Coordination Chemistry Reviews, 49 (1983) 193—279
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

Chapter 4

ELEMENTS OF GROUP IV

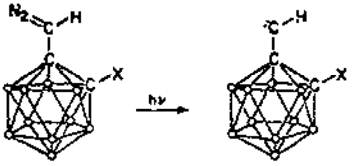
P.G.Harrison

0010-8545/83/$26.10

4.1 UNSTABLE INTERMEDIATES OF CARBON, SILICON AND GERMANIUM

4.1.1 Carbenes and Related Species

Triplet e.p.r. spectra of o-carboranylcarbene and its methyl analogue (1) (from photolysis of the diazo precursor (2)), observed at 5K in frozen solution, indicate little delocalisation of the π spin density into the carboranyl moiety (cf. benzenoid systems).[1]

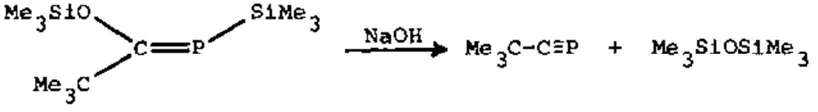


(1)
a) X = H
b) X = CH_3

(2)
a) X = H
b) X = CH_3

The interaction of the alkadienylidenecarbenes, $R_2C{=}C{=}C{=}C{:}$, with the triorganometal hydrides, R'_3MH (M = Si, Ge, Sn), leads to the formation of the novel silicon-, germanium- and tin-functionalised cumulenes, $R_2C{=}C{=}C{=}CHMR'_3$. The reaction is general for both alkyl- and aryl-substituted carbenes giving 26-88% yields of product, which are relatively stable, although somewhat air-sensitive, pale yellow oils.[2]

2,2-Dimethylpropyliynephosphine, $Me_3C{-}C{\equiv}P$, has been obtained by the decomposition of [2,2-dimethyl-1-(trimethylsiloxy)propylidene]-trimethylsilylphosphine in the presence of small amounts of solid sodim hydroxide at 20°C:[3]

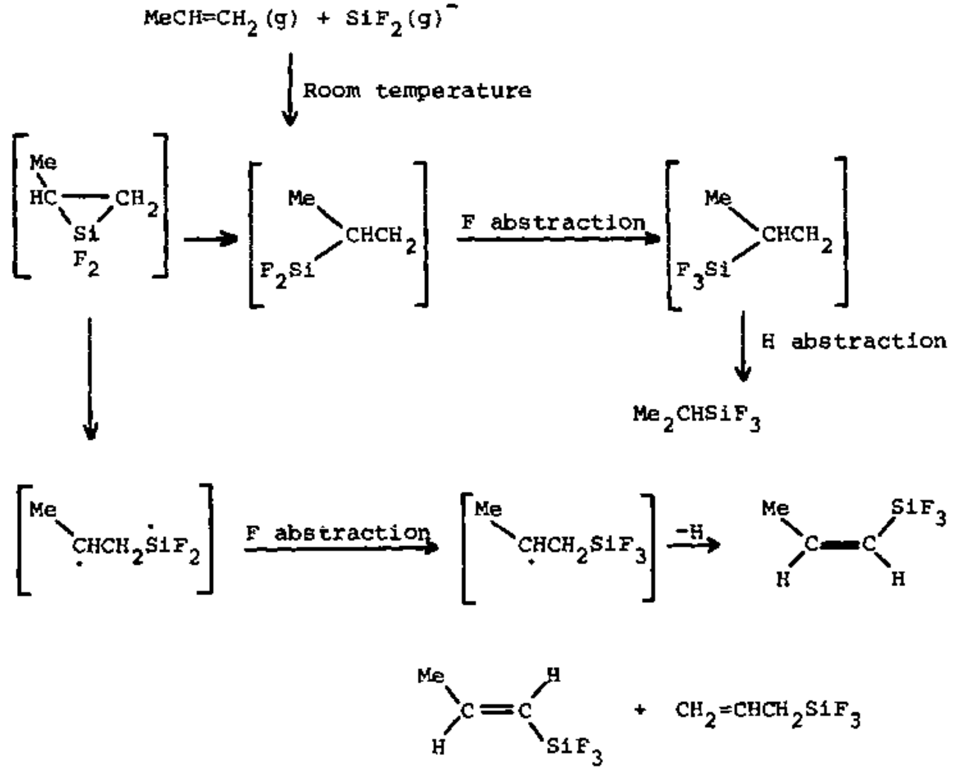


$$(Me_3SiO)(Me_3C)C{=}P{-}SiMe_3 \xrightarrow{NaOH} Me_3C{-}C{\equiv}P + Me_3SiOSiMe_3$$

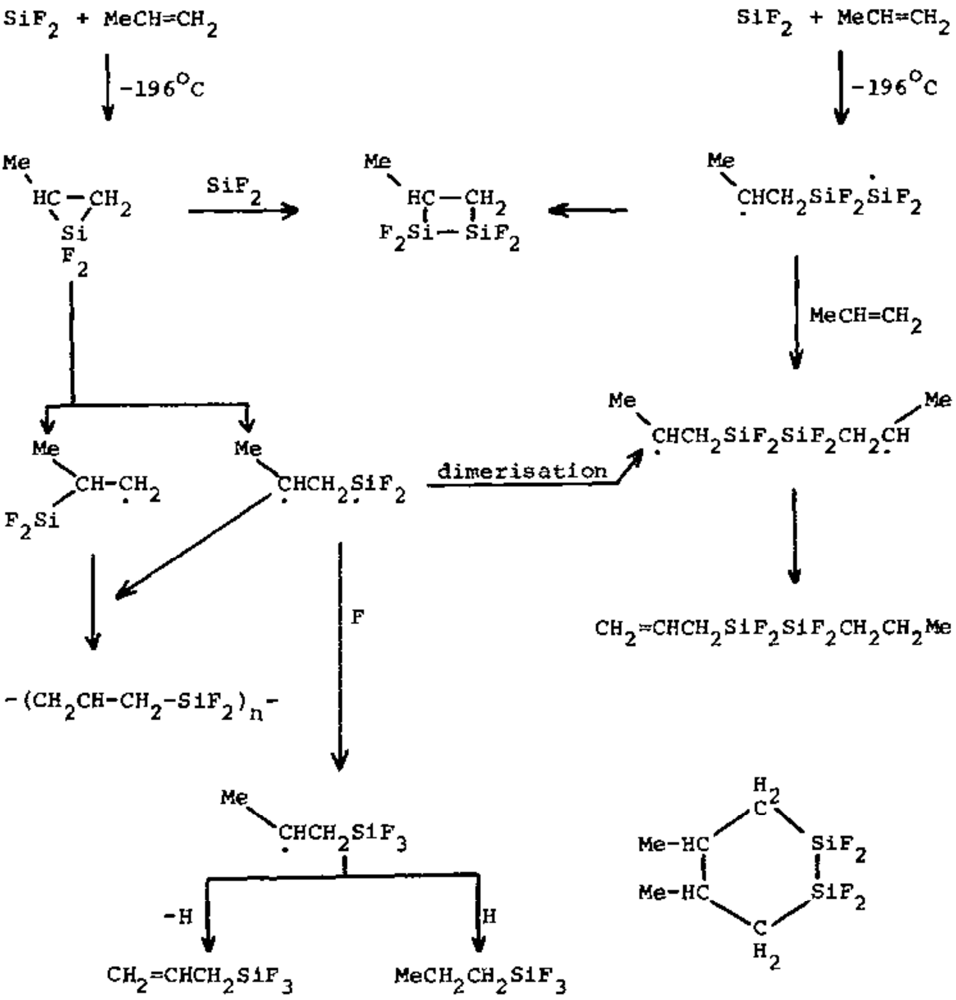
An electron diffraction and microwave study has shown that the $C{\equiv}P$ bond distance in $Me_3C{-}C{\equiv}P$ (1.536(2)Å) is somewhat shorter than in either $H{-}C{\equiv}P$ (1.542(3)Å) or $Me{-}C{\equiv}P$ (1.544(4)Å). The C-C(P) bond is shorter (1.473(4)Å) than the (Me)C-C distance (1.543(2)Å).[4] The structural parameters of phosphaethene, $CH_2{=}PH$, have also been deduced from microwave data. Relevant data are: C=P : 1.671Å, P-H : 1.425Å, $HCP_{(2)}$ = 124.5°, $HCP_{(E)}$ = 119.1°, CPH; 95.5°.[5]

4.1.2 Silylenes, Silaethylenes and other Miscellaneous Species

An ab initio (SCF + MP2 methods) study of the insertion of carbene and silylene into dihydrogen predicts that the former species reacts with no energy barrier, but that the latter has to overcome a 36 kJ mol^{-1} barrier.[6] Monomeric $^{31}SiF_2$ reacts with two moles of ethylene to yield 1,1-difluoro[^{31}Si]silacyclopentane as the final product. Competition experiments, however, indicate that ethylene is about ten times less reactive than butadiene (giving 1,1-difluoro[^{31}Si]silacyclopentene) for the trapping of difluorosilylene.[7] In the gas phase, SiF_2 reacts with propene to afford products which contain only the (SiF_2) unit expected for carbene-like behaviour (Scheme 1). The product mixture from cocondensation experiments is much more complex (Scheme 2), and comprises several products containing (SiF_2SiF_2) units as well as polymeric species.[8]

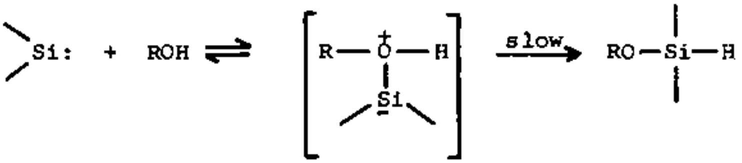


Scheme 1

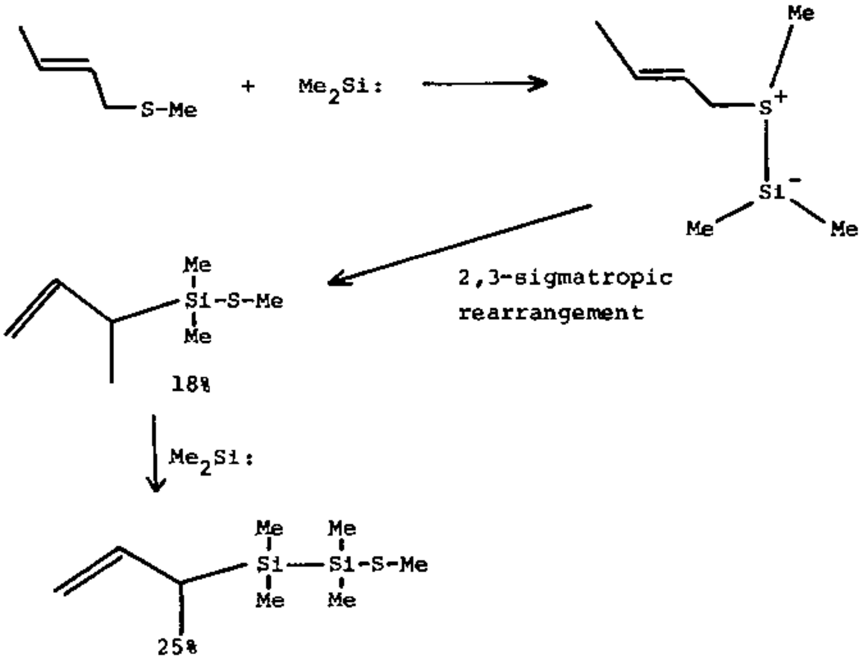


Scheme 2

Dimethylsilylene insertion into the Si-H bonds of trimethylsilane, pentamethyldisilane, and sym-tetramethyldisilane occurs with zero activation energy and relative rate constants of 1:3.1:4.3, respectively. The activation energy for insertion into HCl was deduced to be 28 kJ mol^{-1}. Photochemical reactions with methylchlorosilanes are much more complex, involving little or no silylene chemistry. Rather the reactions which occurred in these systems appear to proceed almost entirely by radical mechanisms.[9] A kinetic isotope effect for the insertion of dimethylsilylene into O-H and Si-H bonds has been demonstrated. For insertion into $BuMe_2SiH$, $^{K}H/^{K}D$ is 1.3, and for the insertion into the O-H bond of alcohols, the ratio varies between 1.8 and 2.3, favouring the mechanism[9a]

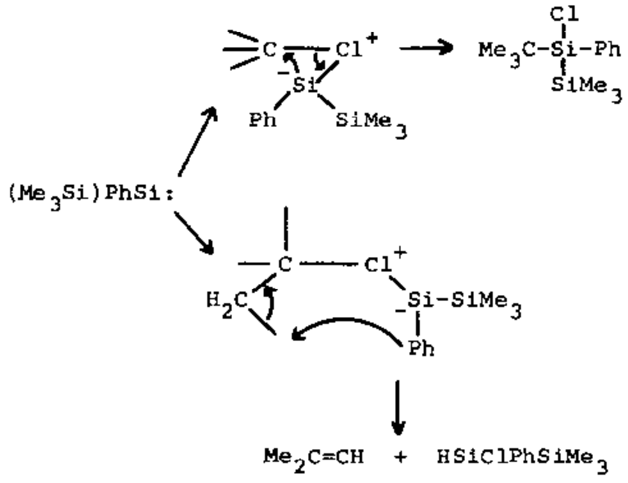


Insertion of dimethylsilylene into Si-S, S-S and C-S bonds has also been demonstrated. Reaction with the silylthioethers, Me_3SiSR and $Me_3SiSSiMe_3$, gives the disilanylthiethers, Me_5Si_2SR and $Me_5Si_2SSiMe_3$ respectively, whilst insertion into the S-S bond of dialkyldisulphides yields the bis(thiolato)silanes, $Me_2Si(SR)_2$.[10] Insertion into allylic·methylsulphides proceeds regiospecifically leading to the formation of allylic dimethyl(methylthio)silanes (Scheme 3).[11]



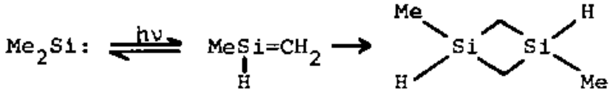
Scheme 3

(Trimethylsilyl)phenylsilylene, $(Me_3Si)PhSi:$, generated by the photolysis of $(Me_3Si)_3SiPh$, inserts clearly into the C-Cl bonds of allyl chloride, 2-methylallyl chloride and 2-octyl chloride affording the adducts, $Me_3Si-SiPhRCl$ (R = $CH_2=CHCH_2$, $CH_2-C(Me)CH_2$, C_8H_{17}). With sec-butyl chloride, however, a second reaction involving the elimination of iso-butene also occurs, which with tert-butyl chloride becomes the sole reaction (scheme 4).[12,13]



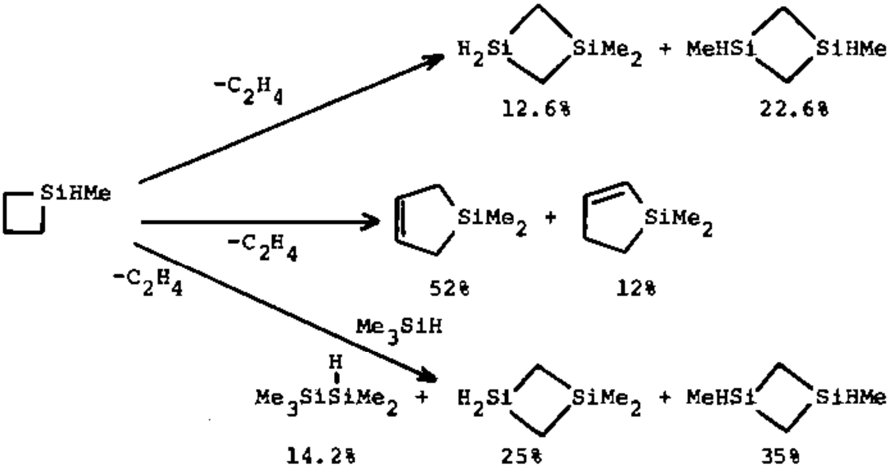
Scheme 4

Dimethylsilylene, generated in an argon matrix at 10K, undergoes photoisomerisation to 2-silapropene, which forms 1,3-dimethyl-1,3-disilacyclobutane on annealing. Similar processes also occur in hydrocarbon matrices at 77K, but in this case annealing leads to rapid reversion to the silylene (Scheme 5).[14]



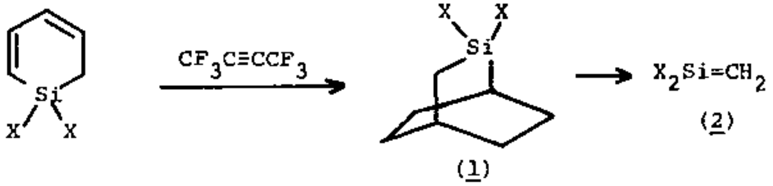
Scheme 5

Products characteristic of dimethylsilylene reactions such as pentamethyldisilane (formed by insertion into the Si-H bond of trimethylsilane), dimethylsilacyclopentenes (by trapping with butadiene), and dimethyldisilacyclobutanes (by dimerisation) have been identified in the pyrolysis products of the 1-methylsilaethylene precursor, methylsilacyclobutane, thereby providing strong evidence for an isomerisation of the intermediate silaethylene to dimethylsilylene (Scheme 6). Trapping of the silylene by Me_3SiH is particularly characteristic of silylenes, since it shows no reactivity towards silaolefins. Although the formation of 1,3-dimethyl-1,3-disilacyclobutane could have arisen from the dimerisation of 1-methylsilaethylene, it was shown to be the major product resulting from initial dimerisation of dimethylsilylene followed by rearrangement of tetramethyldisilene.



Scheme 6

Although silaethylenes have generally been prepared by the thermolysis of silacyclobutanes, decomposition of this type of precursor has also been accomplished using a tunable pulsed CO_2 laser. Thus, irradiation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane in the presence of methanol affords Me_3SiOMe via intermediate $Me_2Si{=}CH_2$. Decomposition of 1,1-dimethylsilacyclobutane, using SF_6-sensitisation generates the silaolefin in 80±10% yield.[16] Vacuum flash photlysis of the adducts (1) at 650°C and 0.2 Torr affords silaolefins (2) with hydrogen, deuterium or chlorine substituents on silicon:



(1) (2)

X = H, ^2H or Cl.

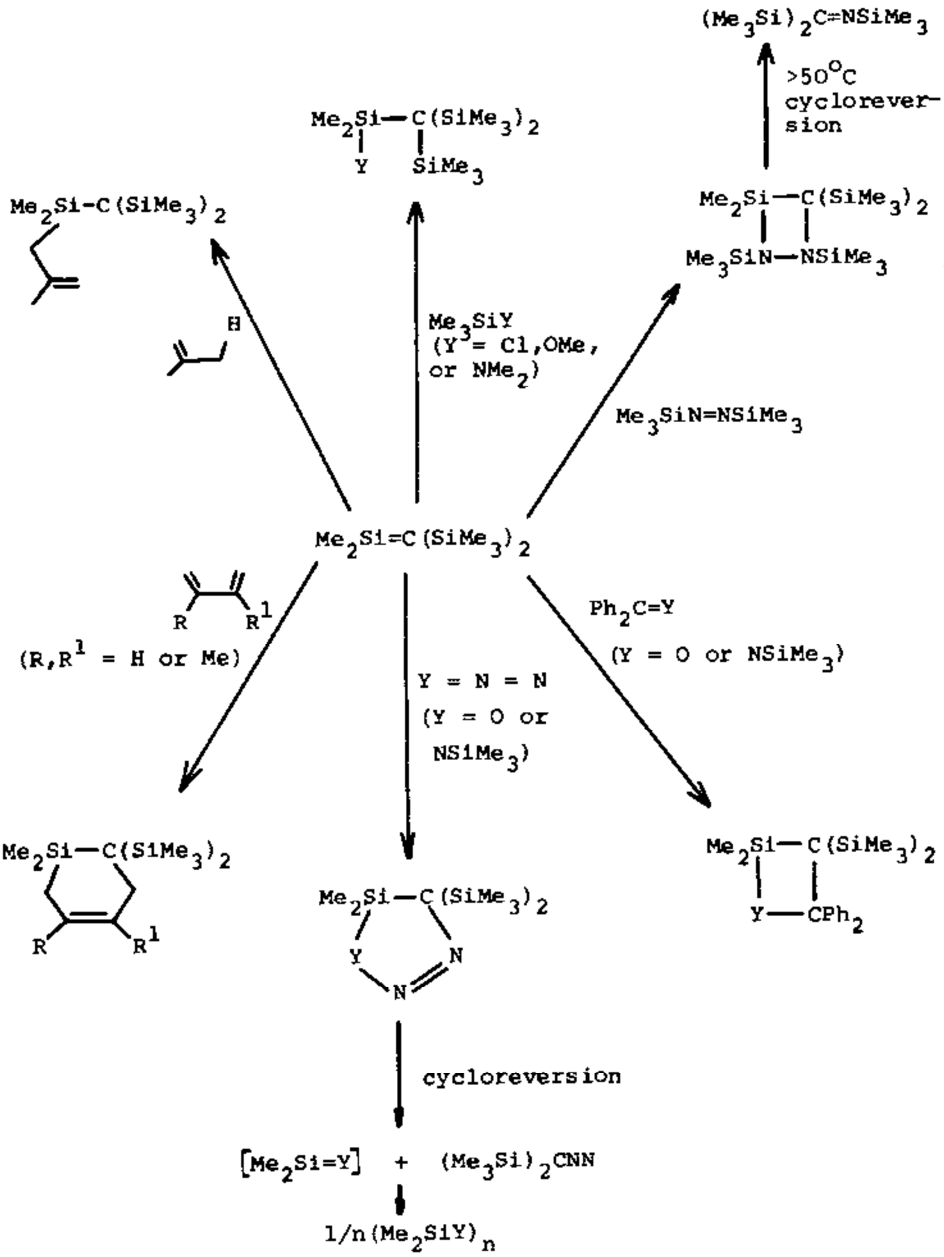
The silaolefins (2) may be subsequently trapped and characterised spectroscopically in argon matrices at 10K.[17] The thermal decomposition of 1,1-dimethylsilacyclobutane in the presence of methanol gives, in addition to the main product Me_3SiOMe, another product (3) resulting from a rapid secondary addition of Me_3SiOMe to the silaolefin in the early stages of the reaction:

$$Me_2Si{=}CH_2 + Me_3SiOMe \longrightarrow \underset{(3)}{Me_3SiCH_2SiMe_2OMe}$$

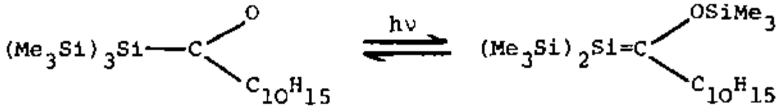
The same adduct is formed when the pyrolysis of 1,1-dimethylsilacyclobutane is carried out with added Me_3SiOMe at 681K, but no reaction other than those producing normal products were observed in the presence of added dimethylether.[18]

Butyllithium and phenyllithium convert the silylated bromides, $(Me_3Si)_2(Me_2XSi)CBr$, at low temperature into the corresponding lithium derivatives, $(Me_3Si)_2(Me_2XSi)CLi$, which in some cases (X = R, RO) are thermostable, whereas in others (X = halide, tosylate, $(PhO)_2PO_2$, PhS) readily eliminate LiX generating the silaethene intermediate, $Me_2Si{=}C(SiMe_3)_2$. In the absence of trapping reagents, the silaethene dimerises to the 1,3-disilacyclobutane, $[Me_2SiC(SiMe_3)_2]_2$, but undergoes a variety of insertion, [2+4]-, [2+3]-, [2+2]-, and [2+2+2]-cycloaddition, and ene-type reactions, as illustrated in Scheme 7. Some of the cycloadducts are thermolabile, undergoing cycloreversion to either the silaethene or to the silaimine, $Me_2Si{=}NSiMe_2$.[19-21]

The first example of a stable solid silaethene has been reported. The compound, 2-adamantyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silaethene (4), is produced by photolysis of a solution of the isomeric acylsilane (5).

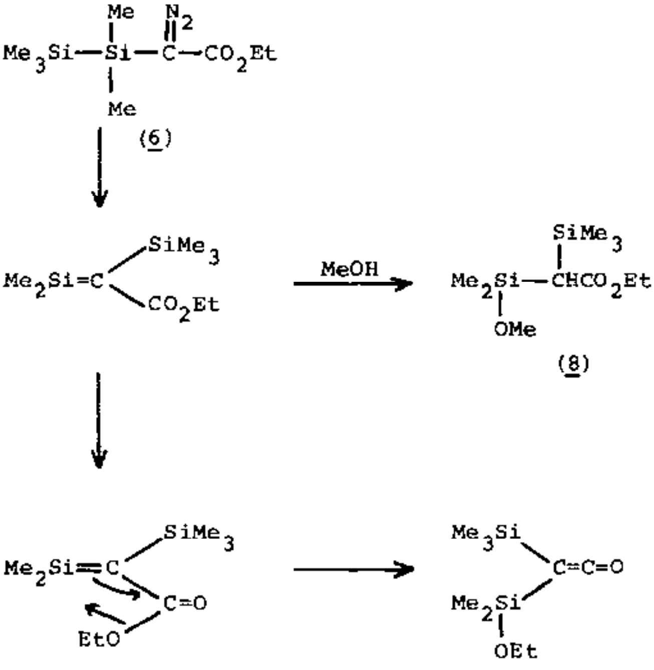

(Me3Si)2C=NSiMe3
>50°C cycloreversion
Me2Si—C(SiMe3)2
Y SiMe3
Me2Si-C(SiMe3)2
H
Me3SiY (Y = Cl,OMe, or NMe2)
Me2Si—C(SiMe3)2
Me3SiN—NSiMe3
Me3SiN=NSiMe3
Me2Si=C(SiMe3)2
R R1
(R,R1 = H or Me)
Y = N = N (Y = O or NSiMe3)
Ph2C=Y (Y = O or NSiMe3)
Me2Si—C(SiMe3)2
R R1
Me2Si—C(SiMe3)2
Y N N
Me2Si—C(SiMe3)2
Y—CPh2
cycloreversion
[Me2Si=Y] + (Me3Si)2CNN
1/n(Me2SiY)n

Scheme 7



(5) (4)

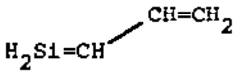
Solid (4), m.p. 95°, is stable at room temperature under argon, but on exposure to air immediately reacts exothermically producing white smoke.[22] Photolysis of ethylpentamethyldisilanyldiazoacetate (6) in THF affords the disilylketene (7) cleanly in quantitative yield. That the process involves an intermediate silaolefin is supported by the formation of alkoxysilanes (8) in high yield when the photolysis is performed in the presence of alcohols:[23]



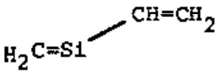
(6) (8) (7)

Ab initio SCF calculations have been carried out on fifteen isomers with the chemical formula C_2SiH_4 including isomers with formal double and triple bonds to silicon, as well as carbenes and silylenes, thus enabling a direct comparison to be made.

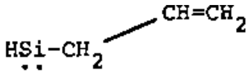
The principal conclusions are: (i) the magnitudes of the energies favouring C=C over Si=C are not huge, (ii) the situation for Si≡C is quite different; R_2C=Si competes favourably with RC≡SiR. The calculations also suggest C=Si=C is also unstable, (iii) methyl substitution stabilises Si=C relative to hydrogen, (iv) vinyl substitution stabilises R_2Si: relative to methyl substitution, (v) cyclic silylenes are relatively less strained than their cyclic isomers, (vi) the energy difference between silylenes and their π-bonded isomers are much smaller than the energy differences between comparable carbenes and their unsaturated isomers.[24] The calculated SCF relative stabilities of 1-silabutadiene (9), 2-silabutadiene (10), and their respective singlet silylene isomers, allylsilylene (11) and methylvinylsilylene (12) are in the order (12) < (10) < (9) < (11).



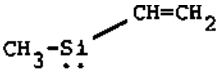
(9)



(10)



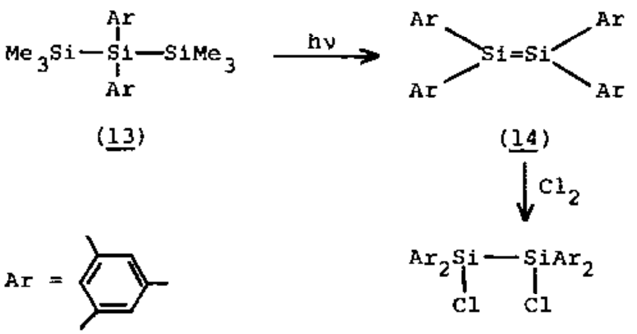
(11)



(12)

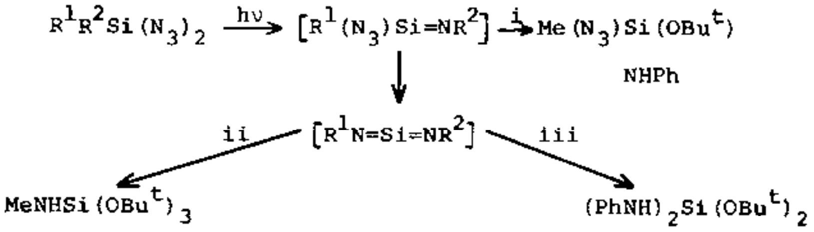
Analysis of energy shifts indicates the occurrence of π-conjugation in the silabutadienes, and the π-charge transfers are predominantly in the direction $Si=C \rightarrow C=C$ in (9) whilst in the sense $C=Si \leftarrow C=C$ in (10). This conjugation strongly stabilises (9) with respect to (11), while conjugation in (10) is balanced by the $\pi_{C=C} \rightarrow 3p_{ZSi}$ delocalisation occurring in (12).[25] The structure and stability of the Si≡C triple bond in silaethyne, HC≡SiH, has been investigated via an analysis of its isomerisation to silylidene, H_2C=Si and through a study of its hydrogenation energy relative to acetylene and silaethylene. It was deduced that silaethyne is rather unstable in a thermodynamic sense. However, whilst SCF calculations predict that this species should rearrange to its more stable isomer with no energy barrier, the introduction of perturbation corrections suggest the existence of a small barrier separating the two isomers.[26]

Photolysis of 2,2-dimesitylhexamethyltrisilane (13) in a hydrocarbon solvent affords tetramesityldisilane (14), the first stable compound containing a Si=Si double bond. The yellow-orange solid is stable at room temperature in the absence of air, but reacts rapidly with Cl_2, EtOH and oxygen. U.v. indicates that the Si=Si π bond is distinctly weaker than the equivalent C=C bond in alkenes.[27]



(13) (14)

Photolysis of diazidosilanes affords highly reactive Si=N double-bonded intermediates which may be trapped by reaction with t-butyl alcohol (Scheme 8).[28]



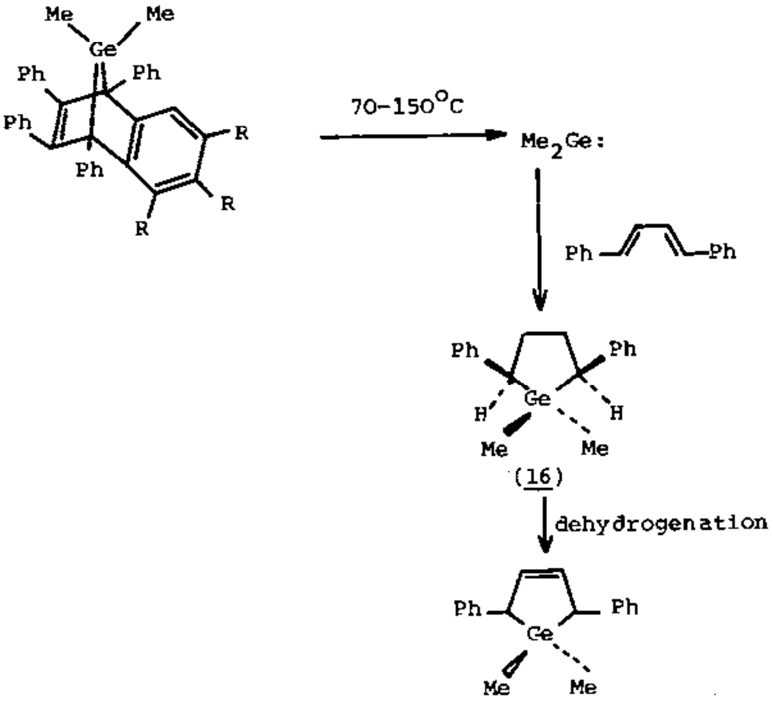
i, $Bu^tOH(R^1 = Me, R^2 = Ph)$; ii, $Bu^tOH(R^1 = R^2 = Ph)$; iii, Bu^tOH $R^1 = R^2 = Me)$.

Scheme 8

Matrix i.r. of argon resonance photolysis products of $SiCl_4$ include the previously identified $SiCl_2$ and $SiCl_3$ radicals, $SiCl_3^+$ and possibly $SiCl_4^+$. Similar studies with $GeCl_4$ and $SnCl_4$ give MCl_2 and MCl_3 (M = Ge, Sn).[29]

4.1.3 Germylenes

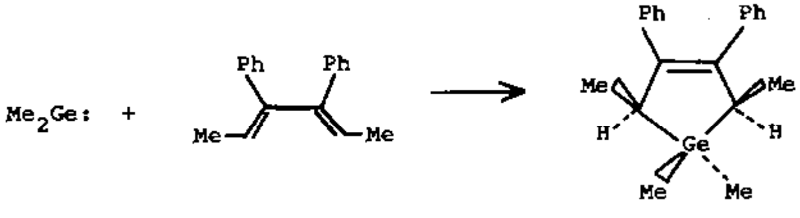
Dimethylgermylene may be smoothly generated by the thermolysis of (15) in the temperature range 70-150°C. Trapping of the germylene using the (E),(E)-isomer of diphenylbutadiene results in the exclusive formation of the cis adduct (16), whose dehydrogenation leads to the formation of (17).



(16)

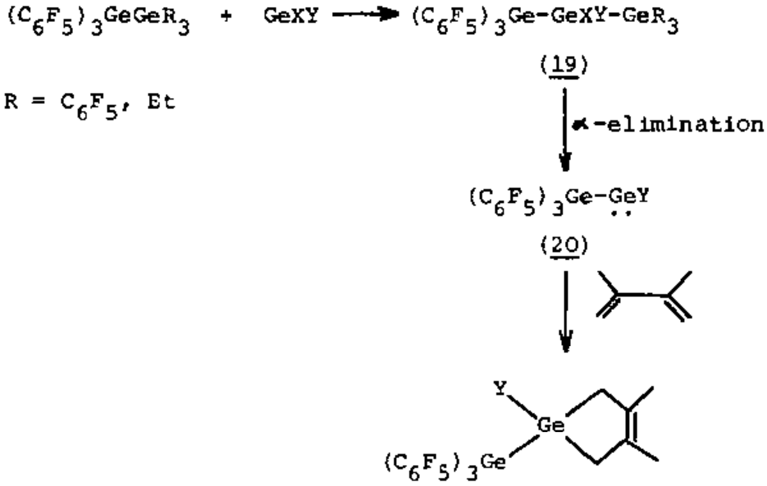
(17)

The adduct (18) is similarly obtained by trapping with 3,4-diphenylhexa-2,5-diene:



(18)

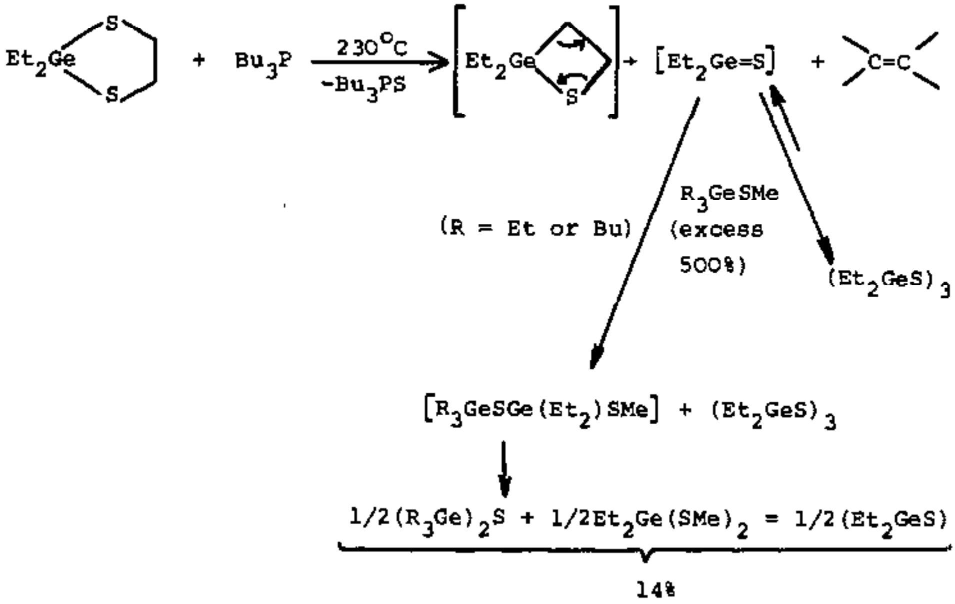
The results indicate that thermally-generated dimethylgermylene reacts as a singlet germylene, in accord with theoretical studies which place the singlet states of germylene and dimethylgermylene 19 and 14 kcals mol^{-1}, respectively, lower in energy than the corresponding triplet states.[30] Halogenogermylenes of the types GeXY (X = F, Cl; Y = F, Ph) insert into the Ge-Ge bond of digermanes, affording the trigermanes (19) which decompose thermally by an α-elimination process giving halogermanes and germylgermylenes (20). The latter may be trapped by 2,3-dimethyl butadiene.[31]



Ab initio calculations with double ζ(+d orbitals) basis sets and full optimisation at the SCF level predict planar structures for both germanone and germathione. Calculated parameters are: $H_2Ge{=}O$ Ge-O = 1.63Å, Ge-H = 1.55Å, HGeH = 112°. $H_2Ge{=}S$ Ge-S = 2.02Å, Ge-H = 1.55Å, HGeH = 110°. The σ and π $Ge\overset{(+)\ (-)}{\text{—}}O$ bond polarities suggest that the bonding is intermediate between π ($H_2Ge{=}O$) and semipolar ($H_2Ge{:}\rightarrow O$) bonding.[32]

Germadithiolanes undergo desulphuration on treatment with trialkylphosphines yielding germathiones *via* intermediate germathietanes (Scheme 9).

The formation of germylenes also observed in these systems arises from the further reduction of the germathiones by trialkylphosphine.[33] Di- or trimercurated geminal polygermanes are generally of low stability and undergo thermal or photochemical decomposition to germynes, germylenes or germanium-



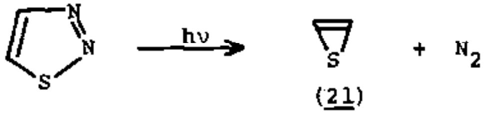
Scheme 9

centred radical species, and also to intermediate $\dot{G}e$-$\dot{G}e$ biradicals, which may be considered as limiting forms of germanium-germanium doubly-bonded species. The intermediates were characterised chemically and spectroscopically.[34]

Reaction of GeO and difluorine in an argon matrix after photolysis using a high pressure mercury lamp affords F_2GeO. Isotopic splittings and force-constant calculations show that the observed fundamentals correspond to a planar structure. The force constant for the Ge=O double bond ($7.43 \times 10^2 N\ m^{-1}$) is as expected (cf. GeO_2 $7.32 \times 10^2 N\ m^{-1}$), but the Ge-F bond is unexpectedly weak ($5.0 \times 10^2 N\ m^{-1}$).[35]

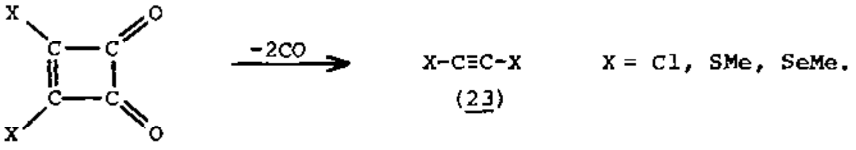
4.2 MOLECULAR CARBON COMPOUNDS

The elusive thiirene molecule (21) has been obtained by photolysis of 1,2,3-thiadiazole:[36]



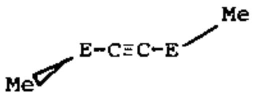
(21)

Pyrolysis of the substituted cyclobutene-1,2-diones (22) leads to the formation of the corresponding disubstitbted acetylenes (23):



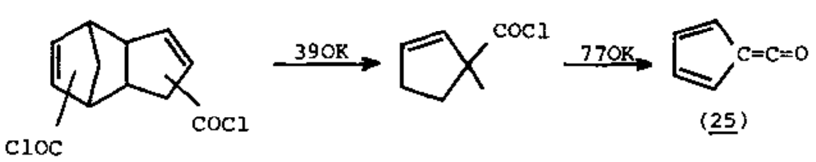
(22) (23)

Spectroscopic data indicate the C_2 conformation (24) in the gas phase for the sulphur and selenium compounds.[37]

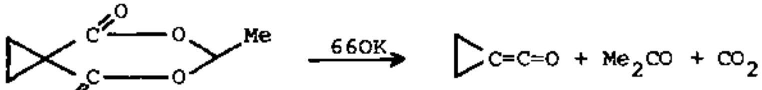


(24)

The alkylketenes, $R_2C{=}C{=}O$ (R = H, Me, Et), chloroketene, $ClHC{=}C{=}O$, and cycloketene, $NC{-}HC{=}C{=}O$, can be generated by elimination of HCl from the appropriate acyl derivative, $R_2CHCOCl$. Dichloroketene, $Cl_2C{=}C{=}O$, is obtained by reduction of CCl_3COBr with zinc metal, whilst monobromoketene, $BrHC{=}C{=}O$, results from pyrolysis of 2-bromocyclobutanone. Similar methods have been employed to generate 'fulvene-ketene' (25) and ethylene ketene (26) from cyclopentene, carbonyl chloride and cyclopropyl spiro-substituted Meldrun's acid:[38]



(25)

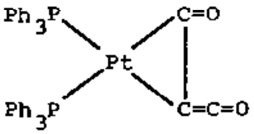


(26)

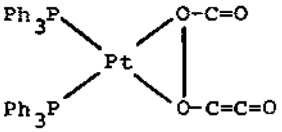
The thermally-induced elimination of HCl from the unsaturated acyl chlorides, $MeRC{=}CHCOCl$ (R = H, Me), gives the vinylketenes, $H_2C{=}CRHC{=}C{=}O$. Iomeric alkylideneketenes, $MeRC{=}C{=}C{=}O$, are produced in the 760K short-path pyrolysis of alkylidenemalonates, but rearrange on prolonged residence time in the heating zone into the thermodynamically more stable vinylketenes.[39] The heavy atom skeleton of methyleneketene, $CH_2{=}C{=}C{=}O$, has been shown by microwave spectroscopy to be bent at the middle carbon atom by approximately 26° from linearity. This non-linearity is confirmed by the identification of *cis* and *trans* forms of monodeuterio methyleneketene, by the lack of intensity alternation in the spectral lines, and by a substantial perpendicular component of the dipole moment.[40]

The thermal decomposition of carbon dioxide has been studied thermodynamically by calculation the equilibrium concentration of the decomposition products as a function of temperature and total pressure. Over a fairly wide range of these two variables, carbon dioxide dissociates into carbon monoxide and oxygen with no precipitation of carbon. At each total pressure, however, there is a critical temperature above which the carbon monoxide disproportionates and the decomposition products are carbon and oxygen.

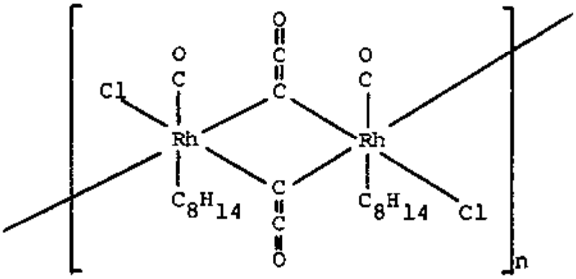
The reactions of carbon suboxide with several platinum and rhodium complexes have been reported. The complexes (27) and (28) are obtained with $[Pt(PPh_3)_2(C_2H_4)]$ and $[Pt(PPh_3)_2O_2]$, respectively. No reaction occurs with either $[Rh(C_8H_{12})Cl]_2$ or $[Rh(C_5H_5)(C_2H_7)_2]$ in dichloromethane, but with $[Rh(PPh_3)Cl]$ the carbonyl complex $[Rh(PPh_3)(CO)Cl]$, PPh_3 and polymeric $(C_2O)_n$ are produced. Reaction with $[Rh(C_8H_{14})_2Cl]_2$ yields the complex $[Rh(C_8H_{14})(CO)C_2O)Cl]$ for which the ketenyl-bridged polymeric structure (29) was proposed.[42]



(27)

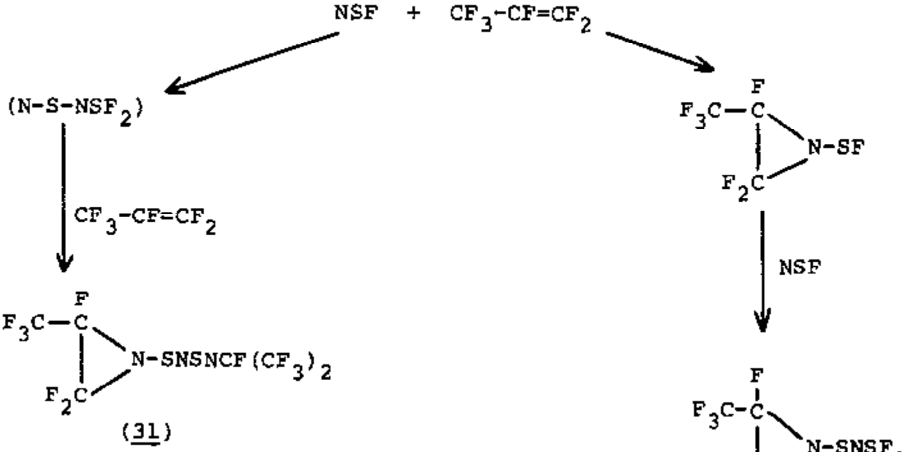


(28)



($\underline{29}$)

Irradiation of thiazyl fluoride and hexafluoropropene affords the sulphenylaziridines ($\underline{30}$) and ($\underline{31}$) in 28 and 12% yields, respectively:[43]



($\underline{31}$)

($\underline{30}$)

The chlorofluorination of nitriles using a 1:1 mixture of $ClF-F_2$ leads to the formation of $\underline{N}$-chloro-$\underline{N}$-fluoroalkylamines according to the process:[44]

$$\begin{tikzcd}
RCN + ClF \arrow[r] & {[RCF{=}NCl]} \arrow[r, "ClF"] \arrow[d, "F_2"] & RCF_2NCl_2 \arrow[dl, "{F_2, -ClF}"] \\
& RCF_2NClF &
\end{tikzcd}$$

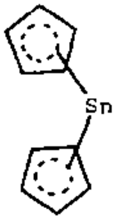
The structural parameters of several molecules have been reported from either microwave or electron diffraction studies. Electron diffraction data for bromotrichloromethane,[45] and monofluoro- and pentafluoroethane[46] are not unusual. Cis-1,3-dichloro-1-propene has a conformation in which the chlorine atom of the methyl group and the C=C double bond are mutually gauche.[47] 2,3-Dichloro-1-propene comprises a mixture of two conformers with the chlorine atoms anti (torsion angle $\phi=0^\circ$) or gauche ($\phi=109^\circ$) to each other, the anti form being the more stable. The composition (mole fraction) of the vapour changed on increase in temperature according to 0.55 (24°C), 0.49 (90°C) and 0.41 (273°C), corresponding to an energy difference of 0.7(3) kcal mol^{-1} between the two forms.[48] 1-Chloro-2-methylpropane has an unsymmetrical conformation.[49] Two conformers also exist for dichloroacetyl chloride in which the hydrogen and oxygen atoms are syn and gauche to each other. Temperature/composition studies indicate almost equal energy for both forms with an almost invariant composition (0.73 syn isomer).[50] Carbonyl bromide has expected dimensions with C=O = 1.178(9)Å and C-Br = 1.923(5)Å.[51] A pyramidal configuration at nitrogen has been found for both tetramethylurea (C=O 1.240(5)Å) and tetramethylthiourea (C=S 1.676(3)Å).[52] Thioacetamide exhibits a conformation in which one C1H bond eclipses the C=S double bond, (C=S 1.647(3)Å).[53] A unique structure could not be determined for 1,4-pentadiyne by microwave spectroscopy. However, analysis of moments of inertia indicates that the bond distances are close to typical values found in other related compounds. The data are consistent with either the central CCC angle being close to the tetrahedral value with the acetylene groups pushed away from linearity by ca. 3-4°, or opening of the central CCC angle to about 113° with linear acetylene groups. A range of structures between these two extremes is also possible.[54] Normal coordinate analysis of the possible rotamers favours a planar trans structure for methylvinylether.[55]

4.3 BIVALENT COMPOUNDS OF GERMANIUM, TIN AND LEAD

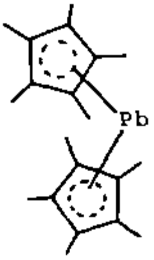
4.3.1 Bonds to Carbon

The crystal structures of both bis(cyclopentadienyl)tin(II) (32) and bis(pentamethylcyclopentadienyl)lead(II) (33) (a deep red solid from the organolithium reagent and lead(II) chloride in

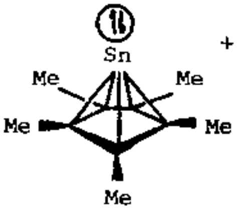
THF), have been reported. Both are monomeric in the solid with pentahapto cyclopentadienyl rings, in contrast to the chain structure determined for bis(cyclopentadienyl)lead(II). The ring centroid-metal-ring centroid for each compound is larger than expected. The values for the two crystallographically independent molecules of bis(cyclopentadienyl)tin(II) (148.0° and 143.7°) are marginally greater than in bis(pentamethyl)tin(II), suggesting strongly that electronic rather than steric factors control the value of this angle. The value of ca. 125° quoted for bis(cyclopentadienyl)tin(II) iin the rather old vapour phase electron diffraction study is probably now in need of a redetermination. The angle in bis(pentamethylcyclopentadienyl)-lead(II) is even larger (151°). Although the metal-carbon bond distances in both compounds vary substantially [$(C_5H_5)_2Sn$ 2.56-2.85Å; $(Me_5C_5)_2Pb$ 2.69-2.90Å], the bonding is nevertheless best regarded as pentahapto.[56] Monocyclopentadienyltin(II) derivatives of the type $(C_5R_5)SnX$ (R = H or Me) assume both covalent and ionic structures depending upon the nature of X. When the group X is poorly nucleophilic (e.g. BF_4^-, $AlCl_4^-$, $CF_3SO_3^-$), the compounds are ionic and contain the pentagonal pyramidal cation (34). With more nucleophilic groups, covalent compounds such as $(C_5Me_5)SnO_2CR$ (R = CF_3, CCl_3) are obtained. This type of compound,is, however, sometimes unstable with respect to disproportionation to bis(pentamethylcyclopentadienyl)-lead(II) and the tin(II) carboxylate (e.g. R = H, Ph, CH_2Cl).[57] The products of the reaction of bis(cyclopentadienyl)tin(II) with $[W(C_5H_5)(CO)_3H]$ in chlorinated hydrocarbon solvent has been shown to be the complex, $ClSn[W(C_5H_5)(CO)_3]$, and not $Sn[W(C_5H_5)(CO)_3]_2$ as proposed previously.[58,59] The ionic compounds $R^+SnPh_3^-$ (R = Me_4N, $(Ph_3P)_2N$, Na(15-crown-5) or K(18-crown-6)), containing the triphenyltin(II) anion, have been prepared from the alkalimetal



(32)



(33)

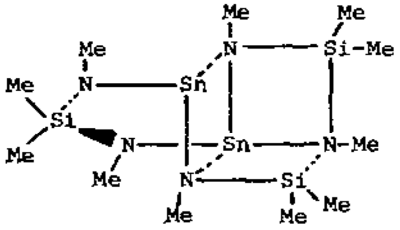


(34)

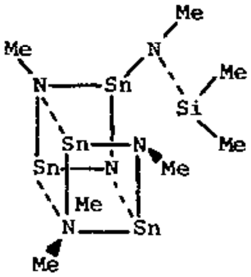
Ph_3SnM derivatives by reaction in liquid ammonia. The products are yellow crystalline solids, which are soluble in weakly basic solvents. Nmr and vibrational spectra indicate a C_{3v} structure for the Ph_3Sn^- anion.[60]

4.3.2 Bonds to Nitrogen, Phosphorus and Arsenic

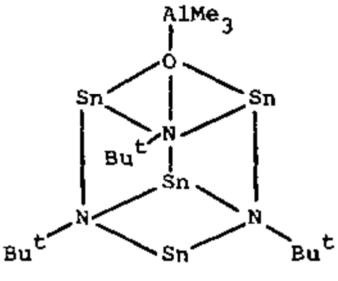
Reaction of tin(II) chloride with the lithium amide $(LiNMe)_2SiMe_2$ affords the cage compound $(Me_2Si)_3(NMe)_5Sn_2$ together with polymeric $(SnNMe)_n$. The structure of the former compound is best regarded as a four-membered $[Sn_2N_2]$ ring bridged in the [1,3]-positions by a $[Me_2Si\text{-}NMe\text{-}SiMe_2]$ group and by a $[NMe\text{-}SiMe_2\text{-}NMe]$ group across the [2,4]-positions as illustrated in (35).



(35)



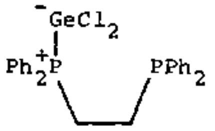
(36)



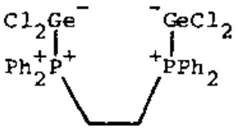
(37)

The same compound also results from the reaction of $Me_2Si(NBu^t)_2Sn$ and $Me_2Si(NMeH)_2$, a reaction which also affords another cage compound, $(Me_2Si)(NMe)_5Sn_4$, as a byproduct, when the reaction is carried out without solvent. The structure of this compound resembles a 'basketane', in which four tetrahedrally orientated tin and four nitrogen atoms form a cube, one edge of which is enlarged by the $[Me_2Si-NMe]$ bridge as shown in (<u>36</u>). N.m.r. studies of (<u>36</u>) indicate the occurrence of valence fluctuations at ordinary temperatures in organic solvents.[61] The structure of the trimethylaluminium adduct of the $[(Bu^tN)_3OSn_4]$ cage (<u>37</u>) has been confirmed by crystallographic studies.[62]

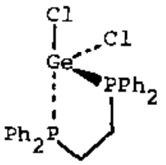
Depending on the molar ratio of the reactants, both 1:1 and 1:2 adducts (<u>38</u>) and (<u>39</u>), respectively, can be obtained from the interaction of $GeCl_2$-dioxan with 1,2-bis(diphenylphosphino)ethane (dppe). ^{31}P n.m.r. data indicates a rapid equilibration of germanium between the two phosphorus centres in the 1:1 adduct. This observation is not in fact surprising in view of the solid-state structure of the adduct shown in (<u>40</u>). Although the germanium atom is much closer to one of the phosphorus atoms (Ge-P = 2.51Å), the second phosphorus is only 3.34Å away. The overall geometry of the adduct can be described as a pseudo-trigonal bipyramidal in which the axial sites are occupied by a chlorine and the long Ge-P interaction, and the equatorial sites by the second chlorine, the shorter Ge-P bond, and a stereochemically active lone pair.[63] In nitromethane, tin(II) and lead(II) hexafluoroantimonates), $M(SbF_6)_2$ (M = Sn, Pb) forms 1:1 complexes with the di- and polyphosphines $Ph_2P{\frown}PPh_2$, $PhP{\frown}PPh_{2\ 2}$, $MeC(CH_2PPh_2)_3$, $[Ph_2PCH_2CH_2]_2PCH_2CH_2\overset{+}{P}HPh_2$, $Ph_2P[(CH_2)_2PPh]_2(CH_2)_2\overset{+}{P}HPh_2$, $P[{\frown}PPh_2]_3$ and $Ph_2P[{\frown}PPh_2]_2(CH_2)_2PPh_2$. The phosphonium ligands are formed <u>in situ</u>. Slow inter- and intramolecular exchange is observed for all the complexes except for the last two ligands, which may be involved in rapid intramolecular exchange. In most cases, the ligands were shown to function with maximum denticity. 1:2 and 1:3 complexes have been observed with triphenylphosphine oxide



(<u>38</u>)



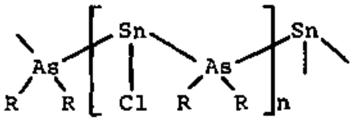
(<u>39</u>)



(<u>40</u>)

and isolable 1:1 complexes with $Ph_2(O)P{\frown}P(O)Ph_2$, $PhP(O)[{\frown}P(O)Ph_2]_2$ and $(O)P[{\frown}P(O)Ph_2]_3$.[64]

The associated structure (41) has been proposed for the ylidic arsenic-tin complex, $Bu^t_2\overset{+}{As}-\overset{-}{Sn}Cl_2$, (from tin(II) chloride and Bu^t_3As or $Bu^t_2(Me_3Si)As$), with bridging arsino groups and terminal chlorines.[65]



(R = Bu^t)

(41)

4.3.3 Bonds to Oxygen

The two ternary tin(II) oxides $M_2Sn_2O_3$ (M = K, Cs) have been prepared by heating mixtures of tin(II) oxide with either $KO_{0.48}$ or $CsO_{0.46}$ under argon using Al_2O_3 cylinders at 550°(K) or 480° (Cs). The compounds are yellow in colour, and have layer structures with pyramidal $[SnO_3]$ units.[66,67] Bis(trimethylsiloxy)-germanium(II) and -lead(II) have been obtained via the routes:

$$GeCl_2.dioxan + 2NaOSiMe_3 \rightarrow Ge(OSiMe_3)_2$$

$$PbO + 2Me_3SiOH \rightarrow Pb(OSiMe_3)_2$$

Both are fairly soluble in all inert organic solvents. The lead compound is dimeric in benzene.[68]

The structures of four lead(II) carboxylates have been reported. All, $Pb(O_2CC_6H_4NH_2\text{-}\underline{p})_2$,[69] $[Pb(O_2CC_6H_4OH\text{-}\underline{p})_2.H_2O]H_2O$,[70] $Pb(O_2CC_6H_4NH_2\text{-}\underline{p})(NO_3)$,[71] and $Pb(O_2CC_6H_4NH_2\text{-}\underline{m})(NO_3)$,[72] are polymeric with coordination numbers varying from 6 to 9. In $Pb(O_2CC_6H_4NH_2\text{-}\underline{p})_2$, both carboxylate groups chelate the metal although one also acts as a bridging group linking adjacent metal atoms into a one-dimensional chain structure. The coordination polyhedron is quite distorted, and is closest to a trigonal prism.[69] Both carboxylate groups in $[Pb(O_2CC_6H_4OH\text{-}\underline{p})_2.H_2O]H_2O$ function as both chelating and bridging ligands, although one employs both oxygen atoms to bridge adjacent lead atoms, whereas the other uses only one. The second oxygen atom of this carboxylate group forms hydrogen bonds with the two water molecules. The hydroxy function of the aryl group also participates in the hydrogen-bonding network to form a three-dimensional network, and does not coordinate to lead.[70] Adjacent lead atoms in the two lead(II) carboxylate nitrates are bridged by both types of ligand. The lead atoms in the carboxylato-bridged chains in $Pb(O_2CC_6H_4NH_2\text{-}\underline{p})(NO_3)$ are connected laterally by the amino group to a lead atom in an adjacent chain to form a layer structure. The layers are further bonded together by the nitrate groups and by hydrogen-bonding between nitrato oxygen atoms and the amino group. The coordination number of lead is eight.[71] In the other lead(II) carboxylate nitrate, $Pb(O_2CC_6H_4NH_2\text{-}\underline{m})(NO_3)$, the coordination number is nine, the lead atom being coordinated by four oxygen atoms from three carboxylate groups, four oxygen atoms from two nitrate groups, and the amino group nitrogen atom. Again, adjacent lead atoms are bridged by carboxylate groups forming a two-dimensional layer structure, which is interconnected by a network of hydrogen bonds.[72] In lead(II) bis(dihydrogenphosphate), the lead atom is coordinated by seven oxygen atoms from seven different dihydrogenphosphate groups. The coordination polyhedron is irregular with five short and two longer lead-oxygen distances. Hydrogen-bonding links the infinite chains into a three-dimensional polymeric network.[73]

The structure of the mixed-valence tin carboxylate $[Sn^{II}Sn^{IV}O(O_2CCF_3)_4]_2.C_6H_6$ comprises independent centrosymmetric $[Sn^{II}Sn^{IV}O(O_2CCF_3)_4]_2$ units, in which two symmetry-related tin(IV) atoms are bridged by two triply-bridging oxygen atoms forming a central $[Sn_2^{IV}O_2]$ four-membered ring. Octahedral coordination at tin(IV) is completed by trifluoroacetate groups which bridge both tin(II) and tin(IV) atoms. The tin(II) atoms have a distorted square-based pyramidal geometry with the apical site occupied by a triply-bridging oxygen atom, and the basal positions by oxygen atoms from the bridging carboxylate groups. The remaining apical site is presumably occupied by the lone pair.[74]

Hydrolytic reactions of lead(II) ions have been studied calorimetrically at 25° in an aqueous solution and dioxan-water mixtures (0.1 and 0.2 mole fraction dioxan) containing 3 mol dm^{-3} $LiClO_4$ as a constant ionic medium. Values of enthalpies and entropies for the formation of the complexes $Pb_2(OH)_3^{3+}$, $Pb_4(OH)_4^{4+}$, $Pb_3(OH)_4^{2+}$ and $Pb_6(OH)_8^{4+}$ in aqueous solution.[75] A solvent deuterium isotope effect on the hydrolysis of lead(II) has also been reported.[76]

Complexes of tin(II) chloride, perchlorate and isothiocyanate with 15-crown-5 have been described. The 2:1 complex with tin(II) perchlorate, $(15\text{-crown-}5)_2Sn(ClO_4)_2$, exhibits one of the highest Mössbauer isomer shifts yet recorded, and may be regarded as a "bare" tin(II) cation sandwiched by the two polyether molecules. The two other complexes have stoichiometry $(15\text{-crown-}5)_2[SnX_2]_2$ (X = Cl, SCN), and contain tin in two different chemical environments, one of which is similar to that in the perchlorate, and the other corresponding to a $[SnX_3^-]$ anion.[77]

4.3.4 Bonds to Sulphur

The structure of tin(II) sulphide has been determined, and comprises layers parallel to the [100] plane. Each tin atom is surrounded by six sulphur atoms forming a distorted octahedron with three short (2.622(1), 2.662(2), 2.662(2)Å) and three longer (3.385, 3.287, 3.287Å) tin-sulphur interactions. The layers are linked by weak Sn-S---S and Sn---Sn interactions.[78]

The solubilized thiolate-ligand, 2-(morpholin-4-yl)ethanethiolate (mes) and its ammonium conjugated acid (Hmes) form the crystalline complexes, $Pb_2(Hmes)_3(NO_3)_4$, $Pb(mes)_2$, $Pb(mes)(NO_3)$, $Pb(mes)(O_2CCH_3)$ and $Pb(mes)(O_2CCF_3)$, which are soluble in aqueous media. Crystals of the complex $Pb(mes)(NO_3)$ contain chains of alternating lead and bridging thiolato-sulphur atoms (Pb-S = 2.646(4), 2.795(4)Å), with the lead also coordinated by the tertiary nitrogen atom (Pb-N = 2.61(1)Å). The nitrate ions weakly bridge lead atoms along the chain (Pb-O = 2.69(2), 2.88(2), 2.98(2), 3.03(2)Å).[79]

4.3.5 Bonds to Halogen

Mössbauer data have been recorded for the three known phases of tin(II) fluoride. In the monoclinic α-phase, the two structurally different tin environments have Mössbauer parameters which are undistinguishable from one another. A discontinuity in the temperature dependence of the Mössbauer parameters occurs at the $\alpha \rightarrow \gamma$ phase transition at ca. 425K. The high temperature γ-phase exhibits a very large asymmetry in line intensity of the quadrupole split doublet. No such discontinuity is observed at the $\gamma \rightleftharpoons \beta$ second-order phase transition; instead progressive changes occur.[80] Tin-119 Mössbauer studies of a single crystal of α-SnF_2 and partially oriented α-$PbSnF_4$ shows that the sign of eQV_{zz} in both is positive.[81]

The nature of solutions of tin(II) halides in various donor solvents has been investigated by tin-119 n.m.r. All spectra comprise single resonances, the chemical shifts of which are markedly solvent, concentration and temperature dependent in most cases. The chemical shift values increase in the order $SnF_2 < SnCl_2 < SnBr_2 < SnI_2$, the same order observed previously for heats of solution and adduct stabilities. Significant solution conductivity was found for SnI_2 in DMSO and HMPA. Chemical shift data were interpreted in terms of adduct formation and ionisation processes.[82]

The correct composition of "basic" tin(II) chloride has been shown to be $Sn_{21}Cl_{16}(OH)_4O_6$, the structure of which is characterised by two different nets, M1 = ${}^{2}_{\infty}[Sn_5(OH)_6Cl_6]^{2-}$ and M2 = ${}^{2}_{\infty}[Sn_8O_3(OH)_4Cl_5]^{3+}$, stacked along [001] with intercalated chloride ions. M1 and M2 comprise condensed $[Sn(OH)_3]$ and $[Sn(OH)_2Cl_2]$ or $[Sn(OH)_3]$ and $[Sn(OH)_2Cl]$-type groups, respectively. Additionally, M2 contains the new cubane group $[Sn_4O_3(OH)]$, which is linked by $[Sn(OH)_3]$ and SnCl fragments, All but one of the tin atoms exhibit typical pseudo-trigonal bipyramidal coordination.[83] DTA and XRD studies of the $SnBr_2$-SnI_2 system indicate the presence of SnBrI besides the two symmetrical halides.[84] Matrix isolation studies show that tin(II) halides and alkalimetal halides form ion pairs in the matrices. The species SnF_3^-, $SnClF_2^-$, $SnCl_2F^-$ and (tentatively) SnF_4^{2-} were identified.[85]

The structure of molten lead(II) chloride has been reexamined by XRD. In the melt, each lead atom is surrounded by three chlorines at an average distance of 2.63 as well as four at 3.14Å. The lead-lead interaction is within 10Å and is similar to the same distance in the face-centred-cubic arrangement.[86] Matrix isolation studies of lead(II) fluoride and caesium fluoride indicate the formation of $Cs^+PbF_3^-$ ion pairs. The force constant for the C_{3v} PbF_3^- anion (1.83 mdyn $Å^{-1}$) is appreciably lower than for other lead fluoride species.[87] Activities, activity coefficients and partial molar free energies have been calculated for each component in the systems $PbBr_2$-MBr (M = K, Rb, Cs). The systems contain complex ions, most probably mixtures of $PbBr_4^{2-}$, $PbBr_6^{4-}$ and some $PbBr_3^-$.[88]

4.4 TETRAVALENT COMPOUNDS OF SILICON, GERMANIUM, TIN AND LEAD

4.4.1 General

Heats of formation and dissociation of the methylsilanes and chlorosilanes and radicals derived therefrom have been determined, leading to calculated values for bond dissociation energies in these molecules as well as the Si-Si bond dissociation energy in the disilanes X_3SiSiX_3 (X = H, Me, Cl) (Tables 1-4).[89]

4.4.2 Bonds to Hydrogen

The structures of several silyl derivatives have been reported, including the cis and skew isomers of methylvinylsilane (barriers to internal rotation = 1866±39 cal mol^{-1} (cis) and 1698±22 cal mol^{-1} (skew)),[90] silacyclopentane (Si-H (assumed) = 1.478Å, Si-C = 1.891(4)Å, CSiC = 96.4(6)°),[91] silylchloroacetylene, $H_3SiC{\equiv}CCl$, (linear skeleton, Si-C = 1.812(5)Å, C≡C = 1.234(6)Å, Si-H = 1.488(12)Å, C-Cl = 1.620(5)Å),[92] and silylmethylacetylene (linear skeleton, Si-C = 1.802(4)Å, C≡C = 1.219(4)Å).[93] Microwave and i.r. data for the (deuterio)germyl halides, GeD_3X and $GeHD_2X$ (X = F, Cl, Br, I) have been recorded, affording improved structural data for these molecules. Values of the HGeX angles show a correlation with the Ge-H stretching frequency, but no correlation with the Ge-H bond distance was apparent.[94]

Substitution at both silicon and germanium centres of H_3SiGeH_3 can occur depending on the reagent. With tin(IV) chloride substitution at silicon occurs, but iodine reacts at the germanium centre:[95]

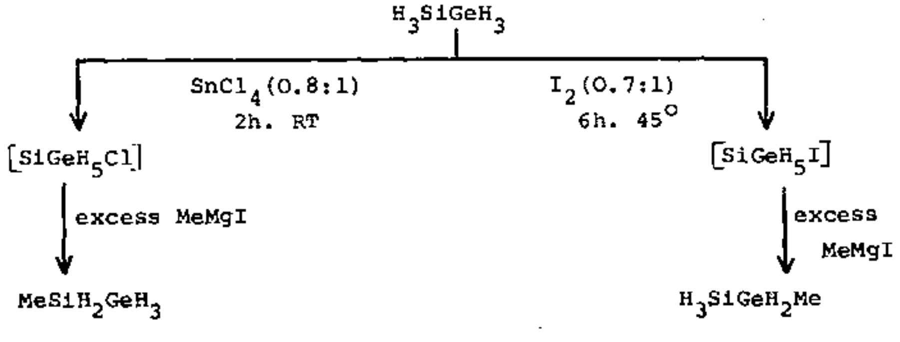


Table 1. Bond-dissociation energies D(R-X) in monosilanes.

radical R	X = H calculated D(R-H)/kJ mol^{-1}	X = H experimental D(R-H)/kJ mol^{-1}	X = Me calculated D(R-Me)/kJ mol^{-1}	X = Me experimental D(R-Me)/kJ mol^{-1}	X = Cl calculated D(R-Cl)/kJ mol^{-1}	X = Cl experimental D(R-Cl)/kJ mol^{-1}
SiH_3	388.7	398.0	385.4	377.3	485.5	527.3
		397.0		355.6		
		366.1				
SiH_2Cl	385.2		379.9		463.1	
$SiHCl_2$	386.6		375.1		438.0	
$SiCl_3$	384.7	382.0	371.7	377.0	415.0	466.0
		383.7		358.1		435.1
SiH_2Me	384.3	376.6	373.0		479.1	
		384.9				
$SiHMe_2$	377.7	376.0	360.6	320.1	468.6	
		383.7				
$SiMe_3$	377.1	376±11	355.0	355±6	462.8	477.0
				384.0		485.3
$SiMe_2Cl$	376.1		353.7		442.3	
$SiMeCl_2$	376.7		355.8		426.6	
$SiHMeCl$	379.9		364.5		451.7	

Table 2. Bond-dissociation energies D(M-X) in silicon radicals

group M	X = H		X = Me		X = Cl	
	calculated D(M-H)/ kJ mol^{-1}	experimental D(M-H)/ kJ mol^{-1}	calculated D(M-Me)/ kJ mol^{-1}	experimental D(M-Me)/ kJ mol^{-1}	calculated D(M-Cl)/ kJ mol^{-1}	experimental D(M-Cl)/ kJ mol^{-1}
SiH_2	260.7	246.0	261.7		360.9	
		249.0				
SiHCl	249.9		250.3		326.5	
$SiCl_2$	216.4		214.8		269.7	272.0
SiHMe	242.4	288.7	237.6		341.6	
$SiMe_2$	235.3	309.6	218.8	288.0	327.9	
SiMeCl	232.1		222.0		307.2	

Table 3. Bond-dissociation energies D(YSi-X) in SiXY molecules.

group YSi	X = H		X = Me		X = Cl	
	calculated D(YSi-H)/ kJ mol^{-1}	experimental D(YSi-H)/ kJ mol^{-1}	calculated D(YSi-Me)/ kJ mol^{-1}	experimental D(YSi-Me)/ kJ mol^{-1}	calculated D(YSi-Cl)/ kJ mol^{-1}	experimental D(YSi-Cl)/ kJ mol^{-1}
SiH	346.5	353.0	365.8		468.7	
SiCl	374.2		392.4		484.3	484.0
SiMe	390.3		393.0		511.2	

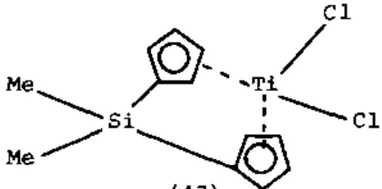
Table 4. Si-Si Bond-dissociation energies.

molecule	calculated Si-Si bond-dissociation energy/kJ mol^{-1}	experimental Si-Si bond-dissociation energy/kJ mol^{-1}
$Me_3Si-SiMe_3$	336.1	337 280.3
$H_3Si-SiH_3$	330.9	338.9±16.7
$Cl_3Si-SiCl_3$	326.3	322.2

The reaction of the silyl and germyl molecules MH_3Q (M = Si, Ge; Q = H, F, Cl, Br, I) with $[HPt(PEt_3)_3]^+BPh_4^-$ affords products which depend on M and Q. When M = Ge and Q = F, Cl or I, triphosphino cations of 6-coordinate platinum(II) are identified as the initial products at 213K by n.m.r. These decompose on warming eliminating $Et_3PH^+BPh_4^-$ and forming trans-$[PtH(PEt_3)_2(MH_2Q)]$, the only product identified when Q = Br and M = Ge or Si. With SiH_4 or SiH_3Cl, the only products detected were the $[Pt(PEt_3)_3SiH_2Cl]^+$ cations. No reaction occurred with GeH_4 or SiH_3F, and none of the products was isolable.[96] The reactions of the iridium complex, trans-$[Ir(PEt_3)_2(CO)I]$ (42) with several silyl derivatives have also been studied. With $(H_3Si)_2Y$ (Y = O, S, Se) in benzene, both $[Ir(CO)HI(PEt_3)_2(SiH_2YSiH_3)]$ or $[\{Ir(CO)HI(PEt_3)_2(SiH_2)\}_2Y]$ are formed, although when Y = O, the formation of the former species is difficult to detect. Reaction of (42) with $P(SiH_3)_3$ leads to the formation of $[Ir(CO)HI(PEt_3)_2\{SiH_2P(SiH_3)_2\}]$, $[\{Ir(CO)HI(PEt_3)_2(SiH_2)\}_2PSiH_3]$, or $[\{Ir(CO)HI(PEt_3)_2(SiH_2)\}_3P]$, depending on the proportions of the reactants taken. Reaction between (42) and $N(SiH_3)_3$ gives $[Ir(CO)HI(PEt_3)_2\{SiH_2N(SiH_3)_2\}]$ and $[\{Ir(CO)HI(PEt_3)_2(SiH_2)\}_2NSiH_3]$, but no tris(iridiosilyl)amine was detected. Structures in which the two phosphine ligands, the iodo- and carbonyl ligands, and the hydride and silyl ligands are mutually trans were proposed for the products.[97] Cleavage of the E-E bonds in ligands of the types R_2EER_2' and $R_2EE'R'$ (R,R' = CH_3, CF_3; E = P, As; E' = S, Se, Te) coordinated to $M(CO)_5$ (M = Cr, Mo) fragments by trimethyltin hydride has been studied by ^1H and ^{19}F n.m.r. In comparison to the analogous reactions with the free ligands, the rate of reaction is considerably reduced, whereas the direction of cleavage is generally retained.[98]

4.4.3 Bonds to Carbon

An electron diffraction study of $(Me_3Si)_3CH$ shows that the SiCSi bond angles are unusually large (117.2(4)°), implying an unusually high degree of p-character in the orbital used to form the C-H bond. A slight lengthening of the Me_3Si-C (1.887Å) bond (cf. Me-Si 1.873Å) is also observed. The high acidity associated with a C-H bond of high p-character can be most simply attributed to delocalisation of the lone pair of the conjugate carbanion into the d-orbitals of the silicon atoms, and the inherent effect may be substantially enhanced by the geometry whereby the near planarity of the three silicon and central carbon atoms means that very little movement of atoms will be needed to give the maximum conjugative stabilisation on going to the carbanion.[99] Molecules of bis di-tert- butyl(tert-butylamino)silyl acetylene has a crystallographic centre of symmetry, with the two (NHBu)$SiBu_2$ substituents attached to the central C C bond.[100] In $Me_2Si(C_5H_5)_2TiCl_2$, the titanium atom is sandwiched between the two cyclopentadienyl rings as in (43).[101] The vapour phase structure



(43)

of tetraphenyltin has been investigated by electron diffraction at 310°. An S_4 symmetry model gave a better fit to the data than an "open" D_{2d} model with Sn-C = 2.160(7)Å. The geometry of the phenyl rings appears to be almost unaffected by bonding to tin.[102]

Tetrakis(trifluoromethyl)germanium and -tin are obtained in reasonable yields (43% and 66%, respectively) by treatment of GeI_4 or $SnBr_4$ with $(CF_3)_2Cd$.glyme.[103] Vibrational spectra, normal coordinate analysis, and electron diffraction structural data have been reported for $Sn(CF_3)_4$. The molecule has T_d symmetry with C-F = 1.338(2)Å, Sn-C = 2.201(5)Å and FCF = 108.2(2)°. Compared with $SnMe_4$, the Sn-C bonds are weakened and lengthened by 5.8(6)pm.[104]

The cleavage of phenyl groups from Ph_4Sn or $PhSnBu_3$ by $[^{18}F]F_2$ in $CFCl_3$ or CCl_4 at 178° is a rapid synthesis of $[^{18}F]$fluorobenzene.[105] Phosphorus(V) fluoride cleaves methyl groups from $CH_2(SnMe_3)_2$:[106]

$$CH_2(SnMe_3)_2 \ + \ 2PF_5 \ \rightarrow \ 2MePF_4 \ + \ CH_2(SnMe_2F)_2$$

Phenyl groups are cleaved from tetraphenyltin and -lead by $MeSO_2NBrCl$:[107]

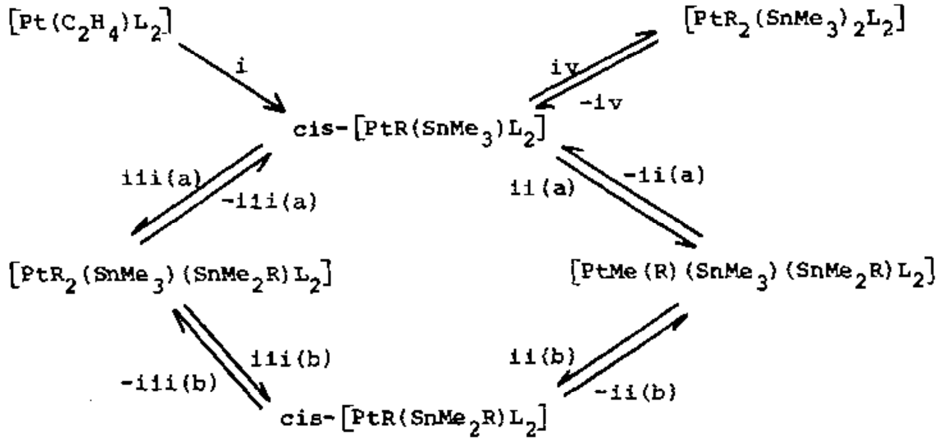
$$MPh_4 \ + \ MeSO_2NBrCl \ \rightarrow \ MeSO_2N(Cl)MPh_3$$

M = Sn, Pb.

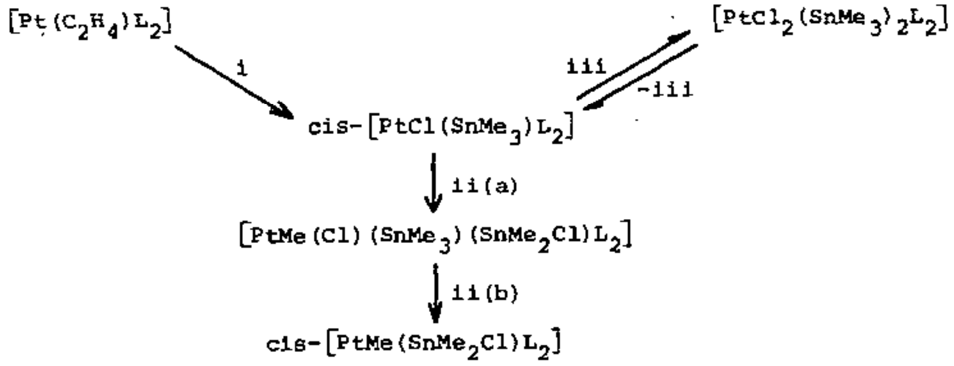
Mechanisms involving platinum(IV) intermediates have been proposed for the homogeneous catalysis by platinum(II) complexes of the redistribution reactions:

$$2Me_3SnR \overset{Pt\,(II)}{\rightleftharpoons} Me_4Sn \; + \; SnMe_2R_2 \qquad R = aryl$$

(Scheme 10), and for the formation of *cis*-$[PtMe(SnMe_2Cl)(PPh_3)_2]$ from $[Pt(C_2H_4)(PPh_3)_2]$ and Me_3SnCl (Scheme 11).[108]



Scheme 10 (L = PPh_3) i, $+SnMe_3R$, $-C_2H_4$, ii, (a) $+SnMe_3R$, (b) $-SnMe_4$, iii, (a) $+SnMe_2R_2$, (b) $-SnMe_3R$, iv, $+SnMe_3R$.



Scheme 11 (L = PPh_3) i, $+SnMe_3Cl$, $-C_2H_4$, ii, (a) $+SnMe_3Cl$, (b) $-SnMe_3Cl$, iii, $+SnMe_3Cl$.

Arylmethylstannanes, $Me_{4-n}R_nSn$ (R = aryl; n = 1-3) react with $[Pt(C_2H_4)(PPh_3)_2]$ (*44*) to yield the complexes, *cis*-$[PtR(SnMe_{4-n}R_{n-1})(PPh_3)_2]$ (n = 1 or 2), but with excess of Me_3RSn (if R has no 2-substituents), the complex, *cis*-$[PtR(SnMe_2R)(PPh_3)_2]$ is also formed. *cis*-$[PtR(SnMe_3)R)(PPh_3)_2]$ reacts with Me_2R_2Sn to form *cis*-$[PtR(SnMe_2R)(PPh_3)_2]$. The system catalyses the redistribution reaction:

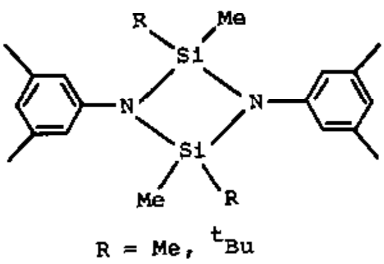
$$2Me_3SnR \rightleftharpoons SnMe_2R_2 + SnMe_4$$

and *cis*-$[PtR(SnMe_2R)(PPh_3)_2]$ catalyses the redistribution of aryl groups (R,R') between $SnMe_2R'_2$ and $SnMe_2R_2$.[109]

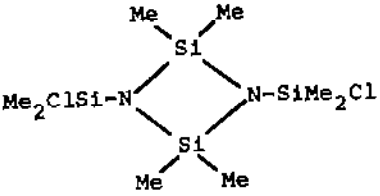
4.4.4 Bonds to Nitrogen

Electron diffraction studies of the silylamines, $(MeH_2Si)_3N$,[110] $F_2P(H_3Si)_2N$[111] and $(F_2P)_2(H_3Si)N$,[111] and the germylamine, $(F_2P)GeNH_2$,[112] show that in all four the central $[NM_3]$ skeleton is planar. In $(MeH_2Si)_3N$, one silicon-carbon bond lies perpendicular to the plane, whilst the other two silicon-carbon bonds are twisted up to 20° out-of-plane to give overall C_s symmetry. The Si-N bond distances in $F_2P(H_3Si)_2N$ and $(F_2P)_2(H_3Si)N$ are substantially longer than in other silylamines. In each of these compounds, the conformation adopted by the $[F_2P]$ groups is such that the axes of the nitrogen and phosphorus lone pair orbitals are approximately orthogonal. A similar lengthening of the Ge-N bond is observed in $(F_2P)GeNH_2$. Again, the conformation adopted is such that the nitrogen and phosphorus lone pair orbitals are almost orthogonal, whilst those of the two phosphorus atoms lie approximately *cis* to each other in the skeletal plane.

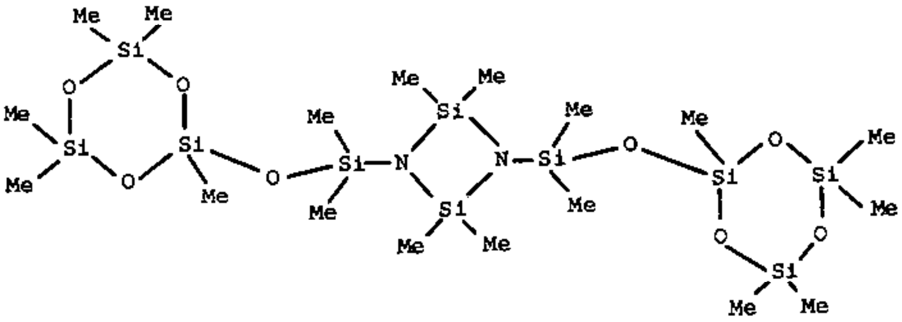
The structures of several ring and cage silazanes have been determined, including the 1,3-diaza-2,4-disilacyclobutanes (*44*)-(*46*),[113-115] the heterocycle (*47*), in which the three rings are planar with the $[SiN_2C_2]$ rings attached to the same side of the central ring and interplanar angles of 114.4 and 114.8°,[116] the cyclosilazanes (*48*), in which two boat conformation $[Si_3N_3]$ rings are joined by a $[SiF_2]$ bridge,[117] and (*49*), which possesses an approximately planar trisilazane ring joined by three silicon spiro atoms to three trisiloxane rings,[118] the cyclotetrasilazane (*50*), which has the general boat conformation,[119] and the


R
Me
Si
N
N
Si
Me
R
R = Me, ^{t}Bu

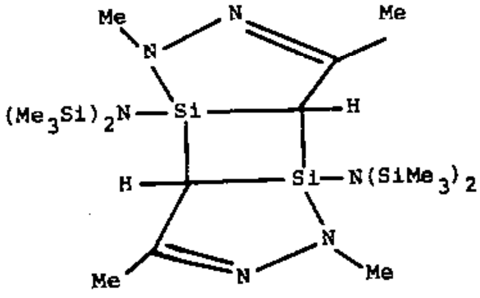
(44)


Me
Me
Si
$Me_2ClSi-N$
$N-SiMe_2Cl$
Si
Me
Me

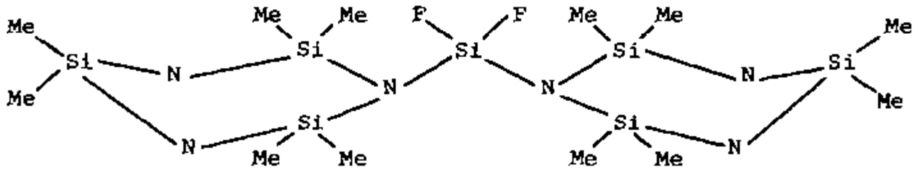
(45)



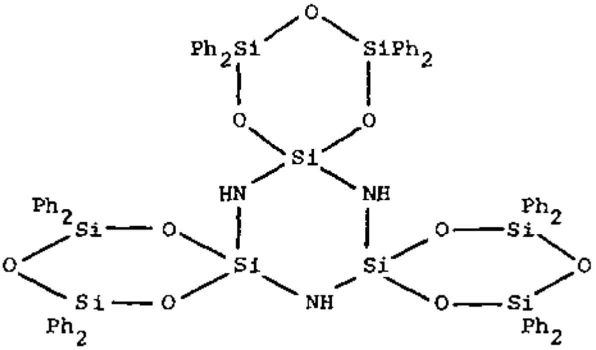
(46)


Me
N
Me
N
$(Me_3Si)_2N$
Si
H
H
Si
$N(SiMe_3)_2$
N
Me
N
Me

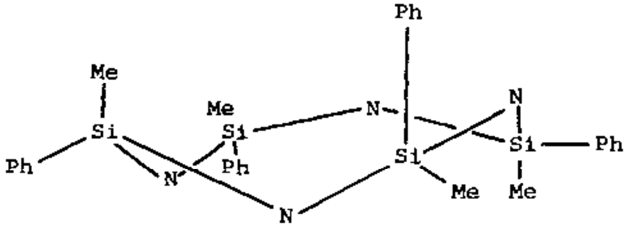
(47)



(48)

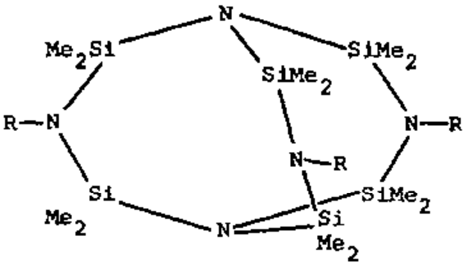


(49)



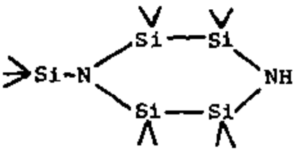
(50)

bicyclo-[3.3.3]-hexasilazane cage compound (51), the tricyclic silazane core of which has non-crystallographic C_{3h} symmetry. Unusually, the nitrogen atoms lying on the $\bar{3}$ axis have an almost planar configuration (mean Si-N-Si (apical) 119.1(5)°).[120]

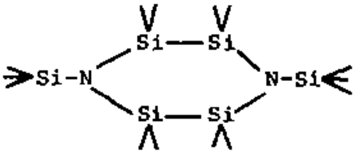


(51)

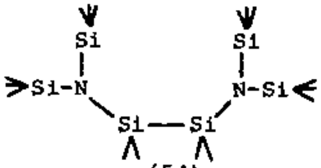
Other novel silazane frameworks which have been synthesised include (52)-(56).[121]



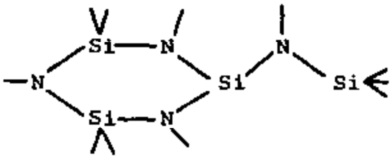
(52)



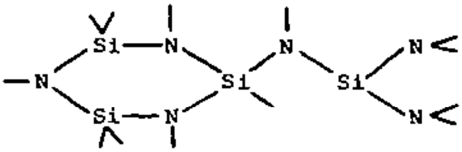
(53)



(54)



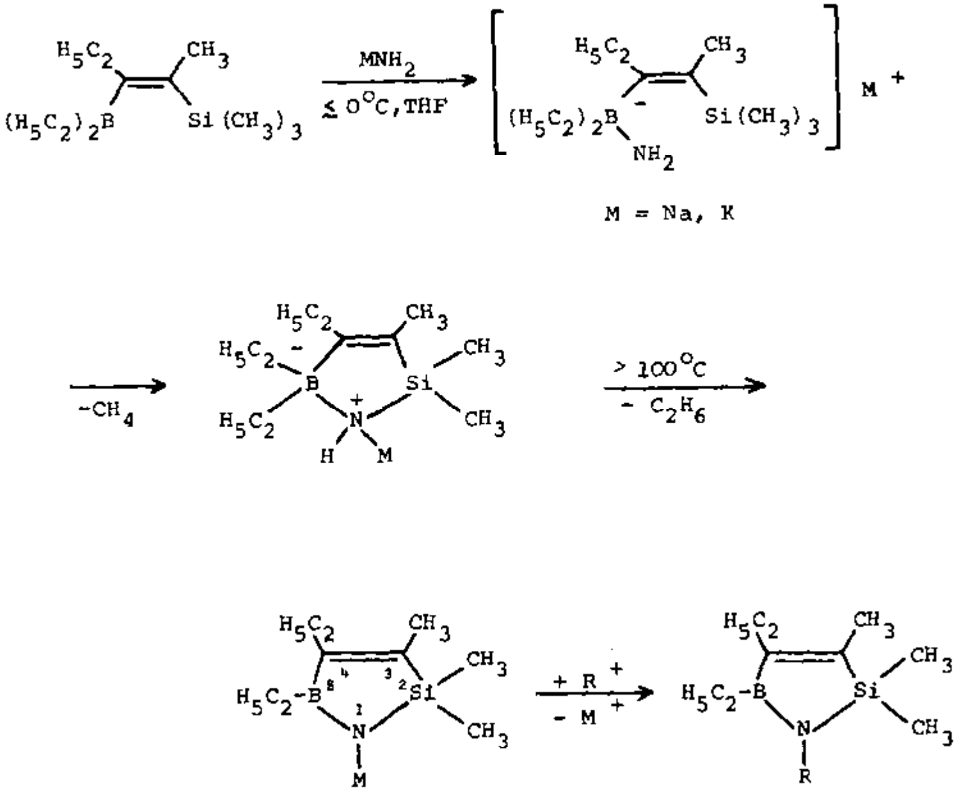
(55)



(56)

The new (silylamino)boranes, $(Me_2SiH)_2N$-BPhNMe$_2$ and $Me_2\overline{Si\text{-}CH_2CH_2SiMe_2N}$-BPhNMe$_2$ have been prepared by the reaction of Me$_2$NBPhCl and the N-lithio derivatives of the corresponding silylamine. Similar reaction with PhBCl$_2$ afforded the mono(silylamino)borane, $Me_2\overline{SiCH_2CH_2SiMe_2N}$BPhCl, from which the corresponding B-methyl and B-amino derivatives may be obtained by treatment with methyllithium and ammonia. Boron trichloride reacted with two equivalents of the cyclic N-lithio silylamide to yield $[Me_2\overline{SiCH_2CH_2SiMe_2N}]_2BCl$.[122] The dialkyl[(trimethylsilyl)-

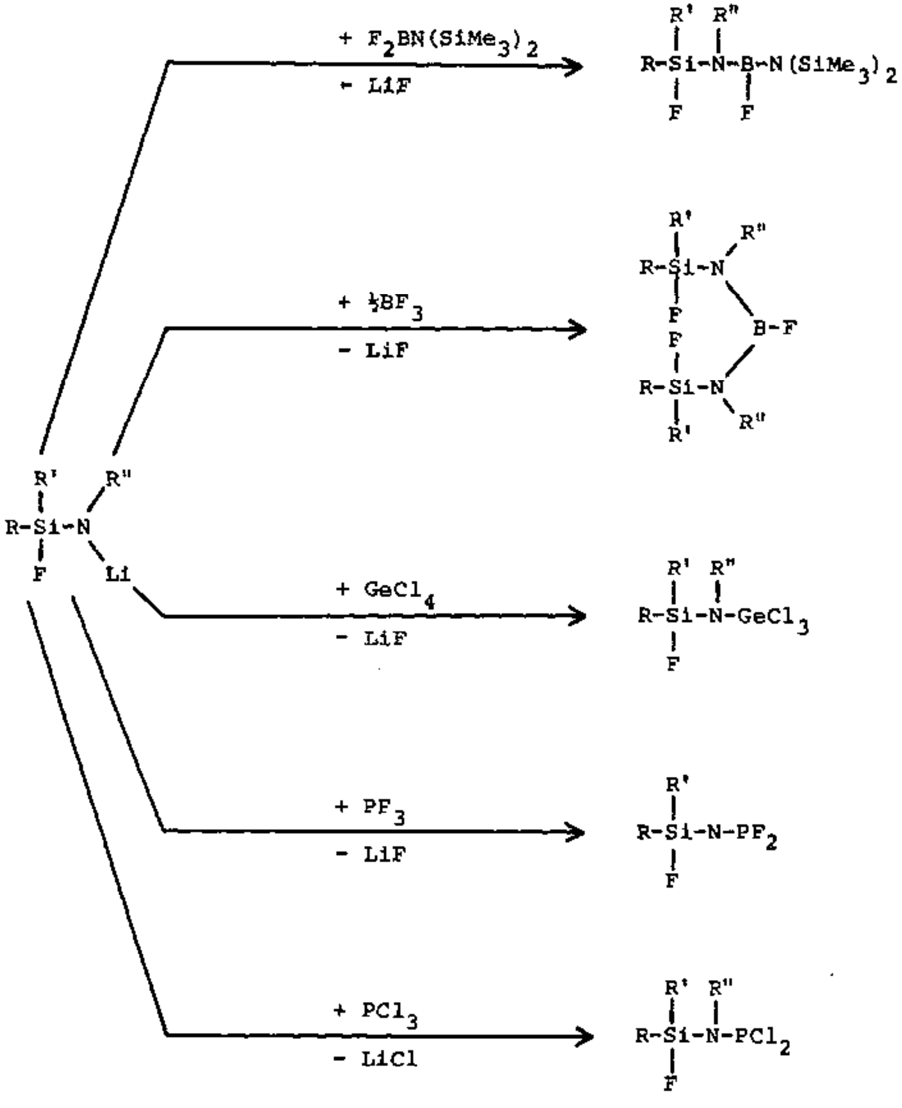
(trimethylsiloxy)amino boranes, $R_2B-N(OSiMe_3)SiMe_3$, prepared from $(Me_3Si)_2N-OSiMe_3$ and R_2BCl, can be thermolysed in the liquid phase at -70°, eliminating hexamethyldisiloxane and giving a mixture of $R_2B-NR-BR-N(OSiMe_3)SiMe_3$ and $(RBNR)_3$.[123] The novel five-membered $[C_2BNSi]$ ring compounds (57) have been prepared according to the route:[124]



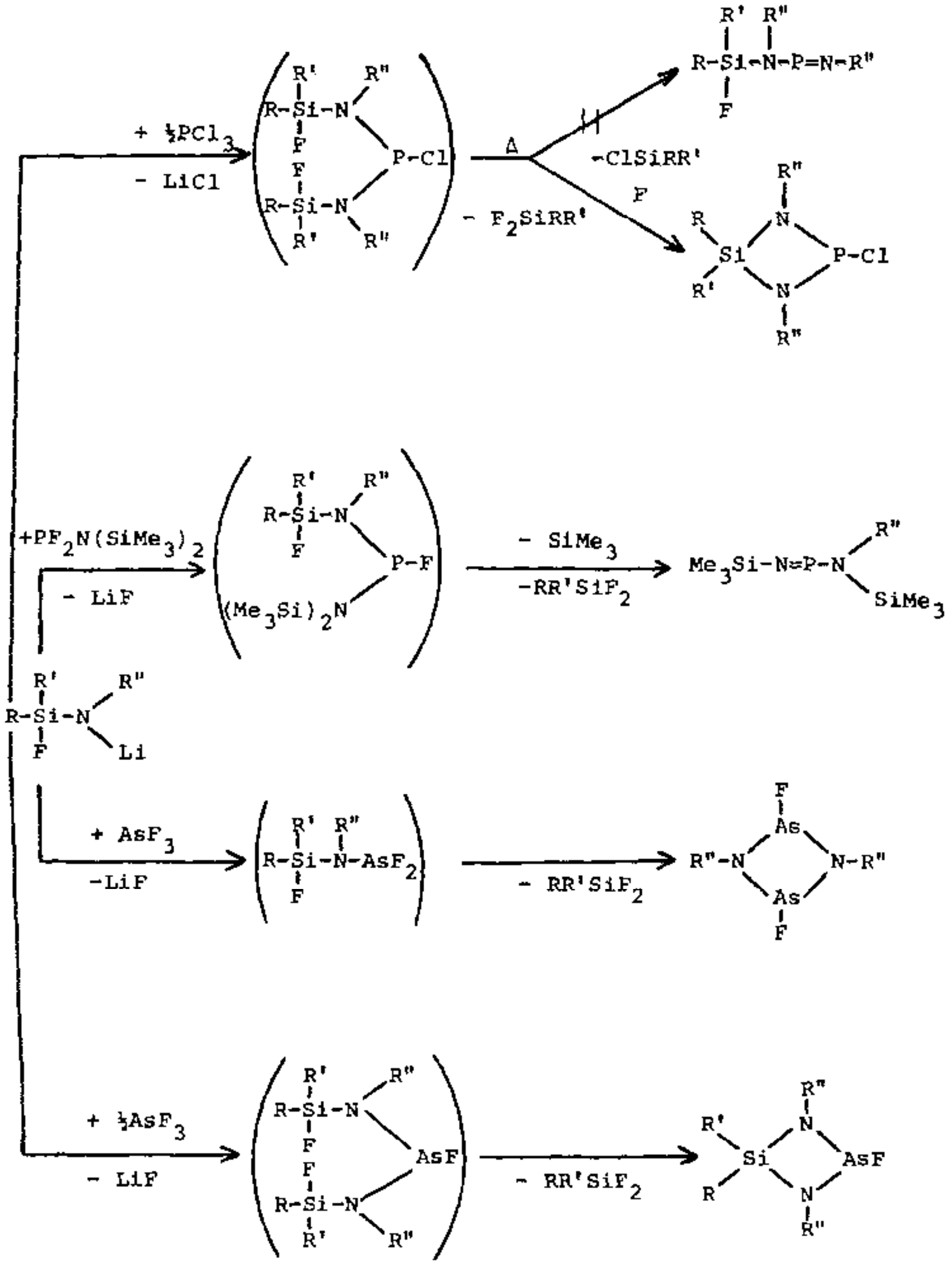
R = Me, $SiMe_3$ (57)

Several fluorosilylamino derivatives of various elements have been obtained by substitution. Representative examples are illustrated in Schemes 12 and 13.[125]

The stable silylated methylenephosphine, $(Me_3Si)_2N-P=CHSiMe_3$, results from the dehydrohalogenation of $(Me_3Si)_2N-PCl-CH_2SiMe_3$ using $LiN(SiMe_3)_2$.[126] The cations, $[(Me_2N)(^tBuMe_2Si)_2NP]^+$, $[(Me_2N)(Me_3Si)_2NP]^+$ and $[\{(Me_3Si)_2N\}_2P]^+$ are obtained by treatment of the appropriate precursor chlorides and a

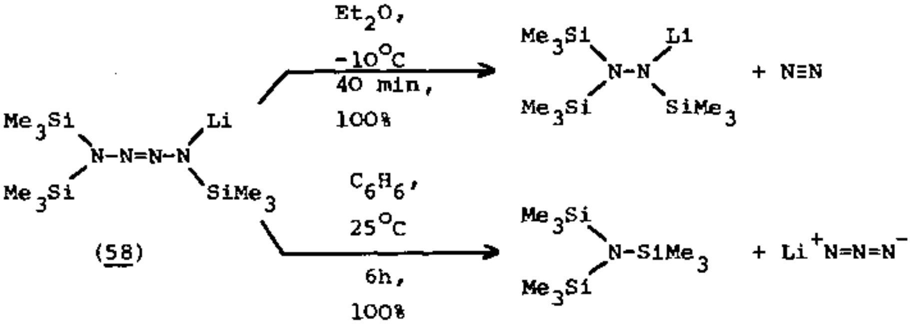

+ $F_2BN(SiMe_3)_2$
- LiF
+ ½BF_3
- LiF
+ $GeCl_4$
- LiF
+ PF_3
- LiF
+ PCl_3
- LiCl
R'
R"
R-Si-N
F
Li
R-Si-N-B-N$(SiMe_3)_2$
B-F
R-Si-N-$GeCl_3$
R-Si-N-PF_2
R-Si-N-PCl_2

<u>Scheme 12</u>

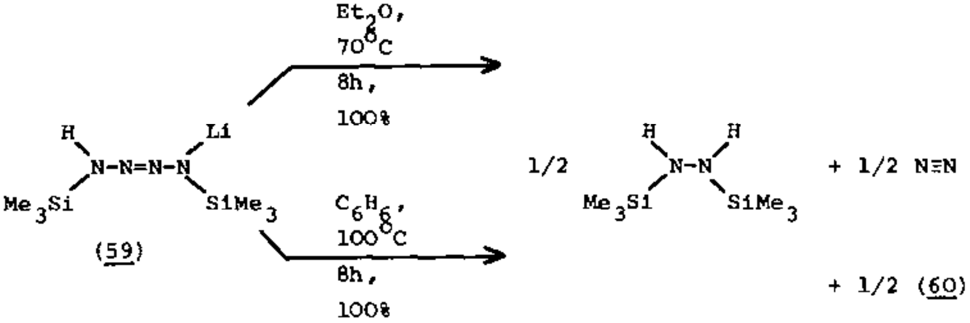

+ ½PCl3
- LiCl
R-Si-N
P-Cl
Δ
-ClSiRR'
F
- F2SiRR'
R-Si-N-P=N-R"
Si
+PF2N(SiMe3)2
- LiF
(Me3Si)2N
P-F
- SiMe3
-RR'SiF2
Me3Si-N=P-N
SiMe3
R'
R"
Li
+ AsF3
-LiF
R-Si-N-AsF2
- RR'SiF2
R"-N
As
N-R"
+ ½AsF3
- LiF
AsF

Scheme 13

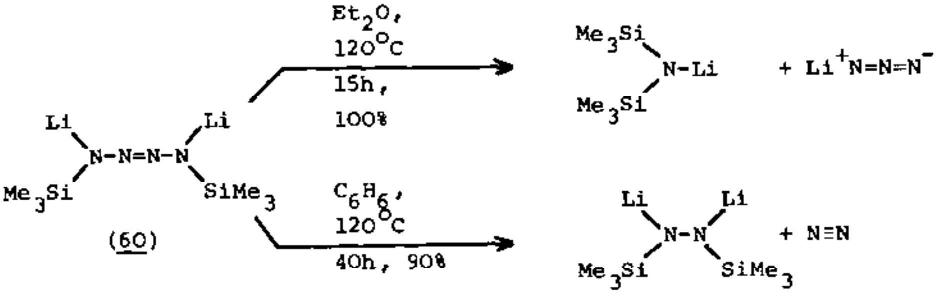
stoichiometric amount of aluminium(III) chloride in dichloromethane.[127] The reactions of $Me_2Si(NMe_2)_2$ and the Group IV metal chlorides, MCl_4 (M = Ti, Zr, Hf, Si, Ge, Sn) fall into two categories: (a) N-donor chelation leading to 1:1 complex formation (M = Ti, Zr, Hf, Sn), and (b) halide-NMe_2 exchange (M = Si, Ge). Decomposition of $TiCl_4{\cdot}SiMe_2(NMe_2)_2$ to $TiCl_3(NMe_2)$ occurs in both solution and the solid-state.[128] Reaction of butyllithium with tris- or bis(trimethylsilyl)tetrazenes leads to the formation of the tetrazenides, (58)-(60), which are sensitive to hydrolysis, thermolysis, and molecular oxygen:[129]



(58)



(59)



(60)

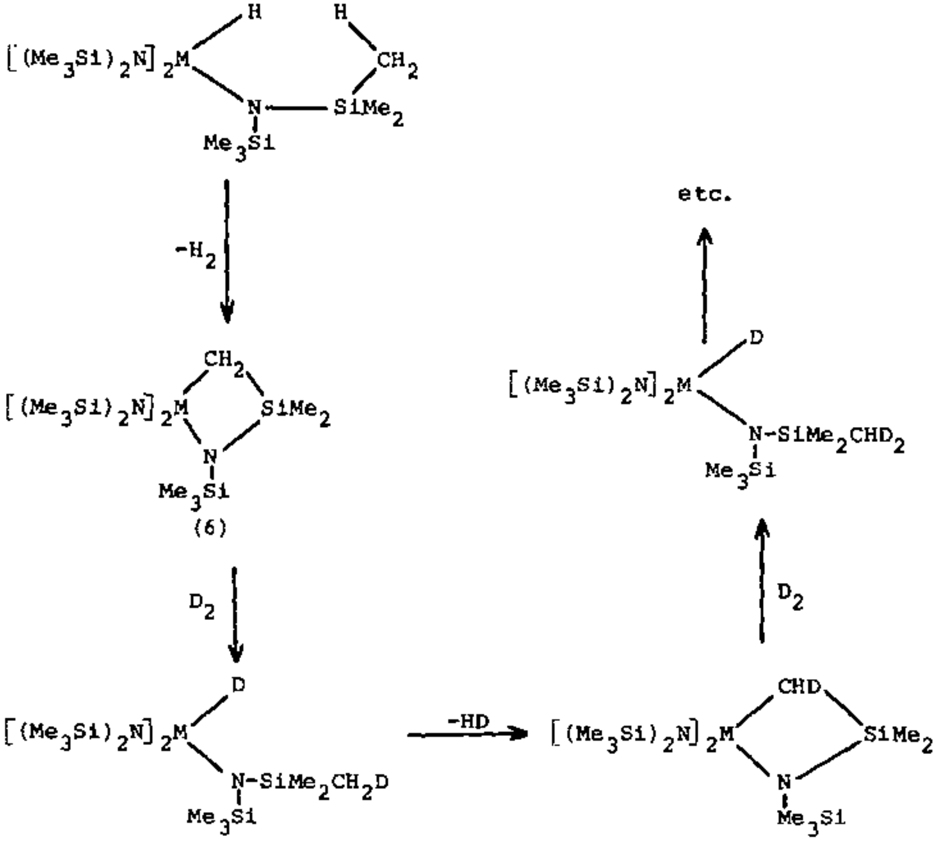
Treatment of $(C_5H_5)TiCl_2$ with one or two equivalents of $LiN(SiMe_3)_2$ affords the previously described metallocycle, $(C_5H_5)_2\overline{Ti{-}CH_2SiMe_2N}SiMe_3$ and HCl. The analogous zirconium metallocycle was isolated from the reaction of $(C_5H_5)_2Zr(H)Cl$ and $LiN(SiMe_3)_2$. The trimethylsilyl groups of $(C_5H_5)_2Zr[N(SiMe_3)_2]_2$, from $(C_5H_5)_2ZrCl_2$ and two equivalents of $LiN(SiMe_3)_2$, are megnetically non-equivalent at 27°, but coalesce at 84° on the ^1H n.m.r. time-scale.[130] Yellow, hydrocarbon-soluble silylamido-europium derivatives of the types $[(Me_3Si)_2N]_2Eu(L)_2$ (L = THF or DME) and $[(Me_3Si)_2N]_2Eu(bipy)$ have been prepared via the route:

$$\begin{tikzcd}
2Eu[N(SiMe_3)_2]_3 + EuCl_3 \arrow[r, "THF"] & 3ClEu[N(SiMe_3)_2]_2 \arrow[d, "{THF,\ Na^+Np^-}"] \\
Eu[N(SiMe_3)_2]_2(L_2) & Eu[N(SiMe_3)_2]_2(THF)_2 \arrow[l, "\substack{DME\\ or}"', "bipy"]
\end{tikzcd}$$

The crystal structure of the DME complex shows the europium to be hexacoordinated by two mutually *trans* $[N(SiMe_3)_2]$ groups [NEuN = 134.2°] and two chelating DME groups.[131] The silylamido uranium complex, $[(Me_3Si)_2N]_2UCl_2{\cdot}DME$, from UCl_4 and two equivalents of $NaN(SiMe_3)_2$ in DME, THF followed by addition of DME, also has a six-coordinated structure with *cis* silylamido groups and *trans* chlorines.[132] The uranium atom in $H[(Me_3Si)_2N]_3U$ lies on a crystallographic 3-fold axis, and is bonded to three nitrogen atoms with NUN = 115.0(1)°. The structure is disordered in the **z** direction, with uranium atoms at locations 0.51Å above and below the plane at **z** = $^1/4$.[133] Monomeric monohydrides and mono-deuterides of thorium and uranium of this type are prepared by the two routes:

$$\begin{tikzcd}
MCl_4 + NaN(SiMe_3)_2 \arrow[dr, "refluxing"] & \\
 & HM[N(SiMe_3)_2]_3 \\
ClM[N(SiMe_3)_2]_3 + NaN(SiMe_3)_2 \arrow[ur, "THF"'] &
\end{tikzcd}$$

The metal-bonded hydrogen atom may be methylated by treatment with methyllithium followed by methylbromide. Reaction with diborane leads to the formation of the corresponding borohydrides, $BH_4M[N(SiMe_3)_2]_3$. Pyrolysis of the hydrides yields the four-membered metallacycles, $[(Me_3Si)_2N]_2MCH_2SiMe_2NSiMe_3$, which are key intermediates in the H-D exchange reaction which yields the perdeuteriated analogue, $[\{[(CD_3)_3Si\}_2N]_2\overline{MCD_2Si(CD_3)_2N}Si(CD_3]_3$, according to Scheme 14.[134]



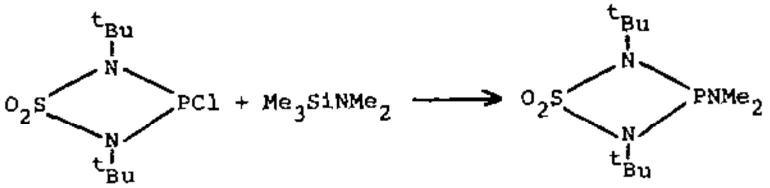
Scheme 14

Silylamino compounds have been used as reagents in a large number of transformation reactions, and several examples are shown below:

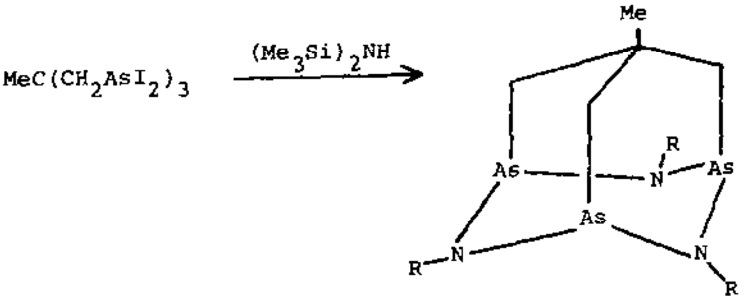
$S_4N_4Cl_2 + 2Me_3SiNMe_2 \longrightarrow S_4N_4(NMe_2)_2$ refs. 135 and 136

$(Me_5C_5)ECl_2 + Me_3SiNMe_2 \longrightarrow (Me_5C_5)(Me_2N)ECl$ ref. 137

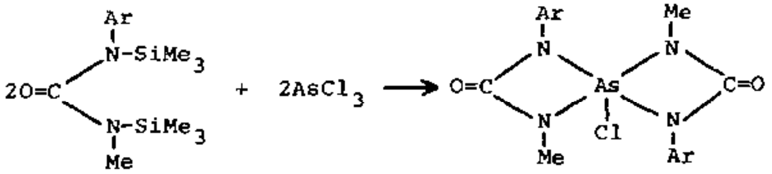
E = P, As.



ref. 138

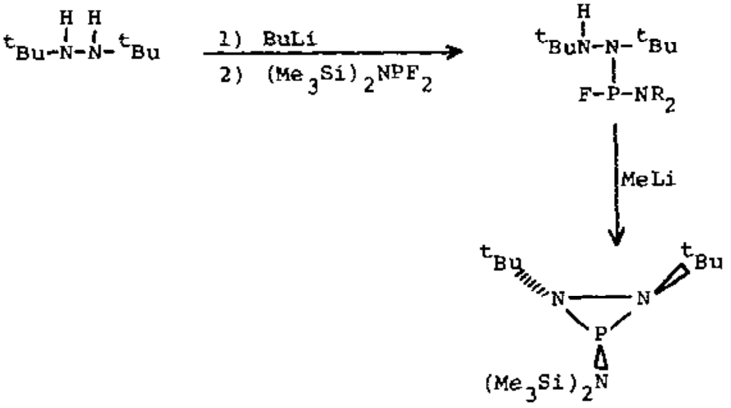


ref. 139

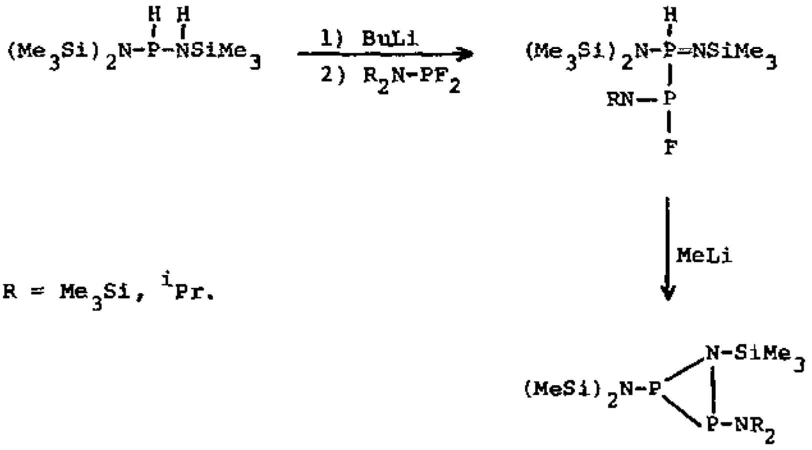


Ar = $C_6H_4CF_3$-3

ref. 140

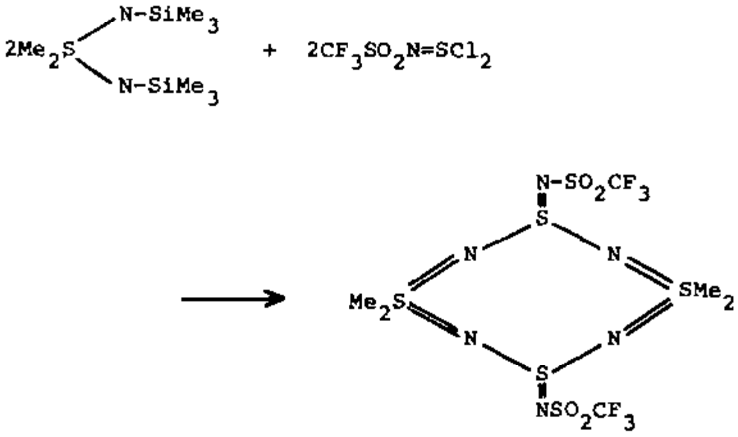


ref. 141



R = Me_3Si, ^iPr.

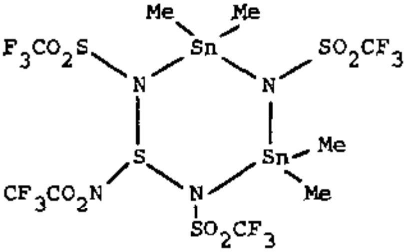
ref. 142



ref. 143

The vibrational spectrum of germyl azide-do and -d_3 has been assigned on the basis of C_s symmetry. Normal coordinate analysis (modified valence force field) shows that the Ge-N stretching force constant has a significantly smaller value than the corresponding value in germyl isocyanate or isothiocyanate. A considerable amount of mixing was found between the Ge-N stretching and in-plane NNN deformation modes.[144]

Treatment of $Me_2SnNO_2SCF_3$ with $CF_3SO_2N=S=O$ yields the six-membered heterocycle (61).[145]

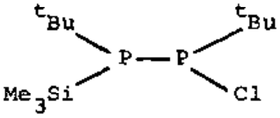


(61)

N-Bromo-N-sodiocarbamidate, $C_2H_5OC(O)NBrNa$, reacts with Me_3SnBr and Ph_3PbCl to afford, respectively, $C_2H_5OC(O)NBrSnMe_3$ and $C_2H_5OC(O)NBrPbPh_3$.[146] Tin-119 Mössbauer data and reduction potentials have been reported for six tin porphyrin derivatives. The Mössbauer spectra exhibit a resolvable quadrupole splitting of 0.47-0.99 mm s^{-1}. The dichlorotin porphyrins are ring reduced about 380mV more easily than the corresponding free base porphyrin.[147]

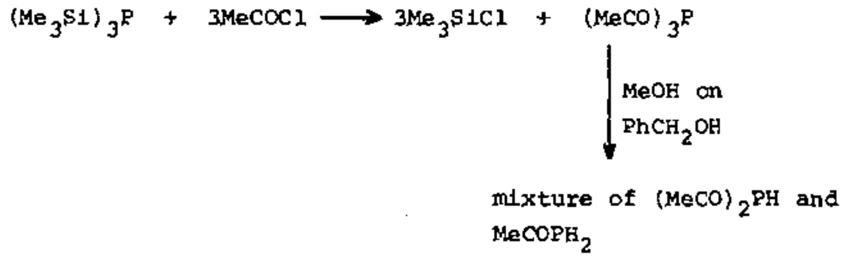
4.4.5 Bonds to Phosphorus and Arsenic

Although previous attempts to prepare a P-halo-P-silylphosphane always proved unsuccessful due to the elimination of halosilane, $^tBuPCl-SiMe_3$ has now been synthesised from the reaction of $^tBu(SiMe_3)_2P$ with a stoichiometric amount of C_2Cl_6. With excess reagent, the second silyl group is also cleaved giving $^tBuPCl_2$. Even at room temperature, $^tBuPCl-SiMe_3$ reacts slowly in toluene with the elimination of Me_3SiCl to afford the unsymmetrical diphosphine (62), which in the presence of $^tBu(Me_3Si)_2P$ cyclises to $(^tBuP)_3$ and $(^tBuP)_4$.[148]



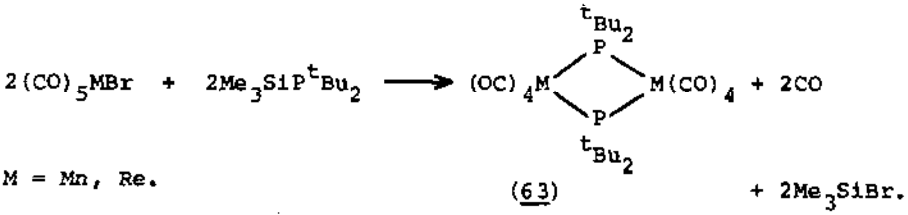
(62)

Treatment of tris(trimethylsilyl)phosphine with excess acetyl chloride in cyclopentane affords triacetylphosphine:[149]



$$(Me_3Si)_3P + 3MeCOCl \longrightarrow 3Me_3SiCl + (MeCO)_3P \xrightarrow{MeOH\ or\ PhCH_2OH} \text{mixture of } (MeCO)_2PH \text{ and } MeCOPH_2$$

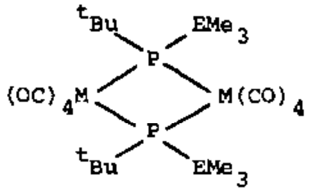
The α,ω-disilyltetraphosphine, $Me_3(PPh)_4SiMe_3$, has been obtained by metathesis between $K_2(PPh)_4$ and Me_3SiCl, but of the six possible isomers, only the *erythro*, *meso*, *erythro*, *erythro*, *d*, *ℓ*, *erythro*, *threo*, *d*, *ℓ*, *threo*, and *erythro*, *threo*, *threo* could be detected by ^{31}P n.m.r. Inversion at phosphorus is rapid leading to a dynamic equilibrium between the isomers. Alcoholysis gives $H(PPh)_4H$ as the main product.[150] Reaction between $Me_3SiP^tBu_2$ and pentacarbonylmanganese or -rhenium bromide leads to the formation of the cyclic compound (63):



M = Mn, Re.

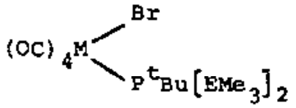
(63)

Similarly prepared were the compounds (64)-(67).[151]



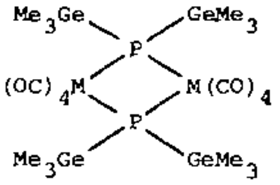
M = Re, E = Si
M = Mn, E = Ge
M = Re, E = Ge

(64)



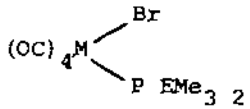
M = Mn, E = Si
M = Mn, E = Si
M = Re, E = Sn

(65)



M = Mn, Re

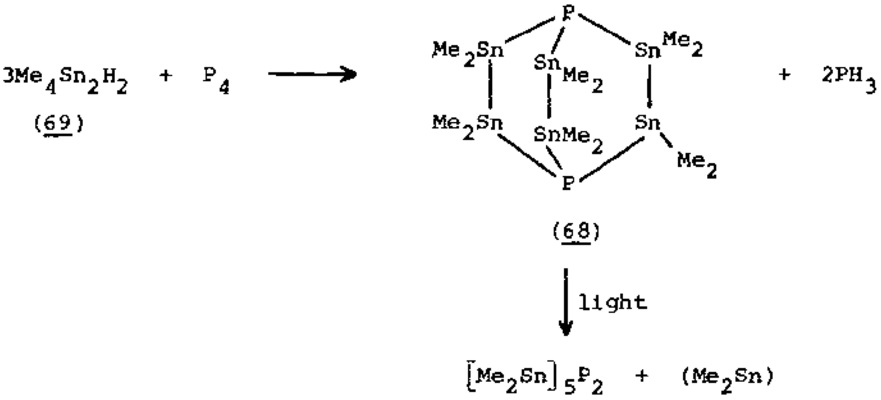
(66)



M = Mn, E = Si
M = Re, E = Si
M = Mn, E = Sn
M = Re, E = Sn

(67)

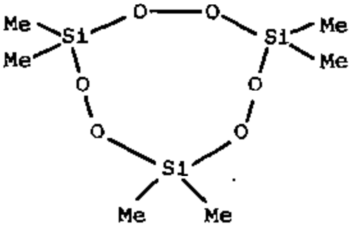
The bright yellow crystalline compound (68) has been synthesised by the reaction of the hydride (69) with elemental phosphorus in ether at 0^o in the dark:

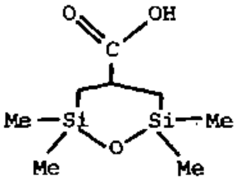


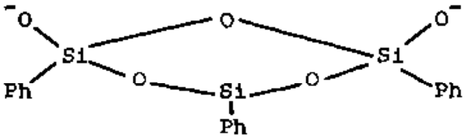
Exposure of (68) to light converts it to $[Me_2Sn]_5P_2$. Crystallographic studies of (68) show it to be a chiral molecule with D_{3h} symmetry; a bicyclo constructed from three $[Sn_4P_2]$ rings which share three bonds with each other and adopt the conformation of a boat twisted by 26^o.[152] Tin-119 Mössbauer data have been reported for compounds of the type $(Me_3Sn)_n(^tBu)_{3-n}P$ (n = 1-3)(L), as well as the complexes, $Mn(NO)_3L$, $Fe(CO)(NO)_2L$, $Co(CO)_2(NO)L$, and $Ni(CO)_3L$.[153]

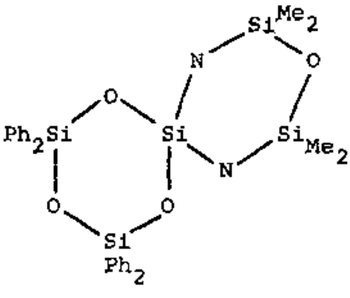
4.4.6 Bonds to Oxygen

The structures of several silicon-oxygen bonded compounds have been reported. That of silyl acetate has been determined in both the gas phase and in the solid at 150K, the Si-O bond distances being 1.685(3)Å and 1.696(4)Å, respectively. In both phases, the heavy atom skeleton is almost planar with the Si-O and C=O arranged cis to each other leading to intramolecular Si---O(carbonyl) distances of 2.795(14)Å (gas phase) and 2.832(4)Å (solid). The crystal structure is characterised by unusually short Si---O(carbonyl) intermolecular contacts of 2.721(4)Å, which exhibit the stereospecificity associated with secondary bonds.[154] The intramolecular Si---N distances in the compounds $(Me_2C{=}NO)_2MeClSi$[155] and $PhSi(ON{=}CMe_2)_3$[156] are ca. 2.50Å (cf. the corresponding distance in silatranes of 2.1 - 2.3Å), showing little bonding interaction. In the bissilylperoxides, $Me_2RSiOOSiRMe_2$ (R = C_6H_4Cl-p, CH_2Ph), molecules sit on a centre of symmetry and have an ideal trans-conformation for the peroxide group. Bond distances and angles are similar in both molecules.[157] The cyclic silylperoxide (70) has approximate D_3 symmetry. The ring has the TBC conformation according to Hendrickson's nomenclature.[158] Molecules of $(Me_3SiO)_4Si$ sit on a two-fold axis in the crystal at -120°. The Si-O bonds to the central silicon atom are shorter (1.602(3)Å) than to the peripheral silicon (1.634(3)Å). The average SiOSi bond angle is 146.0(2)°.[159] Molecules of (71) are joined by hydrogen bonds between the carbonyl groups to form dimers in the crystal.[160] The core of the cis-1,3,5-triphenylcyclotrisiloxane-1,3,5-triolate anion (72) (as the sodium salt octahydrate) consists of a

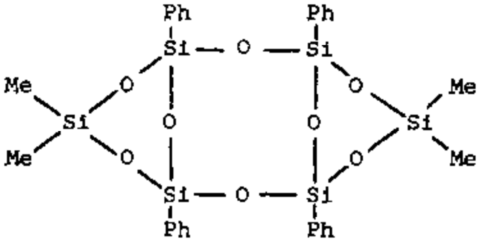

(70)


(71)


(72)

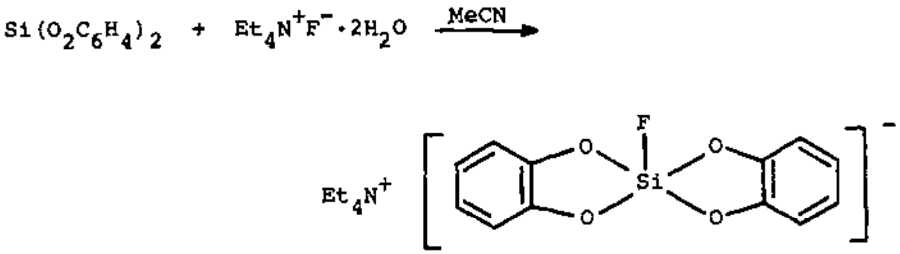


(73)



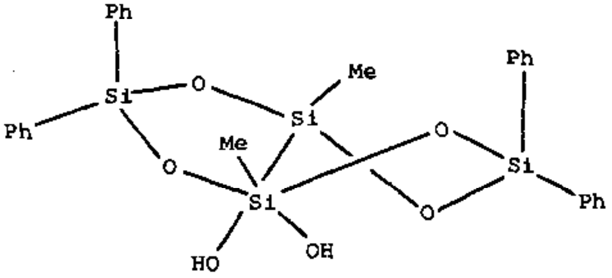
(74)

practically planar trisiloxane ring. Crystals are made up of layers of anions having polar and non-polar surfaces. The space between the polar surfaces, turned towards one another, of neighbouring layers is occupied by a layer of Na^+ cations and water molecules. SiOH---O$<$ and Na^+---O ionic interactions lead to formation of three-layer packets, which are superimposed on one another through their non-polar surfaces, between which van der Waals forces operate. The crystal thus represents a mica-like layer hybrid of siloxane and silicate structures.[161] The two rings of the spiro compound (73) are almost perpendicular to each other. The $[Si_3N_2O]$ ring has the boat conformation.[162] Molecules of the isomer of (74) melting at 222.5° sit at a centre of symmetry and has the trans structure. The end trisiloxane rings are bent away from the central tetrasiloxane through angles 82.4°. The SiOSi angles of the tetrasiloxane ring have an unusually low value (mean 132.5°).[163] Molecules of the other isomer, m.p. 162.5°, lie on a two-fold axis with the cis structure; the lateral trisiloxane rings being bent away from the central tetrasiloxane ring by 118°.[164] The tetrasiloxane ring of the cyclic diol (75) has the boat conformation (mean SiOSi = 144°, mean Si-O (ring) = 1.622Å, mean Si-OH = 1.643Å). In the crystal, molecules are joined by hydrogen bonds to form chains.[165] The two silasesquisiloxane derivatives, $[C_2H_3SiO_{1.5}]_8$ (C_2H_3 = vinyl)[166] and $[MeSiO_{1.5}]_{10}$,[167] have the cage structures (76) and (77), respectively. Crystals of tetraethylammonium bis(1,2-benzenediolato)fluorosilicate(IV), (78), prepared according to the route:

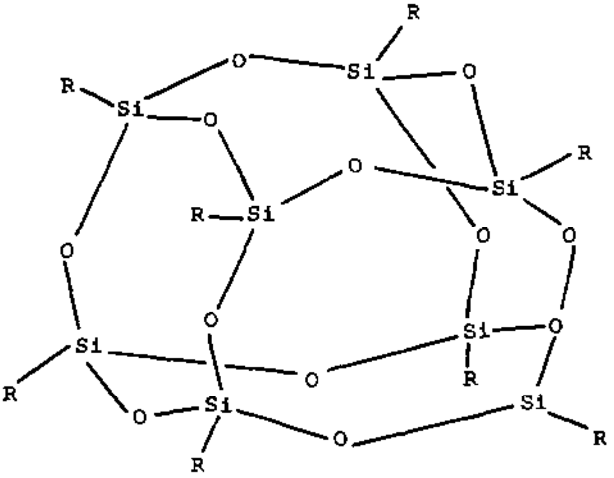


(78)

comprise two crystallographically independent square-pyramidal anions. On the basis of dihedral angle data, the geometry about the silicon atom is displaced ca. 55% or ca. 70% from ideal trigonal bipyramidal geometry towards square pyramidal.

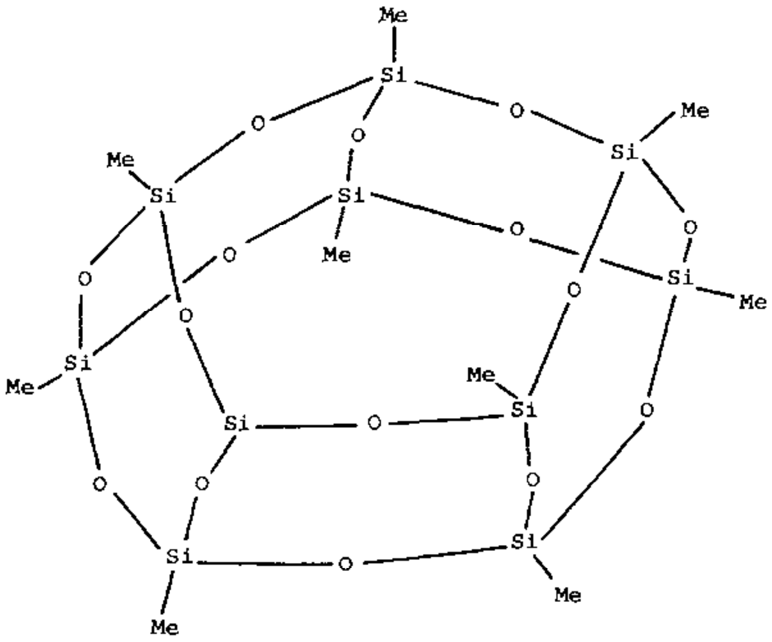


(75)

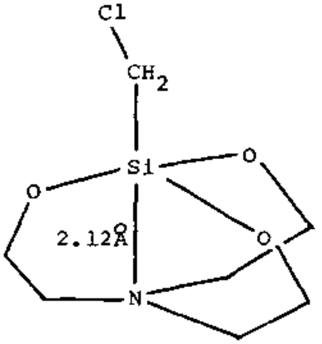


$R = C_2H_3$

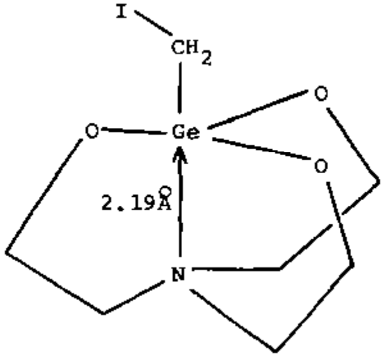
(76)



(77)



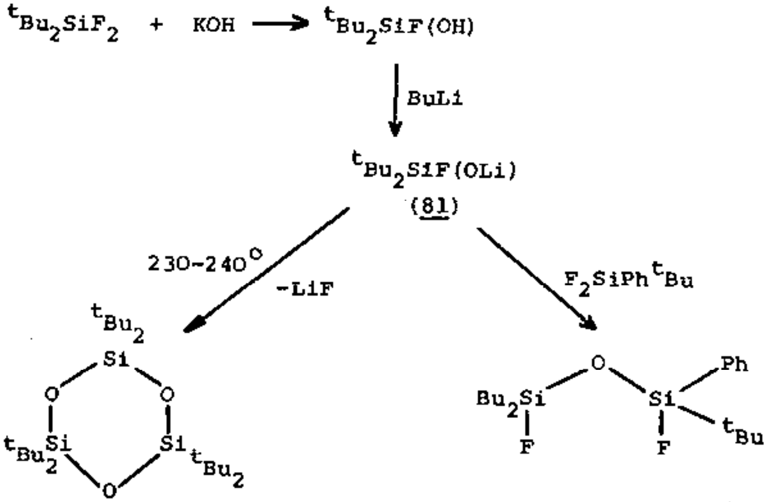
(79)



(80)

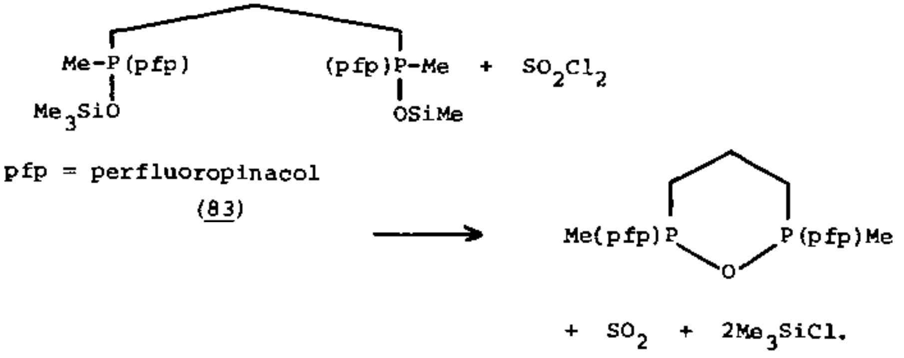
Substituent effects appear to be the major force determining the structure.[168] Short intramolecular N→Metal interactions occur in both the silatrane (79)[169] and the germatrane (80).[170]

3,3,7,7-Tetraphenylcyclotetrasiloxane-1,1,5,5-tetrol forms a complex with pyridine.[171] Potassium hydroxide reacts with difluorosilanols, RR'Si(OH)F, which maybe converted into the corresponding lithium salts are employed as building blocks for directed siloxane synthesis, e.g:[172,173]



(82)

The silanolate salt (81) is unexpectedly stable, melting at 238° with partial decomposition, giving the sterically-trisiloxane ring compound (82). Trimethylsilyl dimethylcarbamate and -dithiocarbamate react with $Me(CF_3)_3PX$ (X = Cl, F) affording $Me(CF_3)_3\overline{P\text{-}EC(E)N}Me_2$ (E = O, S).[174] Treatment of hexamethyldisilazane with sulphur dioxide gives ammonium trimethylsilylsulphite, $NH_4[Me_3SiOSO_2]$, which readily "sublimes" at ambient temperature. Spectral (i.r., n.m.r., and XDS) data ruled out the presence of ammonium and bisulphite ions.[175] The Si-O bonds of the siloxyphosphorane (83) are cleaved by SO_2Cl_2:[176]



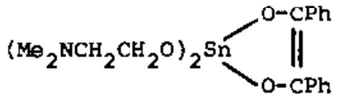
pfp = perfluoropinacol

(83)

The nature of the species present in aqueous solutions of potassium silicate has been studied by ^{29}Si n.m.r. Definitive evidence was obtained for eleven silicate species including five ions which involve a ring containing three siloxy units.[177]

Substitution of germanium(IV) chloride by trimethyl- and trifluoroacetic acids lead to the formation of the chlorogermanium (IV) carboxylates, $Cl_{4-n}Ge(O_2CCR_3)_n$ as colourless oils, separable by fractional distillation.[178] With catechol, 3.5-di-tert-butylcatechol and toluene-3,4-dithiol in the presence of triethylamine, germanium(IV) chloride yields the spirocyclic derivatives, $Ge(O_2C_6H_4)_2.2H_2O$, $[ClGe(O_2C_{14}H_{20})_2]NEt_3H$, and $Ge(S_2C_7H_6)_2$, respectively. The physical properties and solution behaviour of the neutral derivatives suggest a polymeric structure for both, whilst $[ClGe(O_2C_{14}H_{20})_2]NEt_3H$ contains pentacoordinated germanium and reacts with water to yield the corresponding hydroxy species, $[(HO)Ge(O_2C_{14}H_{20})_2]NEt_3H$. Further reaction of $Ge(O_2C_6H_4)_2{\cdot}2H_2O$ with triethylamine, or carrying out the original reaction in triethylamine alone, leads to the exclusive formation of the spirocyclic hexacoordinated germanium(IV) complex, $[Ge(O_2C_6H_4)_3]NEt_3H$. Metathesis of this latter complex with $NEt_4^+Cl^-$ affords the corresponding tetraethylammonium salt.[179] The effect of pressure on the intramolecular racemisation of tris(acetylacetonato)germanium(IV) perchlorate has been studied in various organic solvents. The volume of activation ($\Delta V^{\ddagger}$) in 1,1,2,2-tetrachloroethane, propylene carbonate, acetonitrile, and DMF fall in the range +15 - -4 $cm^3\ mol^{-1}$ in the pressure region 0.1-284 MPa at 50° and 60°, but does not depend on pressure and temperature. The values obtained correlate best with the donor number of the solvent, and are accounted for by the intramolecular mechanism involving an intermediate containing one unidentate acetylacetonate ligand. $\Delta V^{\ddagger}$ seems to reflect direct participation of the solvent molecule in the transition state, rather than the change in the second-sphere coordination around the complex cation. The size of the solvent molecules appears to play a less important but appreciable role in determining the $\Delta V^{\ddagger}$ values than does the basicity.[180]

Crystallographic studies of the hexaphenyl Group IV ethers, Ph_3MONPh_3 ($M \neq N$ = Si, Ge, Sn) show that the metalloid atoms are disordered between the two possible sites, as has been shown previously for $Ph_3SiOPbPh_3$. In $Ph_3SiOGePh_3$, the disorder is total (population parameter = 0.503) with a MON angle of 142.5°. Population parameters for $Ph_3GeOSnPh_3$ and $Ph_3SiOSnPh_3$ are 0.532 and 0-642, respectively.[181] Trimeric di-*tert*-butyltin oxide, $({}^tBu_2SnO)_3$, has been obtained by hydrolysis of ${}^tBu_2SnCl_2$ using sodium hydroxide in boiling toluene. Unusually for this class of compound, it is readily soluble in organic solvents in the cold, and X-ray studies show the six-membered $[Sn_3O_3]$ ring to be planar (OSnO = 106.9°, SnOSn = 133.1°).[182] Th- discrete molecular, *cis*-octahedral structure for bis(acetylacetonato)dichlorotin(IV) has been confirmed.[183] Spectroscopic evidence indicates a similar six-coordinated geometry for the bis(3-cyanopentane-2,4-dionato)dihalotin(IV) derivatives, with no metal-cyanide interactions.[184] The addition product,



$(Me_2NCH_2CH_2O)_2Sn\begin{matrix}O{-}CPh\\ \| \\ O{-}CPh\end{matrix}$

, results from the reaction of $Sn(OCH_2CH_2NMe_2)_2$ with benzil.[185] 8-Hydroquinoline reacts with the tris(trimethylsilyl)methyltin halides, $RSnX_3$, $RR'SnX_2$ and RR'_2SnX (R' = Me or Ph, R = $(Me_3Si)_3C$, X = halogen), in ethanol to afford the corresponding oxinate derivatives, $RSn(OX)_3$, $Sn(OEt)R(OX)_2$, $SnR'R(OX)_2$ and $R'_2RSn(OX)$. The $RR'Sn(OX)_2$ complexes exist in two *cis* isomeric forms. Heating the di- or tri-oxinates results in nucleophilic cleavage of one trimethylsilyl group yielding the bis(trimethylsilyl)methyl compounds, $Sn(OEt)\{CH(SiMe_3)_2\}(OX)_2$ and $SnR'\{CH(SiMe_3)_2\}(OX)_2$. The latter compound (R' = Me) has the *cis*- octahedral structure, with the nitrogen atoms *trans* to both Sn-C bonds. Hydrobromic acid readily converts the oxinates to the corresponding bromides.[186]

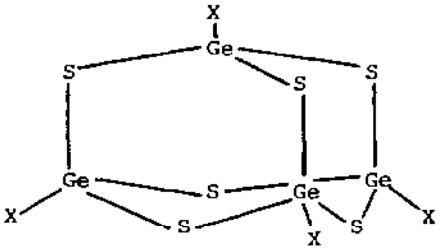
Triphenyltin nitrate and diphenyltin dinitrate react with bis(diphenylphosphino)ethane and -ethylene in methanol/benzene or acetonitrile/benzene to give adducts of the general formula, $\{Ph_{4-n}Sn(NO_3)_n\}_2.L$ (n = 1,2). Infrared and Mössbauer data suggest a *meridional* six-coordinated geometry when n = 1, and a pentagonal bipyramidal structure with mutually *trans* axial phenyl groups when n = 2. In each case the nitrate groups are bidentate and the diphosphine ligands bridge two tin centres. Reaction in other solvents leads to oxidation of the diphosphine ligand.[187] α-(Phenylphosphonato)trimethyltin forms colourless crystals in which $[Me_3SnOP(O)(OH)Ph]$ molecular units are associated to form infinite one-dimensional chains in which planar $[Me_3Sn]$ units are axially bridged by $[OPO]$ linkages giving almost perfect trigonal bipyramidal geometry at tin. The chains are linear at tin, but bent at phosphorus, and are propagated helically through the crystal. Hydrogen-bonds hold together adjacent helical chains, which turn in opposite directions resulting in a two-dimensional sheet structure. Tin atoms occupy two non-equivalent environments, with alternating metal atoms forming either two short or two long bonds to oxygen, an arrangement best described as a combination of $[Me_3Sn^+]$ cations and $[Ph(OH)OSnMe_3OP(O)(OH)Ph]_n^-$ polymeric anions.[188] Barium oxobisoxalatostannate(IV), $BaSnO(OX)_2.8H_2O$, obtained by the coprecipitation method decomposes at 850° to $BaSnO_3$.[189]

4.4.7 Bonds to Sulphur and Selenium

Methylthiosilanes of the types $Me_nH_{3-n}SiSMe$ (n = 0-3) and $MeHSi(SMe)_2$ have been synthesised from the lithium thioaluminate, $Li\,Al(SMe)_4$, eg:

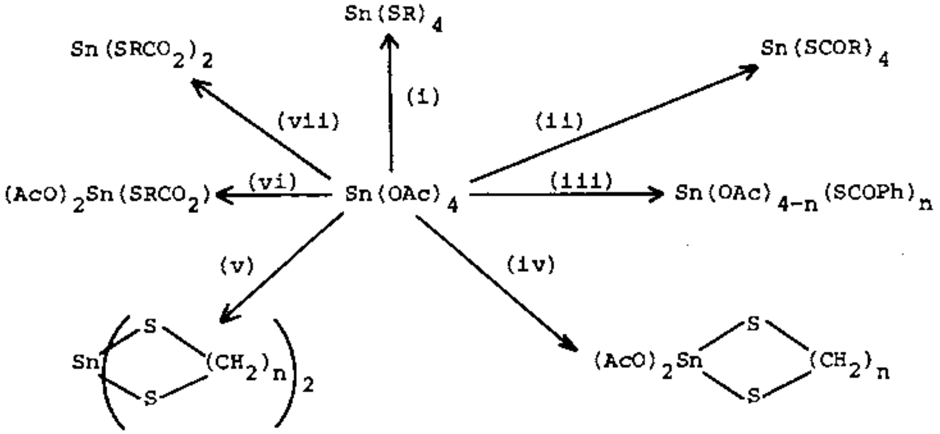
$$\begin{tikzcd}
LiAlH_4 + 4MeSH \arrow[r, "ether"] & Li[Al(SMe)_4] + 4H_2 \arrow[d, "4Me_2HSiI"] \\
& 4Me_2HSiSMe + AlI_3 + LiI
\end{tikzcd}$$

Normal coordinate analysis was carried out using a modified valence force field.[190] The reaction of germanium(IV) bromide and iodide with hydrogen sulphide in carbon disulphide leads to the formation of the mixed germanium(IV) halide sulphides, $Ge_4S_6X_4$ (X = Br, I), which both possess the adamantane framework (84).[191]



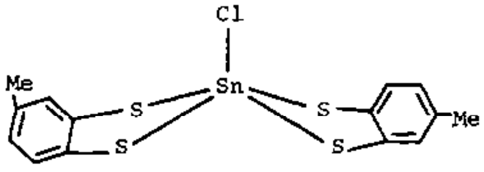
(84)

5,5-Diphenyl-1,4,6,5-oxodithiastannocane, $Ph_2Sn(SCH_2CH_2)_2O$, has a ring conformation which is near the saddle point of the energy surface between chair-chair and chair-boat conformations. The configuration around the tin is intermediate between four-coordinate tetrahedral and five-coordinate trigonal bipyramidal (Sn---O (transannular) = 2.660(7)Å).[192] Metathesis between bis(trimethyltin)sulphide or selenide and Cl^tBuPP^tBuCl gives the three-membered ring compounds $^tBuP\text{-}E\text{-}P^tBu$ (E = S, Se).[193] The reactions of tin(IV) acetate with thiols, thiocarboxylic acids and mercaptocarboxylic acids in chloroform or toluene with the azeotropic removal of acetic acid are very facile, leading to the formation of Sn-S bonds (Scheme 15).[194]

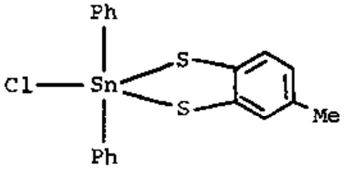


(i) RSH (R = Bu, C_6H_{13}), (ii) RCOSH (R = Me, Et), (iii) nPhCOSH (n = 1-4), (iv) $HS(CH_2)_nSH$ (n = 2-6), (v) $2HS(CH_2)_nSH$ (vi) $HSRCO_2H$ (R = CH_2, $(CH_2)_2$, *o*-C_6H_4), (vii) $2HSRCO_2H$.

The anion $[(C_7H_6S_2)_2SnCl^-]$ (as the tetramethylammonium salt) is the first characterised example of a rectangular-bipyramidal geometry for tin (85). The similar $[(C_7H_6S_2)SnPh_2Cl^-]$ anion has the usual trigonal-bipyramidal geometry (86).[195] Bis(dimethyldithiophosphinato)dimethyltin(IV), $Me_2Sn(S_2PMe_2)_2$ has a distorted octahedral structure with the four sulphur atoms of the anisobidentate chelating $[S_2PMe_2]$ ligands resulting in a CSnC angle of 122.6(8)°. The diodotin analogue is also octahedral with the two iodine atoms placed mutually *cis* and opposite the longer Sn-S



(85)



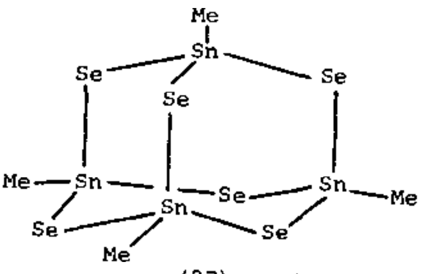
(86)

bonds.[196] The dihalogenotin bis(dithiocarbonates), [Sn(S$_2$COEt)$_2$X$_2$] (X = Cl, Br, I) are stable crystalline compounds, although the corresponding mono- and tri-dithiocarbonato compounds, Sn(S$_2$COEt)X$_3$ and Sn(S$_2$COEt)$_3$X, cannot be isolated. Crystallographic studies of the dibromide and diiodide show that in these two compounds also, the two halogen atoms are mutually cis but trans to the longer Sn-S bond.[197] The interaction of tin(IV) with thiourea in perchloric acid leads to the formation of the complex [Sn(thiourea)$_2^{4+}$] cation, with logβ_2° = -1.53(7).[198]

Both Ph$_3$PbSC$_6$H$_3$Me$_2$-2,6 and Ph$_3$PbSC$_6$H$_4$Br-2 are essentially tetrahedral. In the latter compound however, there is a relatively short intermolecular Pb---Br interaction of 3.77Å.[199]

The complexation of trimethllead(IV) by cysteine, penicillamine, glycine, N-acetylpenicillamine and mercaptoethanol has been studied by ^{11}H n.m.r. Of the potential binding sites, the deprotonated sulphydryl group binds trimethyllead(IV) most strongly at intermediate and high pH. The binding is pH dependent due to competitive protonation of the sulphydryl group at low pH and competitive complexation of [Me$_3$Pb] by hydroxide ion at high pH. At low pH, there is also some complexation by the carboxylate groups.[200]

Mercury selenide reacts with diodosilane at 120° in benzene to afford a polymer which on heating depolymerises to yield trimeric

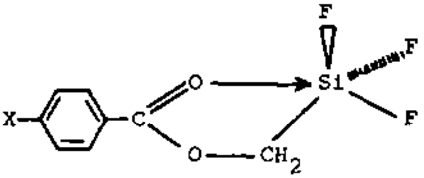


(87)

$(H_2SiSe)_3$.[201] $Me_4Sn_4Se_6$, from $MeSnBr_3$ and NaHSe in water, has the adamantane structure (87).[202]

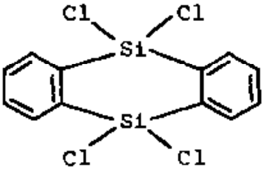
4.4.8 Bonds to Halogen

Electron diffraction data for dimethyldichlorosilane yield the following values: Si-C = 1.858(4)Å, Si-Cl = 2.053(2)Å, ClSiCl = 101(2)°, and CSiC = 109(4)°.[203] The structures of four organosilyl trihalides have been determined. The conformation of (dichloromethyl)trichlorosilane is unambiguous staggered, with the barrier to internal rotation about the Si-C bond estimated to be between 10.5 and 13.0 kJ mol^{-1}. The Si-C bond distance of 2.024(9)Å is in line with the gradual decrease observed from the $MeSiCl_3$ to Cl_3CSiCl_3.[204] The Si-C bond distance in (gem-difluorocyclopropyl)trichlorosilane is 1.84(5)Å.[205] The orientation of the Si-C bond in allyltrifluorosilane is such as to optimise interaction of the Si-C bonding electrons with the π system of the C=C double bond.[206] The three (4-halogenobenzoyloxymethyl)trifluorosilanes, $4\text{-}XC_6H_4CO_2CH_2SiF_3$ (X = F,Cl,Br) have a five-coordinated structure (88), in which the silicon atom is situated at the centre of a trigonal bipyramid.[207]



(88)

The energy difference between the trans and gauche isomers of ethylfluorosilane is 55±50 cal mol^{-1} (gauche isomer more stable (microwave).[208] 9,9,10,10-Tetrachloro-9,10-disiladihydroanthracene (89) is non-planar, the central ring having the boat conformation.[209]



(89)

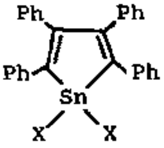
Methanolysis of $(Me_3Si)_3CSiPhI$ is not significantly accelerated by sodium methoxide, indicating ionisation as the rate-determining step (cf. methanolyses of the corresponding nitrate and bromide which are markedly accelerated by sodium methoxide).[210] U.v. irradiation of $(Me_3Si)_3CSiPh_2I$ in methanol, n-hexane, carbon tetrachloride, ether and PhOMe can be interpreted in terms of the formation of cationic as well as free-radical organosilicon intermediates, i.e.:[211]

$$\begin{array}{lcc} \geqslant\mathrm{Si{-}I} \xrightleftharpoons{h\nu} & [\geqslant\mathrm{Si}\cdot\ \cdot\mathrm{I}] \rightarrow & [\geqslant\mathrm{Si}^{+}\ \mathrm{I}^{-}] \\ & \downarrow & \downarrow \\ & \text{products} & \text{products} \end{array}$$

Codeposition of ammonia and silicon(IV) fluoride in inert matrices at dilutions as high as 1/1/4000 give spectra assignable to the 1:1 adduct $SiF_4 \cdot NH_3$, as well as the previously assigned 1:2 adduct. The spectra suggest a trigonal bipyramidal arrangement about the central silicon, with the ammonia ligand in the axial position. Codeposition of ammonia and silicon(IV) chloride give product bands, but only at relatively high concentrations, which may also be ascribed to a 1:1 adduct but considerably less strongly bound. No adduct is formed between silicon(IV) fluoride and dimethyl ether.[212] The matrix reaction of caesium fluoride and methylfluorosilanes leads to the formation of $MeSiF_4^-$ and $Me_2SiF_3^-$ anions. Distinct anions containing more than two methyl groups and $MeSiClF_3^-$ could not be formed. The C_{2v} structure was preferred for the $MeSiF_4^-$ anion, whilst no structural information could be gleaned for $Me_2SiF_3^-$.[213]

Crystals of hydrazinium hexafluorogermanate(IV) monohydrate comprise discrete anions and cations and water molecules, interconnected by a three-dimensional network of N-H---O and N-H---F hydrogen bonds.[214]

Mixed tin bromide iodides are not formed in mixtures of tin(IV) bromide and iodide.[215] New second and third stage intercalates of trimethyltin chloride and tin(IV) chloride into graphite have been prepared by irradiation in stringently dry carbon tetrachloride using a high pressure mercury lamp for 3-40 days. In the Mössbauer spectra, a decrease in isomer shift and absence of a quadrupole splitting for the tin(IV) chloride intercalate implies donation of electrons from graphite to guest with the retention of overall tet ahedral symmetry. The corresponding changes for the trimethyltin chloride intercalate may rather imply a difference in geometry upon intercalation.[216] The direct and indirect coupling constants between tin and hydrogen atoms in $MeSnCl_3$ and Me_3SnCl partially oriented in nematic phases have been separated by the dilution spinning method. The structural parameters obtained are comparable to those from gas phase studies.[217] Methyltin trichloride is the product of alkylation of tin(II) chloride by methylcobalamin in aqueous hydrochloric acid under aerobic conditions. The reaction follows a second-order rate expression, and is first-order in both reactants. Reaction does not occur under anaerobic conditions, but does occur in the presence of stoichiometric ammounts of aquocobalamin. The mechanism appears to involve direct bimolecular homolytic attack by $SnCl_2$ at the saturated carbon centre producing a strongly reducing methyltin(III) radical.[218] The stannoles (<u>90</u>) (X = I,Br) can be derivatised into a wide range of products in which X = N_3, NCS,SCN,OAc,S_2CNEt_2,NMe_2,PPh_2, and F.[219]



(<u>90</u>)

The adducts $SnCl_4.L_2$ (L = DMF,DMA,DMSO) and $SnBr_4.2DMF$ are isolated as the <u>cis</u> isomers from a wide range of solvents (CH_2Cl_2, $CHCl_3$,MeCN,Et_2O,EtOH,Et_2CO_3), but undergo transformation in the solid state to the <u>trans</u> isomers. The <u>cis</u> $SnBr_4.2DMA$ adduct also exhibits a solid-state transition which cannot unequivocally be characterised as an isomerisation.[220] The complex, $SnCl_4.4C_6H_{11}OH$, prepared from its components, has a centre of symmetry at the tin atom with two <u>trans</u> oxygen and four chlorine atoms in an octahedral arrangement. The two other cyclohexanol molecules are linked by hydrogen bonds to the $[SnCl_4.2C_6H_{11}OH]$ molecules. Further OH---Cl hydrogen bonds link the structure.[221] The structures of the two hexachlorostannate(IV) salts, Me_2 $Me_2NH_2{}^+SnCl_6{}^-$ [222] and $Et_3NH^+SnCl_6{}^-$ [223] have been determined. In the former, anions and cations are connected by a weak bifurcated hydrogen bond. In the latter, each anion is associated with two cations centrosymmetrically through bifurcated hydrogen bonds to four of the chlorine atoms leaving two unengaged. The bifurcation is nearly symmetrical, with a nearly planar N-H---2Cl group.

4.4.9 Bonds to Main Group Metals

X-ray studies of benzene, hexane and THF solutions of Et_3GeLi yield radical distribution functions which show directly that molecules associate in solution. The associated structures are, however, different in hydrocarbon and electron donor solvents. Nearest neighbour distances between the germanium atoms of coupled molecules is 4.5Å in benzene and hexane, and 4.0Å in THF. Diameters of the aggregates are estimated as 12.5-14Å in hydrocarbon solvents and 10Å in THF.[224] Ph_3SnLi reacts with carbon disulphide giving the salt $[Ph_3Sn^-CS_2^-]Li^+$, which reacts with alkyl halides triphenylstannane dithiocarboxylates, Ph_3SnCS_2R.[225]

The first magnesium-germanium bonded compound, $(Me_3Ge)_2Mg.2DME$, has been obtained as colourless crystals by treating the mercurial $(Me_3Ge)_2Hg/DME$ with metallic magnesium. Decomposition occurs immediately upon contact with air.[226] Bis(trimethylsilyl)- and bis(trimethylgermyl)mercury are both readily obtained in high yields by the reaction of the trimethylmetal chloride with lithium amalgam.[227] The structures of both $(Ph_3Ge)_2Hg$[228] and $[(C_6F_5)_3Ge]_2Hg$[229] have been reported. In each, the GeHgGe system is practically collinear. The latter molecule has crystallographic C_2 symmetry. The orientation of the pentafluorophenyl groups (as calculated by the atom-atom potential method) is, however, not the most favourable due to the formation of two intramolecular Ge---F and Hg---F secondary bonds which fix the aryl rings. This results in increasing shielding of the mercury atom, and raises the electron density on both germanium and mercury. Both factors lead to an increase in the thermal stability and chemical inertness of the compound towards nucleophiles compared to the phenyl analogue.

Reaction of $(Me_3Si)_3SiLi$ (isolated as a tri-THF solvate) with boron halides, methoxides, alkyls and hydrides leads to the formation of Si-B bonded compounds, eg. $Me_2B-Si(SiMe_3)_3$, 9-$[(Me_3Si)_3Si]$-9-BBN, $(Me_3Si)_3Si-B(NMe_2)_2$, $[(Me_3Si)_3Si]_2-BNMe$, and $[(Me_3Si)_3Si]-BOMe$.[230] The system $TiCl_4/Al(SiMe_3)_3.Et_2O$ (5:2) is a suitable catalyst for the polymerisation of ethylene.[231]

The synthesis of $Me_3SnB(NR_2)_2$, $Me_3SnBCl(NR_2)$ and $(Me_3Sn)_2BNR_2$ has been accomplished by treatment of Me_3SnLi with the appropriate aminochloroboranes. The former stannylboranes are relatively thermally stable. The Sn-B bonds are cleaved by hydrogen, chalcogens and alcohols.[232] Reaction of Me_3SnLi with borane-THF yields the salt, $Li[H_3B\text{-}SnMe_3]$. Multinuclear n.m.r. data for a large number of stannylboranes have been reported.[233]

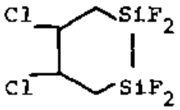
γ-Irradiation of solid solutions of hexamethyldisilane and digermane in CCl_3F at 77K generates $Me_6M_2^+$ species, whose e.s.r. parameters establish that the unpaired electron is localised in a σ-bonding orbital between the two metal atoms.[234] Analysis of the methyltin hyperfine tensor components of $Me_6Sn_2^+$ generated similarly shows that the metal-metal orbital is largely $4p_s + 4p_z$ in character, and that the 4S contribution is negligible. It was inferred that the configuration about each tin atom is nearly planar.[235]

An electron diffraction study of Si_3Cl_8 gives values of SiSiSi as 118.7(16)° and Si-Si = 2.329(7)Å, very similar to other disilanes.[236] Aluminium(III) chloride catalyses skeletal rearrangement of permethylated acyclic polysilanes. The linear polysilanes, $Me(Me_2Si)_nMe$ ($n = 4\text{-}10,12$) undergo rearrangement to branched isomers in almost quantitative yield. When $n = 4\text{-}6$, the products are $(Me_3Si)_3SiMe$, $(Me_3Si)_4Si$ and $(Me_3Si)_3SiSiMe_2SiMe_3$, respectively as single isomers. When $n = 7\text{-}9$, conversion leads to an equilibrium mixture each consisting of a pair of branched isomers, viz. $(Me_3Si)_2SiSiMe_2SiMe_2SiSiMe_3$ + $(Me_3Si)_3SiSiMe(SiMe_3)_2$, $(Me_3Si)_3SiSiMe_2SiMe(SiMe_3)_2$ + $[(Me_3Si)_3Si]_2$, and $(Me_3Si)_3SiSiMe_2SiMe_2SiMe(SiMe_3)_2$ + $[(Me_3Si)_3Si]_2SiMe_2$, respectively. The compounds, $[(Me_3Si)_3SiSiMe_2]_2$ and $[(Me_3Si)_3SiSiMe_2SiMe_2]_2$ are obtained as single products when n = 10 and 12, respectively.[237]

Octa-iso-propylcyclotetrasilane has been obtained by the reaction:

$$4\,{}^{i}Pr_2SiCl_2 \;+\; 8Li \;\rightarrow\; ({}^{i}Pr_2Si)_4 \;+\; 8LiCl.$$

Ring-opening occurs readily with various reagents including hydrogen chloride, acetyl chloride, aluminium(III) chloride, iodine and aqueous iodine. Displacement of propyl groups from silicon was not observed.[238] Permethylated cyclosilanes with ring sizes varying from five to thirtyfive silicon atoms are formed when dimethyldichlorosilane is added slowly to a Na/K alloy in THF.[239] Treatment of benzene suspensions of the perphenylated cyclosilanes, $(Ph_2Si)_n$ (n = 4-6) with anhydrous and iodine-free aluminium(III) iodide together with passage of hydrogen iodide gives the corresponding periodated cyclosilanes in quantitative yield. The presence of iodine leads to ring cleavage.[240] The six-membered $[Si_6]$ ring in $(Ph_2Si)_6$.heptabenzene has a centrosymmetric chair conformation.[241] Crystals of cis-4,5-dichloro-1,1,2,2-tetrafluoro-1,2-disilacyclohexane (91) comprise enantiomeric pairs of molecules related by the n glide symmetry. The conformation of the six-membered ring is close to a half-chair, with the disilane part of the ring considerably flattened.[242]



(91)

$I(Ph_2Ge)_4I$ has an 'all trans' structure with a fully staggered conformation of substituents.[243] The five-membered ring in cyclo-$[(Ph_2Ge)_4Se]$ is approximately planar.[244] In cyclo-$(Ph_2Ge)_6$.2toluene, the six-membered $[Ge]_6$ ring is sandwiched between the two toluene solvate molecules.[245]

The germasilanes, $R_3SiGePh_3$ (R = Me,Et), undergo cleavage in NaOMe/MeOH to give triphenylgermane. From rate measurements and solvent isotope effects, it was concluded that a Ph_3Ge^- anion separates in the rate-determining transition state, the mechanism being either:

$$\begin{tikzcd}
MrO^- + Me_3SiGePh_3 \arrow[r, shift left, "fast"] & {[(MeO)Me_3SiGePh_3]^-} \arrow[l, shift left] \arrow[d, "slow"] \\
 & MeOSiMe_3 + Ph_3Ge^- \arrow[d, "{MeOH,\ fast}"] \\
 & Ph_3GeH + MeO^-
\end{tikzcd}$$

or

$$\begin{tikzcd}
MeO^- + Me_3SiGePh_3 \arrow[r] & {[MeO \text{——} \cdot Me_3Si\text{-----}GePh_3]^-} \arrow[d, "slow"] \\
 & MeOSiMe_3 + Ph_3Ge^- \arrow[d, "{MeOH,}"', "fast"] \\
 & MeO^- + Ph_3GeH
\end{tikzcd}$$

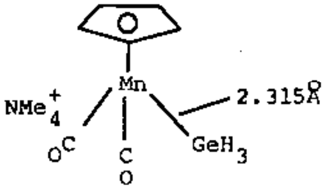
An unusually large steric effect was observed, with $Me_3SiGePh_3$ being methanolysed ca. 1300 times as reactive as the ethyl analogue.[246]

The structures of the compounds $(K\text{-}2,2,2\text{-crypt})_2Sn_4.en$ and $(Na\text{-}2,2,2\text{-crypt})_2Ge_4$ (crypt = $N(C_2H_4OC_2H_4OC_2H_4)_3N$; en = ethylenediamine), containing the Sn_4^{2-} and Ge_4^{2-} anions, respectively, have been determined. The Sn_4^{2-} anion, an 18 electron tetrahedral cluster, is only slightly distorted from T_d towards C_{2v} symmetry, with one edge shorter than the other five. The actual structure bears little resemblance to the predicted minimum energy structure. (a compressed tetrahedron with four short and two long bonds). E.s.r. spectra show no evidence for unpaired electrons.

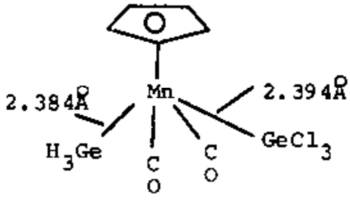
The Ge_4^{2-} anion is slightly elongated towards C_{3v} symmetry.[247] The anions Sn_4^{2-}, $TlSn_8^{5-}$, $Sn_{9-x}Ge_x^{4-}$ (x = 0-9) and, $SnTe_4^{4-}$ have been studied by tin-119 n.m.r.[248] Relativistic parametized extended Hückel calculations have been reported for the homonuclear clusters, Ge_9^{4-}, Ge_9^{2-}, Sn_4^{2-}, Sn_9^{2-}, Sn_9^{4-}, Pb_5^{2-}, Pb_9^{4-}, and the heteronuclear clusters $PbSn_4^{2-}$, $SnGe_8^{4-}$, $GeSn_8^{4-}$, $PbSn_8^{4-}$ and $TlSn_8^{5-}$, as well as the exopolyhedral cluster $MePb_9^{3-}$.[249]

4.4.10 Bonds to Transition Metals

The reaction of $[(MeC_5H_4)Mn(CO)_3]$ with GeH_3K gives the potassium salt $K[(MeC_5H_4)Mn(CO)_2GeH_3]$, which reacts with Me_4NCl and $GeCl_4$ forming (<u>92</u>) and (<u>93</u>), respectively. X-ray studies of both (<u>92</u>) and (<u>93</u>) show significant shortening of the Mn-Ge bond.[250] Reactions of $(OC)_5MnSiMe_3$ (<u>94</u>) with organic carbonyl compounds have been reported. Over two weeks at 5°C, (<u>94</u>) reacts with benzaldehyde to give the addition product (<u>95</u>), which undergoes

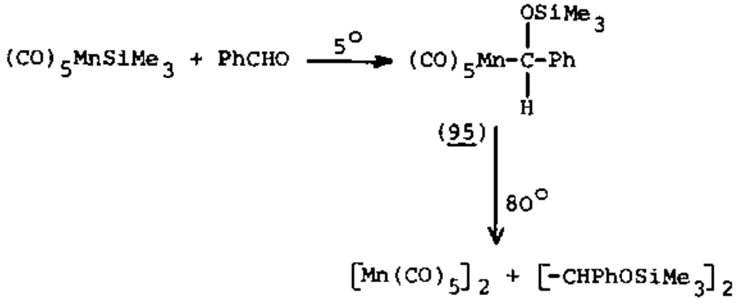


(92)

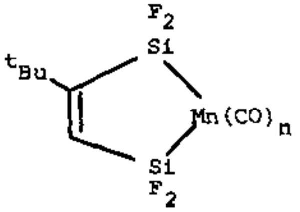


(93)

rapid homolysis at 80°:



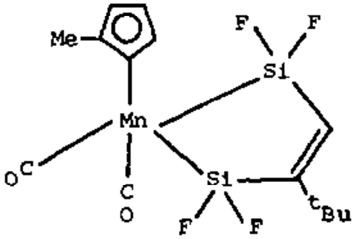
The reactions with p-MeC_6H_4CHO and p-$(Me_2N)C_6H_4CHO$ are much faster, yielding organometallic products which are much less stable towards homolysis. With butyraldehyde, $(CO)_5MnH$ and the (E)- and (Z) isomers of silylallylether are obtained. When this reaction is performed under an 10 atmospheres pressure of carbon monoxide, $(CO)_5MnCOCH^nPr(OSiMe_3)$ may be isolated, thus providing good evidence for the intermediate formation of $(CO)_5MnCH^nPrOSiMe_3$. Acetone, cyclohexanone and 2-methylcyclohexanone react similarly to give $(CO)_5MnH$ and trimethylsilyl enol ethers.[251] Irradiation of a mixture of $(MeC_5H_4)Mn(CO)_3$ and Ph_2SiH_2 in hexane results in the cleavage of one Si-H bond and the formation of $(MeC_5H_4)(CO)_2CH)MnSiHPh_2$, which can be converted to the halogen compounds $(MeC_5H_4)(CO)_2HMnSiXPh_2$ (X = F,Cl,Br,I) by the reagents Ph_3CBF_4/CH_2Cl_2, CCl_4 + trace PCl_5, Br_2 and I_2, respectively. Under 50-60 bar pressure of carbon monoxide at 100-120°, these compounds are cleaved to $(MeC_5H_4)Mn(CO)_3$ and Ph_2SiXH.[252] Irradiation of 1,1,2,2-tetrafluoro-1,2-disilacyclobutenes with molybdenum, manganese,iron and cobalt carbonyls leads to the formation of the products (96)-(98).[253]



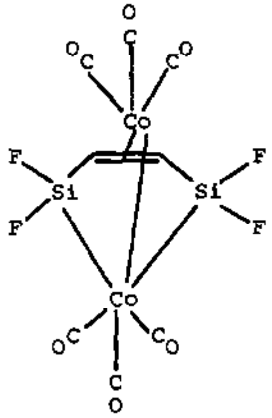
M = Mo, n = 5

M = Fe, n = 4

(96)



(97)

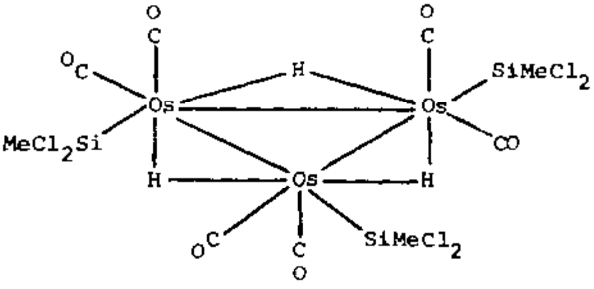


(98)

The reaction mechanism was rationalised by an initial dissociation of a carbonyl group from the transition metal, followed by oxidative-addition of the Si-Si bond to the coordinatively unsaturated metal carbonyl species. Petroleum ether slurries of $M_2Fe(CO)_4$ (M = Na,K) react with Me_3SiBr to form $(OC)_4Fe[SiMe_3]_2$. In THF, the potassium salt gives fair yields of $K^+[(OC)_4FeSiMe_3^-]$, which is also formed from $(OC)_4Fe(H)SiMe_3$ and potassium hydride. With sodium hydride, $Na^+[(CO)_4FeSiMe_3^-]$ is obtained.[254] The complex, $Ge[Co(CO)_7]_2$ may be prepared from GeF_4 and $Na[Co(CO)_4^-]$ or GeH_4 and $[Co_2(CO)_8]$. The molecule has approximately C_2 symmetry, with the Ge atom bridging the Co-Co bonds of two $[Co_2(CO)_7]$ units. The germanium bridge is unsymmetrical with Ge-Co distances of 2.38Å and 2.34Å. The corresponding bridging carbonyl group is also asymmetrically disposed but in the opposite sense.[255] The anion of $(NEt_4)[Ge\{Co_2(CO)_7\}\{Co_2(CO)_6\}$-

$[HgCo(CO)_4]\}]$ from Ge-F_4 and $Na[Co(CO)_4]$ in the presence of mercury, contains a common germanium atom bridging the Co-Co bonds of both a $[Co_2(CO)_7]$ and a $[Co_2(CO)_6]$ unit, which is also bridged by a $[HgCo(CO)_4]$ unit.[256] $[W_2(Br_2Ge)(CO)_{10}]$ exhibits the hitherto unknown $[GeW_2]$ three-membered ring. The carbonyl groups form a distorted square pyramid around each tungsten, with the metal approximately in the middle of a square plane.[257]

The reaction of $M_3(CO)_{12}$ (M = Ru,Os) with Cl_2XSiH (X = Me,Cl) in hexane under vacuum at elevated temperatures gives the complexes $M(CO)_4(SiXCl_2)_2$ and $M_3(\mu\text{-}H)_3(CO)_9(SiXCl_2)_3$. The structure of $Os_3(\mu\text{-}H)(CO)_9(SiMeCl_2)_3$ comprises two independent molecules which differ with respect to the orientation of the methyl and chlorine ligands. Each molecule has a triangular arrangement of osmium atoms in which each metal is presumably bridged by a hydrogen atom (99). The same structure persists in solution, except rapid rotation about the Os-Si bond occurs.[258]



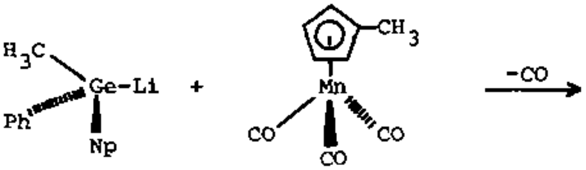
(99)

The iridium complex $(CO)(H)(PPh_3)_3Ir$ reacts with H_3MCl (M = Si, Ge; Cl = H,F,Cl,Br,I; M = Si, Q = SiH_3 or Me) giving the complexes $[IrH_2(CO)(PPh_3)_2(MH_2Q)]$. When M = Ge, the predominant isomer contains mutually trans phosphine lignads, whereas when M = Si, the predominant (and in some cases the sole) product contains cis phosphines.[259] Complexes in which platinum is chelated by phosphinoethylsilyl lignads have been obtained by the reaction:

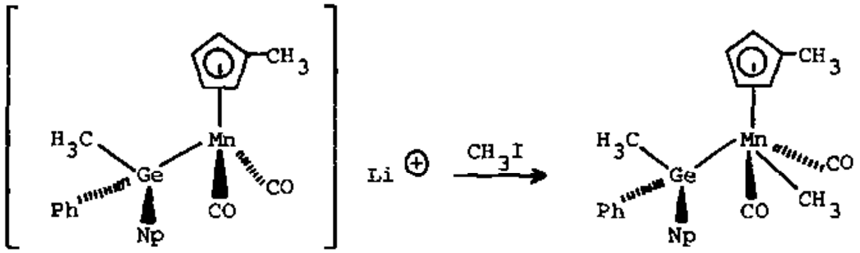
$$[Pt(COD)_2] \quad + \quad Ph_2PCH_2CH_2SiHR^1R^2 \xrightarrow{ether} cis\text{-}[Pt(PPh_2CH_2CH_2SiR^1R^2)_2]$$

The geometry was confirmed by X-ray for the case $R^1 = R^2 = Me$. When $R^1 \neq R^2$, racemic and mesodiastereoisomers are formed in varying ratios consistent with asymmetric induction during stepwise chelation.[260]

The optically active anion (100), as the tetraethylammonium salt, has been synthesised from the (R)-enantiomer of the germyllithium compound (101). The anion (100) reacts with methyl iodide affording the neutral complex (102):



(P)-(101)

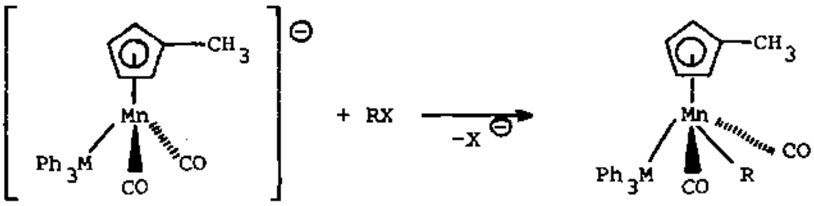


(S)-(100)

(102)

Np = 1-Naphthyl

The same type of reaction has also been employed for the preparation of the manganese complexes (103) and molybdenum and tungsten complexes (104).[261]



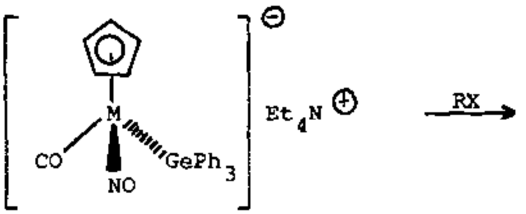
(103)

M = Si

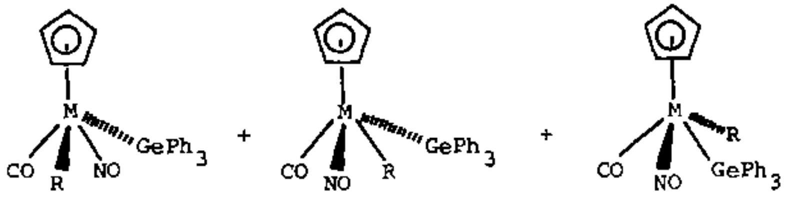
M = Ge

RX = CH_3I, $C_6H_5CH_2Br$

M = Si, R = CH_3; M = Si, R = $CH_2C_6H_5$; M = Ge, R = CH_3; M = Ge, R = $CH_2C_6H_5$



M = Mo
M = W
RX = CH_3I, $C_6H_5CH_2Br$



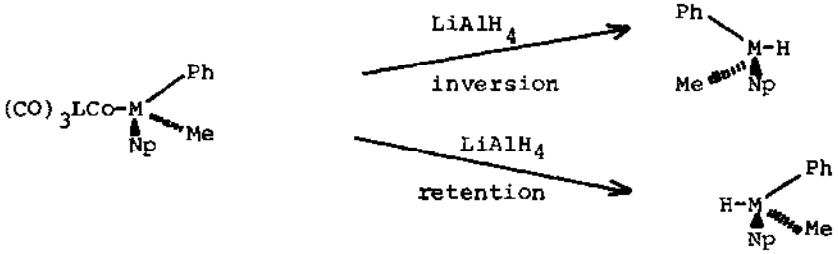
M = Mo, R = CH_3; M = Mo, R = $C_6H_5CH_2$;
M = W, R = CH_3 (104)

The cobalt complexes (105) have been obtained by the reaction:

$$[(CO)_3LCo]_2 + 2R^1R^2R^3MH \longrightarrow 2(CO)_3LCoMR^1R^2R^3 + H_2$$

M = Si; M = Ge (105)

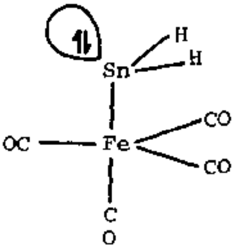
The stereochemical course of the $LiAlH_4$-cleavage are quite similar for both silyl- and germyl-cobalt complexes, but vary, depending on the ligands at cobalt, from a high degree of inversion of configuration to poor retention:[262]



The silyl-rhenium complexes, cis-$[C_5H_5)Re(CO)(H)(SiR_3)]$ (R = Ph, CH_2Ph) and cis-$[(C_5H_5)Re(CO)_2(SiPh_2H)(H)]$ have been obtained by uv irradiation if $(C_5H_5)(CO)_3Re$ and the appropriate silane. Trans-$[(C_5H_5)Re(CO)_2XH]$ (X = $SiPh_3$, $GeCl_3$, $GeBe_3$, $SnCl_3$) complexes were prepared by protonation of the corresponding anions. Reaction of $(C_5H_5)(CO)_3Re$ with Cl_3GeH or Ph_3SnH affords trans-$[(C_5H_5)Re(CO)_2(GeCl_3)_2]$ and trans-$[(C_5H_5)Re(CO)_2(SnPh_3)]_2$, respectively.[263]

Several new trihalogenstannate complexes have been prepared. The complexes $B_2[MoCl_4(SnX_3)_2]$ (B = NMe_4, NEt_4, NH_4; X = Br, Cl) are the first examples of molybdenum complexes containing such ligands. $[NEt_4]_2[MoCl_4(SnCl_3)_2]$ (and presumably the others in the series) is an effective reducing agent for small oxyanions such as ClO_4^-, ClO_3^-, NO_3^- and NO_2^-. A tentative conclusion from the study was that Mo(IV) is a particularly effective site at which oxoanions or other oxidised non-metals can bind, and that it allows rapid transfer of electrons from electron donor to the substrate.[264] Two n.m.r. studies of Rh-Sn-Cl systems have been reported. The species present in aqueous hydrochloric acid solutions of $RhCl_3$ and $SnCl_2$ have been investigated by tin-119 n.m.r., which indicate fast intramolecular scrambling of the ligands. A redox process between Rh(III) and tin(II) giving a Rh(I) complex with five tin(II) ligands occurs at a molar ratio of [Sn]:[Rh] = 6:1.[265] Tin-119 and phosphorus-31 n.m.r. data for the reaction of $[RhCl(NBD]_2$ with four equivalents of tertiary phosphine and two of tin(II) bromide suggests that halogen scrambling occurs during the preparation, resulting in the formation of a mixture of complexes containing $[SnBr_3]$, $[SnClBr_2]$, $[SnCl_2Br]$ and $[SnCl_3]$ as ligands.[266] The structure of $(NH_4)_4[OsCl(SnCl_3)_5]$ comprises two crystallographically independent complex anions with similar geometries, in which five $[SnCl_3]$ ligands and a chlorine form a slightly deformed octahedron around osmium.[267] The complex $SnCl[Mn(PPh_3)(CO)_4]_3$ has a distorted tetrahedral geometry at tin.[268]

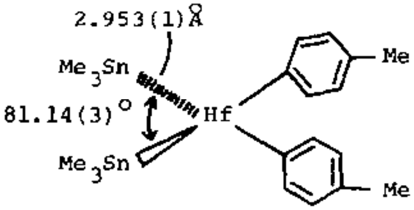
Extended Hückel MO calculations carried out on $[(H_2Sn)Fe(CO)_4{}^{2-}]$ show that the most stable geometry corresponds to a trigonal bipyramidal structure at iron with a highly pyramidal $[SnH_2]$ group in an axial position as in (106). The tin lone pair of electrons are essentially localised in a hybrid orbital on tin.



(106)

Another stable geometry has a basically trigonal $[SnH_2]$ group, with the two electrons in a $\underline{a}_2$ equatorial carbonyl-based orbital. However, there is a symmetry-imposed barrier on going from one geometry to another, i.e. there is a highly unusual double-well potential for pyramidalisation at tin.[269] As has been shown previously, the complexes $[Fe(CO)_4(SnR_2)]_2$ establish a dimer monomer equilibrium with the solvated, unbridged monomer $[Fe(CO)_4\{SnR_2(B)\}]$. For B = THF, pyridine, 4-MeC$_5$H$_4$NO, the monomer undergoes a two-electron reduction in the presence of strongly hydridic reagents such as sodium hydride, or by treatment with sodium amalgam. The complexes produced are proposed to contain the $[Fe(CO)_4(SnR_2)]^{2-}$ anion. The reduction process may be formulated as the population of a non-bonding $\underline{sp}^3$ lone-pair orbital on tin, with possible back-bonding. Spectroscopically, both iron and tin undergo a one-electron reduction. The $[Fe(CO)_4(SnR_2)]^{2-}$ anions have been isolated as sodium salts, which show tight ion-pairing in acetonitrile. In solution, the base appears to be cation-associated.[270]

Treatment of Hf(η-toluene)$_2$PMe$_3$ with Me$_6$Sn$_2$ at 45° leads to the formation of [Hf(η-toluene)$_2$(SnMe$_3$)$_2$], a $\underline{d}^2$ bent bis-arene, whose structure is illustrated in (107). The analogous zirconium complex was prepared similarly.[271]



(107)

The Group VI metal-lead complexes, $(C_5H_5)M(CO)_3PbR_3$ (M = Cr,Mo, W; R = Me,Et), have been obtained by metathesis from R_3PbCl. The methyllead compound is photochemically (and to a lesser extent) thermally unstable with respect to methyl group transfer giving $(C_5H_5)M(CO)_3Me$, lead metal and tetramethyllead. The related ethyl complexes behave differently, rearranging to $[(C_5H_5)M(CO)_3]_2PbEt_2$ and tetraethyllead. Treatment with sulphur dioxide gives the complexes $(C_5H_5)M(CO)_3(SO_2R)$.[272]

4.5 OXIDES, SULPHIDES, SELENIDES AND TELLURIDES

High-resolution, solid-state Silicon-29 n.m.r. continues to be applied to the study of silicate systems. The spectrum of the product of the reaction between zeolite Na-Y with silicon(IV) chlorides, highly crystalline essentially aluminium-free faujasite structure, exhibits a single sharp peak characteristic of regular Si(4Si) lattice ordering.[273] Detailed information concerning the Si-Al ordering in the aluminosilicate framework of zeolites can also be obtained by this technique. In particular, the arrangement of silicon and aluminiumatoms of an NaX zeolite with Si/Al = 1.4 was shown to be not centrosymmetrical.[274] Zeolites containing five-membered rings of silicon tetrahedra (Hz mordenite, Na-2S M-5, and H-ZSM-11) exhibit a spectral line at ca. -113ppm in contrast with other zeolites which do not contain this building unit (Na-A, Na-X, Na-Y and H-L), for which resonance occurs in the -80 - -106ppm range depending on the Si-Al ratio.[275]

Theoretical studies indicate that lattices of the chain and ring varieties of $CaSiO_3$ fit together with only a slight mis-match. High resolution electron microscopic studies of a sample undergoing conversion from chain-to-ring structure, however, indicate that intergrowths do not occur. Instead, the chain structure recrystallises via a glassy phase into the ring structure of the same composition.[276]

The direct trimethylsilylation of olivine yields partial trimethylsilyl derivatives of ortho- and disilicates, the unsilylated silanol groups are esterified with the alcohol used as the organic solvent. GC/mass spectral measurements indicate the presence of the tri-, di- and monoalkyl-substituted trimethylsilyl derivatives of monosilicic acid, $[SiO_4(SiMe_3)_{4-n}R_n]$ (n = 1-3), in addition to the fully silylated monomeric derivative, $[SiO_4(SiMe_3)_4]$. Dimeric derivatives have also been detected containing both the completely trimethylsilylated derivative $[Si_2O_7(SiMe_3)_6]$, and the alcohol-estified derivatives, $[Si_2O_7(SiMe_3)_{6-n}R_n]$ (n = 1-4). The ratio of esterified products varies with the volume of alcohol or water in the silylating reagent as well as the reaction time.[277]

Heating together α-quartz and Na_2O in a 1:2 molar ratio at 800° overnight under nitrogen affords crystalline sodium orthosilicate, Na_4SiO_4, containing discrete $[SiO_4]$ tetrahedra.[278] High-temperature trisodium hydrogen silicate dihydrate consists of chains of $[HSiO_4]^{3-}$ tetrahedra held together by Si-O---H-O-Si hydrogen bonds. Adjacent chains are linked by sodium atoms and by hydrogen bonds to water molecules.[279] All the metal atoms in Na_2MgSiO_4 are tetrahedrally coordinated. The structure is derived from the hexagonally close packed Würtzite structure by replacing sulphur by oxygen and zinc by sodium, magnesium and silicon. The conductivity (3.0×10^{-3} $(\Omega m)^{-1}$ at 573K) is attributed to diffusion in the 101 direction, in which there are chains of sodium atoms separated by distances of 3.21Å and 3.27Å. In order to move from one site to another, the sodium atoms must pass through unoccupied tetrahedra and/or octahedral sites of the framework.[280] Crystals of α-$CaSiO_3$ (ψ-Wollastonite) have been grown using a flux of $CaCl_2$. Four-layer, six-layer and disordered stacking types could be detected in different samples by XRD. One of the four-layer polytypes is composed of ternary rings of three $[Si_3O_9]$ tetrahedra and an apparent octahedral layer. The structure is therefore similar to that of $SrGeO_3$ except that the latter is of a six-layer type.[281] Metastable $SrSiO_3$ is formed during the course of the reaction between an equimolar mixture of $SrCO_3$ and SiO_2. The reaction proceeds in four stages:

$$2SrCO_3 + SiO_2 \rightarrow Sr_2SiO_4 + 2CO_2 \quad ...(1)$$

$$SrCO_3 + SiO_2 \rightarrow SrSiO_3(\text{metastable}) + CO_2 \quad ...(2)$$

$$SrSiO_3(\text{metastable} \xrightarrow{\text{transformation}} SrSiO_3(\text{stable}) \quad ...(3)$$

$$Sr_2SiO_4 + SiO_2 \rightarrow 2SrSiO_3(\text{stable}) \quad ...(4)$$

The overall reaction, (1) + (2), is best described by the Jander equation with an apparent activation energy of 215.5 kJ mol^{-1}, irrespective of the ball milling time. Reaction isotherms for (4) were best described by the Ginstling-Brownshtein equation with an activation energy of 510 kJ mol^{-1}.[282] The equilibrium diagram for the $SrSiO_3$-$BaGeO_3$ system shows four regions of solid solution, based on the ψ-Wollastonite forms of α-$BaGeO_3$, α-$SrSiO_3$ and $(Sr_{1-x}Ba_x)_3(Si_{1-x}He_x)_3O_9$ (x = 0.5 - 0.7), and a pyroxenoid β-, $BaGeO_3$.[283] The two new stable lead silicate phases, Pb_5SiO_7 and $Pb_{11}Si_3O_{17}$, have been observed in the PbO-$PbSiO_3$ system above 650°. The stability of the previously described phase, Pb_4SiO_6, could not be confirmed.[284] Lead "orthosilicate", 2PbO.SiO_2, contains $[Si_4O_{12}{}^{8-}]$ rin-s and oxide ions, but not $[SiO_4{}^{4-}]$ groups, and is therefore not a true orthosilicate. It would more properly be termed 'basic lead metasilicate' or 'Lead oxide metasilicate'.[285] The thermal behaviour upto 1000° of double silicates of the lanthanides with rubidium and caesium has been studied.[286]

The structures of several other silicate minerals have been determined including sodium β-hydrogenneatungstosilicate hydrate, $Na_9(\beta\text{-}SiW_9Os_4H).23H_2O$,[287] the new minerals, Jasmundite, $Ca_{22}(SiO_4)_8O_4S_2$, containing a mixture of orthosilicate, oxide and sulphur ions, and related to alinite, $Ca_{22}[(Si_{0.75}Al_{0.25})O_4]_8O_4Cl_2$,[288] medaite, manganese(II) vanadatopentasilicate, $(Mn_{5.774},Ca_{0.190},Fe_{0.035})$ $(V_{0.815},As_{0.188})$-$Si_5O_{18}(OH)$, containing the vanadatopentasilicate anion, $[VSi_5O_{18}(OH)]^{12-}$ with some As-for-V substitution,[289] dicupro(II)-18-molybdosilicate(12-), $(NH_4)_{12}[Cu_2Si_2Mo_{18}O_{66}].14H_2O$, in which each $[SiO_4]$ tetrahedron is surrounded by nine $[MoO_6]$ octahedra. The two $[SiO_6]$ octahedra, which share a common edge are attached to both silicon atoms.[290] A single crystal Raman study of the layer silicate Apophyllite, $KCa_4(Si_4O_{10})_2(F/OH).8H_2O$, has been carried out.[291] Methods of preparation and XRD data have been described for pollucite, $C_5AlSi_2O_6$.[292]

Synthetic dimercury(II) germanate(IV), Hg_2GeO_4, is isostructural with menardite, Na_2SO_4, and comprises isolated $[GeO_4]$ tetrahedra and mercury atoms with an irregular six-fold coordination.[293] The dependence of the phases formed in the Na_2O-Ln_2O_3-GeO_2-H_2O system on the size of the lanthanide has been investigated at 250° at a molar ratio Ln_2O_3:GeO_2 = 1:7. The ranges of existence of the germanates, $Ln_2O_3.2GeO_2$ (Ln = La-Tm,Y), $7Ln_2O_3.9GeO_2$ (Ln = La-Nd), $Na_2O.Ln_2O_3.2GeO_2$ (Ln = Tb-Lu,Y), $Na_2O.3Ln_2O_3.4GeO_2.nH_2O$ (Ln = Sn-Tb), and $Na_2O.Ln_2O_3.4GeO_2$ (Ln = Tm-Lu), were determined.[294] In the equilibrium state, only α-$PbGeO_3$ and R-GeO_2 exist in the GeO_2-$PbGeO_3$ system. The equilibrium in the annealing of $xPbCO_3.(100-x)Q$-GeO_2 ($0 \leqslant x \leqslant 50$) proceeds extremely slowly with the formation of the metastable phases, $PbGe_3O_7$ and $PbGe_4O_9$. Single crystals of two modifications of $PbGeO_3$, four modifications of $PbGe_4O_9$, and the rutile form of GeO_2 have been obtained by slowly cooling melts of GeO_2-PbO mixtures.[295] The structure of lead α-tetragermanate, α-$PbGe_4O_9$, is based on a mixed Ge–O lattice with the lead atoms situated in lattice vacancies formed by $[GeO_4]$ and $[GeO_6]$ polyhedra.[296] The solid phases, $PbSeO_3$ and $PbSeO_3.H_2SeO_3$, have been isolated from the PbO-SeO_2-H_2O system at 100°. Only $PbSeO_4$ could be observed in the PbO-SeO_3-H_2O system.[297] The defect structure of antimony oxide-tin oxide has been investigated by profile refinement of powder neutron diffraction data. The structure, based on the occupation by Sb(III) of interstitial positions within the rin(IV) oxide rutile-type lattice, was used to rationalise some of the properties of the mixed oxide.[298]

Crystalline Ba_3SiS_5 has a structure based on a partly filled Sb_3Ca_5 type.[299] Cu_8SiS_6 is isotypic with $Ag_8GeSe_6(\beta')$ and contains $[SiS_4]$ tetrahedra.[300] Pure thiohydroxygermanates can be prepared from aqueous solution by reaction of stoichiometric amounts of either sodium sulphide and GeO_2 or sodium hydroxide and GeS_2. The structure of $Na_2GeS_2(OH)_2.5H_2O$ contains the novel mononuclear $[GeS_2(OH)_2]^{2-}$ anions, which are connected to the octahedrally coordinated sodium cations by an extensive system of S---HO and O---HO hydrogen bonds.[301] $Tl_2Sn_2S_5$ has been prepared by fusion of stoichiometric amounts of the two sulphides at 300° w with prolonged heating. The tin atoms are coordinated by five sulphur atoms forming a considerably distorted trigonal bipyramid. The $[SnS_5]$ bipyramids are linked by common edges into chains extending in the [110] and [$1\bar{1}0$] direction, and are cross-linked by sharing the remaining equatorial vertices of the $[SnS_5]$ bipyramids into a three-dimensional framework.[302] Crystalline $Tl_4Ge_4Se_{10}$, prepared by fusion of Tl_2Se and GeS_2, is characterised by adamantane-like $[Ge_4Se_{10}]^{4-}$ and thallium(I) cations.[303] $Na_6Si_2Te_6$ is isotypic with $K_6Sn_2Te_6$, containing $[Si_2Te_6]^{6-}$ anions.[304] The interaction of Me_3SiCl with cis- and trans-

$(HO)_2TeF_4$ and cis- and trans-$HOTeF_4(OMe)$ affords cis- and trans-$(Me_3SiO)_2TeF_4$ and cis- and trans-$(Me_3SiO)TeF_4(OMe)$ respectively.[305]

REFERENCES

1 R. S. Hutton, H. D. Roth and S. Chari, J. Phys. Chem., 85(1981)753.

2 P. J. Stang and M. R. White, J. Am. Chem. Soc., 103 (1981)5429.

3 G. Becker, G. Gresser and W. Uhl, Z. Naturforsch., 36b (1981) 16.

4 H. Oberhammer, G. Becker and G. Gresser, J. Mol. Structure, 75(1981) 282.

5 R. D. Brown, P. D. Godfrey and D. McNaughton, Aust. J. Chem., 34(1981) 465.

6 M.S. Gordon, J. Chem. Soc. Chem. Comm., (1981)890.

7 E.E. Siefert, S. D. Witt and Y. N. Tang, J. Chem. Soc., Chem. Comm., (1981) 217.

8 C. C. Shiau, T. L. Hwang and C. S. Liu, J. Organomet. Chem., 214(1981)31.

9 I. M. T. Davidson and N. A. Ostah, J. Organomet. Chem., 206(1981)149.

10 A. Chihi and W. P. Weber, J. Organomet. Chem., 210(1981) 163.

11 A. Chihi and W. P. Weber, Inorg. Chem., 20(1981)2822.

12 M. I. Ishikawa, K. I. Nakagawa and M. Kumada, J. Organomet. Chem., 214(1981)277.

13 N. Ishikawa, K. I. Nakagawa, S. Katayama and M. Kumada, J. Organomet. Chem., 216(1981)C48.

14 J. Drahnak, J. Michl and R. West, J. Am. Chem. Soc., 103 (1981)1845.

15 R. T. Conlin and D. L. Wood, J. Am. Chem. Soc., 103(1981) 1843.

16 H. M. Frey, A. Kashoulis, L. M. Ling, S. P. Lodge, I. M. Pidgeon and R. Walsh, J. Chem. Soc., Chem. Comm., (1981) 915.

17 G. Maier, G. Mihm and H. P. Reisenauer, Angew. Chem., Int. Ed. Engl., 20(1981)597.

18 P. John, B. G. Gowenlock and P. Groome, J. Chem. Soc., Chem. Comm., (1981)806.

19 N. Wiberg, G. Preiner and O. Schieda, Chem. Ber., 114 (1981)2087.

20 N. Wiberg, G. Preiner, O. Schieda and G. Fischer, Chem. Ber, 114(1981)3505.

21 N. Wiberg, G. Preiner and O. Schieda, Chem. Ber., 114 (1981)3518.

22 A. G. Brook, F. Abdesaken, B. Gutekunst. G. Gutekunst and R. K.Kallury, J. Chem. Soc., Chem. Comm., (1981)191.

23 W. Ando, A. Sekiguchi and T. Sato, J. Am. Chem. Soc., 103 (1981)5573.

24 M. S. Gordon and R. D. Koob, J. Am. Chem. Soc., 103(1981) 2939.

25 G. Trinquier and J. P. Malneu, J. Am. Chem. Soc., 103 (1981)6313.

26 M. S. Gordon and J. A. Pople, J. Am. Chem. Soc., 103 (1981)2945.

27 R. West and M. J. Fink, Science, 214(1981)1343.

28 W. Ando, H. Tsumaki and M. Ikeno, J. Chem. Comm., (1981) 597.

29 J. H. Miller and L. Andrews, J. Mol. Structure, 77(1981) 65.

30 M. Schriewer and W. P. Neumann, Angew. Chem., Int Ed. Engl., 20(1981)1019.

31 A. Castel, J. Escudie, P. Riviere, J. Satge, M. N. Bochkarev, L. P. Maiorova and G. A. Razuvaev, J. Organomet. Chem., 210(1981)37.

32 G. Trinquier, M. Pelissier, G. Saint-Roch and H. Lavayssiere, J. Organomet. Chem., 214(1981)169.

33 J. Barrau, H. Lavayyssiere, G. Dousse, C. Couret and J. Satge, J. Organomet. Chem., 221(1981)271.

34 P. Riviere, A. Castel and J. Satge, J. Organomet. Chem., 212(1981)351.

35 H. Schnöckel, J. Mol. Structure, 70(1981)183.

36 A. Krantz and J. Laureni, J. Am. Chem. Soc., 103(1981) 486.

37 H. Bock, W. Ried,and U. Stein, Chem. Ber., 114(1981)673.

38 H. Bock, T. Hirabayashi and S. Mohmand, Chem. Ber., 114 (1981)2595.

39 S. Mohmand, T. Hirabayashi and H. Bock, Chem. Ber, 114 (1981)2609.

40 R. D. Brown, P. D. Godfrey, R. Chapman and D. McNaughton, J. Am. Chem. Soc., 103(1981)5711.

41 M. H. Lietzke and C. Mullins, J. Inorg. Nucl. Chem., 43 (1981)1769.

42 G. Paioro and L. Pandolfo, Angew. Chem., Int. Ed. Engl., 20(1981)288,289.

43 W. Bludssus and R. Mews, Chem. Ber., 114(1981)1539.

44 A. Sekiya and D. D. Desmarteau, Inorg. Chem., 20(1981)1.

45 S. Konaka, K. Yamagata and M. Kimura, Bull. Chem. Soc. Jpn., 54(1981)2435.

46 B. Beagley, M. O. Jones and P. Yavari, J. Mol. Struct., 71 (1981)203.

47 Q. Shen, J. Mol. Struct., 75(1981)303.

48 Ø. Trongmo, Q. Shen, K. Hagen and R. Seip, J. Mol. Struct., 71(1981)185.

49. W. V. F. Brooks, J. A. Gosselin, M. A. Mohammadi and J. D. Thibault, J. Mol. Struct., 72(1981)17.

50 Q. Shen, R. L. Hilderbrandt and K. Hagen, J. Mol. Struct., 71(1981)161.

51 M. Nakata, T. Fukuyama, C. J. Wilkins and K. Kuchitsu, J. Mol. Struct., 71(1981)195.

52 L. Fernholt, S. Samdal and R. Seip, J. Mol. Struct., 72 (1981)217.

53 M. Hargattai, S. Samdal and R. Seip, J. Mol. Struct., 71(1981)147.

54 R. L. Kuczkowski, F. J. Lovas, R. D. Suenram, R. P. Latimer, K. W. Hillig and A. J. Ashe, J. Mol. Struct., 72(1981)143.

55 I. S. Ignatyev, A. N. Lazarev, M. B. Smirnov, M. B. Alpart and B. A. Trofimov, J. Mol. Struct., 72(1981)25.

56 J. L. Atwood, W. E. Hunter, A. H. Cowley, R. A. Jones and C. A. Stewart, J. Chem. Soc., Chem. Comm., (1981)925.

57 P. G. Harrison, J. Organomet. Chem., 212(1981)183.

58 T. S. Dory, J. J. Zuckerman, C. D. Hoff and J. W. Connolly, J. Chem. Soc., Chem. Comm., (1981)521.

57 F.X.Kohl and P.Jutzi, Chem. Ber., 114(1981)488.

58 P.G.Harrison, J. Organomet. Chem., 212(1981)183.

59 T.S.Dory, J.J.Zuckerman, C.D.Hoff and J.W.Connolly, J. Chem. Soc., Chem. Commun., (1981)521.

60 W.R.Bullard and M.J.Taylor, Aust. J. Chem., 34(1981)1337.

61 M.Veith, M. Grosser and O. Recktenwald, J. Organomet. Chem., 216(1981)27.

62 M.Veith and O.Recktenwald, Z. Naturforsch., 36b(1981)144.

63 N. Bruncks, W. W. Du Mont, J. Pickardt and G. Rudolph, Chem. Ber., 114(1981)3572.

64 P. A. W. Dean, D. D. Plillips and L. Polensek, Canad. J. Chem., 59(1981)50.

65 W. W. Du Mont and G. Rudolph, Z. Naturforsch., 36b(1981) 1215.

66 R. M. Braun and R. Hoppe, Z. anorg. allg. Chem., 478(1981) 7.

67 R. M. Braun and R. Hoppe, Z. anorg. allg. Chem., 480(1981) 81.

68 W. W. Du Mont and M. Grenz, Chem. Ber., 114(1981)1180.

69 I. R. Amiraslanov, N. Kh. Dzhafarov, G. N. Nazhafov, Kh. S. Mamedov, E. M. Movsumov and B. J. Usubakiev, J. Struct. Chem., 22(1980)104.

70 N. Kh. Dzhafov, I. R. Amiraslanov, G. N. Nadzhafov, E. M. Movsumov, F. R. Kerimova and K. S. Mamedov, J. Struct. Chem., 22(1981)245.

71 I. R. Amiraslanov, N. Kh. Dzhafarov, G. N. Nadzhafov, Kh. S. Mamedov, E. M. Movsumov and B. T. Usubaliev, J. Struct. Chem., 21(1980)109.

72 N. Kh. Dzafarov, I. R. Amiraslanov, G. N. Nadzhafov, E. M. Movsumov and Kh. S. Mamedov, J. Struct. Chem., 22(1981) 242.

73 P. Vasic, B. Prelesnik, R. Herak and M. Giric, Acta Crystallogr., B37(1981)660.

74 T. Birchall and J. J. Johnson, J. Chem. Soc., Dalton Trans., (1981)69.

75 S. I. Ishiguro and H. Ohtaki, Bull. Chem. Soc., Jpn., 54(1981)335.

76 K. Kogura, M. Okamoto, H. Kakihana and M. Maeda, J. Inorg. Nucl. Chem., 43(1981)1561.

77 R. H. Herber and G. Carrassquillo, Inorg. Chem., 20(1981) 3693.

78 S. del Bucchia, J. C. Jumas and M. Maurin, Acta Crystallogr., 37B(1981)1903.

79 I. G. Dance and P. J. Guerney, Aust. J. Chem., 34(1981)57.

80 T. Birchall, G. Denes, K. Ruebenbauer and J. Pannetier, J. Chem. Soc., Dalton Trans., (1981)1831.

81 T. Birchall, G. Denes, K. Ruebenbauer and J. Pannetier, J. Chem. Soc., Dalton Trans., (1981)2296.

82 H. M. M. Yeh and R. A. Geanangel, Inorg. Chim. Acta, 52(1981)113.

83 H. G. von Schnering, R. Nesper and H. Pelshenko, Z. Naturforsch., 36b(1981)1551.

84 N. N. Zhamskay, Russ. J. Inorg. Chem., 26(1981)780.

85 C. J. Kallendorf and B. S. Ault, J. Phys. Chem., 85(1981) 608.

86 H. Morikawa, M. Miyake, Y. Takagi and F. Marumo, J. Chem. Soc., Farad. Trans.1,77(1981)1967.

87 B. S. Ault, J. Phys. Chem., 85(1981)3083.

88 H. Bloom and M. S. White, Aust. J. Chem., 34(1981)479.

89 T. N. Bell, K. A. Perkins and P. G. Perkins, J. Chem. Soc., Fraad. Trans. I, 77(1981)1779.

90 M. Imachi, A. Nagayama, J. Nakagawa and M. Hayashi, J. Mol. Struct., 77(1981)81.

91 V. S. Mastriyukov, A. V. Golobinskii, E. G. Atavin, L. V. Vilkov, B. N. Cyvin and S. J. Cyvin, J. Struct. Chem., 20(1979)615.

92 S. Cradock, A. Fraser and D. W. H. Rankin, J. Mol. Structure, 71(1981)209.

93 S. Cradock, J. Koprowski and D. W. H. Rankin, J. Mol. Struct., 77(1981)113.
94 S. Cradock, D. C. McKean and M. W. MacKenzie, J. Mol. Struct., 74(1981)265.
95 Y. M. Choo and K. M. Mackay, J. Chem. Res. (S), (1981)76.
96 E. A. V. Ebsworth, S. G. D. Henderson and D. W. H. Rankin, Inorg. Chim. Acta, 48(1981)159.
97 E. A. V. Ebsworth, H. M. Ferrier and T. E. Fraser, J. Chem. Soc., Dalton Trans., (1981)836.
98 J. Grobe and D. Le Van, Z. Naturforsch., 36b(1981)866.
99 B. Beagley, R. G. Pritchard, C. Eaborn and S. S. Washburne, J. Chem. Soc., Chem. Comm., (1981)710.
100 W. Clegg, U. Klingebiel, J. Neemann, G. M. Sheldrick and N. Vater, Acta Crystallogr., 37B(1981)987.
101 H. Köpf and J. Pickardt, Z. Naturforsch., 36b(1981)1208.
102 A. V. Belyakov, L. S. Khaikin, L. V. Vilkov, E. T. Bogoradovskii and V. S. Zavgorodnii, J. Mol. Struct., 72(1981)233.
103 L. J. Krause and J. A. Morrison, J. Am. Chem. Soc., 103(1981)2995.
104 R. Eujen, H. Bürger and H. Oberhammer, J. Mol. Struct., 71(1981)109.
105 M. J. Adam, B. D. Pate, T. J. Ruth, J. M. Berry and L. D. Hall, J. Chem. Soc., Chem. Comm., (1981)733.
106 W. Althoff, M. Fild and R. Schmutzler, Chem. Ber., 114 (1981)1082.
107 S. Mohr, J. Jander and H. P. Latscha, Z. Naturforsch., 36b(1981)901.
108 T. A. K. Al-Allaf, C. Eaborn, K. Kundu and A. Pidcock, J. Chem. Soc., Chem. Comm., (1981)55.
109 C. Eaborn, K. Kundu and A. Pidcock, J. Chem. Soc., Dalton Trans., (1981)1223.
110 E. A. V. Ebsworth, E. K. Murray, D. W. H. Rankin and H. E. Robertson, J. Chem. Soc., Dalton Trans., (1981)1501.
111 G. S. Laurenson and D. W. H. Rankin, J. Chem. Soc., Dalton Trans., (1981)425.
112 G. S. Laurenson and D. W. H. Rankin, J. Chem. Soc., Dalton Trans., (1981)1047.
113 W. Clegg, U. Klingebiel, G. M. Sheldrick and N. Vater, Z. anorg. allg. Chem., 482(1981)88.
114 S. N. Gurkova, A. I. Gusev, N. V. Alekseev, Yu. M. Varezhkin, M. M. Morgunova and D. Ya. Zhinkin, J. Struct. Chem., 22(1981)142.
115 V. E. Shklover, P. Adaasuren, G. V. Kotrelev, E. A. Zhdanova, V. I. Svistunova and Yu. T. Struchkov, J. Struct. Chem., 21,(1980)198.
116 W. Clegg, U. Klingebiel, G. M. Sheldrick and P. Werner, Angew. Chem., Int. Ed. Engl., 20(1981)384.
117 W. Clegg, M. Nottemajen, G. M. Sheldrick and N. Vater, Acta Crystallogr., 37B(1981)986.
118 V. E. Shklover, Yu. T. Struchkov, G. V. Solomatin, A. B. Zachernyuk and A. A. Zhdanov, J. Struct. Chem., 21(1980) 772.
119 V. E. Shklovev, Y. T. Struchkov, B. A. Astapov and K. A. Andrianov, J. Struct. Chem., 20(1979)77.
120 V. E. Shklover, Yu. T. Struchkov, G. V. Kohelev, W. Kazakova and K. A. Andrianov, J. Struct. Chem., 20(1979)73.
121 U. Wannagat, T. Blumenthal, G. Eisole, A. König and R. Schacter, Z. Naturforsch., 36b(1981)1479.
122 Y. F. Beswick, P. Wisian-Neilson and R. H. Neilson, J.

Inorg. Nucl. Chem., 43(1981)2639.

123 P. Paetzola and T. von Bennigsen-Mackiewicz, Chem. Ber., 114(1981)298.

124 R. Koster and G. Seidel, Angew. Chem., Int. Ed. Engl., 20(1981)972.

125 J. Neemann and U. Klingebiel, Chem. Ber., 114(1981)527.

126 R. H. Neilson, Inorg. Chem., 20(1981)1679.

127 A. H. Cowley, M. Lattman and J. C. Wilburn, Inorg. Chem., 20(1981)2916.

128 S. R. Wade and G. R. Willey, J. Chem. Soc., Dalton Trans., (1981)1264.

129 N. Wiberg, H. Bayer and S. K. Vasisht, Chem. Ber., 114 (1981)2658.

130 S. J. Simpson and R. A. Anderson, Inorg. Chem., 20(1891) 3627.

131 T. D. Tilley, A. Zalkin, R. A. Andersen and D. H. Templeton, Inorg. Chem., 20(1981)551.

132 L. G. McCullough, H. W. Turner, R. A. Andersen, A. Zalkin and D. H. Templeton, Inorg. Chem., 20(1981)2869.

133 R. A. Andersen, A. Zalkin and D. H. Templeton, Inorg. Chem., 20(1981)622.

134 S. J. Simpson, H. W. Turner and R. A. Andersen, Inorg. Chem., 20(1981)2991.

135 H. W. Roesky, M. N. S. Rao, C. Graf, A. Gieren and E. Hädicke, Angew. Chem., Int. Ed. Engl., 20(1981)592.

136 H. W. Roesky, C. Petz, A. Gieren and E. Hädicke, Z. Naturforsch., 36b(1981)1437.

137 S. G. Baxter, A. H. Cowley and S. K. Mehrotra, J. Am. Chem. Soc., 103(1981)5572.

138 A. H. Cowley, S. K. Mehrotra and H. W. Roesky, Inorg. Chem., 20(1981)712.

139 J. Ellermann and M. Lietz, J. Organomet. Chem., 215(1981) 165.

140 H. W. Roesky, H. Djarral, D. Amirzadeh-Asl and W. S. Sheldrick, Chem. Ber., 114(1981)1554.

141 E. Niecke, K. Schwichtenhövel, H. G. Schäfer and B. Krelos, Angew. Chem., Int. Ed. Engl., 20(1981)963.

142 E. Niecke, A. Nickloweit-Lüke and R. Rüger, Angew. Chem., Int. Ed. Engl., 20(1981)385.

143 H. W. Roesky, L. Schöngelder, B. Krebs and G. Henkel, Z. anorg. allg. Chem., 475(1981)191.

144 J. R. Dürig, J. F. Sullivan and P. L. Trowell, J. Mol. Struct., 72(1981)41.

145 H. Fuess, J. W. Bats, M. Diehl, L. Schönfelder and H. W. Roesky, Chem. Ber., 114(1981)2369.

146 E. Wagner, V. Münch, J. Jander and H. P. Latscha, Z. Naturforsch., 36b(1981)1185.

147 L. May, R. F. X. Williams, P. Hambright, C. Burnham and M. Krishnamurthy, J. Inorg. Nucl. Chem., 43(1981)2577.

148 R. Appel and W. Paulen, Angew. Chem., Int. Ed. Engl., 20(1981)869.

149 G. Becker, Z. anorg. allg. Chem., 480(1981)21, 38.

150 M. Baudler, G. Reuschenbach and J. Hanh, Z. anorg. allg. Chem., 482(1981)27.

151 H. Schumann and H. Neumann, Z. Naturforsch., 36b(1981)708.

152 M. Dräger and B. Mathiasch, Angew. Chem., Int. Ed. Engl., 20(1981)1029.

153 M. Meisner, H. J. Kroth, K. H. Köhricht and H. Schumann, Z. Naturforsch., 36b(1981)904.

154 M. J. Barrow, S. Cradock, E. A. V. Ebsworth and D. W. H.

Rankin, J. Chem. Soc., Dalton Trans., (1981)1988.

155 S. N. Gurkova, A. I. Gusev, N. V. Alekseev, N. S. Fedotov, G. V. Ryasin, M. V. Polyakova and V. V. Solokov, J. Struct. Chem., 20(1979)133.

156 S. N. Gurkova, A. I. Gusev, N. V. Alekseev, M. G. Los, V. E. Zavednik, V. K. Bel'skii, G. V. Ryasin and N. S. Fedotov, J. Struct. Chem., 20(1979)906.

157 V. E. Shklover, T. V. Timofeeva, Yu. T. Struchkov, A. V. Ganyushkin and V. A. Yablokov, J. Struct. Chem., 22(1981) 366.

158 V. E. Shklover, P. Ad'yansuren, I. Tsinker, V. A. Yablokov, A. V. Ganyushkin and Yu. T. Struchkov, J. Struct. Chem., 21(1980)342.

159 M. Yu. Antipin, V. E. Shklover, Yu. T. Struchkov, T. V. Vasil'eva, T. V. Snegireva and N. M. Petrovnina, J. Struct. Chem., 21(1980)553.

160 I. L. Dubchack, T. V. Timofeeva, V. E. Shklover, Yu. T. Struchkov, A. A. Zhdanov, E. A. Kashutina and O. I. Shchegotikhina, J. Struct. Chem., 22(1981)54.

161 I. L. Dubchak, V. E. Shklover, M. M. Lavitskii, A. A. Zhdanov and Yu. T. Struchkov, J. Struct. Chem., 21(1980) 778.

162 V. E. Shklover, Yu. T. Struchkov, G. V. Solomatin, A. B. Zachernyuk and K. A. Andrianov, J. Struct. Chem., 20(1979) 257.

163 V. E. Shklover, I. Yu. Klement'ev and Yu. T. Struchkov, J. Struct. Chem., 22(1981)372.

164 V. E. Shklover, Yu. T. Struchkov, I. Yu. Klement'ev, V. S. Tikhonov and K. A. Andrianov, J. Struct. Chem., 20(1979)1251.

165 V. E. Shklover, I. L. Dubchak, Yu. T. Struchkov, V. P. Mileshkovich, G. A. Nikolaev and Yu. V. Tsyganov, J. Struct. Chem., 22(1981)225.

166 I. A. Baidina, N. V. Podberezskaya, V. I. Alekseev, T. N. Marktynova, S. V. Borisov and A. N. Kanov, J. Struct. Chem., 20(1979)550.

167 I. A. Baidina, N. V. Podberezskaya, S. V. Borisov, V. I. Alekseev, T. N. Martynova and A. N. Kanov, J. Struct. Chem., 21(180)352.

168 J. J. Harland, R. O. Day, J. F. Vollano, A. C. Sau and R. R. Holmes, J. Am. Chem. Soc., 103(1981)5269.

169 M. G. Voronkov, M. P. Denvidov, V. E. Shklover, V. P. Baryshok, V. M. D'yakov and Yu. L. Frolov, J. Struct. Chem., 21(1980)203.

170 S. N. Gurkova, A. I. Gusev, I. R. Segel'man, N. V. Alekseev, T. K. Gar and N. V. Khromova, J. Struct. Chem., 22(1981) 461.

171 V. E. Shklover, I. L. Dubchak, Yu. T. Struchkov, E. S. Khynku and A. A. Zhdanov, J. Struct. Chem., 22(1981)229.

172 U. Klingebiel, Chem. Ber., 114(1981)3366.

173 U. Klingebiel, Angew. Chem., Int. Ed. Engl., 20(1981)678.

174 R. G. Cavell, K. I. The and L. V. Griend, Inorg. Chem., 20(1981)3813.

175 D. W. Bennett and L. D. Spicer, J. Am. Chem. Soc., 103 (1981)5522.

176 D. Svhemburg, N. Weferling and R. Schmutzler, J. Chem. Soc., Chem. Comm., (1981)810.

177 R. K. Harris, C. T. G. Knight and W. E. Hull, J. Am. Chem. Soc., 103(1981)1577.

178 P. Sostrand, K. Taugbol and T. Skorstad, Inorg. Nucl. Chem. Letters, 17(1981)91.

179 A.C.Sau and R.R.Holmes, Inorg. Chem., 20(1981)4129.
180 F.B.Ueno, A.Najasawa and K.Saito, Inorg. Chem., 20(1981)3504.
181 B.Morosin and L.A.Harrah, Acta Crystallogr., 37B(1981)579.
182 H.Puff, W.Schuh, R.Sievers and R.Zimmer, Angew. Chem., Int. Ed. Engl., 20(1981)591.
183 M.Webster and J.S.Wood, J. Chem. Res. (S), (1981)40.
184 F.S.Delk and D.W.Thompson, J. Chem. Soc., Dalton Trans., (1981)1231.
185 I.Wakeshima and I.Kijima, Bull. Chem. Soc. Jpn., 54(1981)2345.
186 F.G.Glockling and W.K.Ng, J. Chem. Soc., Dalton Trans., (1981)1101.
187 P.G.Harrison, O.A.Idowu, C.Pelizzi, G.Pelizzi and P.Tarasconi, J. Organomet. Chem., 216(1981)159.
188 K.C.Molloy, M.B.Hossain, D. van der Helm, D.Cunningham and J.J.Zuckerman, Inorg. Chem., 20(1981)2402.
189 V.P.Karlov, G.N.Butuzov, T.F.Dotorokhotova and V.I.Volkov, Russ. J. Inorg. Chem., 26(1981)332.
190 J.E.Drake, B.M.Glavincevski and L.N.Khasrou, Canad. J. Chem., 59(1981)2909.
191 S.Pohl, U.Seyer and B.Krebs, Z. Naturforsch., 36b(1981)1432.
192 M.Dräger, Chem. Ber., 114(1981)2051.
193 M.Baudler, H.Suchomel, G.Fürstenberg and U.Schings, Angew. Chem., Int. Ed. Engl., 20(1981)1044.
194 R.C.Mehrotra, G.Srivastrava and E.N.Vasanta, Inorg. Chim. Acta, 47(1981)125.
195 A.C.Sau, R.O.Day and R.R.Holmes, Inorg. Chem., 20(1981)3076.
196 K.C.Molloy, M.B.Hossain, D. van der Helm, J.J.Zuckerman and F.P.Mullins, Inorg. Chem., 20(1981)2172.
197 R.W.Gable, C.L.Raston, G.L.Rowbottom, A.H.White and G.Winter, J. Chem. Soc., Dalton Trans., (1981)1392.
198 V.P.Vasil'ev, V.I.Shorokhava and A.V.Katrovtseva, Russ. J. Inorg. Chem., 26(1981)327.
199 N.G.Furmanova, A.S.Batsanov, Yu.T.Struchkev, D.N.Kravtsov and E.M.Rohhlina, J. Struct. Chem., 20(1979)245.
200 S.J.Backs and D.L.Rabenstein, Inorg. Chem., 20(1981)410.
201 A.Haas and R.Hitze, Z. Naturforsch., 36b(1981)1069.
202 A.Blecher, M.Dräger and B.Mathiasch, Z. Natuforsch., 36b(1981) 1361.
203 V.S.Mastryukov, A.V.Golubinskii and L.V.Vilkov, J. Struct. Chem., 21(1980)37.
204 E.Vajda, T.Szekely, M.Hargitta, A.K.Maltsev, E.G.Baskir and O.M.Nefedov, J. Mol. Struct., 73(1981)243.
205 T.M.Kuznetsova, N.V.Alekseev and N.V.Veniaminov, J. Struct. Chem., 20(1979)823.
206 T.M.Kuznetsova, N.V.Alekseev and N.N.Veniaminov, J. Struct. Chem., 20(1979)281.
207 E.A.Zel'bst, V.E.Shklorov, Yu.T.Struchkov, Yu.L.Frolov, A.A.Kashaev, L.I.Gubanova, V.M.D'yakov and M.G.Voronkov, J. Struct. Chem., 22(1981)377.
208 M.Hayashi, M.Imachi and M.Oyamada, J. Mol. Struct., 74(1981)97.
209 V.A.Sharapov, A.I.Grusev, Yu.T.Struchkov, N.G.Komalenkova, L.N.Shamshin and E.A.Chernyshev, J. Struct. Chem., 21(1980)786.
210 C.Eaborn and F.M.S.Mahmoud, J. Chem. Soc. Chem. Commun., (1981)63.
211 C.Eaborn, K.D.Safa, A.Ritter and W.Binder, J. Chem. Soc., Chem. Commun., (1981)175.
212 B.S.Ault, Inorg. Chem., 20(1981)2817.
213 B.S.Ault and U.Tandoc, Inorg. Chem., 20(1981)1937.

214 B.Frlec, D.Gantar, L.Golic and I.Leban, Acta Crystallogr., 37B(1981)666.
215 N.N.Zhamskay, Russ. J. Inorg. Chem., 26(1981)738.
216 P.Barron, W.Jones, J.M.Thomas and R.Schlögl, J. Chem. Soc., Chem. Commun., (1981)677.
217 H.Fujiwara and Y.Sasaki, J. Chem. Soc., Chem. Commun., (1981)35.
218 Y.T.Fanchiang and J.M.Wood, J. Am. Chem. Soc., 103(1981)5100.
219 W.A.Gustavson, L.M.Principe, W.-Z. Min Rhee and J.J. Zuckerman, Inorg. Chem., 20(1981)3460.
220 C.U.Daranzo and Y.Gushikem, J. Chem. Soc. Dalton Trans., (1981)843.
221 F.Fourner and F.Theobald, Inorg. Chim. Acta, 52(1981)15.
222 M.H.Ben Ghozlen, A.Daoud and J.W.Bats, Acta Crystallogr., 37B(1981)1415.
223 O.Knop, T.S.Cameron, M.A.James and M.Falk, Canad. J. Chem., 59(1981)2550.
224 V.I.Korsunsky, M.B.Taraban, T.V.Lestrina, O.I.Margovskaya and N.S.Vyazankin, J. Organomet. Chem., 215(1981)179.
225 U.Kunze, P.-R.Bolz and W.Winter, Chem. Ber., 114(1981)2744.
226 L.Rösch, Angew. Chem., Int. Ed. Engl., 20(1981)872.
227 L.Rösch, G.Altnau, E.Hahn and H.Havemann, Z. Naturforsch., 36b(1981)1234.
228 S.N.Titova, V.T.Bychkov, G.A.Domrachev, G.A.Razuvaev, L.N.Zakharov, G.G.Alexandrov and Yu.T.Struchkov, Inorg. Chim. Acta, 50(1981)71.
229 L.G.Kuz'mina, T.V.Timofeeva, Yu.T.Struchkov and M.N.Bochkarov, J. Struct. Chem., 22(1981)44.
230 W.Biffar and H.Nöth, Z. Naturforsch., 36b(1981)1509.
231 L.Rösch and G.Altnau, Angew. Chem., Int. Ed. Engl., 20(1981)582.
232 H.Nöth and R.Schwerthöffer, Chem. Ber., 114(1981)3056.
233 W.Biffar, H.Nöth, H.Pommerening, R.Schwerthöffer, W.Storch and B.Wrackmeyer, Chem. Ber., 114(1981)49.
234 J.T.Wang and F.Williams, J. Chem. Soc., Chem. Commun., (1981)660.
235 M.C.R.Symons, J. Chem. Soc., Chem. Commun., (1981)1251.
236 A.Almenningen and T.Fjeldberg, J. Mol. Struct., 77(1981)315.
237 M.Ishikawa, J. Iyoda, H.Ikeda, K.Kotake, T.Hashimoto and M.Kumada, J. Am. Chem. Soc., 103(1981)4845.
238 M.Watanabe, T.Muraoka, M.-A.Kageyama and Y.Nagai, J. Organomet. Chem., 216(1981)C45.
239 L.F.Brough and R.West, J. Am. Chem. Soc., 103(1981)3049.
240 E.Hengge and D.Korav, Angew. Chem., Int. Ed. Engl., 20(1981)678.
241 M.Dräger and K.G.Walter, Z. Anorg. Allg. Chem., 479(1981)65.
242 T.-H.Hsem, T.-L.Hwang and C.-S.Liu, Inorg. Chem., 20(1981)2182.
243 M.Dräger and D.Simm, Z. Anorg. Allg. Chem., 472(1982)120.
244 L.Ross and M.Dräger, Z. Anorg. Allg. Chem., 472(1982)109.
245 M.Dräger and L.Ross, Z. Anorg. Allg. Chem., 476(1981)95.
246 C.Eaborn and F.M.S.Mahoud, J. Organomet. Chem., 205(1981)47.
247 S.C.Critchlow and J.D.Corbett, J. Chem. Soc., Chem. Commun., (1981)236.
248 M.J.Rothman, L.S.Bartell and L.L.Lohr, J. Am. Chem. Soc., 103(1981)2482, 2480.
249 L.L.Lohr, Inorg. Chem., 20(1981)4229.
250 W.Gäder and E.W.eiss, Chem. Ber., 114(1981)2399.
251 D.L.Johnson and J.A.Gladysz, Inorg. Chem., 20(1981)2508.
252 U.Schubert, B.Wörle and P.Jandik, Angew.Chem.Int.Ed. Engl., 20(1981)695.

253 Y.Chi and C.-S.Lim, Inorg. Chem., 20(1981)3456.
254 A.J.Blakeney, D.L.Johnson, P.W.Donovan and J.A.Gladysz, Inorg. Chem., 20(1981)4415.
255 R.F.Gerlach, K.M.Mackay, B.K.Nicholson and W.T.Robinson, J. Chem. Soc. Dalton Trans., (1981)80.
256 D.N.Duffy, K.M.Mackay, B.K.Nicholson and W.T.Robinson, J. Chem. Soc. Dalton Trans., (1981)381.
257 C.Burschka, K.Stroppel and P.Jutz, Acta Crystallogr., 37B(1981)1397
258 G.N.van Buuren, A.C.Willis, F.W.B.Einstein, L.K.Peterson, R.K.Pomeroy and D.Sutton, Inorg. Chem., 20(1981)4361.
259 E.A.V.Ebsworth, J.E.Fraser, S.G.Henderson, D.M.Leitch and D.W.H.Rankin, J. Chem. Soc., Dalton Trans., (1981)1010.
260 R.D.Holmes-Smith, S.R.Stobart and S.Cameron and K.Jochen, J. Chem. Soc., Chem. Commun., (1981)937.
261 E.Colomer, R.J.P.Corriu and A.Vioux, Angew. Chem., Int. Ed. Engl., 20(1981)476.
262 G.Cerveau, E.Colomer and R.J.P.Corriu, Angew. Chem., Int. Ed. Engl., 20(1981)478.
263 D.F.Dong, J.K.Hoyano and W.A.G.Graham, Canad. J. Chem., 59(1981)1455.
264 I.W.Boyd, G.P.Haight and N.C.Howlader, Inorg. Chem., 20(1981)3115.
265 H.Moriyama, T.Aoki, S.Shinoda and Y.Saito, J. Chem. Soc., Dalton Trans., (1981)639.
266 M.Garralda, V.Garcia, M.Kretschmer, P.S.Pregosin and H.Ruegger, Helv. Chim. Acta, 64(1981)1150.
267 T.S.Khodashava, M.A.Porai-Koshits, V.P.Nikolaev and V.N.Shchurkina, J. Struct. Chem., 21(1980)220.
268 H.Preut and H.J.Haupt, Acta Crystallogr., 37B(1981)688.
269 J.Silvestre, T.A.Albright and B.A.Sosinsky, Inorg. Chem., 20(1981)3937.
270 B.A.Sosinsky, J.Shelly and R.Strong, Inorg. Chem., 20(1981) 1370.
271 F.G.N.Cloke, K.P.Cox, M.L.H.Green, J.Bashkin and K.Prout, J. Chem. Soc., Chem. Commun., (1981)117.
272 K.H.Pannell and R.N.Kapoor, J. Organomet. Chem., 214(1981) 47.
273 J.Klonowski, J.M.Thomas, M.Audiev, S.Vasudevan, C.A.Fyfe and J.S.Hartman, J. Chem. Soc., Chem. Commun., (1981)570.
274 G.Engelhardt, E.Lippmaa and M.Mägl, J. Chem. Soc.,Chem. Commun., (1981)712.
275 J.B.Nagy, J.P.Gilson and E.G.Derovane, J. Chem. Soc., Chem. Commun., (1981)1129.
276 W.Shu-Lin, S.Ramdas and D.A.Jefferson, J. Chem. Soc., Chem. Commun., (1981)662.
277 K.Kuroda, T.Koike and C.Kato, J. Chem. Soc., Dalton Trans., (1981)1957.
278 M.G.Barker and P.G.Gadd, J. Chem. Res. (S), (1981)274.
279 R.L.Schmid, L.Szolnai, J.Felsche and G.Huttner, Acta Crystallogr., 37B(1981)789.
280 W.H.Baur, T.Ohta and R.D.Shannon, Acta Crystallogr., 37B(1981)1483.
281 T.Yamanaka and H.Mori, Acta Crystallogr., 37B(1981)1010.
282 O.Yamaguchi, K.Yabuno, S.Yamamoto and K.Shimizu, J. Chem. Soc., Dalton Trans., (1981)1300.
283 R.G.Grebenshchikov, V.I.Shitova and L.Yu.Dmitrieva, Russ. J. Inorg. Chem., 26(1981)120.
284 K.Hirota and Y.T.Hasegawa, Bull. Chem. Soc. Jpn., 54(1981) 754.

285 L.S.Dent Glasser, R.A.Howie and R.M.Smart, Acta Crystallogr., B37(1981)303.

286 V.A.Masloboev, E.B.Panasenko and N.F.Sklokina, Russ. J. Inorg. Chem., 26(1981)185.

287 F.Robart and A.Teze, Acta Crystallogr., 37B(1981)318.

288 L.S.Dent Glasser and C.K.Lee, Acta Crystallogr., 37B(1981)803.

289 C.M.Gramaccioli, G.Liborio and T.Pilati, Acta Crystallogr., 37B(1981)1972.

290 H.F.Fukushima, A.Kobayashi and Y.Sasaki, Acta Crystallogr., 37B(1981)1613.

291 D.M.Adams, R.S.Armstrong and S.P.Best, Inorg. Chem., 20(1981)1771.

292 S.A.Gallagher and G.J.McCarthy, Inorg. Nucl. Chem., 43(1981)1773.

293 K.F.Hesse and W.Eysol, Acta Crystallogr., 37B(1981)429.

294 N.I.Zaginaichenko, E.B.Panasenko, N.F.Sklokina and M.N.Ryskina, Russ. J. Inorg. Chem., 26(1981)672.

295 A.A.Bush and Yu.N.Venevtsev, Russ. J. Inorg. Chem., 26(1981)249.

296 A.Yu.Shashkov, V.A.Efremov, I.Matsichek, N.V.Rannev, Yu.N.Venevtsev and V.K.Trunov, Russ. J. Inorg. Chem., 26(1981)316.

297 T.Oikova and G.Gospodinov, Russ. J. Inorg. Chem., 26(1981)266.

298 F.J.Berry and C.Greaves, J. Chem. Soc., Dalton Trans., (1981)2447.

299 D.Schmitz, Acta Crystallogr., B37(1981)578.

300 M.Levalois and G.Allais, Acta Crystallogr., 37B(1981)1816.

301 B.Krebs and H.J.Wallstab, Z. Naturforsch., 36b(1981)1400.

302 G.Eulenberger, Z. Naturforsch., 36b(1981)687.

303 G.Eulenberger, Z. Naturforsch., 36b(1981)521.

304 B.Eisenmann, H.Schwerer and H.Schäfer, Z. Naturforsch., 36b(1981)2538.

305 B.Bildstein, W.Tötsch and F.Sladky, Z. Naturforsch., 36b(1981)1542.