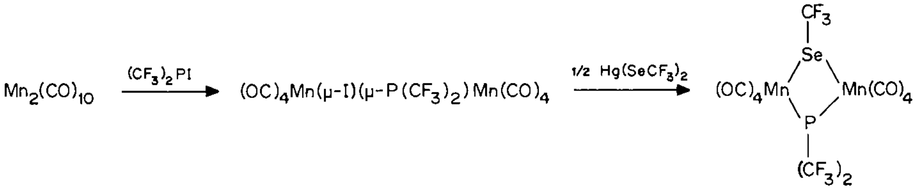
(Ref. 339) (111)

$$M = Mn,\ Re;\ R = Me,\ Ph$$

Metathetical reactions with $Al(SePh)_3$ (equation 112) and $Hg(SeCF_3)_2$ (equation 113) have also been used to form transition-metal selenolate complexes.

$$\mathrm{MCl}_n + \mathrm{Al(SePh)_3} \xrightarrow{\mathrm{Et_2O/C_6H_6}} \mathrm{M(SePh)}_n \qquad \text{(Ref. 328)} \qquad (112)$$

$$n = 3;\ \mathrm{M} = \mathrm{Cr}$$
$$n = 4;\ \mathrm{M} = \mathrm{Ti,\ Zr}$$



(Ref. 343) (113)

The derivatives prepared by the metathesis route in equation (112) were formulated as monomeric species on the basis of their solubility in organic solvents and molecular weight measurements in certain cases (Table 26). Similar reactions with niobium and tantalum pentachlorides reduced the metals to the + 3 states[328] (equation 114).

$$5\,\mathrm{Al(SePh)_3} + 3\,\mathrm{MCl_5} \rightarrow 3\,\mathrm{M(SePh)_5} + 5\,\mathrm{AlCl_3} \qquad (114)$$
$$\mathrm{M} = \mathrm{Nb,\ Ta}$$
$$(3\,\mathrm{M(SePh)_5} \rightarrow \mathrm{M(SePh)_3} + \mathrm{PhSeSePh})$$

These complexes were also formulated as monomeric, although all of the monomers slowly polymerized in solution[328].

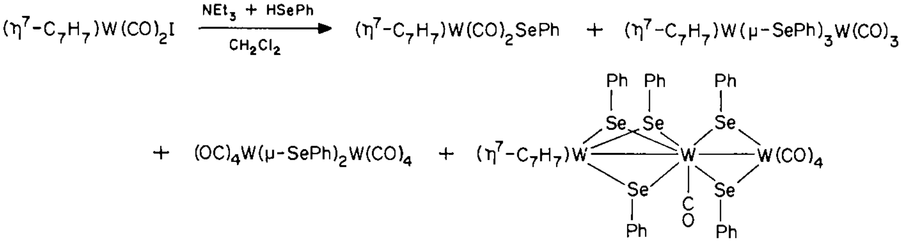
Reaction of metal acetylacetonates with selenophenol also provided a route to the corresponding selenolate complexes (equation 115). These products were formulated as polymeric on the basis of their insolubility in all common organic solvents, but a monomeric Ni(II) complex was formed by reaction with $\mathrm{P(Bu\text{-}}n)_3$ (equation 116).

$$\mathrm{M(acac)_2} + 2\,\mathrm{PhSeH} \xrightarrow[-2\,\mathrm{Hacac}]{\mathrm{C_6H_6}} \mathrm{M(SePh)_2} \qquad \text{(Ref. 328)} \qquad (115)$$
$$\mathrm{M} = \mathrm{Ni,\ Co}$$

$$\{\mathrm{Ni(SePh)_2}\}_n \xrightarrow[\mathrm{PhMe}/\Delta]{\mathrm{P(Bu\text{-}}n)_3} [\mathrm{Ni(SePh)_2(P(Bu\text{-}}n)_3)_2] \qquad \text{(Ref. 328)} \qquad (116)$$

Ziegler and coworkers prepared a number of complexes with terminal and bridging $\mathrm{SeR^-}$ ligands by metathetical reactions[336,351]. Included in this work is the single-crystal X-ray diffraction characterization of the monomeric complex $(\eta^7\text{-}\mathrm{C_7H_7})\mathrm{W(CO)_2SePh}$[337], the dimeric complexes $\mathrm{Cp(ON)Cr(\mu\text{-}SePh)_2Cr(NO)Cp}$ and $\mathrm{Cp(ON)Cr(\mu\text{-}SeBu\text{-}}n)(\mu\text{-}\mathrm{OH)Cr(NO)Cp}$[351] and the unique triply bridged dimer $(\eta^7\text{-}\mathrm{C_7H_7})\mathrm{Mo}(\mu_2\text{-}\mathrm{SePh})_3\mathrm{Mo(CO)_3}$[337].

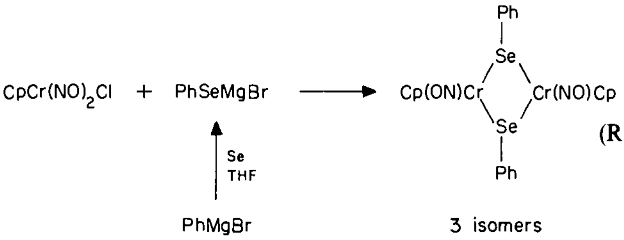
The metathetical reactions between a halo complex and a $\mathrm{SeR^-}$ reagent generally give a mixture of products, which can be isolated by column chromatography (equation 117).



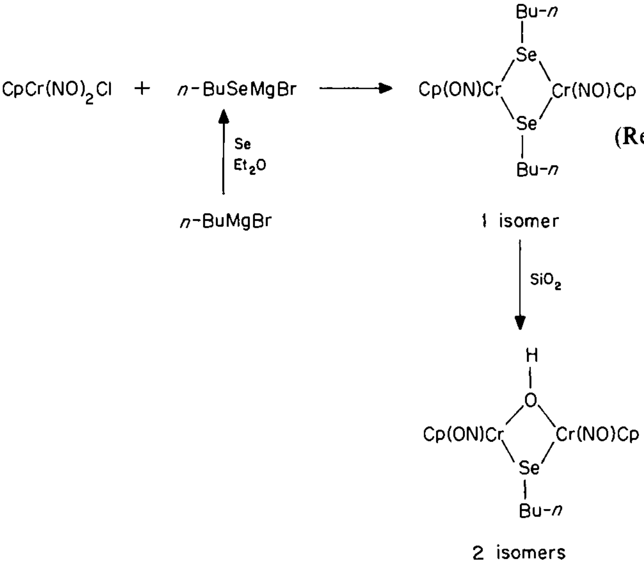
(Ref. 336) (117)

The structure of the sulphur analogue of the non-cyclic trinuclear cluster has been established by X-ray crystallography[362].

The reaction of CpCr(NO)$_2$Cl with RSeMgBr (R = *n*-Bu, Ph) gave dimeric SeR-bridged products (equations 118 and 119).



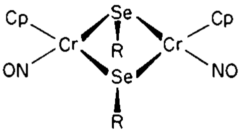
(Ref. 351) (118)



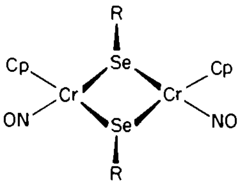
(Ref. 351) (119)

The hydroxy-bridged species, isolated along with the diselenium-bridged complex, apparently formed during the chromatographic purification of this product on a silica gel column.

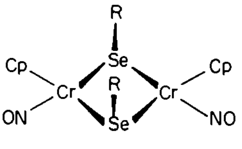
Five isomers are possible for dimeric Cp(ON)Cr(μ-SeR)$_2$Cr(NO)Cp complexes, although fewer have been isolated (equations 118 and 119):



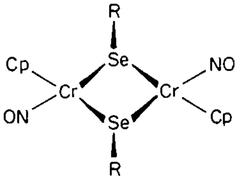
(*cis*-I)



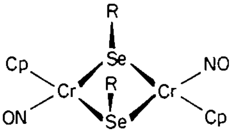
(*cis*-II)



(*cis*-III)



(*trans*-I)

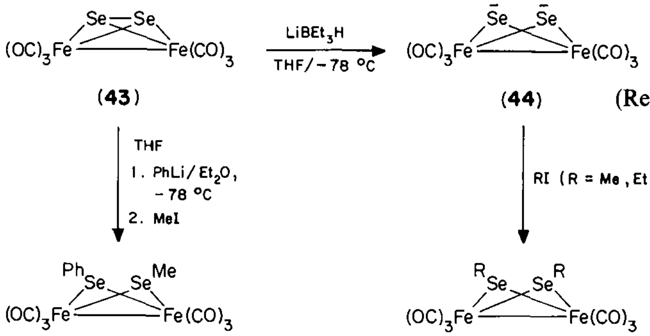


(*trans*-II)

Recently, novel routes involving alkylation of coordinated Se atoms have been described (equations 120–122).

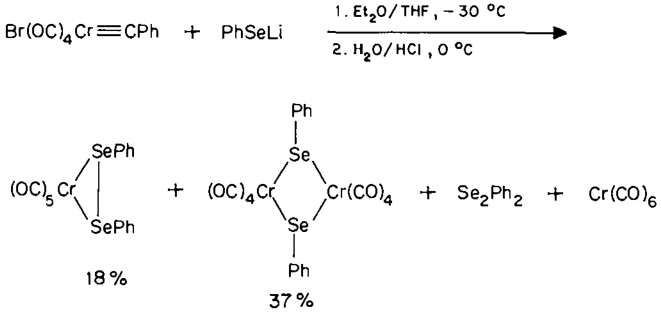
$$(OC)_4Mn(\mu\text{-}SeH)_2Mn(CO)_4 + CH_2N_2 \rightarrow (OC)_4Mn(\mu\text{-}SeMe)_2Mn(CO)_4$$ (Ref. 363) (120)

$$\begin{tikzcd} (ON)_2Fe(\mu\text{-}I)_2Fe(NO)_2 + Li_2Se \arrow[r] & (ON)_2Fe(\mu\text{-}Se)_2Fe(NO)_2{}^{2-} \arrow[d, "PhCH_2Cl"] \\ Se \arrow[u, "THF", "LiBEt_3H"'] & (ON)_2Fe(\mu\text{-}SeCH_2Ph)_2Fe(NO)_2 \end{tikzcd}$$ (Ref. 353) (121)



(**43**) (**44**) (Ref. 354) (122)

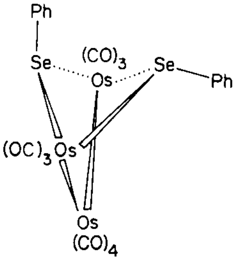
Röll and coworkers[250] reported a reaction involving the displacement of a carbyne ligand with formation of a dimeric complex incorporating SePh⁻ bridges (equations 123). In this reaction the use of aqueous HCl rather than an alkylating agent enhanced the yields of the first two products (i.e. vs. $(OC)_5Cr(SePhEt)$, equation 59).



(123)

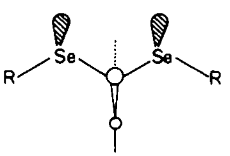
The only reported transition-metal cluster compound incorporating a bridging selenol ligand was prepared by an oxidative addition reaction[358] (equation 124). The structure **45**

$$Os_3(CO)_{11}(NCMe) \xrightarrow[CH_2Cl_2/r.t.]{Se_2Ph_2} Os_3(CO)_{10}(\mu_2\text{-}SePh)_2 \qquad (124)$$

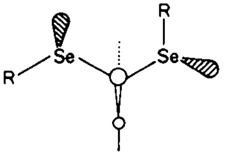


(45)

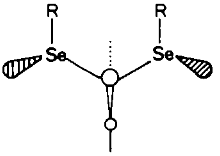
was proposed on the basis of mass spectroscopy and infrared spectroscopy. The latter was similar to that of $Os_3(CO)_{10}(\mu_2\text{-}X)_2$ (X = Cl, Br, I) which have this general structure. Three isomers, differing in the stereochemistry about the SePh bridges, are possible for this structural type, and, based on the inequivalence of the phenyl groups in its NMR spectrum, it was assigned form **B**:



(A)



(B)



(C)

No isomerization was observed by NMR over the range 30–100 °C, although refluxing a solution of the cluster in *n*-octane gave a low yield of isomer **C** (ca. 3%) as well as a decarbonylation product, $Os_3(CO)_9(\mu_2\text{-}Se)_2$ (ca. 13%; this cluster is discussed in Section II.G.5).

3. *SeH⁻*

Only a few complexes containing the SeH^- ligand, both terminal and bridging, have been reported[108,144,363–368]. Metal–SeH bonds have been formed by several different routes as described below.

a. Oxidative addition of H_2Se to a metal substrate. The oxidative addition of H_2Se to Pt(0) (equation 125), Pt(II) (equation 126) and Ir(I) (equation 127) complexes has been described.

$$[Pt(PPh_3)_2] \xrightarrow[C_6H_6/r.t.]{H_2Se} [Pt(PPh_3)_2(SeH)(H)] \qquad \text{(Refs. 364, 365)} \qquad (125)$$

white air-stable solid
m.p. 135 °C

MW(CHCl₃) = 740 (calc. 798)

$\nu_{Pt-H} = 2140\,cm^{-1}$

$$trans\text{-}PtH(SeH)(PEt_3)_2 \xrightarrow[\substack{CH_2Cl_2 \\ -85\,^{\circ}C}]{H_2Se} Pt(H)_2(SeH)_2(PEt_3)_2 \qquad \text{(Ref. 366)} \qquad (126)$$

$\delta(PtH) = -13.1$ ppm

$^1J_{PtH} = 1004$

$^2J_{PtH} = -22$

$^2J_{PH} = -8$

$^3J_{HH} = 3.5$

$\delta(SeH) = -5.0$ ppm

$$trans\text{-}IrCl(CO)(PPh_3)_2 \xrightarrow[C_6H_6/r.t.]{H_2Se} [IrCl(CO)(PPh_3)_2(SeH)(H)]$$

(Ref. 367) (127)

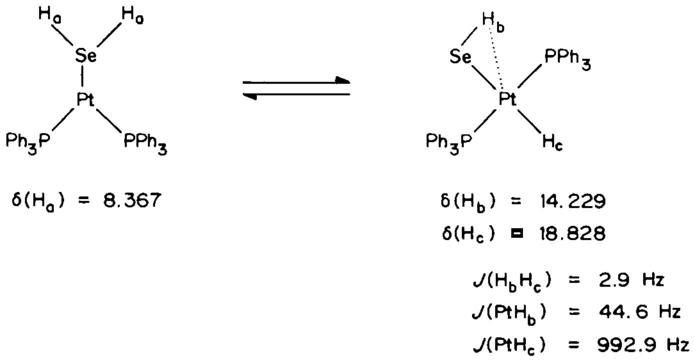
air-sensitive solid

m.p. dec. > 160 °C

$\nu_{C\equiv O} = 1950$vs 2018vs

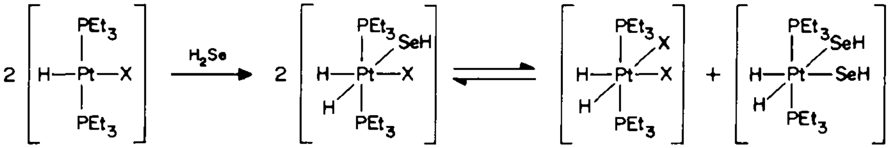
$\nu_{Ir-Cl} = 325$vs 262s

The ^{1}H-NMR of [Pt(PPh$_3$)$_2$(SeH)(H)] (equation 125) in CDCl$_3$ at room temperature has been interpreted in terms of the following equilibrium[365]:



On the basis of detailed analysis of the ^{1}H-NMR spectra and D$_2$O exchange experiments, the broadening of the resonances as the temperature was decreased was attributed to rapid dissociation of the phosphine ligands rather than exchange of H$_b$ and H$_c$. With the H$_2$S analogue, the H$_b$ and H$_c$ resonances split into triplets at -80 °C (J (PH$_b$) = 10 Hz; J(PH$_c$) = 11 Hz). The latter coupling constants also indicate that the two phosphine ligands are mutually *trans*[141].

The reaction described in equation (126) was carried out in an NMR tube at low temperature. On warming the tube to room temperature, H$_2$ was evolved with the formation of *trans*-Pt(SeH)$_2$(PEt$_3$)$_2$. Multinuclear NMR studies (^{1}H, ^{31}P, ^{77}Se, ^{195}Pt) of the Pt(IV) complex indicated a *cis, cis, trans* stereochemistry. Similar reactions between H$_2$Se and *trans*-Pt(H)X(PEt$_3$)$_2$ (X = Cl, Br, I) gave the expected Pt(IV) complexes as well as the two redistribution products, on the basis of detailed multinuclear NMR studies (equation 128).



(Ref. 366) (128)

b. Metathetical reactions between a metal halide complex and SeH⁻:

$$trans\text{-}PtCl(H)(PEt_3)_2 \xrightarrow[\text{EtOH}]{\text{SeH}^-} trans\text{-}Pt(H)(SeH)(PEt_3)_2 \qquad \text{(Ref. 366)} \qquad (129)$$

pale yellow crystals

$\nu_{Pt-H} = 2110$; $\nu_{Se-H} = 2288w$; $\nu_{Pt-Se} = 194$

$\delta(^1H)$:

Pt—H, -10.7 ($^1J_{PtH} = 1108$; $^3J_{HH} = 3$
$^2J_{PH} = -14$)

Se—H, -4.5 ($^2J_{PtH} = -44$; $^3J_{HH} = 3$;
$^3J_{PH} = 13$)

$$trans\text{-}PtCl_2(PEt_3)_2 \xrightarrow[\text{EtOH}]{2\text{SeH}^-} trans\text{-}Pt(SeH)_2(PEt_3)_2 \qquad \text{(Ref. 366)} \qquad (130)$$

yellow crystals

$\delta(^1H)$:

SeH, -4.0 ($^2J_{PtH} = -56$;
$^3J_{PH} = 11$)

$$PPN[Cr(CO)_5Cl] \xrightarrow[\text{EtOH}]{\text{Na}_2\text{Se}} PPN[Cr(CO)_5SeH] \qquad \text{(Ref. 105)} \qquad (131)$$

slightly air-sensitive yellow solid

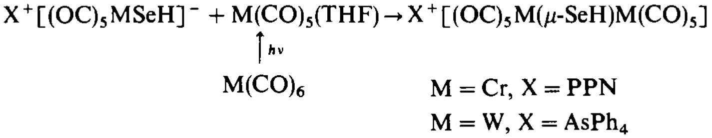
m.p. 94 °C dec.

$\nu_{C\equiv O}$(THF) = 2035vw, 1904vs, 1850m

$\delta(^1H)$, d_6-DMSO: SeH, -7.47s;
PPN, 7.79m

The complexes $PtH(SeH)(PEt_3)_2$[366] and $Pt(SeH)_2(PEt_3)_2$[366] are very air-sensitive, in contrast to the air-stable $PtH(SeH)(PPh_3)_2$[365]. A *trans* stereochemistry of $PtH(SeH)(PEt_3)_2$ was established by multinuclear NMR spectroscopy. The ^1H spectrum gave a complex pattern characteristic of mutually *trans* PEt_3 groups in square-planar Pt(II) complexes and two triplets each showing coupling to ^{195}Pt (equation 129). In addition, the ^{31}P, $\delta = 19.3$ (vs. external 85% H_3PO_4), ^{195}Pt, $\delta = -205$ (vs. external 0.5M *trans*-$PtCl(H)(PEt_3)_2$ in CH_2Cl_2), $^1J_{PtP} = 2654$, and the ^{77}Se spectra, $\delta = -312$ (vs. 10% $SeMe_2$ in CH_2Cl_2), $^1J_{PtSe} = 322$, $^1J_{SeH}$ not observed, $^2J_{PSe} = 9$, $^2J_{SeH} = 50$, were recorded[366]. Similar data were recorded for *trans*-$Pt(SeH)_2(PEt_3)_2$, but a Se—H coupling constant was measured ($\delta(^{77}Se) = -232$, $^1J_{SeH} = 116$, $^1J_{PtSe} = 166$, $^2J_{PSe} = 12$).

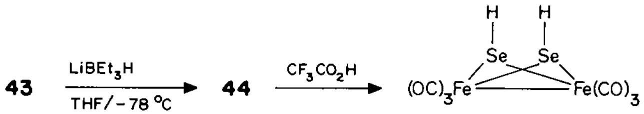
The derivatives $M(CO)_5SeH^-$ (M = Cr, Mo, W) (equation 131) were also obtained by reactions of the $M(CO)_5THF$ derivatives, prepared by photolysis of the hexacarbonyls in THF, with ethanol solutions of Na^+SeH^- followed by precipitation of the anionic complex with PPN^+ or Ph_4As^+. In these reactions addition of ethanol to M_2Se (M = Li, Na, K) results in solvolysis to M^+SeH^-. This latter species can also be formed directly by borohydride reduction of elemental Se in ethanol[369]. These anionic complexes were also formed directly, thermally or photochemically, from solutions of $M(CO)_6/NaHSe$ in THF/EtOH[108]. Two reactions of these monomeric complexes were investigated: (*i*) alkylation of the selenol ligand to the neutral diorganoselenide ligand (equation 15) and (*ii*) reaction with the labile $M(CO)_5THF$ species to give selenol-bridged dimers (equation 132).



$$X^+[(OC)_5MSeH]^- \underset{\substack{\uparrow h\nu \\ M(CO)_6}}{} + M(CO)_5(THF) \rightarrow X^+[(OC)_5M(\mu\text{-}SeH)M(CO)_5] \qquad M = Cr, X = PPN \quad M = W, X = AsPh_4$$

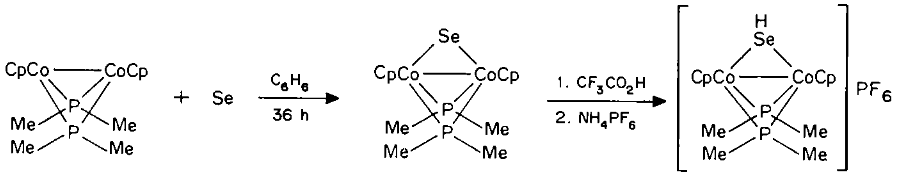
(Ref. 108) (132)

c. Protonation of coordinated selenium. The reactivity of coordinated chalcogen atoms and rings has been an area of considerable recent interest in organometallic chemistry (see Section II.G), and two examples from this work illustrate the transformation of coordinated Se to the SeH^- ligand. Seyferth and Henderson[354] in their study of the chemistry of $Fe_2(CO)_6(\mu_2,\eta^2\text{-}Se_2)$ (**43**) formed the $Fe_2(CO)_6(\mu_2\text{-}SeH)_2$ dimer in a two-step sequence (equation 133). This product was not isolated but reacted *in situ* with MeI and Et_3N to give $(OC)_3Fe(\mu_2\text{-}SeMe)_2Fe(CO)_3$, a compound which can also be formed by the more direct reaction of **44** with MeI[354].



(Ref. 354) (133)

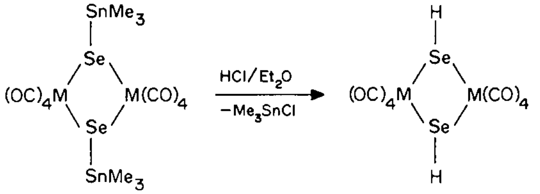
A reaction sequence involving insertion of Se into a metal–metal bond followed by protonation has been used to form a selenol-bridged dimer (equation 134).



red-brown air-stable salt

(Ref. 368) (134)

d. Elimination reactions. Finally, an elimination reaction involving the bridging —$SeSnMe_3$ ligand has provided a route to the corresponding air-sensitive selenol-bridged dimer (equation 135).



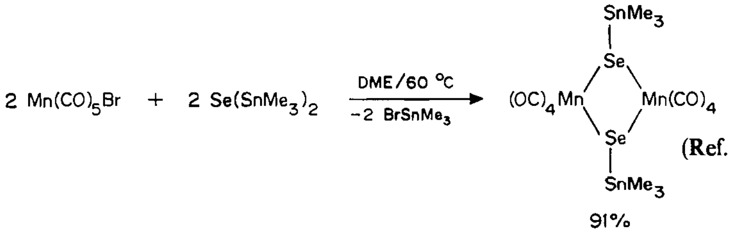
(Ref. 363) (135)

M = Mn	M = Re
ν_{Se-H} = 2285s, 2263m, 2223s	2280s, 2235s
^{1}H-NMR $\delta(CH_2Cl_2)$: −6.20 (SeH)	−4.13

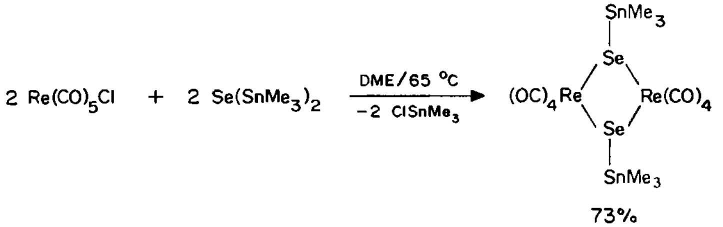
These dimers can be *Se*-alkylated to give the corresponding alkylselenol-bridged dimers (equation 120).

4. $SeER_3^-$ ($E = Ge$, $R = Ph$; $E = Sn$, $R = Me$)

Only a few examples of complexes incorporating ligands of this class, both terminally bonded and bridging, have been reported[144,335,363,370]. Dimeric —$SeSnMe_3$-bridged complexes were prepared by elimination reactions with metal carbonyl halides (equations 136 and 137). These air-sensitive brownish-red crystalline solids were characterized by infrared and ^1H-NMR spectroscopy. Reactions for the conversion of the bridging group to —SeH (equation 135) and —$SeEMe_2$ ($E = P$, As) (equation 21) have been described above. Heating the dimers in refluxing hexane gave high yields of the tetrameric $[Me_3SnSeM(CO)_3]_4$ compounds, which were formulated as cubane-type clusters[363] (e.g. see structure **42**).



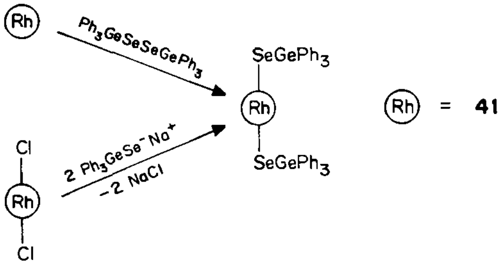
(Ref. 363) (136)



(137)

The reaction of $[(OC)_4ReSeSnMe_3]_2$ with PMe_3 in benzene at room temperature gave $(Me_3P)_2(OC)_3Re\text{-}Se\text{-}Re(CO)_3(PMe_3)_2$, which was characterized by single-crystal X-ray diffraction[370] (Figure 4).

The only reported example of a ligand of this class terminally bonded to a metal was prepared by oxidative addition of a Rh(I) substrate with $Ph_3GeSeSeGePh_3$ or by an equivalent metathetical reaction (equation 138).



(Ref. 335) (138)

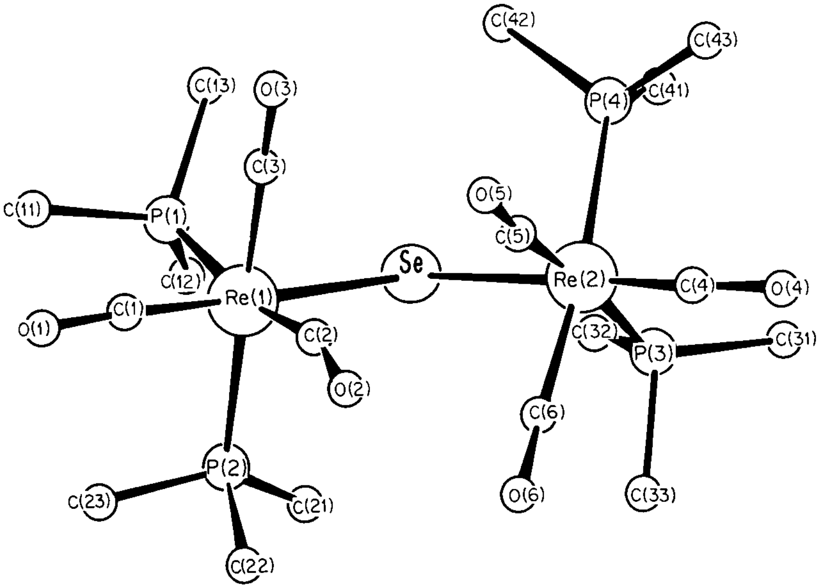


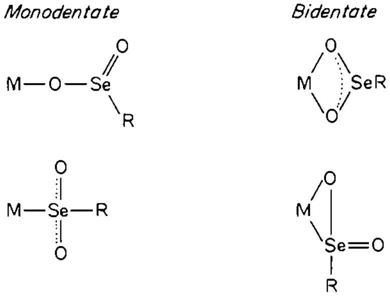
FIGURE 4. Molecular structure of $(Me_3P)_2(OC)_3Re—Se—Re(CO)_3(PMe_3)_2$. Reproduced with permission from Ref. 370

The bis(triphenylgermanium) diselenide was prepared as shown in equation (139)[335].

$$\begin{tikzcd} 2\,Na_2Se + 2\,Ph_3GeBr \arrow[r, "EtOH", "C_6H_6"'] & 2\,NaSeGePh_3 \arrow[d, "MeSO_2Cl", "C_6H_6"'] \\ & (Ph_3Ge)_2Se_2 \end{tikzcd} \qquad (139)$$

5. Organoseleninates ($RSeO_2^-$)

A variety of organoseleninate metal complexes have been prepared by metathetical reactions between a metal chloride salt or complex and a sodium organoseleninate[371–388]. In two cases methylseleninate complexes have been formed by insertion of SeO_2 into a metal–Me bond ($CpFe(CO)_2Me$[389] and η^7-$C_7H_7Mo(CO)_2Me$[390]). No



linkage isomeric pairs have been isolated with ligands of this class, as in the case of sulphinato ligands[153e]; nevertheless, they have an interesting ambidentate ligand chemistry. Although no definitive single-crystal X-ray diffraction studies have been reported, the bonding modes illustrated above have been proposed on the basis of infrared spectroscopy (Table 28).

Many transition-metal complexes with phenylseleninato and substituted phenyl analogues have been prepared by Preti and coworkers[371–387].

Since the ring substituents, while causing relatively minor changes in spectroscopic properties, have not changed the bonding mode in any case, the spectroscopic data in Table 28 are, for the most part, restricted to the parent ligand. Infrared spectral changes,

TABLE 28. Infrared spectral data (cm^{-1}) for seleninate complexes[a]

Compound	$\nu_{Se-O,sym}$	$\nu_{Se-O,asym}$	ν_{Se-C}	Ref.
$Na^+SeO_2Ph^-$	768	781	666	371
Monodentate O bonding				
		$(\nu_{Se-O-M,asym})$		
$Cd(OSe(O)Ph)_2$[b]	815	725	675	374
$Co(bipy)_2(OSe(O)Ph)_2\cdot 3H_2O$[c]	810	698	659	378
$[Ni(phen)_2(OSe(O)Ph)_2]$[d]	850	700	650	378
$Zn(phen)_2(OSe(O)Ph)_2$	866	752	668	386
Monodentate Se bonding				
$[Pt(SeO_2Ph)_2(H_2O)_2]$	730	830	680	371
$Hg(SeO_2—C_6H_4Cl\text{-}m)_2$	830[e]	860[f]	655	374
$Cp(OC)_2FeSeO_2Me$	728	859	570	389
$(\eta^7\text{-}C_7H_7)Mo(CO)_2SeO_2Me$	970	887	565	390
Bidentate (O, O) bonding				
$[Cu(O_2SePh)_2]$	725	745	670	372
$[Co(O_2SePh)_2(OH_2)_2]$	690	740	670	371, 377
$[Ni(O_2SePh)_2(OH_2)_2]$	680	750	670	371, 377
$[Rh(O_2SePh)_3]\cdot 2H_2O$	710, 690	740	670	373
$[Ir(O_2SePh)_3]\cdot 2H_2O$	700, 690	740	670	373
$[Zn(O_2SePh)_2(H_2O)_2]$	690	778	670	374
$[Cd(O_2Se(C_6H_4Cl\text{-}m))_2(OH_2)_2]$	730	790	655	374
$[Hg(O_2Se(C_6H_4Cl\text{-}m))_2(OH_2)_2]$	760	790	655	374
$Cr(O_2Se(C_6H_4Br\text{-}p))_3$[g]	726	795, 776	708	381
$Mn(O_2SePh)_2$[h]	735	751	667	381
$Fe(O_2Se(C_6H_4Br\text{-}p))_3$[i]	—	785, 728	708	381
$V(O_2SePh)_2$[j]	714	778	680	388
$Cr(O_2SePh)_3$[k]	726	802	674	388
$Fe(O_2SePh)_3$[l]	723	807	673	388
$Ti(O_2SePh)_4$[m]	738, 724	803, 795	675	388
$Ru(O_2SePh)_3$	729, 700	765	680	383
Bidentate (Se, O) bonding				
$[IrH_2(PPh_3)_2(OSe(O)Ph)]$	865	720	640	375

[a] Measured as KBr discs.
[b] $\nu_{Cd-O} = 450\,cm^{-1}$.
[c] $\nu_{Co-O} = 443\,cm^{-1}$.
[d] $\nu_{Ni-O} = 432\,cm^{-1}$.
[e] The corresponding value for the ionic sodium salt is $795\,cm^{-1}$ [376].
[f] The corresponding value for the ionic sodium salt is $817\,cm^{-1}$.
[g] $\nu_{Cr-O} = 530\,cm^{-1}$.
[h] $\nu_{Mn-O} = 420\,cm^{-1}$.
[i] $\nu_{Fe-O} = 420\,cm^{-1}$.
[j] $\nu_{V-O} = 540\,cm^{-1}$.
[k] $\nu_{Cr-O} = 545\,cm^{-1}$.
[l] $\nu_{Fe-O} = 508\,cm^{-1}$.
[m] $\nu_{Ti-O} = 434\,cm^{-1}$.

TABLE 29. Infrared spectral characterization of organoseleninato ligand bonding modes

Bonding mode	$\nu_{\mathrm{Se-O,sym}}$[a]	$\nu_{\mathrm{Se-O,asym}}$[a]	Δ[b]	$\nu_{\mathrm{Se-C}}$
M—Se	Decrease	Increase	80–90	Little change
M—O	Increase	Decrease	80–90	Little change
M—(O, O)	Decrease	Decrease	30–88	Little change
M—(Se, O)	Increase	Decrease	ca. 150	Little change

[a] Shifts vs. the ionic Na salts of the ligands.

[b] $\nu_{\mathrm{Se-O,asym}} - \nu_{\mathrm{Se-O,sym}}$ of the complexes.

compared to the Na salt of the ligand, have been established as criteria of the bonding mode of the ambidentate organoseleninato ligand (Table 29).

In some cases the proposed bonding mode was further supported by the measurement of a metal–O or metal–Se vibration (Table 28). The insolubility of some of the simple complexes (e.g. Cu[372], Co[371], Ni[371]) suggests polymeric structures involving O,O coordination via bridging ligands rather than intramolecular chelation. For $M(O_2SeAr)_3$ (M = Rh[373], Ir[373], Ru[383], Cr[381], Fe[381]), however, the solubility in alcohols suggested monomeric formulations.

The removal of water from the coordination sphere of the Cd(II) and Hg(II) complexes, $[M(O_2SePh)_2(H_2O)_2]$, changes the bonding mode of the seleninato ligand (to monodentate O bonding in the Cd(II) complex and to monodentate Se in the Hg(II) complex)[374]. With the Zn(II) analogue, however, the O,O bonding mode is retained in the anhydrous compound[374].

The first example of SeO_2 insertion into a metal–alkyl bond involved the facile reaction of freshly sublimed SeO_2 with a benzene solution of a Fe(I) complex[389] (equation 140).

$$\mathrm{CpFe(CO)_2Me + SeO_2 \rightarrow CpFe(CO)_2SeO_2Me + Fe(O_2SeMe)_3 + [CpFe(CO)_2]_2} \tag{140}$$

brown, moderately air-stable solid

MW (CH_2Cl_2): 300

EIMS: $[M]^{+\cdot} = 302, 304$

^{1}H-NMR $\delta(CD_3OD)$: 3.02 (s, Me), 5.05 (s, Cp)

The Me chemical shift, the downfield shift of the Cp resonance vs. the starting Me compound, and the $\nu_{C\equiv O}$ values (2056, 2009; ca. 50 cm^{-1} higher energy than the precursor Me compound) all support the presence of a —SeO_2Me ligand in this product. The infrared spectrum in the 700–900 cm^{-1} region (Table 28) and the independent synthesis of the same complex by a metathetical reaction between $CpFe(CO)_2Cl$ and $NaSeO_2Me$ further confirm the proposed insertion reaction.

A similar SeO_2 insertion reaction, with activated SeO_2 generated in a metal atom reactor, has been reported with a molybdenum alkyl[390] (equation 141).

$$(\eta^7\text{-}\mathrm{C_7H_7})\mathrm{Mo(CO)_2Me + SeO_2} \xrightarrow[\text{8 days}]{\text{THF}, -78\,^\circ\text{C}} (\eta^7\text{-}\mathrm{C_7H_7})\mathrm{Mo(CO)_2SeO_2Me} \tag{141}$$

30%

red–brown

$\nu_{C\equiv O}(CH_2Cl_2) = 2000\text{vs}, 1940\text{vs cm}^{-1}$

$\nu_{Se-C}(\text{mull}) = 565\text{vs cm}^{-1}$

$\nu_{Se-O}(\text{mull}) = 1070\text{s}, 887\text{s}, 790\text{s cm}^{-1}$

^{1}H-NMR $\delta(CDCl_3)$: 5.28 (s, C_7H_7),
2.32 (s, Me)

The Me proton signal in the SeO_2 insertion product is significantly shifted downfield (-0.25 ppm) compared to the precursor Me complex. The product, which was purified by medium-pressure gradient chromatography on SiO_2 at $-20\,°C$, was stable in an inert atmosphere for a few days at $-78\,°C$ but decomposed in a few minutes at room temperature. An analogous reaction with $(\eta^7\text{-}C_7H_7)Mo(CO)_2Ph$ failed to give SeO_2 insertion[390].

6. *Dialkylselenocarbamates* $(\text{—}SeC(O)NR_2^-)$

Although the dialkylselenocarbamate hybrid ligand system can bond in a (Se, O) bidentate coordination mode (Section II.D.2a), several examples of monodentate Se coordination have been described[391-400]. Ni(II)[391], Pd(II)[392,393] and Pt(II)[392,393] complexes were prepared by metathetical reactions with selenocarbamate salt generated *in situ* (equation 142).

$$\begin{array}{lll} L_2MCl_2 + 2\,R_2NH_2[SeC(O)NR_2] \xrightarrow{C_6H_6} L_2M(SeC(O)NR_2)_2 & & (142) \\ M = Pd, Pt \qquad \uparrow \text{CO/THF}^{401} & R = Me, Et, n\text{-Pr}, n\text{-Bu};\ L = PPh_3 & \\ \qquad\qquad\quad Se + R_2NH & R = Me;\ L = PPh_2Me & \end{array}$$

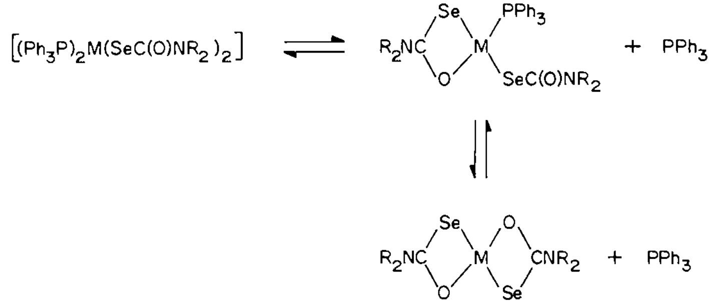
As would be expected on the basis of the stoichiometry of the Pd(II) and Pt(II) complexes and the well-established Class B Lewis acid character of these metals[309], the complexes are square-planar with monodentate Se-bonded selenocarbamate. The infrared spectra of these complexes in the solid state show $\nu_{C=O}$ absorptions at ca. 1600 cm^{-1}, characteristic of this bonding mode with a free carbonyl group (Table 30).

TABLE 30. Infrared data (cm^{-1}) for complexes with monodentate Se-bonded dialkylselenocarbamate ligands

Complex	$\nu_{C=O}$	Reference
$(Ph_3P)_2Ni(SeC(O)NEt_2)_2$	1581s (1598m, 1521s)[a]	391
$(Ph_3P)_2Pd(SeC(O)NBu_2)_2$	1600s (1592s, 1532m)[a]	392, 393
$(Ph_3P)_2Pt(SeC(O)NBu_2)_2$	1603s (1595s, 1540sh)[a]	392, 393
$(Ph_2MeP)_2Pd(SeC(O)NMe_2)_2$	1599s (1592s, 1540vw)[a]	393
$(Ph_2MeP)_2Pt(SeC(O)NMe_2)_2$	1603s (1603s)[a]	393
$Me_3SnSeC(O)NMe_2$	1620	394
$(Ph_3P)AuSeC(O)NC_5H_{10}$[b]	1605, 1595[c]	395
$(Ph_3P)AuSeC(O)NMe_2$	1605, 1595[c]	395
$(Ph_3P)_2Rh(CO)SeC(O)NC_5H_{10}$[b]	1585	395
$Mn(CO)_5SeC(O)NMe_2$	1623	396
$[Mn(CO)_4SeC(O)NMe_2]_2$ (**48a**)	1660	397
$Re(CO)_5SeC(O)NMe_2$	1621	398
$[Re(CO)_4SeC(O)NMe_2]_2$ (**48b**)	1665	398
$CpFe(CO)_2SeC(O)NMe_2$	1600	399
$CpMo(CO)_3SeC(O)NMe_2$	1618	400

[a] CH_2Cl_2 *solution*.
[b] NC_5H_{10} = piperidyl.
[c] Coupled (C$\cdots$O) and (C$\cdots$N) stretching modes.

In CH_2Cl_2 solution, molecular weight, infrared and NMR studies[392,393] have shown that the PPh_3 complexes undergo dissociation of the phosphine ligand and chelation of the selenocarbamate (equation 143). This dissociation reaction occurs to a greater extent for Pd(II) than Pt(II), as expected on the basis of the greater kinetic stability of the latter complexes, whereas the complexes with the more basic phosphine, PPh_2Me, show essentially no dissociation in solution, as evidenced by molecular weight measurements and the presence of only one $\nu_{C=O}$ band due to uncoordinated carbonyl in both the solid state and solution (Table 30).



(143)

The exchange process was confirmed by ^{31}P-NMR for $(Ph_3P)_2Pd(SeC(O)NBu_2)_2$, which gave a broad resonance, whereas the other three complexes that were soluble enough for such measurements all gave sharp singlets that did not change with added phosphine $[(Ph_3P)_2Pt(SeC(O)NBu_2)_2$; $(Ph_2MeP)_2M(SeC(O)NMe_2)_2$, M = Pd, Pt]. The ^{31}P–^{195}Pt coupling constants for the Pt compounds indicated a *trans* geometry (2860 and 2713 Hz).

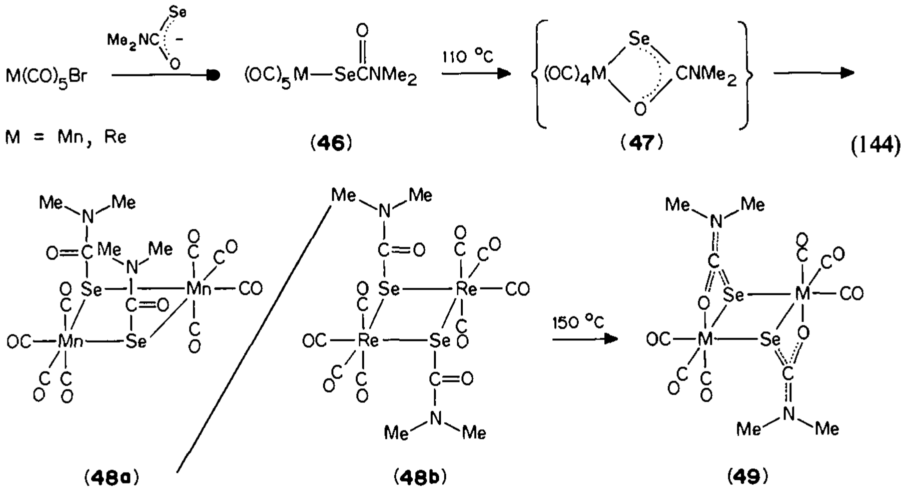
^1H-NMR spectroscopy established free rotation about the C—N bond at room temperature for $(Ph_2MeP)_2M(SeC(O)NMe_2)_2$, but at lower temperature the single broad N—Me resonances were split into two signals (Pd: $\delta = 2.56$ (r.t.), 2.57, 2.46 (– 15 °C); Pt: $\delta = 2.57$ (r.t.), 2.56, 2.49 (– 15 °C)[393]).

The diamagnetism of the Ni(II) complex, $Ni(PPh_3)_2(SeC(O)NEt_2)_2$, and its infrared spectrum (Table 30) indicated that the complex was square planar with two Se-bonded selenocarbamate ligands[391]. The solution infrared spectrum and low molecular weight in CH_2Cl_2 (439 vs. calculated value of 941) indicated significant dissociation as in the Pd(II) and Pt(II) complexes (equation 143). Treatment of a THF solution of this complex with CO resulted in facile displacement of the selenocarbamate ligand and formation of $Ni(PPh_3)_2(CO)_2$ in ca. 70% yield[391].

Monodentate Se bonding of the selenocarbamate in $Me_3SnSeC(O)NMe_2$[394], prepared by a metathetical reaction from Me_3SnCl, was indicated by its infrared spectrum (Table 30). Related compounds, $Me_2Sn(OSeCNR_2)_2$ and $Me_2ClSn(OSeCNMe_2)$, contain (Se, O) bidentate selenocarbamate (Section II.D.2.a). A tetrahedral structure with monodentate dialkyldithiocarbamate has been established by single-crystal X-ray diffraction of $Me_3SnSC(S)NMe_2$[402].

In contrast to the Pd(II)[393], Pt(II)[393], Au(I)[395] and Rh(I)[395] complexes, restricted rotation about the C—N bond occurs in this Sn complex at room temperature ($\delta(CCl_4)$, NMe_2: 3.28, 3.09)[394].

Manganese[396,397] and rhenium[398] pentacarbonyl complexes containing monodentate Se-bonded selenocarbamate (**46**) undergo successive solid-state thermal decarbonylation reactions to give dimeric complexes with more highly coordinated forms of this ligand (equation 144).



(144)

Although the initial report[396] on the thermolysis of the manganese pentacarbonyl complex indicated that the tetracarbonyl complex formed as the initial thermolysis product was monomeric **47** with chelating selenocarbamate ligand, a subsequent report[397] showed that this complex was actually a dimeric species with Se-bridging selenocarbamate (**48**). Thermolysis in cyclohexane did, however, allow the unstable monomeric species **47** to be identified by infrared spectroscopy ($\nu_{C=O} = 1550\,cm^{-1}$).

Isolation of pure tetracarbonyl dimers required that the thermolysis be carried out under flowing CO[397]. Thermolysis under N_2 always gave contamination with the tricarbonyl dimer **49**. The identification of the tetracarbonyls as dimers with bridging Se-bonded selenocarbamates rather than monomers with chelating selenocarbamates was based on infrared and mass spectroscopy[396–398]. A detailed analysis of the infrared spectra of the dimers in the carbonyl region ($M—C\equiv O$, 1900–2100 cm^{-1}) and comparison of the number of observed bands with those expected for the various symmetry types allowed assignments of the detailed stereochemistries (equation 144). The conversion of the manganese tetracarbonyl **48a** to tricarbonyl dimer **49** involves inversion of configuration with respect to the orientation of the selenocarbamate ligand[397], but for the Re dimers this net decarbonylation process is accompanied by retention of configuration[398] (**48b** → **49**).

The Fe(II) and Mo(II) complexes (Table 30) were prepared by substitution reactions (equations 145 and 146).

$$\begin{tikzcd}
\text{[CpFe(CO)}_2\text{(Me}_2\text{CO)]BF}_4 \arrow[r, "SeC(O)NMe_2^-"] & CpFe(CO)_2SeC(O)NMe_2 \quad \text{(Ref. 399)} \\
CpFe(CO)_2Cl \arrow[u, "AgBF_4 \; Me_2CO"', "(-AgCl)"]
\end{tikzcd} \tag{145}$$

$$CpMo(CO)_3Cl \xrightarrow[THF]{SeC(O)NMe_2^-} CpMo(CO)_3SeC(O)NMe_2 \quad \text{(Ref. 400)} \tag{146}$$

The electrochemical oxidation of these complexes in MeCN and CH_2Cl_2 has been investigated along with the corresponding analogues with SeSe, SeS, SS and SO donors[399,400].

7. *Miscellaneous ligands*

A single example of a monodentate Se-bonded dialkyldiselenocarbamate complex has been reported ($CpFe(CO)_2SeC(Se)NMe_2$)[399,403]. This complex has been prepared by a substitution reaction[399] (equation 147a) and a CSe_2 insertion reaction[403] (equation 147b). There is a discrepancy in the infrared data of the two reports. The lower value of ν_{C-N}, $1460\,cm^{-1}$ [399] vs. $1500\,cm^{-1}$ [403], is probably a more reasonable one for monodentate coordination of dialkyldiselenocarbamate, values of ca. $1510-1525\,cm^{-1}$ being generally found for the usual bidentate coordination mode (Section II.D.C).

$$\begin{tikzcd}
 & {[CpFe(CO)_2(OCMe_2)]BF_4} \arrow[d, "\text{(a)}\ [Me_2NH_2][Se_2CNMe_2]"] \\
 & CpFe(CO)_2SeC(Se)NMe_2 \\
CpFe(CO)_2^{Cl} \arrow[r, "\substack{1.\ HNMe_2\\ \text{neat}}", "\substack{-21\,^{\circ}C\\ 2.\ NaPF_6(aq)}"'] & \{CpFe(CO)_2NHMe_2\}PF_6 \arrow[u, "\substack{\text{(a)}\ CSe/KOBu\text{-}t\\ \text{acetone}/-20^{\circ}C}"']
\end{tikzcd} \qquad (147)$$

A single example of a complex with monodentate selenothiocarbamate, $CpFe(CO)_2SC(Se)NMe_2$, has also been prepared by the substitution route described in equation (147a). The position of the $\nu_{C\doteq N}$ band, $1460\,cm^{-1}$, supports a monodentate bonding mode, a value of $1515\,cm^{-1}$ being found for the related complex with (S, Se) bidentate coordination ($CpFe(CO)SeSCNMe_2$). This assignment of a Fe—S rather than a Fe—Se bonding mode of this ambidentate ligand was based on the observation of a $[FeS]^+$ fragment peak, but no $[FeSe]^+$ peak in its mass spectrum[399].

The two-step formation of an unusual —SeSeMe ligand has been achieved by alkylation of a coordinated η^2-Se_2 ligand (see equation 215) followed by reductive cleavage of one of the metal—Se bonds[404] (equation 148).

$$Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2 \xrightarrow[2.NaClO_4/EtOH]{1.CF_3SO_3Me/CH_2Cl_2} [Os(\eta^2\text{-}Se_2Me)(CO)_2(PPh_3)_2]ClO_4 \qquad (148)$$

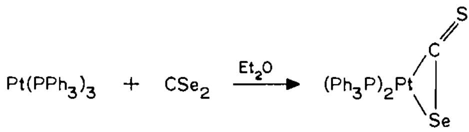
$$\xrightarrow{NaBH_4/EtOH} Os(\eta^1\text{-}Se_2Me)H(CO)_2(PPh_3)_2$$

C. Neutral Bidentate Ligands

1. *(Se, C) donors*

a. CSe_2 complexes. Because of the instability of CSe_2[405] relatively few complexes[214,217,224,406-408] of this molecule have been isolated compared to the extensive coordination chemistry of CS_2[204,409]. This molecule has also been used in the synthesis of selenocarbonyl complexes (Section II.A.7).

Jensen and Huge-Jensen prepared the first examples of complexes with coordinated CSe_2 by reactions with coordinatively unsaturated low-valent metal species[406] (equations 149–151).



(149)

light green solid

$\nu_{C=Se} = 995\,cm^{-1}$

($1270\,cm^{-1}$ in free CSe_2)

$$\mathrm{Ni(PPh_3)_2(CO)_2 + CSe_2 \rightarrow Ni(PPh_3)_2(CSe_2)_2} \qquad (150)$$

$$\nu_{\mathrm{C{=}Se}} = 870\,\mathrm{cm^{-1}}$$

$$\mathrm{Rh(PPh_3)_3Cl + CSe_2 \rightarrow Rh(PPh_3)_2Cl(CSe_2)_2} \qquad (151)$$

$$\nu_{\mathrm{C{=}Se}} = 865\,\mathrm{cm^{-1}}$$

In the Ni and Rh systems, only complexes with two CSe_2 units could be isolated, and these have been formulated as tetraselenooxalate complexes on the basis of infrared spectroscopy (no $\nu_{C=Se}$ band at $\sim 1000\,cm^{-1}$ and a strong band at $\sim 870\,cm^{-1}$ characteristic of the tetraselenooxalate anion).

Although no single-crystal X-ray diffraction structure determination has been reported for a CSe_2 complex, the CS_2 analogue of the product of equation (149) has been shown to have the proposed structure with η^2-CS_2 coordination[410]. Several other complexes with η^2-CS_2 have also been structurally characterized[409].

Similar reactions were subsequently used to prepare Ir[217,407], Pt[407], Pd[408], Ru[214] and Co[224] complexes of CSe_2 (equations 152–156).

$$trans\text{-}\mathrm{IrCl(CO)(PPh_3)_2 \xrightarrow[C_6H_6]{CSe_2} IrCl(CO)(CSe_2)(PPh_3)_2} \qquad \text{(Ref. 407)} \qquad (152)$$

$$\nu_{\mathrm{C{\equiv}O}} = 1960\,\mathrm{cm^{-1}} \qquad \nu_{\mathrm{C{=}Se}} = 1008\,\mathrm{cm^{-1}}$$

$$\nu_{\mathrm{Ir{-}Cl}} = 317\,\mathrm{cm^{-1}} \qquad \nu_{\mathrm{C{\equiv}O}} = 2025\,\mathrm{cm^{-1}}$$

$$\nu_{\mathrm{Ir{-}Cl}} = 265\,\mathrm{cm^{-1}}$$

$$\mathrm{IrCl(CSe)(PPh_3)_2 \xrightarrow{CSe_2} IrCl(CSe)(\eta^2\text{-}CSe_2)(PPh_3)_2} \qquad \text{(Ref. 217)} \qquad (153)$$

$$\nu_{\mathrm{C{=}Se}} = 1175\,\mathrm{cm^{-1}}$$

$$\nu_{\mathrm{C{=}Se(CSe_2)}} = 1010\,\mathrm{cm^{-1}}$$

$$\mathrm{Pt(PPh_2R)_4 \xrightarrow[hexane]{CSe_2} Pt(PPh_2R)_2(CSe_2)} \qquad \text{(Ref. 407)} \qquad (154)$$

$$\mathrm{R = Ph};\ \nu_{\mathrm{C{=}Se}} = 999\,\mathrm{cm^{-1}}$$

$$\mathrm{R = Me};\ \nu_{\mathrm{C{=}Se}} = 985\,\mathrm{cm^{-1}}$$

$$\mathrm{Ru(CO)_2(PPh_3)_3 \xrightarrow{CSe_2} Ru(CSe_2)(CO)_2(PPh_3)_2} \qquad \text{(Ref. 214)} \qquad (155)$$

$$\nu_{\mathrm{C{=}Se}} = 953\,\mathrm{cm^{-1}}$$

$$\nu_{\mathrm{C{\equiv}O}} = 2020,\ 1950\,\mathrm{cm^{-1}}$$

$$\mathrm{Pd(PPh_3)_4 \xrightarrow{CSe_2} Pd(PPh_3)_2(CSe_2)} \qquad \text{(Ref. 408)} \qquad (156)$$

$$\nu_{\mathrm{C{=}Se}} = 990\,\mathrm{cm^{-1}}$$

Coordinated CSe_2 can be readily alkylated, and this reaction has been used to prepare selenocarbonyl complexes (M—CSe) from CSe_2 complexes (equations 43 and 46). Only two other brief reports have described the reactivity of complexes containing η^2-CSe_2: (*i*) phosphine substitution reactions (equation 157)[408] and (*ii*) reaction of the coordinated CSe_2 with a difunctional halide to give a cyclic carbene complex (equation 158)[411].

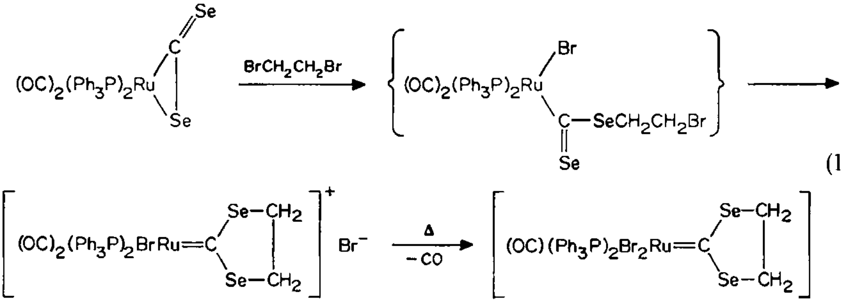
$$\mathrm{Pd(PPh_3)_2(CSe_2) \xrightarrow[hexane]{L} LPd(CSe_2) + 2\,PPh_3} \qquad (157)$$

$$\mathrm{L = dppe}$$

$$\nu_{\mathrm{C{=}Se}} = 990\,\mathrm{cm^{-1}}$$

$$\mathrm{L} = o\text{-}\mathrm{(Ph_2PCH_2)_2C_6H_4}$$

$$\nu_{\mathrm{C{=}Se}} = 995\,\mathrm{cm^{-1}}$$



(158)

The initial cationic carbene complex was isolated as its perchlorate salt and characterized by infrared and ^{1}H-NMR spectroscopy. Warming a solution of the cationic complex results in evolution of CO and formation of the neutral dibromo complex.

b. CSSe complexes. Several complexes of CSSe with transition metals (Co[224,412], Rh[224,412], Ru[215], Os[215], Ni[413], Pd[414,415] and Pt[408]) have been prepared by reaction of an appropriate metal precursor and CSSe, and an η^2 bonding mode via C and Se has been found in a recent single-crystal X-ray diffraction characterization of (o-$(Ph_2PCH_2)_2C_6H_4$)Pd(η^2-CSSe)[414] (Figure 5.)

As previously described in connection with the synthesis of selenocarbonyl complexes (Section II.A.7, equation 44) stable linkage isomers of the η^2-CSSe ligand have been isolated (**33a**, $\nu_{C=S} = 1063\,cm^{-1}$; **33b**, $\nu_{C=Se} = 1027\,cm^{-1}$)[215]. The analogous Os linkage isomers have also been isolated (Os(η^2-$\underline{CS}$eS), orange, $\nu_{C=S} = 1066\,cm^{-1}$; Os($\eta^2$-$\underline{CS}$Se), pink, $\nu_{C=Se} = 1015\,cm^{-1}$)[215].

Complexes with η^2-CSSe have been used as precursors to thiocarbonyl complexes via phosphine-induced Se extrusion reactions[412] (equation 159 and 160). A Ni(o) complex with CSSe has been prepared at low temperature by displacement of the labile 1,3-cyclooctadiene (COD) ligand[413] (equation 161).

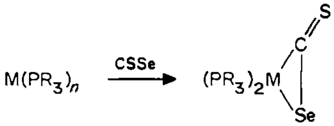
$$\begin{tikzcd}[column sep=small] CpCo(PMe_3)_2 \arrow[r, "CSeS", "-20\,^{\circ}C/PhMe"'] & CpCo(PMe_3)(\eta^2\text{-}CSeS) \arrow[r, phantom, "+"] \arrow[rr, bend right, "PPh_3/C_6H_6"', "50\,^{\circ}C\quad -SePPh_3"'] & {} & CpCo(PMe_3)(CS) \end{tikzcd} \qquad (159)$$

$$CpRh(C_2H_4)(PMe_3) \xrightarrow{CSeS} CpRh(\eta^2\text{-}CSeS)(PMe_3) \xrightarrow[-SePPh_3]{PPh_3} CpRh(PMe_3)(CS) \qquad (160)$$

$$Ni(bipy)(COD) + CSeS \xrightarrow{Et_2O/-80\,^{\circ}C} Ni(bipy)(CSeS) + COD \qquad (161)$$

$$\nu_{C=S} = 1103\,cm^{-1}$$

The Pd(II)[414] and Pt(II)[408] complexes were prepared by reaction of the appropriate tetrakis(triorganophosphine) complex with CSSe and, as in the CSe_2 analogues[408], the monodentate phosphine ligands can be readily displaced by chelating phosphines (equation 162).



(162)

$M = Pd$; $n = 2, 3$; $R = i\text{-}Pr$[414]

$n = 4$; $R = Ph$[414]

$M = Pt$; $n = 4$; $R = Ph$[408]

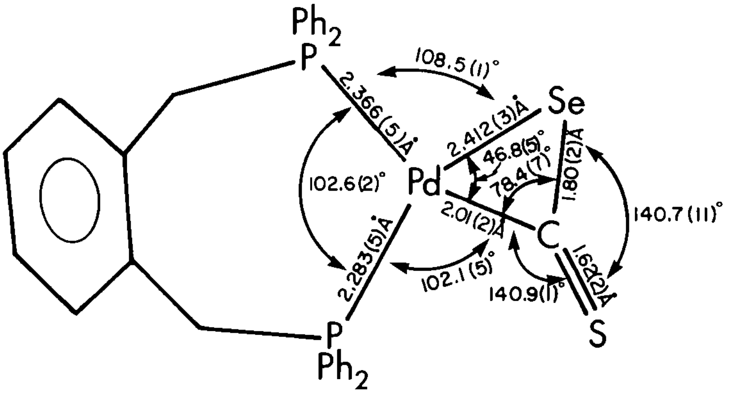


FIGURE 5. Molecular structure of $(o\text{-}(Ph_2PCH_2)_2C_6H_4)Pd(\eta^2\text{-}CSeS)$

Bonding via C and Se was proposed for all of these complexes, based on infrared spectroscopy ($\nu_{C=S} = 1160\text{–}1175\,cm^{-1}$)[414], a conclusion confirmed by single-crystal X-ray diffraction for $(o\text{-}(Ph_2PCH_2)_2C_6H_4)Pd(\eta^2\text{-}CSSe)$[414] (Figure 5).

Noteworthy also is the significant *trans* influence of the C atom on the Pd—$P_{trans(C)}$ distance vs. the Pd—$P_{trans(Se)}$ (Figure 5). A similar *trans* effect has been observed in $Pd(PPh_3)_2(\eta^2\text{-}CS_2)$.

c. *Selenoformaldehyde complexes.* Although polymeric forms of selenoformaldehyde have been prepared and characterized both in the free state (e.g. the cyclic trimer 1,3,5-triselane[416]) and coordinated to a metal (e.g. $[[(CH_2Se)_3]_2Ag]AsF_6$[417]) monomeric selenoformaldehyde has never been isolated. The latter complex, isolated as yellow crystals in 98% yield, was prepared by the reaction of $AgAsF_6$ and $(CH_2Se)_3$ in liquid SO_2[417]. Single-crystal X-ray diffraction showed the presence of discrete $[Ag\{(CH_2Se)_3\}_2]^+$ cations with all Se atoms irregularly coordinated to the Ag (the next shortest Ag—Se distance is 3.71 Å) (Figure 6).

In 1983 four reports described the first examples of monomeric selenoformaldehyde coordinated as both an $\eta^2\text{-}CH_2Se$ chelate (equations 163[418], 164[419] and 165[420]) and a bridging ligand (equation 166[421]).

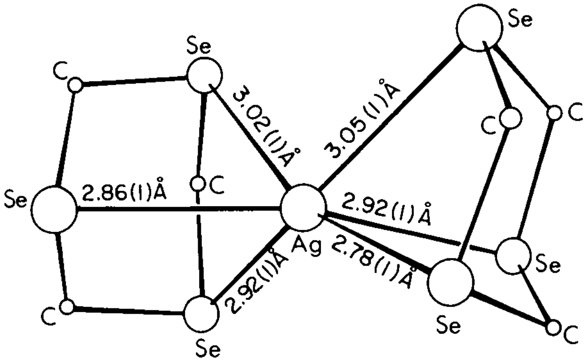
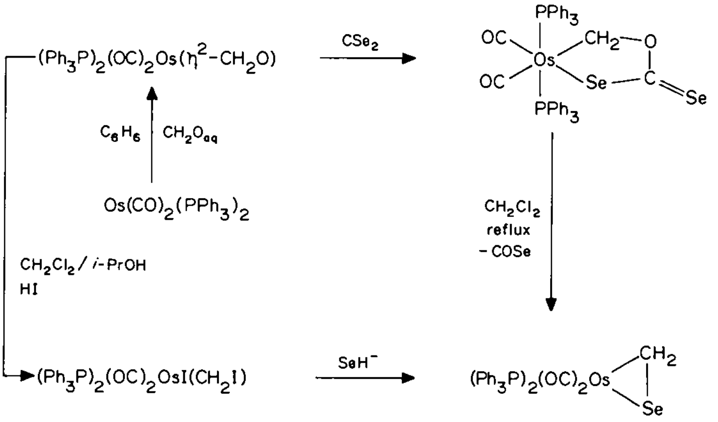


FIGURE 6. Molecular structure of $[Ag\{(CH_2Se)_3\}_2]^+$

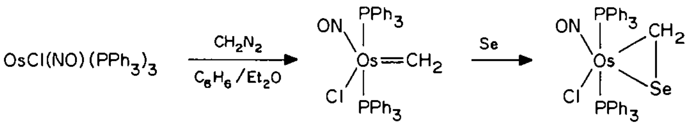


pale yellow crystals

$\nu_{C\equiv O}$ = 1986, 1919 cm^{-1}

^{1}H-NMR, δ(CDCl$_3$): 1.78 (t, SeCH$_2$, $^3J_{PH}$ = 4.8 Hz)

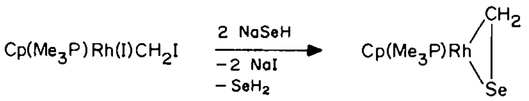
(163)



82%

tan air-stable crystals
m.p. 209-210 °C

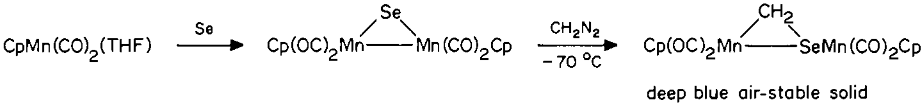
(164)



(165)

red–violet slightly air-sensitive solid (72%)

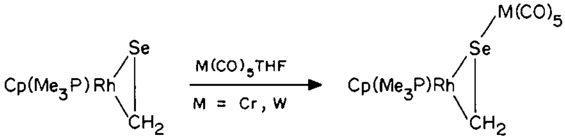
δ(CH$_2$) = 4.26 (ddd, J_{HH} = 1.2 Hz, J_{RhH} = 0.8 Hz, J_{PH} = 8.3 Hz); 5.31 (ddd, J_{HH} = 1.2 Hz, J_{RhH} = 2.2 Hz, J_{PH} = 0.6 Hz)



$\nu_{C\equiv O}(CCl_4) = 2000vs, 1955s, 1934vs, 1882s\,cm^{-1}$ (166)
$\nu_{C-H}(KBr) = 3115s, 2965s, 2930vs\,cm^{-1}$
^1H-NMR (270 MHz, C_6D_6)
$\delta(Cp) = 4.34$ (s), 3.71 (s)
$\delta(CH_2) = 4.88$ (d, $^2J_{HH} = 1.5$ Hz)
$= 4.66$ (d, $^2J_{HH} = 1.5$ Hz)

The structure of the selenoformaldehyde-bridged dimer $\{Cp(OC)_2Mn\}_2(CH_2Se)$ has been confirmed by single-crystal X-ray diffraction[421].

Heterometallic binuclear complexes with bridging selenoformaldehyde have also been prepared by acid–base reactions between a complex with η^2-$SeCH_2$ and complexes with the very labile THF ligand[422] (equation 166a).



(166a)

The ^1H-NMR spectra of these dimers give two signals for the diastereotopic CH_2Se protons (δ(Rh, Cr) = 4.88 (dd), 3.56 (ddd); δ(Rh, W) = 5.18 (ddd), 3.76 (ddd)), the differences in δ values of the CH_2 signals being significantly greater than for the Mn dimer (equation 166).

The basicity of the coordinated η^2-selenoformaldehyde ligand was further demonstrated by the formation of Cp′ $(OC)Rh(\mu_2,\eta^2(Rh)\text{-}CH_2Se)M(CO)_5$ by the two-step synthesis (e.g. equations 165 and 166a) starting with $Cp'(OC)Rh(I)(CH_2I)$[422].

2. *(Se, N) and (Se, P) donors*

Only a few examples of neutral (Se, N) ligands have been reported (Table 31), and no definitive structural information is available for these complexes.

Complexes of selenosemicarbazide ($RHNC(Se)NHNH_2$; ssc-R, **50**) were readily isolated from a solution of the ligand and the appropriate metal salt. A tetrahedral monomeric structure with (Se, N) bidentate selenosemicarbazide (ssc-H) was assigned to $[Zn(ssc\text{-}H)Cl_2]$[424] on the basis of the similarity of its X-ray powder pattern with that of the analogous thiosemicarbazide complex, the structure of which has been solved by single-crystal X-ray diffraction[435]. A green complex, $Cu(ssc\text{-}H)Cl_2$ was precipitated if an aqueous solution of the ligand, acidified with HCl, was added to cold aqueous $CuCl_2$ in a 1 : 1 molar ratio. The structure of this complex is unknown, but the similarity of its infrared spectrum with that of the thiosemicarbazide analogue indicates a bidentate (Se, N) coordination mode, and its insolubility suggests a polymeric structure with bridging chloro ligands. The magnetic susceptibility ($\mu_{eff} = 1.78$ B.M.) confirmed the presence of Cu(II).

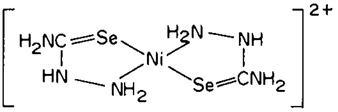
Reaction of CuX_2 ($X = Cl, NO_3$) or $CuSO_4$ with ssc-H in a 1:2 molar ratio gave

TABLE 31. Complexes with neutral (Se,N) and (Se,P) donors

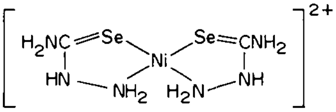
Ligand	Complex	Ref.
(Se,N) donor sets		
ssc-R (**50**)	$[Ni(ssc\text{-}Ph)_2]Cl_2$	423
	$[Zn(ssc\text{-}H)Cl_2]$	424
	$[Zn(ssc\text{-}H)_2](NO_3)_2$	424
	$[Cu(ssc\text{-}H)Cl_2]$	424
	$Cu(ssc\text{-}H)_2X_2$; $X = Cl, NO_3, \frac{1}{2}SO_4$	424
	trans-$[Ni(ssc\text{-}H)_2]SO_4 \cdot 3H_2O$ (**51a**)	425
	cis-$[Ni(ssc\text{-}H)_2]SO_4$ (**51b**)	425
	trans-$[Ni(ssc\text{-}H)_2]2X$; $X = Cl, Br, NO_3$	425
	$[Ni(ssc\text{-}H)_3]2X \cdot 2H_2O$; $X = Cl, Br$	425
pbs (**52**)	$[MCl_2(pbs)]$; M = Pd, Pt	426
$MeSeCH_2CH_2NH_2$ (mse)	$[Co(en)_2(mse)](ClO_4)_3$	427–429
	$[Co\{N(CH_2CH_2NH_2)_3\}(mse)]Cl_3$	430
(Se,P) donor sets		
spp (**53**)	$[Co(spp)_2Br]ClO_4$	431
	$[Ni(spp)_2Br]ClO_4$	432, 437
	$[Ni(spp)_2(NCS)_2]$	433
	$[Pd(spp)(SCN)_2]$	433, 434
	$[Pd(spp)I_2]$	434
	$[Ru(spp)_2Cl_2]$	434

complexes reported to be $Cu(ssc\text{-}H)_2X_2$ ($X = Cl, NO_3, \frac{1}{2}SO_4$)[424]. The insolubility and red–brown colour of the chloride and nitrate complexes, however, suggest that reduction has occurred with formation of Cu(I) complexes, $[Cu(ssc)]_n$. The magnetic susceptibilities of these complexes were not reported. In contrast, the sulphate complex was reported to be green, characteristic of Cu(II)[424].

Addition of solid ssc-H to a concentrated aqueous solution of $NiSO_4$ gave a precipitate of a diamagnetic red solid, which was assigned a *trans* square-planar structure (**51a**)[425] on the basis of the similarity of its X-ray powder pattern with the structurally characterized thiosemicarbazide analogue[436].



(51a)



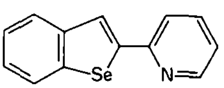
(51b)

A pale brown complex, formulated as the *cis* isomer (**51b**), was prepared by addition of a hot ethanol solution of $NiSO_4$ to a hot dilute ethanol solution of ssc-H[425].

The pale brown, diamagnetic square-planar complex $[Ni(ssc\text{-}H)_2]Cl_2$ precipitated on mixing hot ethanol solutions of ssc-H and $NiCl_2 \cdot 6H_2O$ in a 2:1 molar ratio[425]. An aqueous solution of this complex was, however, blue–green and paramagnetic. Concentration of this solution gave green crystals of the octahedral complex $[Ni(ssc\text{-}H)_3]Cl_2 \cdot 2H_2O$ ($\mu_{eff} = 3.14$ B.M.)[425].

Addition of aqueous ammonia to solutions of $[Ni(ssc\text{-}Ph)_2]Cl_2$[423] and $[Ni(ssc\text{-}H)_2]Cl_2$[425] precipitated the corresponding neutral complexes containing the anionic form of the selenosemicarbazide ligand.

A study[426] of the use of 2-(2-pyridyl)benzo[*b*]selenophene (**52**) as a reagent for the



pbs, (**52**)

gravimetric determination of Pd(II) and Pt(II) included the isolation of the yellow complexes $MCl_2(pbs)$. They were formulated as monomeric, square-planar species with (N, Se) bidentate pbs, although no spectroscopic data were presented.

Alkylation of a coordinated Se atom was used to prepare Co(III) complexes with the chelating $RSeCH_2CH_2NH_2$ ligand (equation 167).

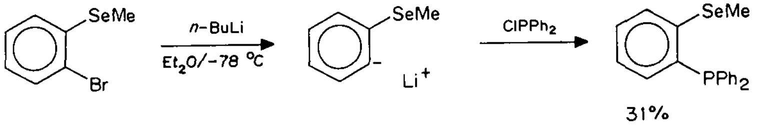
$$[Co(en)_2(SeCH_2CH_2NH_2)]^{2+} \xrightarrow{RCl} [Co(en)_2(RSeCH_2CH_2NH_2)]^{3+} \quad (167)$$

$R = Me$[427,428], Et[428], CH_2Ph[428], $CH_2CH_2C(O)Me$
($MeC(O)CH{=}CH_2$ was used as the alkylating agent[428])

The kinetics of the reaction with MeI was studied, and the relative nucleophilicities of various coordinated S and Se centres were determined: $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+} < [(en)_2Co(o\text{-}SC_6H_4NH_2)]^{2+} < [(en)_2Cr(SCH_2CH_2NH_2)]^{2+} \sim [(en)_2Co(SCH_2CO_2)]^{+} \approx [(en)_2Co(SCH_2CH_2NH_2)]^{2+} < [(en)_2Co(SeCH_2CH_2NH_2]^{2+}$ [427].

Optical isomers of the octahedral complexes $[Co(en)_2(MeSeCH_2CH_2NH_2)]^{2+}$ [429] and $[\{N(CH_2CH_2NH_2)_3\}Co(MeSeCH_2CH_2NH_2)]^{2+}$ [430] have also been isolated and characterized by electronic and circular dichroism spectra. These complexes were synthesized by alkylation of the corresponding selenolato complexes (e.g. equation 167). The complex with the tetradentate amine, $N(CH_2CH_2NH_2)_3$, gave two geometrical isomers differing in the relative orientation of the bidentate (Se, N) ligand, which were separated by chromatography[430].

Although a large number of hybrid bidentate ligands with various (P, E) (E = Group 5a or 6a element) donor sets have been reported[10], only one example with a (Se, P) set is known (**53**). The ligand was prepared by the two-step route shown in equation (168)[431]. This ligand forms complexes with Co(II)[431], Ni(II)[432,433], Ru(II)[434] and Pd(II)[433,434]. The Co(II)[431] and Ni(II)[432] bromo complexes were formulated as square-pyramidal on the basis of solution conductivities (1:1 electrolytes in MeCN and $MeNO_2$), magnetic susceptibilities (Co complex, $\mu_{eff} = 2.54$ B.M.; Ni complex, diamagnetic) and electronic spectroscopy. The thiocyanate complex $[Ni(spp)_2(NCS)_2]$[433] was assigned an octahedral structure with N-bonded thiocyanate, but no spectroscopic data were given in support.



(168)

spp, (**53**)

The Pd(II)[433,434] complexes are square-planar with S-bonded thiocyanate, although no spectroscopic evidence has been presented to support the latter conclusion[434]. These complexes readily undergo thermal *Se*-demethylation in solution to give the corresponding neutral complexes (e.g. $[Ni(ps)_2]$[433], $[(ps)Pd(\mu\text{-}SCN)_2Pd(ps)]$[433,434], $[Pd(ps)_2]$[410]; see Section II.D.1). The kinetics of the demethylation of $[Pd(spp)(SCN)_2]$ with SCN^- in CD_3CN/CH_2Cl_2 (3:1) has been studied[434], and under these conditions the reaction goes under milder conditions than in neat solvent (i.e. 55 °C[434] vs. refluxing DMF or *n*-butanol[433]).

3. (Se, E) (E = O, S, Se) donors

Relatively few ligands of this class have been described. The heterocycles 1,4-diselenan and 1,4-oxaselenan, which could coordinate as chelating (Se, Se) and (Se, O) ligands, were discussed in Section II.A.4 (see Tables 10 and 11). No good evidence for such chelation has been published. The Se_n ligands ($n = 2$, 4, 5), which can be formally considered to be neutral (Se, Se) chelates, are discussed in Section II.G.2–4.

The neutral bidentate (Se, E) (E = O, S, Se) ligands and their transition-metal coordination complexes are summarized in Table 32. The complex formation constants of $Se(CH_2CH_2CO_2H)_2$ and its related ligands with various divalent metals were measured in aqueous solution.

Complexes with 1:1 stoichiometries with both neutral and deprotonated forms of the ligands were present in such solutions. Chelation via the Se and O sites of these ligands was suggested, although no spectroscopic data were reported in this work[91].

The hybrid ligand $MeSCH_2SeMe$ functions as a bridging ligand in Pt(IV) complexes (e.g. $Me_3Pt(\mu\text{-}X)_2(\mu\text{-}MeSCH_2SeMe)PtMe_3$)[257]. Abel and coworkers, as a continuation of their detailed NMR studies of pyramidal inversion and intramolecular rearrangements in metal complexes with chalcogen ligands, have shown that increasing the methylene group by one unit allows the resulting ligand to function as a (Se, S) chelate in Pt(IV)[437], Pt(II)[439] and Re(I)[438] complexes (Table 32). This chelating ligand (msmte) was prepared as shown in equation (169)[437]. The metal complexes were prepared from appropriate halo complexes (equations 170–172). Facial geometry of the octahedral Re(I) complexes was established by infrared spectroscopy (e.g. three observed $\nu_{C\equiv O}$ bands of similar intensities).

$$\mathrm{MeSCH_2CH_2Cl} + \underset{\substack{\uparrow\ \text{liq. NH}_3\\ \mathrm{Me_2Se_2 + Na}}}{\mathrm{MeSe^-\,Na^+}} \rightarrow \underset{\substack{\text{msmte}\\ \text{pale yellow liquid}\\ \text{b.p. } 82\,^\circ\text{C (10 mm Hg)}\\ 88\%\ \text{yield}}}{\mathrm{MeSCH_2CH_2SeMe}} \qquad (169)$$

$$\mathrm{Me_3PtX} \xrightarrow[\substack{\text{CHCl}_3\\ \text{reflux}}]{\text{msmte}} \mathrm{Me_3PtX(msmte)} \quad \text{(Ref. 437)} \qquad (170)$$

$$X = Cl, Br, I$$

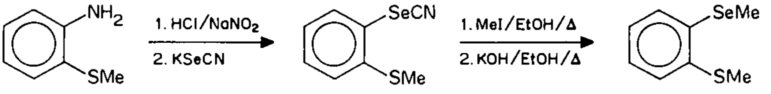
$$\mathrm{PtXMe(COD)} \xrightarrow[\substack{\text{CHCl}_3\\ \text{reflux}}]{\text{msmte}} \mathrm{PtXMe(msmte)} \quad \text{(Ref. 439)} \qquad (171)$$

$$X = Cl, Br, I$$

$$\begin{array}{l}\mathrm{(OC)_4Re(\mu\text{-}X)_2Re(CO)_4} \xrightarrow[\substack{\text{CHCl}_3\\ \text{reflux}}]{\text{msmte}} fac\text{-}\mathrm{[ReX(CO)_3(msmte)]}\\ \text{(or } \mathrm{[ReX(CO)_3(THF)]}\text{)} \end{array} \quad \text{(Ref. 438)} \qquad (172)$$

$$X = Cl, Br, I$$

The aromatic (Se, S) hybrid ligand msta (**54**) was first prepared by Pierpont[455] (equation 173).



(173)

msta, (**54**)

yellow oil
b.p. 104–105 °C (1 mm Hg)

TABLE 32. Complexes with neutral (Se, E) (E = O, S, Se) ligands

Ligand (L)	Complex	Reference
(Se, O) donors		
$Se(CH_2CH_2CO_2H)_2$ $Se(CH_2CO_2H)_2$ $Se(CH(Me)CO_2H)_2$	[ML] M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), Ag(I)	91
(Se, S) donors		
msta (**54**)	$PdCl_2$(msta)	434
	$PtMe_3X$(msta) X = Cl, Br, I	437
	$ReX(CO)_3$(msta) X = Cl, Br, I	438
$MeSeCH_2CH_2SMe$ (msmte)	$PtMe_3X$(msmte) X = Cl, Br, I	437
	PtMeX(msmte) X = Cl, Br, I	439
	$ReX(CO)_3$(msmte) X = Cl, Br, I	438
(Se, Se) donors		
$NCSeCH_2CH_2SeCN$ (dse)	$[M(dse)Cl_2]$ (**56**) M = Pd, Pt	440
	$[Co(dse)Cl_2]_n$	441
	$[M(dse)Cl_3]$ (**57**) M = Rh, Ir	441
$MeSeCH_2CH_2SeMe$	$MCl_n \cdot L$ $n = 2$; M = Pd, Hg $n = 3$; M = Au, Fe $n = 4$; M = Ti, V, Pt, Sn	442
	$M(CO)_3XL$ M = Mn, Re; X = Cl, Br	443
	$Cr(CO)_4L$	443
	$[PtXMe_3L]$ X = Cl, Br, I	444, 445
	$[ReX(CO)_3L]$	446
i-$PrSeCH_2CH_2SePr$-i	$[MX_2L]$ M = Pd, Pt; X = Cl, Br	447–450
	$[NiX_2L_2]$ X = Cl, Br	451
	$[Ni(NCS)_2L]$	451
	$[M(CO)_4L]$ M = Cr, Mo, W	450, 452
$PhSeCH_2CH_2SePh$	$[TiCl_4L]$	453
	$[Ru(CO)_2Br_2L]$	98
$MeSeCH_2CH_2CH_2SeMe$	$MCl_n \cdot L$ $n = 2$; M = Pd, Hg $n = 3$; M = Au $n = 4$; M = Ti, V, Pt, Sn	442
	$(FeCl_3)_2 \cdot L$	442
	$TeBr_4 \cdot L$	442
	$[PtXMe_3L]$ X = Cl, Br, I	444, 445
	$[ReX(CO)_3L]$ X = Cl, Br, I	446
$EtSeCH_2CH_2CH_2SeEt$	$[MCl_2L]$	
	M = Pd	6
	M = Pt	5

TABLE 32. (*Continued*)

Ligand (L)	Complex	Reference
$MeSeCH_2CMe_2CH_2SeMe$	$[M(CO)_4L]$ M = Cr, Mo, W	454
$Ph_2P(Se)CH_2P(Se)Ph_2$	$[CoLX_2]$ X = Cl, Br, I	140d
	$[(COD)RhL]ClO_4$	128
	$[ML_2]ClO_4$ M = Cu, Ag	134
	$[MLX_2]$ M = Pd, Pt; X = Cl M = Hg; X = Cl, Br	134
$Ph_2P(Se)CH_2CH_2P(Se)Ph_2$	$[AgL_2]ClO_4$	134
	$[HgLCl_2]$	134

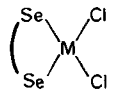
A more recent paper[434] described a synthesis via lithiation of *o*-bromoselenoanisole, followed by sulphur insertion and methylation (equation 174). Since the starting *o*-bromoselenoanisole was prepared from *o*-bromoanisole by a route analogous to that described in equation (173), the more direct synthesis via the latter route seems more efficient.

$$o\text{-}BrC_6H_4SeMe \xrightarrow[\text{2. } S_8 \quad \text{3. MeI}]{\text{1. } n\text{-BuLi/hexane/Et}_2\text{O}} \mathbf{54} \qquad (174)$$

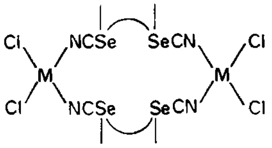
The monomeric Pd(II) complex of this hybrid ligand, [Pd(Se, S)Cl$_2$], shows a typical doublet in the far-infrared region characteristic of a *cis*-PdCl$_2$ group (300, 320 cm^{-1})[434].

Total NMR band-shape fitting methods have been used to determine accurate energy data for inversion barriers at S and Se in the complex $[PtXMe_3(o\text{-}MeSC_6H_4SeMe)]$[437] and *fac*-$[ReX(CO)_3(o\text{-}MeSC_6H_4SeMe)]$[438] (X = Cl, Br, I).

Poorly characterized complexes of Pd(II)[440], Pt(II)[440], Co(II)[441], Rh(III)[441] and Ir(III)[441] with 1,2-diselenocyanatoethane have been reported. This ligand, prepared by reaction of KSeCN and 1,2-dibromoethane in refluxing ethanol, was isolated as white needles after recrystallization from EtOH to remove elemental Se (m.p. 136–137 °C)[440]. The Pt(II) complex[440] gave ν_{Pt-Cl} bands at 320 and 303 cm^{-1}, characteristic of a *cis* terminal PtCl$_2$ group, but no far-infrared data were reported for the Pd complex. Shifts of the $\nu_{C\equiv N}$ and ν_{C-Se} vs. the free ligand suggest that both N and Se sites interact with the metals in these complexes. The insolubility of the complexes precluded molecular weight measurements. The data suggest polymeric structures for these complexes (**56**) rather than monomeric structures with chelating (Se, Se) (**55**).



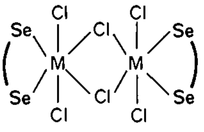
(**55**)



(**56**)

Spectroscopic and magnetic data support an octahedral polynuclear formulation for the pink, very hygroscopic complex with CoCl$_2$[441].

The more stable, brown, diamagnetic Rh(III) and Ir(III) complexes, however, were assigned chloro-bridged dimeric structures (**57**) with chelating Se ligands (infrared spectra, MW in sulpholan solution, non-electrolytes in DMSO). These dimers undergo typical bridge cleavage reactions to give monomeric products[441] (equation 175).



$\nu_{\mathrm{Ir-Cl}} = 315,\ 276\,\mathrm{cm}^{-1}$
$\nu_{\mathrm{Rh-Cl}} = 339,\ 278\,\mathrm{cm}^{-1}$
$\nu_{\mathrm{Rh-Cl-Rh}} = 238\,\mathrm{cm}^{-1}$

(57)

$$[\mathrm{MCl_3(Se,\ Se)}]_2 \xrightarrow[\substack{\mathrm{MeC(O)Et}\\ \text{reflux}}]{p\text{-}\mathrm{MeC_6H_4NH_2}} \mathrm{Cl_3}(p\text{-}\mathrm{MeC_6H_4NH_2})\mathrm{M(Se,\ Se)} \qquad (175)$$

$\nu_{\mathrm{Rh-Cl}} = 336,\ 275\,\mathrm{cm}^{-1}$
$\nu_{\mathrm{Ir-Cl}} = 312,\ 275\,\mathrm{cm}^{-1}$

Complexes of the (Se, Se) chelating ligand, $\mathrm{EtSeCH_2CH_2SeEt}$, with Pt(II)[5] and Pd(II)[6] were prepared in the early work of Fritzmann (equations 176 and 177).

$$\mathrm{K_2[PtCl_4]} \xrightarrow[\mathrm{(Se,\ Se)}]{\mathrm{EtSe(CH_2)_3SeEt}} cis\text{-}[\mathrm{PtCl_2(Se,\ Se)}] + [\mathrm{Pt(Se,\ Se)_2}][\mathrm{PtCl_4}] \qquad \text{(Ref. 5)} \qquad (176)$$

yellow
m.p. 176.5 °C
soluble in $\mathrm{CHCl_3}$

brown
m.p. 176 °C
insoluble in $\mathrm{CHCl_3}$

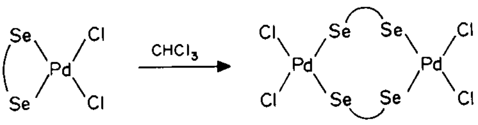
$$\mathrm{K_2[PdCl_4]} \xrightarrow[\mathrm{(Se,\ Se)}]{\mathrm{EtSe(CH_2)_3SeEt}} \mathrm{PdCl_2(Se,\ Se)]} \qquad \text{(Ref. 6)} \qquad (177)$$

yellow
insoluble in organic solvents
m.p. 181 °C dec.

The pure monomeric *cis*-Pt complex (equation 176) was prepared by using 2 equiv. of the Se ligand and heating the reaction mixture on a steam bath or by heating the reaction mixture of equation (176) to 110 °C, which isomerizes the Magnus-type salt to the monomer[5].

A number of other complexes with $\mathrm{RSe(CH_2)}_n\mathrm{SeR}$($n = 2$, R = Me, *i*-Pr, Ph; $n = 3$, R = Me) have been reported (Table 32). Much of the interest in these complexes centred on variable-temperature ^{1}H-NMR studies of inversion processes in such ring systems[444–446,449,450,452,454].

The complexes $[\mathrm{MX_2}(i\text{-}\mathrm{PrSeCH_2CH_2CH_2SePr}\text{-}i)]$ (X = Cl, Br; M = Pd, Pt)[447] were isolated from aqueous ethanol reaction solutions as monomers, but on dissolution in $\mathrm{CHCl_3}$, dimerization occurred with formation of Se bridges (equation 178). The



(178)

MW(acetone) = 468 MW = 950
(calc.) = 449.5
$\nu_{\mathrm{Pd-Cl}} = 319,\ 298\,\mathrm{cm}^{-1}$

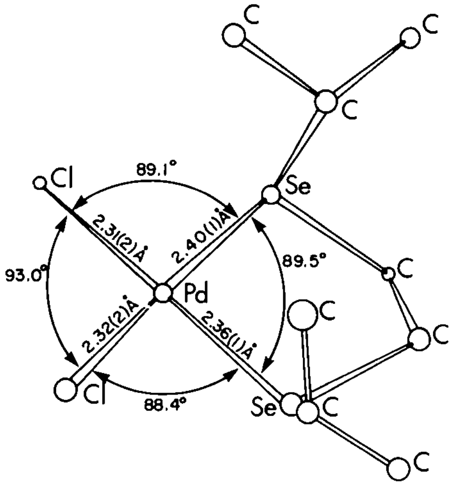


FIGURE 7. Molecular structure of $PdCl_2$(*i*-$PrSeCH_2CH_2SePr$-*i*)

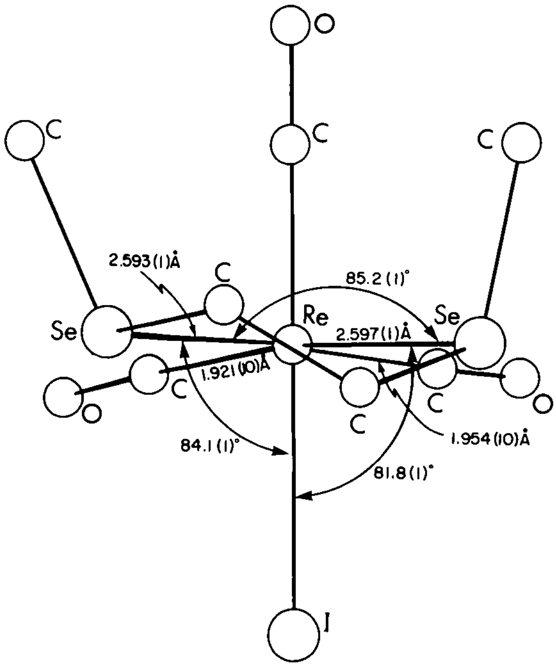


FIGURE 8. Molecular structure of *fac*-[$ReI(CO)_3(MeSeCH_2CH_2SeMe)$]

formulation of the dimers as Se-bridged species rather than the isomeric halo-bridged compounds was based on their failure to give bridge-cleavage monomeric products with *p*-toluidine, a reaction typical of the latter dimers (e.g. equation 175). In addition, the $\nu_{M—Cl}$ vibrations are essentially identical in the monomers and dimers, but bridging halo ligands would be expected to have decreased values for such vibrations.

Octahedral monomeric Ni(II) complexes, $[NiX_2(i\text{-}PrSeCH_2CH_2SePr\text{-}i)_2]$, were formulated on the basis of conductometric, magnetic and spectroscopic (infrared and electronic) evidence[451]. Reaction of these complexes with KSCN gave the square-planar, paramagnetic ($\mu_{eff} = 3.40$ B.M.) $[Ni(NCS)_2(i\text{-}PrSeCH_2CH_2SePr\text{-}i)]$, assigned an isothiocyanato bonding mode ($\nu_{C\equiv N} = 2105$, $\nu_{C—S} = 776$, $\delta_{N\equiv C—S} = 467, 458\,cm^{-1}$).

Two complexes with chelating ligands of this class have been characterized by single-crystal X-ray diffraction: $[PdCl_2(i\text{-}PrSeCH_2CH_2SePr\text{-}i)]$[424] (Figure 7) and *fac*-$[ReI(CO)_3(MeSeCH_2CH_2SeMe)]$[422] (Figure 8). Several examples of complexes containing chelating phosphine selenides have been described ($Ph_2P(Se)(CH_2)_nP(Se)Ph_2$, $n =$ 1[128,134], 2[134]; Table 32). Difunctional phosphine selenides with longer methylene chains ($n = 3, 4, 6$) bridge metal centres rather than chelate to a single metal (see Section II.A.3). The difunctional phosphine selenides $Ph_2P(Se)(CH_2)_nP(Se)Ph_2$ ($n = 1, 2$), prepared by reaction of the phosphine with KSeCN in MeCN[140], form (Se, Se) chelate complexes with Cu(I), Ag(I), Hg(II), Pd(II) and Pt(II).

The copper complex $[Cu(Ph_2P(Se)CH_2P(Se)Ph_2)_2]ClO_4$[134] precipitated from an $EtOH/CHCl_3$ solution of $Cu(ClO_4)_2\cdot 6\,H_2O$ and the selenide in a 1:2 molar ratio. In contrast, the analogous phosphine sulphide gave either a Cu(II) or Cu(I) complex, depending on the reaction conditions (e.g. acetone solvent, Cu(II) complex isolated; acetone solvent/hypophosphorous acid or ethanol solvent, Cu(I) complex isolated)[134].

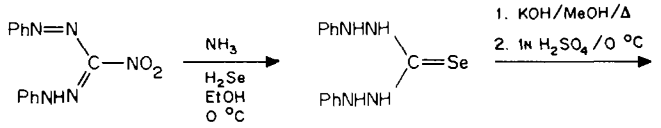
As discussed for monodentate phosphine selenides, a shift of the $\nu_{P=Se}$ band to lower energy is characteristic of Se coordination of this class of ligands. This band was not assigned in $[Co(Ph_2P(Se)CH_2P(Se)Ph_2)X_2]$ (X = Cl, Br, I)[140d], but in several other complexes of Rh(I)[128], Cu(I)[134], Ag(I)[134] and Hg(II)[134] with this chelating phosphine selenide, shifts of ca. $10\,cm^{-1}$ to lower energy were observed vs. the value for the free ligand ($Ph_2P(Se)(CH_2)_nP(Se)Ph_2$; $n = 1$: $531\,cm^{-1}$; $n = 2$: $530\,cm^{-1}$). Although no complex with a chelating phosphine selenide ligand has been characterized by single-crystal X-ray diffraction, $[Cu(Ph_2P(S)CH_2P(S)Ph_2)Cl]$ has been so characterized and shown to contain bidentate phosphine sulphide in a distorted trigonal-planar Cu(I) complex[134]. The decrease in $\nu_{P=S}$ vs. the free ligand was ca. $60\,cm^{-1}$ for this complex[134].

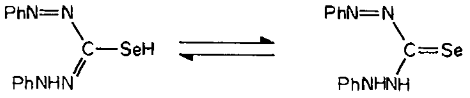
D. Anionic Bidentate Ligands

1. (Se, N)$^-$ and (Se, P)$^-$ donors

Only a few complexes with anionic (Se, N) and (Se, P) hybrid chelates have been reported (Table 33), but examples of both classes have been characterized by single-crystal X-ray diffraction ($[Co(en)_2(SeCH_2CH_2NH_2)](NO_3)_2$[457] and *trans*-$[Ni(o\text{-}Ph_2PC_6H_4Se)_2]$[464]).

The first reported hybrid ligand of this class was the Se analogue of dithizone, the reagent widely used in trace-metal analysis. This ligand (diphenylselenocarbazone, 3-seleno-1,5-diphenylformazan, 'selenazone', szH, **58**) was prepared in two steps from 3-nitro-1,5-diphenylformazan[456] (equation 179).





(58a) **(58b)**

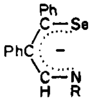
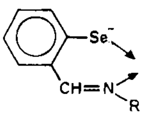
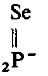
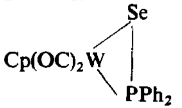
black microcrystals ($CHCl_3$) (179)
m.p. 116 °C
$\nu_{C=Se} = 705\,cm^{-1}$

This reagent forms highly coloured complexes with many metals that can be extracted into organic solvents over a range of pH values, but none of these complexes was isolated and structurally characterized.

A number of dithizone (dzH, i.e. S analogue of **58**) complexes, however, have been characterized, and bonding modes of this ambidentate ligand involving (S, N) chelation ($[MeHg(dz)]$[465], $[Zn(dz)_2]$[466], $[Ni(dz)_2]$[467]) and monodentate S coordination ($[Hg(dz)_2(pyr)_2]$[468]) have been established by single-crystal X-ray diffraction.

An unusual trigonal-bipyramidal structure has been established for $In(dz)_3$[469], one

TABLE 33. (Se, N)$^-$ and (Se, P)$^-$ ligands and their coordination complexes

Ligand	Complex	Reference
(Se, N)$^-$ donors		
sz$^-$, (**58** – H)	$[M(sz)_2]$	456
	M = Mn, Ni, Fe, Co, Cu, Zn, Cd, Hg, Pb	
$H_2NCH_2CH_2Se^-$	$[Co(en)_2(Se,N)]X_2$ (**59**)	
	X = NO_3	457[a]
	X = ClO_4,	427–429, 458, 459
	$[Co(tren)(Se,N)](ClO_4)_2$	430
	tren = $N(CH_2CH_2NH_2)_3$	
$H_2NCH_2CH(Me)Se^-$	$[Co(en)_2(Se,N)]^{2+}$	460
	$[Co(tren)(Se,N)]^{2+}$	
 R = Me, Et, *i*-Pr	$[Ni(Se,N)_2]$ (**60**)	461
	$[M(Se,N)_2]$ (**61**)	
	M = Zn, Ni; R = *p*-Tol, *p*-An	462
	M = Ni; R = Ph, *o*-Tol, *n*-Bu, *i*-Pr, C_6H_{11}	
	M = Co; R = *i*-Pr, C_6H_{11}, *o*-Tol	463
	M = Zn; R = Ph, *n*-Bu	463
(Se, P)$^-$ donors		
o-$Ph_2PC_6H_4Se^-$ (ps)	$[Ni(ps)_2]$ (**62**)	433, 464[a]
	$[Pd(ps)SCN]_2$ (**63**)	433
	$[Pd(ps)_2]$ (**64**)	433
 $\overset{Se}{\overset{\Vert}{R_2P^-}}$		143

[a] Single-crystal X-ray diffraction structure determination.

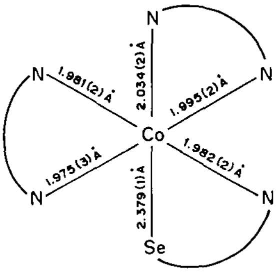
ligand being coordinated only through a S atom in an equatorial position while the other two dz ligands are bidentate (N, S), spanning axial and equatorial positions.

The tris-chelate Co(III) complex $[Co(en)_2(SeCH_2CH_2NH_2)]^{2+}$ has been prepared by oxidation of a deaerated Co(II)(en) solution with the diselenide[457] (equation 180). The X-ray structural characterization of this complex (**59**) showed a *trans* effect, reflected in a lengthening of the Co—N bond *trans* to the Se donor[457]. This redox route to metastable Co(III) complexes containing reducing ligands has also been applied to the corresponding thiolate complex[457].

$$2\,Co(ClO_4)_2 + 5\,en + (H_3NCH_2CH_2Se)_2SO_4 \xrightarrow{H_2O} \qquad (180)$$

$$2\,[Co(en)_2(Se,N)](ClO_4)_2 + [enH_2]SO_4$$

$$\begin{array}{c} 53\% \\ \text{brown needles} \end{array}$$



(**59**)

Subsequent studies of this complex have demonstrated the nucleophilicity of the Se atom[427–429] (e.g. alkylation of the coordinated Se; see Section II.C.2). Optical isomers of this chelate system (and the related $[Co\{N(CH_2CH_2NH_2)_3\}SeCH_2CH_2NH_2]^{2+}$[430] and $[Co\{N(CH_2CH_2NH_2]_3\}SeCH(Me)CH_2NH_2]^{2+}$[460] chelates) have been isolated and characterized by electronic and circular dichroism spectra. A detailed study of the solution photochemistry of this complex by Adamson and coworkers[458] showed only photoredox decomposition at all wavelengths. The 2-selenolatoethylamine ligand was also oxidized to

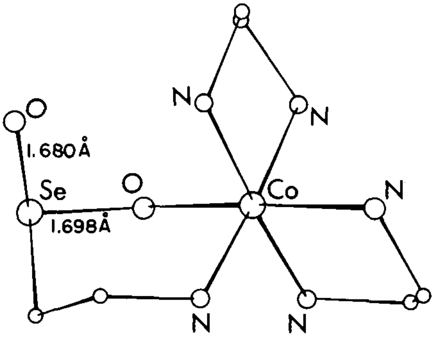
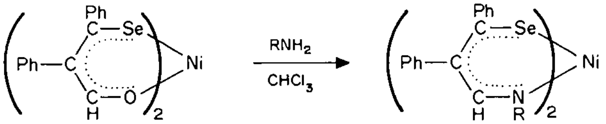


FIGURE 9. Coordination geometry of $[Coen_2(SeO_2CH_2CH_2NH_2)]^{2+}$

the seleninato derivative ($—Se(O)_2CH_2CH_2NH_2$) by treatment of the Co(III) chelate with aqueous H_2O_2. Single-crystal X-ray diffraction of this complex established an (N, O) bonding mode of this ambidentate ligand (Figure 9). The six-membered chelate ring has a chair conformation. The spontaneous resolution of the nitrate salt to give the $(-)^{CD}_{500}$ isomer occurred on cooling an aqueous solution of the racemic salt[470].

Ni(II) aldimine chelates (**60**) have been prepared by reaction of the 1,2-diphenyl-2-formylvinylselenol chelate (equation 181) with primary amines[461].



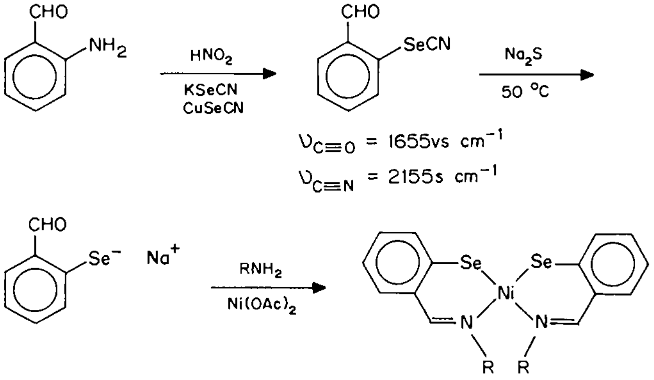
(181)

(60)

$\nu_{C\cdots O} = 1560\,cm^{-1}$

R = Me	Et	*i*-Pr
$\nu_{C\cdots N} = 1608$	1605	$1610\,cm^{-1}$

Selenosalicylideneamine chelates of Ni(II)[462,463] (**61**), Zn(II)[462,463] and Co(II)[463] have been prepared by template-type reactions (equation 182). The air-stable Ni(II) chelates (**61**) can be recrystallized from dioxane, melt without decomposition and are readily soluble in organic solvents. They are diamagnetic in the solid state and solution and have been assigned square-planar geometries. The retention of this stereochemistry in solution contrasts with the square-planar (solid state) → tetrahedral (solution) transition observed in the analogous salicylideneaminato complexes[471,472]. The analogous bis(thiosalicylideneaminato) chelates give tetrahedral paramagnetic complexes at high temperature in DMSO[473]. The order of stability of the square-planar geometry in these complexes, therefore, is (Se, N) > (S, N) > (O, N). The dipole moments of several of these complexes have been determined, the high values (5.8–7.7 D) in C_6H_6 indicating a *cis* configuration.



(182)

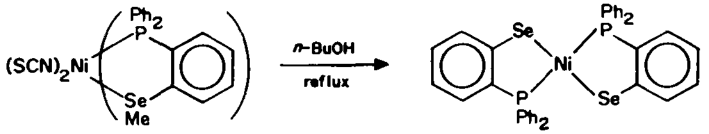
(61)

The Co(II) complexes (Table 33), however, have tetrahedral geometries in the solid state at room temperature ($\mu_{eff} = 4.81$ B.M., $R = C_6H_{11}$; $\mu_{eff} = 4.96$ B.M., R = *i*-Pr; $\mu_{eff} = 4.21$ B.M., R = *o*-Tol). In the one case where solubility allowed a dipole-moment measurement (R = c-HeX) the dipole moment of 4.16 D agreed with the proposed tetrahedral structure.

The Zn(II) chelates have the expected tetrahedral structures.

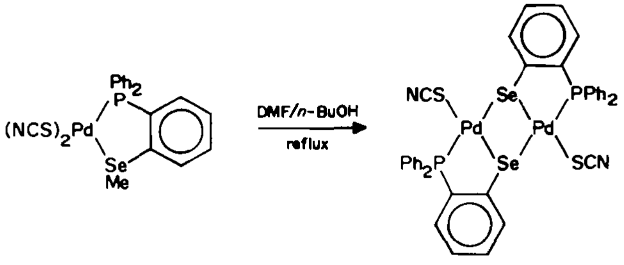
Axial ligation of $^{-}SeCH_2CH_2NMe_2$ in the bleomycin—Fe(III)—$SeCH_2CH_2NMe_2$ and haemoglobin—Fe(III)—$SeCH_2CH_2NMe_2$ complexes has been confirmed by the rapid-freezing ESR technique[474]. Here the *N,N*-dimethylselenocysteamine functions as a monodentate Se ligand because of the stable planar arrangement of the FeN_4 coordination spheres in these systems.

Other than the tungsten complex with chelating $SePPh_2^-$ (equation 20), the only example of an anionic bidentate (Se, P) ligand is diphenyl-*o*-selenatophenylphosphine (ps)[433]. Complexes of the latter chelate have been readily prepared by thermolysis of the diphenyl(*o*-methylselenophenyl)phosphine precursors (equations 183–185).



(183)

(62)



(184)

(63)

(185)

(64)

The Ni(II) complex (**62**) was very soluble in $CHCl_3$, and its ^1H-NMR spectrum confirmed that *Se*-demethylation occurred on thermolysis[433]. Its diamagnetism and electronic absorption spectrum indicated a square-planar geometry[433], a formulation subsequently confirmed by single-crystal X-ray diffraction, which established a *trans*-NiP_2Se_2 coordination sphere[464].

The thermolysis product **63** was formulated as a Se-bridged dimer on the basis of molecular weight measurement in $CHCl_3$ and the single sharp $\nu_{C\equiv N}$ band at $2110\,cm^{-1}$, characteristic of a terminal S-bonded thiocyanate[433]. The insolubility of the complex **64**, however, indicated a polymeric formulation[433].

2. *(Se, E)$^-$ (E = O, S, Se) donors*

Although not as numerous as the various classes of dithio ligands[12], a number of complexes with anionic (Se, Se) ligands and their (Se, O) and (Se, S) hybrid analogues have

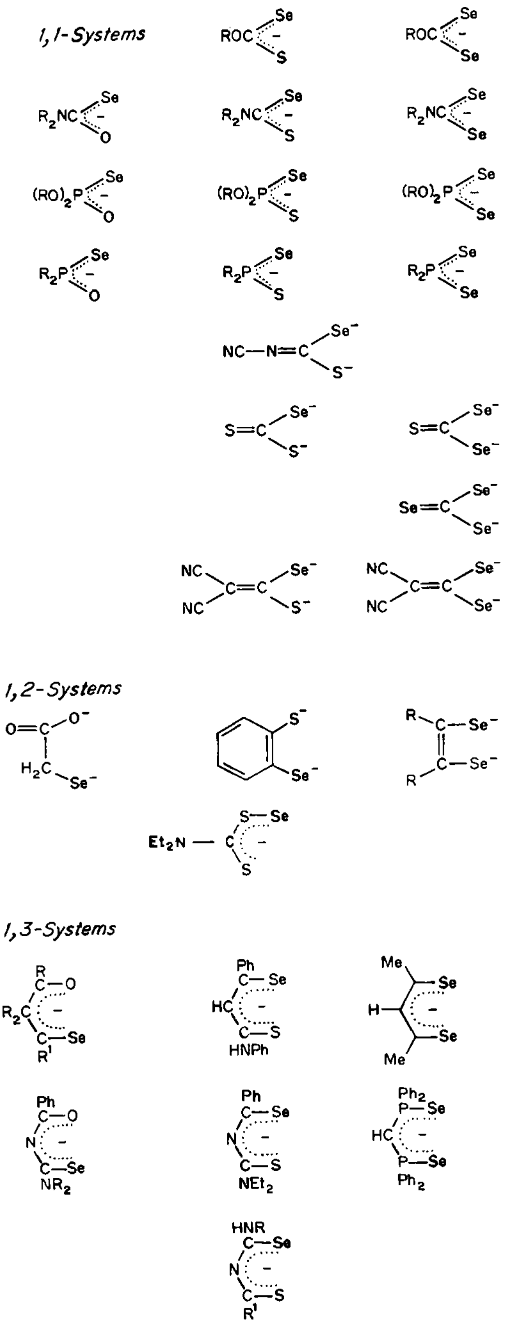


FIGURE 10. Anionic (Se, E)$^{n-}$ (E = O, S, Se; n = 1, 2) ligands

TABLE 34. Complexes with anionic (Se,O) chelating ligands

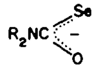
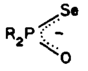
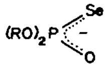
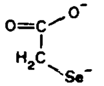
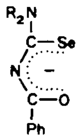
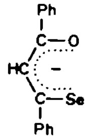
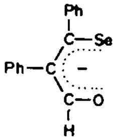
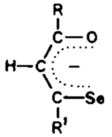
Ligand	Complex
1,1-(Se,O)⁻ donors	
 (65)	$Me_2Sn(SeOCNR_2)_2$[394] R = Me, Et
 (66)	$Pd(SeOCNEt_2)_2$[393] $M(SeOPEt_2)_2$[475] M = Zn, Cd, Ni, Pb $Ph_2Sn(SeOP(OPr\text{-}i)_2)_2$[476]
 (67)	$M(SeOP(OPr\text{-}i)_2)_n$[477] n = 1; M = Ag n = 2; M = Zn, Cd, Pb n = 4; M = Th
1,2-(Se,O)⁻ donors	
 (68)	$[Co(en)_2(Se,O)]ClO_4$[457]
1,3-(Se,O)⁻ donors	
 (69)	$[M(Se,O)_n]$ R = Et[478] $n = 2$; M = Ni, Pd $n = 3$; M = Co R = *i*-Bu[479] $n = 2$; M = Ni, Cu (73)
 (70)	$[M(Se,O)_n]$[480,481] $n = 1$; M = Tl $n = 2$; M = Ni, Pd, Hg, Zn, Pb, Cd $n = 3$; M = Co, In
 (71)	$[Ni(Se,O)_2]$[461]
 (72)	$[M(Se,O)_2]$[482] M = Fe, Co, Ni, Cu, Zn, Hg, Pb, Cd, Pd; R = CF_3, R^1 = 2-thienyl

TABLE 35. Infrared data (cm^{-1}) for bidentate selenocarbamate complexes

Complex	$\nu_{C=O}$[a]	Misc. bands	Ref.
$Me_2Sn(SeOCNMe_2)_2$	1592s	337m[b]	394
$Me_2Sn(SeOCNEt_2)_2$	1586s	322m[b]	
$Me_2ClSn(SeOCNMe_2)$	1590s	343m[b]	
$Me_2ClSn(SeOCNEt_2)$	1587s	325m[b]	
$Me_3Sn(SeCONMe_2)$[c]	1620s	328m[b]	
$(SeC(O)NMe_2^-)$	1620		
$(Ph_3P)_2Pd(SeOCN(Pr\text{-}i)_2)_2$	1590s		393
	(1589s, 1537m)[d]		
$(Ph_3P)_2Pt(SeOCN(Pr\text{-}i)_2)_2$	1598s		393
	(1599s, 1540sh)[d]		
$(OC)_4Mn(SeOCNMe_2)$	1550[e]		397
$CpMo(CO)_2(SeOCNMe_2)$	1560		400

[a] Values for $\nu_{C=O}$ for monodentate Se-bonded complexes are given in Table 30.

[b] ν_{Sn-Se}.

[c] Contains monodentate selenocarbamate.

[d] In CH_2Cl_2.

[e] The spectrum of this unstable monomeric chelate was measured in cyclohexane (see equation 144).

been prepared (Figure 10). The following sections summarize the complexes reported for each of these three structural types of ligands along with their characteristic chemical and spectroscopic properties.

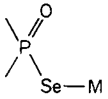
a. (Se, O)⁻ donors. Complexes with monodentate Se-bonded selenocarbamates were discussed in Section II.B.6. Typical complexes containing (Se, O)-chelated selenocarbamates (**65**), selenophosphinates (**66**) and selenophosphates (**67**) along with other anionic (Se, O) ligands are listed in Table 34.

The first reported bidentate selenocarbamate complexes, $Me_2Sn(OSeCNR_2)_2$, $Me_2ClSn(SeOCNR_2)$ (R = Me, Et), are air-stable solids whose infrared spectra give $\nu_{C\cdots O}$ bands (Table 35) at lower energy than that found for the complexes with Se-bonded monodentate selenocarbamate (see Section II.B.6). Weak Sn—O bonds were suggested for these chelates because of the large intensity ratios of $\nu_{sym}(Sn—C)/\nu_{asym}(Sn—C)$ ($Me_2Sn(Se, O)_2$, ca. 0.6–0.95 vs. values of ca. 0.2 for the corresponding $Se_2CNR_2{}^-$ and $SeSCNR_2{}^-$ complexes; $Me_2ClSn(Se,E)$ (E = O, S, Se), ca. 0.95).

The ^1H-NMR spectra of these chelates show doublets for the N—Me (and doublets of a quartet and a triplet for $N—CH_2CH_3$) due to restricted rotation about the C—N bond. The coalescence temperatures for these proton signals are in the range 50–55 °C ($PhNO_2$ solvent). The latter values, compared to a coalescence temperature of 110 °C for $Me_2ClSn(SSeCNMe_2)$, indicate a rather low double-bond character for these selenocarbamate complexes.

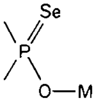
A series of complexes $(Ph_3P)_2M(SeOCNR_2)_2$ (M = Pd, Pt; R = Me, Et, *i*-Pr, *n*-Bu) have been prepared and characterized in the solid state and in solution by infrared, ^1H- and ^{31}P-NMR spectroscopy[392,393]. These data, together with molecular weight measurements, established a solution equilibrium (equation 143) involving phosphine dissociation and chelation of the selenocarbamate which is monodentate Se-bonded in the solid state. This reaction is reflected in the appearance of a new $\nu_{C\cdots O}$ band at ca. 1540 cm^{-1} due to the coordinated C=O in the solution infrared spectra of these complexes (the uncoordinated C=O in the solid-state structure has its absorption at ca. 1590 cm^{-1}; Table 35). A similar equilibrium was found for $(Ph_3P)_2Ni(SeC(O)NEt_2)_2$[391] (Table 30).

A brief report of the diethylselenophosphinato (**67**) chelates, $[M(SeOPEt_2)_2]$ (M = Co, Zn, Cd) has appeared[475]. Owing to the instability of these complexes, they were not characterized, and attempts to prepare chelates of Ni(II), Pd(II), Pt(II) and Bi(III) led only to decomposition products[475].



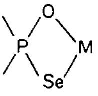
(selenol)

$Me_3SiSeP(O)(OPr\text{-}i)_2$
$Ph_3GeSeP(O)(OPr\text{-}i)_2$
$As(SeP(O)(OPr\text{-}i)_2)_3$



(selenone)

$Me_3SnOP(Se)(OPr\text{-}i)_2$
$P(OP(Se)(OPr\text{-}i)_2)_3$



(chelate)

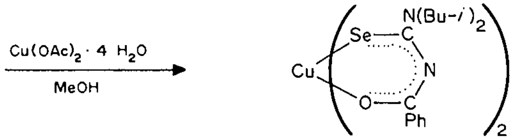
$Ph_2Sn(SeOP(OPr\text{-}i)_2)_2$
$PhSn(SeOP(OPr\text{-}i)_2)_3$

Complexes of diisopropylselenophosphate, $SeOP(OPr\text{-}i)_2^-$, with a variety of main-group elements[476] and transition metals[477] have been isolated (Table 34). The main-group compounds were isolated as air-stable liquids but are very sensitive to heat and light, readily depositing elemental Se[476]. The three bonding modes illustrated above were suggested by the infrared and ^{31}P-NMR spectra of these complexes[476].

The infrared evidence for the bidentate coordination mode was equivocal, but the ^1J values measured for $Me_3Sn(SeOP(OPr\text{-}i)_2)$ (644.1 Hz) and $Ph_2Sn(SeOP(OPr\text{-}i)_2)_2$ (545.9 Hz) supported (Se, O) chelates[476]. Similar spectroscopic evidence suggested (Se, O) chelation in other complexes (Table 34, $850\,\text{Hz} > {}^1J_{PSe} > 550\,\text{Hz}$) and monodentate Se coordination ($^1J_{PSe} < 550\,\text{Hz}$) in $M(SeP(O)(OPr\text{-}i)_2)_n$ ($n = 2$, M = Hg, Se, Te; $n = 3$, M = As, Sb, Bi)[77]. All of these complexes are unstable.

The tris-chelate $[Co(en)_2SeCH_2CO_2]ClO_4$[457] was prepared by the oxidation of a $Co(ClO_4)_2$/en solution with $(HO_2CCH_2Se)_2$ as previously described (equation 180) for the $^-SeCH_2CH_2NH_2$ analogue. Stable chelates derived from 1,1-dialkyl-3-benzoylselenourea, $R_2NC(Se)NHCOPh$ (**69**) (Table 34) readily precipitated from solutions of the neutral precursor and appropriate metals salts[478,479] (equation 186).

$$KSeCN + PhC(O)Cl + (i\text{-}Bu)_2NH \xrightarrow{\text{acetone}} (i\text{-}Bu)_2NC(Se)NHC(O)Ph \qquad (186)$$



(73)

The Ni(II) chelate was also prepared in a one-step procedure in which $Ni(OAc)_2 \cdot 4\,H_2O$ was added to the 1,1-diisobutyl-3-benzoylselenourea formed *in situ*[479].

Hoyer and coworkers, who have extensively studied metal chelates with various anionic (Se, E) (E = O, S, Se) donors, have reported a mass spectroscopic investigation of these complexes[479].

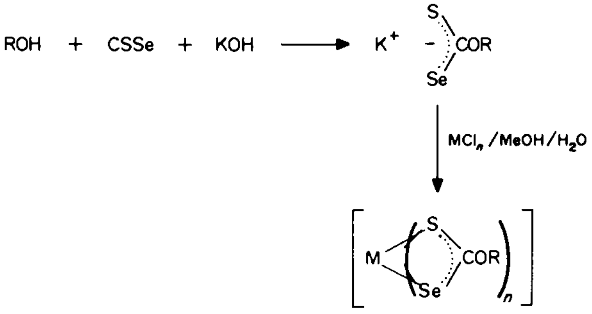
The anion of monoselenodibenzoylmethane (**70**) gives chelates with a variety of metals (Table 34) on reaction of a $CHCl_3$ solution of the ligand with the metal salt in ethanol solution mixed with an aqueous NaOAc buffer[481]. The Ni chelate gave 1:1 adducts with phen and bipyr. Characterization of these complexes was limited to elemental analysis and electronic spectroscopy[481].

The chelate ligand 1,1,1-trifluoro-4-(2-thienyl)-4-seleno-3-butene-2-one (**72**) was obtained as an air-sensitive red oil by the reaction of H_2Se with the corresponding diketone in absolute ethanol in the presence of HCl[482]. This ligand was evaluated as an extractant in $CHCl_3$ solution for various metals salts (Table 34). All of these gave highly coloured solutions, which were characterized by electronic spectroscopy.

b. *(Se, S)⁻ donors.* Complexes of several classes of ligands of this general type are known (Table 36) and in two cases molecular structures have been established by single-crystal X-ray diffraction ($[Cu(SeSCNEt_2)_2]$[504], $[(n\text{-}Bu)_4N]_2[Ni(SeSC{=}C(CN)_2)_2]$[485]).

A number of complexes of monoselenoxanthates (**74**) have been prepared (Table 36)[485] (equation 187).

Anionic tris-chelates $[Ni(Se, S)_3]^-$, (Se, S) = **74**, were also isolated by use of the appropriate Ni/selenoxanthate stoichiometry[486]. The magnetic moments and electronic spectra of these complexes indicated a trigonally distorted $NiSe_6$ coordination sphere[486].



(187)

TABLE 36. Complexes with $(Se, S)^-$ donors

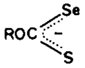
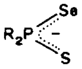
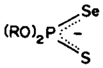
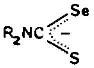
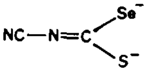
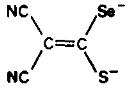
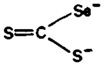
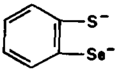
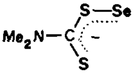
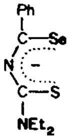
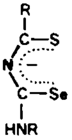
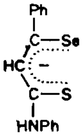
Ligand	Complex	Reference
1, 1-*Selenothio type*		
	M(SeSCOEt)$_n$	483
	M = Fe, Cu, Pb, Ni; $n = 2$	
	M = Ag; $n = 1$	
(74)		
	Ni(SeSCOEt)$_2$	484
	M(SeSCOCH$_2$CH$_2$OMe)$_n$	485
	M = Ni, Pd, Pt, Zn; $n = 2$	
	M = Co, Rh, Cr; $n = 3$	
	[Ni(SeSCOCH$_2$CH$_2$OMe)$_3$]	486
	M(SeSPEt$_2$)$_n$	
	M = Tl; $n = 1$	475, 487
	M = Zn, Cd, Pb, Ni, Pd; $n = 2$	462, 463
(75)	M = Bi, Rh; $n = 3$	
	M(SeSP(OR)$_2$)$_n$	488–490
	M = Pb, Ni, Cu, Zn, Cd, Hg, Pd, Pt; $n = 2$	
	M = Co, Rh, Ir, Cr; $n = 3$	
(76)		
	Me$_2$Sn(SeSCNMe$_2$)$_2$	491
	M(SeSCNR$_2$)$_n$	
	$n = 1$	492
(77)	M = Tl, Ag; R = Et	
	$n = 2$	
	M = Ni, Pd, Pt; R = Me, Et	492
	M = Zn, Cd, Pb, Ni, Pd, Cu; R = Et	493
	$n = 3$	494
	M = Ga, In, Tl, Fe, Co, Rh, Cr, Mn; R = Et	
	L$_2$Au(SSeCNR$_2$)	494
	L = Cl, Br, I, Me, Et; R = Me, Et	
	FeCl(SSeCNR$_2$)	495
	R = Me, Et	
	(OC)$_4$Mn(SeSCNMe$_2$)	396
	Pd(PR$_3$)Cl(SeSCNR$^1_2$)	496
	PR$_3$ = PPh$_3$, PMePh$_2$, PMe$_2$Ph; R^1 = Me, Et	

TABLE 36. (*Continued*)

Ligand	Complex	Reference
	$M(SeSCNR_2)_2$ $M = Ni, Cu; R = C_6H_{11}, Et, CH_2Ph$	497
 **(78)**	$(Et_4N)_2[M(SeSC{=}NCN)_2]$ $M = Ni, Pd$	485
 *i*-mnts, **(79)**	$[(n\text{-}Bu)_4N]_a[M(i\text{-}mnts)_n]$ $M = Au; a = 1; n = 2$ $M = Ni, Pd, Pt, Zn, Cd; a = n = 2$	485
	$(Ph_4As)_n[M(i\text{-}mnts)_n]$ $M = Se, Te; n = 2$ $M = Cr, Co, Rh, Fe, In; n = 3$	485
 **(80)**	(triphos)CoSSeC=Se	498
1,2-*selenothio type*		
 tbs, **(81)**	$Pr_4N[M(tbs)_2]$ $M = Ni, Co, Cu$	455,499
 **(82)**	$[Os_2(SeS_2CNMe_2)_2(S_2CNMe_2)_3]PF_6$	500
1,3-*Selenothio type*		
 **(83)**	$[Ni(Se,S)_2]$ **(86)**	501
 **(84)**	$[Ni(Se,S)_2]$ **(87)** $R^1 = Me; R = Ph, p\text{-}An$ $R^1 = Ph; R = Ph, p\text{-}Tol, p\text{-}An$	502
	$[M(Se,S)_2]$ **(87)** $M = Co, Cu, Zn; R^1 = Ph; R = p\text{-}An$	502
	$[M(Se,S)_2]$ **(88)** $M = Ni, Cu, Co$	502

Because of the poor stability of the selenoxanthate complexes, as well as selenothiophosphates (**76**) and selenothiophosphinates (**75**) little work beyond their isolation has been reported.

The selenothiocarbamate (**77**) complexes are substantially more stable, and spectroscopic data for some of these complexes have been reported. In addition, the complex $[Cu(SeSCNEt_2)_2]$ has been characterized by single-crystal X-ray diffraction[503]. This complex has a *trans*-$[CuS_2Se_2]$ square-planar coordination geometry. The single-crystal ESR spectrum of this complex has also been recorded[504,505].

The rather air-sensitive thioselenocarbamate salts are readily synthesized by reaction of carbon sulphide selenide with a secondary aliphatic amine in a 1:2 molar ratio[492] (equation 188).

$$2\,R_2NH + CSSe \rightarrow [H_2NR_2]^+[SeSCNR_2]^- \qquad (188)$$

Reaction of these salts with appropriate metal salts in aqueous or methanolic solutions gives the metal chelates (Table 36), which are generally air-stable. The Mn(II) and Co(II) salts oxidize during work-up to give the tris-chelates with the trivalent metals[493].

The stereochemistries of these complexes were investigated by the standard methods of coordination chemistry (e.g. electronic spectroscopy and magnetic susceptibility measurements). Because of the nuclear spin of $^{77}Se(I = 1/2$, natural abundance $= 7.58\%)$, ESR spectroscopy can provide useful information on electron density delocalization onto such ligands and therefore has been widely used to study the bonding[504,505] as well as ligand-exchange reactions in these and related Se ligands[480,493,506,507].

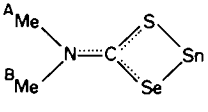
Although most of the complexes with selenothiocarbamates were prepared by metathetical reactions, a cleavage reaction involving coordinated Se was used to prepare a Sn(IV) complex[491] (equation 189).

$$3\,Me_2NC(S)Cl + [Me_2SnSe]_3 \xrightarrow{C_6H_6} 3\,Me_2ClSn(SSeCNMe_2) \qquad (189)$$

Repeated extraction of a benzene solution of this product with water gave the bis-chelate[491] (equation 190).

$$2\,Me_2ClSn(SSeCNMe_2) \rightarrow Me_2Sn[SSeCNMe_2]_2 + Me_2SnCl_2 \qquad (190)$$

The strong $\nu_{C\cdots N}$ bands in these complexes above $1500\,cm^{-1}$ (Table 37) and the ν_{Sn-Se} and ν_{Sn-S} bands in the $285-385\,cm^{-1}$ region all support a planar $SnSSeCNC_2$ arrangement:



Two Me resonances appear in the ^{1}H-NMR spectra of these complexes (Table 38), indicative of restricted rotation about the C—N bond. The broader lower-field signal is assigned to Me(A) *trans* to the Se atom, since stronger coupling with the ^{77}Se would be expected in this position.

Reaction of $Me_2ClSn(SeSCNR_2)$ (R = Me, Et) with $FeCl_3$ gave the pentacoordinate Fe(III) complexes $[FeCl(SeSCNR_2)_2]$. Characterization by electronic spectroscopy and magnetic susceptibility measurements indicated a square-pyramidal structure for these complexes. In contrast, reaction of $FeCl_3$ with $[Et_2NH_2][SeSCNEt_2]$ gave the tris-chelate[493].

An investigation of the electrochemistry of the chelates $[M(EE^1CNR_2)_2]$ ($E = E^1 = S$, Se; $E = S$, $E^1 = Se$; $R = C_6H_{11}$, Et, CH_2Ph)[497] in acetonitrile showed that the ease of oxidation followed the orders Cu > Ni and $Se_2 > SeS > S_2$.

TABLE 37. Infrared data (cm^{-1}) for some selenothiocarbamate complexes

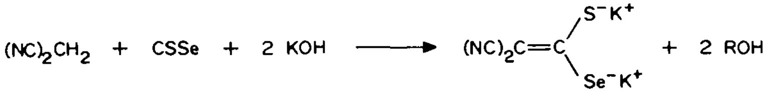
Complex	$\nu_{C=N}$	ν_{C-S}	ν_{C-Se}	Ref.
$Me_2ClSn(SeSCNMe_2)$	1538s	951s 935s	867w	491
$Me_2Sn(SeSCNMe_2)_2$	1511s	958s	861m	491
$Ni(SeSCNEt_2)_2$	1520s			492
$Pd(SeSCNEt_2)_2$	1515s			492
$Pt(SeSCNEt_2)_2$	1525s			492
$Fe(SeSCNEt_2)_3$	1495			493
$Co(SeSCNEt_2)_3$	1503			493
$Cr(SeSCNEt_2)_3$	1510			493
$Mn(SeSCNEt_2)_3$	1500			493
$Zn(SeSCNEt_2)_2$	1505			493
$Cd(SeSCNEt_2)_2$	1518			493
$Ni(SeSCNEt_2)_2$	1530			493
$Pd(SeSCNEt_2)_2$	1530			493
$Cu(SeSCNEt_2)_2$	1507			493
$Ag(SeSCNEt_2)$	1510			493
$Cl_2Au(SeSCNMe_2)$	1580s			494
$Cl_2Au(SeSCNEt_2)$	1570s			494
$Me_2Au(SeSCNMe_2)$	1545s			494
$Et_2Au(SeSCNMe_2)$	1530s			494
$(OC)_4Mn(SeSCNMe_2)$	1551			396
$(Ph_3P)ClPd(SeSCNMe_2)$	1553			496

TABLE 38. ^{1}H-NMR data for some selenothiocarbamate complexes

Complex	δ(—NR_2)	Ref.
$Me_2Sn(SeSCNMe_2)_2{}^a$	3.40, 3.37	491
$Me_2ClSn(SeSCNMe_2)^a$	3.38, 3.31	491
$Ni(SeSCNEt_2)_2{}^b$	CH_2: 3.65(q), 3.61(q) Me: 1.26(t), 1.23(t)	492
$Pd(SeSCNEt_2)_2{}^b$	CH_2: 3.77(q), 3.72(q) Me: 1.32(t), 1.29(t)	492
$Pt(SeSCNEt_2)_2{}^b$	CH_2: 3.60(q), 3.54(q) Me: 1.32(t), 1.29(t)	492
$Et_2Au(SeSCNMe_2)^b$	3.35, 3.37	494
$Me_2Au(SeSCNMe_2)^b$	3.31, 3.33	494

[a] In CH_2Cl_2.
[b] In $CHCl_3$.

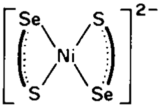
Complexes of several metals with the dianionic chelate isomaleonitrile–thioselenolate (*i*-mnts, **79**; Table 36) have been isolated. The ligand was prepared in good yields (80%) from malononitrile and CSSe[485] (equation 191).



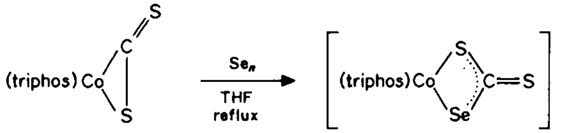
(191)

All of the reported complexes contain the transition metals in their normal oxidation state. In the case of the diseleno analogue **92**, a stable Ni(III) tris-chelate was isolated by oxidation of the Ni(II) precursor (Section II.D.2.c).

A single-crystal X-ray diffraction of $[(n\text{-Bu})_4N]_2[Ni(SeSC{=}C(CN)_2)_2]$ confirmed the proposed *trans* square-planar structure[485]:



Elemental Se inserts into Co—C bonds of η^2-CS_2 complexes to give new (S, Se) chelates[498] (equations 192 and 193). These facile insertion reactions were cited as evidence for the carbenoid nature of the metal–(η^2-CS_2) and metal–(η^2-CS_2Me) functions[480].

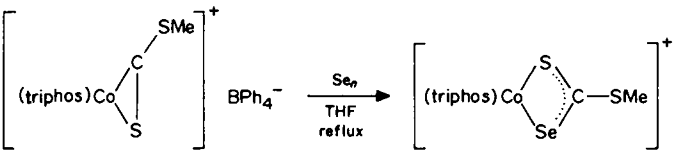


(192)

$\nu_{C-S} = 790\ cm^{-1}$

$\nu_{C=S} = 1040\ cm^{-1}$

$\mu_{eff}(293\ K) = 2.03$ B.M.



(193)

$\nu_{C-S} = 960\ cm^{-1}$

$\mu_{eff}\ (293\ K) = 2.10$ B.M.

The 1,2-selenothio dianion (**81**) (tbs) was prepared by the Na/liquid NH_3 reduction of *o*-methylthioselenoanisole[455,499]. Reaction of this anion with metal halides in ethanol solution gave the $[M(tbs)_2]^{2-}$ (M = Ni, Co, Cu) anions initially, but these oxidized in air to give the monoanionic complexes, which were isolated as their $(n\text{-Pr})_4N^+$ salts. Characterization of these complexes by magnetic susceptibility measurements and electronic spectroscopy indicated square-planar geometries. The polarographic half-wave reduction potentials were also measured as well as the ESR spectrum of the Ni salt. The latter suggested the presence of both *cis* and *trans* isomers at 100 K in DMF–$CHCl_3$ glass.

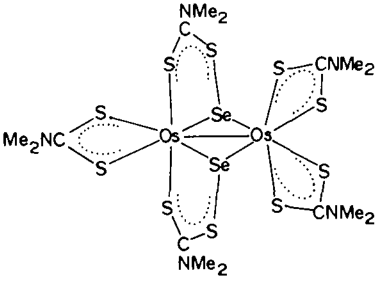
The first example of a selenodithiocarbamate chelating ligand was prepared recently[500] (equation 194).

$$[Os(S_2CNMe_2)_3] \xrightarrow[\text{2. }NaPF_6/\text{MeOH}]{\text{1. }Se_8/\text{DMF reflux}} [Os_2(\mu\text{-}SeS_2CNMe_2)_2(S_2CNMe_2)_3]PF_6 \qquad (194)$$

10%

$\nu_{C{=}N} = 1530\,cm^{-1}$

Single-crystal X-ray diffraction established an η^2,μ_2 bonding mode of the selenodithiocarbamate ligands with the dithiocarbamate ligands chelating in the usual manner (**85**)[500].

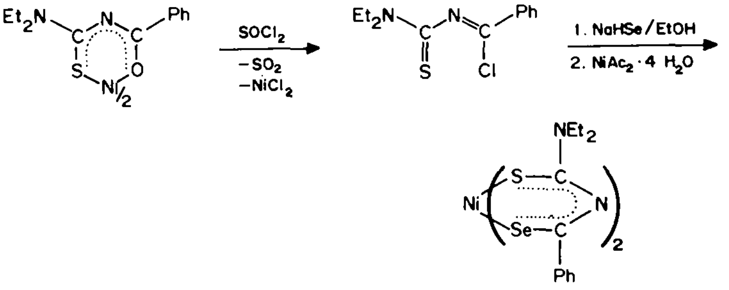


(85)

The structure is analogous to the previously characterized trithiocarbamate complex $[Os_2(S_3CNMe_2)_2(S_2CNMe_2)_3]PF_6$[508], although the synthesis of this complex (e.g. equation 194, reaction with elemental S) also gave a product $[Os_2(S_5)(S_3CNMe_2)(S_2CNMe_2)_3]$ with bridging S_5 and S_3CNMe_2 ligands[508].

The location of Se only in the bridging positions of **85** suggests a mechanism involving initial coordination of Se_8 or a lower fragment to $Os(S_2CNMe_2)_3$. A rich and interesting chemistry of complexes with such proposed Se_n ligands is being developed (Section II.G). Brief reports describe the synthesis of the 1,3-selenothio ligands, 1,1-diethyl-3-selenobenzoylthiourea (**83**)[501], 1-thioacyl-3-arylselenoureas (**84**)[502] and 3-selenobenzoylthioacetanilide[502] and some chelates of the deprotonated forms of these ligands (Table 36).

The Ni(II) chelate of 1,1-diethyl-3-selenobenzoylthiourea (**86**)[501] was prepared as shown in equation (195) without isolation of the neutral thiourea[509]. The highest nickel-containing fragment in the mass spectrum of this chelate is m/z 532, $[M - CSSe]^{+\cdot}$.

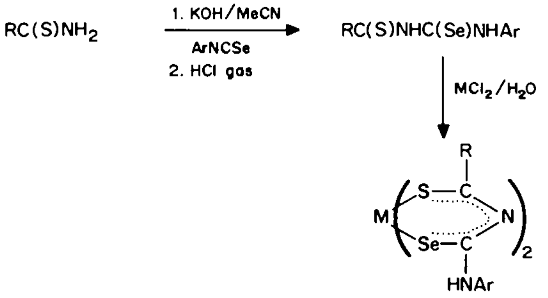


(195)

(86)

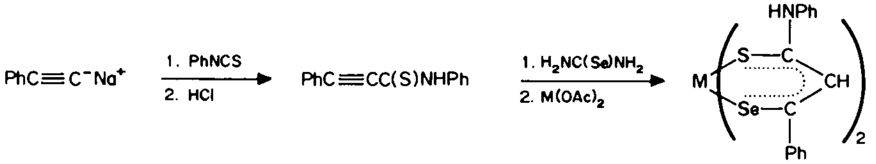
Brown-black crystals (EtOH)
m.p. 147–148 °C

The 1-thioacyl-3-arylselenourea chelates (**87**)[502] were prepared by addition of an aqueous metal chloride solution to a $CHCl_3$ solution of the freshly prepared selenourea (equation 196). The structurally related 2-selenobenzoylthioacetanilide chelates were prepared as shown in equation (197)[502].



(196)

(87)



(88) (197)

c. *(Se, Se)⁻ donors.* A variety of complexes incorporating anionic (Se, Se) chelating ligands have been described. Except for the dialkyl diselenocarbamates, the coordination chemistry of these ligands is relatively unexplored, although complexes of several of these types have been structurally characterized by single-crystal X-ray diffraction.

A variety of transition-metal and main-group dialkyldiselenocarbamates have been prepared (Table 39) since the original synthesis of dialkyldiselenocarbamate salts and some transition-metal derivatives by Barnard and Woodbridge[515] (equation 198). In these reactions the dialkyldiselenocarbamate salt solution is used immediately after its preparation.

$$\begin{tikzcd}
CSe_2 + R_2NH + NaOH \arrow[rr, "dioxane/H_2O", "N_2/-10\,^{\circ}C"'] & & Na[Se_2CNR_2] \arrow[d, "ZnSO_4/H_2O"] \\
Cu(Se_2CNR_2)_2 & & {[Zn(Se_2CNR_2)_2]} \arrow[ll, "CHCl_3"', "CuSO_4/H_2O"]
\end{tikzcd} \qquad (198)$$

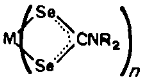
$R = Me, Et, n\text{-}Bu$

Jensen and coworkers, early investigators in Se ligand chemistry[17b], reported the first detailed study of the synthesis[510] and the infrared[511] and electronic[512] spectra of dialkyldiselenocarbamate complexes. These chelates readily precipitated from solution by the procedure of equation (198), although in this work the $Et_2NH_2[Se_2CNEt_2]$ salt was isolated by carrying out the reaction in ether and then dissolving it in 0.5M NaOH for the subsequent reactions with aqueous solutions of the metal salts[510]. The resulting air-stable chelates can be recrystallized unchanged from organic solvents (e.g. $CHCl_3$)[510] and have d–d transition bands red-shifted vs. the analogous dithiocarbamates[512].

The most characteristic infrared bands of these complexes (Table 40) are the $\nu_{C\cdots N}$ (ca. $1500\,cm^{-1}$) and the ν_{C-Se} (800–$900\,cm^{-1}$) absorptions, the latter showing more dependence on the nature of the alkyl groups than the former[511]. The location of the $\nu_{C\cdots N}$ band was also dependent on the stereochemistry of the metal complex: square-planar (Ni,

TABLE 39. Dialkyldiselenocarbamate complexes

Complex



$n = 1$
M = Tl; R = $Et^{510-512}$
M = Ag; R = Et^{513}
M = Cu; R = Et^{514}
$n = 2$
M = Zn; R = Me, Et, *n*-Bu^{515}
M = Cu; R = $Et^{514,515}$
M = Zn, Ni, Pd, Pt; R = Et, *i*-$Bu^{516-519}$
M = Ni, Cu, Zn; R = Et[520a]
M = Ni, Pd, Pt, Cd; R = Et^{510}
M = Ni, Pd; R = Et^{521}
M = Co; R_2 = morpholino[521]
M = Ni, Pd, Pt, Cu; $R_2 = (CH_2CH_2)_2X$
(X = CH_2, O, S)[522]
M = Ni, Cu; R = Et, CH_2Ph, C_6H_{11}[497]
$n = 3$
M = As, Sb, Bi[523]
M = In, Tl, Cr, Rh; R = Et^{510}
M = Co, Cr; R = Et^{521}
M = Co; R = Et^{516}
M = Co, Cr, Fe; $R_2 = (CH_2CH_2)_2X$
(X = CH_2, O, S)[524]
$n = 4$
M = Ti, V; R = Et^{525}
M = Pt; R = *i*-Bu^{516}

Complex

$Se(Se_2CN(CH_2CH_2)_2)_2$[526a]
$Pt(Se_2CN(Bu\text{-}i)_2)_2$[516a,518,519,527]
$Pt(Se_2CN(Bu\text{-}i)_2)(PPh_3)Me$[517a,518,519]
$Pt(Se_2CN(Bu\text{-}i)_2)_2(PPh_3)$[518,519,527]
$M(Se_2CNEt_2)(Cl)(PEt_3)$[405,516,519]
M = Ni, Pd, Pt
$[M(Se_2CNR_2)_3]BF_4$
M = Ni, Fe, Mn; R = Et^{528}
M = Fe; R = Et, CH_2Ph[a]; R_2
= $(CH_2CH_2)_2X$ (X = O, NH)[529]
$[Ni(Se_2CN(Bu\text{-}n)_2)_3]Br$[530]
$Cu(Se_2CNEt_2)_2I_3$[514]
$[Pt(Se_2CN(Bu\text{-}i)_2)_2X_2]$[518]
X = Br, I

---

[a] Characterized by single-crystal X-ray diffraction.

TABLE 40. Infrared data (cm^{-1}) for dialkyldiselenocarbamate complexes

Complex	$\nu_{C=N}$	ν_{C-Se}	Ref.
$Ni(Se_2CNMe_2)_2$	1550vs	890	511
$Co(Se_2CNMe_2)_2$	1528vs	900	511
$Mn(CO)_4(Se_2CNMe_2)$	1537		396
$[Fe(Se_2CNEt_2)_3]BF_4$	1525vs		528
$[Fe(Se_2CN(CH_2Ph)_2)_3]BF_4$	1510vs		529
$Cu(Se_2CNEt_2)$	1489		514
$Cu(Se_2CNEt_2)_2$	1500		514
$Cu(Se_2CNEt_2)_2I_3$	1535		514
$Pt(Se_2CNC_5H_{10})_2$[a]	1510vs		522
$Pd(Se_2CNC_5H_{10})_2$[a]	1500vs		522
$Zn(Se_2CNC_5H_{10})_2$[a]	1480vs		524
$Fe(Se_2CNC_5H_{10})_3$[a]	1480		524
$Cr(Se_2CNC_5H_{10})_3$[a]	1488		524

---

[a] NC_5H_{10} = piperidyl.

Cu, Pd, Pt; 1510–1525 cm^{-1}) > tetrahedral (Zn, Cd; 1502–1506 cm^{-1}) > octahedral (Cr, Co, Rh, In, Tl; 1495–1500 cm^{-1}).

The Fe(II) and Co(II) complexes, like the analogous dithiocarbamates, readily react with NO to give $M(Se_2CNEt_2)_2(NO)$, with characteristic strong $\nu_{N=O}$ bands (Co, 1623 cm^{-1}; Fe, 1682 cm^{-1}).

$Ni(Se_2CNEt_2)_2$, again like the dithiocarbamate analogue, reacts with bromide to give the black $Ni(Se_2CNEt_2)_2Br_2$, a formally Ni(IV) complex[510].

The electronic spectra of $CHCl_3$ solutions of these chelates are unchanged on addition of pyridine, indicating the retention of the original coordination spheres in such a solvent system. In contrast, the red $CHCl_3$ solution of the square-planar $Ni(Se_2COEt)_2$ turns yellow on addition of pyridine as a result of formation of the octahedral complex $Ni(Se_2COEt)_2(pyr)_2$, which presumably has the pyridine ligands in the axial positions[510].

The monomeric complex $[Mn(CO)_4(Se_2CNMe_2)]$ undergoes solid-state thermolysis to form the diselenocarbamate-bridged dimer, $(OC)_3Mn(\mu\text{-}Se_2CNMe_2)_2Mn(CO)_3$[396] (e.g. see equation 144). The $\nu_{C\cdots N}$ band of this bridged dimer (1540 cm^{-1}) differs little from that of the monomer (Table 40).

Fackler and coworkers prepared a large number of dialkyldiselenocarbamate complexes[516–519,527] and their characterization of these included ^{77}Se-NMR spectroscopy[518,527] as well as single-crystal X-ray diffraction for $Pt(Se_2CN(Bu\text{-}i)_2)_2$[516], $Pt(Se_2CNEt_2)(PPh_3)(Me)$[517], $Pt(Se_2CNEt_2)(PPh_3)(Cl)$[519] and $Ni(Se_2CNEt_2)(PPh_3)(Cl)$[519].

Diselenocarbamates, like dithiocarbamates, stabilize metal complexes in high formal oxidation states (e.g. Ni(IV)[479,528–530], Cu(III)[479,514], Fe(IV)[528,529]). The structures of the Ni(IV) complex, $[Ni(Se_2CN(Bu\text{-}n)_2)_3]Br$[530], and the Fe(IV) complex, $[Fe(Se_2CN(CH_2Ph)_2)_3]BF_4$[529], were determined by single-crystal X-ray diffraction.

The complex $[Ni(Se_2CN(Bu\text{-}n)_2)_3]$ Br contains an octahedral arrangement of Se atoms about the Ni(IV) centre (Ni—Se = 2.391(5) Å)[530]. The complex $[Fe(Se_2CN(CH_2Ph)_2)_3]BF_4$ has a D_3 macrosymmetry with the $FeSe_6$ coordination core having six Se atoms at the apices of a coordination polyhedron intermediate between the idealized trigonal prismatic and trigonal antiprismatic geometries[529]. Infrared, ESR and Mössbauer spectral data as well as the magnetic susceptibility are all consistent with Fe(IV), but the XPS data (Fe $2P_{3/2}$ binding energy = 708.1 eV) indicate the presence of Fe(II)[529]. The latter problem of *in situ* photoreduction of inorganic compounds involving metal ions in high oxidation states has been observed in a number of other cases.

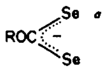
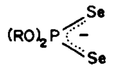
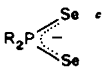
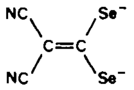
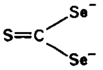
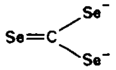
The other types of 1,1-diseleno ligands and their metal complexes are summarized in Table 41. Only a few reports have described complexes of 1,1-diseleno ligands of the type XSe_2^- (X = ROC, $(RO)_2P$, R_2P) (Table 41).

The complex $Ni(Se_2COEt)_2$ was prepared by the addition of an aqueous solution of $NiCl_2 \cdot 6H_2O$ to a cold solution of freshly prepared KSe_2COEt (from $KOH/CSe_2/EtOH$)[510]. The complex, which immediately precipitated, was isolated by extraction with $CHCl_3$. A dark red $CHCl_3$ solution of this complex instantly became yellow on addition of pyridine[510]. This behaviour was attributed to the conversion of the low-spin square-planar complex to the high-spin octahedral $[Ni(Se_2COEt)_2(pyr)_2]$[510].

Sodium diethyldiselenophosphinate was obtained by the multistep route shown in equation (199).

$$\begin{aligned}
&\mathrm{Et_2P(S)P(S)Et_2} \xrightarrow[-\mathrm{PCl_3}]{\mathrm{PCl_5/CCl_4/80\,^{\circ}C}} \mathrm{Et_2P(S)Cl}\\
&\xrightarrow[-(n\text{-}\mathrm{Bu})_3\mathrm{PS}]{(n\text{-}\mathrm{Bu})_3\mathrm{P}/150\,^{\circ}\mathrm{C}} \mathrm{Et_2PCl} \xrightarrow{\mathrm{Se}} \mathrm{Et_2P(Se)Cl} \qquad (199)\\
&\xrightarrow[-\mathrm{NaCl}]{2\,\mathrm{NaSeH/EtOH}} \mathrm{Et_2P(Se)Se^-Na^+}
\end{aligned}$$

TABLE 41. Complexes with miscellaneous 1,1-diseleno ligands

Ligand	Complex	Reference
 [a] (89)	$M(Se_2COC_{12}H_{25}\text{-}n)_2$ M = Co, Ni, Zn, Fe, Cu	513
	$Cu(Se_2COEt)_2$	513
	$Ni(Se_2COEt)_2$	510
 [b] (90)	$M(Se_2P(OEt)_2)_3$ M = Cr, Rh, Ir	531
	$M(Se_2P(OEt)_2)_n$ n = 1; M = Tl n = 2; M = Pb, Sn n = 3; M = As, Sb, Bi, In	532
	n = 3; M = Cr	533
	$Ni(Se_2P(OEt)_2)_2$	534[g]
 [c] (91)	$M(Se_2PEt_2)_n$ n = 1; M = Tl n = 2; M = Zn, Cd, Pb, Pd n = 3; M = Bi, In	535
	$Ni(Se_2PPh_2)_2$	536[g]
 [d] (92)	$(Ph_4P)_n[M(Se_2C{=}C(CN)_2)_2]$ n = 1; M = Au n = 2; M = Ni, Zn, Cd, Pt, Cu n = 3; M = Co, Rh, Cr	537
	$(Ph_4As)_2[Ni(Se_2C{=}C(CN)_2)_3]$	538, 539[g]
 [e] (93)	$Cp(Me_3P)CoSe_2C{=}Se$	224
 [f, h] (94)	$Cp(Me_3P)CoSe_2C{=}S$ $Cp(Me_2PhP)CoSe_2C{=}S$	224

[a] Diselenoxanthate.
[b] Diorganodiselenophosphate.
[c] Diorganodiselenophosphinate.
[d] Isomaleonitrilediselenolate.
[e] Triselenocarbonate.
[f] Diselenothiocarbonate.
[g] Structure characterized by single-crystal X-ray diffraction.
[h] A complex with (Se, S) coordination of this ambidentate ligand has also been reported (equation 192).

Stable colourless crystals of the hydrate $Et_2P(Se)SeNa \cdot 2H_2O$ were obtained by addition of ligroin to an acetone/water (95:5 v/v) solution of the above product[535]. Complexes (Table 41) readily precipitated from aqueous solutions of the appropriate metal halides by addition of $Et_2P(Se)SeNa \cdot 2H_2O$[535].

Several diethyldiselenophosphate (**91**) complexes (Table 41) were isolated by a similar route[531,532] (equation 200). Because of the instability of the potassium salt, the chelates were generally prepared by addition of the appropriate metal chloride to a freshly prepared solution of the former. The resulting complexes have good stability (e.g. $Cr(Se_2P(OEt)_2)_3$ can be recrystallized from hot EtOH to give air-stable black crystals[533]).

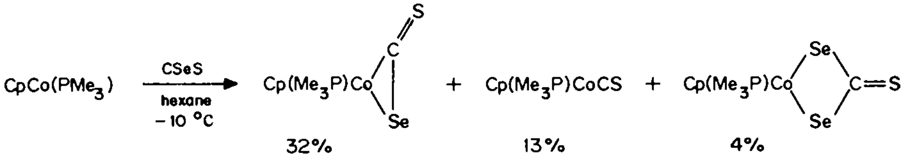
$$4\,\mathrm{EtOH} + \mathrm{P_2Se_5} \rightarrow 2\,\mathrm{(EtO)_2P(Se)SeH} + \mathrm{H_2Se}$$

$$\xrightarrow{\mathrm{KOH/EtOH}} \mathrm{KSe(Se)P(OEt)_2} \xrightarrow[-n\,\mathrm{KCl}]{\mathrm{MCl}_n} \mathrm{M(Se_2P(OEt)_2)}_n \qquad (200)$$

A complex of isomaleonitrilediselenolate (**92**) with nickel in the formal + 4 oxidation state was prepared by oxidation of the Ni(II) chelate[538] (equation 201). The oxidation product was isolated as the Ph_4As^+ salt in the form of black needles. The other products of this reaction, which involves both oxidation and increase in the coordination number of the Ni, were not characterized[538]. A distorted octahedral coordination of the six Se atoms about the Ni atom has been established for this complex by single-crystal X-ray diffraction (average Ni—Se distance = 2.387(1) Å)[539]. The ligands are planar, and the C=C (1.36 Å) and C≡N (1.15 Å) distances suggest that the stabilization of the Ni(IV) chelate does not result from an extended delocalization of charge on the ligands, but the oxidation should rather be described as loss of electrons from the $NiSe_6$ function exclusively[539].

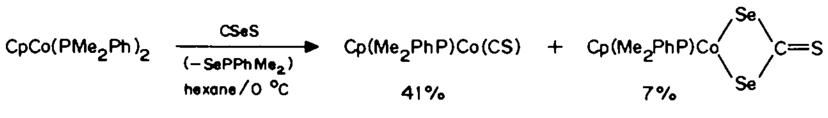
$$[\mathrm{Ni(Se_2C{=}C(CN)_2)_2}]^{2-} \xrightarrow{\mathrm{I_2/MeCN}} [\mathrm{Ni(Se_2C{=}C(CN)_2)_3}]^{2-} \qquad (201)$$

Low yields of diselenothiocarbonate (equations 202 and 203) and triselenocarbonate (equation 204) were obtained by column chromatography of the products obtained in reactions of Co(I) complexes with CSeS and CSe_2, respectively[224].



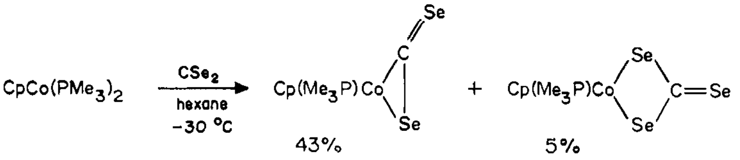
(202)

m.p. 122 °C dec.
$\nu_{C=S}$ (KBr) = 1007 cm^{-1}
ν_{C-Se} (KBr) = 812 cm^{-1}
^{1}H-NMR (δ, acetone-d_6): 5.25 (d, Cp), J_{PH} = 0.3 Hz; 1.75 (d, Me), J_{PH} = 10.8 Hz



(203)

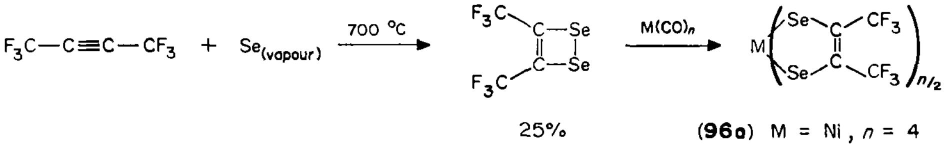
m.p. 136 °C dec.
$\nu_{C=S}$ (KBr) = 1018 cm^{-1}
ν_{C-Se} (KBr) = 825 cm^{-1}
^{1}H-NMR (δ, acetone-d_6): 5.05 (d, Cp), J_{PH} = 0.3 Hz; 1.90 (d, Me), J_{PH} = 10.6 Hz; 7.76 (m, Ph)


(204)

$\nu_{C=Se}$ (KBr) = 879 cm^{-1}
ν_{C-Se} (KBr) = 810 cm^{-1}
^{1}H-NMR (δ, C_6D_6): 5.30 (d, Cp), J_{PH} =
0.4 Hz; 1.67 (d, Me), J_{PH} = 11.2 Hz

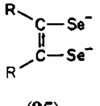
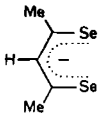
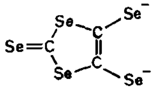
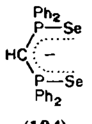
As discussed in Section II.A.7, the η^2-CSeS and η^2-CSe_2 complexes readily undergo PPh_3-induced Se extrusion reactions to give the corresponding Co—CS and Co—CSe complexes under more forcing reaction conditions (e.g. 50 °C)[224].

Only two types of 1,2-diseleno ligands have been reported (Table 42). Davison and Shaw[540] prepared 1,2-diseleno chelates by oxidative addition reactions of metal carbonyls and bis(trifluoromethyl)-1,2-diselentene (equation 205).


(**96a**) M = Ni, n = 4
(**96b**) M = Mo, n = 6
(**96c**) M = W n = 6

(205)

TABLE 42. Complexes with 1,2- and 1,3-diseleno-type anionic ligands

Ligand	Complex	Ligand	Complex
1,2-*Type*		1,3-*Type*	
 [a] (95)	**96a–c**[540] **96b**[541] [b] **98**, **99**[542]	 [d] (102)	(**103**)[543,544]
 [c] (100)	**101**[27]	 [e] (104)	(**105**)[545]

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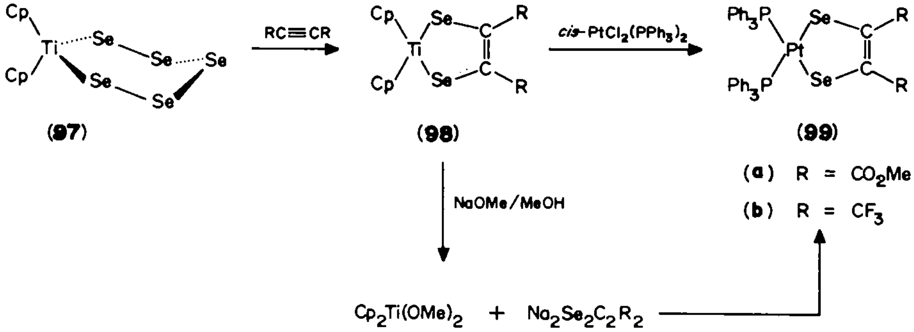
[a] *cis*-1,2-Di(organo)ethylene-1,2-diselenato.
[b] Structure characterized by single-crystal X-ray diffraction.
[c] 2-Selenoxo-1,3-diseleno-4,5-diselenato.
[d] Diselenoacetylacetonato.
[e] Methinotetraphenyldiselenodiphosphino.

The crystal structure of tris(*cis*-1,2-di(trifluoromethyl)ethylene-1,2-diselenato)-molybdenum (**96b**) established a trigonal prismatic arrangement of six Se atoms about the Mo[541]. The relatively short interligand Se····Se distances (3.222(3) Å) compared with the intraligand value of 3.317(5) Å was suggested to indicate a significant interligand Se····Se interaction, which is important in the stabilization of the relatively unusual trigonal prismatic coordination of this hexacoördinate complex.

Bolinger and Rauchfuss[542] recently described the synthesis of the similar 1,2-diseleno chelates **98** and **99** (equation 206). This route, via the readily prepared Cp_2TiSe_5 (**97**) reagent[542], offers considerable advantage over the reaction of Se vapour at high temperature to give the diselentene (equation 205).

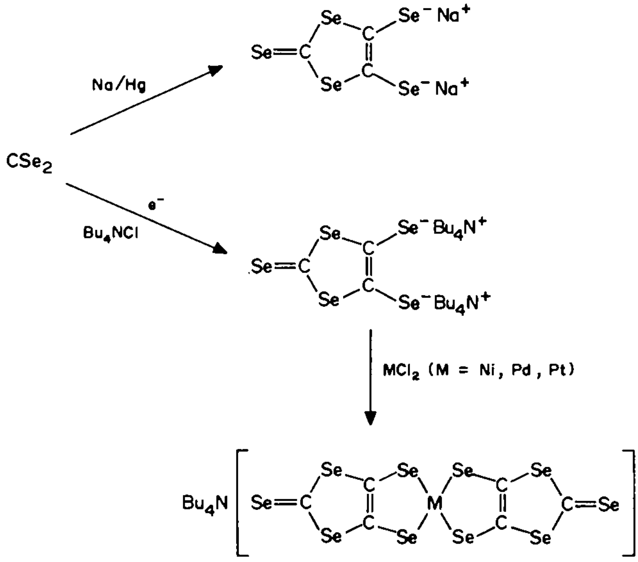


(97) **(98)** **(99)**

(**a**) R = CO_2Me
(**b**) R = CF_3

(206)

Chemical or electrochemical reductive coupling of CSe_2 has also provided 1,2-diseleno anions, which react with various metal salts to give the corresponding square-planar bis-chelates[27] (equation 207).

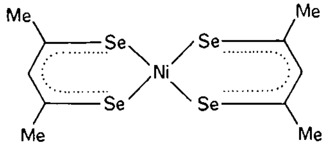


(207)

(101)

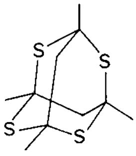
Ligands of the 1, 3-diseleno type are also restricted to two structural types (**102** and **104**; Table 42).

The diamagnetic square-planar Ni(II) complex (**103**) with the chelating ligand diselenoacetylacetonate (**102**) was prepared by passing H_2Se into an acidified ethanol solution of acetylacetone containing $NiCl_2$[543,544].



(103)

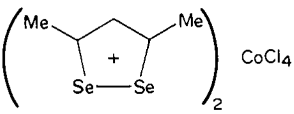
In the absence of the metal salt the reaction presumably gave the dimer of diselenacetylacetone, as has been confirmed by NMR and mass spectroscopy for the reaction of acetylacetone and H_2S in HCl-saturated ethanol (i.e. the product is **106**[544]).



(106)

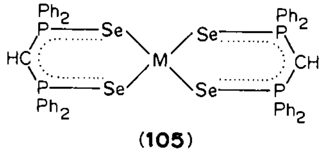
The dark red-brown Ni(II) complex is moderately stable in the solid state at room temperature but slowly decomposes over several weeks. Its thermal instability (decomposes > 120 °C) has precluded the recording of its mass spectrum. It is less stable in solution, but it can be recrystallized from hot $CHCl_3$ if done rapidly to prevent the deposition of elemental Se. The square-planar formulation is supported by its diamagnetism and the similarity of its infrared spectrum with that of the bis-dithioacetylacetonate complex of Co(II), which has been characterized by single-crystal X-ray diffraction[546].

Attempts to prepare the Co(II) complex of **102** by a similar procedure gave the tetrachlorocobaltate(II) salt of the 3,5-dimethyl-1,2-diselenolium cation **107**.



(107)

The chelating ligand **104** was prepared by selenation of $(Ph_2P)_2CH_2$ with KSeCN in acetonitrile followed by deprotonation with *n*-BuLi in THF at $-70\,^\circ C$[545]. Reaction of solutions of the lithium salt with $(Et_4N)_2[MBr_2X_2]$ ($M = Fe, Co, X = Cl; M = Ni, X = Br$) gave the neutral bis-chelates **105** after evaporation of the reaction solution and extraction with hot toluene[545].

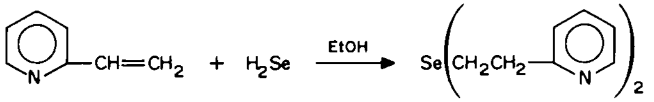


(105)

Electronic spectroscopy and magnetic moment measurements (Fe(II), $\mu_{eff} = 5.33$ B.M.; Co(II), $\mu_{eff} = 4.68$ B.M.; Ni(II), diamagnetic) support tetrahedral geometries for the Fe and Co complexes and a square-planar configuration for the Ni complex[545].

E. Tridentate Ligands

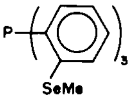
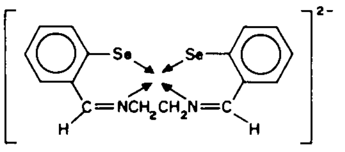
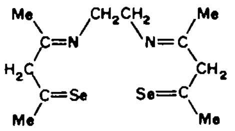
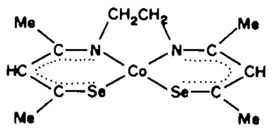
The two reported examples of tridentate Se ligands are of the SeN_2 hybrid type (**108**, **109**). Bis(β-(2-pyridyl)ethyl) selenide (bpes, **108**) was prepared according to equation (208)[547]. Several 1:1 complexes of Cu(II) were formed with this ligand in ethanolic or aqueous solution (Cu(bpes)X_2; X = Cl, Br, NO_3, ClO_4)[547].



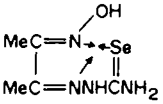
(208)

(108)

TABLE 43. Complexes with tetradentate Se ligands

Ligand	Complex	Ref.
Se_4 Donor set		
$MeSe(CH_2)_2Se(CH_2)_3Se(CH_2)_2SeMe$ 1,3-Bis(methylselenoethylseleno) propane (bsep)	$[Pd_2(bsep)X_4]$ X = Cl, Br, I	549
Se_3P Donor set		
 Tris(*o*-methylselenophenyl)phosphine (TSeP)	$[Ni(TSeP)X]ClO_4$ X = Cl, Br, I, NCS $[Ni(TSeP)_2](ClO_4)_2$	550
Se_2N_2 donor sets		
 α,α′-(Ethylenedinitrilo)di-*o*-tolueneselenolato	$[Ni(Se_2N_2)]$	462, 463
 *N*,*N*′-Ethylenebis(monoselenoacetylacetonimine) (seacn-H_2)	 $[Co(seacn)_2]$	551

The other ligand of this type, diacetylselenosemicarbazone oxime (**109**), was prepared by the reaction of diacetyl monoxime and acetone selenosemicarbazone in aqueous ethanol[548]. Complexes with Cu(II) involving coordination of the neutral ligand ($CuX_2(H_2dso)$; X = Cl, Br), the monoanionic form (CuX(Hdso); X = Cl, Br), and the dianionic form ($Cu(dso)\cdot\frac{1}{2}H_2O$), have been isolated[548]. The coordination sites indicated in **109** are based on the similarity of the X-ray powder patterns of these complexes with those of the analogous diacetylthiosemicarbazone oxime complexes, for which these bonding sites have been established. The complexes with the neutral form of the ligand crystallize from methanol solutions of the cupric halide and the ligand, and the ionized forms of the ligand are generated by addition of NaOAc to the reaction solution. These Cu(II) complexes resist reduction to Cu(I) even in boiling solution.

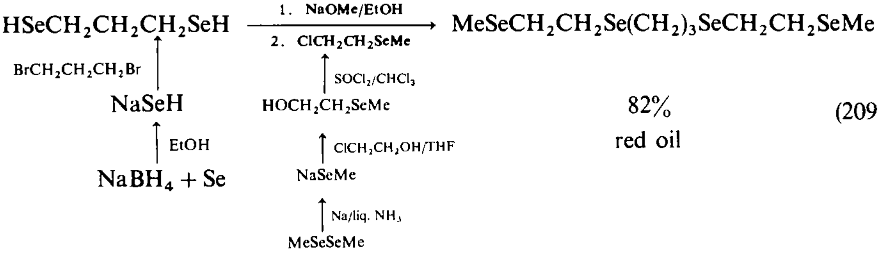


H_2dso, (**109**)

F. Tetradentate Ligands

Tetradentate ligands with Se_4, Se_3P and Se_2N_2 donor sets have been reported (Table 43).

The open-chain tetraseleno ether 1,3-bis(methylselenoethylseleno)propane (bsep) was prepared according to equation (209)[549]. In attempts to prepare the analogous ethylene diselenol intermediate, $HSeCH_2CH_2SeH$, by this route, H_2Se was evolved, presumably by reaction (210). Attempts to distil bsep gave decomposition, and the material was simply heated under vacuum to remove impurities. Characterization of the ligand was limited to ^1H-NMR: δ 2.1 (s, Me), 2.7 (m, $(CH_2)_3$), 3.0 (m, $-CH_2-$).



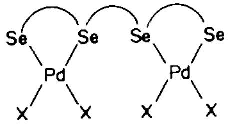
$$\begin{tikzcd}
HSeCH_2CH_2CH_2SeH \arrow[r, "1.\ \text{NaOMe/EtOH}", "2.\ ClCH_2CH_2SeMe"'] & MeSeCH_2CH_2Se(CH_2)_3SeCH_2CH_2SeMe \\
NaSeH \arrow[u, "BrCH_2CH_2CH_2Br"] & HOCH_2CH_2SeMe \arrow[u, "SOCl_2/CHCl_3"'] \\
NaBH_4 + Se \arrow[u, "EtOH"'] & NaSeMe \arrow[u, "ClCH_2CH_2OH/THF"'] \\
 & MeSeSeMe \arrow[u, "\text{Na/liq. }NH_3"']
\end{tikzcd}$$

82%
red oil

(209)

$$2\,NaSeH + BrCH_2CH_2Br \rightarrow \{HSeCH_2CH_2SeH\} \xrightarrow{-\,C_2H_4} \{HSeSeH\} \rightarrow H_2Se + Se \qquad (210)$$

Reaction of bsep with Na_2PdX_4 (X = Cl, Br, I) in $EtOH/CHCl_3$ gave immediate precipitates of $[Pd_2(bsep)X_4]$ regardless of the molar ratios of the reactants[549]. The chloro complex had ν_{Pd-Cl} bands at 312 and 308 cm^{-1}, characteristic of a *cis* terminal $PdCl_2$ group, and all three complexes gave electronic reflectance spectra characteristic of a $PdSe_2X_2$ square-planar chromophore. Dimeric structures with bridging seleno ether ligands were proposed on the basis of this spectroscopic evidence:



The insolubility, magnetic moment (2.98 B.M.), and electronic reflectance spectrum of $Ni_2(bsep)I_4$ suggest an octahedral polymeric complex with bridging iodo and bsep ligands[549].

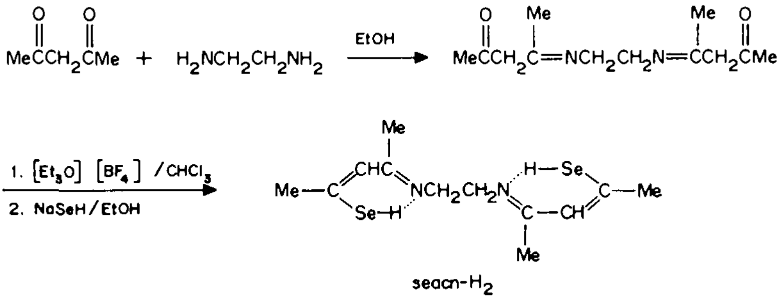
The Se_3P hybrid ligand, tris(*o*-methylselenophenyl)phosphine (TSeP), was synthesized in 7% yield as colourless air-stable crystals[550] (equation 211). This ligand forms intensely blue, paramagnetic Ni(II) complexes, $[Ni(TSeP)X]ClO_4$ (X = Cl, Br, I, NCS)[550]. The molar conductances of these complexes in nitromethane solution support their formulation as 1:1 electrolytes ($\Lambda_M = 80\text{–}90\,cm^2\,ohm^{-1}\,M^{-1}$), and their electronic spectra are characteristic of trigonal-bipyramidal structures. With the weakly coordinating perchlorate anion a 2:1 electrolyte-type complex, $[Ni(TSeP)_2](ClO_4)_2$, was obtained. The structure of this complex was not determined.

$$o\text{-BrC}_6H_4NH_2 \xrightarrow[2.\ KSeCN]{1.\ H_2SO_4,\ NaNO_2} o\text{-BrC}_6H_4SeCN \xrightarrow[2.\ KOH]{1.\ MeI/EtOH} \tag{211}$$

$$o\text{-BrC}_6H_4SeMe \xrightarrow[Et_2O,\ 0^\circ C]{n\text{-BuLi}} o\text{-MeSeC}_6H_4{}^-\ Li^+ \xrightarrow[Et_2O]{PCl_3} \underset{\text{(TSeP)}}{(o\text{-MeSeC}_6H_4)_3P}$$

A diamagnetic, square-planar nickel(II) chelate of the Se_2N_2 tetradentate Schiff base derived from selenosalicylaldehyde and ethylenediamine (Table 43) was prepared by the template reaction previously described for related bidentate (Se, N) chelates (equation 182). The dipole moment of this complex (7.28 D in $CHCl_3$) is consistent with the *cis* geometry imposed by the tetradentate structure of the macrocycle[551].

A tetradentate seleno Schiff base derived from acetylacetone has also been reported[551] (equation 212).



(212)

$$MeC(=O)CH_2C(=O)Me + H_2NCH_2CH_2NH_2 \xrightarrow{EtOH} MeC(=O)CH_2C(Me)=NCH_2CH_2N=C(Me)CH_2C(=O)Me$$

A detailed ESR study of the Co(II) chelate prepared by reaction of the neutral seleno Schiff base with $Co(OAc)_2$ adduct in frozen CH_2Cl_2 has been reported[551].

G. Complexes Incorporating Se_n

The synthesis of metal complexes with terminal Se^{2-} ligands dates back to the early part of the century (e.g. 1927, $(NH_4)_2[WSe_4]$)[552]. The chemistry of selenometallates has been the subject of several reviews[553]. Within the past few years a number of novel

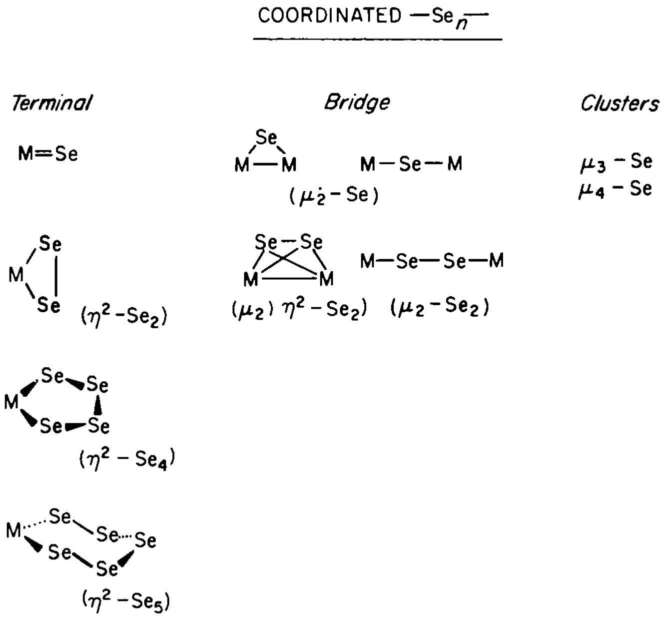


FIGURE 11. Bonding modes of coordinated Se_n

molecular complexes incorporating Se_n (n = 1, 2, 4, 5; Figure 11) have been prepared, and the reactivity of such coordinated Se ligands has been investigated.

In addition to having an interesting chemistry of their own, recent work suggests that such complexes may have considerable utility as precursors of various other organoselenium ligand systems.

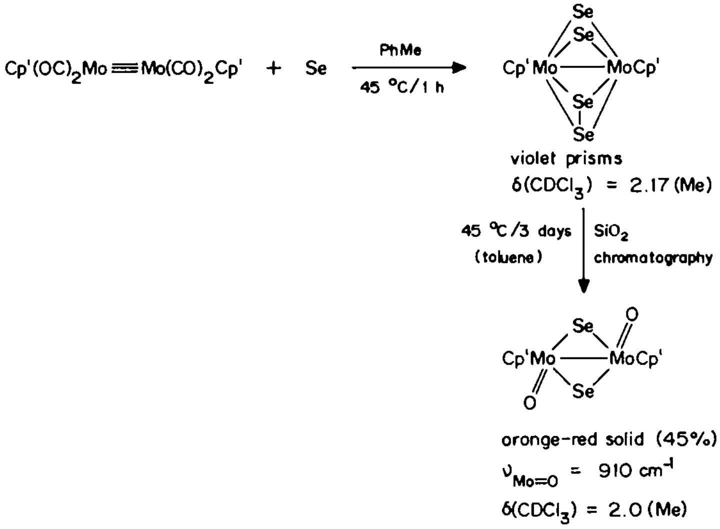
1. μ_2-Se ligand

The complex $(Me_3P)_2(OC)_3Re—Se—Re(CO)_3(PMe_3)_2$[370] (Figure 4) was the first structurally characterized complex containing a bridging Se atom. Since this initial report, several dimeric complexes with bridging Se atoms have been prepared by insertion reactions of elemental Se into metal–metal bonds[554–556]. The complex $CpCo(\mu\text{-}PMe_2)_2(\mu\text{-}Se)CoCp$ was prepared in 55% yield by such a route (equation 134). This general reaction has provided a route to related Mo, W and Rh Se-bridged dimers (equations 213–215).

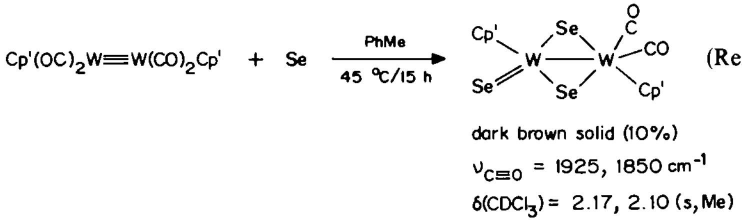
Complexes with labile ligands react with elemental Se (equation 166) or COSe (equation 216) to give Se-bridged dimers.

The μ_2-Se complex was obtained in only small yield from the initial reaction (ca. 10:1 μ_2-Se_2 : μ_2-Se products) but was obtained in high yields by extrusion of a Se atom from the μ_2-Se_2 dimer with triphenylphosphine[557]. The presence of a Mn—Mn bond in the μ_2-Se complex was proposed by analogy with related complexes (e.g. $[Cp''(OC)_2Mn]_2CH_2$ and $[Cp(OC)_2Mn]_2CHR$). The crystal structure of the μ_2-Se complex was reported in the same paper[557].

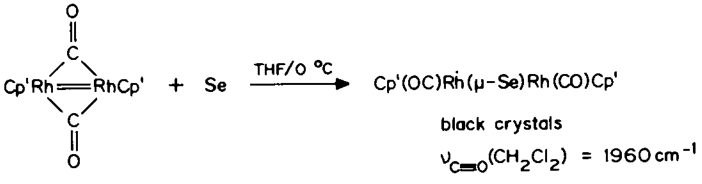
These two dimers, identical with those isolated by the route of equation (166), were separated by low-temperature (−20 °C) chromatography on SiO_2.



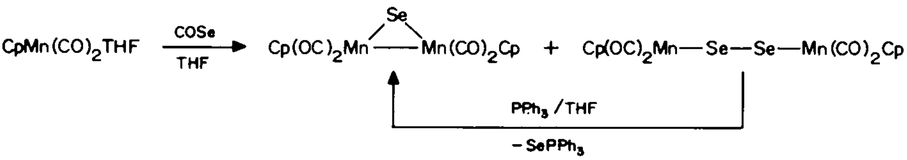
(Ref. 555) (213)



(Ref. 555) (214)



(Ref. 556) (215)



(Ref. 557) (216)

Redox reactions of organometallic anions and sodium selenite have provided another route to Se-bridged dimers (equations 217 and 218).

$$\mathrm{Na^+\,[Cp'Cr(CO)_3]^-} \xrightarrow[\mathrm{HCl}]{\mathrm{Na_2SeO_3}} \mathrm{Cp'(OC)_2Cr{\equiv}Se{\equiv}Cr{\equiv}(CO)_2Cp'}$$

(Ref. 558) (217)

$$Na^+[V(CO)_4(dppe)]^- \xrightarrow[H_3PO_4]{Na_2SeO_3/H_2O} [(OC)_3(dppe)V{\equiv}Se{\equiv}V(dppe)(CO)_3] \qquad (218)$$

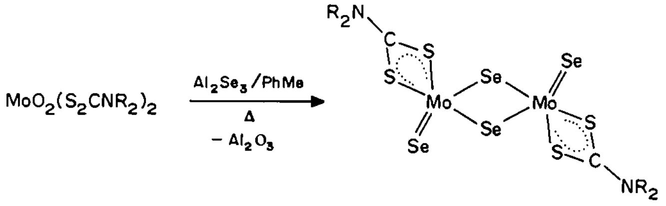
$$25\% \qquad \text{(Ref. 559)}$$

$$\nu_{C\equiv O}(CH_2Cl_2)\text{: 1980, 1930s}$$
$$\text{1885vs, 1852vs}$$

The crystal structure of $[V(CO)_3(dppe)]_2S$ (e.g. S analogue of product of equation 218) revealed a very short V—S bond (2.172 Å vs. normal single-bond values of ca. 2.30 Å). A bond order between 2 and 3 is suggested for these linear $V{\equiv}E{\equiv}V$ (E = S, Se, Te) dimers[559].

Reaction of some of these Se-bridged dimers with diazomethane is a convenient route to μ,η^2-selenoformaldehyde complexes[554,558] (e.g. equation 166).

The high oxophilicity of Al(III) has been used to form metal–Se bonds in equation (219)[560]. The dimeric formulation was assigned on the basis of magnetic and infrared spectral data and by analogy with the S analogue, which has been unequivocally characterized by single-crystal X-ray diffraction.



(219)

R = Me, Et

R_2 = pyrrolidinyl, morpholinyl

$\nu_{Mo=Se} = 360\,cm^{-1}$

$\nu_{Mo-Se-Mo} = 250\,cm^{-1}$

Detailed resonance Raman and infrared spectroscopic studies[561] of the dimeric $[(PhE)_2Fe(\mu_2\text{-}Se)_2Fe(EPh)_2]^{2-}$ (E = S, Se) and $[(o\text{-}C_6H_4(CH_2S)_2Fe(\mu_2\text{-}Se)_2Fe(SCH_2)_2C_6H_4\text{-}o)]^{2-}$ and an ESR study[562] of their reduced forms have been reported. These dimers are coordination analogues of the Fe–S proteins, ferredoxins.

2. *η^2-Se$_2$ ligand*

The structure of the complex $[Ir(dppe)_2(Se_2)]Cl$, first briefly described in 1971[563] (equation 220), has been reported[564].

$$[Ir(dppe)_2]Cl + Se_8 \xrightarrow[20\,^\circ C/\,days]{CH_2Cl_2} [Ir(dppe)_2Se_2]Cl \qquad (220)$$

green air-stable solid
m.p. 200–201 °C
$\nu_{Se-Se} = 310\,cm^{-1}$

As previously proposed on the basis of its ^{31}P-NMR spectrum[563], single-crystal X-ray diffraction showed the presence of side-on bonded Se_2 (η^2-Se_2; Figure 11).

This complex was prepared more recently with Cp_2TiSe_5 as a Se-transfer agent (equation 221).

$$[Ir(dppe)_2]Cl + Cp_2TiSe_5 \xrightarrow{CH_2Cl_2/THF} [Ir(dppe)_2(Se_2)]Cl \qquad \text{(Ref. 565)} \quad (221)$$

A similar bonding mode had previously been found for $\mathrm{Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2}$[404] (equation 222).

$$\mathrm{Os(CO)_2(PPh_3)_3 + red\ Se \xrightarrow{C_6H_6} Os(\eta^2\text{-}Se_2)(CO)_2(PPh_3)_2} \qquad (222)$$

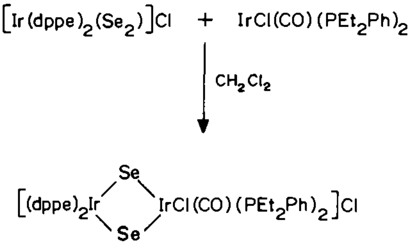
60%

red-purple crystals ($\mathrm{CHCl_3}$/EtOH)

m.p. 192–195 °C

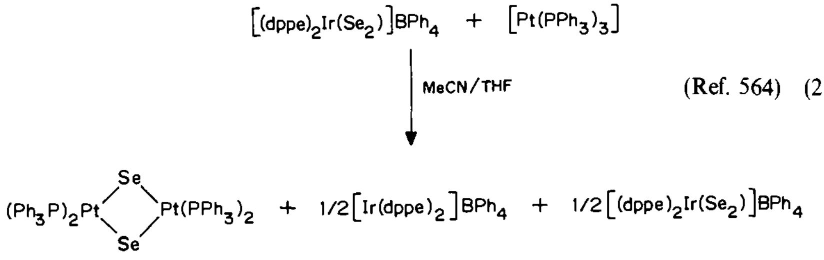
$\nu_{\mathrm{Se-Se}} = 310\,\mathrm{cm^{-1}}$

The Se—Se bonds in such complexes are reactive to electrophilic alkylating reagents (e.g. equation 148) with retention of the Se—Se bond and to low-valent transition-metal species, which undergo oxidative insertion into the Se—Se bond (equation 223).

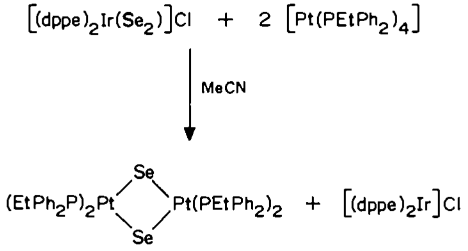


(Ref. 564) (223)

Although the complexes $\mathrm{[(dppe)_2Ir(S_2)]Cl}$ and $\mathrm{[(Me_2PCH_2CH_2PMe_2)_2Rh(S_2)]Cl}$ undergo oxidative addition reactions with $\mathrm{Pt(PPh_3)_3}$ and $\mathrm{Pt(PEtPh_2)_4}$ to give the $\mathrm{M(\mu_2\text{-}S)_2Pt}$ (M = Rh, Ir) dimers, the reactions with the (η^2-$\mathrm{Se_2}$) complex not only result in addition across the Se—Se bond but also displace the Ir from Se (equations 224 and 225).



(Ref. 564) (224)



(Ref. 564) (225)

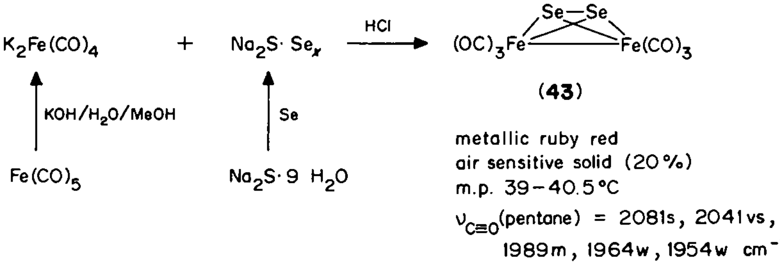
SCF-Xα-SW calculations on the model compounds $\mathrm{[M(X_2)(PH_3)_4]^+}$ (M = Rh, Ir; X = S, Se) predict an X—X bond order of about 1 and $\mathrm{M—X_2}$ covalent interaction in the order $RhSe_2 < IrSe_2 < RhS_2 < IrS_2$, both in agreement with the observed properties of the analogues with the bidentate phosphines discussed above[566].

The complex $Cp'Mn(CO)_2(\eta^2\text{-}Se_2)$ has been prepared by reaction of elemental Se with $Cp'Mn(CO)_2THF$[567]. The spectroscopic data for this complex support the 'side-on' coordination of Se_2, an assignment confirmed by preliminary X-ray structure analysis (Se—Se = 2.263(8) Å, Mn—Se = 2.463(4) Å)[567]. These data suggest the Se_2 is best considered as an uncharged two-electron ligand.

3. μ_2-Se_2 and μ_2, η^2-Se_2 ligands

The complex $Cp(OC)_2Mn(SeSe)Mn(CO)_2Cp$ (equation 216) is the only example reported with a bridging M—SeSe—M linkage.

The complex $(OC)_3Fe(\mu_2,\eta^2\text{-}Se_2)Fe(CO)_3$ was first prepared in 1958 by Hieber and Gruber[568]. A detailed description of the synthesis of the dimer, based on their original method, was reported by Seyferth and Henderson[354] (equation 226).



(226)

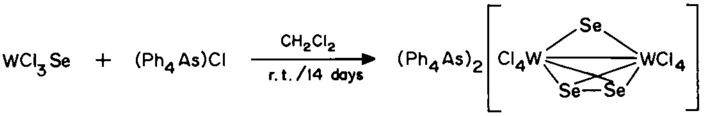
(43)

metallic ruby red
air sensitive solid (20%)
m.p. 39–40.5 °C
$\nu_{C\equiv O}$(pentane) = 2081s, 2041vs, 1989m, 1964w, 1954w cm^{-1}

The proposed structure, involving both Se—Se and Fe—Fe bonds, was confirmed by single-crystal X-ray diffraction[569]. Work by Seyferth and Henderson[354] and Rauchfuss and coworkers[570,571] has established an extensive chemistry of this dimer based on the reactivity of the Se—Se bond (Figure 12). The use of this dimer as a substrate in oxidative addition reactions with low-valent metal (e.g. Pt(o), Co(i), Ni(o)) complexes offers a route to a wide variety of mixed-metal clusters[570,571]. Substitution reactions in which the terminal CO ligands are replaced by phosphines have also been reported[571–573].

The S analogue, $(OC)_3Fe(\mu_2,\eta^2\text{-}S_2)Fe(CO)_3$, exhibits the same general reactivity pattern but has been the subject of more study[570,571,574,575], owing to its enhanced stability and ease of preparation compared to **43**.

The μ_2,η^2-Se_2 ligand also occurs in the dimers $Cp'_2Mo_2Se_4$ (equation 213), $[W_2Se_3Cl_8]^{2-}$ (equation 227) and $[Nb_2Se_4Cl_4(SMe_2)_4]$ (equation 228) as well as the cluster $Nb_4Se_3Br_{10}(MeCN)_4$ (equation 229).



(Ref. 576) (227)

$$NbCl_3Se \xrightarrow{Me_2S} (Me_2S)_2Cl_2Nb(\mu_2,\eta^2\text{-}Se_2)_2NbCl_2(SMe_2)_2$$

(Ref. 577) (228)

$$(3\,NbCl_5 + Sb_2Se_3 \xrightarrow{CSe_2} 3\,NbCl_3Se + 2\,SbCl_3)$$

$$4\,NbBr_4(MeCN)_2 + Sb_2Se_3 \xrightarrow{MeCN} Nb_4(MeCN)_4Br_6(\mu_2\text{-}Br)_4(\mu_2,\eta^2\text{-}Se_2)(\mu_4\text{-}Se)$$

(Ref. 578) (229)

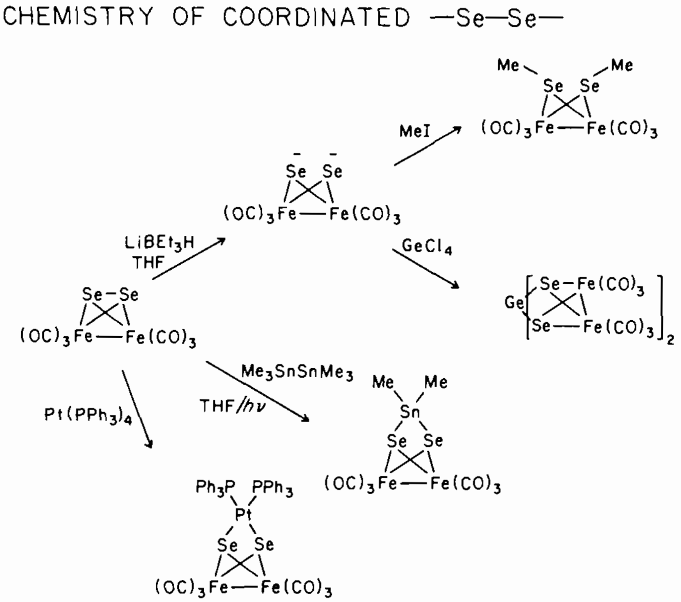


FIGURE 12. The chemistry of $Fe_2Se_2(CO)_6$

The compound $Nb_2Se_2Br_6$, prepared in the form of air-stable, diamagnetic metallic grey crystals from the elements in a sealed quartz tube at 1073 K, has been shown by single-crystal X-ray diffraction to contain the μ_2,η^2-Se_2 ligand[579]. The structure consists of one-dimensional infinite chains of $[Nb_2(Se_2)Br_4]$ units having single side-on bonded Nb_2 and Se_2 dumb-bells forming a quasi-tetrahedral Nb_2Se_2 cluster asymmetrically bridged along the Nb—Nb edge by two bromo ligands (Figure 13).

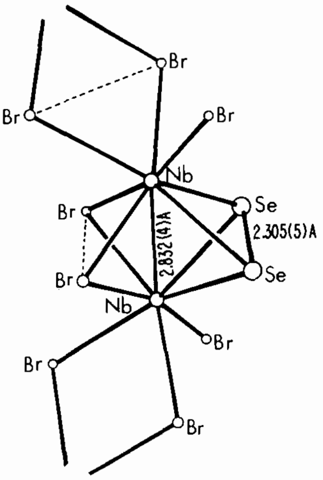


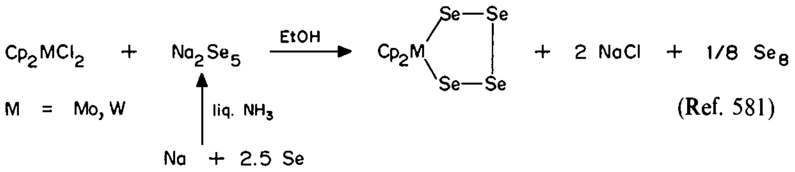
FIGURE 13. Crystal structure of $Nb_2Se_2Br_6$

The interatomic distances show that there is no significant interaction between the chains. The short Nb—Nb and Se—Se distances (Figure 13) support the formal oxidation state assignments Nb(4 +) and Se(1 −). The Se—Se and Nb—Nb bond orders are approximately 1 and 0.62, respectively.

The diamagnetic compounds $NbSe_2X_2$ (X = Cl, Br, I) have been prepared by similar chemical vapour transport reactions and were formulated with similar structural features (i.e. Nb_2^{4+}, $(Se_2)_2^{2-}$, X_4^-) on the basis of crystallographic and XPS data[580].

4. *η^2-Se_4 and η^2-Se_5 ligands*

Three complexes have been reported involving the chelating η^2-Se_4 ligand (equations 230 and 231).



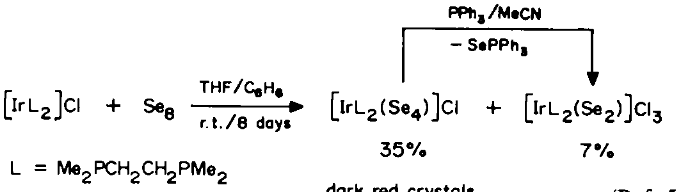
(Ref. 581) (230)

M = Mo

red-black air-stable platelets
(36%; recryst. from DMF)
m.p. 215 °C dec.
^{1}H-NMR δ(DMF): 5.17 (s, Cp)

M = *W*

Brownish violet air-stable platelets
(86%; recryst. from DMF)
m.p. 225 °C dec.
^{1}H-NMR δ(DMF): 5.22 (s, Cp)



dark red crystals
(MeCN / PhMe)
m.p. 277–280 °C dec.

(Ref. 582) (231)

An X-ray structure determination of $[Ir(Me_2PCH_2CH_2PMe_2)_2(Se_4)]Cl$[582] confirmed a *cis*-octahedral geometry with the Se_4 ligand symmetrically chelated to the Ir at equatorial positions. The $IrSe_4$ ring has a half-chair conformation with the two central Se atoms equidistant from and on opposite sides of the $IrSe_2$ (coordinated) plane. The Ir—Se (2.545 Å) and Se—Se (2.307 Å) distances are similar to the corresponding values in $[Ir(dppe)_2(Se_2)]Cl$[564]. As found for the Se_2 ligand[566], SCF-Xα-SW calculations on the model compound $[Ir(PH_3)_4(Se_4)]^+$ indicate that the Se_4 ligand is best described as an excited Se_4 molecule[582].

The reaction of Cp_2TiCl_2 with Na_2Se_5 gave Cp_2TiSe_5 (97)[583] (rather than the η^2-Se_4 derivative as in the Mo and W analogues) (equation 230). This dark violet air-stable solid (m.p. 211 °C) gave two signals of equal intensity in the ^{1}H-NMR spectrum; this was the first example of the splitting of the Cp proton signal in a Cp_2Ti^{4+} derivative and indicated that at room temperature and below the $TiSe_5$ ring is in a fixed conformation. The crystal structure of the S_5 analogue has shown that the six-membered TiS_5 ring exists in a cyclohexane-like chair conformation[584]. These two bands broaden with increasing temperature (S_2Me_2 solution) and finally coalesce at ca. 90 °C. This reversible process becomes irreversible above 100 °C, owing to reaction of Cp_2TiSe_5 with the solvent.

The utility of Cp_2TiSe_5 as a convenient reagent for the synthesis of transition-metal ethylene-1,2-diselenate complexes was described previously (equation 206). As with $Fe_2Se_2(CO)_6$, the enhanced stability and ease of preparation of Cp_2TiS_5[584,585] compared to its Se analogue[542] have resulted in more work with the former derivative, although the reactivity patterns for both complexes are similar.

5. Se incorporated in metal clusters

The synthesis and structural characterization of transition-metal cluster compounds has been an active area of research for 25 years[1,586]. Several such clusters incorporating Se in the framework have been reported (Table 44). These clusters most commonly incorporate a Se atom bonded to three transition metals in the cluster framework (i.e. a μ_3-Se ligand), although the first example of a μ_4-Se ligand has been structurally characterized[600].

The first example of such a transition-metal cluster compound incorporating Se was reported by Hieber and Gruber in 1958[568] (equation 232). Such cluster compounds generally require a single-crystal X-ray diffraction analysis for an unequivocal structural characterization. Indeed, the crystal structures of most of the known Se-containing clusters have been reported (Table 44). The first such structurally characterized compound was $Fe_3(\mu_3\text{-Se})_2(CO)_9$[587], which consists of an $Se_2Fe_2(CO)_6$ fragment of idealized C_{2v}-2 mm symmetry bonded to an $Fe(CO)_3$ group via two bent Fe—Se bonds and two bent Fe—Fe bonds (Figure 14). The cluster framework can be described as a square pyramid with an Fe at the apex (a seven-coordinated Fe atom) and alternate Se and Fe atoms at the corners of the basal plane.

$$3\,Fe(CO)_4{}^{2-} + 2\,SeO_3{}^{2-} + 10\,H^+ \rightarrow Fe_3(\mu_3\text{-Se})_2(CO)_9 + CO_2 + 2\,CO + 5\,H_2O \qquad \text{(Ref. 568)} \quad (232)$$

The reaction of $Os_3(CO)_{12}$ with elemental Se in refluxing *n*-octane followed by thin-layer chromatographic separation of the products gave $H_2Os_3Se(CO)_9$, $Os_3Se_2(CO)_9$ (Figure 15), and $H_2Os_4Se_2(CO)_{12}$ (Figure 16)[540]. Carrying out the reaction under CO/H_2 pressure (35 atm, 1:1) gave improved yields of all three clusters, whereas in a CO atmosphere the yields of the hydrido clusters decreased significantly. Initial characterization of these clusters, as for such compounds in general, was by infrared and mass

TABLE 44. Transition-metal cluster compounds containing μ_3-Se ligands

Complex	Ref.	Complex	Ref.
$Fe_3(\mu_3\text{-Se})_2(CO)_9$	568, 587[a]	$Os_3(\mu_3\text{-Se})_2(CO)_9$	593, 594[a]
$Fe_4(\mu_3\text{-Se})_4(CO)_{12}$	588	$H_2Os_4(\mu_3\text{-Se})_2(CO)_{12}$	590[a]
$FeCo_2(\mu_3\text{-Se})(CO)_9$	589[a]	$Co_3(\mu_3\text{-Se})(CO)_9$	589[a], 595
$Fe_2Co(\mu_3\text{-Se})(CO)_9$	589	$Co_6C(\mu_3\text{-Se})_2(CO)_{12}$	595[a]
$Ru_3(\mu_3\text{-Se})_2(CO)_9$	590	$(Me_4N)[Rh_3(\mu_3\text{-Se})_2(CO)_6]$	596[a]
$H_2Ru_3(\mu_3\text{-Se})(CO)_9$	590, 591	$[(Ph_3PAu)_3(\mu_3\text{-Se})](PF_6)$	597[a]
$RuCo_2(\mu_3\text{-Se})(CO)_9$	592	$[(Et_3P)_6Ni_3(\mu_3\text{-Se})_2](BPh_4)_2$	598[a]

[a] Single-crystal X-ray diffraction structure determination.

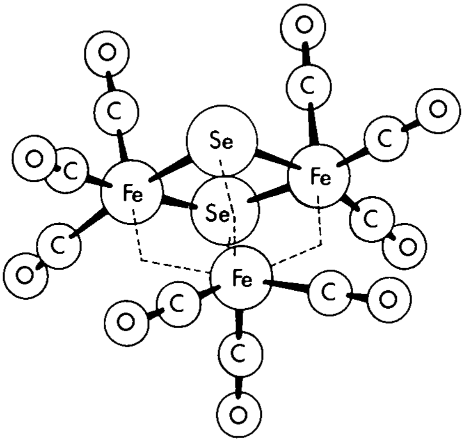


FIGURE 14. Molecular structure of $Fe_3Se_2(CO)_9$. Reproduced with permission from Ref. 587

spectroscopy[590]. The structure of $Os_3Se_2(CO)_9$ (Figure 15) was shown[594] to contain a triangle of Os atoms with one long non-bonding edge (Os—Os = 3.791(1) Å) and Se atoms capping the triangle on both sides to give a trigonal bipyramidal cluster geometry.

The structure of $H_2Os_4Se_2(CO)_{12}$ (Figure 16) has been shown to have a novel trigonal-prismatic Os_4Se_2 core with each Se atom capping a triangle of Os atoms[590]. Two Os—Os distances in each 'Os_3Se' unit are non-bonding (ca. 4 Å). All 12 carbonyl ligands are terminally bonded to the four Os atoms, and the two hydride ligands were formulated as

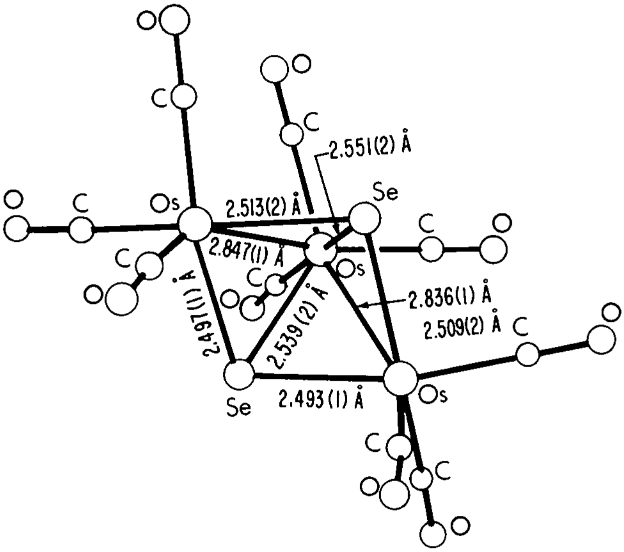


FIGURE 15. Molecular structure of $Os_3Se_2(CO)_9$

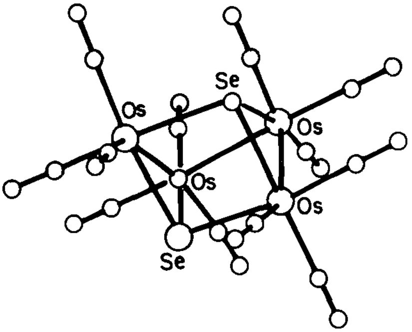


FIGURE 16. Molecular structure of $H_2Os_4Se_2(CO)_{12}$

edge-bridging the two long Os—Os bonds, since the carbonyl ligands bend away from these edges.

Two types of selenide ligands, including a unique μ_4-Se, occur in the cluster $Nb_4(MeCN)_4Br_6(\mu_2\text{-}Br)_4(\mu_2,\eta^2\text{-}Se_2)(\mu_4\text{-}Se)$[578] (Figure 17).

Reaction of H_2Se with $[Ni(OH_2)_6](ClO_4)_2$ and PEt_3 in $H_2O/CHCl_3$ gave the polynuclear complex $[Ni_3(\mu_3\text{-}Se)_2(PEt_3)_6]^{2+}$, which was isolated as its air-stable, red tetraphenylborate salt[598]. The molecular structure[598,599] of this complex contains a triangle of Ni atoms capped on both sides by triply bridging Se atoms forming an almost regular trigonal bipyramid. Each Ni atom is further coordinated to two terminal PEt_3 ligands, the phosphorus atoms lying in the appropriate Ni—Se_2 plane. The average Ni—Ni distance (3.16(2) Å) precludes any significant direct metal–metal interaction, and the cluster geometry can be considered as three d^8 $NiSe_2P_2$ square planes sharing two bridging ligands.

The supertetrahedral clusters, $[(\mu_3\text{-}Se)_4M_{10}(SPh)_{16}]^{4-}$ (M = Zn, Cd) have been prepared in 80–100% yields by reactions of elemental Se with the adamantanoid clusters $[M_4(SPh)_{10}]^{2-}$ and isolated as their tetramethylammonium salts[600].

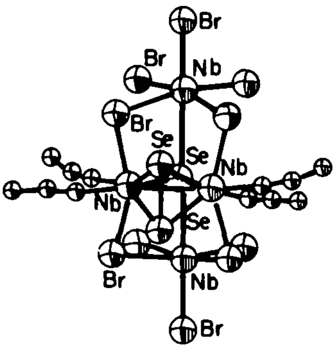


FIGURE 17. Molecular structure of $Nb_4(MeCN)_4Br_6(\mu_2\text{-}Br)_4(\mu_2,\eta^2\text{-}Se_2)(\mu_4\text{-}Se)$. Reproduced with permission from Ref. 578

TABLE 45. Summary of complexes with monodentate tellurium ligands

Ligand	Complex	Ref.
$Te(alkyl)_2$		
terminal	$PtCl_2(Te(CH_2CH_2Ph_2)_2)_2$	605
	$Pd(SCN)_2(Te(CH_2CH_2CH_2SiMe_3)_2)_2$	606[a]
	$[CpNi(TeMe_2)_2]BF_4$	607
	$(OC)_5Cr(TeEt_2)$	108
bridging	$[n\text{-}Bu_4N]_2[Cl_3Pt(\mu\text{-}TeMe_2)PtCl_3]$	608
	$BrAg(\mu\text{-}Te(Bu\text{-}n)_2)AgBr$	609
	$[CuCl(TeEt_2)]_n$	610[a]
$Te(aryl)_2$		
terminal	$RhCl(TePh_2)_3$	611
	$HgI_2(TePh_2)]_4$ (**110**)	612, 613[a]
	$PdCl_2(Te(C_6H_4OEt\text{-}p)_2)_2$	614
	$CuI(Te(C_6H_4Me\text{-}p)_2)_2$	615
bridging	$IAg(\mu\text{-}TePh_2)AgI$	609
Te(alkyl)(aryl)		
terminal	$HgBr_2(TeMePh)$	612
bridging	$BrAg(\mu\text{-}TePhC(O)Ph)AgBr$	609
(alkyl)TeTe(alkyl)		
bridging	$[CuCl(Te_2Et_2)]_n$	616
	$[CpNi(\mu\text{-}Te_2Me_2)NiCp](BF_4)_2$	617
(aryl)TeTe(aryl)		
bridging	$[CuBr(Te_2(C_6H_4OEt\text{-}p)_2)_2]_n$	616
	$[(OC)_3M(\mu\text{-}Br)_2(\mu\text{-}Te_2Ph_2)M(CO)_3$	
	M = Re, Mn	190[a], 191
Heterocycles		
L = **111**	$Mn(CO)_3L_2Cl$	618
L = **112**	$LCr(CO)_3$	619
L = **113**, **114**	$L_2Rh(CO)Cl$	620
$Te(EMe_3)_2$	$[Cr(CO)_5(Te(EMe_3)_2)]$	196
	E = Ge, Sn, Pb	
$(CF_3)ETeMe$	$Mo(CO)_5\{(CF_3)_2PTeMe\}$[b]	194
E = P, As		
Tellurourea		
L = **115**	$M(CO)_5L$	621
	M = Cr, Mo, W	
	$Fe(CO)_4L$	622
CTe[c]	$OsCl_2(CO)(CTe)(PPh_3)_2$	216
	$(Et_4N)[LMo(CO)_2(CTe)]$	223
	L = **37**	
Telluroketone	$(OC)_5W(Te{=}CPh_2)$	623
Carbenes	$(OC)_5Cr{=}C(NEt_2)(TePh)$	624
Telluroxides	$MeTeCl_3(OTePh_2)_2$[d]	625
	$(p\text{-}ROC_6H_4)TeCl_3(OTePh_2)_2$	
	R = Me, Ph	

[a] Structure determined by single-crystal X-ray diffraction.

[b] Mo—P bonding of ambidentate (P, Te) ligand.

[c] M—CTe bonding.

[d] $Te{-}O{=}TePh_2$ bonding.

III. ORGANOTELLURIUM LIGANDS

Because transition-metal complexes with Te ligands have been the subject of recent reviews[15,18] and these complexes are generally prepared by routes described above for the analogous Se complexes, discussion of the former complexes will be limited to a general consideration of the various ligand types and very recent developments.

The extensive ligand chemistry developed for 1,1- and 1,2-dithio[12] and -diseleno (Section II.D.2) anionic ligands has not been extended to the Te analogues. Likewise, no examples of tridentate or tetradentate ligands containing one or more Te donor sites have been reported.

Although several papers have described the syntheses of phosphine tellurides (R_3PTe, $(R_2N)_3PTe$; R = alkyl)[601], no complexes of these donors analogous to those of the lower chalcogens (R_3PX; $X = O$[602], $X = S$[603], Se (Section II.A.3)) have been described. Similarly, although several salts of the tellurocyanate anion[604] have been isolated and characterized, no complexes with this ambidentate ligand are known, in contrast to the extensive ligand chemistry of thiocyanate[302] and selenocyanate (Section II.B.1).

Recent advances in the synthetic methodology of organotellurium chemistry as illustrated in other chapters of this volume can be expected to provide impetus for the development of this coordination chemistry. The most diverse class of Te ligands are neutral monodentate (Table 45).

A. Neutral Monodentate Ligands

1. *Diorganotellurides*

a. Dialkyl tellurides. The first reported coordination complex with a Te ligand, *cis*-$PtCl_2(Te(CH_2Ph)_2)_2$, was reported by Fritzmann in 1915[8]. Since then a number of transition-metal and Group IIb complexes with dialkyl and diaryl tellurides have been prepared[18]. Early work in this area generally involved lower molecular weight dialkyl tellurides, and the air sensitivity and foul odour of these ligands no doubt led to the belief among inorganic chemists that these were general characteristics of Te compounds. In fact, the aromatic ligands are air-stable solids that can be readily prepared with a variety of functional groups[15]. The alkyl derivatives can also be made more amenable to convenient handling by increasing the alkyl chain length. The slightly air-sensitive dialkyl tellurides $Te(CH_2CH_2Ph)_2$[605] and $Te((CH_2)_nSiMe_3)_2$[606] ($n = 1, 3$) can be readily prepared in high yields by alkylation of Na_2Te. The complex *trans*-$Pd(SCN)_2(Te(CH_2CH_2CH_2SiMe_3)_2)_2$ has been characterized by single-crystal X-ray diffraction[606]. The complex is square-planar with S-bonded thiocyanate (Figure 18).

The complex *trans*-$[Pd(SCN)_2(Te(CH_2SiMe_2Ph)_2)_2]$ also has S-bonded thiocyanate initially (i.e. $\nu_{C\equiv N} = 2111\ cm^{-1}$), but on aging for several weeks at room temperature, its infrared spectrum indicates a partial Pd—SCN → Pd—NCS isomerization (i.e. $\nu_{C\equiv N} = 2077\ cm^{-1}$) as well as a *trans* → *cis* isomerization of the S-bonded isomer (i.e. $\nu_{C\equiv N} = 2106,\ 2098\ cm^{-1}$)[626]. This linkage isomerism is presumably the result of the increased steric bulk introduced around the Pd by the $Te(CH_2SiMe_2Ph)_2$ ligand vs. $Te(CH_2CH_2CH_2SiMe_3)_2$.

^{125}Te-NMR has been used to study the solution structure of the complex $PtCl_2(Te(CH_2CH_2Ph)_2)_2$[605]. This complex has a *cis* configuration in the solid state (a ν_{Pt-Cl} doublet characteristic of C_{2v} symmetry in the far-infrared) (Figure 19a). On dissolution in CH_2Cl_2 the solution initially contains the *cis* isomer (Figure 19b), but *cis–trans* isomerization occurs over several hours to reach an equilibrium mixture

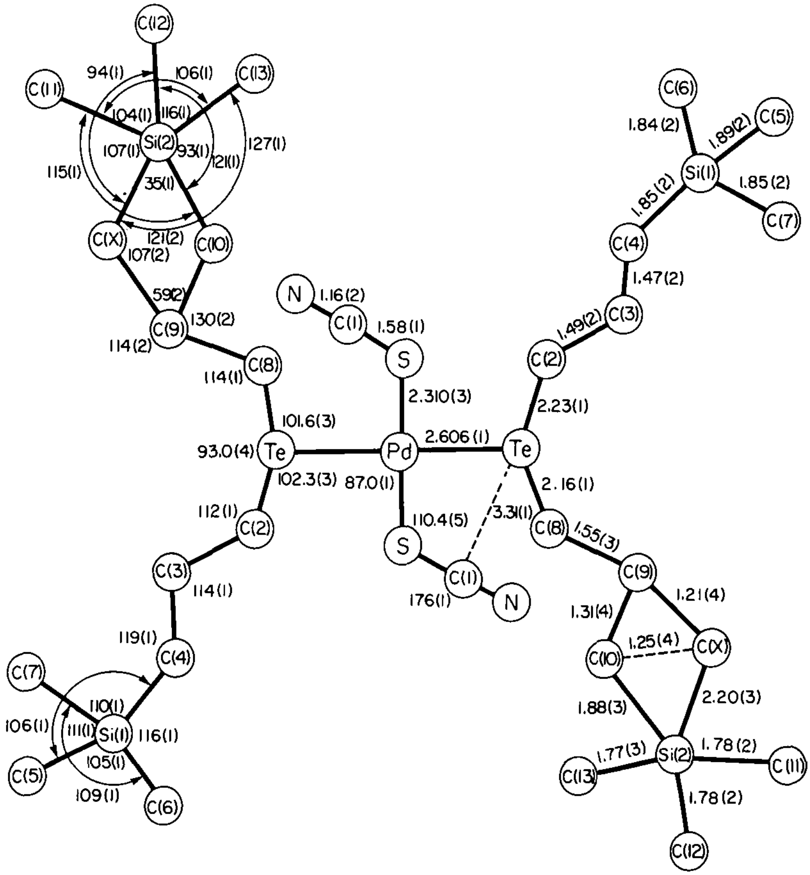


FIGURE 18. Molecular structure of *trans*-$Pd(SCN)_2(Te(CH_2CH_2CH_2SiMe_3)_2)_2$. Reproduced with permission from Ref. 606

of the two isomers. The *trans* isomer has a single ν_{Pt-Cl} at higher energy than the *cis* isomer (Figure 19b) and a ^{125}Te resonance downfield from the *cis* isomer as well as a smaller $J(^{125}Te\text{-}^{195}Pt)$ (Figure 19b). In toluene solution, however, the complex exists exclusively as the *trans* isomer ($\nu_{Pt-Cl} = 337\,cm^{-1}$; $\delta(^{125}Te) = -430$ ppm, $J(^{125}Te\text{-}^{195}Pt) = 601$ Hz).

The largest number of dialkyl telluride complexes involve Pt(II) and Pd(II). A variety of techniques have been applied to the characterization of their solid-state and solution structures (e.g. infrared, Raman, NMR, dipole-moment measurements)[18]. In such square-planar complexes, $MX_2(TeR_2)_2$ (M = Pd, Pt; X = Cl, Br, I), *cis–trans* isomerization, intramolecular ligand exchange and tellurium inversion processes have all been observed by detailed far-infrared and variable-temperature ^{1}H-NMR studies[18].

A CH_2Cl_2 solution of $(Bu_4N)[Pt(CNS)_3TeMe_2]$, prepared by equilibration of $(Bu_4N)_2[Pt(SCN)_4]$ with $[Pt(SCN)_2(TeMe_2)_2]$, was shown by $^1H\text{-}\{^{195}Pt\}$ INDOR spectroscopy to contain the following four isomers (relative amounts in parentheses)[627]:

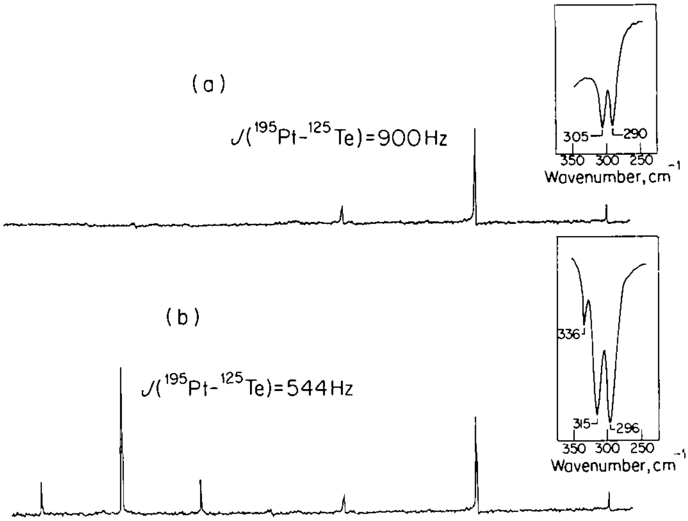
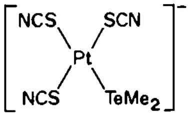
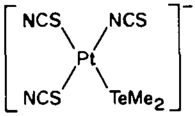
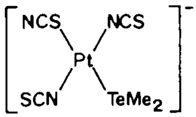
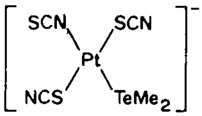


FIGURE 19. ^{125}Te-NMR and far-infrared spectra of $PtCl_2(Te(CH_2CH_2Ph)_2)_2$, (a) in the solid state and (b) in CH_2Cl_2 solution. Reproduced with permission from Ref. 605

		δ(Me)	$^3J(^{195}Pt-^1H)$	$^1J(^{195}Pt-^{14}N)$
	(1)	2.25	33.6 Hz	
	(0.3)	2.24	35.7 Hz	367 ± 5 Hz
	(0.04)	2.20	35 Hz	450 Hz
	(0.006)	2.14		

The multiplicity of the ^{14}N coupling pattern in the spectrum was used to determine the number of N-bonded thiocyanate ligands in a particular isomer. Specific assignments of the mixed complexes were made by assuming a regular upfield shift of the methyl resonances when S^- is replaced by N-bonded thiocyanate in the position *cis* to the telluride ligand and a somewhat large shift for the *trans* position.

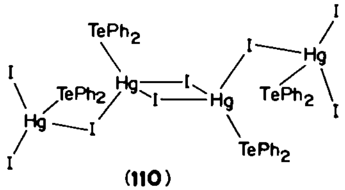
A few examples of bridging diorganotelluride ligands in Ag(I), Pt(II) and Cu(I) complexes have been reported (Table 45). In the Ag(I) complexes ($(AgX)_2TeR_2$; X = Br, I), XPS showed an increase in the Te 3d binding energy of 0.7–0.9 eV vs. the free ligand[609].

A bridging dialkyl telluride ligand in the complexes $(Bu_4N)_2[X_3Pt(\mu\text{-}TeMe_2)PtX_3]$ (X = Cl, Br) has been proposed on the basis of ^{125}Te-NMR spectroscopy[608]. The $J(^{125}Te{-}^{195}Pt)$ coupling constants in the dimeric complexes, in which both lone pairs of the bridging Te ligand are involved in bonding, are much larger than in complexes containing terminal dialkyl telluride ligands (e.g. $(Bu_4N)_2[Cl_3Pt(\mu\text{-}TeMe_2)PtCl_3]$, 5923 Hz vs. $(Bu_4N)[Cl_3PtTeMe_2]$, − 1553 Hz)[608].

The first structure characterization by X-ray diffraction of a complex containing a bridging diorganotelluride ligand was reported recently for $[CuCl(TeEt_2)]_n$[610]. The structure contains infinite sheets in which two $TeEt_2$ ligands bridge two $(Cu(\mu\text{-}Cl)_2Cu)$ dimeric units to give distorted tetrahedral coordination about both the Cu and Te atoms (Cu—Te distances = 2.535(1) and 2.625(1) Å). The synthesis of this complex involved the *in situ* reduction of Cu(II) (equation 233).

$$2\,CuCl_2 + 3\,TeEt_2 \xrightarrow{EtOH} 2\,[CuCl(TeEt_2)] + TeEt_2Cl_2 \qquad (233)$$

b. Diaryl tellurides. Adducts of diaryl tellurides with mercuric halides were prepared as easily crystallized derivatives in Lederer's early work involving the syntheses of these organotellurides (see Ref. 18 for a discussion of this early work). Few data, other than melting points, were reported for these complexes. More recently some of these complexes have been studied by far-infrared[628] and ^{125}Te Mössbauer spectroscopy[628], and a tetrameric structure (**110**) has been found for $[HgI_2(TePh_2)]$ by X-ray diffraction[613].



(**110**)

Relatively few other complexes of transition metals with terminal diaryl telluride ligands (primarily $TePh_2$) have been reported (e.g. Pd(II), Pt(II), Cu(I), Mn(I), Fe(I, II), Ru(II), Rh(I, III), Re(I))[18].

Although diorganotelluride complexes are generally stable, in two cases Te—C bond cleavage has been reported to give complexes with bridging tellurol ligands (equations 234 and 235).

$$Mn_2(CO)_{10} + 2\,TePh_2 \xrightarrow{-Ph_2} (OC)_4Mn(\mu\text{-}TePh)_2Mn(CO)_4 \qquad \text{(Ref. 618)} \quad (234)$$

$$RhCl_3\cdot 3\,H_2O + TePh_2 \xrightarrow[EtOH/reflux]{40\%\,aq.\ CH_2O/KOH} [Rh(TePh)_3]_n \qquad \text{(Ref. 611)} \quad (235)$$

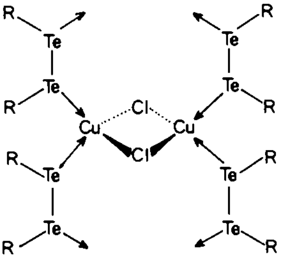
2. Diorganoditellurides

Although ditellurides (and diselenides, Section II.A.5) most commonly undergo cleavage of their E—E (E = Se, Te) bond with formation of terminal or bridging ER^- ligands (e.g. equations 95–104 and 107–109), examples of intact coordinated diorganoditellurides have been described. The crystal structure of the dimeric bridged ditelluride

$[(OC)_3Re(\mu\text{-}Br)_2(\mu\text{-}Te_2Ph_2)Re(CO)_3]$ was reported[184] recently. This complex and the analogous Mn dimer[191] were prepared by the route described for the Se_2R_2 dimers (equation 32, Section II.A.5).

Unique mixed complexes of unsymmetrical diaryl ditellurides were prepared recently by reaction of CuCl with mixtures of the symmetrical ditellurides[629]. The orange-red precipitates formed in these reactions had the composition $PhTeTe(C_6H_4OEt\text{-}p)\cdot 2\,CuX$ (X = Cl, Br), but their insolubility and thermal sensitivity precluded unequivocal characterization. Previous ^{125}Te-NMR studies, however, demonstrated that solutions of two symmetrical ditellurides also contain the unsymmetrical ditelluride[630]. The presence of intact ditelluride was confirmed by the observation of the characteristic ν_{Te-Te} at ca. 175 cm^{-1} in the Raman spectra of these complexes.

Several 1:1 complexes with symmetrical ditellurides have also been prepared ($CuX(Te_2R_2)$: X = Cl, Br; R = Et, *n*-Bu, *n*-C_5H_{11}, Ph, *p*-$EtOC_6H_4$)[616]. The presence of bands assigned to ν_{Te-Te} (170–180 cm^{-1}) and $\nu_{Cu-X-Cu}$ vibrations in the far-infrared spectra of these complexes and their insolubility in organic solvents suggested a polymeric formulation (**116**).



(**116**)

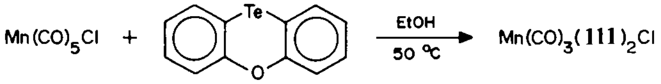
Complexes of Cu(I) and Cu(II) with the potentially chelating ditelluride (o-$H_2NC_6H_4)TeTe(C_6H_4NH_2$-$o$) have also been reported[631], but their structures were not established.

A complex proposed to contain an intact Me_2Te_2 ligand ($[CpNi(Te_2Me_2)]BF_4$) has been prepared by treatment of $[CpNi(C_5H_6)]BF_4$ with the ditelluride in ether[617]. The bonding mode of the Te ligand, however, is not well characterized. Structures involving bridging and chelating MeTeTeMe have been suggested[617].

ESR and infrared spectroscopy were employed in a kinetic and mechanistic study of the oxidative addition of the ditellurides Te_2Ar_2 (Ar = Ph, *p*-MeC_6H_4, *p*-ClC_6H_4, *p*-$EtOC_6H_4$) to *trans*-$(OC)Cl(Ph_3P)_2Ir$[632].

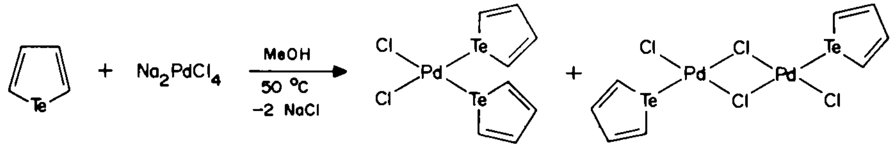
3. Miscellaneous ligands

Only a few examples of transition-metal complexes with Te heterocycles are known. Phenoxtellurine (**111**) forms a complex (Mn—Te bonding) with Mn(I)[618] (equation 236). The reaction of tellurophene (**112**) with Na_2PdCl_4 gave two products, which were separated by their solubility differences in acetone and $CHCl_3$[619] (equation 237).



(236)

(**111**)



(112) **(117)** 70% **(118)** 27% (237)

Treatment of a suspension of **118** in $CHCl_3$ with excess tellurophene gave **117**.

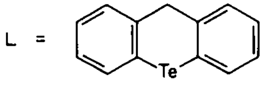
The analogous reaction of Na_2PdCl_4 with tetrachlorotellurophene (tct) gave exclusively *trans*-$PdCl_2(tct)_2$, on the basis of elemental analyses and the observation of only one $\nu_{Pd—Cl}$ band in its far-infrared spectrum ($354\,cm^{-1}$)[619].

Reaction of **112** with $Cr(CO)_6$ at high temperature failed to give any substitution product, but the π complex $(\eta^5\text{-}TeC_4H_4)Cr(CO)_3$ was obtained in 80% yield from the reaction of **112** with $Cr(CO)_3(MeCN)_3$ in Bu_2O at 60 °C[619]. The purple-red complex dissolves in benzene as a monomer and can be vacuum sublimed at 65 °C without decomposition.

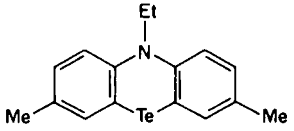
Monomeric complexes result from the reactions of 9-*H*-telluroxanthene (**113**) and 10-ethyl-3,7-dimethylphenotellurazine (**114**) with the dimeric complex **119**[620] (equation 238).

$$4\,L + (OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2 \rightarrow 2\,L_2Rh(CO)Cl \qquad (238)$$

(119)



(113)



(114)

Chromium complexes with $Te(EMe_3)_2$ (E = Ge, Sn, Pb) were prepared[196] by a two-step route (equation 239) involving the initial photochemical generation of a labile THF adduct rather than by direct substitution (e.g. $Se(SnMe_3)_2$ complexes, equation 38) because of the high photosensitivity of the telluride ligands.

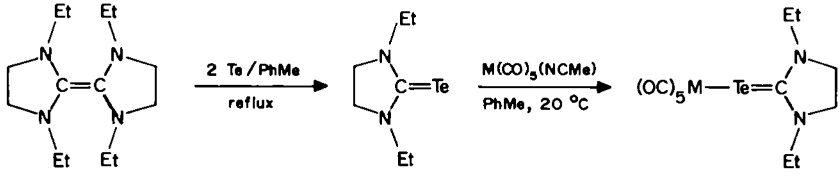
$$Cr(CO)_6 \xrightarrow[\text{THF}]{h\nu} \{Cr(CO)_5(THF)\} \xrightarrow[0\,^\circ C]{Te(EMe_3)_2} Cr(CO)_5Te(EMe_3)_2 \qquad (239)$$

$$E = Ge, Sn, Pb$$

These complexes are quite sensitive to air and moisture and slowly decompose in the solid state even at 0 °C. They all exhibited satellites about the singlet Me signal in their ^1H-NMR spectra ($J(^1HC\text{-}^{119}Sn) = 54.5\,Hz$, $J(^1HC\text{-}^{117}Sn) = 52.5\,Hz$, $J(^1HC\text{-}^{207}Pb) = 57.8\,Hz$ and a three-bond $J(^1HCGe\text{-}^{125}Te) = 8.5\,Hz$).

A similar indirect photochemical substitution route was used to prepare the complexes $(OC)_5Cr\{(CF_3)_2ETeMe\}$ (E = P, As). These monomeric complexes were isolated as air-sensitive red-brown oils in 23% and 14% yields, respectively. The $(CF_3)_2PTeMe$ complex has good thermal and light stability in the solid state and solution, but the complex with the weaker donor, $(CF_3)_2AsTeMe$, decomposes in solution slowly over a few days even in the absence of air and light. Spectroscopic results indicate that the $(CF_3)_2AsTeMe$ complex contains both As- and Te-bonded linkage isomers, whereas the $(CF_3)_2PTeMe$ complex is isomerically pure (Cr—P bonding). The NMR characterization of the bonding mode of these ambidentate ligands was similar to that previously described for the Se analogues (Section II.A.5).

The instability of tellurourea-type compounds has precluded the synthesis of the wide variety of complexes described for selenourea (Section II.A.1). Lappert and coworkers[621,622], however, have reported two examples of complexes with the cyclic tellurourea derivatives (**115**) (Table 45). The Cr, Mo and W complexes were prepared by the substitution route shown in equation (240) using the electron-rich olefin **120**[621].

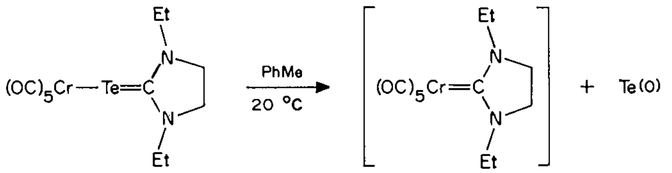


(120) **(115)**

75%, M = Cr
52%, M = Mo
71%, M = W

(240)

The Cr complex readily undergoes Te extrusion to give the corresponding carbene complex[621] (equation 241).



(241)

The Mo and W analogues are somewhat more stable but also undergo the detelluration reaction at high temperatures. The molecular structure of the Cr derivative has been determined by single-crystal X-ray diffraction (Figure 20)[621].

These complexes, an Fe(I) complex with the same ligand and the telluroketone complex $(OC)_5W(Te{=}CPh_2)$, are the only reported complexes with a tellurocarbonyl group ($>$C=Te) (Table 45), although two other examples of organotellurium derivatives of this class were described recently (*o*-alkyltellurocarboxylates, $RC(Te)OR^1$ [633] and telluroamides, $RC(Te)NR^1R^2$ [634]).

Two complexes of tellurocarbonyl have been prepared as shown in equations (242) and (243).

$$Cl_2(Ph_3P)_2(OC)Os{=}CCl_2 \xrightarrow[C_6H_6,\ EtOH]{Na^+\,TeH^-} Cl_2(Ph_3P)_2(OC)Os{-}C{\equiv}Te \quad \text{(Ref. 216)} \quad (242)$$

(121)

30%

air-stable orange crystals

m.p. 221–223 °C

$\nu_{C\equiv O} = 2040\text{s}\ \text{cm}^{-1}$

$\nu_{C\equiv Te} = 1046\text{s}\ \text{cm}^{-1}$

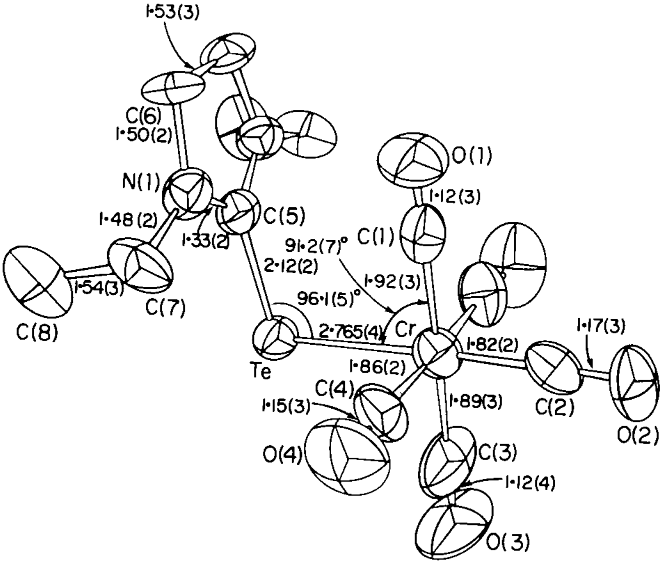


FIGURE 20. Molecular structure of $(OC)_5Cr\{Te{=}\overline{CN(Et)CH_2CH_2N}Et\}$. Reproduced with permission from Ref. 621

$$\begin{array}{lcl} L(OC)_2Mo{\equiv}CCl & \xrightarrow[\text{2. } Et_4NCl]{\text{1. } Li_2Te \quad THF} & Et_4N^+[L(OC)_2Mo{\equiv}C{-}Te^-] \quad \text{(Ref. 223)} \quad (243) \\ L = 37 & & \updownarrow \\ & & Et_4N^+[L(OC)_2Mo^-{-}C{\equiv}Te] \\ & & \mathbf{(122)} \\ & & 60\% \\ & & \nu_{C\equiv O} = 1924,\ 1840\text{vs}\,cm^{-1} \\ & & \nu_{C\equiv Te} = 951\text{s}\,cm^{-1} \end{array}$$

The stereochemistry of the octahedral Os complex **121** was assigned (e.g. **35**, Te in place of Se) on the basis of the similar infrared spectra of all three CX (X = S, Se, Te) derivatives and the characterization of the thiocarbonyl complex by single-crystal X-ray diffraction[225]. The low yield of the tellurocarbonyl complex after silica gel chromatography was attributed to the difficulty of preparing pure TeH^- ($NaBH_4$ reduction of powdered Te in refluxing ethanol followed by cooling to −20 °C and acidification with HOAc/EtOH[635]).

The Mo complex **122** is less stable than its S and Se congeners, but it was converted to the more stable telluromethylidyne complex[223] (equation 244).

$$\begin{array}{lcl} Et_4N[L(OC)_2Mo{\equiv}C{-}Te] & \xrightarrow[-Et_4NI]{MeI} & L(OC)_2Mo{\equiv}C{-}TeMe \qquad (244) \\ L = 37 & & 20\% \\ & & \nu_{C\equiv O} = 1992,\ 1911\text{s}\,cm^{-1} \\ & & {}^{13}C\text{-NMR } (\delta,\ CDCl_3)\text{: } 266.22\ (C{-}Te), \\ & & \qquad 226.62\ (CO) \end{array}$$

The first example of a telluroketone complex was prepared recently by insertion of Te from tellurocyanate into a metal–carbene bond[623] (equation 245).

$$(OC)_5W{=}CPh_2 + PPN[TeCN] \xrightarrow[-\,PPN[CN]]{CH_2Cl_2/-90\,^{\circ}C} (OC)_5W{-}Te{=}CPh_2 \qquad (245)$$

18%

m.p. 35 °C dec.

$\nu_{C\equiv O}$ (hexane): 2066m, 1953, 1941 cm^{-1}

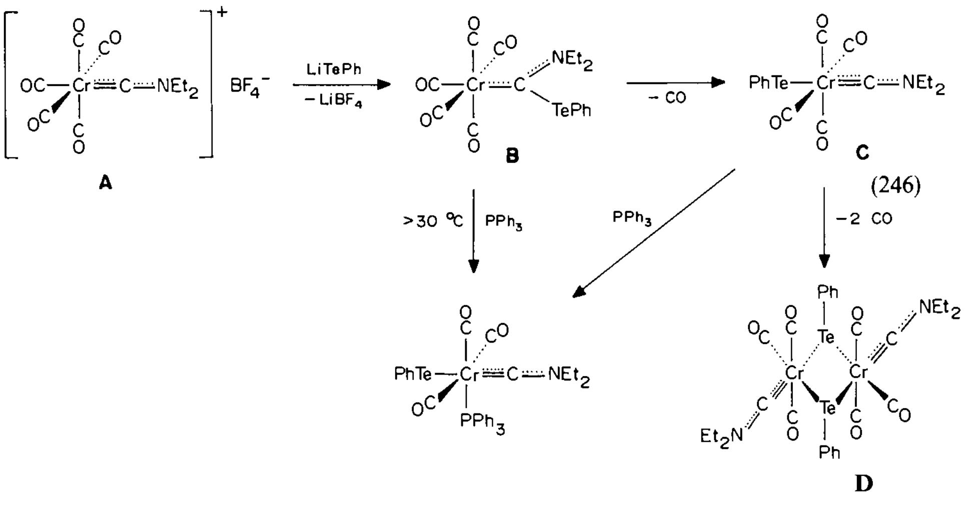
^{1}H-NMR δ(acetone-d_6): 7.66(m)

^{13}C-NMR δ(acetone-d_6): 160.4, 130.4, 128.1, 127.0, 123.8 (Ph); 197.3 (CO_{cis}); 231.9 (Te=C)

The product was isolated as thermally unstable, black crystals by column chromatography (SiO_2/pentane–CH_2Cl_2 10:1) at −50 °C followed by recrystallization from pentane. The formulation of the product as a telluroketone complex was based on spectroscopic evidence, especially the position of the Te=C—^{13}C resonance (equation 245).

Free diaryl telluroketones are not known, although a brief report[636] described the synthesis of a dialkyl telluroketone. This is, therefore, another example of the stabilization of an unstable organic molecule by coordination to a transition-metal centre.

Fischer and coworkers[624] recently reported the first example of a Te-functionalized metal carbene complex and studied its reactivity (equation 246). Rearrangement of the initial Te-functionalized carbene complex **B** occurs spontaneously over a few hours at 30 °C to give quantitatively the carbyne complex **C**, which readily eliminates CO on further stirring in ether at room temperature to give the thermally unstable Te-bridged dimer **D**. Because the latter dimerization is inhibited by free CO, whereas the rearrangement of **B** to **C** is independent of CO concentration, the carbyne **C** can be synthesized in good yield by carrying out the reaction under CO pressure. Heating **B** in an



(246)

autoclave at 40 °C under 40 atm of CO for 2 h gave C, after recrystallization from 1:1 CH_2Cl_2/pentane, in 77% yield as an orange crystalline solid (m.p. 42 °C dec.). All of the above compounds were characterized by elemental analysis and infrared and ^1H-NMR spectroscopy, and the carbene complex **B** was shown to be isostructural with $(OC)_5Cr{=}C(SePh)(NEt_2)$ (**38**), which was previously characterized by single-crystal X-ray diffraction[248]. The rearrangement of **B** to **C** in 1,1,2-trichloroethane follows a first-order rate law ($-d[B]/dt = k[B]$; $\Delta H^{\neq} = 108 \pm 1\ kJ\,mol^{-1}$; $\Delta S^{\neq} = 42 \pm 4\ J\,mol^{-1}\,K^{-1}$).

Diphenyl telluroxide, $Ph_2Te{=}O$, reacts with Sn(IV), Ti(IV) and Sb(V) chlorides to give Ph_2TeCl_2, but 2:1 adducts have been isolated from reactions with organotellurium trichlorides[625] (equation 247). The Te—O=$TePh_2$ bonding mode for these air-stable white complexes was proposed on the basis of infrared spectroscopy ($\nu_{Te=O}$ decreases from 708 cm^{-1} in $Ph_2Te{=}O$ to 658–613 cm^{-1} in the complexes). The presence of two strong $\nu_{Te=O}$ bands in the octahedral complexes suggests a *cis* arrangement of the two $Ph_2Te{=}O$ ligands[625].

$$RTeCl_3 + 2\,Ph_2Te{=}O \xrightarrow{CHCl_3} RCl_3Te[O{=}TePh_2]_2 \qquad (247)$$

$$R = Me,\ C_6H_4OMe\text{-}p,\ C_6H_4OPh\text{-}p$$

B. Anionic Monodentate Ligands

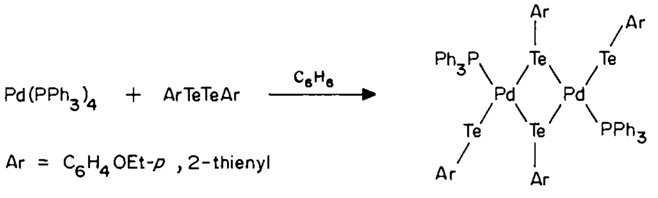
The synthesis of complexes containing terminal and bridging tellurol ligands (Table 46) parallels the routes described above for selenol complexes (Section II.B.2). The most common preparative route involves oxidative addition of a diorganoditelluride to a low-valent metal substrate (equations 248–250).

$$2\,Fe(NO)_2(CO)_2 + ArTeTeAr \xrightarrow[\text{r.t.}\ -4\,CO]{C_6H_6} \underset{\mathbf{(123)}}{(ON)_2Fe(\mu\text{-}TeAr)_2Fe(NO)_2} \qquad \text{(Ref. 640)} \quad (248)$$

$$Ar = C_6H_4OMe\text{-}p$$

$$CpFe(\mu\text{-}CO)_2FeCp + PhTePh \xrightarrow[\text{reflux}]{C_6H_6} \underset{\mathbf{(124)}}{CpFe(CO)_2TePh} \qquad \text{(Ref. 329)} \quad (249)$$

$$\xrightarrow[\text{reflux}/h\nu]{C_6H_6} \underset{\mathbf{(125)}}{Cp(OC)Fe(\mu\text{-}TePh)_2Fe(CO)Cp}$$



(Ref. 641) (250)

(126)

The diamagnetic dimer **123** is isostructural with Roussin's salt, $[Fe(NO)_2SEt]_2$, the structural determination of which has established tetrahedral coordination about the Fe atoms (two terminal NO ligands and two bridging S atoms; Fe—Fe = 2.72 Å[640]).

TABLE 46. Complexes with anionic tellurium ligands

Ligand	Complex	Ref.
Te(alkyl)$^-$		
terminal	$(OC)_2(Ph_3P)_2(Me)OsTeMe$	418
bridging	$[EtTeCu]_n$	616
	$(ON)_2Fe(\mu\text{-}TeCH_2Ph)_2Fe(NO)_2$	353
	$Cp(ON)_2Cr(\mu\text{-}Te(Bu\text{-}n))_2Cr(NO)_2Cp$	351
Te(aryl)$^-$		
terminal	$CpFe(CO)_2TePh$	305
	$(\eta^7\text{-}C_7H_7)Mo(CO)_2TePh$	337[a]
	$(\eta^7\text{-}C_7H_7)W(CO)_2TePh$	336
	$[Ph_4P][Hg(TePh)_3]$	637[a]
	$CpNi(P(Bu\text{-}n)_3)(TeC_6H_4X)$	330
	X = H, p-Cl, p-MeO, p-Me, m-CF_3	
	$Cp_2W(TeAr)_2$	332
	Ar = Ph, $C_6H_4Me\text{-}p$	
	$Cp_2Nb(TePh)_2$	332
bridging	$Cp(OC)Fe(\mu\text{-}TeAr)_2Fe(CO)Cp$	
	Ar = Ph, p-$EtOC_6H_4$	329, 638[a]
	$(\eta^7\text{-}C_7H_7)W(\mu\text{-}TePh)_3W(CO)_3$	336
	$(OC)_4W(\mu\text{-}TePh)_2W(CO)_4$	336
	$Cp(ON)_2Cr(\mu\text{-}TePh)_2Cr(NO)_2Cp$	351
	$(\eta^7\text{-}C_7H_7)(OC)Mo(\mu\text{-}TePh)_2Mo(CO)(\eta^7\text{-}C_7H_7)$	639
$Te(SnMe_3)^-$		
bridging	$(OC)_4Re(\mu\text{-}TeSnMe_3)_2Re(CO)_4$	363
TeH^-		
terminal	$PPN[Cr(CO)_5TeH]$	108
bridging	$(AsPh_4)[(OC)_5W(\mu\text{-}TeH)W(CO)_5]$	108
$Te(O)_2Me^-$	$(\eta^7\text{-}C_7H_7)Mo(CO)_2Te(O)_2Me$	390

[a] Structure determined by single-crystal X-ray diffraction.

The monomeric complex **124** with terminally bonded TePh$^-$ gave the dimeric complex **125** when the reaction solution was refluxed with infrared irradiation[329]. The dimeric complex was obtained as a mixture of two isomers on the basis of TLC and ^{1}H-NMR evidence, but the pure isomers could not be isolated. Spectroscopic evidence (Table 47) indicated the formulations **127a** and **127b** (Ar = Ph) for the two dimers[329]. Five stereoisomers (**127a**–**e**) of such a dimer are possible, and each of these can exist in two conformational forms for a non-planar Fe_2Te_2 ring[642].

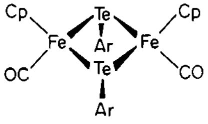
TABLE 47. Spectroscopic data for $Cp(OC)Fe(\mu\text{-}EPh)_2Fe(CO)Cp$ (E = S, Se, Te) dimers (**127a**) and (**127b**)

	127a		**127b**	
E	$\nu_{C\equiv O}$ (cm^{-1})[a]	δ_{Cp} (ppm)[b]	$\nu_{C\equiv O}$ (cm^{-1})[a]	δ_{Cp} (ppm)[b]
S[c]	1982s	4.43	1953s, 1937s	4.03
Se	1975s	4.46	1947s, 1931s	4.02
Te	1965m	4.48	1937, 1921	4.11

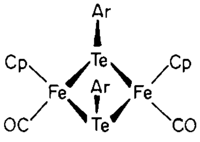
[a] In C_6H_{12} solution.

[b] In CS_2 solution.

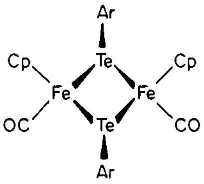
[c] The crystal structure of isomer **127a** of this dimer has been reported[643].



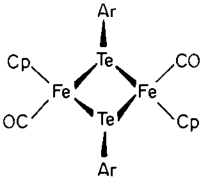
(127a)



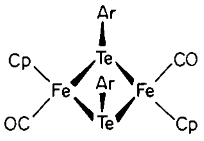
(127b)



(127c)



(127d)



(127e)

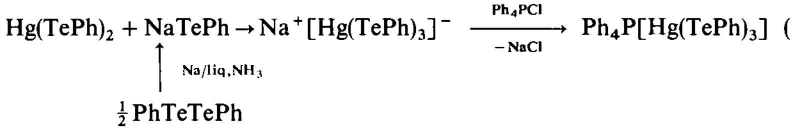
The relative stabilities of the isomers **127a** and **127b** vary significantly with the nature of the chalcogen atom. The amounts of isomer **127b** obtained from equation (249) and related reactions for Ph_2E_2 (E = S, Se) are: Te (major product) > Se (~ 25%) > S (~ 1%). The related reaction with $Te_2(C_6H_4OEt\text{-}p)_2$ gave two isomers, which could be mechanically separated after recrystallization from CH_2Cl_2/hexane[638]. Single-crystal X-ray diffraction of the isomer obtained in lower yield (ca. 5%) showed it to be isomer (**127a**) while the other isomer, obtained as 95% of the total yield, has the structure (**127d**)[638].

The unique dimeric complexes **126** contain both terminal and bridging tellurol ligands[641]. These complexes were characterized by elemental analysis and molecular weight measurements in benzene. Although ^{125}Te Mössbauer spectroscopy failed to resolve the chemically inequivalent Te atoms in these dimers, X-ray photoelectron spectroscopy resolved the two types (Te $3d_{5/2} \simeq 572.5, 573.5$ eV)[644].

Elemental Hg also undergoes oxidative addition reactions with diorganoditellurides (equation 251).

$$Hg + ArTeTeAr \rightarrow Hg(TeAr)_2 \qquad (251)$$
$$Ar = Ph^{357}, C_6H_4OEt\text{-}p^{645}$$

A monomeric trigonal planar anionic complex (Figure 21) was obtained from $Hg(TePh)_2$ and isolated as its air-stable Ph_4P^+ salt as shown in equation (252).



$$Hg(TePh)_2 + \underset{\underset{\frac{1}{2}PhTePh}{\uparrow\, Na/liq,NH_3}}{NaTePh} \rightarrow Na^+[Hg(TePh)_3]^- \xrightarrow[-NaCl]{Ph_4PCl} Ph_4P[Hg(TePh)_3] \qquad (252)$$

Attempts to form $[Hg(TePh)_4]^{2-}$ by reaction of $[Hg(TePh)_3]^-$ with an equivalent of $[Ph_4P]TePh$ in $CHCl_3$ gave $[Hg_3(TePh)_{11}]^{5-}$, isolated as its orange-red crystalline Ph_4P^+ salt. The structure of this complex is unknown.

Several Cr, Mo and W complexes containing both terminal and bridging $PhTe^-$ have been isolated by metathetical reactions with organometallic halide precursors (Table 46). As discussed for the analogous $SePh^-$ complexes (Section II.B.2; equations 117–119), these reactions generally give mixtures of monomeric and dimeric complexes, which can be separated by column chromatography. The crystal structure of the monomeric

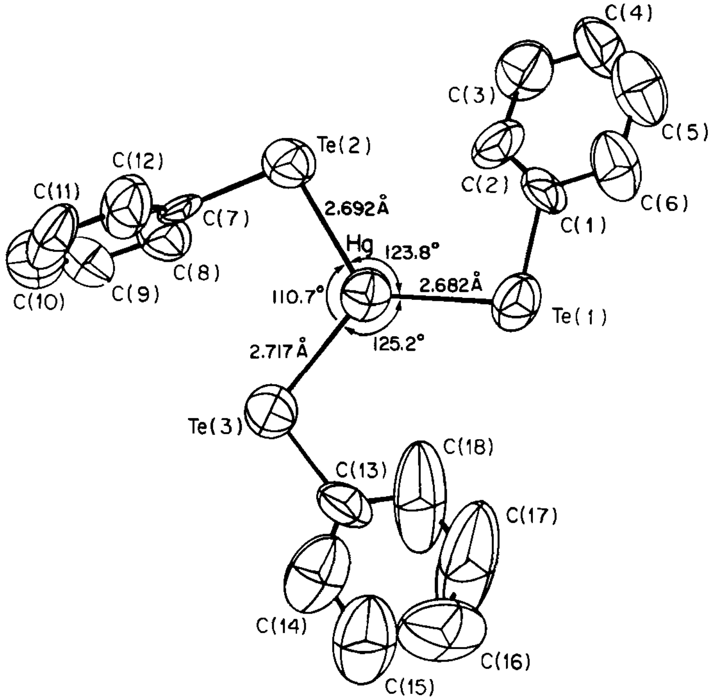


FIGURE 21. Molecular structure of $[Hg(TePh)_3]^-$. Reproduced with permission from Ref. 637

complex $(\eta^7\text{-}C_7H_7)(OC)_2MoTePh$ (Figure 22) has been reported[337]. The Mo—Te bond distance in this complex (2.797 Å) is 0.15 Å shorter than the sum of the covalent radii, indicating a considerable double-bond character.

The monomeric complex $(Ph_3P)_2(OC)_2(Me)OsTeMe$ was prepared by Te methylation (i.e. MeI) followed by borohydride reduction of the telluroformaldehyde complex, $(Ph_3P)_2(OC)_2Os(\eta^2\text{-}CH_2Te)$ (see next section).

The only example of a $—TeO_2R^-$-type ligand was prepared by insertion of TeO_2 into a metal–alkyl bond (equation 253).

$$(\eta^7\text{-}C_7H_7)Mo(CO)_2Me \xrightarrow{TeO_2} (\eta^7\text{-}C_7H_7)Mo(CO)_2Te(O)_2Me \qquad (253)$$

$$\nu_{C\equiv O}\ (CH_2Cl_2) = 1990,\ 1930\,cm^{-1}$$

$$\nu_{Te-C}\ (\text{Nujol mull}) = 470\,cm^{-1}$$

$$\nu_{Te=O}\ (\text{Nujol mull}) = 960,\ 785,\ 750,\ 695\,cm^{-1}$$

$$\delta(CDCl_3) = 2.33\ (Me),\ 5.30\ (C_7H_7)$$

The TeO_2 was an active form of the reagent generated in an ether matrix at − 196 °C in a metal-atom reactor and subsequently reacted with the methyl compound at − 78 °C for 8 weeks. The thermal instability of the red microcrystalline product precluded its X-ray structural characterization, the proposed formulation being based on the similarity of its spectral properties with those of the more stable S and Se analogues.

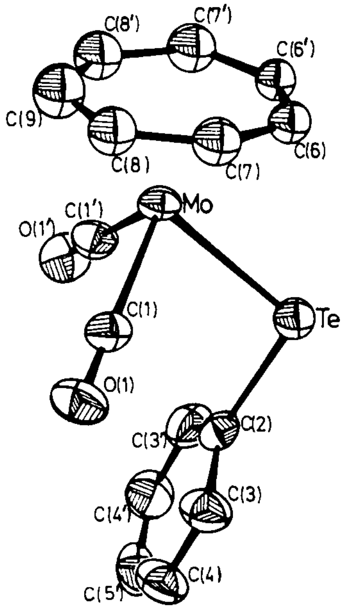


FIGURE 22. Molecular structure of $(\eta^7\text{-}C_7H_7)Mo(CO)_2TePh$. Reproduced with permission from Ref. 337

Complexes containing both terminal (equation 254) and bridging (equation 255) TeH^- have been prepared.

$$\begin{tikzcd} M(CO)_5THF + Na_2Te \arrow[r, "EtOH", "-60\ ^\circ C"'] & Na[M(CO)_5TeH] \arrow[r, "X^+Cl^-", "-NaCl"'] & X[M(CO)_5TeH] \qquad (254) \\ M(CO)_6 \arrow[u, "-CO", "h\nu/THF\ -40\ ^\circ C"'] & & \end{tikzcd}$$

$X = PPN, M = Cr$
$X = Ph_4As, M = W$

$$X[M(CO)_5TeH] \xrightarrow{M(CO)_5(THF)} X[(CO)_5M(\mu\text{-}TeH)M(CO)_5] \qquad (255)$$

$X = PPN,\ M = Cr$
$X = Ph_4As, M = W$

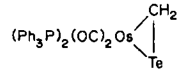
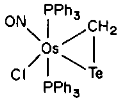
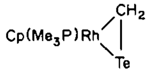
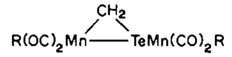
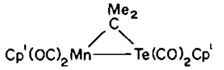
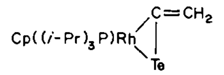
The terminal TeH^- ligand can be alkylated to the neutral dialkyl telluride analogue (equation 256).

$$PPN[Cr(CO)_5TeH \xrightarrow[EtOH]{[Et_3O][BF_4]} (OC)_5CrTeEt_2 \qquad (256)$$

C. Bidentate Ligands

Only three well-characterized examples of bidentate Te ligands have been reported (Table 48).

TABLE 48. Complexes with bidentate tellurium ligands

Ligand	Complex	Ref.
Telluroformaldehyde		
η^2-CH_2Te		418
		419
		420
η^2,μ-CH_2Te		
	R = Cp	421
	R = Cp'	646, 647
η^2,μ-CMe_2Te		647
Telluroketene		648
(128)	$[Pt(128)_2][Pt(SCN)_4]\cdot 2$ DMF	57[a]

[a] Structure determined by single-crystal X-ray diffraction.

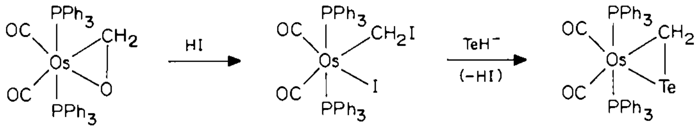
In 1983 the first examples of telluroformaldehyde complexes, involving both chelating η^2-CH_2Te (equations 257–259) and bridging η^2,μ_2-CH_2Te (equations 260 and 261) bonding modes of this ligand, were reported.

These reactions are further examples of coordination stabilization of an unstable organic molecule; monomeric telluroformaldehyde is not known, although a trimer has been reported but not characterized[649]. All four derivatives in the series $(Ph_3P)_2(OC)_2Os(\eta^2\text{-}CH_2E)$ ($E = O$[650], S[651], Se[418], Te[418]) have been prepared.

The rigid RhCTe three-membered ring in $Cp(Me_3P)Rh(\eta^2\text{-}CH_2Te)$ produces two ^{1}H-NMR signals for the CH_2Te protons ($\delta = 5.50$ (ddd, $J_{HH} = 0.6$ Hz, $J_{RhH} = 0.6$ Hz, $J_{PH} = 10.2$ Hz), 6.63 (ddd, $J_{HH} = 0.6$ Hz, $J_{RhH} = 2.0$ Hz, $J_{PH} = 0.6$ Hz)[420]). Similarly, the asymmetry of the dimer $Cp(OC)_2Mn(\eta^2,\mu\text{-}TeCH_2)Mn(CO)_2Cp$ results in an AB system for the CH_2 protons in its ^{1}H-NMR spectrum (equation 260)[421].

The synthesis of μ-alkylidene organotransition-metal complexes (e.g. $M(\eta^2,\mu\text{-}CH_2Te)M$) by carbene transfer from diazoalkane precursors to multiply bonded main-group/transition-metal compounds (e.g. equations 260 and 261) is a recently developed route, which may have general utility for such derivatives[421,554,647].

The previously unknown telluroketene molecule has been stabilized by coordination to Rh(I) in a two-step reaction involving insertion of elemental Te into the metal–carbon bond of an initially formed vinylidene complex[648] (equation 262).

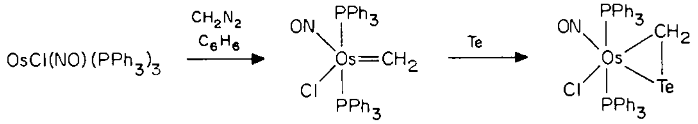


(Ref. 418) (257)

bright yellow air-stable crystals

$\nu_{C\equiv O}$(Nujol mull) ▫ 1991, 1922 cm^{-1}

$\delta(CDCl_3)$: 2.08 (t, CH_2; $^3J(^{31}P-^1H)$ = 6.0 Hz)



(Ref. 419) (258)

$\nu_{N=O}$ = 1740 cm^{-1}

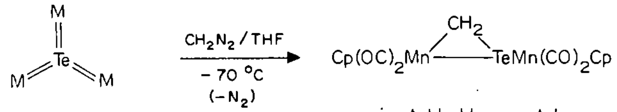
$\delta(CDCl_3)$: 4.88 (t, CH_2; $J(^{31}P-^1H)$ = 3 Hz)

$$Cp(Me_3P)Rh(C_2H_4) \xrightarrow{CH_2I_2} Cp(Me_3P)Rh(I)(CH_2I) \xrightarrow[-2\ NaI,\ -TeH_2]{2\ NaTeH/THF,\ 25\ ^\circ C} Cp(Me_3P)Rh(\eta^2\text{-}CH_2Te)$$

24%

dark green, slightly air-sensitive crystals

(Ref. 420) (259)



M = $CpMn(CO)_2$

air-stable blue crystals

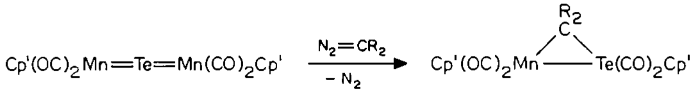
(Ref. 421) (260)

$\nu_{C\equiv O}$(THF) = 1994, 1939, 1922, 1871 cm^{-1}

$\delta(C_6D_6)$: 4.29 (s, Cp), 3.79 (s, Cp),

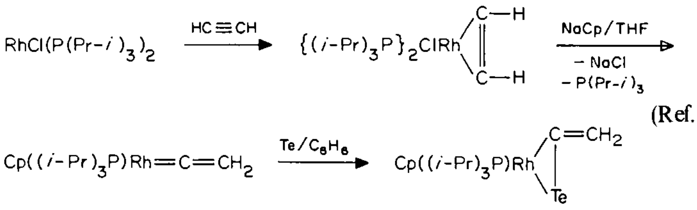
5.96 (d, CH_2; $^2J_{HH}$ = 3.7 Hz),

6.02 (d, CH_2; $^2J_{HH}$ = 3.7 Hz)



R = H, Me

(Ref. 647) (261)



(Ref. 648) (262)

70%

air-sensitive green solid

m.p. 102 °C

$\nu_{C=C}$ ▫ 1572 cm^{-1}

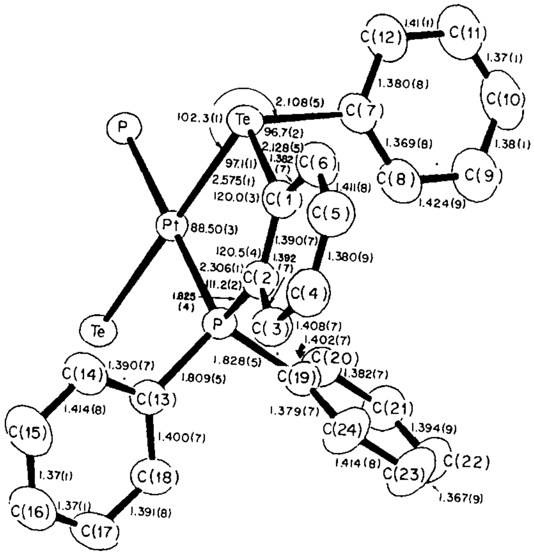
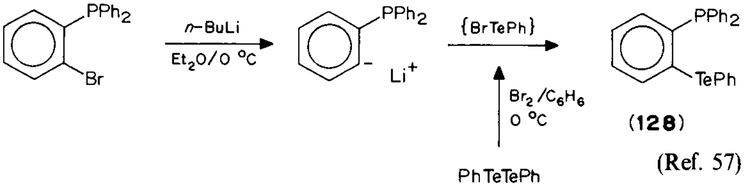


FIGURE 23. Molecular structure of $[Pt(Ph_2PC_6H_4TePh\text{-}o)_2]^{2+}$. Reproduced with permission from Ref. 57

Single-crystal X-ray diffraction has confirmed the proposed coordination mode for the more stable thioketene analogue[648].

The first example of a stable hybrid bidentate ligand containing a Te donor site was prepared recently (equation 263). Reaction of **128** with $K_2Pt(SCN)_4$ gave a complex formulated as the neutral square-planar $[Pt(\mathbf{128})(SCN)_2]$ ($\nu_{C\equiv N} = 2102$, $2118\,cm^{-1}$). Upon recrystallization from hot DMF, however, the complex rearranged to give the Magnus-type salt $[Pt(\mathbf{128})_2][Pt(SCN)_4]\cdot 2\,DMF$[57] ($\nu_{C\equiv N} = 2108\,cm^{-1}$). Single-crystal X-ray diffraction confirmed the proposed bidentate P, Te coordination of the hybrid ligand (Figure 23).



(Ref. 57) (263)

Complexes of Cu(I) and Cu(II) with the potentially chelating ligand di-2-aminophenyl ditelluride (e.g. $[CuCl_n(C_{12}H_{12}N_2Te_2)]_m$; $n = 1, 2$) have been described, but their low solubility, presumably due to polymeric structures, precluded their definitive characterization[631].

D. Complexes Incorporating Te_n ($n = 1, 2$)

Although not as extensive as S_n and Se_n ligand chemistry, several types of transition-metal dimers and cluster compounds incorporating Te atoms are known (Table 49). The

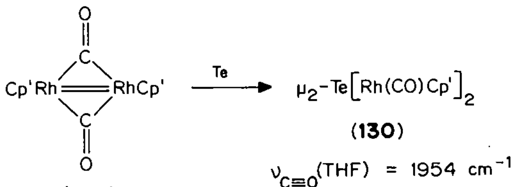
TABLE 49. Complexes with Te_n ligands

Ligand	Complex	Ref.
μ_2-Te	$Li_2[(ON)_2Fe(\mu_2\text{-}Te)_2Fe(NO)_2]$	353
	μ_2-Te[Cp′(OC)Rh]$_2$	556^a
	μ_2-Te[V(CO)$_3$dppe]$_2$	559
	μ_2-Te[Mn(CO)$_2$Cp′]$_2$	646, 647^a
	$(OC)_3Fe(\mu_2\text{-}Te\{Pt(PPh_3)_2\})Fe(CO)_3$	570, 571
μ_2, η^2-Te_2	$(OC)_3Fe(\mu_2,\eta^2\text{-}Te_2)Fe(CO)_3$	570, 571, 562
	$Nb_2Te_2X_6$ X = Br, I	579
μ_3-Te	μ_3-Te[Mn(CO)$_2$Cp]$_3$	653
	$Fe_3(\mu_3\text{-}Te)_2(CO)_9$	568, 654–661^a
	$Fe_3(\mu_3\text{-}Te)_2(CO)_nL_m$ L = P(Bu-n)$_3$, P(OPh)$_3$, AsPh$_3$ $n = 9, 8, m = 1; n = 7, m = 2$ L = PPh$_3$^{a}, $Ph_2P(CH_2)_nPPh_2$ (n = 1–3), CO, t-BuNC	655 660
	$Fe_3(\mu_3\text{-}E)(\mu_3\text{-}Te)(CO)_9$ E = S, Se	662, 663
	$Fe_3(\mu_3\text{-}E)(\mu_3\text{-}Te)(CO)_nL_m$ E = S, Se $n = 8, m = 1; n = 7, m = 2$ L = AsPh$_3$, P(OPh)$_3$	663
	$Fe_4(\mu_3\text{-}Te)_4(CO)_{12}$	652, 661
	$FeCo_2(\mu_3\text{-}Te)(CO)_9$	589^a, 661
	$CpRhFe_2(\mu_3\text{-}Te)_2(CO)_x$ $x = 6, 7$	664
	$H_2Ru_3(\mu_3\text{-}Te)(CO)_9$	591
	$Ru_3(\mu_3\text{-}Te)_2(CO)_9$	590
	$Os_3(\mu_3\text{-}Te)_2(CO)_9$	590
μ_4-Te	$Co_4(CO)_8(\mu_2\text{-}CO)_2(\mu_2\text{-}Te)_2$	618, 661, 665^a
	$Co_4Te_2(CO)_{11}$	661

^{a}Structures determined by single-crystal X-ray diffraction.

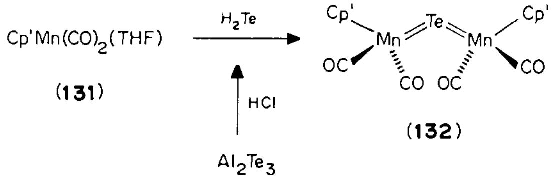
low tendency of Te to form Te_n ($n > 2$) rings and chains comparable to S and Se (e.g. Section II.G.4) is no doubt responsible for this less diverse ligand chemistry of the heaviest member of the chalcogen elements. Te vapour, for example, consists primarily of Te_2 with less than 1% Te_3[666].

Dimeric complexes incorporating bridging Te atoms, **130** and **132**, were prepared recently by insertion of elemental Te into the reactive Rh=Rh double bond of **129** (equation 264) and by reaction of TeH_2 with a substitution labile organomanganese(I) complex (**131**) (equation 265).



(129) **(130)** (Ref. 556a) (264)

$\nu_{C\equiv O}$(THF) = 1954 cm^{-1}

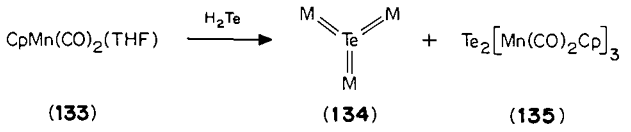


(Ref. 647) (265)

The reactivity of M—M multiple bonds has been shown to be useful for the synthesis of a variety of alkylidene-bridged organometallics[554] as well as S[556], Se (equation 215) and Te (equation 264) insertion products. These reactions generally go under mild conditions in quantitative yields[554,556]. Although elemental S reacts with **129** at -20 °C to give $(\eta^2$-$S_4)Rh(\mu$-$CO)Rh(\eta^2$-$S_4)$[556a] with CO elimination, the analogous reactions with Se (equation 215) and Te (equation 264) (-80 to 0 °C) gave products containing only one chalcogen atom. The detailed structures of these latter complexes (three-membered Rh_2E ring systems or Rh=E=Rh geometries) await definitive crystallographic studies.

The structure of **132** has been confirmed by single-crystal X-ray diffraction[647]. The complex contains a bent Mn—Te—Mn framework with multiple bonding (Mn—Te = 2.459(2) Å vs. 2.70 Å for the sum of the covalent radii). The intramolecular Mn—Mn distances (4.209 Å) show that no metal-metal bonding is present. In contrast, the S analogue, $[\mu$-$S[Cp'Re(CO)_2]_2]$[647], has been shown to contain a Re—Re bond. The dimer **132** readily reacts with diazoalkanes to give alkylidene addition products (equation 261)[647].

Replacement of the Cp' ligand in **131** by the less sterically demanding unsubstituted Cp ligand in **133** in equation (265) results in the formation of a μ_3-bridged product **134** as well as a small amount of another product (**135**) of uncertain structure (equation 266).



(266)

M = CpMn(CO)$_2$

	(134)	(135)
	black crystals(47%)	black crystals (0.8%)
$\nu_{C\equiv O}(Et_2O)$	1998m, 1992m (sh), 1940s, 1928vs, 1909m, 1886w cm^{-1}	1994s, 1982m(sh), 1935vs, 1919vs, 1901s, 1886m(sh) cm^{-1}
^{1}H-NMR $\delta((CD_3)_2CO)$	5.23 (s,Cp)	5.23

The propeller-type arrangement of the $MnTe_3$ core of **134** has been confirmed by X-ray diffraction. The central Te atom lies 0.034(1) Å above the centre of the triangular Mn_3 plane, and as in **132**, formal Mn=Te double bonds have been proposed on the basis of bond distances ($Mn—Te_{av.}$ = 2.485 Å vs. 2.54 Å for the sum of the covalent radii) and the inert gas formalism[652].

A redox route was used to prepare the Te-bridged dimer (**136**) (equation 267).

$$Na[V(CO)_4dppe] + Na_2TeO_3 \xrightarrow{H_3PO_4} [V(CO)_3dppe]_2Te \qquad \text{(Ref. 559)} \qquad (267)$$

(136)

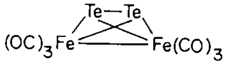
25%

$\nu_{C\equiv O}$ = 1970m, 1925s, 1880vs cm^{-1}

A linear V$\doteq$Te$\doteq$V arrangement was proposed for **136** because of its spectral similarity with the S analogue, whose structure has been determined by single-crystal X-ray diffraction.

The dimeric complex $[(ON)_2Fe(\mu\text{-}Te)_2Fe(NO)_2]^{2-}$ was prepared by the previously described metathetical route (e.g. $(ON)_2Fe(\mu\text{-}I)_2Fe(NO)_2 + Li_2Te$; equation 121)[353]. Like the Se analogue, this dimer can undergo μ_2-Te alkylation to give the corresponding neutral dimers (e.g. equation 121)[353].

The complex **137** was first described by Lesch and Rauchfuss[570], who obtained it, contaminated with **138**, in less than 1% yield from fractional sublimation (0.1 mm Hg/45 °C/36 h) of the crude product obtained by Hieber and Gruber's[568] original synthesis of **138** (equation 268).



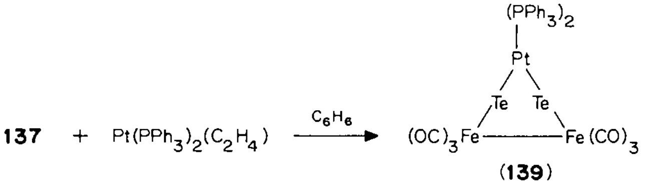
(137)

$$3\,Fe(CO)_5 \xrightarrow{NaOH/MeOH} 3\,[Fe(CO)_4]^{2-} + 2\,TeO_3^{2-} + 10\,H^+ \xrightarrow[-2\,CO]{-5\,H_2O} \underset{\mathbf{(138)}}{Fe_3(\mu_3\text{-}Te)_2(CO)_9} + \mathbf{137} \qquad (268)$$

$\nu_{C\equiv O}$ (hexane; cm^{-1}): 2045s 2025s 2004s; 2067m 2028s 1995s

Although the dimer **137** could not be obtained pure, it was characterized by infrared spectroscopy of the sublimate (**137** + **138**), the latter cluster being a well-characterized compound (Table 49). In contrast, the S and Se dimers obtained in reactions analogous to equation (268) were readily separated from $Fe_3(\mu_3\text{-}E)_2(CO)_9$ (E = S, Se) by fractional sublimation.

An effective separation of **137** from **138** was, however, achieved by using the selective reactivity of **137** in an oxidative addition reaction with a Pt(o) substrate[570,571] (equation 269).



(269)

(139)

red needles (70%)

$\nu_{C\equiv O}$ = 2034s, 1995vs, 1960s cm^{-1}

The cluster **138**, lacking a reactive Te—Te bond, is unreactive to oxidative addition, and the product (**139**) can be readily separated from the former cluster by adsorption chromatography. Surprisingly, Te_2Ph_2 was reported to be unreactive towards $Pt(PPh_3)_2(C_2H_4)$[570]. In contrast, $Pd(PPh_3)_4$ readily undergoes oxidative addition reactions with ditellurides (equation 250)[641], and $Pt(PPh_3)_2(C_2H_4)$ oxidatively adds S_2Ph_2 and Se_2Ph_2[571].

The molecular structure of the Se analogue of **139** has been confirmed by single-crystal X-ray diffraction, and an analogous structure for the Te dimer was inferred from the similar spectral and chemical properties of the two derivatives[571].

In subsequent work[652] non-aqueous gel permeation chromatography with 8% cross-linked polystyrene was an effective method for the separation of the thermally labile $(OC)_3Fe(\mu_2, \eta^2\text{-}Te_2)Fe(CO)_3$ from $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ (products of equation 268). By using this size-exclusion method, yields of ca. 4% of **137**, based on starting $Fe(CO)_5$, were obtained. In an additional modification of the original Hieber and Gruber method (equation 268), the reaction solution was kept at 0 °C to minimize decomposition of the thermally labile **137**. After acidification and CH_2Cl_2 extraction of the black reaction residue, the mixture was applied to a column of Bio-Beads SX-8 resin swelled with CH_2Cl_2 and eluted with the same solvent. A purple band of **138** (58%) eluted first, followed by an orange band of **137** (4.3%). Solutions of **137** were air-stable, but attempts to isolate the solid dimer by evaporation of the solvent under a stream of Ar or CO resulted in decomposition to an insoluble black material, which was tentatively formulated as $Fe_4(\mu_3\text{-}Te)_4(CO)_{12}$. Although this cubane-type cluster was not previously reported, an analogous insoluble and non-volatile cluster, $Co_4(\mu_3\text{-}Sb)_4(CO)_{12}$, has been structurally characterized[667]. Thermolysis of an acetonitrile solution of $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ (80–90 °C) under 2000 psi of CO gave $Fe_4Te_4(CO)_{12}$ in 69% yield (black crystals; $\nu_{C\equiv O}$ (mull): 2043vs, 2035sh, 1994sh, 1988sh, 1982s, 1968w cm^{-1})[661].

The dimer **137** was characterized by mass spectroscopy, which showed peaks for all $Fe_2Te_2(CO)_x$ ($x = 0$–6) fragments, and by infrared and ^{125}Te-NMR spectroscopy[652].

The instability of **137** was rationalized in terms of the considerable strain imposed on the tetrahedral Fe_2Te_2 framework because of the large size of the Te atoms vs. S and Se atoms, which gave stable $Fe_2(\mu_2\text{-}E_2)(CO)_6$ dimers.

Compound (**137**) was later obtained in 40% yield by treatment of methanolic solutions of **138** with NaOMe, followed by acidification with 6M HCl[661].

On the basis of the reactions illustrated in equations (270) and (271), $Fe_2(\mu_2\text{-}Te_2)(CO)_6$ was proposed to be an intermediate in the formation of $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ via $Fe_3(\mu_3\text{-}Te)_2(CO)_{10}$[652].

$$\mathbf{137} + Fe(CO)_5 + 2\,Me_3NO \xrightarrow{CH_2Cl_2} \mathbf{138} + 2\,CO_2 + 2\,Me_3N \qquad (270)$$

$$\mathbf{137} + Fe(CO)_5 \xrightarrow[\text{2. 6M HCl}]{\text{1. MeOH/KOH}} \underset{50\%}{\mathbf{138}} + \underset{(\mathbf{140})\ 50\%}{Fe_3(\mu_3\text{-}Te)_2(CO)_{10}} \qquad (271)$$

The formation of **138** from **137** and $Fe(CO)_5$ in neutral solution occurs only in the presence of the decarbonylation reagent Me_3NO[668] (equation 270). Treatment of **137** with a basic solution of $Fe(CO)_5$ ($HFe(CO)_4^-$ forms under the latter condition) gave about equal amounts of **138** and **140**, the latter presumably forming via oxidative addition of $[HFe(CO)_4]^-$ across the Te—Te bond of **137**, analogous to the reaction in equation (269). The decacarbonyl **140**, which has also been prepared by treatment of **138** with CO[655,660], readily loses CO, thermally (refluxing 0.5 h in hexane) or chemically (CH_2Cl_2 solution of Me_3NO at room temperature), to give **138** quantitatively[652]. The decacarbonyl **140** has been obtained in 70% yield by treatment of a well-stirred mixture of CH_2Cl_2 and aqueous K_2TeO_3 with methanolic $K[HFe(CO)_4]$ at 0 °C, followed by acidification and CH_2Cl_2 extraction[652].

The rather low-yield synthesis of **137** has until recently[661] prevented extensive investigation of its chemistry, but the presence of the reactive Te—Te bond should allow its use in the synthesis of a wide variety of mixed metal clusters (e.g. see Figure 12).

As in the Se_n ligands, the first report of a metal cluster complex incorporating a naked Te atom was Hieber and Gruber's synthesis of $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ (equation 268)[568]. Although this stable black cluster compound was first described in 1958, its X-ray structure determination was not reported until 1982[654]. It was shown to be isostructural

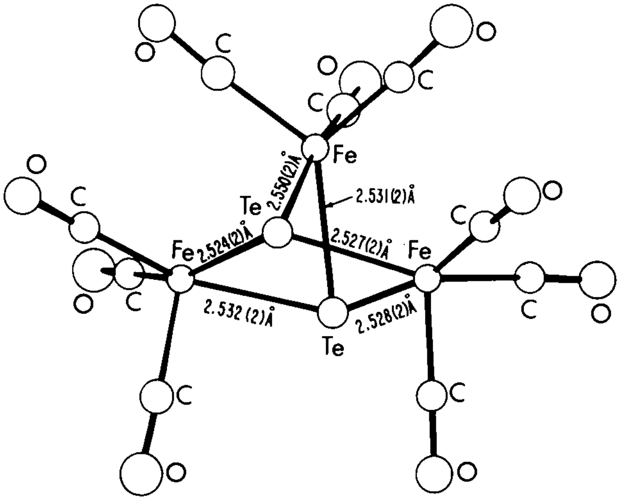


FIGURE 24. Molecular structure of $Fe_3(\mu_3\text{-}Te)_2(CO)_9$

with $Fe_3(\mu_3\text{-}Se)_2(CO)_9$, the Fe_3Te_2 skeleton being square-pyramidal with alternating Fe and Te atoms in the base and an apical Fe atom (Figure 24). These workers[654] obtained the cluster as black needles by cooling a pentane extract of the residue from the reaction of $Fe(CO)_4I_2$ and Na_2Te (equation 272).

$$3\,Fe(CO)_5 + 2\,I_2 + 2\,Na_2Te \xrightarrow[Et_2O]{THF} Fe_3(\mu_3\text{-}Te)_2(CO)_9 + 4\,NaI + 6\,CO \qquad (272)$$

The mass spectrum of **138** shows a molecular peak and nine peaks corresponding to the successive loss of the nine CO ligands, the $[Fe_3Te_2]^+$ peak being the most intense[658].

A variable-temperature ^{13}C-NMR investigation of **138**[659] showed that two discrete CO exchange processes occur in this cluster (Figure 25). At room temperature only two resonances are observed, corresponding to the equivalent carbonyls on the apical iron, Fe(1), and the two basal iron atoms, Fe(2). At −87 °C the carbonyls on the apical iron, Fe(1), remain equivalent, but two of the three chemically inequivalent types of CO ligands on the basal iron atom, Fe(2), are resolved. Delocalized exchange between CO ligands on the apical and basal iron atoms does not occur.

The ^{125}Te-NMR spectrum of this cluster showed an unexpectedly large downfield shift compared to the $(OC)_3Fe(\mu_2,\eta^2\text{-}Te_2)Fe(CO)_3$ dimer[652] (Table 50). Indeed, ^{125}Te-NMR spectroscopy has been shown to be a useful structural probe for a variety of Te compounds, a range of some 5000 ppm having been observed for the compounds measured to date[669]. In addition, in complexes with metals having NMR active nuclei, ^{125}Te–M coupling constants can provide useful structural information (e.g. Figure 19).

Reactions of **138** with Lewis bases (phosphines, CO, *t*-BuNC) initially give adducts $(Fe_3(\mu_3\text{-}Te)_2(CO)_9L)$ followed by substitution reactions under more forcing conditions to give $Fe_3(\mu_3\text{-}Te)_2(CO)_nL_m$ ($n = 8$, $m = 1$ and $n = 7$, $m = 2$; Table 49)[659,660].

The adduct $Fe_3(\mu_3\text{-}Te)_2(CO)_9PPh_3$ has been characterized by single-crystal X-ray diffraction[660]. The structure contains an isosceles triangle of Fe atoms joined by capping μ_3-Te atoms. Each Fe atom contains three terminal CO ligands, and the phosphine coordinates to a unique Fe atom. A variable-temperature ^{13}C-NMR

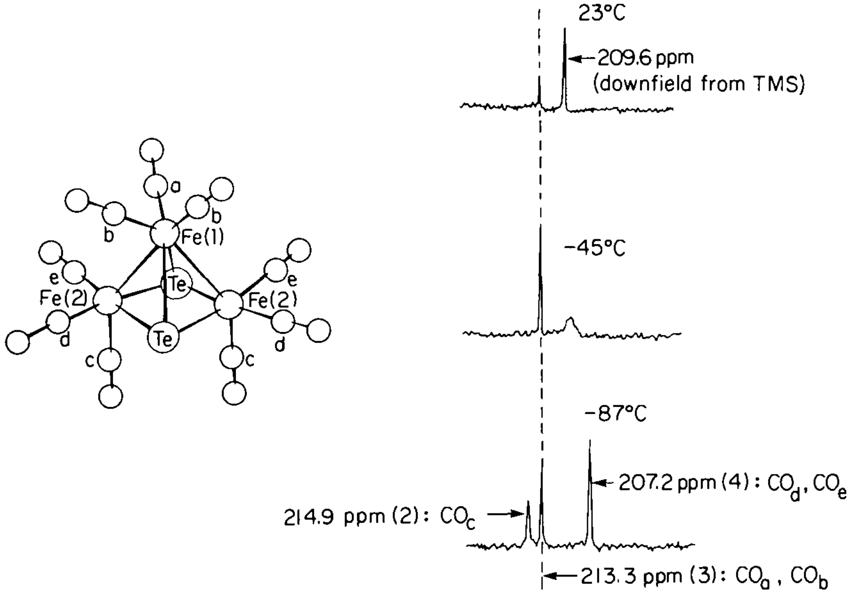


FIGURE 25. Variable-temperature ^{13}C-NMR spectra of $Fe_3(\mu_3\text{-}Te)_2(CO)_9$ ($CDCl_3$ solution). Reproduced with permission from Ref. 659

investigation[659] of the adduct $Fe_3(\mu_3\text{-}Te)_2(CO)_9(P(Bu\text{-}n)_3)$ had been unable to establish the coordination site (Fe or Te) of the phosphine ligand.

Mixed cluster compounds $Fe_3(\mu_3\text{-}Te)(\mu_3\text{-}E)(CO)_9$ (E = S, Se) have been prepared by the route described in equation (268) with appropriate equimolar mixtures of TeO_3^{2-}/EO_3^{2-} [662]. The reactions gave the three possible clusters, $(\mu_3\text{-}E)_2$, $(\mu_3\text{-}Te)_2$, and $(\mu_3\text{-}Te)$ $(\mu_3\text{-}E)$, which were separated by repeated preparative thin-layer chromatography.

TABLE 50. ^{125}Te-NMR data for metal complexes containing Te ligands

Complex	δ (ppm)[a]	$J(^{125}\text{Te–M})$ (Hz)	Ref.
$Fe_2(\mu_2\text{-}Te_2)(CO)_6$	−733		652
$Fe_3(\mu_3\text{-}Te)_2(CO)_9$	+1123		652
$Fe_2(CO)_6Te_2Pt(PPh_3)_2$	−861	M = ^{195}Pt, 561	571
$CpCoFe_2Te_2(CO)_7$	−825		661
$CpCoFe_2Te_2(CO)_6$	1103, 1087[b]		661
$Fe_3(\mu_3\text{-}Te)_2(CO)_9PPh_3$	−887		664
	−938	M = ^{31}P, 42	
$Fe_3(\mu_3\text{-}Te)_2(CO)_8PPh_3$	1062		664
$CpRhFe_2Te_2(CO)_6PPh_3$	−925	M = ^{103}Rh, 100	664
	−838	M = ^{31}P, 21	
$CpRhFe_2Te_2(CO)_7$	−973	M = ^{103}Rh, 93	664
$CpRhFe_2Te_2(CO)_6$	1081		664
	1109		

[a] Measured in $CDCl_3$ vs. external neat $TeMe_2$; positive chemical shifts are downfield.
[b] The cluster gives two isomers in solution[661].

Like the parent cluster **138**, these mixed derivatives are air-stable and give substitution reactions with $\mathrm{AsPh_3}$ and $\mathrm{P(OPh)_3}$[663].

The cluster $\mathrm{Fe_3(\mu_3\text{-}Te)_2(CO)_9}$ has been shown to be a useful precursor for the synthesis of a variety of mixed metal cluster compounds[661,664]. This reagent is especially attractive since it is one of the relatively few transition-metal carbonyl cluster compounds that can be prepared easily in good yields from inexpensive starting materials[652].

The utility of this cluster has been attributed to its conversion to the reactive $\mathrm{Fe_2(\mu_2,\eta^2\text{-}Te_2)(CO)_6}$ in polar solvents (e.g. acetonitrile). Indeed, the mixed metal cluster $\mathrm{Fe_2Te_2Pt(CO)_6(PPh_3)_2}$ (**139**), originally prepared from $\mathrm{Fe_2(\mu_2,\eta^2\text{-}Te_2)(CO)_6}$ (equation 269), can be isolated in 76% yield from the reaction of $\mathrm{Fe_3(\mu_3\text{-}Te)_2(CO)_9}$ (**138**) and $\mathrm{Pt(PPh_3)_2C_2H_4}$ in MeCN at room temperature[661]. Other syntheses of mixed metal clusters are illustrated in equations (273)–(276).

$$\mathbf{138} + \mathrm{CpCo(CO)_2} \xrightarrow[\text{reflux}]{\text{MeCN}} \mathrm{CpCoFe_2Te_2(CO)_7} \qquad \text{(Ref. 661)} \qquad (273)$$

70%

FDMS: 687 ([M]$^+$)

$$\mathbf{138} + \mathrm{Co_2(CO)_8} \xrightarrow[\substack{180\ ^\circ\mathrm{C} \\ 1700\ \text{psi CO}}]{\text{hexane}} \mathrm{Co_2FeTe(CO)_9} \qquad \text{(Ref. 661)} \qquad (274)$$

76%

$$\mathbf{138} + \mathrm{Co_2(CO)_8} \xrightarrow[\substack{150\ ^\circ\mathrm{C} \\ 2000\ \text{psi CO}}]{\mathrm{CH_2Cl_2}} \mathrm{Co_4Te_2(CO)_{11}} \qquad \text{(Ref. 661)} \qquad (275)$$

64%

$$\mathbf{138} + \mathrm{CpRh(CO)_2} \xrightarrow[\text{reflux}]{\text{MeCN}} \mathrm{CpRhFe_2Te_2(CO)_7} \qquad \text{(Ref. 664)} \qquad (276)$$

73%

FDMS: 731 ([M]$^{+\cdot}$)

The clusters $\mathrm{CpMFe_2Te_2(CO)_7}$ (M = Co[661], Rh[664]) can both be decarbonylated by $\mathrm{Me_3NO}$ to give $\mathrm{CpMFe_2Te_2(CO)_6}$ clusters, which exist in two isomeric forms as evidenced by ^{125}Te-NMR (Table 50), but the isomers cannot be separated by chromatography.

All of these clusters have been characterized by infrared and ^{125}Te-NMR (Table 50) spectroscopy as well as by field-desorption mass spectroscopy (FDMS), a technique especially useful for thermally labile compounds[670].

In two cases (equations 277 and 278), diorganotellurides have been used as precursors to introduce Te into transition-metal cluster frameworks.

$$\mathrm{Co_2(CO)_8} + \mathrm{Fe_3(CO)_{12}} + \mathrm{Et_2Te} \xrightarrow{\text{hexane}} \mathrm{FeCo_2(\mu_3\text{-}Te)(CO)_9}$$

30% (Ref. 589) (277)

air-stable brown crystals

$$2\,\mathrm{Co_2(CO)_8} + 2\,\mathrm{TePh_2} \xrightarrow[\substack{20\ ^\circ\mathrm{C} \\ -6\ \mathrm{CO}}]{\mathrm{C_6H_6}} \mathrm{Co_4(\mu_4\text{-}Te)_2(CO)_8(\mu_2\text{-}CO)_2} + \mathrm{PhPh}$$

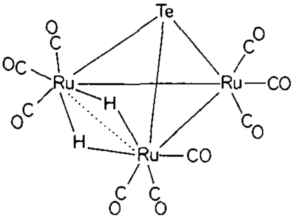
(Ref. 618) (278)

Diphenyl telluride was previously shown to be a precursor for μ_2-$\mathrm{TePh^-}$ bridging ligands (equations 234 and 235). The formation of transition-metal cluster compounds containing 'naked' main-group elements by using organometallic compounds of the latter has, however, been demonstrated recently in other systems (e.g. $[Rh_9P(CO)_{21}]^{2-}$[671], $[Rh_{10}P(CO)_{22}]^{3-}$[672], $[Rh_{12}Sb(CO)_{27}]^{3-}$[673] and $[Rh_{10}As(CO)_{22}]^{3-}$[674] from $Rh(CO)_2acac$ and PPh_3, $SbPh_3$ and $AsPh_3$, respectively).

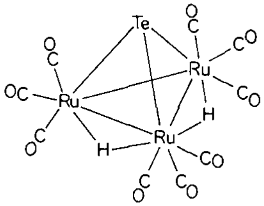
The molecular structure of $FeCo_2(\mu_3\text{-}Te)(CO)_9$ has been described as a tetrahedral $FeCo_3Te$ cluster system formed by the symmetrical coordination of an apical Te atom to a basal $FeCo_2(CO)_9$ fragment containing three $M(CO)_3$ groups at the corners of an equilateral triangle and linked to one another by metal–metal bonds[589].

The cluster $Co_4(\mu_4\text{-}Te)_2(CO)_8(\mu_2\text{-}CO)_2$ (equation 278) is the only reported structure involving a μ_4-Te bridging ligand[665], although other related structures involving a Co_4E framework with an apical main-group element bridging four Co atoms in a basal rectangle are known[665,675].

Attempts to prepare $Ru_3Te_2(CO)_9$ by reaction of $Ru_3(CO)_{12}$ in alkaline tellurite (TeO_2 + aqueous KOH), conditions used for $Fe_3Te_2(CO)_9$ (equation 268), gave instead the hydride cluster $H_2Ru_3Te(CO)_9$ in 0.5% yield after acidification of the reaction solution with 2N H_2SO_4 and CCl_4 extraction of the resulting precipitate[591]. Two structures (**141a** and **b**) were proposed for this cluster. The reaction of $Ru_3(CO)_{12}$ with Te powder in *n*-octane under a pressure of CO/H_2 (35 atm, 1:1) was reported to give a mixture of $H_2Ru_3Te(CO)_9$ and $Ru_3Te_2(CO)_9$[590]. These workers also reported that under a pure CO atmosphere the yield of the hydrido cluster was significantly decreased. These two clusters were separated by thin-layer chromatography, although data (elemental analysis, infrared and mass spectroscopy) are reported only for $H_2Ru_3Te(CO)_9$[590].



(141a)



(141b)

A similar reaction of $Os_3(CO)_{12}$ with elemental Te in refluxing *n*-octane gave a mixture of $H_2Os_3Te(CO)_9$, $Os_3Te_2(CO)_9$ and $H_2Os_4Te_2(CO)_{12}$ although again only data for $Os_3Te_2(CO)_9$ were reported[590]. As usual for such complex metal clusters, definitive structural characterization requires single-crystal X-ray diffraction.

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