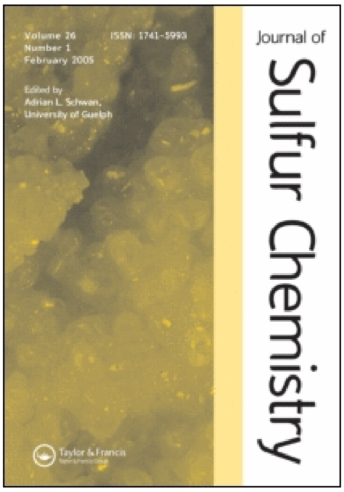

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STRUCTURAL AND CHEMICAL CONSEQUENCES OF INTRAMOLECULAR N(O)→Te COORDINATION IN ORGANOTELLURIUM COMPOUNDS

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The structural characteristics of organotellurium compounds possessing intramolecular coordinate N→Te and O→Te bonds are systematised and critically analysed. Particular emphasis has been placed on the enhancement of the stability and the description of the characteristic reactivity of compounds with this type of bond.

Key words: Organotellurium compounds, intramolecular coordination, N→Te and O→Te bonds.

CONTENTS

1. INTRODUCTION

Intramolecular coordination has long been recognised as a key factor influencing the structure, stability and reactivity of organoelement compounds. The most widespread intramolecularly coordinated compounds are those associated with the formation within a molecule of a donor-acceptor bond between a main group or transition metal atom and a lone-pair coordinating atom (pnictogen or chalcogen). Whereas the structural types of these compounds have been thoroughly systematised and their properties amply reviewed, see for example[1-4] and references therein, much less attention has been paid to another type of intramolecular coordination which involves attractive interactions between electron-rich heteroatoms. A large number of organosulfur and organoselenium compounds are known, where the actual conformation is defined by intramolecularX···Y contacts (X = S, Se; Y = N, O, S).[5,6] The importance of such attractive interactions in biology is particularly apparent due to their role in controlling the secondary or tertiary structure of biomolecules.[7] The X···Y distances between mutually attracted electron-rich centres span the whole range of values corresponding to purely covalent σ-bonds and those exceeding the sum of the van der Waals radii. Whereas the nature and properties of the former type of bond are well understood, and the latter case corresponds to nonbonded contacts, the gap remaining represents a critical region with a specific type of bonding that cannot be assigned to any conventional interaction. Considered as so-called secondary bonds,[8] the intermediate-distance X···Y contacts contain contributions from different types of interaction, including for example electrostatic, negative hyperconjugation, d-orbital participation, or cyclic delocalization. At the closest approach of the attracting centres, the bonding may be attributed to a three centre-four electron (3c-4e) interaction, of the hypervalent type. Depending upon the relative contribution of distinct binding forces to the X···Y attractive interaction, the properties and the reactivity of compounds containing such contacts may vary broadly. In many cases intramolecular coordination drastically changes the chemical behaviour of chalcogen-containing compounds. Thus, the mechanism and kinetics of the chlorination of arenesulfenyl chlorides,[9] the hydrolysis of *N*-sulfonylsulfilimines,[10] oxidation of sulfides by chloramine-T[11] and 2-(organylseleno)benzoic acids by *t*-butyl hydroperoxide,[12] and the Pummerer rearrangement of aryl benzyl sulfoxides[13] drastically differ for compounds containing *o*-substituents (COOH, NO_2) capable of forming intramolecular coordinate O→S and O→Se bonds and their *p*-isomers where this interaction is sterically impossible.

In recent years interest has rapidly grown in compounds in which intramolecular (secondary) bonds (O→Te and N→Te) are formed with the participating Te atom in different oxidation states. The presence of such bonds considerably increases the thermal and hydrolytic stability of organotellurium compounds and permits access to novel examples of such materials. Two concise reviews have recently appeared which were chiefly focused on a discussion of the contributions to the area of the Rostov[14] and Birmingham[15] research groups. The present review aims to present an updated and more detailed treatment of the subject. The data on the structural characteristics of organotellurium compounds possessing intramolecular coordinate N→Te and O→Te bonds with tellurium in various oxidation states, are systematised according to structural types and critically analysed. Attention has been given to both X-ray structural studies in the solid state and manifestations of intramolecular coordination in solution as evidenced by NMR, IR and Raman spectral studies. The origin of the interactions causing the attraction between the centres participating in the intramolecular coordination is briefly considered in comparison with relevant organosulfur and organoselenium compounds. Particular emphasis has been placed on the enhancement of stability and the characteristic of reactivity of the compounds with intramolecular Te←N and Te←O coordination.

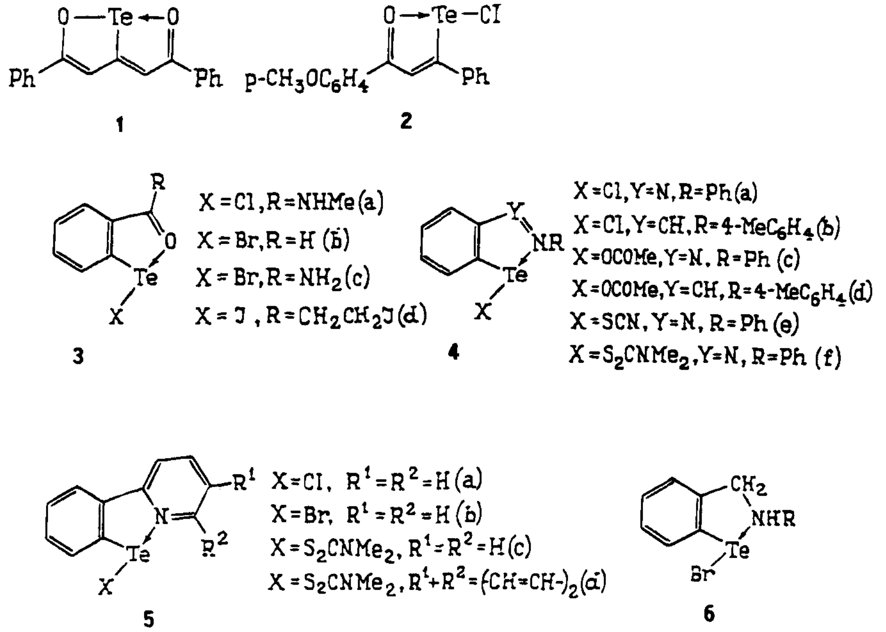
2. MOLECULAR AND CRYSTAL STRUCTURES OF ORGANOTELLURIUM COMPOUNDS WITH INTRAMOLECULAR TE←N AND TE←O COORDINATION

Coordination by tellurium of electron-rich nitrogen or oxygen centres leads to expansion of its valence electron shell owing to partial incorporation of one additional electron pair. At distances Te···X (X = N, O) approaching the covalent bond lengths Te-X (X = N, O), the coordination polyhedron of tellurium is defined by the rules of the VSEPR (valence state electron pair repulsion) theory. At larger distances the donation of the electron pair of nitrogen or oxygen to tellurium is incomplete, but the coordination polyhedron, although distorted, retains the general features of the coordinatively saturated type as defined by the total number of atoms attached to and lone pairs associated with tellurium.

This section contains a complete list of the X-ray structural data on organotellurium compounds possessing intramolecular coordination Te←X (X = N, O) bonds. These are systematised according to the structures of the organotellurium compounds.

2.1. *Tellurenyl Derivatives RTeX*

Compounds with this structure, **2–5** are the most thoroughly studied group of organotellurium compounds, to which 1,6-dioxa-6a-tellurapentalene **1** is also closely related. All compounds **1–5** possess a slightly distorted T-shaped configuration at the tellurium centre with two lone-pair phantom ligands formally occupying equatorial positions of its ψ-trigonal bipyramidal coordination polyhedron.[14,16–22,24–28] Such an arrangement of bonds at the tricoordinated tellurium atoms in **1–5** provides for their inclusion into virtually planar five-membered rings. However, in **6** with an sp^3-hybridised nitrogen centre, the N atom lies out of the plane (0.84 Å) of the remaining four atoms of the chelate ring.[23]



SCHEME 1

Table 1 contains data on bond lengths and valence angles at the tellurium centre in **1–6**. Noteworthy is the fact that, in contrast to organotellurium compounds without intramolecular coordination involving tellurium centres,[29] no marked secondary interactions with appreciably shortened Te···X contacts were observed in the crystals of **1–6**. The intermolecular Te···Cl distances in the tellurenyl chlorides **4a**[19] and **4b**[14,20] in the crystalline state were found to be 3.66 Å and 3.756 Å, respectively, whereas the sum of the van der Waals radii is 4.0 Å.[30] In the case of the tellurenyl bromide **3b**,[22] the intermolec-

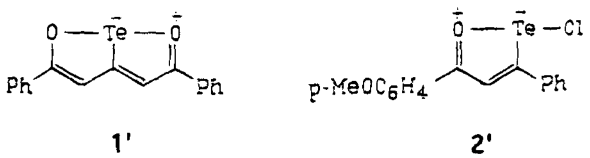
TABLE 1 Bond Lengths and Valency Angles

			Bond Length, Å			Angle	
No.	X	Y-Z	Te-C	Te-X	Te-Z	Z-Te-X	Ref.
1	O	C=O	2.043	2.124	2.130	156.9	16
2[a)]	Cl	C=O	2.080	2.476	2.190	170.1	17
3a	Cl	C=O	2.133	2.516	2.250	168.6	18
4a[a)]	Cl	N=N	2.120	2.550	2.210	166.7	19
4b[a)]	Cl	CH=N	2.097	2.567	2.239	168.4	14, 20
5a[a),b)]	Cl	CH=N	2.08	2.558	2.236	168.4	21
3b	Br	C=O	2.081	2.618	2.31	168.6	22
3c	Br	C=O	2.105	2.646	2.237	170.7	18
5b[a)]	Br	CH=N	2.11	2.707	2.236	169.2	21
6	Br	CH_2-N	2.125	2.663	2.375	165.3	23
3d	I	C=O	2.111	2.784	2.368	169.5	24
4c	OCOMe	N=N	2.074	2.167	2.26	159.0	25
4d	OCOMe	CH=N	2.087	2.160	2.297	159.9	14
4e	SCN	N=N	2.073	2.672	2.243	166.8	25
4f	S_2CNMe_2	N=N	2.101	2.568	2.340	162.3	26
5c	S_2CNMe_2	CH=N	2.111	2.518	2.354	167.6	27
5d[a)]	S_2CNMe_2	CH=N	2.130	2.556	2.375	163.2	28

a) Mean values of bond lengths and angles in two (**2**, **4a**, **4b**, **5d**) or six (**5a** and **5b**) crystallographically independent molecules are given; b) [2-pyridyl)phenyl]tellurium(II) chloride **5a** is part of the inclusion compound formed by two molecules of **5a** and one molecule of 4-ethoxyphenylmercury(II) chloride.

ular Te···Br contact is 3.92 Å, the sum of the van der Waals radii of tellurium and bromine being equal to 4.15 Å. Other values of experimentally observed and van der Waals distances between interacting centres in crystals are 4.02 Å and 4.30 Å (I···I secondary bonds in the tellurenyl iodide **3d**[24]) as well as 3.535 Å and 3.70 Å in the thiocyanate **4e**[25](Te···NCS secondary bonds). In the case of **4** bearing bidentate groups X (OCOMe, S_2CNMe_2) attached to tellurium, secondary Te···O and Te···S bonds are formed within the same molecule. They complete a square planar stereochemical configuration around tellurium. The Te···O=C distances in **4c**[25] and **4d**[14] are 2.953 Å and 3.06 Å, respectively, (the van der Waals contact is 3.60 Å). In the dithiocarbamates **4f**,[26] **5c**[27] and **5d**[28] the Te···S distances equal correspondingly 3.225 Å, 3.667 Å and 3.225 Å, respectively (the van der Waals contact is 4.05 Å).

The lengths of intramolecular coordinate N→Te and O→Te bonds in tellurenyl derivatives fall in the range 2.130–2.375 Å. They increase in the order X = Cl < Br < I < S_2CNMe_2 which is consistent with the decreasing electronegativity of X. At the same time the nature of the functional group containing an sp^2-hybridised nitrogen centre which donates its lone pair to the valence shell of tellurium has little effect on the Te···N distances (Table 1). Due to the marked shortening in **1**–**4** of the Te←X (X = N, O) distance, compared to the van der Waals contacts, the formulation of the structural type of the five-membered rings containing these bonds is not unambiguous. By assuming hypervalent (three centre-four electron) bonds at the tellurium centres, Detty[17] classified compounds **1** and **2** as 10-Te-3 telluranes (**1′** and **2′**) (for the N-X-L formalism see.[31]) Such a description is consistent with the bond lengths and valence angles in the five-membered ring. For example, in 1,2-oxatellurolium chloride the lengths of the C3-C4, C4-C5 and C-O bonds (respectively 1.354 Å, 1.425 Å and 1.269 Å) are in accord with the structural formula **2′**.

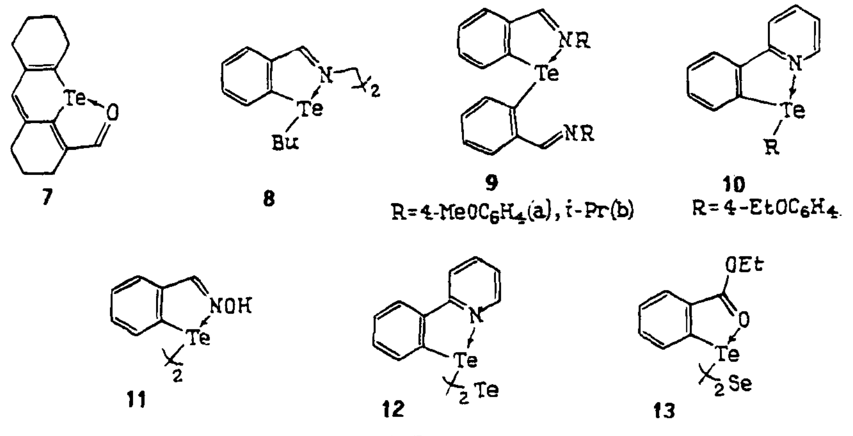


SCHEME 2

From a comparison of the Te···N bond lengths in **5b** (2.236 Å) and **6** (2.375 Å) with identical substituents at the tellurium centre and differently hybridised nitrogen atoms, it follows that the intramolecular coordination bonds of the Te-N_{sp^3} type are weaker than those of the Te-N_{sp^2} type. This conclusion is supported by a ^{125}Te NMR study of **6** in solution.[23]

2.2. *Diorganyl Tellurides R^1TeR^2 and Diorganyl Ditellurides R_2Te_2*

In common with the tellurenyl derivatives **1–6** the diorganyl tellurides **7–10**,[14,27,32-35] the ditelluride **11**[36] and its analogues **12**[37] and **13**[38] belong to the 10-Te-3 structural type leading to similarity in their structural characteristics. Table 2 contains some data concerning the bond lengths and valence angles of **7–13**.



SCHEME 3

As is the case for **1–6** the T-shaped configuration at the tellurium centre is slightly distorted, with R-Te-X (N, O) angles in the range 164.7–170.7°. In general, the intramolecular coordination N→Te and O→Te bonds in tellurides and ditellurides are longer than those in tellurenyl halides which is in accord with the lower electronegativity of the organic (R) and organotellurium groups compared to halogens. The Te···N distances are 2.695–2.773 Å in the tellurides **8–10**, whereas the Te···O intramolecular contact in **7**, the only telluride containing Te···O for which X-ray structural data are available, was found to be 2.575 Å.[32]

TABLE 2 Bond Lengths and Valency Angles in Compounds

		Bond Length (Å)			Angle	
No.	Z	Te-C[a]	Te-C	Te-Z	Z-Te-R	Ref.
7[b]	O	2.075	2.055	2.575	c)	32
8	N	2.111	2.181	2.773	c)	33
9a	N	2.128	2.162	2.702	165.9	15, 34
9b	N	2.125	2.163	2.720	164.7	14, 35
10	N	2.138	2.144	2.695	c)	27
11	N	2.139	-	2.879	c)	36
12	N	2.130	-	2.554	170.7	37
13	O	2.123	-	2.658	169.2	38

a) The carbon atom of the phenyl ring or of the C=C bond which contains group C=Z in position 2; b) mean bond lengths and valency angles in two crystallographically independent molecules are given; c) no data available.

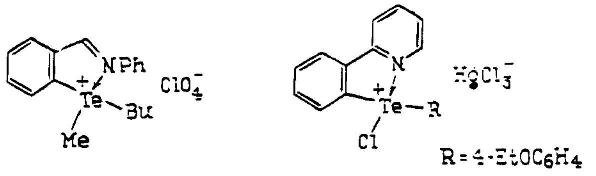
In bis-imines of bis(2-formylphenyl)telluride **9**, owing to the presence of two sterically accessible donor centres, it is possible to form two intramolecular coordination N→Te bonds, in which case the molecular structure may be described as a 12-Te-4 tellurane. It was shown, however, by X-ray structural studies[14,34,35] that the two chemically equivalent iminomethinyl moieties of **9** are differently positioned at the tellurium centre. These compounds exist, therefore, in the crystal form as 10-Te-3 telluranes, in which the lengths of intramolecular coordination N→Te bonds are virtually unaffected by the substituent at the imino nitrogen (Table 2).

The influence of intramolecular coordination on the structural characteristics of the Te-chelated arm-like ligand in **9a**[14,34] may be directly compared with the identical unchelated fragment. The salient features are the noticeable convergence of the bond lengths in the tellurium-containing five-membered ring and the enlarged CH=N-R valence angle. It is noteworthy that in dimethylbis[2(4′-nitrobenzylideneimino)phenyloxy]tellurane (Section 2.6) where the central tellurium atom forms intramolecular coordination bonds with two equivalent imino nitrogens, the geometry of both coordinated ligand fragments is identical.[39]

2.3. *Telluronium Salts* $R^1R^2R^3Te^+X^-$

X-Ray structural data are available for three representatives of this class of organotellurium compound possessing intramolecular N→Te bonds, namely methylbutyl(2-phenyliminomethinylphenyl)telluronium perchlorate **14**,[14,40] chloro-4-ethoxyphenyl-2-(2′-pyridyl)phenyl telluronium trichloromercurate **15**,[41a] and [bromo(phenyl)({2-dimethylaminoethyl}-phenyl)]telluronium bromide,[41b] the latter compound providing interesting evidence for such intermediates in the oxidative addition of halogens to tellurium(II) centres.

Both crystals exhibit only slight intermolecular contacts between the cationic fragments and the corresponding counter-ions. For instance, in **14** the tellurium centres and the oxygen atoms of the perchlorate anions are separated in the solid by distances of 3.33–3.56 Å, very close to the sum of the van der Waals radii of tellurium and oxygen (3.60 Å[30]). The stereochemical configuration at the tellurium in **14** and **15** is determined by the presence of intramolecular coordination involving N→Te bonds. It is known that the coordination



14 **15**

SCHEME 4

around tellurium in telluronium salts $R^1R^2R^3Te^+X^-$ depends strongly on the nature of the X^- anions. In triorganyltelluronium salts with anions of low nucleophilicity, e.g. $Me_3Te^+BPh_4^-$, no secondary bonds are formed by the telluronium centre, thus, in the crystal, the usual pyramidal configuration pertains.[42] Salts with highly nucleophilic anions, like halides, exist, owing to secondary interactions between these and the tellurium-containing cations, either as dimers in which a penta-coordinate tellurium atom has a distorted square-pyramidal geometry ($Ph_3Te^+Cl^-$ [43] $Et_3Te^+I^-$ [44]) or as cubane-like tetramers with a hexa-coordinate tellurium centre ($Et_3Te^+Cl^-$, [44] $Et_3Te^+Br^-$.[45]) In these salts, the secondary Te···Hal bonds are close in length to ordinary bridging bonds. In the cations of **14** and **15** the pyramidal configuration of the telluronium atom is supplemented by the intramolecular coordination N→Te bonds which gives rise to a ψ-trigonal bipyramidal configuration (assuming one lone-pair phantom ligand) at the telluronium atom. The angles between the two axial bonds N-Te-CH_3 and N-Te-Cl in respectively the cations of **14** and **15** are equal to 164.9°[14] and 166.6°.[47] The Te-C bond lengths in the (Te-C_{ar} 2.120 Å, Te-CH_3 2.37 Å and Te-C_4H_9 2.147 Å) in and **15** (Te-C_{ar} 2.05, 2.11 Å), are normal. The significant difference between the N···Te distances in **14** (2.75 Å) and **15** (2.31 Å) is explained by the difference between the *trans* axial groups. As might be expected (see Section 2.1) the more electronegative chlorine atom in **15** causes substantial shortening of the intramolecular coordination N···Te bonds in **15**.

2.4. *σ-Telluranes RTeX$_3$*

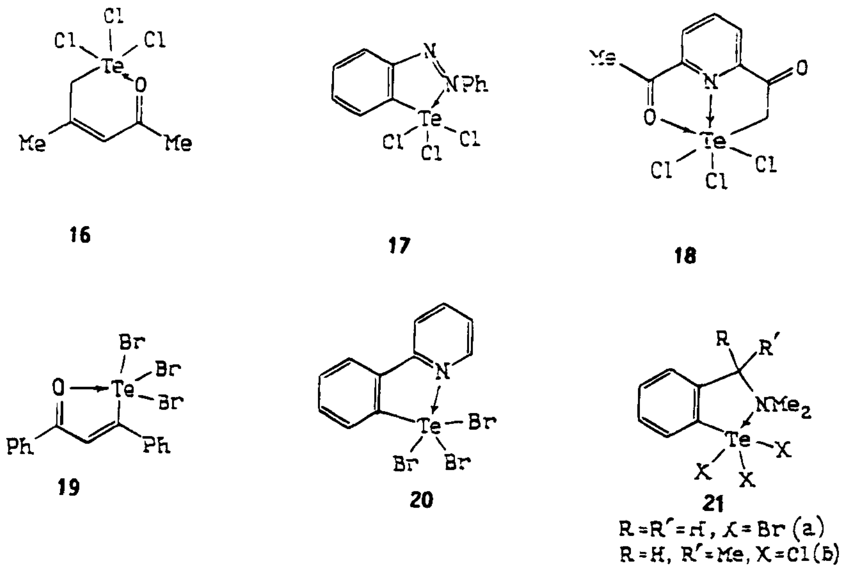
A selection of the X-ray structural data available for **16–21**[27,46–51] is given in Table 3.

TABLE 3 Bond Lengths (Å) and Valency Angles in Compounds

					Bond Length, Å			Angle (°)	
No.	A-B	Y-Z	X	Te-C	Te-X$_{eq.}$	Te-X$_{ax}$	Te-Z	X-TeX	Ref.
16	CH=C(Me)	C=O	Cl	2.135	2.364	2.501	2.438	172.9	46
17	C=C[b]	N=N	Cl	2.114	2.406	2.487	2.417	171.7	47
18	CH_2CO	C=N[c]	Cl	2.129	2.438	2.495	2.402	171.3	48
21[b]	C=C[b]	CH(Me)NMe$_2$	Cl	2.078	2.447	2.502	2.406	175.4	49
19	C(Ph)=CH	C=O	Br	2.175	2.513	2.660	2.362	d)	50
20	C=C[b]	C=N[c]	Br	2.110	2.589	2.665	2.244	172.4	27
21a	C=C[b]	CH_2NMe_2	Br	2.122	2.632	2.696	2.42	178.7	51

a) Mean values are given; b) the C=C bond is part of the phenyl ring; c) and C=N bond is part of the pyridinium ring; d) no data available.

A significant difference is observed in the molecular structure of the σ-telluranes $RTeX_3$ where the organyl substituents possess an arm-like group coordinated to the tellurium and those without such an intramolecular coordination. In crystals, the latter compounds exist either as non-associated monomers possessing a trigonal-bipyramidal configuration at the tellurium atom (2-biphenylyltellurium trihalides) or dimers and polymers in which a pentacoordinated tellurium atom acquires square-pyramidal configuration with the organyl group R taking an apical position.[29] In the case of the σ-telluranes **16**, **17** and **19–21** which have sufficiently strong intramolecular coordination O→Te and N→Te bonds, the configuration around the tellurium atom in crystals may be described as *pseudo*-octahedral, two elongated bonds with tellurium being formed by the halogens. A distinctive feature of the crystal structures of **16**, **17** and **19–21** is the absence (σ-tellurane **17**[47]) or the weakness of the secondary Te···Hal interactions as compared to σ-telluranes without intramolecular coordination. While in the latter case the Te···Cl and Te···Br intermolecular distances lie in the range of respectively 2.717–2.768 Å[29] and 2.829–2.880 Å,[29] in **19m**, **20**, and **21a** the intermolecular Te···Br distances were found to be equal to 3.757 Å, 3.796 Å and 3.896 Å, respectively, thus closely approaching that of the Te-Br van der Waals contact. Compound **18** reveals, apart from an intramolecular N→Te coordination bond (2.402 Å), another somewhat elongated secondary O→Te bond (2.878 Å[48]). The coordination polyhedron of the central tellurium atom in this compound may thus be described as a distorted ψ-pentagonal bipyramid in which two axial positions are taken by two chlorine atoms.



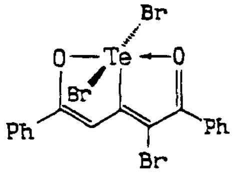
SCHEME 5

A novel feature of the compounds **21a** and **21b** is that the N→Te intramolecular coordination involves an sp^3-hybridized nitrogen atom. Judging from the data on bond lengths listed in Table 3, the N_{sp^3}-Te coordination bonds are slightly weaker than those formed by the sp^2-hybridized nitrogen centres in **17–20**.

1-Trichlorotellur-2-methylpenten-4-one **16** is, to date, the only known representative of organotellurium compounds (where X-ray structural evidence is available) in which an intramolecular coordinate O→Te bond is part of a six-membered chelate ring.[46] The coordination polyhedron of the tellurium atom in **16** is of the same type as that in the σ-telluranes **17–21** with five-membered chelate rings. The Te-Cl axial bonds in **16** are, on average, 0.137 Å longer than the equatorial bonds, the angle Cl_{ax}.-Te-Cl_{ax} being 172.9. The O→Te coordinate bond length is 2.438 Å. Thus, in the tellurium trichlorides **16–18** and **21b** all intramolecular coordination bonds fall into the narrow range of lengths between 2.402 Å and 2.438 Å regardless of the type of C-Te bonds and the hybridization state (sp^2 or sp^3) of the donor centre. The significantly shortened O···Te distances observed in 8-ethoxycyclooct-4-enyltellurium trichloride (2.419 Å[52]) and 2-ethoxycycloheptyltellurium tribromide (2.49 Å[53]) also arise from intramolecular coordination.

2.5. *σ-Telluranes* $R^1R^2TeX_2$

X-Ray structural data are available for only two representatives of this class of compound, i.e. **22**[16] and **23**.[36]



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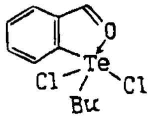


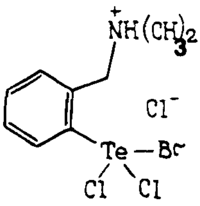
23

SCHEME 6

Whereas **22** shows a strong intramolecular O→Te attractive interaction (the Te···O bond length is 2.171 Å), **23** exemplifies the weakest interaction of this type observed in *o*-telluro compounds (the Te···O distance is 2.839 Å). In both molecules, the bond configuration around the tellurium atoms defines a distorted elongated octahedron with two halogens occupying apical positions. The Te-C bond lengths in **22** (2.11 Å) and **23** (Te-C_{ar} 2.123 Å and Te-Bu 2.242 Å) are of normal magnitude for these types of covalent bonds, and the valence angle (172.4°) deviates somewhat from that (180°) characteristic of a perfect octahedron. Weak intermolecular interactions Te···Br (3.355 Å[16]) and Te···Cl (3.758 Å[36]) are observed in crystals of, respectively, **22** and **23**.

In summary, the intramolecular coordination interaction O→Te and N→Te is substantially stronger in the case of Te(II) compounds than in that of compounds with tellurium in a higher oxidation state, Te(IV). Within the framework of the Te(II) derivatives, tellurenyl halides and acylates RTeX display the shortest intramolecular O···Te and N···Te contacts (i.e. the strongest bonds) falling into the range of 2.130–2.375 Å. The greater the electronegativity of X, the shorter is the intramolecular coordination bond. When replacing X = Hal, OCOR by less electronegative carbon-centred groups in diorganyl tellurides R^1TeR^2, the above indicated range is shifted to the longer distances 2.575–2.773 Å. In σ-telluranes of the $RTeX_3$ type, the intramolecular coordination bond lengths lie in the range 2.245–2.44 Å, intermediate between tellurenyl halides and diorganyl tellurides. Data on other classes of relevant organotellurium compounds (ditellurides, telluronium salts and type $R^1R^2TeX_2$ σ-telluranes) are as yet relatively scarce.

Noteworthy are results of the X-ray study of 2-[(*N*,*N*-dimethylammonium)ethyl]phenyltellurium trichloride **24**.[51] No Te···N coordination exists in this compound since the nitrogen lone pair is engaged in the formation of an N-H bond. The protonated nitrogen atom is turned away from the tellurium centre and found at a distance of 4.38 Å from it. Strong secondary interactions Te···Cl are observed in the crystal, this contact (3.337 Å) being notably shorter than the sum of the van der Waals radii (3.81 Å[30]). The octahedral structure at the tellurium centre has chlorine atoms in the axial (Te-Cl bond lengths 2.487 Å and 2.527 Å) and carbon atoms (Te-C bond lengths 2.134 Å and 2.154 Å) and Cl^- in the equatorial positions.

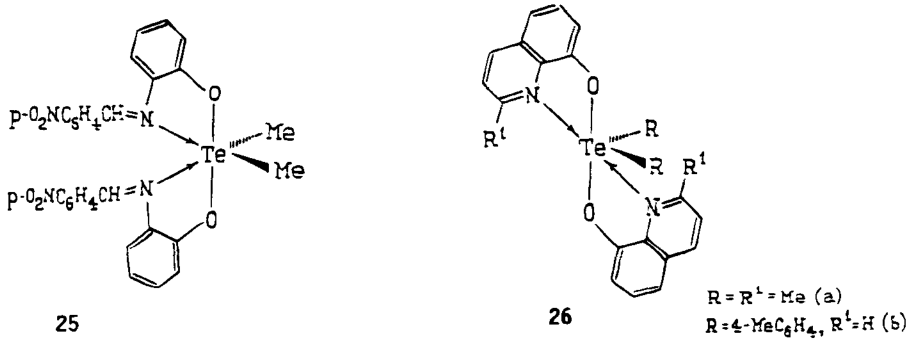


24

SCHEME 7

2.6. *σ-Telluranes $R_2'Te(OR^2)_2$*

This class of material is represented by compounds **25**[39] and **26**.[54]



25 26

SCHEME 8

In contrast to the *o*-telluro bis-imines **9**, in **25** and **26** both imino nitrogen atoms are coordinated to tellurium. The coordination polyhedron of the tellurium in these compounds may initially be viewed as a distorted ψ-trigonal bipyramid with the oxygen atoms taking the axial positions and the organyl groups and the lone electron pair (phantom ligand) being equatorial. The O-Te-O angles deviate substantially from the ideal 180° value and were found to be 164.9° in **25**, 162.1° in **26a** and 167.8° in **26b**.

The intramolecular Te···N bonds in **25** (2.924 Å), **26a** (2.840 Å) and **26b** (2.899 Å) are significantly longer than those found in the organotellurium compounds **4**, **5**, **8–12**, **14**, **15**, **17**, **18**, and **20** possessing similar bonds. Nevertheless, it is these relatively weak intramolecular coordination bonds which define the observed cisoid conformations of both *N*-aryliminoformyl fragments in **25**. Accounting for these bonds, the coordination polyhedron may be described as ψ-pentagonal bipyramidal.

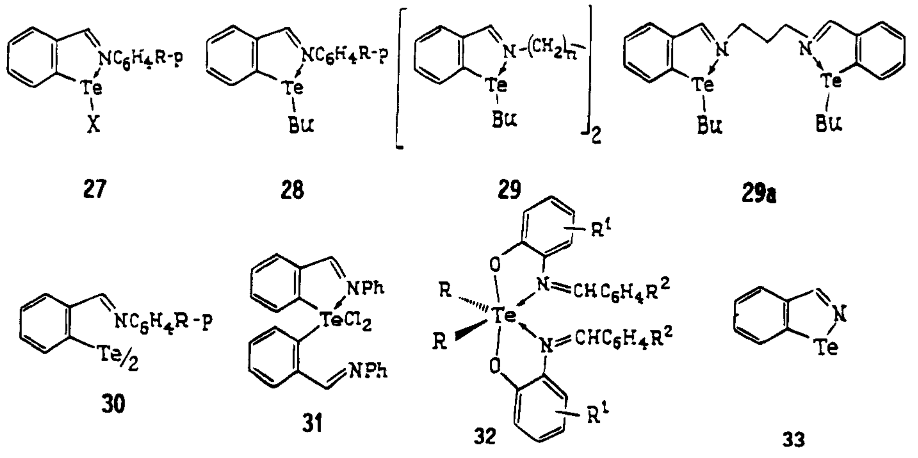
3. THE MOLECULAR STRUCTURE OF COMPOUNDS WITH N(O)→TE INTRAMOLECULAR COORDINATION IN SOLUTION

Evidence for the presence and rupture of intramolecular coordination bonds in organotellurium compounds in solution has been mostly obtained by ^{125}Te NMR spectroscopy, and by measurement of dipole moments and Kerr constants. Important information has been also provided by ^{1}H and ^{13}C NMR, infrared and Raman spectral studies.

3.1. *^{125}Te NMR Spectral Studies*

The principal question of whether secondary intramolecular Te···N bonds in the compounds under consideration are retained in solution in organic solvents may be answered by studying the ^{125}Te NMR spectra of ^{15}N-enriched compounds to determine J(^{15}N-^{125}Te), the scalar one-bond nuclear spin-spin coupling constants. The magnitude of these constants provides insight into the nature and the strength of the respective bond, whereas their temperature dependence may be used for the kinetic characterisation of the stereodynamic behaviour of organotellurium compounds related to the dissociation of N→Te bonds in solution. In Table 4 ^{1}J(TeN) spin-spin coupling constants are listed along with ^{125}Te chemical shifts of **6**, **9**, **14**, **15**, and **27–32**.[14,23,34,36,39,40,41,55] The former constants are to be compared with the recently recorded ^{1}J(^{125}Te-^{15}N) = 157 Hz for the covalent Te-N bond in benzoisotellurazole **33**.[23]

That the intramolecular coordination Te···N is preserved in discrete molecules of **9**, **14**, **28**, **30**, and **31** in solution and provides an effective pathway for spin-spin coupling is manifested by the characteristic high values of ^{1}J(TeN), as shown in Table 4. As might be expected, ^{1}J(TeN) for benzoisotellurazole **33** is higher than the coupling constants listed in Table 4, a consequence of the shorter Te-N distance in **33** (2.11 Å [56]) and a greater degree of s-character in the bonding orbital of the tellurium atom forming the covalent bond with nitrogen. In solution intramolecular coordinated and noncoordinated forms, the latter not showing the Te-N one-bond nuclear spin-spin coupling, exist in a dynamic equilibrium. For a number of compounds the interconversion of these forms is relatively slow (the frequency at room temperature is lower than the difference of the chemical shifts of the two forms) and each conformer displays a distinct ^{125}Te NMR spectral signal. This is, for example, the case with the trichloromercurate **15** whose ^{125}Te NMR spectrum in DMSO solution consists of two single peaks at 1056.4 and 1059.1 (minor conformer) ppm.[41] The spectrum is interpreted to indicate dissociation of the intramolecular coordinate Te-N bond.

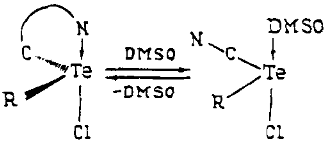


SCHEME 9

TABLE 4 ^{125}Te NMR Chemical Shifts and ^{125}Te-^{15}N Spin-Spin Coupling Constants of *o*-Tellurated Azomethines

Compound		Solvent	^{125}Te′ δ, ppm[a)]	J ^{125}Te-^{15}N, Hz
6		$CHCl_3$	1407, 1511	b)
9	R = Ph	$CDCl_3$	600.0	61.0
14		$CHCl_3$	641.5	62.4
15		DMSO-d_6	1056.4, 1059.1	b)
27	R = H, X = Cl	$CDCl_3$	1355.0	c)
27	R = H, X = Br	$CHCl_3$	1316.0	c)
27	R = H, X = I	$CDCl_3$	1187.0	c)
27	R = Me, X = F	$CDCl_3$	1634.8, 1633.5	b)
28	R = H	$CHCl_3$	483.0	101.4
28	R = Br	$CDCl_3$	484.8	102.0
29	n = 0	$CDCl_3$	464.1	b)
29	n = 1	$CDCl_3$	464.4	b)
29a		$CDCl_3$	464.9	b)
30	R = H	$CDCl_3$	1027.0	135.3
30	R = Br	$CDCl_3$	1036.0	141.4
31		$CDCl_3$	636.0	122.0
32[d)]	R^1 = H, R^2 = 4-NO_2	$CDCl_3$	1056.0, 1076.0, 1104.0	b)
32	R^1 = H, R^2 = 3-NO_2	DMSO-d_6	1055.0, 1122.00	b)
32	R^1 = H, R^2 = 4-Br	$CDCl_3$	1056.0, 1102.0	b)
32	R^1 = R^2 = H	$CDCl_3$	1057.0, 1105.0	b)
32	R^1 = H, R^2 = 4-Me	$CDCl_3$	1055.0, 1108.0	b)
32	R^1 = H, R^2 = 4-Me_2N	DMF-d_7	1056.0, 1105.0	b)
32	R^1 = H, R^2 = 4-OMe	$CDCl_3$	1056.0, 1107.0	b)
32	R^1 = 4-NO_2, R^2 = 4-Me	$CDCl_3$	1104.0 1179.0	b)
32	R^1 = 4-NO_2, R^2 = 4-OMe	DMSO-d_6	998.0 1111.0 1122.0	b)
32	R^1 = 4-Me, R^2 = 4-OMe	CD_2Cl_2	1089.0 1100.0 1052.0	b)

a) Chemical shifts were measured upfield from Me_2Te; b) compounds do not contain ^{15}N; c) ^{125}Te-^{15}N spin-spin coupling given poorly resolved multiplets owing to the quadrupole effects of the halogen atoms; d) R = Me

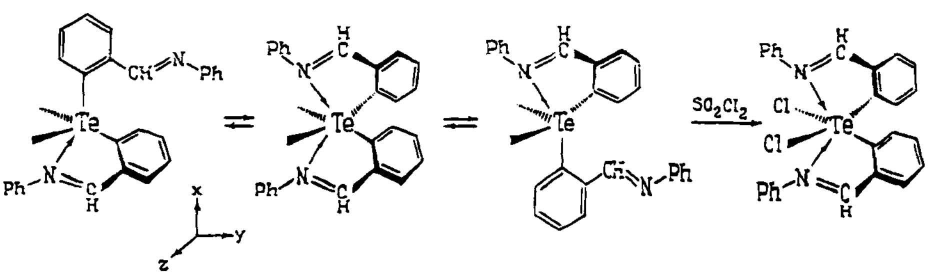


SCHEME 10

The same doubling of ^{125}Te NMR spectral signals was also observed in the spectra of the azomethine derivatives **32** in $CDCl_3$ solution at room temperature. By contrast, the ^{1}H NMR signals of **32** under the same conditions are not doubled, a fact explained by the appreciably smaller difference of proton chemical shifts compared to those of tellurium nuclei. The consequence of this fact is the observation of ^{1}H NMR spectra averaged over two interconverting forms. Also in $CDCl_3$ solutions of ^{15}N-enriched isotopomers of **32** (R^1 = 4-Me, R^2 = 4-OMe), no splitting due to ^{15}N-^{125}Te coupling was observed which may be understood considering the similarity of the ^{1}J(Te-N) constants and the proton chemical shift differences.

Whereas donor and polar solvents like DMSO and $CDCl_3$ compete with the nitrogen atoms positioned within an organotellurium compound for the coordination site at tellurium, more inert solvents, e.g. benzene, do not disturb the intramolecular coordination (Te-N) upon solvation. Thus, the ^{125}Te NMR spectrum of **32** (R^1 = H, R^2 = Me) reveals the existence of a single, presumably intramolecularly Te-N coordinated conformer in benzene solution.[39]

Noteworthy is the dynamic behaviour of **9**, *ortho*-tellurated azomethines, in solution. In the ^{125}Te NMR spectrum of the ^{15}N-labelled compound **9c** (R = Ph) in $CDCl_3$ solution, the signal of the ^{125}Te nucleus appears as a triplet with a ^{15}N-^{125}Te spin-spin coupling constant of 61 Hz.[14,34,55] This value is approximately half as large as similar spin-spin coupling constants of imines of other *ortho*-tellurated azomethines listed in Table 4.



9c **9d** **9e** **31**

SCHEME 11

Both the form of the signal and the value of the spin-spin coupling constant show the presence, in solutions of **9c**, of a very fast (on the NMR time scale) equilibrium **9c** ⇄ **9e**, where **9d** may serve either as an intermediate or a transition state structure for which the lifetime of the 10-Te-3 isomers (**9c**, **9e**) is so short that it does not lead to the reorientation of spins in the transformation to **9d**.[14,34] As in the spectrum of the telluride **9c**, in the ^{125}Te NMR spectrum of the ^{15}N-labelled tellurium dichloride **31** a triplet is observed with a ^{15}N-

^{125}Te spin-spin coupling constant (122 Hz) substantially exceeding the value found for the corresponding telluride.[14,34,55]

3.2. *Dipole Moments and Kerr Constants*

Additional evidence for the existence of intramolecular coordinate N→Te bonds in **28**, **9** and **32** on top of that drawn from the studies of their ^{125}Te NMR spectra was obtained by measuring their dipole moments and molecular Kerr constants.[14,39,57] Table 5 contains these data for the 2-(butyltelluro)benzalanilines **28**.[57] It was found that a sufficiently close agreement between the experimental and the theoretically calculated dipole moments and Kerr constants is achieved only in the case of the conformation of **28** where intramolecular N→Te coordination is present. The azomethine fragment was found to be coplanar with the C-aryl ring, whereas the N-aryl ring is twisted 0–90° out of the plane of the rest of the molecule.[57]

TABLE 5 Dipole Moments and Kerr Constants of 2-(Butyltelluro)-benzalanilines **28** in Dioxane

R	Dipole moment, μ, D	Kerr constant $^\infty$(mk$_2$) 10^{12} un. CGSE
4-NMe$_2$	1.94	730
4-Me	1.50	525
H	1.64	334
4-Cl	2.92	971
2,3,4,5,6-F$_5$	2.98	946

In Table 6, experimental dipole moments for bis-imines of bis(2-formylphenyl)telluride **9**[14] are compared with those calculated by vector addition of group dipole moments under the assumption of two intramolecular coordination Te···N bonds in these compounds. As can be seen from the data, the calculated dipole moments of compounds with regular (the group dipole is aligned with the R-C(Ar) bond) *para*-substituents (compounds **3**, **4** and **8** in Table 6) differ substantially from the experimental values. Hence, the assumption of stable structures of type **9d** with two N→Te coordination bonds is not supported by the dipole moment data.

By contrast, a study of the dipole moments of the azomethines **32** gives evidence of retention of two N→Te coordinate bonds in solution in nonpolar solvents. This conclusion stems from the satisfactory agreement between the experimental and vector addition calculated values of the dipole moments (Table 7),[39] assuming an approximate constancy of the O-Te-O angle in the various compounds. Only in the case of **1**, **15**, **14** and **20** (Table 7) containing a nitro substituent in the aryl moiety, are the calculated dipole moments for the conformation **32** considerably lower than the corresponding experimental values. This indicates that for these compounds the C$_2$-conformation, seen in the crystalline phase, is not stable in solution. The main reason for the destabilization of the conformation **32**, in these compounds lies, most probably, in a sharp decrease in the donor capacity of the imine nitrogen, because a strongly electron-withdrawing substituent (nitro group) is conjugated with the imine nitrogen atom. The energy of the weak intramolecular N→Te bond observed in the crystal seems to be insufficient for maintaining the sterically constrained conformation **32** in solution.[39]

TABLE 6 Dipole Moments of Tellurides **9** (benzene, 25 °C)

No.	R	$\mu_{exp.}$, D	$\mu_{calc.}$, D
1	C_6H_5	2.78	2.78
2	C_6F_5	4.53	-
3	4-ClC_6H_4	3.57	5.50
4	4-$CH_3C_6H_4$	2.68	2.14
5	4-$CH_3OC_6H_4$	3.61	-
6	4-$CH_3COOC_6H_4$	3.75	-
7	4-$(CH_3)_2NC_6H_4$	4.94	-
8	4-$NO_2C_6H_4$	6.89	9.71
9	$CH_2C_6H_5$	2.74	-
10	$CH(CH_3)_2$	3.04	-
11	CH_2CH_2	1.64	-

TABLE 7 Dipole Moments of Diorganyl[bis(2-arylideneamino)aryloxy]telluranes **32** (benzene, 25 °C)

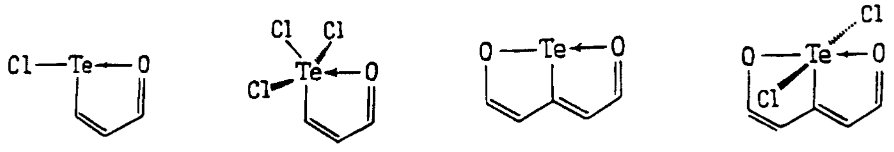
No.	R	R^1	R^2	$\mu_{exp.}$, D	$\mu_{calc.}$, D
1	CH_3	H	4-NO_2	3.54	1.40
2	CH_3	H	3-NO_2	4.50	4.00
3	CH_3	H	4-Br	2.06	2.06$^{a)}$
4	CH_3	H	H	2.41	2.41$^{a)}$
5	CH_3	H	4-CH_3	2.82	2.49
6	CH_3	H	4-OCH_3	3.19	3.08
7	CH_3	H	4-$(CH_3)_2N$	4.64	4.45$^{b)}$
8	CH_3	4-NO_2	4-Br	5.80	5.62$^{b)}$
9	CH_3	4-NO_2	3-F	4.95	4.94$^{b)}$
10	CH_3	4-NO_2	H	5.15	5.24$^{b)}$
11	CH_3	4-NO_2	4-CH_3	4.05	5.17$^{b)}$
12	CH_3	4-NO_2	4-OCH_3	5.16	c)
13	CH_3	4-NO_2	4-$(CH_3)_2N$	5.75	c)
14	CH_3	5-NO_2	4-Br	4.87	3.16$^{b)}$
15	CH_3	5-NO_2	H	5.75	3.51$^{b)}$
16	CH_3	5-NO_2	4-$(CH_3)_2N$	6.20	c)
17	CH_3	4-Br, 6-Cl	4-OCH_3	5.02	c)
18	CH_3	4-NO_2, 6-Cl	4-$(CH_3)_2N$	6.74	c)
19	$CH_2C_6H_5$	H	4-OCH_3	3.52	3.08
20	4-$CH_3C_6H_4$	H	4-NO_2	4.43	1.40
21	4-$CH_3C_6H_4$	H	4-CH_3	2.73	2.49

a) Taken as found experimentally and used for the calculation of the dipole moments of the other compounds; b) the group moments of the NMe_2 and NO_2 groups equal +0.8 D[58] are added to the interaction moments directed along the Ar-N bond line; c) with the presence of two substituents possessing strongly cumulative electron-donating and electron-accepting effects in different aryl nuclei the μ values remain uncertain

4. THE NATURE OF AND TRENDS IN THE PROPERTIES OF INTRAMOLECULAR N(O)→TE BONDS

The X-ray crystallographic and spectral data considered in Sections 2 and 3 offer convincing evidence that organotellurium compounds with pendant functional groups contain five- or six-membered chelate rings formed by rather strong intramolecular N→Te and O→Te bonds. Such examples of attractive interactions between two electron-rich centres seem to be in contradiction with common bonding models although it has been long known that for third and subsequent period elements up to six electron pairs may be accommodated in the valence shell of a central atom, especially when bonded to highly electronegative ligands. Compounds like SF_6 and ClF_5 obey a dodecet rule (see[59,60]) but not the Lewis octet rule and it is the propensity of chalcogen atoms to expand their electron shell beyond the octet that makes possible the formation of intramolecular coordination bonds in compounds similar to **1–5** and others considered in this paper.

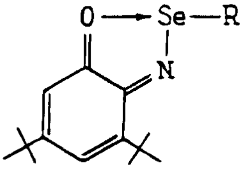
A peculiar feature of the intramolecular coordination bonds in these compounds is the very wide variation in their lengths (see Tables 1–3) and strengths. From an analysis[61] based on *ab initio* calculations of a series of representative organosulfur compounds with sulfur-oxygen intramolecular attractive interactions, it follows that the two most important factors contributing to S···O bonding are electrostatic and n_o-$\sigma^*_{S\text{-}R}$ orbital interactions. The very existence of a chemical bond is confirmed by the non-zero electron population of the S···O bond. CNDO/2 calculations carried out for organotellurium compounds such as **34–37** are also in line with the conclusion that electron density accumulates in the region between the tellurium centre and the coordinated oxygen.[50]



34 **35** **36** **37**

SCHEME 12

Recent *ab initio* calculations of the Laplacian of the electron density in the selenoiminoquinones **38** clearly indicated a significant concentration of electron charge between the selenium and the oxygen centres.[7]



38

a) R = Cl, (Se···O) 2.08Å [62]

b) R = Ph, (Se···O) 2.48Å [7]

SCHEME 13

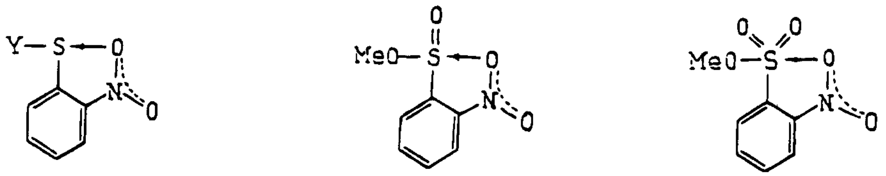
There remains only one step in an unequivocal and consistent theoretical identification of the chalcogen-N(O) bonds, currently considered to be of fractional order, as true chemical bonds; that is a more detailed consideration of Bader's topological analysis of the distribution of the electron density. The location of a "bond critical point" between the two atomic centres would serve to provide convincing evidence of the presence of a chemical bond. Such an approach has been recently applied to an investigation of the nature of the Si-N bond in neutral hypervalent silicon compounds, the silatranes.[63]

Considering that the N···Te and the O···Te contacts in the compounds **1–5**, **8–12**, **14**, **15**, **17**, **19**, **20**, **22**, and **23** fall in a range between the sum of van der Waals radii (3.60 Å for O-Te and 3.70 Å for N-Te) and the sums of the covalent radii (2.00 Å for O-Te and 2.10 Å for N-Te[30]) and thus possess the properties of a real chemical bond, they should be treated as parts of three-centre four-electron hypervalent bonds of the type N-Te-Y and O-Te-Y where Y = Hal, OR, Alk, Ar.

The shortest known Te-N bonds (1.92 Å) have been found in the Te(IV) phosphorane imidates $(Ph_3P{=}N)_2TeCl_2$ and $Ph_3P{=}NTeCl_2Ar$.[64]

The underlying features of the chemical bonding in hypervalent molecules have recently analyzed in much detail.[65–68] The dominance of ionic and covalent ($n \rightarrow \sigma^*$) contributions with d-orbital participation was stressed and the wide spectrum of bond lengths and other bond properties of hypervalent molecules was explained by changes in the relative weight of the ionic and covalent factors.

In the framework of this model of hypervalent bonding, the important trends in structural characteristics observed for organotellurium compounds with intramolecular coordination bonds as well as of their sulfur and selenium analogues may be readily understood. The larger the $n \rightarrow \sigma^*_{Te\text{-}Y}$ interaction, the shorter is the N(O)···Te distance. With increasing electronegativity of the substituent Y on the tellurium atom the $\sigma^*_{Te\text{-}Y}$ energy level is lowered which enhances the $n \rightarrow \sigma^*$ orbital interaction and results in shortened the N(O)→Te intramolecular coordination bonds. As seen from the data of Table 1, this is precisely the order of increase in the electronegativity of the substituents at tellurium in **3–5**, **14**, **15**, **17** and **20**. The same correlation is valid for similar organosulfur compounds,[3,61,69] for example **39–41** and the organoselenium compounds **38**.



39

a) Y = Cl, H (S···O) 2.379 Å

b) Y = OMe, (S···O) 2.458 Å

c) Y = SMe, (S···O) 2.64 Å

40

(S···O) 2.743 Å

41

(S···O) 2.956 Å

SCHEME 14

With increasing electronegativity of Y in the *ortho*-tellurated azomethines **4** the frequencies and intensities of the ν(TeN) vibrations increase, a fact which clearly indicates a strengthening of the intramolecular Te···N bonds.[23]

Another important trend is the lengthening of the N(O)···Te intramolecular coordination bonds in analogous compounds when the tellurium goes from a lower to a higher state of oxidation, i.e. from Te(II) to Te(IV), cf. Tables 1 and 3. This trend is explained by the prevailing role of the electrostatic term of the Te···N bond energy in the case of the intramolecularly coordinated Te(IV) compounds **16–21**. More complete data for the organosulfur compounds **39b**, **40** and **41**[69] are in full accord with the tendency for elongation of intramolecular coordination bonds formed by chalcogens and other lone pair atomic centres.

5. INTRAMOLECULAR N(O)→TE COORDINATION AS THE FACTOR PROVIDING STABILIZATION OF FUNCTIONALIZED TE(II) COMPOUNDS

In contrast to their sulfur and selenium analogues, organotellurium(II) compounds are often prone to disproportionation and decomposition with extrusion of elemental tellurium.[70] Several conceivable approaches aimed at the enhancement of the stability of organic Te(II) compounds include: a) kinetic stabilization through high steric demands of the organic moieties, b) reduction of the Lewis acidity of the central tellurium atom by complexation with electrically neutral ligands or c) by intramolecular coordination. The latter approach should be considered as the most efficient way and sufficiently stable organotellurium compounds bearing functional groups coordinated to the Te(II) centres within a molecule serve as useful synthons in preparative organotellurium chemistry, particularly in the chemistry of tellurium-containing heterocycles.

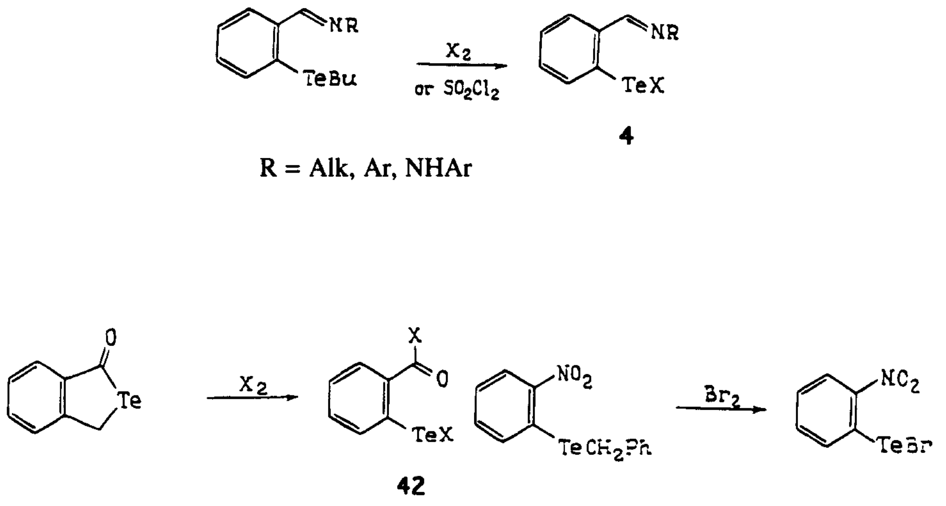
5.1. *Tellurenyl Derivatives RTeX*

5.1.1. *Tellurenyl Halides RTeHal*

Whereas sulfenyl and selenyl halides are known to be rather stable compounds, their tellurenyl analogues obtained by reaction of ditellurides with halogens[71–74] or organyltellurium trichlorides[73,75] rapidly decompose when exposed to air or in solution. Of arenetellurenyl halides, the most resistant to decomposition are the iodides which may be stored in a dry atmosphere for several weeks.[71] Quite the reverse, in the case of alkanetellurenyl halides the highest stability is displayed by the chlorides, whereas alkanetellurenyl iodides at room temperature undergo decomposition in a few minutes.[73]

Intramolecular coordination of TeHal groups in arenetellurenyl halides by *ortho*-positioned functional groups CHO,[22,76] COR,[1,7,24,77–84] $CONH_2$,[18] CH=NR,[14,20,21,23,27,36,37,85–88] N=NR,[19] NO_2,[89] and $CH_2NR'R''$[23,51] strongly stabilizes these compounds. A similar stabilization is also achieved in alkanetellurenyl halides possessing O→Te intramolecular coordination bonds, but the effect is less pronounced compared to their arenetellurenyl analogues.[90]

Although halogenolysis of ditellurides is the most common route to tellurenyl halides, it is rarely employed for the preparation of compounds stabilized by intramolecular coordination. Instead, reactions such as scission of C_{sp^3}-Te bonds by halogens[14,20,36,85,86,88–90] or hydrogen halides[76,77,79,80,91] as well as controlled reduction of aryltellurium trihalides[19,23,27,36,49,51,87,89] have proved useful. The two former reactions have been mostly applied to the preparation of arenetellurenyl halides with carbonyl **3**, **42** or azomethine-containing substituents **4** (Y = CH) in the *ortho*-position.



4

R = Alk, Ar, NHAr

42

X = Cl, Br

SCHEME 15

The presence of COR groups *ortho* to the TeHal group is essential for the formation of the arenetellurenyl halides **3**. In the case of 4-acetylphenyltelluroacetaldehyde diethyl acetal, hydrolysis under analogous conditions leads to the formation of the corresponding ditelluride.[76]

In some cases C_{ar}-Te can also be cleaved by acid hydrolysis.[81]

The synthesis of the 2-chlorotelluro ketones **3** and **2** was realized by use of a specific thermal or Lewis acid catalyzed rearrangement of *o*-(aryltelluro)benzoyl chlorides[78,81,84] and β-(aryltelluro)propenoyl chlorides.[17,82,92]

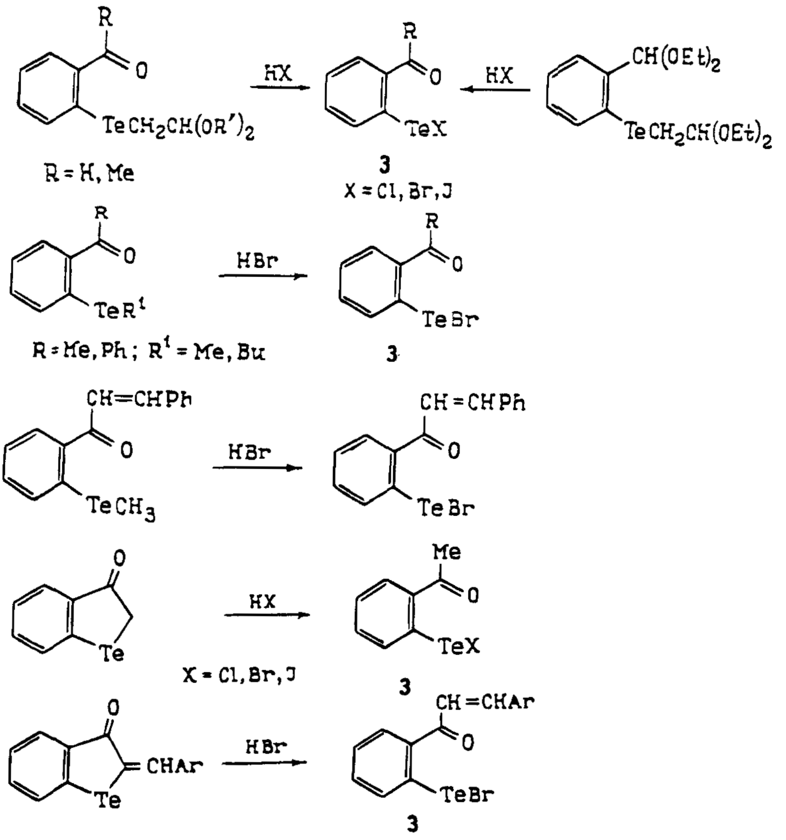
By controlled reduction of aryl(heteroaryl)tellurium trihalides containing 2-pyridyl [27,37,87] substituents, the respective tellurenyl halides have been obtained in good yields.

5.1.2. *Arenetellurenyl Acetates ArTeOAc*

Arenetellurenyl acetates not stabilized by intramolecular coordination have not yet obtained. With azo or azomethine groups located in the *o*-position to the TeOAc substituent, the tellurenyl acetates **4c** and **4d** could be obtained by exchange reactions of the corresponding tellurenyl halides with AcONa[25] or AcOAg.[14,87] Recently a new reaction, the coupling of the anhydrides of arenetellurenic acids **43** with acetic anhydride, has been described[86] to afford type **4c** and **4d** compounds.

5.1.3. *Arenetellurenyl Thiocyanates ArTeSCN*

When diaryl ditellurides are allowed to react with thiocyanogen at low temperature, unstable arenetellurenyl thiocyanates can be obtained isolated as adducts with thiourea, 2-picoline or other nitrogen bases.[93] On the other hand, the tellurenyl thiocyanate **4e** prepared by exchange reaction of the corresponding tellurenyl chloride with NH_4SCN is stable in the crystal line state.[25]

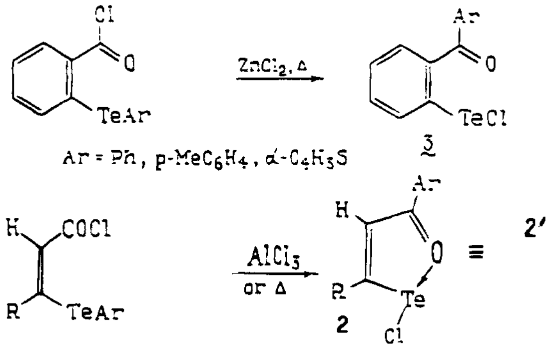


SCHEME 16

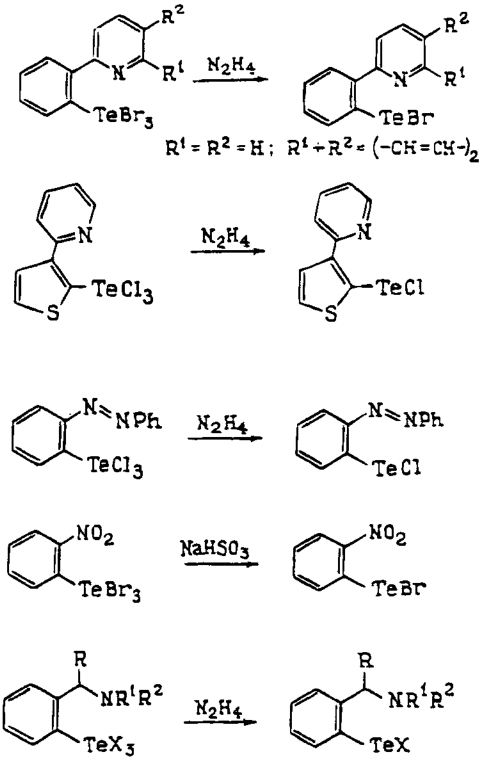
SCHEME 17

5.1.4. *Arenetellurenyl Azides ArTeN$_3$*

Intramolecular N→Te coordination stabilises the arenetellurenyl azides **44** obtained by reaction of tellurenyl bromides with sodium azide.[86] Actually, all attempts to prepare benzeneselenenyl azide by exchange of chlorine in benzenelselenyl chloride with azide ion failed since the initially formed benzeneselenenyl azide immediately decomposes to give diphenyl diselenide[94] (mesityleneselenenyl azide is more stable due to steric hindrance created by the *o*-methyl groups; it can be preparatively isolated). Considering that ArSeX compounds are, in general, more stable than their tellurium analogues, it would be hardly possible to isolate tellurenyl azides in which the tellurium atom does not participate in intramolecular coordination.

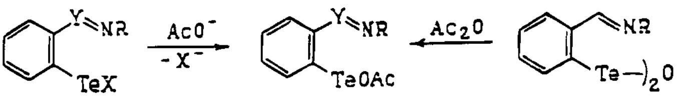


SCHEME 18



X = Cl, Br; R¹ = R² = R² = Me; R = H, Me

SCHEME 19



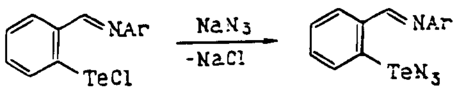
4 c,d **43**

X = Cl; Y = N; R = Ph (c); X = Br; Y = CH; R = 4-MeC_6H_4(d), 4-$MeOC_6H_4$, 2, 4,6-$Me_3C_6H_2$

SCHEME 20

4e

SCHEME 21



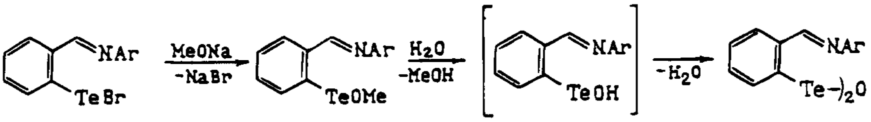
44

Ar = Ph, 4-MeC_6H_4

SCHEME 22

5.1.5. *Esters and Anhydrides of Arenetellurenic Acids*

Stabilized arenetellurenic acid esters **45** have been prepared by treatment of tellurenyl bromides with sodium methoxide in chloroform solution.[86] By hydrolysis of the esters **45**, arenetellurenic acid anhydrides **43** have been prepared by spontaneous dehydration of the intermediate tellurenic acids. Similar reactions are known for areneselenenic acids in which the aryl ring contains *o*-nitro or -carboxy substituents.[95-97]



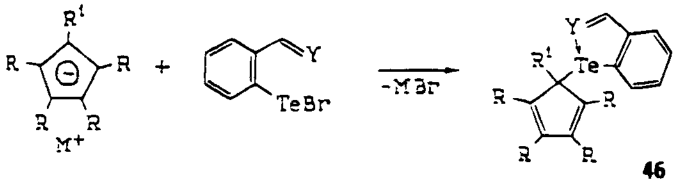
45 **43**

Ar = 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4

SCHEME 23

5.2. *Aryl Cyclopentadienyl Tellurides*

Attempts to prepare aryl cyclopentadienyl tellurides by coupling metal salts of cyclopentadienes with benzenetellurenyl bromide were unsuccessful.[39] Stable tellurides **46** were, however, obtained from this reaction when the arenetellurenyl bromides contained *o*-formyl or *o*-aldimino groups capable of forming strong N(O)→Te intramolecular coordination bonds. These are crystalline compounds with long term stability when stored in air.



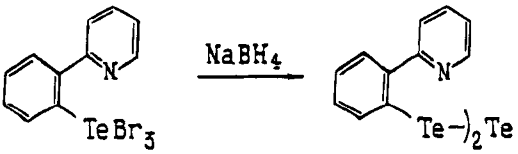
46

R = CO_2Me: R^1 = CO_2Me: Y = O, NPh, 2-MeC_6H_4; R^1 = Me: Y = NPh, 4-$MeOC_6H_4$

SCHEME 24

5.3. *Tritellurides R_2Te_3*

The first representative of diorganyl tritellurides, bis[tris(trimethylsilyl)methyl] tritelluride $[(Me_3Si)_3C]_2Te_3$[99] owes its stability to the steric constraints for any attack at the tritellurium bridge. By contrast, the thermal and kinetic stability of the tritelluride **12** is due to the presence of an intramolecular N→Te coordination bond. Bis[2-(2-pyridyl)phenyl] tritelluride has been synthesized by reduction of 2-(2-pyridyl)phenyltellurium tribromide with $NaBH_4$.[27,37] The mechanism of this reaction, the initial stage of which is the formation of elemental tellurium, remains uncertain.



12

SCHEME 25

For the formation of the quinoline analogue of **12**, prepared in high yield by reduction of a mixture of [2-(2-quinolyl)phenytellurium tribromide and elemental tellurium with $NaBH_4$,[27] the following reaction sequence has been suggested [R = 2-(2-quinolyl)phenyl]:

$$\mathrm{RTeBr_3 + NaBH_4 \rightarrow RTeBr}$$
$$\mathrm{Te + Na\ BH \rightarrow Na_2Te}$$
$$\mathrm{RTeBr + Na_2Te \rightarrow R_2Te_3}$$

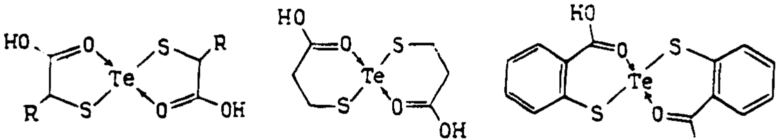
From this scheme it seems that its last stage may have good potential as an independent reaction for the preparation of a number of stabilized diaryl tritellurides from arenetellurenyl bromides and sodium telluride.

5.4. *Bis(organylthio) Tellurides (RS)$_2$Te*

Bis(organylthio) tellurides **47** are generally obtained by treatment of thiols with sodium tellurite.[100]

$$\mathrm{TeO_3^{2-} \xrightarrow[RSH/H^+]{} (RS)_2Te}$$

By this reaction, bis(phenylthio) and bis(2-naphthylthio) telluride have been prepared and isolated. However, both these compounds decompose to disulfide and tellurium when stored as solids and more rapidly in solution. Much more stable are **47a–c** which contain carboxy groups capable of forming chelate rings via intramolecular O→Te coordinate bonds.



47a
R = H,Me

47b

47c

SCHEME 26

The formation of these bonds is clearly indicated by the low-frequency shift of the ν_{co} vibrational bands in compounds **47a–c** relative to the respective ligands. In the case of the five-membered ring compound **47a**, the decrease in the ν_{co} frequency amounts to 30 cm^{-1}, while in the six-membered ring compounds **47b,c** it is only 10–15 cm^{-1}. Such a trend obviously shows stronger O→Te interaction and a greater resulting stabilizing effect in the five-membered chelate ring compound **47a** compared to the six-membered ring analogues **47b,c**. This observation is in line with the fact that virtually all the organotellurium compounds considered above (with the exception of 1-(trichlorotelluro)-2-methylpentan-4-one) belong to the structural type where intramolecular coordinate bonds are involved leading to five-membered chelate rings.

6. INTRAMOLECULAR N(O)→Te COORDINATION AND REACTIVITY OF ORGANOTELLURIUM COMPOUNDS

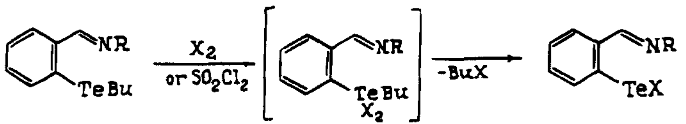
The influence of intramolecular coordination on the reactivity of organotellurium compounds has, as yet, been little studied. The available data are mostly of a qualitative nature, the effects of N→Te intramolecular coordination having being studied in much more detail than those of O→Te coordination.

6.1. *Reduction of C=N Bonds*

Whereas the C=N bonds in aromatic azomethines are known to be readily reduced upon treatment with $NaBH_4$ in ethanol solution at ambient temperature no such reaction occurs with 2-(butyltelluro)benzal-4′-methylaniline upon reflux of its solution with $NaBH_4$ for a long period.[86] On the other hand, the oxygen analog 2-methoxybenzal-4′-methylaniline shows no abnormal behaviour and affords the corresponding secondary amine in high yield. 2-(Trichlorotelluro)benzal-4′-methylaniline when treated with $NaBH_4$ undergoes simultaneous reduction of both the C=N bond and the $TeBr_3$ group, which gives rise to the secondary amine **6.**[23] Replacement of the 4-methyl group by the bulkier *t*-butyl group in the 2,4,6-positions inhibits the former reaction.

6.2. *Oxidative Addition of Halogens*

Oxidative addition of halogens to aryl alkyl tellurides readily affords stable arylalkyltellurium dihalides.[70] By contrast the *o*-tellurated azomethines **28**[14,20,85,86] and **8**[36] when treated with halogens or sulfuryl chloride undergo scission of the C_{sp^3}-Te bond which leads to the formation of the tellurenyl halides **27** and **27a**, respectively, in high yield. The reaction proceeds through the σ-tellurane intermediates **48** which exist in solution at low temperature as proved by ^1H NMR spectral studies.[14] When the temperature is raised to ambient, butyl halide is eliminated giving rise to the tellurenyl halides **27**.

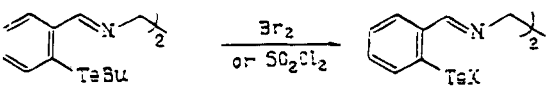


28 **48** **27**

R = Ph, X = Cl; R = 4-MeC_6H_4: X = Cl, Br, I; R = 4-$MeOC_6H_4$: X = Cl, Br, I; R = 2,3,4,5,6-F_5C_6: X = Br, I

SCHEME 27

Such a reaction can be accounted for by two factors: (1) strong stabilization of the 10-Te-3 structures **27** due to the coordination of the azomethine nitrogen to the tellurium atom, (2) by the favourable steric conditions for nitrogen-tellurium n(N)→σ*(Te-Bu) electron delocalization in the intermediate **48**, and (3) the fact that the Te←N coordination will make



8 **27a**

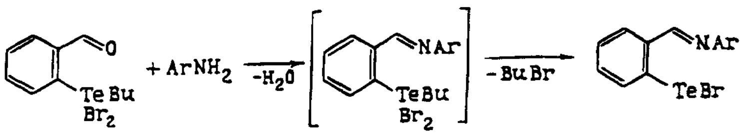
SCHEME 28

the carbon atom adjacent to tellurium susceptible to electrophilic attack. As seen from the orbital interaction pattern such a delocalization leads to a considerable weakening of the Te-C bond which forms with the N→Te fractional bond an angle of about 180°.[14]

48 **51**

SCHEME 29

There are many known examples of reactions facilitating C-X bond rupture which occur when interacting fragments meet each other in appropriate steric positions providing a large n_O-σ*(X-C) or n_N-σ*(X-C) overlap and consequently, a partial population of the antibonding σ*(X-C) orbital. Indeed, 2-benzal-4′-methylaniline(methyl)tellurium **49**, in which the N→Te coordination is sterically inhibited, forms the corresponding tellurium dihalide under the same conditions. *o*-(Halotelluro)benzalanilines **27** rather than σ-telluranes **48** are also formed when 2-(butyldibromotelluro)benzaldehyde reacts upon heating with primary amines, although the tellurium dihalides **48** are obviously the initial products of this reaction.[14,86]

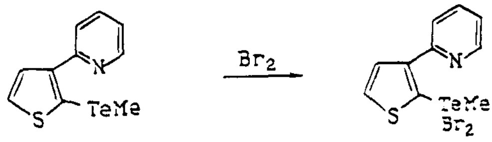


48 **27**

SCHEME 30

It should, however, be noted that **50**, analogous to **48**, obtained by addition of bromine to the respective telluride, is a stable high-melting compound (m.p. 160°.[87])

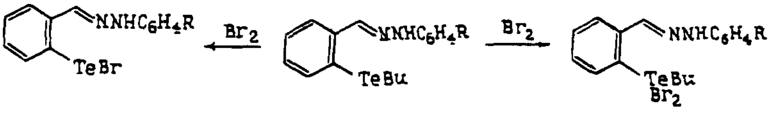
Thus, regardless of the nature of the substituents in the *N*-aryl rings of the aromatic azomethines **28**, their halogenation leads, as a rule, to tellurenyl halides. Similar reactions with arylhydrazones of 2-(butyltelluro)benzaldehyde **51**[88] proceed differently. Whereas the presence of electron-releasing substituents (R = Me) in the arylhydrazone ring favours cleav-



50

SCHEME 31

age of the C_{sp^3}-Te bond upon bromination which results in the formation of the tellurenyl bromide **52**, in the cases with R = H or 2,4-$(NO_2)_2$ arylhydrazones of 2-(butyldibromotelluro)benzaldehyde **53** are formed.



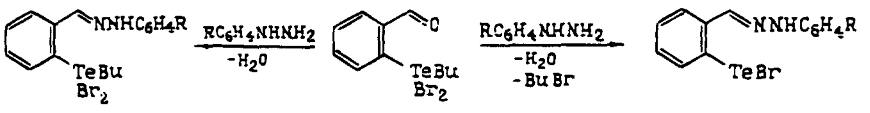
52 R = 4-Me

51

53 R = H, 2,4-$(NO_2)_2$

SCHEME 32

Substituents in the aryl ring of arylhydrazines exert similar influence on the outcome when these compounds react with 2-(butyldibromotelluro)benzaldehyde. When *o*- or *p*-tolylhydrazines are involved, reaction in both toluene or chloroform leads to arylhydrazones of 2-(bromotelluro)benzaldehyde **52** *via* the σ-telluranes **53** which readily eliminate butyl bromide. With the derivative of 2,4-dinitrophenylhydrazine in refluxing toluene solution, the arylhydrazone **53** is the final product as is the case for the reaction of the phenylhydrazine derivative in chloroform solution at room temperature.[88]

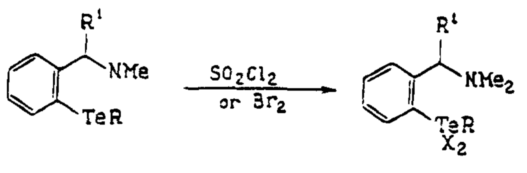


53 R = H, 2,4-$(NO_2)_2$

52 R = H, 4-Me

SCHEME 33

The σ-telluranes **54**, which are formed upon treatment of 2-(alkyltelluro)benzyldimethylamines with sulfuryl chloride [51] or bromine,[49] are also rather stable. Their stability is caused by the intramolecular coordination N_{sp^3}-Te bond which is only slightly weaker than the more extensively studied N_{sp^2}-Te bonds.



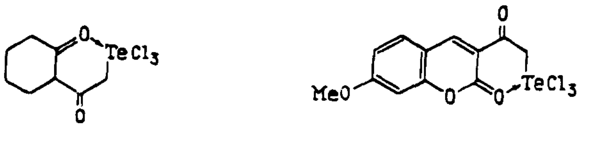
54

$R^1 = H$; R = Me, Et, Bu; $R^1 = R = Me$; X = Cl, Br

SCHEME 34

6.3. *Reactions of σ-Telluranes*

Intramolecular N→Te or O→Te coordination enhances the hydrolytic stability of σ-telluranes. The diorganyl(diaryloxy)telluranes **32** are not subject to hydrolysis even after prolonged contact with water,[39,101] whereas diaryl(dialkoxy)telluranes without N→Te bonds are hydrolyzed instantaneously upon exposure to moist air.[102] Similar properties are characteristic of the intramolecular coordination bonds in the trichlorotellurane **18** considered above, as well as those of **55z** and **56** prepared by coupling of the appropriate ketones with $TeCl_4$.[48] All of these are almost inert to the action of water at room temperature.

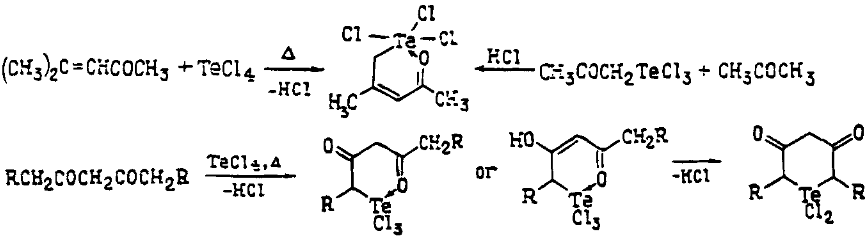


55 **56**

SCHEME 35

As expected the electrophilicity of the Te(IV) centre in $TeCl_3$ groups involved in coordination with nitrogen or oxygen ligating atoms is lowered compared to that of the non-coordinated group. Thus, while acetophenone and its derivatives afford σ-telluranes of the type $(ArCOCH_2)_2TeCl_2$, reactions of $TeCl_4$[102,104] with 2,6-diacetylpyridine, 2-acetylcyclohexanone or 3-acetyl-7-methoxycoumarine stops at the stage of the σ-tellurane $RCOCH_2TeCl_3$ **18**, **55** and **56** even if the carbonyl-containing component is taken in two-fold molar excess. Illustrative is an example of the reaction of mesityl oxide with tellurium tetrachloride in chloroform solution, which gives rise to 1-trichlorotelluro-2-methylpentan-4-one.[105] Therefore, the reaction occurs at the methyl group adjacent to the double bond, but not that adjacent to the carbonyl carbon atom as was the case in analogous reactions with acetophenone[103,104] and other methyl ketones.[70] A possible mechanism might be initial substitution at the C_{sp^3} centre attached to the carbonyl carbon atom with subsequent rearrangement of the intermediate thus formed to **16**. Most probably, the driving force of the reaction is the strong stabilization of **16** by the relatively short intramolecular O—Te coordinate bond (2.44 Å) (see Section 2.4).

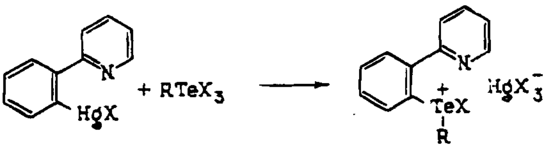
It seems possible,[105] that by the same reason tellurium tetrachloride attacks a terminal rather than the internal carbon centres of 1,3-diketone which leads to formation of 1-telluracyclohexane-3,5-dione 1,1-dichlorides.[70] By substitution of the hydrogen atoms in the terminal groups the tellurane **57** stabilized by an intramolecular coordinate Te←O bond is formed.



57

SCHEME 36

Reaction of organyltellurium trichlorides or bromides with organylmercury halides leads to diorganyltellurium dihalides and $HgHal_2$;[70] It is one of the most important methods of preparation of both symmetrical and unsymmetrical diorganyltellurium dihalides. However, when the formation of an intramolecular coordinate bond with participation of the tellurium centre becomes possible in the final product, the reaction with arylmercury halides gives rise to 2-(2-pyridyl)phenylhalotelluronium trihalomercurates **15**.[27,41]

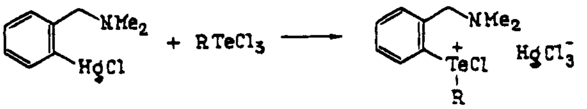


15

X = Cl, Br; R = 4-$EtOC_6H_4$

SCHEME 37

Similar products are formed upon treatment of 2-(chloromercuro)benzyldimethylamine with aryltellurium trichlorides.[51]

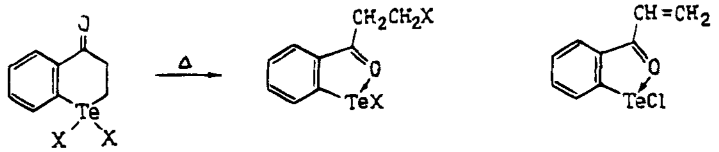


R = 4-$EtOC_6H_4$

SCHEME 38

6.4. *Rearrangement of Dihalotellurochromanones*

Dihalotellurochromanones **58** undergo an unusual rearrangement which involves fission of the C_{sp^3}-Te bond and formation of 2-(β-halopropionyl)phenyltellurenyl halides **3d**.[24] In the case of dichlorotellurochromanone, elimination of hydrogen chloride from **3d** is observed which gives rise to **3d1** as the final product. The rearrangement requires rather severe reaction conditions: 20–30 hours of reflux for solutions of **58** in chloroform, brombenzene or nitrobenzene.

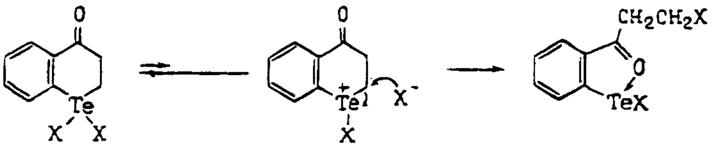


58 **3d** **3d1**

X = Br, I

SCHEME 39

A possible reaction pathway for the rearrangement, the driving force for which is apparently the strong stabilization of the final 10-Te-3 telluranes **3d** and **3d1** by O→Te bonds, may include predissociation of the Te-X bond in **58** with subsequent migration of halide anion to the β-carbon atom.



58 **3d**

SCHEME 40

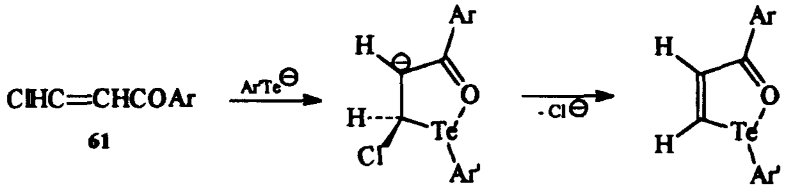
Of particular interest would be to study the tendency of the five- and seven-membered analogues of **58**, i.e. the tellurium dihalides **59** and **60** to undergo the above rearrangement.

59 **60**

SCHEME 41

6.5. *Nucleophilic Substitution of Chlorine at the* sp^2*-Carbon Centre of* β*-Chlorovinyl Carbonyl Compounds by Aryltellurolate Anions*

An interesting example of the influence exerted by intra-molecular O→Te coordination on the stereochemical outcome of nucleophilic vinylic substitution is given by the recently studied reaction of β-chlorovinyl ketones **61a–d** with tellurolate anions.[106] Regardless of the initial configuration at the double bond in **61**, the reaction leads to the formation of only (Z)-isomers of **62a–d**, i.e. inversion of configuration of (E)-**61** and retention of configuration for (Z)-**61**.



61

62

61 and 62 Ar = Ph (A), 4-MeC_6H_4 (B), 4-$MeOC_6H_4$ (C), 4-BrC_6H_4 (D);

62 Ar^1 = Ph (A), 4-MeC_6H_4 (B, C, D), 4-$EtOC_6H_4$ (C).

SCHEME 42

The intramolecular O→Te coordination in the intermediate anion, formed during the addition elimination process, determines the stereochemical course of this reaction.

7. MÖSSBAUER SPECTROSCOPY

Reaction of (2-phenylazophenyl)tellurium(IV) trichloride **63** with dimethyl-, diethyl-, or dibenzyldithiocarbamate (dtc) gives the solids $Te(C_6H_4N_2Ph)(dtc)_3$[26] which surprisingly have the same dark purple colour as the tellurium(II) compounds $Te(C_6H_4N_2Ph)(dtc)$. ^{125}Te NMR data for both $Te(C_6H_4N_2Ph)(dtc)_3$ and $Te(C_6H_4N_2Ph)(dtc)$ show identical chemical shifts characteristic of tellurium(II) demonstrating that, in solution, the *tris*-dithiocarbamate complexes exist as the Te(II) species and the disulfide, $R_2N\text{-}C(S)S\text{-}S(S)C\text{-}NR_2$. The ^{125}Te Mössbauer quadrupole splittings of $Te(C_6H_4N_2Ph)(dtc)_3$ ($\Delta E_Q = 11.4$ mm s^{-1} for dimethyldithiocarbamate = dtc) and of the corresponding $Te(C_6H_4N_2Ph)(dtc)$ ($\Delta E_Q = 12.6$ mm s^{-1}) differ significantly and the difference can be attributed to the existence of a weak charge transfer complex $Te(C_6H_4N_2Ph)(dtc)\cdot$disulfide in the solid "$Te(C_6H_4N_2Ph)(dtc)_3$".

This observation is perhaps another manifestation of the particular stability of intramolecularly coordinated tellurium(II) complexes.

^{125}Te Mössbauer studies of Te($C_6H_4N_2Ph$)Cl show a quadrupole splitting, of 11.8 mm s^{-1}. A simple model[108] based on Towns-Dailey theory predicts a value of ~14 mm s^{-1}. This lower value observed implies that there is less p-lone pair electron density associated with tellurium than anticipated. This may imply some delocalisation of Te p-electron density over the five-membered TeNNCC ring (N=N is longer and C-N shorter than in azobenzene). Thus the rather limited amount of Mössbauer data available for compounds with strong intramolecular Te···N(O) bonds indicate that these materials have novel chemical and electronic properties.

8. SUMMARY

During the preparation of this article another review covering intramolecular coordination in organotellurium chemistry was published.[109] The treatment in that article is more general e.g. Te←P and Te←S systems are included, also there is less emphasis on the influence of intramolecular coordination on reactivity. Thus, rather conveniently the two articles are complementary and together provide a very thorough coverage of the subject.

Some conclusions can be drawn on the basis of the data considered above on the structure and reactivity of organotellurium compounds containing intramolecular N→Te or O→Te coordinate bonds.

1. Strong intramolecular attractive interactions are manifested in organotellurium compounds possessing nitrogen- and oxygen-containing functional groups where nitrogen or oxygen donor centres are spatially positioned with respect to Te(II) or Te(IV) centers to form five- or six-membered rings with N→Te or O→Te coordinate bonds. The strength and lengths of such bonds, which belong to the hypervalent type, show strong dependence on the oxidation state of the tellurium centre and on the electronegativity of the substituents attached to it. The Te···N and Te···O distances cover the full range from close to covalent Te-N and Te-O bonds to their respective van der Waals contacts.
2. The formation of intramolecular coordinate bonds changes the type of coordination polyhedron at the tellurium centre in a way expected according to VSEPR theory.
3. Intramolecular coordinate N→Te and O→Te bonds do not, usually, break down in solution. These bonds define the molecular conformation of the organotellurium compounds in question, as shown by their NMR and IR spectral parameters, dipole moments and Kerr constants.
4. Intramolecular N→Te and O→Te coordination provides for stabilization of certain types of organotellurium compounds and serves as a driving force for their formation in a number of chemical reactions. This fact could be employed as a principle of rational design of kinetically unstable organotellurium compounds.
5. Intramolecular N→Te and O→Te coordination strongly affects the reactivity of organotellurium compounds.

The above generalizations may serve as a basis for further systematic study of the effects exerted by intramolecular hypervalent type coordination on the structure and reactivity of organotellurium compounds. Among many problems to be solved, in the opinion of the authors, the following might be urgently addressed:

1. Synthesis and X-ray structural study of comparatively little studied tellurides, ditellurides and σ-telluranes of the type $R^1R^2TeX_2$; also other σ-telluranes (tellurium oxides, imides and ylides), information on which is completely unavailable at the present time. There is also a surprising paucity of data on organotellurium fluorides stabilised by intramolecular coordination.
2. Extension of the data on structure and reactivity with N_{sp^3}-Te intramolecular coordinate bonds for which only a few examples have been found.
3. Design of organotellurium compounds with six-membered rings chelated by N→Te and O→Te intramolecular coordinate bonds.
4. Structural engineering of 1,2-disubstituted ethenes with intramolecular coordinate bonds involving tellurium centres. Synthesis of novel tellurium-containing heterocycles based on the such precursors.
5. Search for new reactions and rearrangements of organotellurium compounds which would account for structural and chemical reactivity characteristics stemming from the presence of intramolecular hypervalent type bonds.

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References

1. G. R. Newcome, W. E. Puckett, and G. E. Kiefer, *Chem. Ber.* **86**, 451 (1986).
2. J. Omae, Organometallic Intramolecular-Coordination Compounds, *J. Organomet. Chem.* **32** Library 18, Elsevier, Amsterdam, 1986, 402 pp.
3. J. Omae, *Coord. Chem. Rev.* **83**, 137 (1988)
4. J. T. B. H. Jastrzebski and G. Van Vioten, *Adv. Organomet. Chem.* **35**, 241 (1993).
5. I. Hargittai and R. Rozsondai, in: S. Patai and Z. Rappoport (Eds.), *The Chemistry of Organic Selenium and Tellurium Compounds*, John Wiley and Sons, Chichester, New York, Brisbane, Toronto, Singapore, Vol. 1, 1986, pp. 63–156.
6. .A. Kucsman and L. Kapovits, in: I. G. Csizmadia and A. Mangini (Eds.), *Organic Sulfur Chemistry: Theoretical and Experimental Advances*, Amsterdam, 1985, pp. 191–245.
7. D. H. R. Barton, M. B. Hall, Z. Lin, S. I. Parekh and J. Reibenspies, *J. Amer. Chem. Soc.* **115**, 5056 (1993).
8. N. W. Alcock, *Adv. Inorg. Chem. Radiochem.* **15**, 1 (1972).
9. E. N. Givens and H. Kwart, *J. Amer. Chem. Soc.* **90**, 378 (1968).
10. I. Kapovits, F. Ruff, J. Gulyas, and A. Kucsman, *Tetrahedron* **32**, 1811 (1976).
11. F. Ruff, I. Kapovits, J. Rabai, and A. Kucsman, *Tetrahedron* **34**, 2767 (1978).
12. W. Nakanishi, Y. Ikeda, and H. Iwamura, *J. Org. Chem.* **47**, 2275 (1982).
13. H. Kwart and H. Omura, *J. Amer. Chem. Soc.* **73**, 7250 (1971).
14. V. I. Minkin, I. D. Sadekov, A. A. Maksimenko, O. E. Kompan, and Yu. T. Struchkov, *J. Organomet. Chem.* **402**, 331 (1991).
15. W. R. McWhinnie, *Phosphorus, Sulfur, Silicon Relat. Elem.* **67**, 107 (1992).
16. M. R. Detty and H. R. Luss, *J. Org. Chem.* **48**, 5149 (1983).
17. M. R. Detty, B. J. Murray, and D. L. Smith, *J. Amer. Chem. Soc.* **105**, 875 (1983).
18. P. I. Dupont, O. Dideberg, and J. Lamotte, *Acta Cryst.*, **B35**, 849 (1979).
19. R. E. Cobbledick, F. W. B. Einstein, W. R. McWhinnie and F. H. Musa, *J. Chem. Res. (M)*, 1979, 1901.
20. A. A. Maksimenko, I. D. Sadekov, A. G. Maslakov, G. K. Mehrotra, O. E. Kompan, Yu. T. Struchkov, S. V. Lindeman, and V. I. Minkin, *Metallorg. Khim.* **1**, 1151 (1988).
21. M. R. Greaves, T. A. Hamor, B. J. Howlin, T. S. Lobana, S. A. Mbogo, W. R. McWhinnie, and D. C. Povey, *J. Organomet. Chem.* **420**, 327 (1991).

22. P. M. Baiwir, G. Llabres, O. Dideberg, and L. Dupont, *Acta Cryst.* **B30**, 139 (1974).
23. A. G. Maslakov, W. R. McWhinnie, M. C. Perry, N. Shaikh, S. L. W. McWhinnie, and T. A. Hamor, *J. Chem. Soc., Dalton Trans.*, 619 (1993).
24. I. D. Sadekov, A. A. Ladatko, V. L. Nivorozhkin, O. E. Kompan, Yu. T. Struchkov, and V. I. Minkin, *Zh. Obshch. Khim.* **60**, 2764 (1990).
25. M. A. K. Ahmed, W. R. McWhinnie and T. A. Hamor, *J. Organomet. Chem.* **293**, 219 (1985).
26. M. A. K. Ahmed, A. E. McCarthy and W. R. McWhinnie, *J. Chem. Soc., Dalton Trans.*, 771 (1986).
27. N. Al-Salim, A. A. West, W. R. McWhinnie and T. A. Hamor, *J. Chem. Soc., Dalton Trans.*, 2363 (1988).
28. A. A. West, W. R. McWhinnie, and T. A. Hamor, *J. Organomet. Chem.* **356**, 159 (1988).
29. I. D. Sadekov, L. E. Rybalkina, D. Ya. Movshovich, S. B. Bulgarevich, and V. A. Kogan, *Usp. Khim.* **60**, 1229 (1991).
30. L. Pauling, *The Nature of the Chemical Bond*, 3rd Ed., Cornell Univ. Press, Ithaca, New York, 1960.
31. C. W. Perkins, J. C. Martin, A. J. Arduengo, W. Lau, A. Alegria, and J. K. Kochi, *J. Amer. Chem. Soc.* **102**, 7753 (1980).
32. J. Lamotte, H. Campsteyn, L. Dupont, and M. Vermeire, *Cryst. Struct. Commun.* **6**, 749 (1977).
33. N. Al-Salim, T. A. Hamor, and W. R. McWhinnie, *J. Chem. Soc., Chem. Commun.*, 453 (1986).
34. I. D. Sadekov, A. A. Maksimenko, A. G. Maslakov, G. K. Mehrotra, G. S. Borodkin, O. E. Kompan, Yu. T. Struchkov, Yu. T. Fedotov, and V. I. Minkin, *Metallorg. Khim.* **2**, 298 (1989).
35. A. A. Maksimenko, I. D. Sadekov, A. G. Maslakov, O. E. Kompan, A. I. Yanovskii, Yu. T. Struchkov, and V. I. Minkin, *Zh. Strukt. Khim.* **32**, 104 (1991).
36. K. Y. Abid, N. I. Al-Salim, M. R. Greaves, W. R. McWhinnie, A. A. West, and T. A. Hamor, *J. Chem. Soc., Dalton Trans.*, 1697 (1989).
37. T. A. Hamor, N. Al-Salim, A. A. West, and W. R. McWhinnie, *J. Organomet. Chem.* **310**, C5 (1986).
38. N. L. M. Dereu, R. A. Zingaro, and E. A. Meyers, *Cryst. Struct. Commun.* **10**, 1353 (1981).
39. V. I. Minkin, A. A. Maksimenko, A. G. Maslakov, G. K. Mehrotra, O. E. Kompan, I. D. Sadekov, Yu. T. Struchkov, and D. S. Yufit, *J. Organomet. Chem.* **348**, 63 (1988).
40. I. D. Sadekov, A. A. Maksimenko, A. G. Maslakov, O. E. Kompan, Yu. T. Struchkov, and V. I. Minkin, *Metallorg. Khim.* **2**, 1260 (1989).
41a. T. S. Lobana, S. A. Mbogo, and W. R. McWhinnie, *J. Organomet. Chem.* **390**, 29 (1990).
41b. M. R. Detty, A. E. Friedman, and M. McMillan, *Organometallics* **13**, 3338 (1994).
42. R. F. Ziolo, and J. M. Troup, *Inorg. Chem.* **18**, 2271 (1979).
43. R. F. Ziolo, and M. Extine, *Inorg. Chem.* **19**, 2694 (1980).
44. R. K. Chadha, and J. E. Drake, *J. Organomet. Chem.* **299**, 331 (1986).
45. R. K. Chadha, J. E. Drake, and M. A. Khan, G. Singh, *J. Organomet. Chem.* **260**, 73 (1984).
46. C. K. Huang, D. H. O'Brien, K. J. Irgolic, and E. A. Meyers, *Cryst. Struct. Commun.* **11**, 1593 (1982).
47. M. A. K. Ahmed, and W. R. McWhinnie, *J. Organomet. Chem.* **281**, 205 (1985).
48. H. J. Gysling, H. R. Luss, and S. A. Gardner, *J. Organomet. Chem.* **184**, 417 (1979).
49. H. B. Singh, N. Sudha, and R. T. Butcher, *Inorg. Chem.* **31**, 1431 (1992).
50. M. R. Detty, H. R. Luss, J. M. McKelvey, and S. M. Geer, *J. Org. Chem.* **51**, 1692 (1986).
51. H. B. Singh, N. Sudha, A. A. West, and T. A. Hamor, *J. Chem. Soc., Dalton Trans.*, 907 (1990).
52. J. Bergman, and L. Engman, *J. Organomet. Chem.* **181**, 335 (1979).
53. T. S. Cameron, R. B. Amero, C. Chan, and R. E. Cordes, *Cryst. Struct. Commun.* **9**, 543 (1980).
54. A. G. Maslakov, E. Gresham, T. A. Hamor, W. R. McWhinnie, M. C. Perry, and N. Shaikh, *J. Organomet. Chem.* **480**, 261 (1994).
55. V. I. Minkin, I. D. Sadekov, A. A. Maksimenko, A. G. Maslakov, G. K. Mehrotra, and M. A. Fedotov, *Zh. Obshch. Khim.* **58**, 1684 (1988).
56. H. Campsteyn, L. Dupont, J. Lamotte-Brasseur, and M. Vermeire, *J. Heterocycl. Chem.* **15**, 745 (1978).
57. D. Ya. Movshovich, N. A. Ivanova, S. B. Bulgarevich, A. A. Maksimenko, A. G. Maslakov, I. D. Sadekov, and V. I. Minkin, *Zh. Obshch. Khim.* **61**, 739 (1991).
58. V. I. Minkin, Yu. A. Zhdanov, and O. A. Osipov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York, 1970.
59. R. J. Gillespie and E. A. Robinson, *Can. J. Chem.* **41**, 2074 (1963).
60. E. A. Robinson, *J. Mol. Struct.* (THEOCHEM) **186**, 9 (1989).
61. J. G. Angyan, R. A. Poirier, A. Kucsman, and J. G. Csizmadia, *J. Amer. Chem. Soc.* **109**, 2237 (1987).
62. H. W. Roesky, K. L. Weber, U. Seseke, W. Pinter, M. Noltemeyer, W. Clegg, and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, **565** (1985).
63. M. S. Gordon, M. T. Carroll, J. H. Jensen, L. P. Davis, L. W. Burggraf, and R. M. Guidry, *Organometallics* **10**, 2657 (1991).
64. H. W. Roesky, J. Minzeberg, R. Bohra, and N. M. Noltemeyer, *J. Organomet. Chem.* **418**, 339 (1991).
65. A. E. Reed, and P. R. von Schleyer, *J. Amer. Chem. Soc.* **112**, 434 (1990).
66. E. Magnusson, *J. Amer. Chem. Soc.* **112**, 7940 (1990).

67. V. K. Yadav, A. Yadav, and R. Poirier, *J. Mol. Struct.* (THEOCHEM) **186**, 101 (1989).
68. D. A. Dixon, and A. J. Arduengo, *Inorg. Chem.* **29**, 970 (1990).
69. A. Kucsman, I. Kapovits, M. Czugler, L. Parkanyi, and A. Kalman, *J. Mol. Struct.* (THEOCHEM) **198**, 339 (1989).
70. I. D. Sadekov, A. A. Maksimenko, and V. I. Minkin, *Khimiya Tellurorganicheskikh Soedinenii*, Izd. RGU, Rostov-on-Don, 1983.
71. P. Schulz and K. Gunter, *Z. Naturforsch.* **30b**, 40 (1975).
72. P. Schulz and G. Klar, *Z. Naturforsch.* **30b**, 43 (1975).
73. M. Feikus and P. H. Laur, *Phosphorus, Sulfur, Silicon Relat. Elem.* **67**, 73 (1992).
74. N. Petragnani, L. Torres, K. J. Wynne, and D. J. Williams, *J. Organomet. Chem.* **76**, 241 (1974).
75. W. L. Dorn, A. Knochel, P. Schulz, and G. Klar, *Z. Naturforsch.* **31b**, 1043 (1976).
76. J. L. Piette, R. Lysy, and M. Renson, *Bull. Soc. Chim. France*, 3559 (1972).
77. J. L. Piette, and M. Renson, *Bull. Soc. Chim. Belges* **80**, 669 (1971).
78. J. L. Piette, P. Thibaut, and M. Renson, *Chem. Scr.* **A8**, 117 (1975).
79. J. L. Piette, A. Petit, and M. Renson, *Compt. Rend.* **276**, 1035 (1973).
80. J. M. Talbot, M. Renson, and J. L. Piette, *Bull. Soc. Chim. France*, 294 (1976).
81. J. L. Piette, P. Thibaut, and M. Renson, *Tetrahedron* **34**, 655 (1978).
82. M. R. Detty, and B. J. Murray, *J. Amer. Chem. Soc.* **105**, 883 (1983).
83. L. Christiaens, A. Luxen, M. Evers, P. Thibaut, M. Mbuyi, and A. Welter, *Chem. Scr.* **24**, 178 (1984).
84. L. Christiaens, A. Luxen, and M. Renson, *J. Organomet. Chem.* **287**, 81 (1985).
85. A. A. Maksimenko, A. G. Maslakov, G. K. Mehrotra, G. M. Abakarov, I. D. Sadekov, and V. I. Minkin, *Zh. Obshch. Khim.* **58**, 1176 (1988).
86. I. D. Sadekov, A. A. Maksimenko, A. G. Maslakov, and V. I. Minkin, *J. Organomet. Chem.* **391**, 177 (1990).
87. H. B. Singh, and N. Sudha, *J. Organomet. Chem.* **397**, 153 (1990).
88. A. A. Maksimenko, I. D. Sadekov, G. S. Borodkin, and V. I. Minkin, *Zh. Obshch. Khim.* **61**, 778 (1991).
89. P. Wiriyachitra, S. J. Falcone, and M. P. Cava, *J. Org. Chem.* **44**, 3957 (1979).
90. L. Engman, and M. P. Cava, *J. Org. Chem.* **46**, 4194 (1981).
91. W. Lohner and K. Praefcke, *J. Organomet. Chem.* **205**, 167 (1981).
92. M. R. Detty, *Organometallics* **7**, 2188 (1988).
93. T. N. Srivastava and M. M. Singh, *Ind. J. Chem.* **21A**, 305 (1982).
94. T. G. Back and K. G. Russel, *J. Chem. Soc., Chem. Commun.*, **134** (1987).
95. H. J. Reich, W. W. Willis, and S. Wollowitz, *Tetrahedron Lett.* **23**, 3319 (1982).
96. J. L. Kise, F. McAfee, and H. Slebocka-Tilk, *J. Org. Chem.* **49**, 3100 (1984).
97. J. L. Kise, F. McAfee, and H. Slebocka-Tilk, *Tetrahedron Lett.* **23**, 3323 (1982).
98. V. I. Minkin, I. E. Michailov, G. A. Dushenko, I. D. Sadekov, A. A. Maksimenko, and Yu. E. Chernysh, *Dokl. Russ. Akad. Nauk* **322**, 706 (1992).
99. F. Sladky, B. Bildstein, C. Rieker, A. Gieren, H. Betz, and T. Hubner, *J. Chem. Soc., Chem. Commun.*, 1800 (1985).
100. S. A. Gardner, *J. Organomet. Chem.* **199**, 363 (1980).
101. I. D. Sadekov, A. A. Maksimenko, G. K. Mehrotra, and V. I. Minkin, *Zh. Org. Khim.* **23**, 657 (1987).
102. M. Wieber, and E. Kaunzinger, *J. Organomet. Chem.* **129**, 339 (1977).
103. G. T. Morgan, and O. C. Elvins, *J. Chem. Soc.*, 2625 (1925).
104. D. G. Marsh, J. Y. C. Chu., J. W. Lewicki, and J. L. Weaver, *J. Amer. Chem. Soc.* **98**, 8432 (1976).
105. D. H. O'Brien, K. J. Irgolic, and C. K. Huang, *Proceedings of the Fourth Int. Symp. on Org. Chem. of Selenium and Tellurium*, Eds. F. J. Berry, W. R. McWhinnie, Birmingham, 1983, p. 468.
106. I. D. Sadekov, A. V. Zakharov, B. B. Rivkin, and V. I. Minkin, *Dokl. Russ. Akad. Nauk* **339**, 366 (1994).
107. Z. Rappoport, *Acc. Chem. Res.* **25**, 474 (1992).
108. C. H. W. Jones, R. Schultz, W. R. McWhinnie, and N. S. Dance, *Can. J. Chem.* **54**, 3234 (1976).
109. N. Sudha and H. B. Singh, *Coord. Chem. Rev.* **135/136**, 469 (1994).