Coordination Chemistry Reviews, 66 (1985) 190—289
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

Chapter 4

ELEMENTS OF GROUP 4

P.G.Harrison

4.1 GENERAL

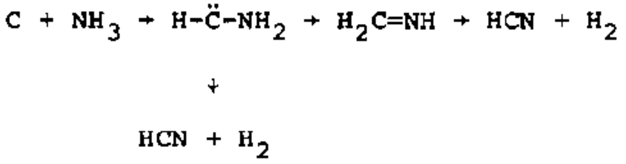
Observed bond distances in the bivalent and tetravalent halide derivatives of the Group IV elements have been used to estimate a new electronegativity scale. Predicted values are: C, 2.6; Si, 1.9; Ge, 2.5 and Sn, 2.3.[1]

4.2 CARBON

Theoretical calculations of the reaction of atomic carbon with water have been compared with experimental data. In the theoretical study for $C(^1D)$ atoms, the process having the lowest activation enthalpy is cleavage of the initially formed carbon-water complex to CO and H_2 along a closed-shell surface ($\Delta H^{\ddagger} = 5.2$ kcal mol^{-1}). Rearrangement of the closed-shell carbon-water complex to hydroxymethylene has $\Delta H^{\ddagger} = 11.6$ kcal mol^{-1}. The most favourable of the initial carbon-water complex for $C(^3P)$ atoms was simple dissociation to the reactants. The barrier to rearrangement of the initial complex to hydroxymethylene was slightly

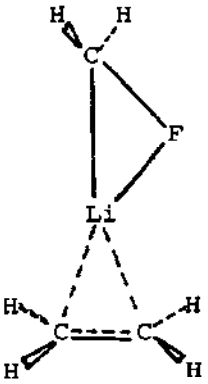
0010-8545/85/$35.00

higher for triplet carbon (22.8 kcal mol^{-1}) than for singlet carbon (18.0 kcal mol^{-1}), although the barriers to rearrangement of the singlet and triplet hydroxymethylenes to formaldehyde are similar. Experimental data bear out the theoretical predictions that singlet carbon atoms are more reactive towards water. Reaction of atomic carbon, generated by the thermolysis of 5-diazatetrazole, affords CO (9.5%) and formaldehyde (2.4%). Addition of O_2, which scavenges triplet carbon atoms, increases the yield of CO to 53.7% whilst leaving the formaldehyde yield unchanged.[2] In a study of arc-generated carbon atoms with ammonia, the primary reactions have been shown to be NH insertion and hydrogen abstraction. The former mode of reaction leads to methyleneamine and HCN, whilst hydrogen abstraction proceeds in a stepwise manner to generate CH_2, which reacts with ammonia to produce methylamine:

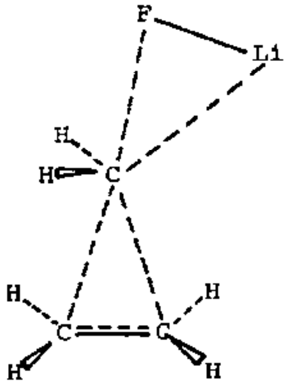


$$\begin{tikzcd} C + NH_3 \arrow[r] & H\text{-}\ddot{C}\text{-}NH_2 \arrow[r] \arrow[d] & H_2C{=}NH \arrow[r] & HCN + H_2 \\ & HCN + H_2 & & \end{tikzcd}$$

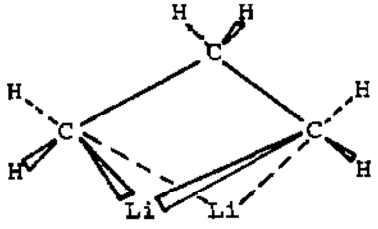
Hydrolysis of the non-volatile residue from this reaction produces the aminoacids, glycine, alanine, N-methylglycine, β-alanine and aspartic acid. Serine is also formed when water is included in the reactants.[3] The detailed reaction pathway for the hydration of ketenimine, $CH_2{=}C{=}NH$ by H_2O and its dimer has been studied by ab initio methods. The preferred reaction pathway is with the water dimer through a "pre-association" mechanism where a small amount of initial bonding occurs via attack by oxygen at the central carbon atom of the ketenimine. Proton transfer to the β-carbon subsequently occurs at or just after the transition state without any appreciable changes in the C-O bond distance. The reaction, which has a calculated activation energy of 22 kcal mol^{-1}, is therefore concerted but highly asynchronous.[4] Calculations for the reaction of $LiCH_2F$ with ethylene show the formation of a complex, (<u>1</u>), in which there are only slight distortions from the geometries of the individual reactants, and a transition state, (<u>2</u>), in which the CH_2 group is in a plane nearly parallel to the ethylene plane. The methylene fragment is aligned so that the LUMO can interact in an electrophilic sense



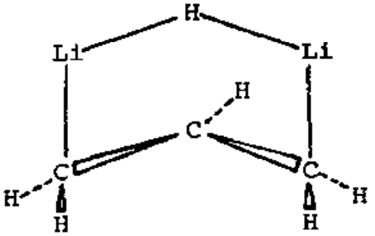
(1)



(2)



(3)

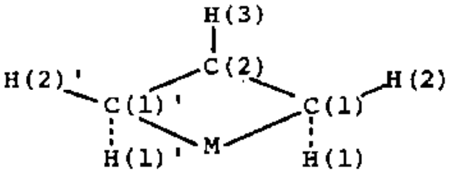


(4)

with the ethylene HOMO on one side and simultaneously with a fluorine lone-pair on the other.[5]

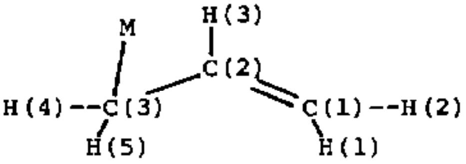
The doubly lithium bridged structure (3) has been shown by ab initio methods to be the lowest-energy geometry of 1,3-dilithiopropane. This form exhibits considerable thermodynamic stability; for example, opening to an extended conformation is endothermic by 24.6 kcal mol^{-1}, and disproportionation with propane into two molecules of n-propyllithium is calculated to require 19.4 kcal mol^{-1}. Conversion of (3) to an allyllithium-LiH complex, (4), (a possible elimination intermediate) is exothermic by 29.0 kcal mol^{-1}. While the second lithiations of ethane and of propane are favourable thermodynamically, both 1,2-dilithioethane and 1,3-dilithiopropane are unstable toward conversion to LiH complexes. When such eliminations are blocked structurally or the carbanionic sites substituted by stabilizing groups, vicinal and 1,3-dilithio derivatives can be expected. Unlike the lower homologues, the doubly bridged form of 1,4-dilithiobutane is indicated to be stable thermodynamically toward elimination to a 3-butenyllithium-

LiH complex. These findings thus rationalise why the higher α,ω-dilithioalkanes are more readily accessible as synthetic reagents.[6] Allyllithium and allylsodium are predicted to have the symmetrically bridged structure (5), whereas allylmagnesium hydride prefers the unsymmetrical geometry (6). Nevertheless, the barriers for 1,3 MgH shift and CH_2 group rotation are quite low. The rotation barrier in unsolvated monomeric allylsodium is predicted to be lower than that in the corresponding lithium compound, in contrast to experimental observation in solution.[7]



M = Li or Na

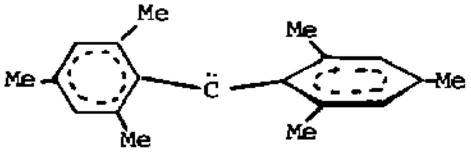
(5)



M = MgH

(6)

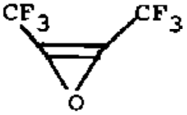
In contrast to diphenylcarbene and essentially all other diarylcarbenes which have bond angles at the central carbon atom of ca. 150°, the skeleton in dimesitylcarbene, (7), is much closer to linearity. When formed from dimesityldiazomethane in n-octane or 1,1-diphenylethylene glasses, dimesitylcarbene is quite persistent at 77K, showing no apparent decay over a period of 4-5 hours.[8] In addition, this carbene appears to be unique amongst diarylcarbenes since its triplet state cannot readily convert into the singlet state.[9]



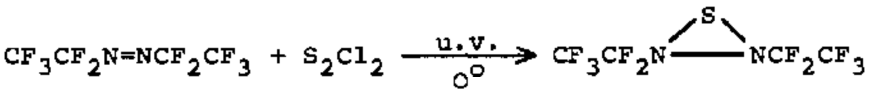
(7)

Photolysis of hexafluoro-3-diazo-2-butanone in an argon matrix affords perfluoroacetylmethylmethylene together with, at lower wavelengths, bis(trifluoromethyl)oxirene:[10]

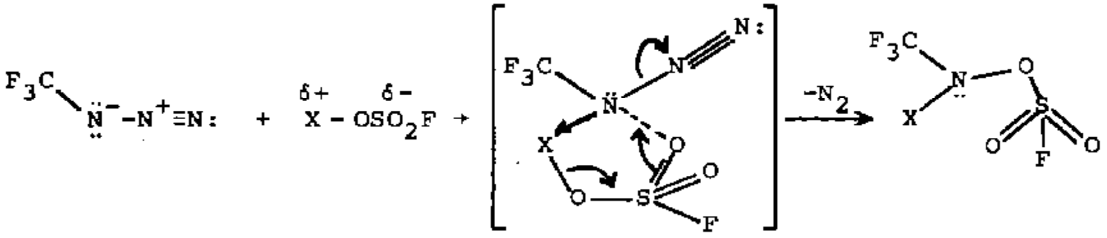
$CF_3CN_2COCF_3 \xrightarrow{h\nu} CF_3\ddot{C}COCF_3$ +



Trifluoronitrosomethane, CF_3NO, has been prepared in good yield by the pyrolysis of nitrosyltrifluoroacetate, CF_3COONO, in a flow of nitric oxide at 190° using perfluorotributylamine as a diluent.[11] Trifluoromethylsulphenyl bromide, CF_3SBr, has been isolated satisfactorily from the products of the reaction between gaseous bromine and either CF_3SAg or $(CF_3S)_2Hg$.[12] Vibrational spectra indicate that $(CF_3S)_2CS$ exists as a complex mixture of conformers in rare gas matrices. Photolysis with $\lambda > 300nm$ modifies the distribution of conformers - a change which may be reversed by irradiation with $\lambda > 530nm$. The threshold for photochemical decomposition to CF_3SCF_3 and CS_2 is about 300nm.[13] Photolysis of $CF_3CF_2N{=}NCF_2CF_3$ with S_2Cl_2 at 0° affords the first known example of a thiadiaziridine:[14]

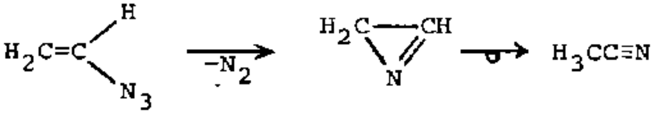


Azidotrifluoromethane reacts readily with halogen fluorosulphates and peroxydisulphuryl difluoride to form the new derivatives, $CF_3NX(OSO_2F)$ (X = F,Cl,Br,OSO_2F) in high yield:

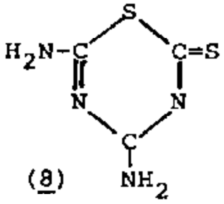


The reactions of ClF and BrF with CF_3N_3 at ambient temperature furnish CF_3NFCl and $CF_3N{=}NCF_3$, respectively. Under similar conditions, however, CF_3N_3 does not react with Cl_2, Br_2, HF or HCl. Photolysis of CF_3N_3 results in rapid decomposition which affords $CF_3N{=}CF_2$ and $(CF_3)_2NN(CF_3)_2$ as the major products.[15] N,N'-Dihalogenoethanediimidoyldifluorides, XN=CF-CF=NX (X = Cl,Br), have been synthesised from the reactions of $(CN)_2$, HgF_2 and the elemental halogen. N-Halogenated amino- or iminoperfluoroethanes, $Cl_2N-CF_2-CF_2-NCl_2$, $ClN{=}CF-CF_2-NCl_2$, $BrN{=}CF-CF_2-NBr_2$ and $Br_2N-CF_2-CF_2-NBr_2$ were also formed as by-products.[16] The electrophilic halides and pseudohalides, $XOSO_2F$ (X = Cl,Br,OSO_2F), add to CF_2=NF in high yield to form FSO_2OCF_2NFX. Other electrophiles such as CF_3OF, CF_3OCl, Cl_2, Br_2 and I_2 are unreactive under the same conditions, and only $FOSO_2F$ resulted in a small yield of the addition product $FSO_2OCF_2NF_2$ on heating. The in situ formation of CF_3NF^- from CF_2=NF and MF (M = K,Cs) in the presence of Cl_2 and Br_2 results in the formation of CF_3NXF (X = Cl,Br). The imines CF_3CF=NF and C_2F_5CF=NF gave similar results with bromine. Chlorofluorination and bromofluorination occurs with the nitriles CF_3CN and XCN (X = Cl,Br) and the elemental halogen in the presence of MF giving products such as $C_2F_5NCl_2$, $C_2F_5N{=}NC_2F_5$, CF_3NCl_2, CF_3CF=NBr, $C_2F_5N{=}NC_2F_5$ and $CF_3N{=}NCF_3$.[17] Trifluoroacetyl derivatives of N,N-dimethylhydrazine, urea, and thiourea, $CF_3CONHNMe_2$, $CF_3CONHCSNHCOCF_3$, $CF_3CONHCSNH_2$ and $CF_3CONHCONH_2$ have been synthesised by treating the appropriate nitrogen compound with trifluoroacetyl chloride in the presence of CsF. With triethylamine as base, $CF_3CONHNMe_2$ was also formed with Me_2NNH_2. Reaction of Me_2NNH_2 with hexafluoroacetone afforded $CF_3C(=NNMe_2)CH=C(OH)CF_3$.[18]

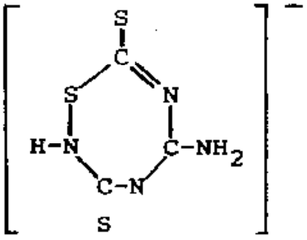
P.E. spectroscopy has been employed to study the gas phase pyrolyses of vinyl azide and 1H-1,2,3-triazide. In accordance with MNDO hypersurface studies, vinyl azide in its lowest thermal decomposition channel eliminates nitrogen to yield predominantly 2H-aziridine, which at higher temperatures rearranges to the most stable C_2H_3N isomer, acetonitrile:[19]



N-Cyanoguanidine reacts with CS_2 in the presence of the appropriate alkali metal hydroxide to form the metal N-cyanoformamidine dithiocarbimates, $M_2[S_2C{=}N{-}C(NH_2){=}N{-}CN]$ (M = K, Rb). With acids and elemental sulphur, the cyclic species (8) and (9), respectively, are formed.[20]

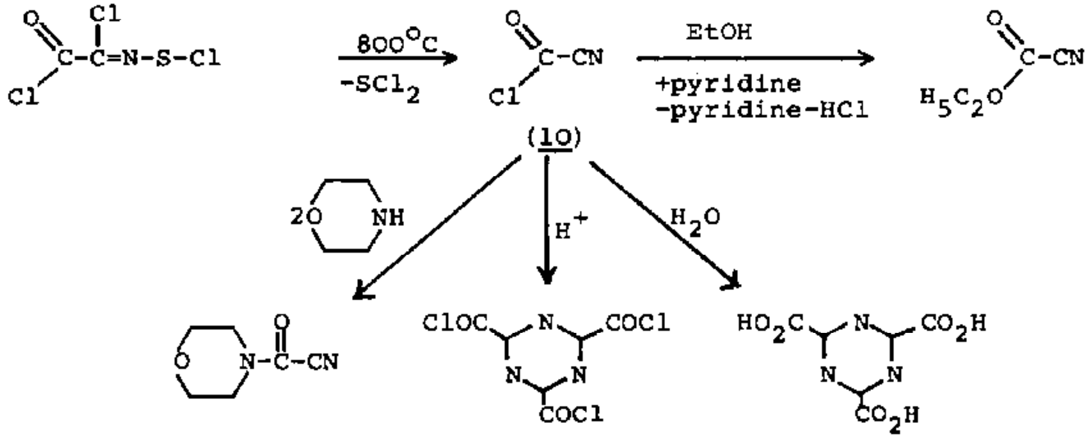


(8)



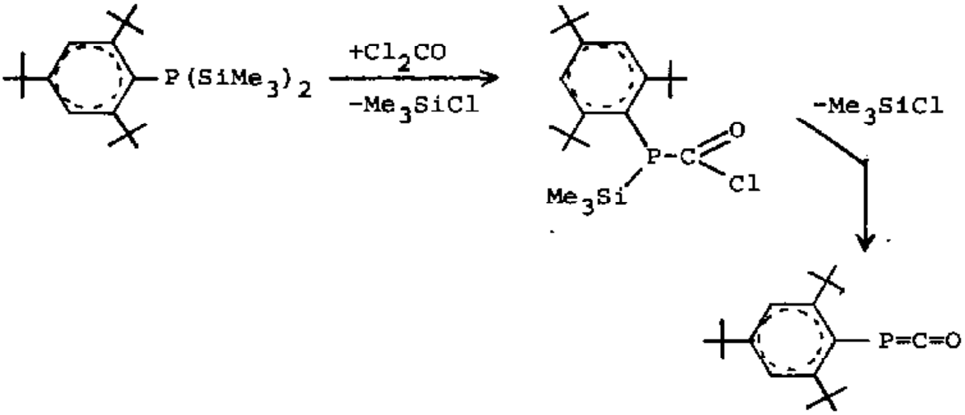
(9)

Cyanoformyl chloride, (10), is formed in high yield by heating 2-chloro-2-(chlorothioimino)acetyl chloride at 800°C in vacuo. Some reactions are shown in Scheme 1.[21]



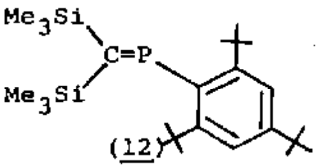
Scheme 1

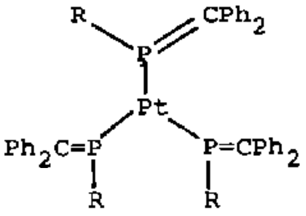
The first phosphaketene stable at room temperature, p-mesitylphosphaketene (11), has been isolated as orange crystals by the route:[22]

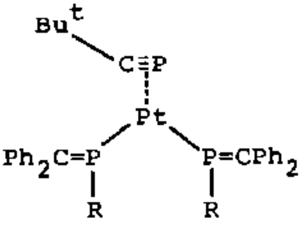


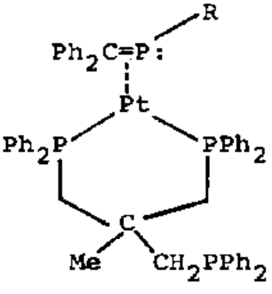
(11)

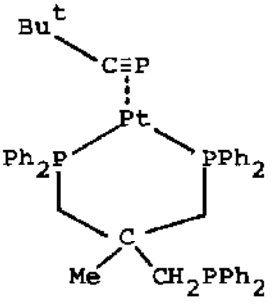
Several other papers deal with compounds containing multiple bonds between carbon and a variety of other elements. He(I) photoelectron spectra of the phosphaalkynes $Bu^tC{\equiv}P$ and $PhC{\equiv}P$ have been obtained and assigned by comparison with the spectra of other species and with the aid of ab initio MO calculations. The first ionisation potentials correspond to electron removal from orbitals with essentially π(CP) bonding character.[23] The new phosphaalkene, (12), is the major product from the reaction of $(Me_3Si)_3CLi$ with $(Me_3Si)_3CPCl_2/(2,4,6\text{-}Bu^t{}_3C_6H_2)PCl_2$ mixtures.[24] Both phosphaalkenes and phosphaalkynes form complexes with transition metals but in a variety of bonding modes.[25-27] Several examples are illustrated in (13 - 17).

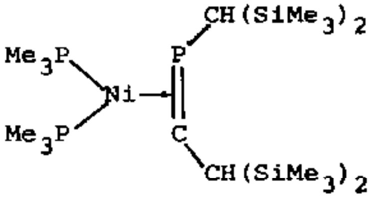

(12)


(13)

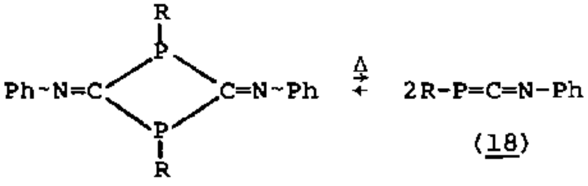

(14)


(15)


(16)

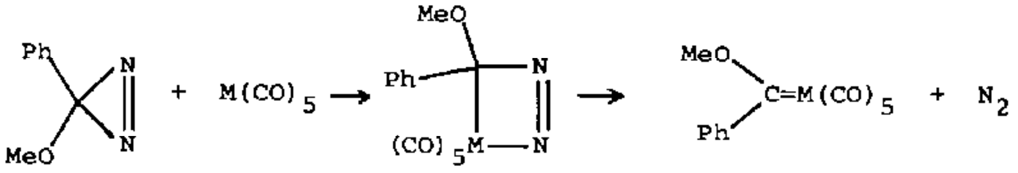

(17)

Flash vacuum pyrolysis of diphosphetanes yields the (iminomethylidene)phosphines (18) containing the P=C=N skeleton:[28]


(18)

Theoretical studies for the phosphonium cyclopropylide, $H_3P{=}C(CH_2)_2$, show that the ground-state equilibrium geometry has a pyramidal carbanion centre.[29] The monomeric phosphorus(II) ylide, $CF_3P{=}CF_2$, has been obtained by the triethylamine catalysed reaction of Me_2Zn with $(CF_3)_2PH$. The ylide is stable as a gas at 100°.[30] Of the new crystal structure determinations of phosphorus ylides, $Ph_3P{=}C(SPh)SePh$ exhibits a planar [PCSSe] skeleton,[31]

$Ph_3P=C(CH_2)_3$ has an approximately tetrahedral 'onium centre inclined to the neighbouring plane of the puckered cyclobutane ring,[32] $Ph_3P=C(PPh_2)_2$ also has a planar $[P=CP_2]$ skeleton,[33] and $(Me_2N)_3P=C=P(NMe_2)_3$ is linear at the central carbon atom.[34] The pyrolysis of $(Me_3SiCH_2)_3AsBr_2$ proceeds via the intermediate formation of the arsenic ylid, $Br(Me_3SiCH_2)_2As=CH_2$.[35] Methylenesulphurtetrafluoride, $CH_2=SF_4$, has been prepared by bromine-lithium exchange on $BrCH_2SF_5$ at low temperatures with subsequent elimination of LiF. The rigid structure is essentially trigonal bipyramidal, with the methylene group occupying an equatorial position. The carbon-sulphur bond is best described as a strong double bond with only little ylidic character, but undergoes numerous addition reactions with polar species. Elimination of SF_4 to yield carbene may occur.[36] Metal-carbene complexes have been obtained by reaction of a diazirine with tungsten or chromium pentacarbonyl via a mechanism not involving free carbene:[37]



M = Cr, W.

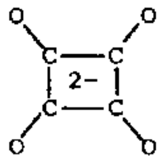
The reaction of $Ru(CO)_2(PPh_3)_2$ with $Cd(CF_3)_2.dme$ produces the zero-valent CF_2-complex $Ru(=CF_2)(CO)_2(PPh_3)_2$, which has a much reduced reactivity towards nucleophiles than the analogous $Ru^{II}-CF_2$ complex.[38]

Single crystals of CO have been examined in a high-pressure Merrill-Bassett diamond cell. The unit cell is hexagonal, $P6_3/mmc$, the same as β-CO near the triple point. At 4.2 GPa, the sample appears to undergo a photochemical change induced by the weak laser light used to make the pressure measurements.[39] The mechanism of the chlorine catalytic oxidation of CO in the gas phase has been investigated. The ratio of the competitive reactions

$$ClCO + Cl_2 \xrightarrow{K_2} COCl_2 + Cl$$

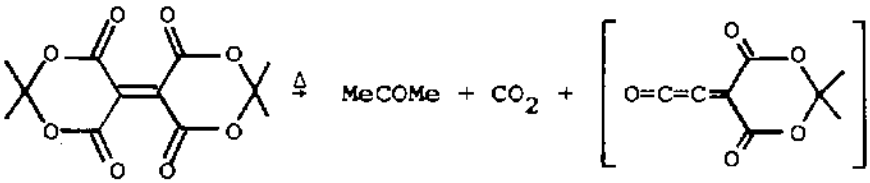
and $$ClCO + O_2 \xrightarrow{K_1} ClC(O)O_2$$

K_1/K_2 was determined to be 6.5×10^{-2}.[40] The $^3\Sigma_g^-$ electronic ground states of OCCO and SCCS have been studied by using non-empirical molecular structure theory, which predicts the presence of strong chemical bonds in these molecules.[41] The ability of CO to form a radical anion, $CO^{\cdot -}$, which can react further with CO or $CO^{\cdot -}$ with the formation of C-C bonds has been suggested by literature data on (i) the reaction of CO with alkali metals, (ii) the electrochemical reduction of CO to the squarate dianion, (18), and (iii) the adsorption of CO on metal oxides.[42]



(18)

A new oxide of carbon, tricarbon monoxide, has been observed amongst the products of (19) at 1000°:



(19)

$\downarrow$

$C_3O + CO_2 + MeCOMe + CO$

Observed microwave frequencies for the new oxide are very close (1 part in 600) to those predicted for C_3O by ab initio calculations. The data are fully consistent with a linear molecule whose electronic structure is well represented by the classical resonance form $^-C{=}C{-}C{=}O^+$.[43] Methane and ethylene are the major products of the reaction of $LiAlH_4$ with CO_2 or $NaHCO_3$ at elevated temperatures. The reaction sequence

$$LiAlH_4 \xrightarrow{\sim 500K} Al + LiH + 3/2H_2$$

$$2Al + 3CO_2 \xrightarrow{\sim 500K} Al_2O_3 + 3CO$$

$$2Al + 3H_2 + 3CO \rightarrow Al_2O_3 + 3CH_2$$

$$CH_2 + H_2 \rightarrow CH_4$$

$$CH_2 + CH_2 \rightarrow C_2H_4$$

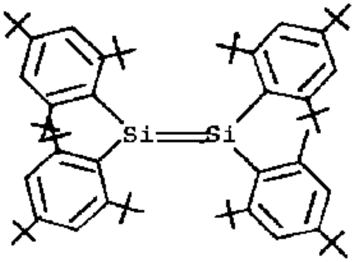
was proposed to account for the observations.[44] Alkali metal chlorides react with CS_2 in acetonitrile in the presence of solid sodium hydroxide as catalyst to form the corresponding yellow unstable metal chlorodithioformates, $M[\dot{S}_2C-Cl]$.[45]

Several papers report novel graphite intercalation compounds. A blue-black first stage graphite fluoride, C_xF $(5 > x > 2)$, in which the planar carbon atom sheets of graphite are preserved, has been made by intercalation of graphite with fluorine in the presence of liquid hydrogen fluoride at ca. 20°, the addition proceeding via a highly conducting second stage salt, $C_{12}{}^+HF_2{}^-$.[46] Graphite-fluorine intercalates have also been prepared in the absence of HF by exposing highly oriented pyrolytic graphite to neat fluorine gas. The rate of intercalation in this case is rather slow and depends strongly on the fluorine pressure, although the presence of catalytic amounts of AsF_5, IF_5 or OsF_6 considerably accelerates the reaction. XRD studies indicate the formation of second-, third-, and fourth-stage compounds. The nature of the intercalating species, however, was not known.[47] Reaction of graphite with $SbCl_5$ at room temperature results in the formation of a dilute first stage intercalate comprising several species including $SbCl_3$, $SbCl_5{}^{2-}$, $SbCl_6{}^-$ and $SbCl_6{}^{3-}$.[48] The course of the intercalation has been monitored in situ by Raman spectroscopy.[49] The reaction of the potassium intercalate C_8K with varying amounts of mercury allows the preparation of a series of compounds of general formula C_8KHg_x.[50] The potassium ions in $C_{36}K$ can react with the three-dimensional cryptand, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane, to yield a first-stage intercalation compound with a very large interlayer spacing (15.5Å), suggesting that the potassium ions are probably within the macroheterobicyclic cage.[51]

4.3 SILICON AND GERMANIUM

4.3.1 Reactive Intermediates

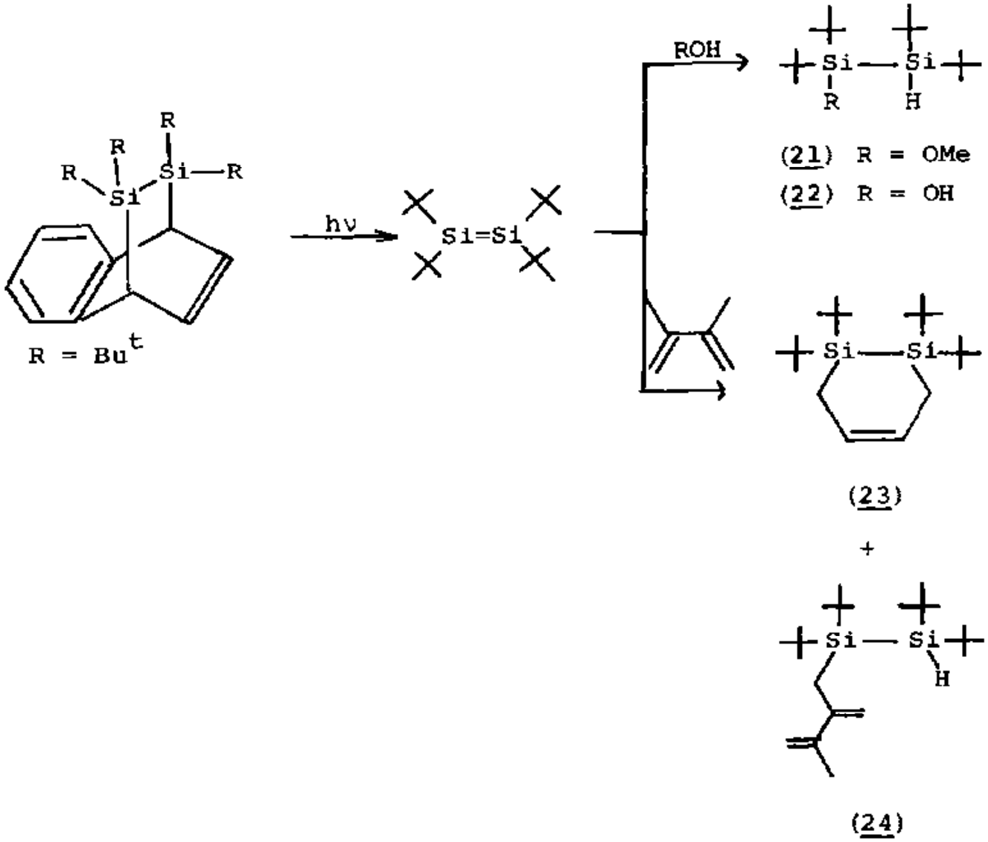
The chemistry of reactive silicon and germanium intermediates continues to prosper. Isolation of the stable disilene derivatives, tetramesityldisilene and tetrakis(2,6-dimethylphenyl)disilene, has been followed by a crystal structure determination of the former. In addition, other, albeit less stable examples have been synthesised. Tetramesityldisilene exhibits a trans-bent geometry (20) in the crystal, with an Si=Si bond distance of 216pm, - ca. 18-20pm shorter than typical single bond distances. Two of the cis aromatic rings are only slightly twisted relative to the approximate plane of the two silicon and four neighbouring carbon atoms, whereas the other two are nearly perpendicular to this plane.[52] The solid ^{29}Si n.m.r. spectrum of this disilene exhibits an anisotropy comparable to that of the solid ^{13}C spectrum of the carbon analogue ethylene. In contrast, the ^{29}Si n.m.r. spectrum of tetramesityldisilene exhibits a much smaller anisotropy, similar to that shown in the ^{13}C spectra of alkanes. Thus, it would appear that the electronic structure of the Si=Si double bond does indeed bear a close resemblance to that of the C=C double bond.[53]



(20)

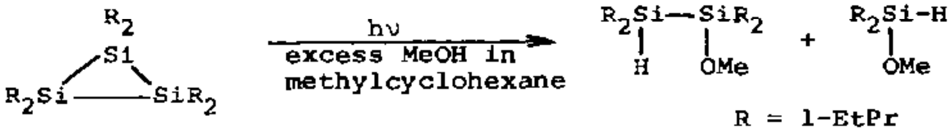
Other methods for the generation of disilene derivatives induce the reduction of 1,2-dihalogenodisilanes using alkali metal naphthalides[54] and the photolysis of cyclotrisilanes[55,56] or strained bridgehead molecules such as 7,7,8,8-tetra-butyl^{t}-7,8-disilabicyclo[2.2.2]octa-2,5-diene (Scheme 2).[57] These routes have been employed for the generation of the tetra-butyl^{t}-, tetra-propyl^{i}-, tetrakis(1-ethylpropyl)-, and tetra-neo-pentyldisilenes, all of which can be trapped by the usual trapping reagents. For example, tetra-butyl^{t}-disilene affords the adducts (21) and (22) with methanol and water, respectively, and the two products (23) and (24) with the diene, 2,3-dimethylbutadiene (Scheme 2).

The photolysis of cyclotrisilanes yields both disilene and the corresponding silylene fragments. Hence, trapping experiments via this method of generation affords products arising from both



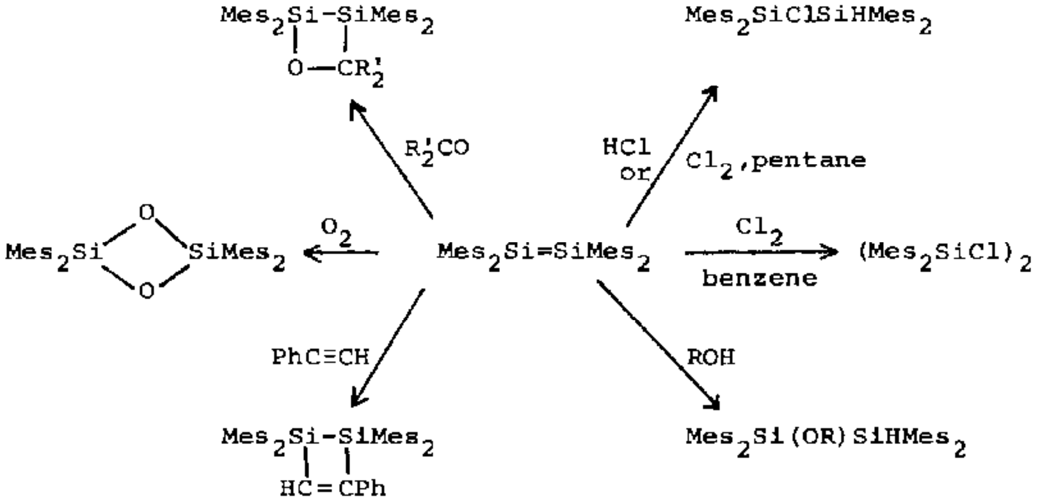
Scheme 2

species, as illustrated , for example, in Scheme 3.



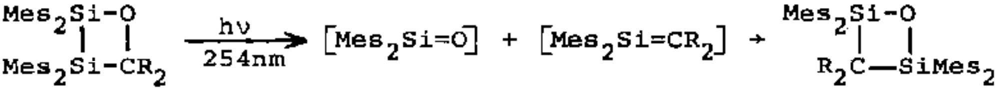
Scheme 3

Disilenes are, not unexpectedly, very reactive. Examples of reactions characterised for tetramesityldisilene are shown in Scheme 4. On photolysis of the acetone adduct (25), rearrangement to 1,3-isomer (26) occurs, probably via cleavage to the silanone and silaethene followed by ring closure in the opposite sense:[58]



Mes = 2,4,6-trimethylphenyl; R = H, or Et; R' = Me or Ph.

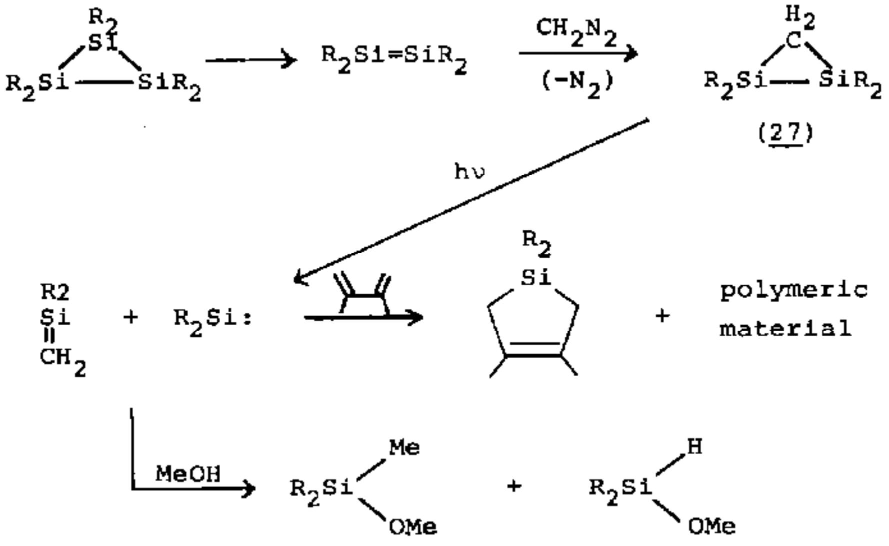
Scheme 4



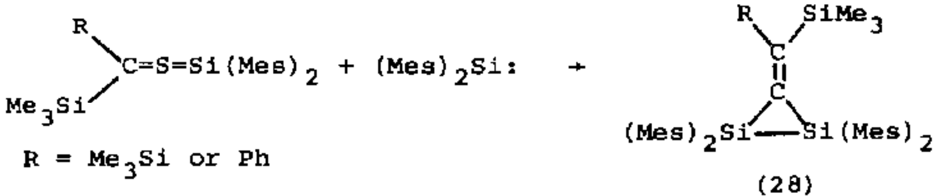
R = Me

(25) (26)

Transformation to $Mes_2HSiSiHMes_2$ occurs on irradiation of tetramesityldisilene in pentane solution. As this product is that expected from abstraction of hydrogen from solvent by silyl radicals, a radical character for the excited state of the disilene is suggested. Reaction of a solution of tetrakis(2,6-dimethylphenyl)disilene in methylcyclohexane at -196° with diazomethane results in the formation of the 1,2-disilacyclopropane derivative (27), which on photolysis in the presence of trapping reagents affords products consistent with the formation of both silaethene and silylene fragments (Scheme 5).[59] Two other stable disilacyclopropanes, (28), have been obtained by the addition of dimesitylsilylene to silapropadiene derivatives.[60] Dimethyl- and diphenylsilylene add stereospecifically to cis and trans-2-butene to give the corresponding siliranes. The facile additions to the cycloadditions are cis. Furthermore, ring-opening of the siliranes by methanol also takes place stereo-

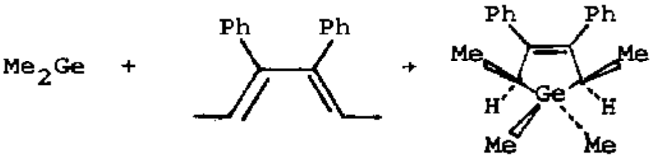


Scheme 5

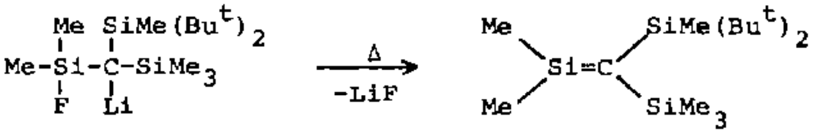


(28)

specifically in a cis fashion.[61] Thermally-generated dimethylgermylene undergoes concerted 1,4-addition of the linear [2+4] cheletropic type with 1,3-dienes under mild conditions:[62]

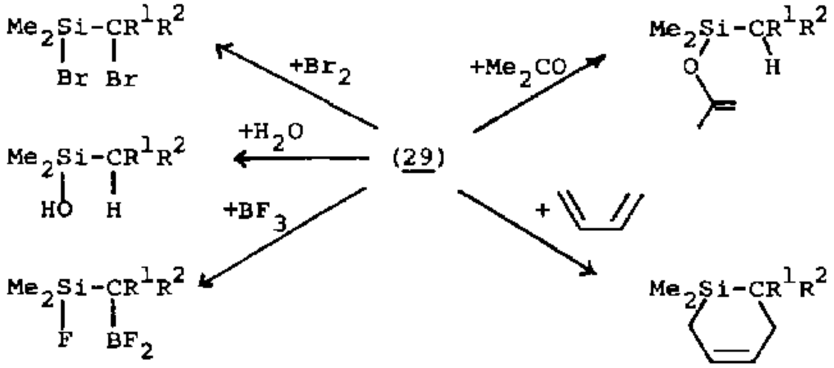


The crystal structure of a stable silaethene was reported in 1982.[63] A second stable silaethene, (29), in which the Si=C double bond is stabilised by bulky silyl groups, has since been described.[64] Synthesis of (29) is achieved by the elimination of LiF from the precursor (30) at temperatures above ca. 100°:



(30) (29)

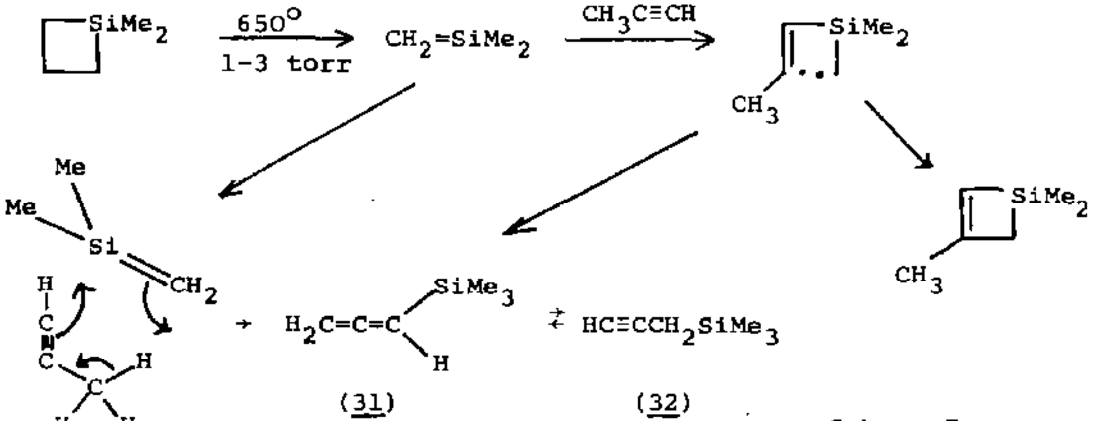
This silaethene may also be obtained in crystalline form by slow recrystallisation from diethylether at -78°, but decomposition occurs within a four days at room temperature or rapidly at 100° to afford secondary products which contain dimers of (29). Several reactions of (29) are shown in Scheme 6.



$R^1 = SiMe_3$; $R^2 = SiMe(Bu^t)_2$

Scheme 6

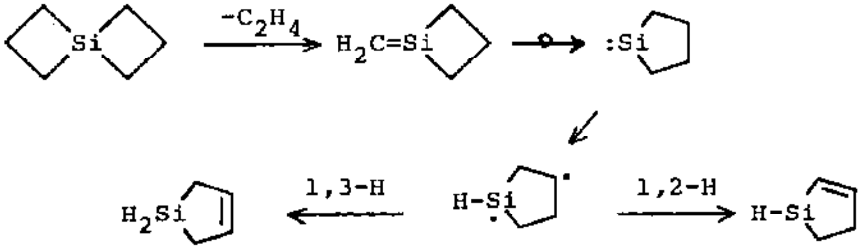
1,1-Dimethylsilaethene, generated by pyrolysis of 1,1-dimethylsilacyclobuta, reacts with alkynes to afford silacyclobutenes and the acyclic products (31) and (32) (Scheme 7):[65]



(31) (32)

Scheme 7

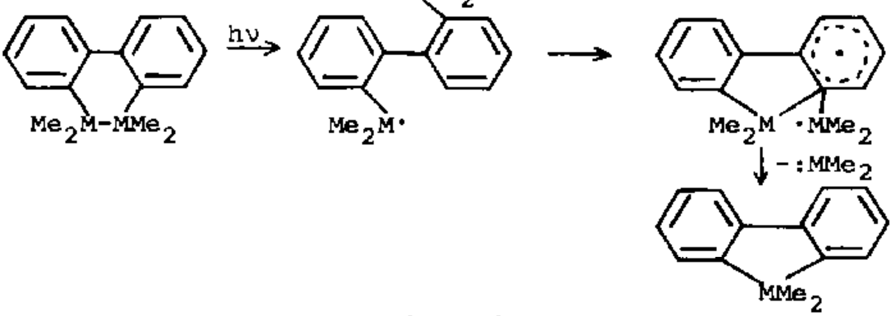
Desorption of trimethylsilane, silacyclobutane, and silacyclohexane from the (110) surface of palladium metal is accompanied by dehydrogenation to silaethylene, silacyclobutadiene, and silabenzene, respectively, which suggests a novel method for the synthesis of these molecules.[66] The conversion of silaspiro 3.3 -cycloheptane into the silacyclopentenes (<u>33</u>) and (<u>34</u>) appears to proceed via a thermally induced silaethene-to-silylene rearrangement (Scheme 8):[67]



(<u>33</u>) (<u>34</u>)

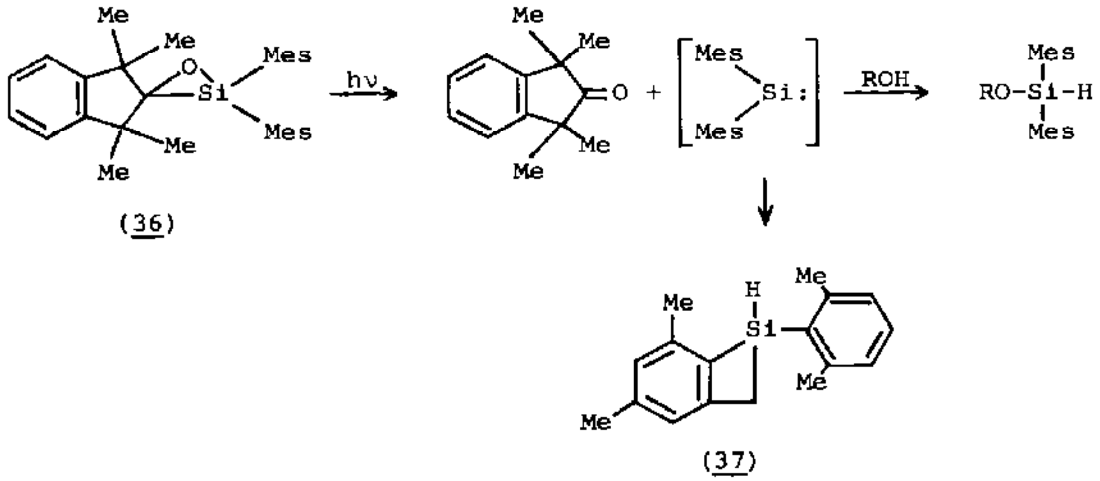
Scheme 8

Thermal decomposition of silacyclobutane leads not only as previously suggested to silaethene and ethene, but also to the silylenes, SiH_2 and SiHMe.[68] Similarly, although the photolysis of 1,1-dimethylsilacyclobutane results predominantly in decomposition to ethene and the silaethene, in the presence of benzene decomposition to cyclopropane and dimethylsilylene also occurs due to sensitization of the silacyclobutane by triplet benzene.[69] The photolysis of dibenzo-1,1,2,2-tetramethyl-1,2-disilacyclohexa-3,5-diene and its germanium analogue (<u>35</u>) results in the exclusive extrusion of the respective silylene or germylene via a route invovling intramolecular ipso aromatic silylation (Scheme 9).[70]



Scheme 9

Dimesitylsilylene is generated by either the photolysis or pyrolysis of the oxasilacyclopropanone (<u>36</u>), and may be trapped by conventional methods. The benzosilacyclobutene (<u>37</u>) was formed in quite large yields in the pyrolysis (Scheme 10).[71]



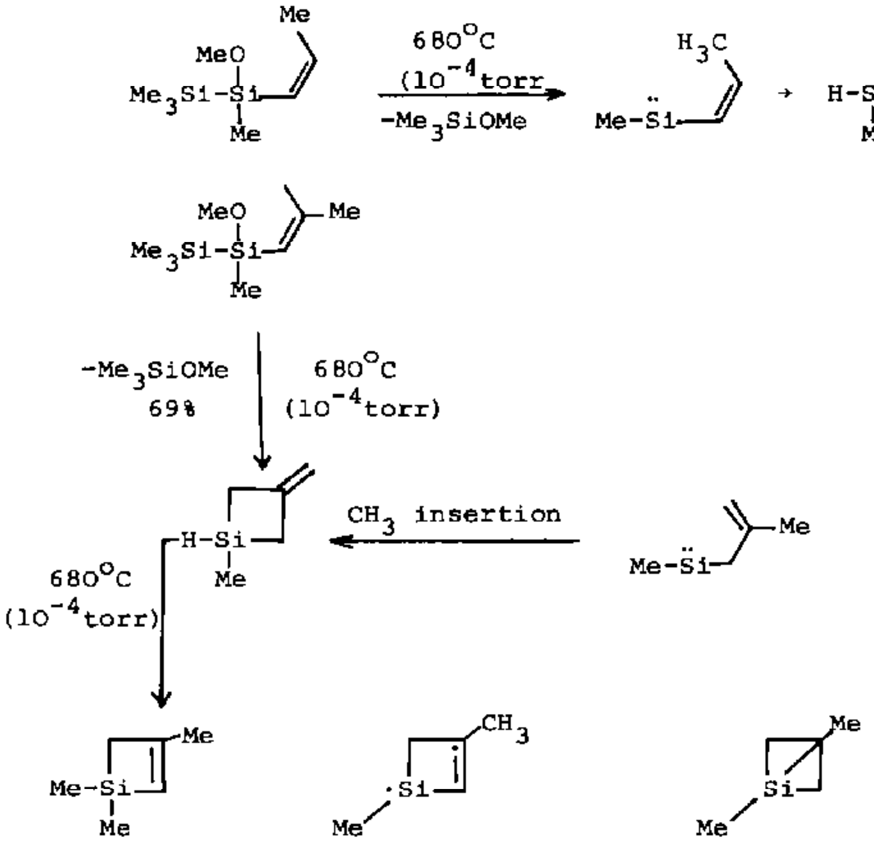
<u>Scheme 10</u>

Silacyclopropenes with silyl or hydride substitution on silicon appear to rearrange thermally to vinylsilylenes.[72]

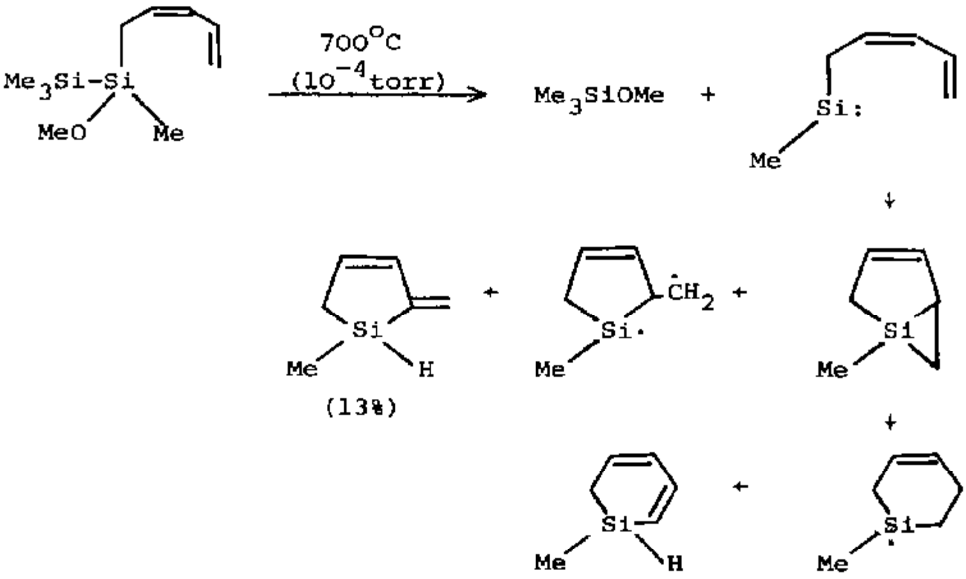
The flash vacuum pyrolysis of methoxydisilanes has been used in order to generate 1-, 2- and 3-proponylsilylenes, each of which affords silacyclobutane products, although probably by different mechanisms (Scheme 11).[73] Methyl-5-(1,3-pentadienylsilylene) reacts similarly (Scheme 12).[74]

Further corroboration of the silylene to disilene rearrangement has been obtained by generating $Me_3SiMe_2SiMeSi$: from 3-methoxyundecamethylpentasilane and observing the rearranged product, $Me_2SiSiMe(SiMe_3)$. In addition, the reverse rearrangement, that is disilene to silylene, has also been demonstrated.[75]

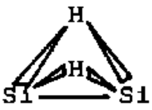
The relative energies of isomers in the Si_2H_2 system have been calculated by ab initio SCF and electron correlation calculations. For the singlet graound state, the global minimum is a non-planar bridged structure, (<u>38</u>), followed by H_2SiSi and trans-bent HSiSiH are predicted to be local minima. For the triplet ground state, H_2SiSi (<u>39</u>) is the global minimum, with the trans-bent structure (<u>40</u>) and a planar bridged structure (<u>41</u>) as local minima.[76] The potential energy hypersurface for the reaction of SiH_2 with H_2 to give SiH_4 has been investigated by a priori quantum mechanical



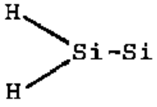
Scheme 11



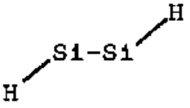
Scheme 12



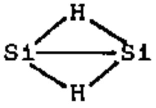
(38)



(39)

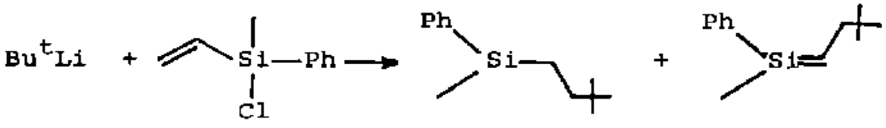


(40)



(41)

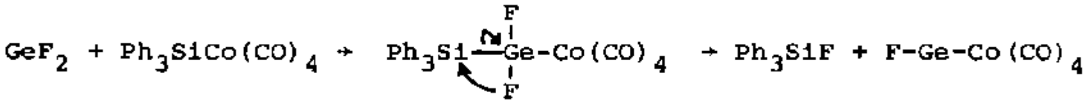
methods, and leads to acceptable agreement with the experimental activation energy.[77] The stability and reactivity of the silicon-metal double bond in $(OC)_5Cr{=}Si(OH)H$ have been studied by the ab initio SCF MO method. The bond dissociation energy of the Cr=Si double bond was calculated to be 29.6 kcal mol^{-1}, indicating the possible existence of a silylene-metal complex.[78] Heats of formation of 1-methylsilaethene and dimethylsilylene of 18 and 46 kcal mol^{-1} have been determined by ion cyclotron double resonance spectroscopy. These data contradict previous studies which indicate that the silylene was favoured in the thermal equilibrium.[79] Highly sophisticated calculations have been performed on the $SiCH_2$ system. The absolute minimum in the potential energy hypersurface is the silylidene, $:Si{=}CH_2$, which lies ca. 50 kcal mol^{-1} below the linear silaacetylene. The vinylidene isomer, $H_2Si{=}C:$, is either a shallow minimum, or, more likely, not a genuine relative minimum at all. Sila-acetylene is predicted to have a trans-bent equilibrium geometry, with a silicon carbon bond distance of 1.635Å, about 0.08Å shorter than a 'standard' Si=C double bond distance. The bond order is suggested to be intermediate between two and three.[80] Ab initio calculations performed on the addition of hydrogen chloride to silaethene predict that the reaction takes place with a small overall barrier and via the formation of a complex and a two-centre transition state in which the Si-C bond distance is lengthened.[81] Both E and Z isomers of 1-methyl-1-phenyl-2-neopentylsilene are generated by the reaction of Bu^tLi with chloromethylphenylvinylsilane, and can be trapped as [4+2] adducts with cyclopentadiene:[82]



(E) (Z)

Both silicon dichloride and silicon difluoride have been studied by electron diffraction, and have valence angles of 102.7°.[83]

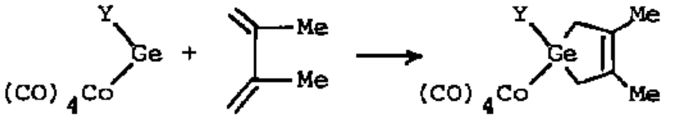
Halogermylenes react readily with dimeric transition metal carbonyl compounds of iron, cobalt and manganese, eg. $Co_2(CO)_8$, $Mn_2(CO)_{10}$, $[Fe(C_5H_5)(CO)_2]_2$ etc., giving the corresponding insertion products. However, in contrast, insertion into Group IVB metal-transition metal bonds results in the formation of unstable adducts leading to the formation of germylenes containing germanium-transition metal bonds:[84]



$$GeF_2 + Ph_3SiCo(CO)_4 \rightarrow Ph_3Si-\overset{F}{\underset{F}{Ge}}-Co(CO)_4 \rightarrow Ph_3SiF + F-Ge-Co(CO)_4$$

$$GeF_2 + 2Ph_3SiCo(CO)_4 \rightarrow 2Ph_3SiF + [(CO)_4Co]_2Ge:$$

Such germylenes undergo the normal types of germylene reactions such as addition to dienes, which unusually are thermally reversible, eg.

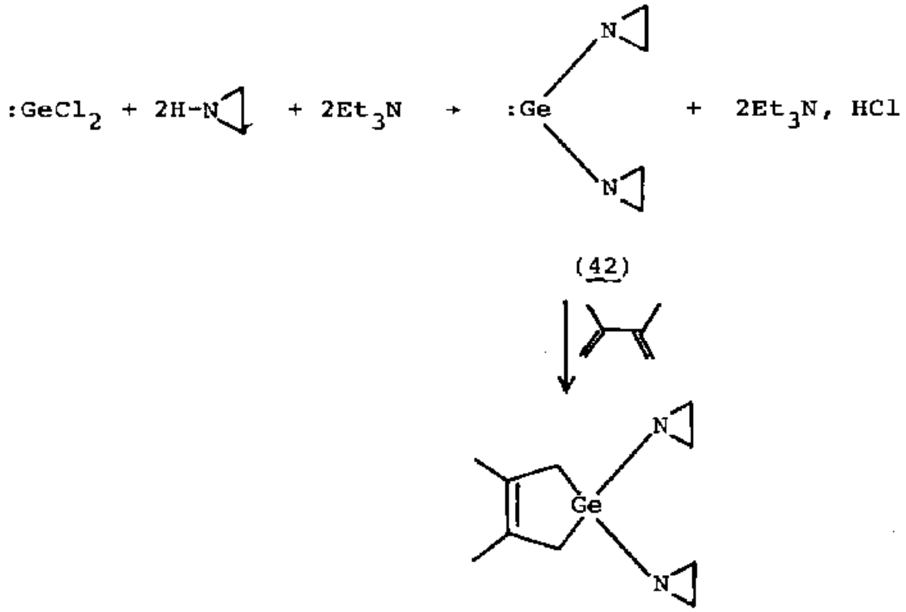


Y = F

Y = $(CO)_4Co$

The singlet potential energy surface of silanone, $H_2Si{=}O$, has been explored by ab initio calculations. The surface differs significantly from the H_2CO potential energy surface. The calculations also show that silanone is expected to be more reactive than silaethene, and disilene.[85] Silathiones and germathiones, previously only characterised by chemical trapping, have now been detected by photoelectron spectroscopy.[86] Transient dialkylgermanones and -germathiones have been generated by β-elimination from oxa- and thia-germacyclobutanes, formed from the condensation of complexed dialkylgermylenes, $R_2Ge{\cdot}NEt_3$ with oxiranes and thiirane, eg:

Dialkylgermylenes did not react with N-substituted aziridine, although :$GeCl_2$ reacted with aziridine to afford the aziridinogermylene (42):

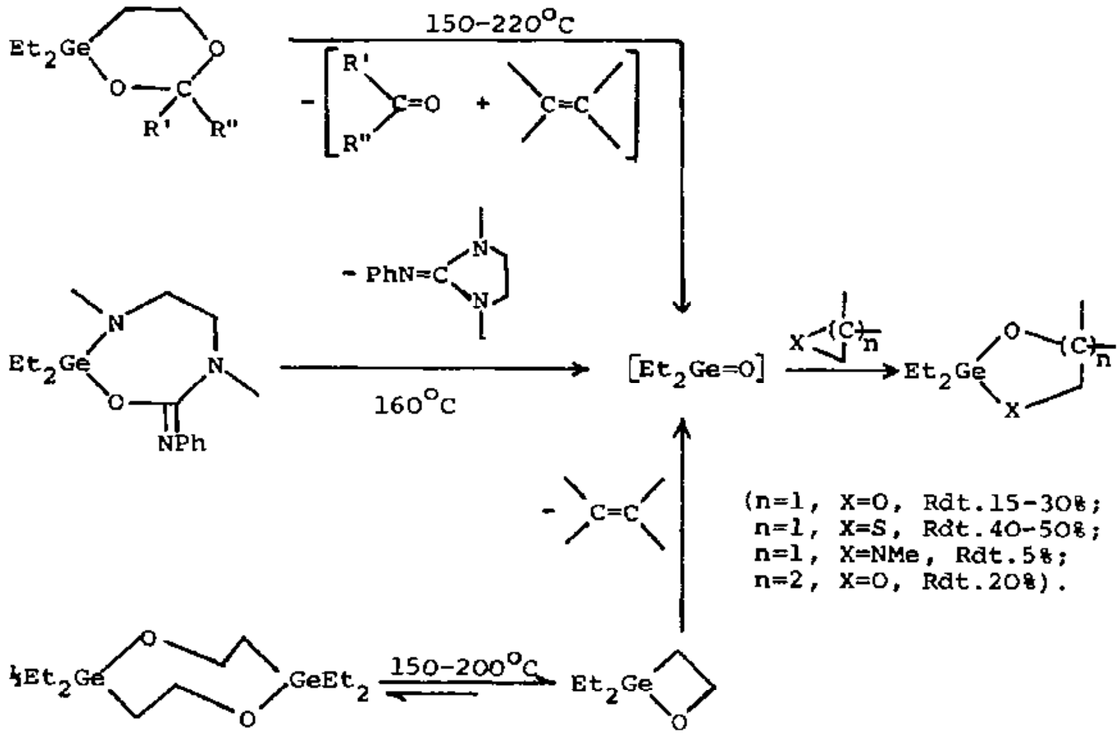


(42)

Complexes are formed between $GeCl_2$ and N-methylaziridine. Dialkylgermylenes insert into the O-H bond of methanol affording the adducts $R_2Ge(H)OMe$.[86] Germanones and germathiones can be generated from a variety of heterocyclic precursors and also the dimeric and trimeric forms, $(R_2GeO)_2$ and $(R_2GeS)_3$. Reaction of the transients with three- and four-membered rings $Y(CH_2)_n$ (n = 2, Y = O, S, NR, CHCN; N = 3, Y = O, S) leads to the formation of ring expanded heterocycles, eg., Schemes 13-15.[87] The trimers $(R_2GeS)_3$ dissociate very readily both thermally and catalytically (eg. with $(Ph_3P)_2PdCl_2$) to the monomeric germathiones, -reactions which are accelerated by the presence of basic solvents such as Et_3N and HMPA.[88]

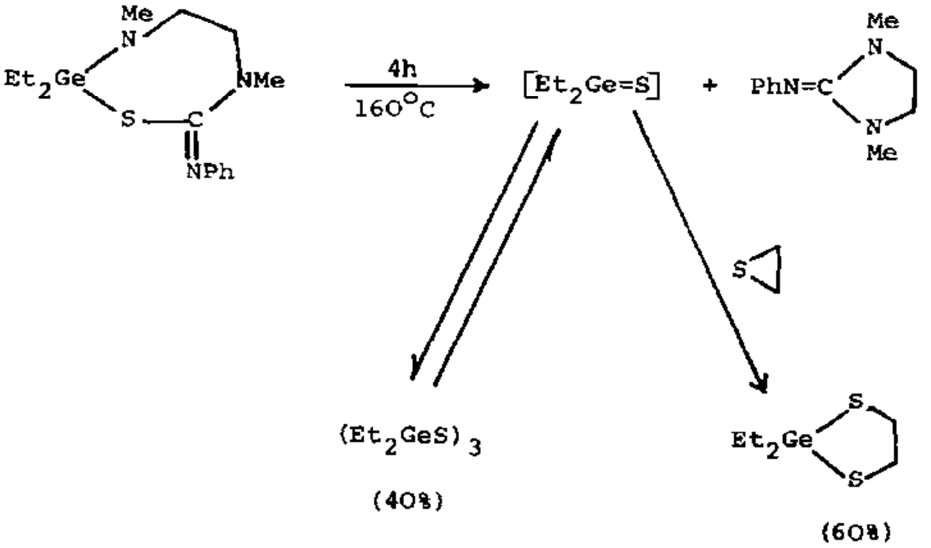
4.3.2 Molecular Compounds

The homogeneous decomposition kinetics of several silanes, including Me_3SiH, Me_2SiH_2, $EtMe_2SiH$, $CH_2{=}CHSiH_3$, $EtSiH_3$ and $PrSiH_3$, have been examined under shock tube conditions.[89] In the reaction of recoil tritium with germane, HT and GeH_3T are produced. Both scavengers and moderators fail to affect the yields of either product.[90] Thermolysis of 1,1-dimethyl-2-phenyl-3-(trimethyl-

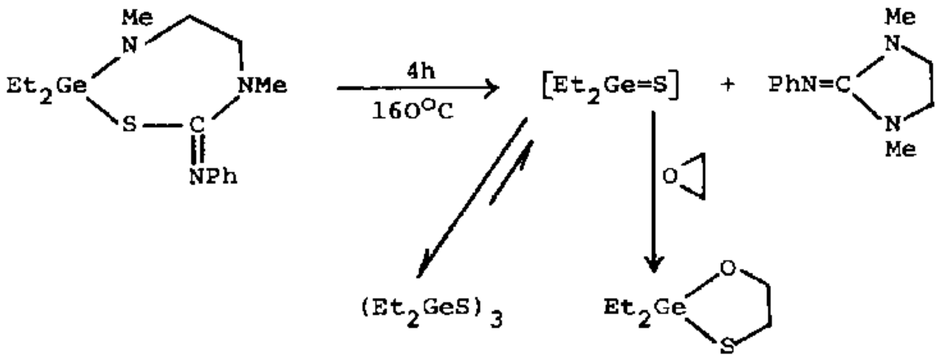


(n=1, X=O, Rdt.15-30%;
n=1, X=S, Rdt.40-50%;
n=1, X=NMe, Rdt.5%;
n=2, X=O, Rdt.20%).

Scheme 13

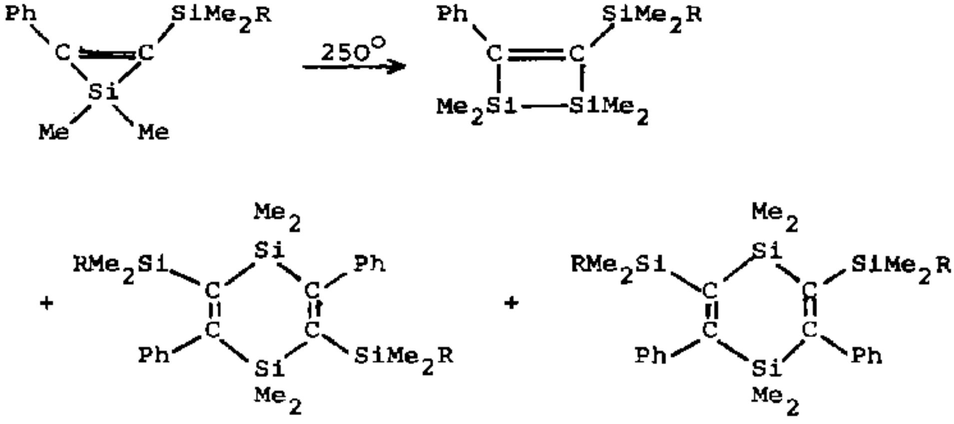


Scheme 14



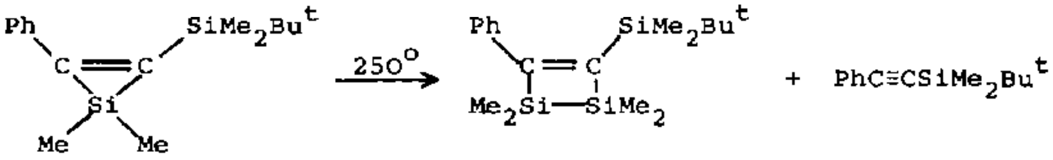
Scheme 15

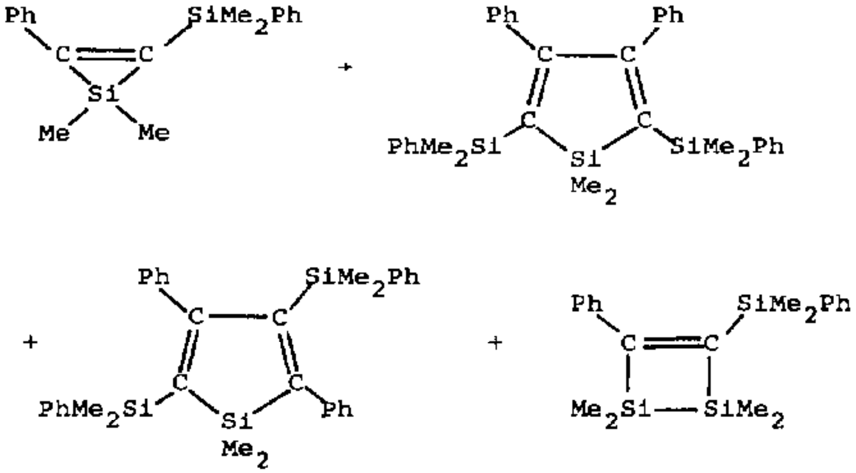
silyl)-1-silacyclopropene and its 3-(ethyldimethylsilyl) homologue in a sealed glass tube at 250° afford two isomers of the respective 1,4-disilacyclohexa-2,5-dienes along with small amounts of the disilacyclobutenes:



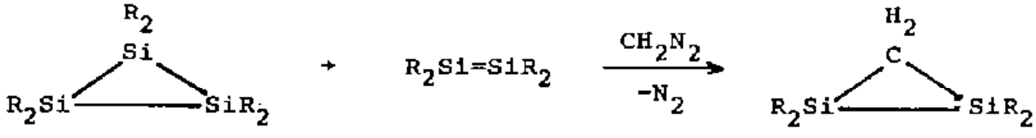
R = Me,Et.

Under identical conditions, the tert-butyldimethylsilyl analogue afforded high yields of the 1,2-disilabutene only, while 1,1-dimethyl-2-phenyl-3-(phenyldimethylsilyl)-1-silacyclopropene gives two isomers of 1-silacyclopenta-2,4-diene and 1,1,2,2-tetramethyl-3-phenyl-4-(phenyldimethylsilyl)-1,2-disilacyclobutene:[91]





1,1,2,2-Tetrakis(2,6-dimethylphenyl)-1,2-disilacyclopropane has been synthesised by the [1+2] addition of carbene to a disilene:[92]

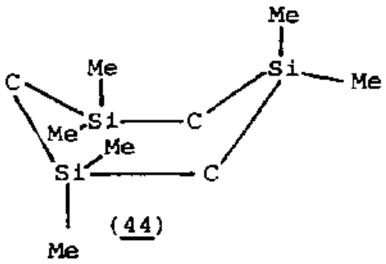


(43)

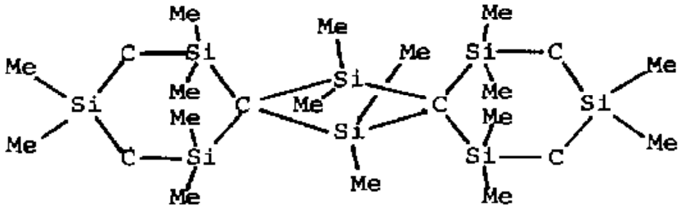
R = 2,6-dimethylphenyl.

Besides that of (43),[92] the structures of two other cyclic carbosilanes have been determined. 1,1,3,3,5,5-hexaphenyl-1,3,5-trisilacyclohexane, (44), has a flattened twist boat conformation,[93] whilst the dispiro system in (45) is formed by a central disilacyclobutane and two C-spiro connected trisilacyclohexane rings. The six-membered rings in this case have a flattened chair conformation. The Si-C bonds at the strained spiro region are distinctly lengthened (192pm) compared to the Si-C bonds at the opposite silicon atoms in the 6-membered rings.[94]

The insertion of difluorocarbene into the Si-Si bond of $(FMe_2Si)_2$ leads to the formation of $(FMe_2Si)_2CF_2$, which undergoes Si- rather than C-alkylation with MeMgCl or MeLi. Treatment with $LiAlH_4$

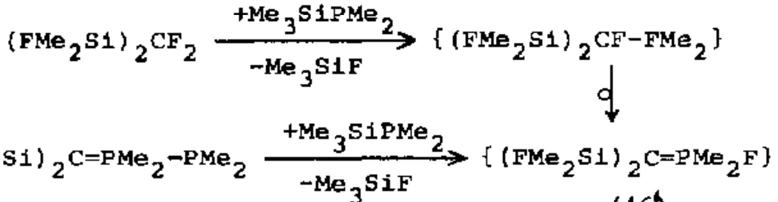


(44)



(45)

affords the corresponding silanes. In all cases the CF_2 group remains inert, although the ylide (46) is formed on treatment with Me_3SiPMe_2:[95]



$$(FMe_2Si)_2CF_2 \xrightarrow[-Me_3SiF]{+Me_3SiPMe_2} \{(FMe_2Si)_2CF\text{-}FMe_2\}$$

$$\{(FMe_2Si)_2CF\text{-}FMe_2\} \xrightarrow{d} \{(FMe_2Si)_2C{=}PMe_2F\}$$

$$(FMe_2Si)_2C{=}PMe_2\text{-}PMe_2 \xleftarrow[-Me_3SiF]{+Me_3SiPMe_2} \{(FMe_2Si)_2C{=}PMe_2F\}$$

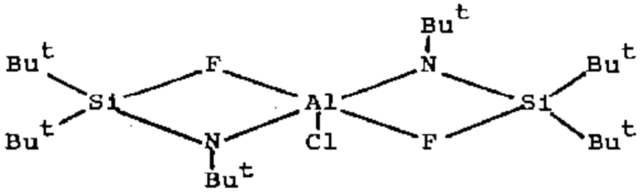
(46)

The preparation of pure diastereoisomers of both 1-naphthylphenylmethyl(1-chloro- and 1-bromoethyl)silanes, optically active at both carbon and silicon, has been described. Crystal structures of both were reported.[96] The reaction of $SnCl_4$ with silanes of the types $R_{3-n}SiH_{n+1}$ (n = 0-2) invariably leads to monochlorination at silicon.[97] The isomerisation of $(Me_3Si)_3CSiMe_2(OCN)$ to the isocyanate is second order in diphenylether at 195°, and is catalysed by ICl in CCl_4 and by NaOMe in MeOH.[98] Mono- and polydentate phosphanes of the types $Me_{4-n}M(CH_2PMe_2)_n$ (n = 1-4, M = Si,Sn) may be prepared by the reaction of the chlorosilane or -stannane with $LiCH_2PMe_2$. The materials are easily deprotonated at the methylene carbon atom.[99] Metathesis employing pentamethylcyclopentadienyllithium has been used to synthesise several monohapto pentamethylcyclopentadienylsilanes and germanes. The other substituents on the metalloid have little influence on the speed of the sigmatropic shift processes.[100] Three products,

$(C_5Me_5)_2Ge$, C_5Me_5GeCl, or $C_5Me_5Ge_2Cl_3$, are produced in the reaction of C_5Me_5Li with germanium dichloride-dioxane depending on the molar ratio of the reactants.[101] The structure of 1,1'-dimethylgermanocene, $(MeC_5H_4)_2Ge$, has been determined by electron diffraction in the gas phase, and shown to be an angular sandwich. The angle between the planes of the two rings is 34(7)°. Ab initio MO calculations on $(C_5H_5)_2Ge$ indicate that metal-to-ring bonding is due primarily to interaction between the e_1 π orbitals of the rings and the $4p_x$ and $4p_y$ orbitals on germanium. The "lone pair" is predominantly on the germanium 4s orbital.[102]

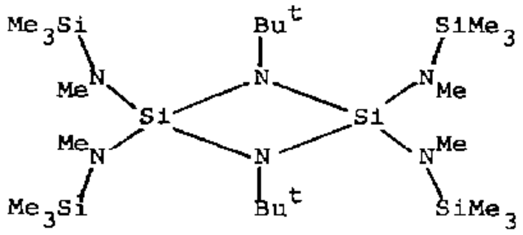
Enthalpies of reaction of several silylamines with phenol, iodine, chloroform and trimethylaluminium have been determined. The data indicate that the alkylsilylamines may not be weaker bases than the corresponding aliphatic amines.[103] Tris(trimethylsilyl)amine and other related silylamines have been studied both by photoelectron spectroscopy and by theoretical (MNDO and ab initio) methods. Ab initio calculations on Me_2NSiH_3 predict a very flat potential surface around nitrogen, suggesting a balance of forces tending toward pyramidal and planar geometries. The results do not wholly support the previous electron diffraction description of this molecule.[104] The conformations of tetramethyl-N,N'-diphenylcyclodisilazane and the corresponding bis-tilylcyclodisilazanes have been studied in solution by ^{13}C n.m.r. Those of the m- and p-tolyl derivatives have also been studied by X-ray crystallography in the solid, and found to be identical with the solution data.[105]

The lithium salts of tert-butylaminodiorganofluorosilanes, $RR'SiFNBu^tLi$, react with aluminium trichloride in petroleum ether, with the elimination of HF, to afford adducts of the silicenium ylide, $(RR'SiNBu^t)AlCl_3$. Hydrolysis of these adducts yields the siloxanes $(RR'SiO)_3$ and $Bu^tNH_2.AlCl_3$. The major product from the reaction of $Bu^t_2SiFNBu^tLi$ with Al_2Cl_6 in thf is the compound $(Bu^t_2SiNBu^t)_2AlClF_2$, which has the structure (46).[106]



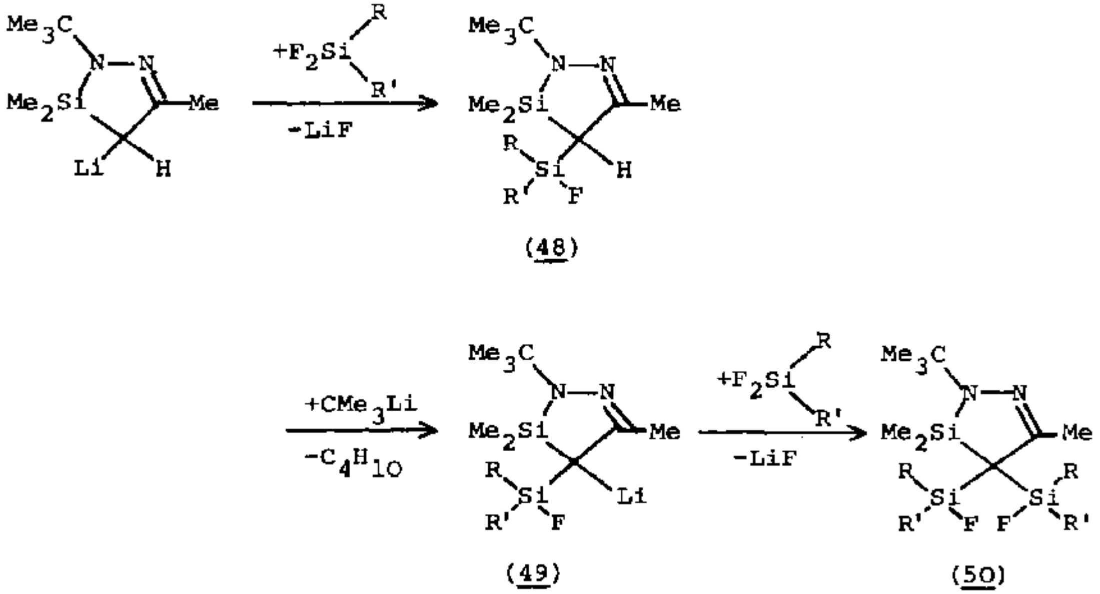
(46)

The dimeric silylaminodichloroalane, $[(Me_2SiNMe)_2SiFNBu^tAlCl_2]_2$, along with small amounts of the cyclodisilazane, $[(Me_3SiNMe)_2SiNBu^t]_2$, is formed with the lithium salt, $(Me_3SiNMe)_2SiFNLiBu^t$, reacts with aluminium trichloride. The cyclodisilazane has a structure in which the central four-membered $[Si_2N_2]$ ring is planar (47).[107]



(47)

Lithium salts of 1,2-diaza-3-sila-5-cyclopentenes react with fluorosilanes and aminofluorosilanes to afford 4-(fluorosilyl)-substituted derivatives (48), which react with tert-butyllithium giving the lithium salts (49). These may then be transformed to the heterocycles (50) by treatment with fluorosilanes:[108]

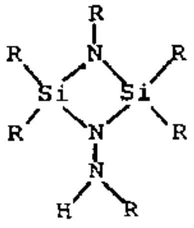


(48)

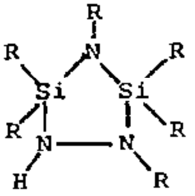
(49)

(50)

N,N-Bis(fluorosilyl)amines react with dilithiated hydrazines to give 4- and 5-membered heterocycles such as (51) and (52).[109]

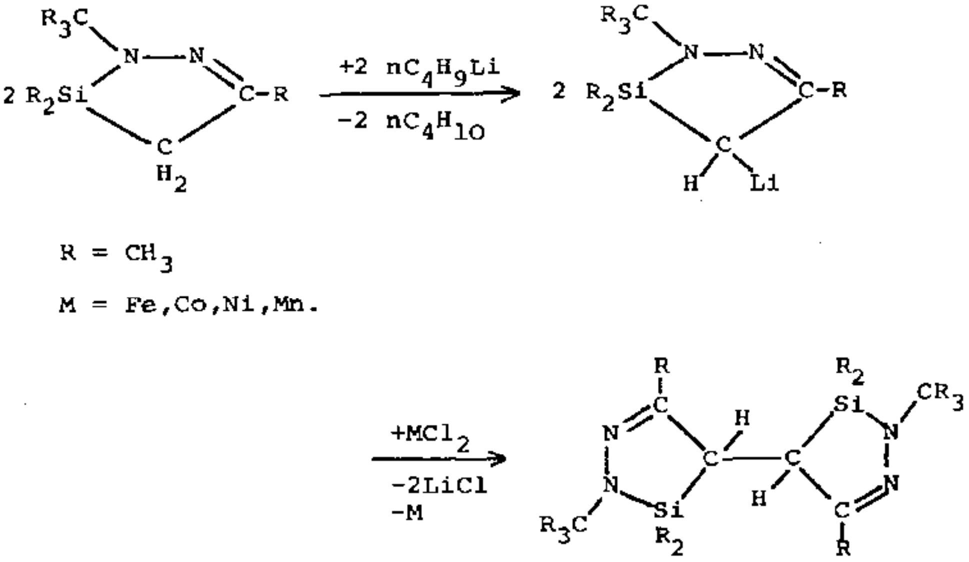


(51)



(52)

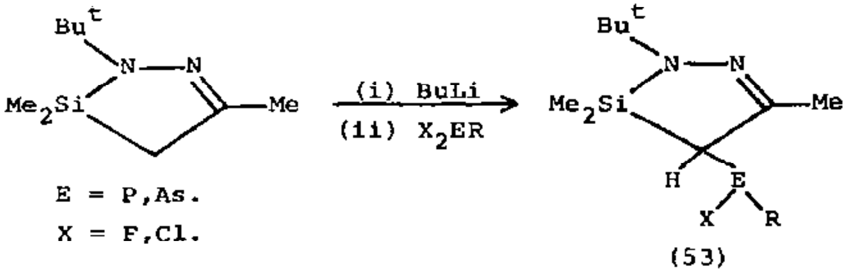
4-Lithium-3,3,5-trimethyl-2-tert-butyl-1,2-diaza-3-sila-5-cyclopentene undergoes oxidation followed by dimerisation on reaction with transition metal chlorides:[110]



R = CH_3

M = Fe,Co,Ni,Mn.

1,2-Diaza-3-sila-5-cyclopentenes which are unsubstituted at the 4-position react, after lithiation, with halophosphanes and arsanes to give the products (53):

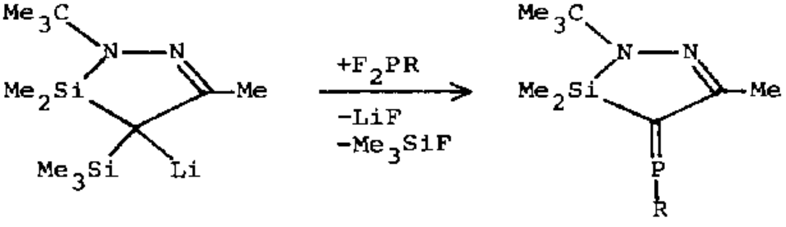


E = P,As.

X = F,Cl.

(53)

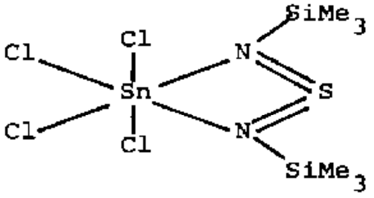
The phosphaethenes, (54), are formed from 4-trimethylsilyl-substituted lithiated rings by reaction with difluorophosphanes and elimination of LiF and chlorosilane:[111]



(54)

R = $N(SiMe_3)_2$, $N(SiMe_3)Bu^t$.

Both Me_3SiNSO and $Me_3SiNSNSiMe_3$ react with tin(IV) chloride to afford the 1:1 adduct $Me_3SiNSNSiMe_3.SnCl_4$, in which the sulphurdiimide functions as a bidentate ligand as in (55):[112]

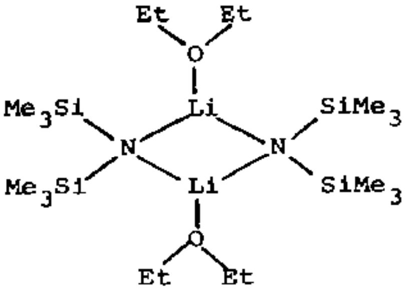


(55)

The reaction of $R_3SiNSOF_2$ with the hexafluoroarsenate salts, $[M(SO_2)_2](AsF_6)_2$ (M = Co,Ni,Cu), yields the metal bis(imidodifluorosulphates), $M(NSOF_2)_2$. The intermediates in the reactions, $[Ni(SO_2)_2\{AsF_4(NSOF_2)_2\}_2]$ and $[Cu(NSOF_2)(AsF_5NSOF_2)]$, were also isolated.[113]

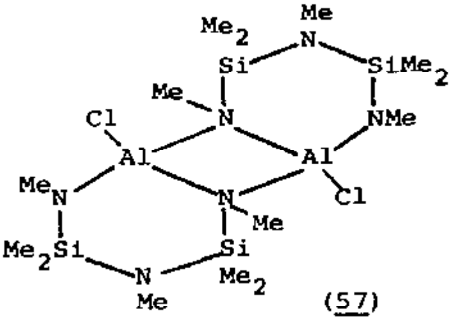
Silylamino derivatives of several elements have been studied. The structures of two silylamino lithium salts have been determined. The 1:1 adduct, $Li[N(SiMe_3)_2].OEt_2$, comprises dimeric molecules, (56), of 222 symmetry with the silazane groups functioning as the bridging ligands.[114,115]

The alkali metal derivatives, $(Me_3SiNM)_2SiMe_2$, have been obtained by the reaction of octamethyldisilatriazane with the metal amide (M = Na,K,Cs), or with the metal in the presence of styrene (M = K,Rb), or with elemental caesium. Both the dilithium and disodium derivatives form stable complexes with ethers, and are both dimeric in benzene solution. However, the

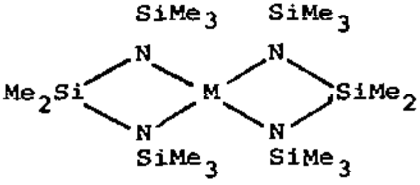


(56)

disodium derivative is trimeric in the solid state. The trimers possess a cluster of six sodium cations which are bridged by the nitrogen atoms of the anions.[116] The dimeric cycloalumadisilatriazane system (57) has been prepared by the reaction of the dilithium salt $MeN(SiMe_2NMeLi)_2$ with aluminium(III) chloride at -60°.[117] Similar methods have also been employed for the synthesis of the spiro compounds (58) and also (59).[118]

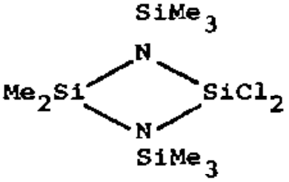


(57)



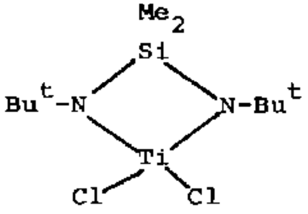
M = Si,Ge,Sn,Ti

(58)



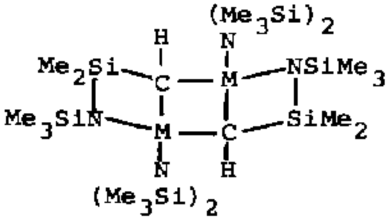
(59)

Several silylamido derivatives of Group IVA metals have been synthesised, and the structures of selected examples determined. The titanium derivative, (60), is monomeric in the crystal.[119]



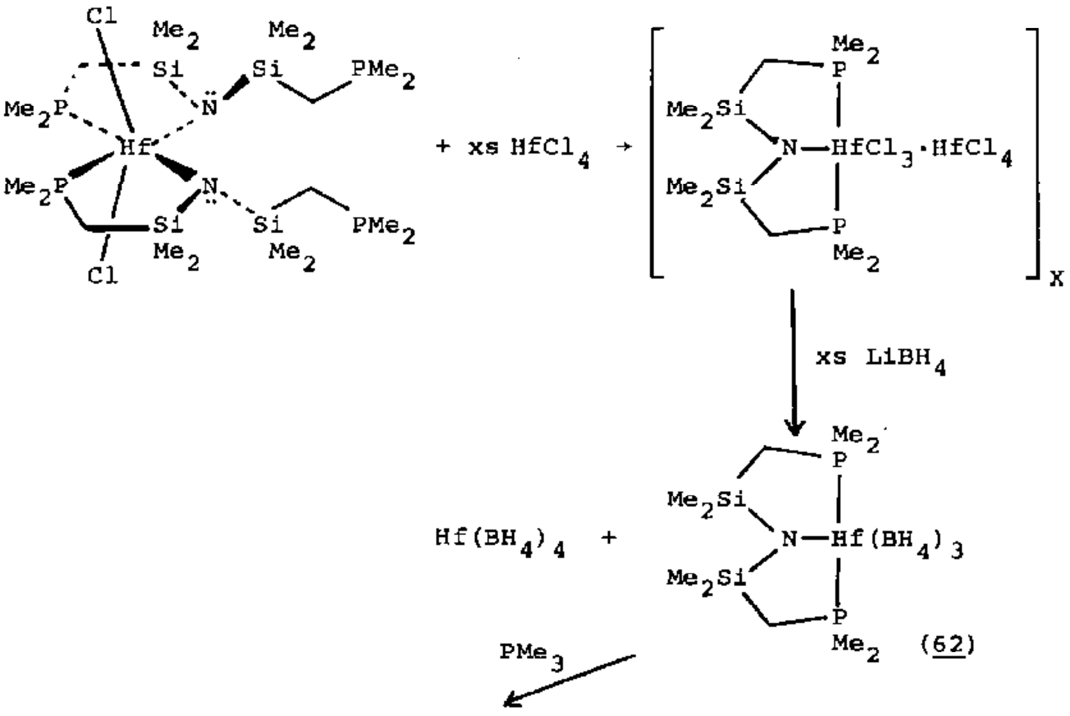
(60)

The reaction of $LiN(SiMe_2CH_2PR_2)_2$ with either zirconium(IV) or hafnium(IV) chloride generates the complexes $MCl_2(NSiMe_2CH_2PR_2)_2$ (M = Zr,Hf; R = Me,Ph). Both of the potentially terdentate hybrid ligands bind in a bidentate fashion only, so that both coordinated and uncoordinated phosphines are present in the same molecule. The crystal structure of the zirconium complex shows it to possess a distorted octahedral geometry with trans chloride and cis phosphine ligands. The molecule is chiral in both the solid and in solution due to the 'gear' effect of the two bulky disilylamide ligands.[120] Zirconium dialkyls of the type $R_2Zr[N(SiMe_3)_2]_2$ (R = Me,Et,CH_2SiMe_3), decompose at 60° (10^{-2} mm Hg) with the elimination of the alkane, CH_4, C_2H_6 or Me_4Si, respectively, to afford the bridged carbene complex $\{ZrCHSiMe_2NSiMe_3[N(SiMe_3)]\}_2$, which forms a 1:1 adduct with pyridine. The related hafnium complexes decompose in a similar manner, although in this case the product could only be characterised as its pyridine adduct. In contrast, the titanium compound, $Me_2Ti[N(SiMe_3)_2]_2$ is thermally stable up to 190°. However, the titanium-carbene complex $\{TiCHSiMe_2NSiMe_3[N(SiMe_3)_2]\}_2$ can be obtained by the sodium amalgam reduction of $Cl_2Ti[N(SiMe_3)_2]_2$. In the solid, the zirconium-carbene complex has the structure (61) comprising three fused planar four-membered rings giving the molecule a "tub" conformation.[121]



(61)

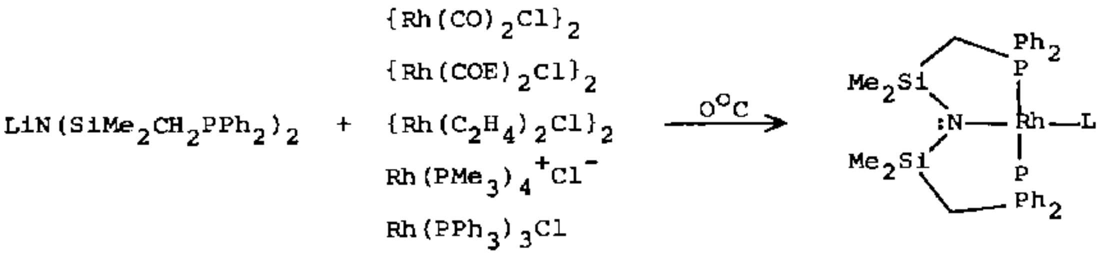
These zirconium- and hafnium-carbene complexes react with 1,2-bis(dimethylphosphino)ethane (dmpe) at room temperature to afford the bis(metallacycle)s $M[CH_2SiMe_2NSiMe_3]_2$(dmpe) in essentially quantitative yield. The same products are also obtained from the phosphine and the dialkyls $R_2M[N(SiMe_3)_2]_2$ at 60°, and are formally derived by addition of a γ-CH bond of a $N(SiMe_3)_2$ group to a metal-carbon (carbene) bond. The zirconium heterocycle has distorted octahedral coordination with idealised C_2 symmetry in which the two phosphorus atoms occupy cis sites trans to the two nitrogen atoms, and the remaining two trans sites are occupied by the carbon atoms of the metallocycle rings. The complex reacts with carbon monoxide under pressure (19 atmos.) at room temperature to afford $Zr[OC(=CH_2)SiMe_2NSiMe_3]_2$(dmpe).[122] Disproportionation of $HfCl[N(SiMe_2CH_2PMe_2)_2]_2$ by excess hafnium(IV) chloride results in the formation of the mono-amide complex, $HfCl_3[N(SiMe_2CH_2PMe_2)_2]HfCl_4$, which is converted into $Hf(BH_4)_3[N(SiMe_2CH_2PMe_2)_2]$ (<u>62</u>) and $Hf(BH_4)_4$ by treatment with excess $LiBH_4$. Reaction of (<u>62</u>) with Lewis bases results in the formation of the hydride:[123]



$\{Hf[N(SiMe_2CH_2PMe_2)_2]\}_2(H)_3(BH_4)_3 + H_3B\text{-}PMe_3$

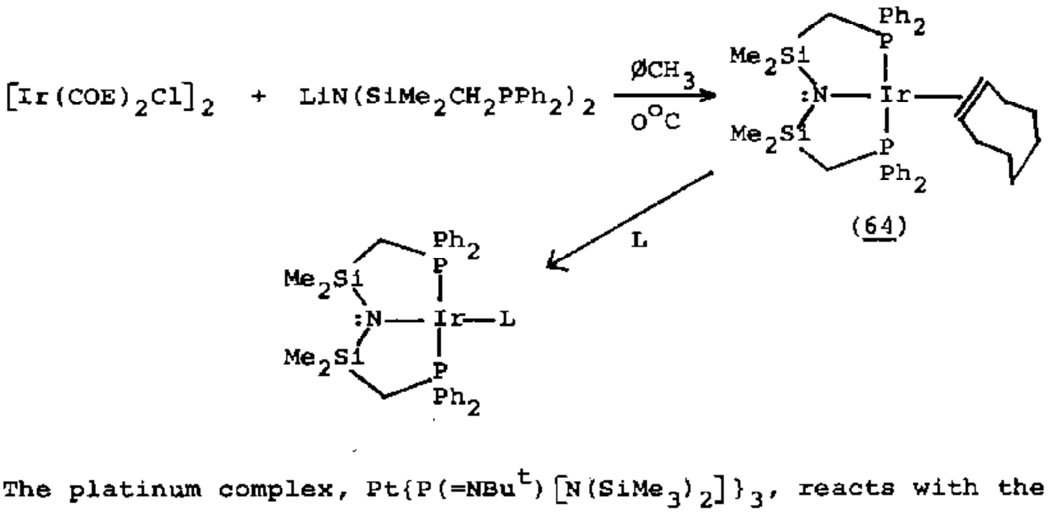
(<u>63</u>)

Reaction of $LiN(SiMe_2CH_2PPh_2)_2$ with a variety of rhodium precursors results in high yields of rhodium(I) amidophosphines:



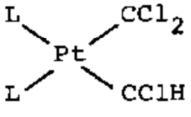
L = CO, cyclooctene, C_2H_4, PMe_3, PPh_3.

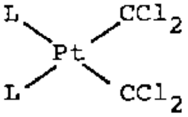
In all of these complexes, the hybrid ligand is also coordinated in a terdentate fashion, resulting in a square-planar, 16-electron species. The analogous iridium derivatives may be prepared in a similar manner, or, more simply, by the reaction of the iridium cyclooctene amide (<u>64</u>) with the desired neutral ligand at room temperature:[124]

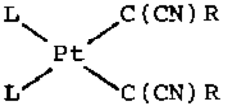


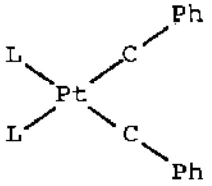
The platinum complex, $Pt\{P(=NBu^t)[N(SiMe_3)_2]\}_3$, reacts with the alkenes, C_2Cl_3H, C_2Cl_4, $C_2H_2(CN)_2$, and $C_2(CN)_4$, to afford the complexes (<u>65</u>-<u>67</u>), respectively. The complex (<u>68</u>) is obtained with diphenylacetylene.[125]

Several papers describe compounds containing the Si-N-P linkage. Treatment of $(Me_3Si)_2N\text{-}P{=}NSiMe_3$ with 2,4,6-tri-tert-butylphenyl lithium and 2,2,6,6-tetramethylpiperidine hydrochloride leads to the formation of (<u>69</u>).[126]


(65)


(66)

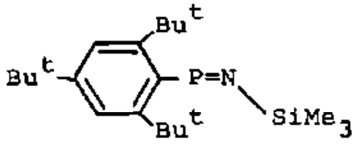

(67)


(68)

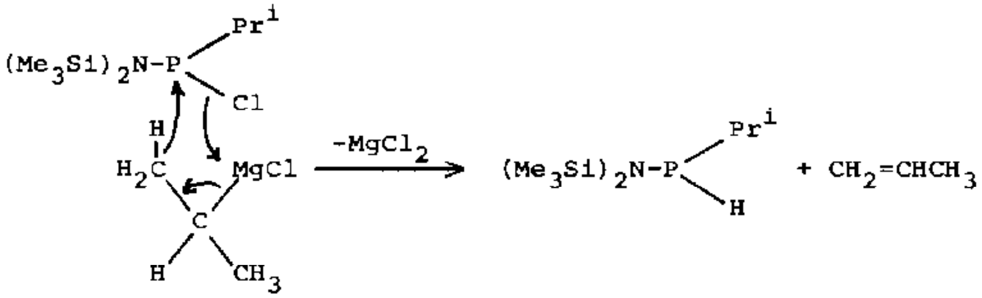
L = $\mathrm{Bu^tN{=}P{-}NBu^t(SiMe_3)}$

R = H

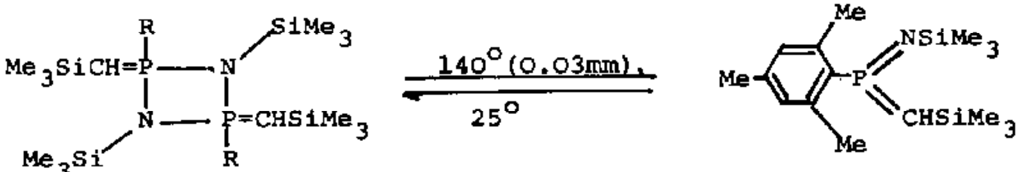
R = CN


(69)

The reactions of [bis(trimethylsilyl)amino]chlorophosphines, $\mathrm{(Me_3Si)_2NPRCl}$, with isopropylmagnesium chloride generally yield mixtures of the isopropyl substitution products $\mathrm{(Me_3Si)_2NPRPr^i}$ together with the unexpected reduction products $\mathrm{(Me_3Si)_2NPRH}$. These latter products appear to be formed by a process in which the Grignard reagent acts as a reducing agent with the elimination of propylene:



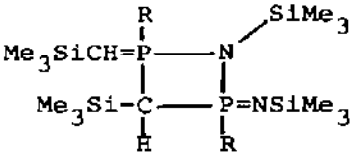
The reaction is catalysed by magnesium salts, and the relative yield of the reduced product increases with the steric bulk of the phosphorus substituents.[127] Bis(disilylamino)phosphines, $\mathrm{[(Me_3Si)_2N]_2PCH_2R}$, have been synthesised by the reaction of Grignard reagents with $\mathrm{[(Me_3Si)_2N]_2PCl}$. Reaction of $\mathrm{[(Me_3Si)_2N]_2PMe}$ with $\mathrm{Me_3SiN_3}$ affords $\mathrm{[(Me_3Si)_2N]_2PMe{=}NSiMe_3}$, and with MeI to give $\mathrm{[(Me_3Si)_2N]_2\overset{+}{P}Me_2\ I^-}$. With $\mathrm{CCl_4}$, mixtures of $\mathrm{(Me_3Si)_2NPCl(Me_3SiCHR){=}NSiMe_3}$ and $\mathrm{(Me_3Si)_2NPCl(CH_2R){=}NSiMe_3}$ are obtained.[128] The thermally unstable mesitylchlorophosphine, $(Me_3Si)_2NP(2,4,6\text{-}Me_3C_6H_2)Cl$, is obtained by the reaction of $2,4,6\text{-}Me_3C_6H_2PCl_2$ with one equivalent of $(Me_3Si)_2NLi$, and can be converted into the more stable derivatives $(Me_3Si)_2NP(Me_3C_6H_2)R$ ($R = H, Me, CH_2SiMe_3$) on further substitution. Treatment with Me_3SiN_3 yields the unstable azide $(Me_3Si)_2NP(Me_3C_6H_2)N_3$.[129] The reaction of CCl_4 with $(Me_3Si)_2NP(C_6H_2Me_3)CH_2SiMe_3$ unexpectedly yields the four-membered $[P_2N_2]$ ring compound, (70), which on heating under a dynamic vacuum dissociates to the monomeric, three-coordinated iminomethylenephosphorane (71). This compound is stable at room temperature for a short time, but reverts to (70) after a few days.



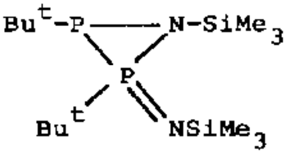
(70) (71)

$R = 2,4,6\text{-}Me_3C_6H_2$.

Treatment of (71) with methanol affords the stable addition product $Me_3SiN{=}P(Me_3C_6H_2)(OMe)CH_2SiMe_3$. When either the dimer (70) or monomer (71) is heated in a sealed tube, the isomeric, four-membered [PCPN] dimer (72) is obtained quantitatively.[130]



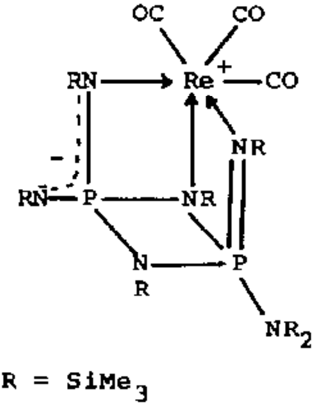
(72)



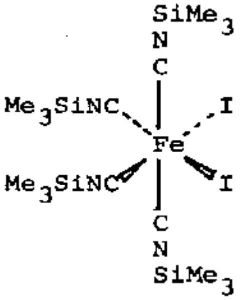
(73)

The azadiphosphirane (73) has been prepared by elimination of Me_3SiCl from $Bu^tP(Cl)N(SiMe_3)_2$.[131] Reaction of $(Me_3Si)N\text{-}P({=}NSiMe_3)$ with $[Re(CO)_3(THF)Br]_2$ affords the complex (74).[132]

The interaction of iron(II) iodide with excess Me_3SiNC in thf affords (75) in high yield.[133] The novel silylaminoarsines, $(CF_3)_2AsN(SiMe_3)$ and $CF_3As[N(SiMe_3)_2]_2$ have been obtained by substitution of $(CF_3)_nAsCl_{3-n}$ using $LiN(SiMe_3)_2$. Chlorination of



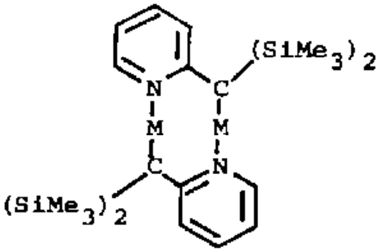
(74)



(75)

the former gives $[(CF_3)_2As(Cl)N(SiMe_3)]_2$, which on refluxing in n-hexane or n-heptane results in the formation of trimeric and tetrameric bis(trifluoromethyl)arsazenes, $[(CF_3)_2AsN]_3$ and $[(CF_3)_2AsN]_4$.[134]

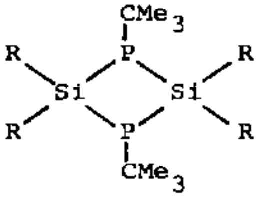
Reactions of 2-bis(trimethylsilyl)methylpyridine with n-butyllithium in hexane-diethylether and n-butyllithium in thf followed by copper(I) chloride yields the thermally robust binuclear complexes (76) (M = Li,Cu), in which the metal is not involved in electron deficient bonding, being bound by C_α of one ligand and the nitrogen of a centrosymmetrically related ligand. There are close metal-metal contacts in each compound (Li...Li 2.560(9)Å; Cu...Cu 2.412(1)Å).[135] The structures of two silylmethyllithium compounds have been determined. That of tris(trimethylsilyl)methyllithium thf solvate is an ate complex with $[Li(thf)_4]$ cations and $\{Li[C(SiMe_3)_3]_2\}$ anions in which the lithium bridges the two organic residues.[136] In the thf adduct of tris(phenyldimethylsilyl)methyllithium, crystals comprise



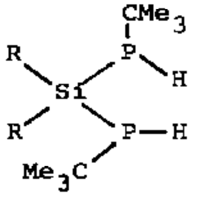
(76)

monomeric species in which the lithium is covalently bonded to oxygen and to the central carbon atom of the $(Me_2PhSi)_3C$ group, and also interacts strongly with the ipso carbon atom of one of the phenyl groups without significantly distorting the hybridisation of the atom.[137] Treatment of $Li[C(SiMe_3)_3]$ with PPh_2Cl affords $P[C(SiMe_3)_3]Ph_2$, which, in spite of the steric crowding may be readily converted into the phosphonium salts, $[P\{C(SiMe_3)_3\}Ph_2H]I$ and $[P\{C(SiMe_3)_3\}Ph_2Me]I$. On heating, the latter salt gives the ylid $MePh_2P{=}C(SiMe_3)_2$.[138]

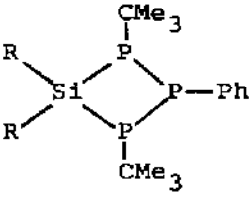
Numerous cyclic and open-chain compounds containing Si-P bonds have been investigated. 1,3-Diphospha-2,4-disilacyclobutanes (77) have been prepared by the ring closure of fluorodialkylsilyl-(t-butyl)phosphines using Bu^{t}Li, whilst ring closure of the bis(phosphane) (78) affords the 1,2,3-triphospha-4-sila-cyclobutane (79).[139,140] The structure of the cis isomer of (80) has been determined.[140] The reaction of $[(Me_3Si)_2P]_2PLi$ with Ph_2PCl affords only small amounts of the expected coupled product $[(Me_3Si)_2P]_2P\text{-}PPh_2$. Instead, the main products are $(Me_3Si)_2P\text{-}PPh_2$ and Ph_2PPPh_2 along with $(Me_3Si)_3P$ and Me_3SiPPh_2.[144] White phosphorus reacts with Bu^{t}Li and Me_3SiCl to afford $P_4(SiMe_3)Bu^t_3$, which with Bu^{n}Li forms $LiP_4Bu^t_3$. Similarly, Bu^{n}Li reacts with trans-$P_4(SiMe_3)_2Bu^t_2$ to give $LiP_4(SiMe_3)Bu^t_2$ which decomposes in a few hours to yield $P(SiMe_3)_2Bu$, $P(SiMe_3)_3$, $LiP(SiMe_3)_2$, and also the cyclic compounds $P_4(SiMe_3)Bu^t_3$, LiP4Bu$^t_3$ and $LiP_3Bu^t_3$. A red colouration is produced immediately when Bu^{n}Li is added to



(77)



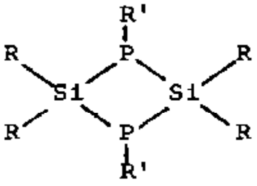
(78)



(79)

R = NMeSiMe$_3$

R' = H



(80)

solutions of $P_4(SiMe_3)_4$, from which, inter alia, Li_3P_7 and $Li_2P_7(SiMe_3)$ are formed, although the initial products of lithiation could not be elucidated.[142] The reaction of $P_7(SiMe_3)_3$ with Li_3P_7 in a molar ratio of 2:1 affords $LiP_7(SiMe_3)_2$, whilst when the molar ratio is 1:2, $Li_2P_7(SiMe_3)$ is formed.[143] Homologues and derivatives of $P_7(SiMe_3)_3$ may be synthesised either from $Li_3P_7.3$ solvent or Na_3P_7, or by cleavage of the P-Si bond with RX, eg.

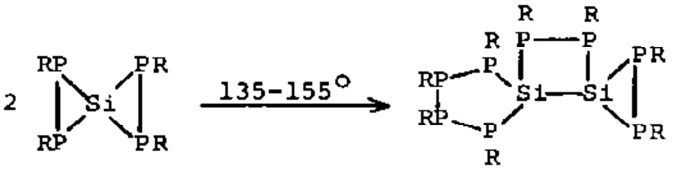
$$Li_3P_7.3DME \; + \; 3Ph_3SiCl \rightarrow P_7(SiMe_3)_3 \; + \; 3LiCl$$

$$Li_3P_7.3DME \; + \; 3Me_3SnBr \rightarrow P_7(SnMe_3)_3 \; + \; 3LiCl$$

$$P_7(SiMe_3)_3 \; + \; nMe_3SnX \rightarrow P_7(SiMe_3)_{3-n}(SnMe_3)_n$$

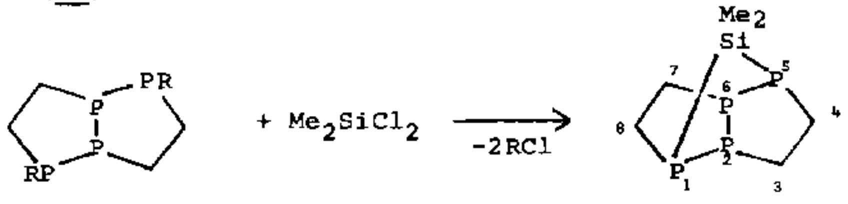
$$X = Cl, Br. \qquad n = 1\text{-}3.$$

X-ray analysis shows that the compounds $P_7(MMe_3)_3$ (M = Si,Ge,Sn,Pb) are isotypic, and crystallise as pure enantiomers.[144] Cyclocondensation of 1,2-dipotassium 1,2-di-tert-butyldiphosphide with silicon(IV) chloride leads to the formation of the tetraphosphasilaspiro[2.2]pentane (<u>81</u>) as a mixture of stereoisomers, the melt of which rearranges at temperatures of 135-155° to the silaphosphane (<u>82</u>):



(<u>81</u>) (<u>82</u>)

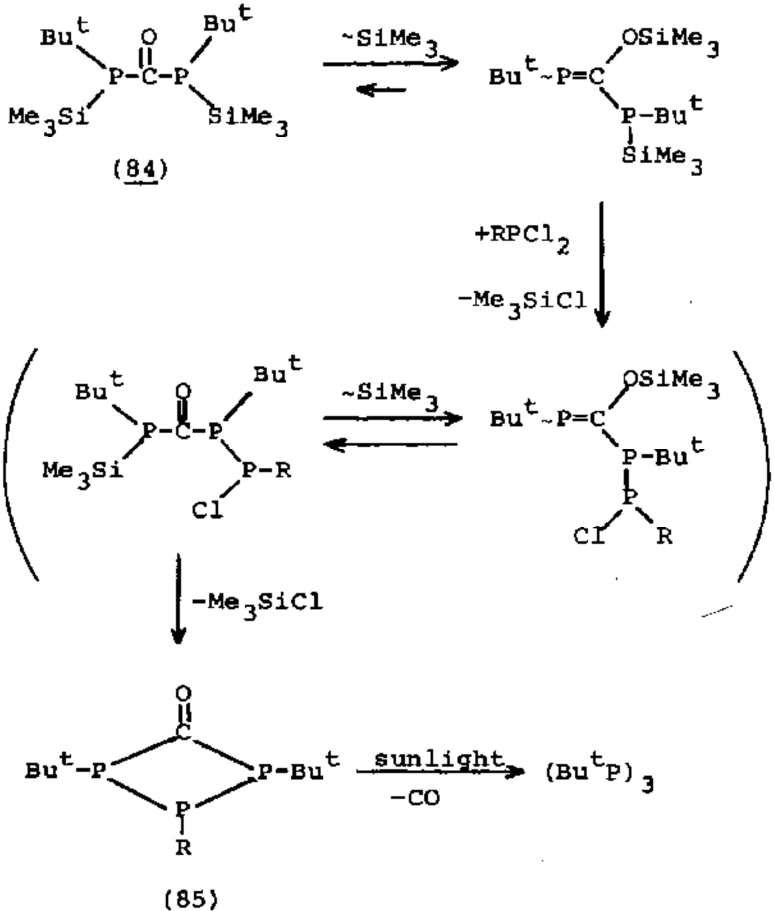
The structure of (<u>82</u>) is most unusual, and comprises three-membered $[SiP_2]$, four-membered $[Si_2P_2]$, and five-membered $[SiP_4]$ rings in the same molecule.[145] Reaction of 1,4-dipotassium-1,2,3,4-tetra-tert-butyltetraphosphide with Me_3SiCl yields the linear tetraphosphane $Me_3Si(Bu^tP)_4SiMe_3$, which is remarkably stable against disproportionation reactions. In solution at temperatures below -30°, only one of the six possible diastereoisomers (erythro/d,e)erythro) appears to be present.[146] 1,2,5,6-Tetraphosphabicyclo[3.3.0]octane and its dilithium salt react with Me_2SiCl_2 forming the tetraphospha-9-silatricyclo[3.3.1.$0^{2,6}$]-nonane (83):[147]



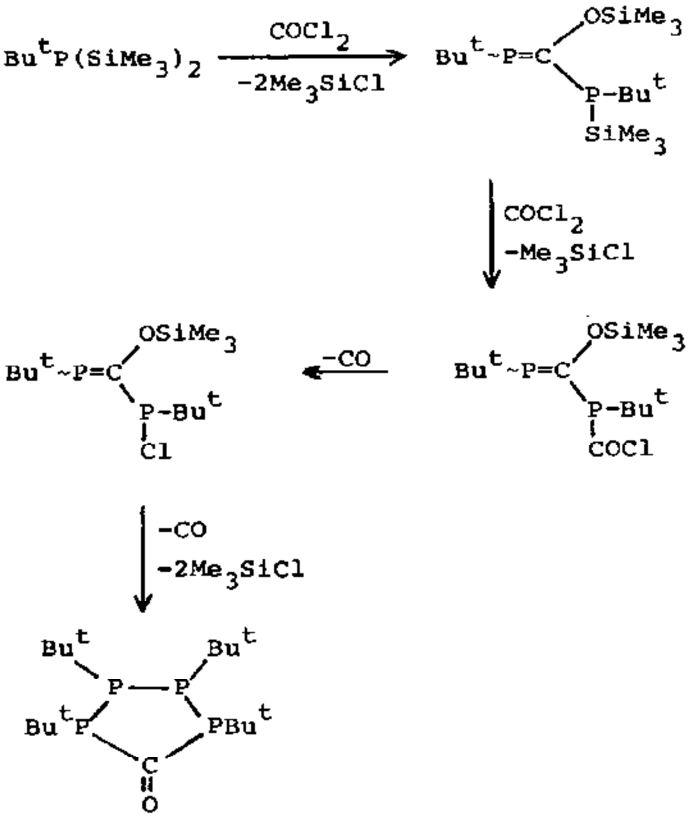
R = H,Li

(83)

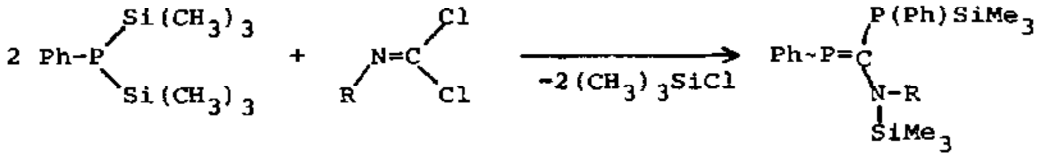
The different reactivities of $P_4(SiMe_2)_3$ and P_7Me_3 has been discussed in terms of simple MO theory.[148] The reaction of the 1,3-bis(trimethylsilyl)-substituted diphospha urea (84) with dichlorophosphanes results in cyclisation and the formation of the triphosphetanones (85), which readily eliminate CO on irradiation with sunlight:[149]



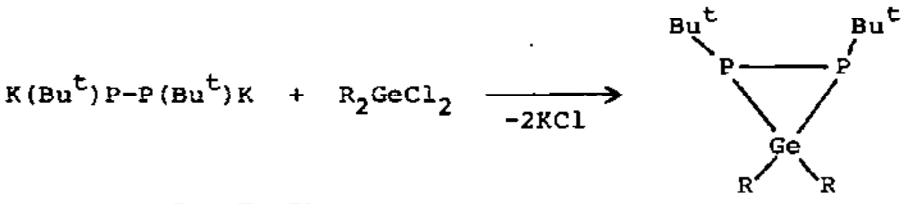
With phosgene, tert-butylbis(trimethylsilyl)phosphane undergoes elimination of Me_3SiCl and CO via several detectable intermediates with the phosphaalkene structure and the formation of a cyclic phospha-urea derivative:[150]



Elimination of Me_3SiCl also occurs in the reaction of phenylbis-(trimethylsilyl)phosphane with isocyanide chlorides:[151]



The first three-membered $[GeP_2]$ heterocycles, (<u>86</u>), have been prepared by [2+1] cyclocondensation:

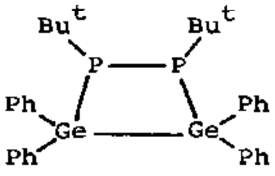


$K(Bu^t)P{-}P(Bu^t)K + R_2GeCl_2 \xrightarrow[-2KCl]{}$ (86)

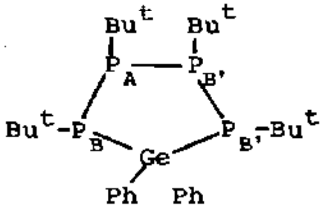
R = Et,Ph.

(86)

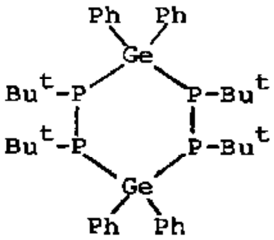
The four-, five-, and six-membered cyclogermaphosphanes (86-88), respectively, are formed as by-products.[152] Under certain conditions, the four-membered heterocycles, (87) and (88), are the main products of the reaction.[153] The four-membered ring of (87) is non-planar.[154]



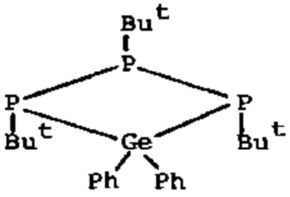
(87)



(88)

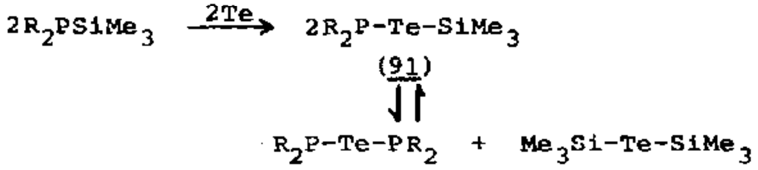


(89)



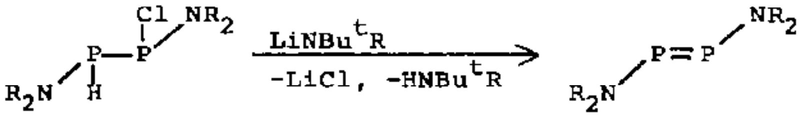
(90)

Tellurium inserts into the Si-P bond of trimethylsilylphosphanes affording (91), which then undergoes symmetrization:[155]



$$2R_2PSiMe_3 \xrightarrow{2Te} \underset{(91)}{2R_2P{-}Te{-}SiMe_3} \rightleftharpoons R_2P{-}Te{-}PR_2 + Me_3Si{-}Te{-}SiMe_3$$

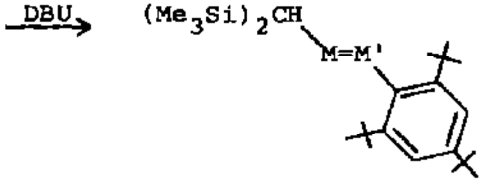
The sterically-demanding bis(trimethylsilyl)amino and bis(trimethylsilyl)methyl groups have been employed, along with other groups such as mesityl, to stabilise compounds involving double bonds between Group V elements. Base-induced dehydrochlorination from (92) has been employed in the synthesis of bis(silylamino)diphosphenes (93):[156,156a]



(92) R = $SiMe_3$ (93)

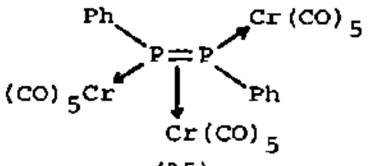
A more general method involves dehydrohalogenation between a dichloro(silylmethyl)phosphine, -arsine, or -stibine and a dihydro(mesityl)phosphine, -arsine, or -stibine using 1,5-diazabicyclo[5.4.0]undec-5-ene:

$(Me_3Si)_2CHMCl_2$ + $(2,4,6\text{-Bu}^t{}_3C_6H_2)M'H_2$

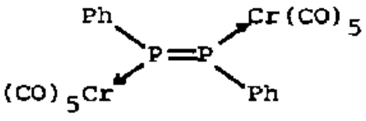


(94)

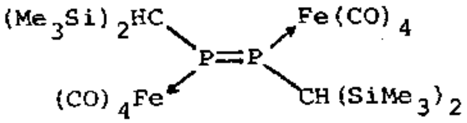
In this way, compounds (94) with P=P, P=As, P=Sb, and As=As double bonds have been synthesised.[157-159] The crystal structures of several of these compounds, as well as that of $(Me_3Si)_3CP{=}PC(SiMe_3)_3$[160] have been determined. Not surprisingly perhaps, such diphosphenes and diarsines have been employed as ligands towards transition metals. Unlike complex (95) in which the π-electrons of the P=P double bond are donated to chromium,[161] only the n-electron pairs on phosphorus or arsenic are used in complexes (96),[161] (97),[162] (98),[163] (99),[164] and (100).[165] In the complex $[Fe(CO)_4\mu\text{-}Fe(CO)_4]$ (ArP=PAr) (Ar = $2,4,6\text{-Bu}^t{}_3C_6H_{2O}$), the diphosphine functions in both ways simultaneously.[164]



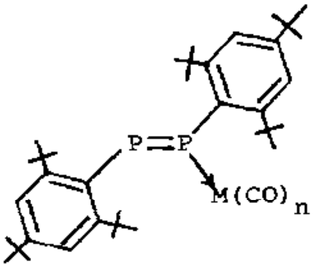
(95)



(96)



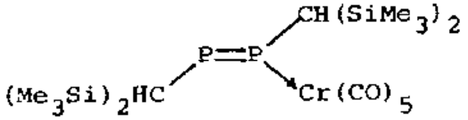
(97)



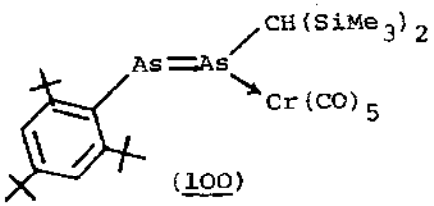
M = Fe; n = 4

M = Ni; n = 3

(98)

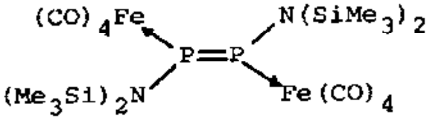


(99)

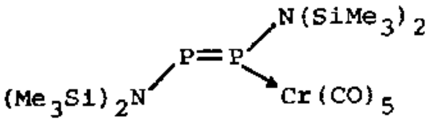


(100)

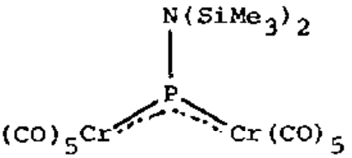
Similar complexes with silylaminodiphosphanes, (101) and (102), silylaminophosphinine, (103) and (104), and silylaminoarsinidine, (105) and (106'), have been synthesised, and in most cases also characterised structurally.[166] The phospha-alkene-nickel complex (107') has also been reported.[167]



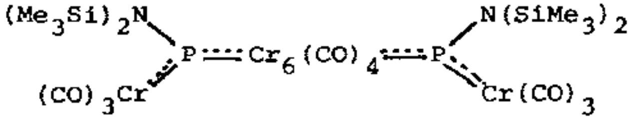
(101)



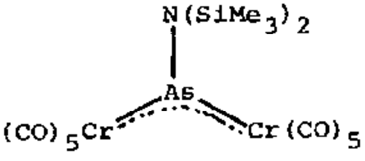
(102)



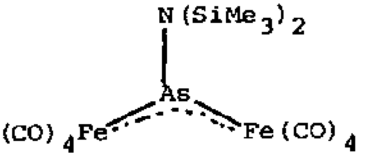
(103)



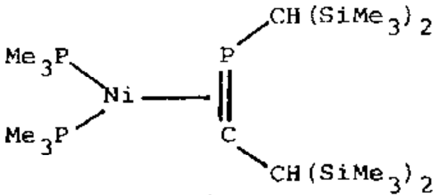
(104)



(105)



(106')



(107')

Trichlorosilanol, Cl_3SiOH, is formed when trichlorosilane and oxygen are photolysed in silicon tetrachloride by the probable free-radical pathway:[168]

$$SiCl_4 \xrightarrow{h\nu} Cl_3Si\cdot + Cl\cdot$$

$$Cl_3SiH \xrightarrow{h\nu} Cl_3Si\cdot + H\cdot$$

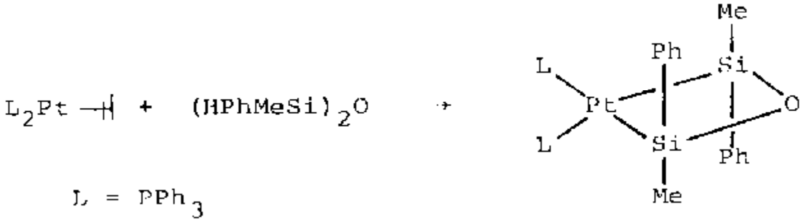
$$Cl_3SiH + Cl\cdot \rightarrow Cl_3Si\cdot + HCl$$
$$Cl_3SiH + H\cdot \rightarrow Cl_3Si\cdot + H_2$$

$$Cl_3Si\cdot + O_2 \rightarrow Cl_3SiOO\cdot$$
$$2Cl_3SiOO\cdot \rightarrow 2Cl_3SiO\cdot + O_2$$
$$Cl_3SiH + Cl_3SiO\cdot \rightarrow Cl_3Si\cdot + Cl_3SiOH$$

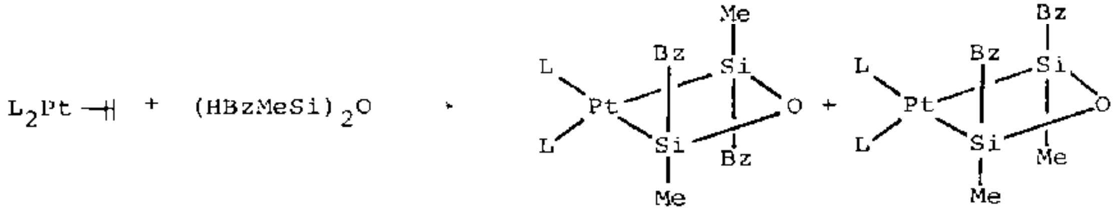
$$Cl_3SiH + Cl_3SiOO\cdot \rightarrow Cl_3Si\cdot + Cl_3SiOOH$$
$$Cl_3SiOOH \rightarrow Cl_3SiO\cdot + \cdot OH$$
$$Cl_3SiH + \cdot OH \rightarrow Cl_3Si\cdot + [HOH]$$
$$SiCl_4 + HOH \rightarrow Cl_3SiOH + HCl$$

$$2Cl_3Si\cdot \rightarrow Cl_3SiSiCl_3$$
$$Cl_3Si\cdot + Cl_3SiO\cdot \rightarrow Cl_3SiOSiCl_3$$
$$2Cl_3SiO\cdot \rightarrow Cl_3SiOOSiCl_3$$
$$Cl_3Si\cdot + H\cdot \rightarrow Cl_3SiH$$
$$Cl_3Si\cdot + Cl\cdot \rightarrow SiCl_4$$

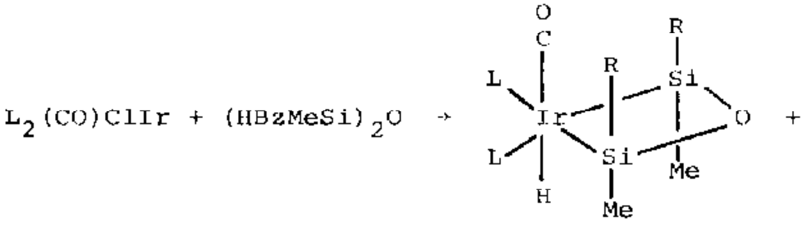
The hydrolysis of dichlorosilane in dichloromethane, either with a stoichiometric amount of water at -30° to -20°, or by slow controlled addition of a slight excess of water at 0°, results in the formation of siloxanes of the type $[H_2SiO]_n$, when n, in the volatile fraction, ranged from 4 to 23.[169] The new cyclometalladisiloxanes (106)-(111) have been prepared by the interaction of disiloxanes with low-valent transition metal complexes:



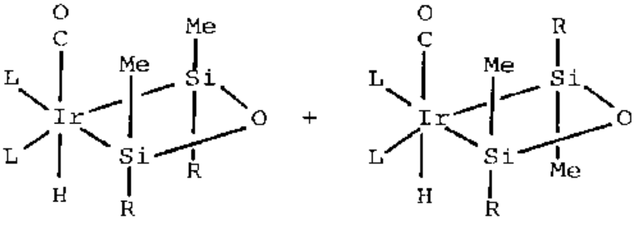
(106)



(107) (108)



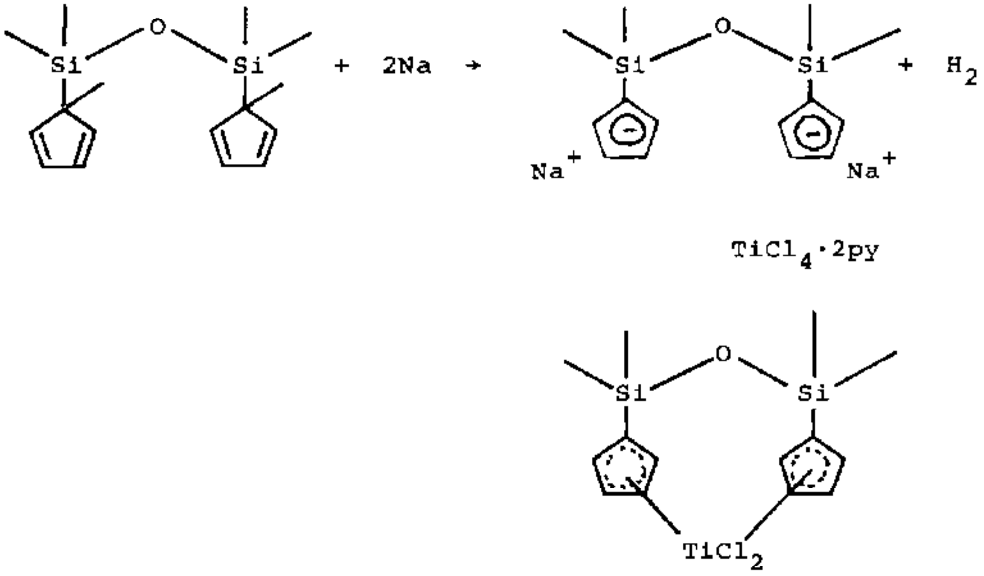
(109)



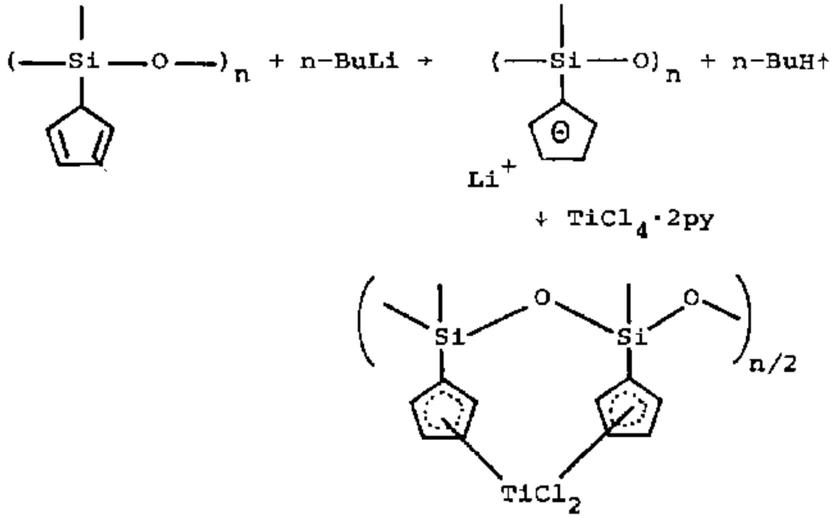
(110) (111)

$R = C_6H_5CH_2;\ C_6H_5$

These metallocycles are catalyst precursors for the extensive redistribution of groups on silicon via Me/H, Ph/H, Ph/Me and SiO/R exchanges.[170] Similar monomeric and polymeric titanoheterosiloxanes (112) and (113) has been prepared by the reaction sequences:



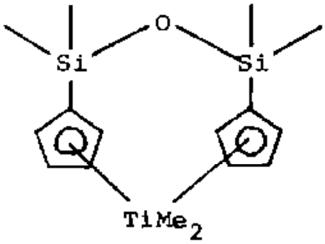
(112)



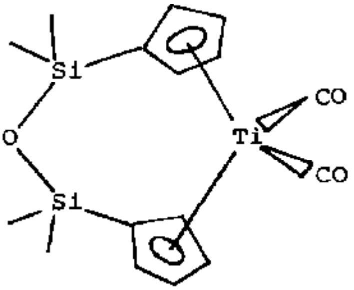
(113)

Complex (112) reacts with methyllithium to give the corresponding dimethyltitanocene derivative, (114), and with carbon monoxide in the presence of aluminium powder to form the dicarbonyl complex, (115).[171] Thermally-induced rearrangements and decompositions of siloxane oligomers have been investigated.[172,173]

The structures of several siloxane compounds have been determined. Electron diffraction studies of the silyl ethers $O(SiH_2Me)_2$ and $O(SiHMe_2)_2$ in the gas phase has shown that the

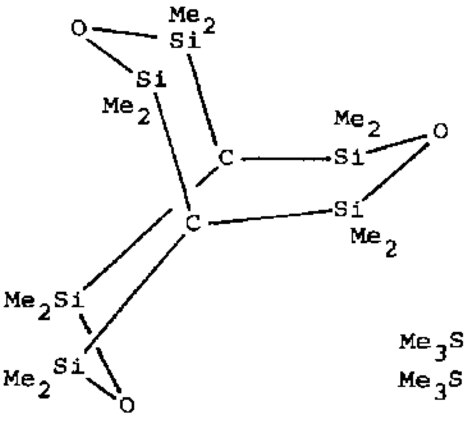


(114)

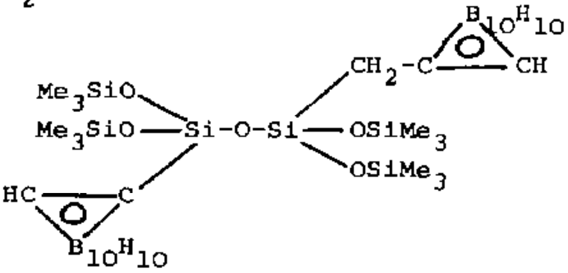


(115)

former compound exists in at least two conformers. In the major component (64%) the methyl groups are twisted by 124(4)° and 58(8)° away from the positions in which the Si-C bonds are trans to the O-Si bonds. In the latter, the silyl groups are twisted by 101(8)° and 41(4)° away from the symmetrical position in which both Si-H bands are cis to O-Si bonds, so that the dimethyl-silyl groups are staggered with respect to each other.[174] Other structure determinations include those of (112),[171] the 3,7,10-trioxa-2,4,6-8,9,11-hexasila[3.3.3]bicycloundecane, (116),[175] and the two carboranesiloxanes, (117) and (118).[176]



(116)

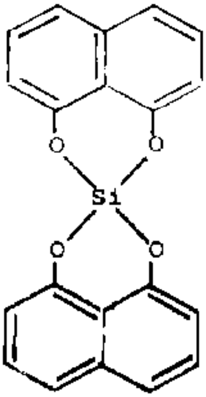


(117)

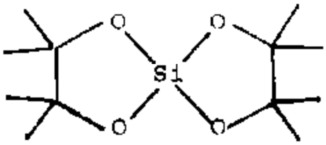
$$Me_2(HO)SiCH_2\text{-}CB_{10}H_{10}C\text{-}CH_2Si(OH)Me_2$$

(118)

Following the contraversy over the claim of a square-planar geometry for bis(o-phenylenedioxy)silane, the structures of two related compounds, bis(1,8-naphthalenedioxy)silane (<u>119</u>),[177] and bis(tetramethylethylenedioxy)silane (<u>120</u>),[178] have been determined, and add additional weight against the original claim. In both the geometry at the spiro silicon atom is distorted tetrahedral, the greater distortion observed in (<u>120</u>) being attributed to the constraints of the five-membered ring rather than to any tendency towards planarization.



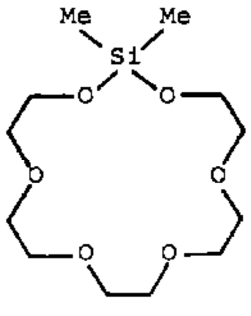
(<u>119</u>)



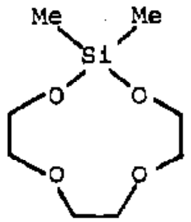
(<u>120</u>)

The kinetics of the racemisation of the tris(tropolonato)silicon-(IV) ion has been studied in 1,1,2,2-tetrachloroethane and acetonitrile in the temperature range 30-70°. The racemisation is promoted by trichloroacetic acid. The proposed mechanism, consistent with the derived activation parameters and the existence of an acid-catalysed pathway, involves a bond-rupture leading to five-coordinated intermediates.[179] Several cyclic poly(alkyleneoxy)silanes such as (<u>121</u>), (<u>122</u>) and (<u>123</u>) have been synthesised by transesterification of alkoxysilanes with polyethylene glycols. Solubility enhancements with lithium, sodium, and potassium ions with these 'sila-crowns' are a function of both the macrocycle and ion size.[180] The co-facially joined metallo-macrocyclic polymer, $\{M(Pc)O\}_n$ (Pc = phthalocyaninato; M = Si, Ge, Sn), are precursors for a new class of electrically conductive polymers, and their synthesis, spectra, and structural, transport, magnetic and optical properties have been reported.[181,182]

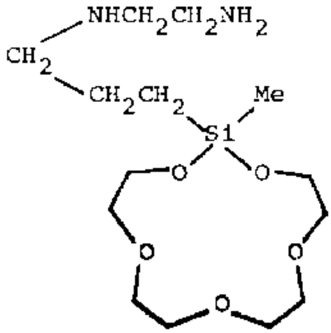
Hydrolysis of di-tert-butylgermanium dichloride affords crystalline di-tert-butylgermanium dihydroxide, the structure of which comprises $[Bu^t_2Ge(OH)_2]$ tetrahedra hydrogen bonded together



(121)

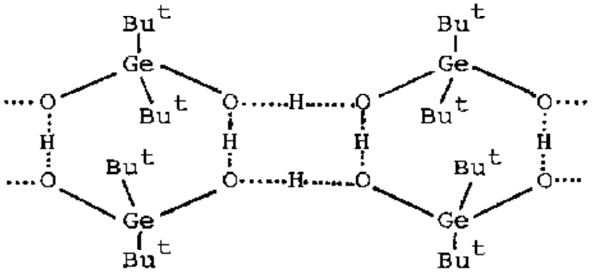


(122)



(123)

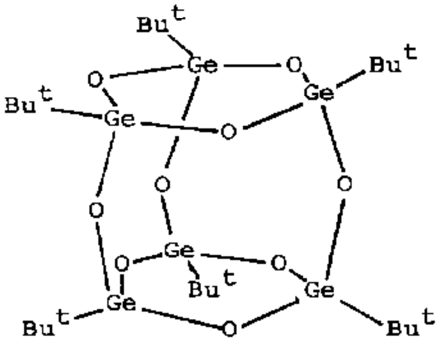
to form one-dimension double chains as in (124). Dehydration of the dihydroxide leads to the formation of trimeric di-tert-butyl-



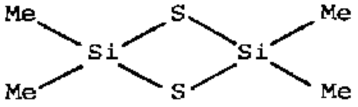
(124)

germanium oxide, crystals of which contain planar $[Ge_3O_3]$ rings.[183,184] The hydrolysis of tert-butylgermanium trichloride gives hexakis(tert-butylgermanium)sesquioxide, $(Bu^tGe)_6O_9$. This compound has a cage structure which has two six-membered and three eight-membered germanium-oxygen rings as in (125).[185]

The structures of a number of compounds containing silicon- or germanium-sulphur bonds have been determined. Crystals of



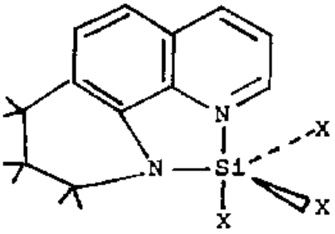
(125)



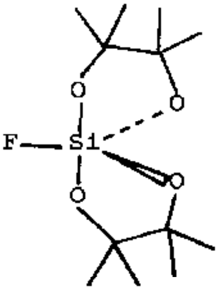
(126)

tetramethylcyclodisilthian, (126), comprise molecules with a planar central four-membered $[SiS_2]$ ring.[186] Both (μ-trithio)-bis[tricyclohexylgermanium] and its triphenylgermanium analogue contain the [Ge-S-S-S-Ge] sequence in a coiled conformation. The organic substituents on germanium have a propeller-like arrangement, which, looking down the Ge-Ge direction, adopt a staggered disposition.[187] The only isomer present in the vapour of germyl monothioacetate, $H_3GeSCOMe$, has the germyl group bonded to sulphur. The heavy atom skeleton is almost planar, with the Ge-S and C=O bonds arranged cis to one another.[188] Bis(trimethylmetal)dithiooxamides of silicon, germanium and tin $(Me_3M)_2(NMe\text{-}CS)_2$, (M = Si,Ge,Sn) have been obtained from the reaction of the metal chlorides and N,N'-di-methyldithiooxamide. The tin derivative has a planar bicyclic structure, in contrast to the silicon and germanium derivatives, which have non-chelated structures.[189]

Silicon and germanium compounds with coordination numbers greater than four continue to arouse interest. Ab initio MO calculations employing double ζ basis sets have indicated that the trigonal bipyramidal geometry (127) is the lowest energy form of the adduct $SiF_4.NH_3$.[190] The silicon atoms in 1-(trichlorosilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline,[191] 1-(trifluorosilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline,[192] and the bis(tetramethylethylenedioxy)fluorosilane anion[193] are all five-coordinated. In the two former compounds, the geometry is distorted trigonal bipyramidal with the dinitrogen ligand spanning an equatorial and an axial site (127). As expected, the coordinate Si...N bond is ca. 14% longer than the covalent Si-N bond in each. In the latter (128), the two crystallographically independent anions are distorted from trigonal bipyramidal geometry towards square pyramidal by 69.1% and 52.3%.[193] Adducts of bromo- and iodotrimethylsilane with pyridine, do not, however, contain five-coordinated silicon. Rather, the halogen is displaced as halide, and crystals comprise tetrahedral $[(Me_3Si)py]^+$ cations and halide anions.[194]



(127)



(128)

Infrared spectra pf solutions of the methyl(aroyloxymethyl)-fluorosilanes, $PhCO_2CH_2SiMeF_2$, $4\text{-}MeC_6H_4CO_2CH_2SiMeF_2$, and $PhCO_2CH_2SiMe_2F$, show that intramolecular coordination of the carbonyl oxygen atom to silicon occurs. With the corresponding (aroyloxymethyl)trifluorosilanes, however, there exists an equilibrium between coordinated and uncoordinated molecules, with the proportion of coordinated molecules being greater in solvent of low polarity. This phenomenon is not governed by enthalpy effects, but rather by entropy changes of the system on coordination.[195] ^{29}Si n.m.r. also has been employed as a probe for intramolecular coordination in compounds of the types $o\text{-}(Me_2NCH_2)C_6H_4SiXYZ$. Upfield shifts of 23-52 ppm upfield of the corresponding uncoordinated compounds are found. The compound $\alpha\text{-}Np[o\text{-}Me_2NCH_2]C_6H_4SiH_2$ is the first silicon compound without halogen or chalcogen to exhibit pentacoordination.[196] The X-ray structure of 1-germatranylmethyl germatrane, $[N(CH_2CH_2O)_3Ge]_2CH_2$, has been determined, and shows that the Ge-C-Ge bond angle (122.3^o and 119.0^o for the two crystallographically independent molecules) is substantially increased from the tetrahedral value due to steric effects.[197]

A new method for the generation of the germanium dihalides GeX_2 (X = F,Cl,Br,I) which involves treatment of germanium(II) sulphide with lead(II) halides has been described.[198]

By studying the equilibrium

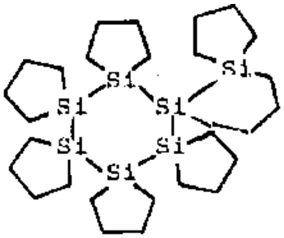
$$Ge + GeCl_4 \rightleftharpoons 2GeCl_2$$

The enthalpy of formation and entropy for $GeCl_2$,g have been determined.[199] The enthalpy and entropy of evaporation of germanium(IV) iodide have been deduced from vapour pressure measurements over liquid GeI_4. Values for the decomposition reaction

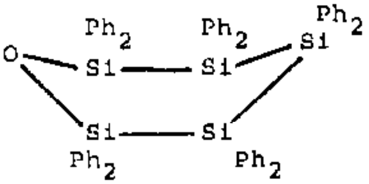
$$2GeI_2,s \rightarrow Ge,s + GeI_4,g$$

and the sublimation of GeI_2 have been derived from measurements of the total pressure over solid GeI_2. The data also yield values of the enthalpies of formation and entropies for both GeI_4,g and GeI_2,g.[200] The syntheses of cyclopropyl-, cyclobutyl-, and cyclopentylgermanium trichlorides have been described.[201]

A new class of polyfunctional polysilanes has been prepared from the Bu_4PCl-catalysed Si-Si/Si-Cl bond redistribution of methylchlorodisilanes, and have a polycyclic structure with approximately seven rings per molecule when the reaction is carried to 250°. Derivatives of the parent polymethylchlorosilane polymer are obtained by modifying the residual silicon-chlorine bonds.[202] Synthesis of cyclic polysilanes can be accomplished by the treatment of diorganodichlorosilane with alkali metals. The diethylcyclosilanes $(Et_2Si)_n$ (n = 4-8) are obtained from Et_2SiCl_2, but distribution of products depends on the alkali metal and the conditions. With two equivalents of lithium in THF, the major products are $(Et_2Si)_5$ and $(Et_2Si)_7$, with excess potassium $(Et_2Si)_5$ is formed, but with sodium in toluene, $(Et_2Si)_4$ is the major product. Photolysis of the penta-, hexa-, hepta-, and octacycles leads to the elimination of $[Et_2Si]$ and the formation of the next smaller ring.[203] Treatment of $PhMeSiCl_2$ with lithium in THF in the presence of $Ph_3SiSiMe_3$ produces a mixture containing 62% of five different isomers of the hexamer $(PhMeSi)_6$ and 25% of three isomers of $(PhMeSi)_5$.[204] Reaction of two equivalents of lithium with $(CH_2)_4SiCl_2$ yields a mixture of cyclopolysilanes, $[(CH_2)_4Si]_n$ (n = 5-12). If, however, an excess of lithium or potassium is used, the hexamer $[(CH_2)_4Si]_6$, and the neovel rearrangement product (<u>129</u>) are formed.[205]



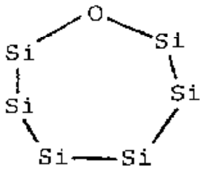
(129)



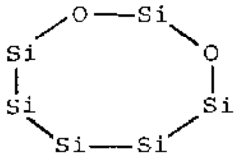
(130)

The crystal structures of two cyclosilanes, octamethylcyclotetrasilane[206] and the all-trans isomer of $(PhMeSi)_6$,[204] as well as that of decaphenyl-1-oxacyclohexasilane,[207] have been reported. In the former, the molecules are located at crystallographic inversion centres, which constrains the $[Si_4]$ ring to be planar.[205] The six-member ring in $(PhMeSi)_6$ is in the chair form with the phenyl groups in the equatorial positions and is somewhat distorted from idealised cyclohexane geometry.[204] The oxacyclohexasilane appears to be the first determination of the structure of cyclosilane containing a heteroatom. The conformation of the molecule is close to the 1,4 boat form (130).[207]

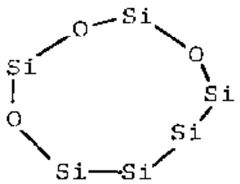
Oxidation of $(Me_2Si)_{12}$ by m-chloroperbenzoic acid leads to the six oxidation products with skeletons (131-136), containing, respectively, one, two, three, four, five and six oxygen atoms.[208]



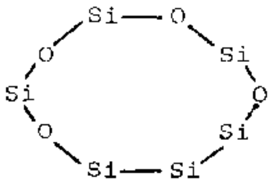
(131)



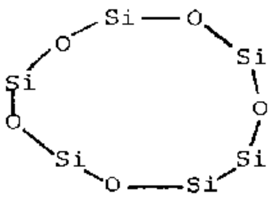
(132)



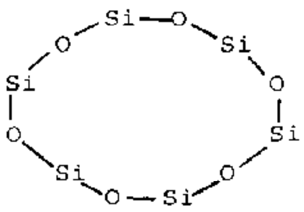
(133)



(134)

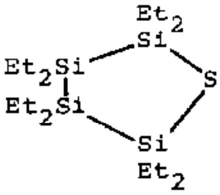


(135)

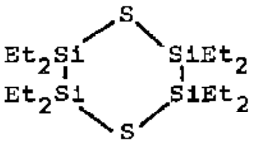


(136)

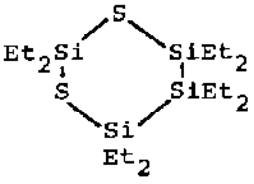
Reaction of $(Et_2Si)_4$ with 1.1 equivalents of elemental sulphur at 50° affords high yields of cyclo-$(Et_2Si)_4S$, (137), whilst reaction with two equivalents of sulphur at 190° gives (138) and (139) as the major products. The latter appears to arise from a reaction of cyclo-$(Et_2Si)_4S_2$ and sulphur that also produces diethylsilanethione, $Et_2Si{=}S$ as a reactive intermediate.[209]



(137)

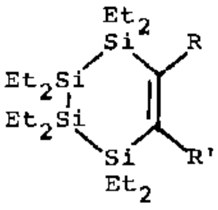


(138)

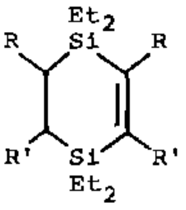


(139)

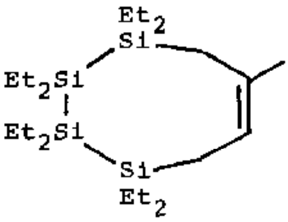
$(Et_2Si)_4$ also reacts with alkynes in the presence of palladium catalysts to yield 3,4,5,6-tetrasilacyclohexenes (140), and, ultimately, 1,4-disilacyclohexa-2,5-dienes, (141). With isoprene, the two addition products, (142) and (143) are formed. Oxidation with m-chloroperbenzoic acid leads to the siloxanes $(Et_2Si)_4O_n$ (n = 1-4). Ring-opening occurs with Cl_2, Br_2, I_2, $LiAlH_4$, HCl, HBr, H_2O, EtOH, HOAc, and, slowly, with PhLi.[210]



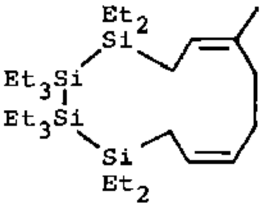
(140)



(141)



(142)

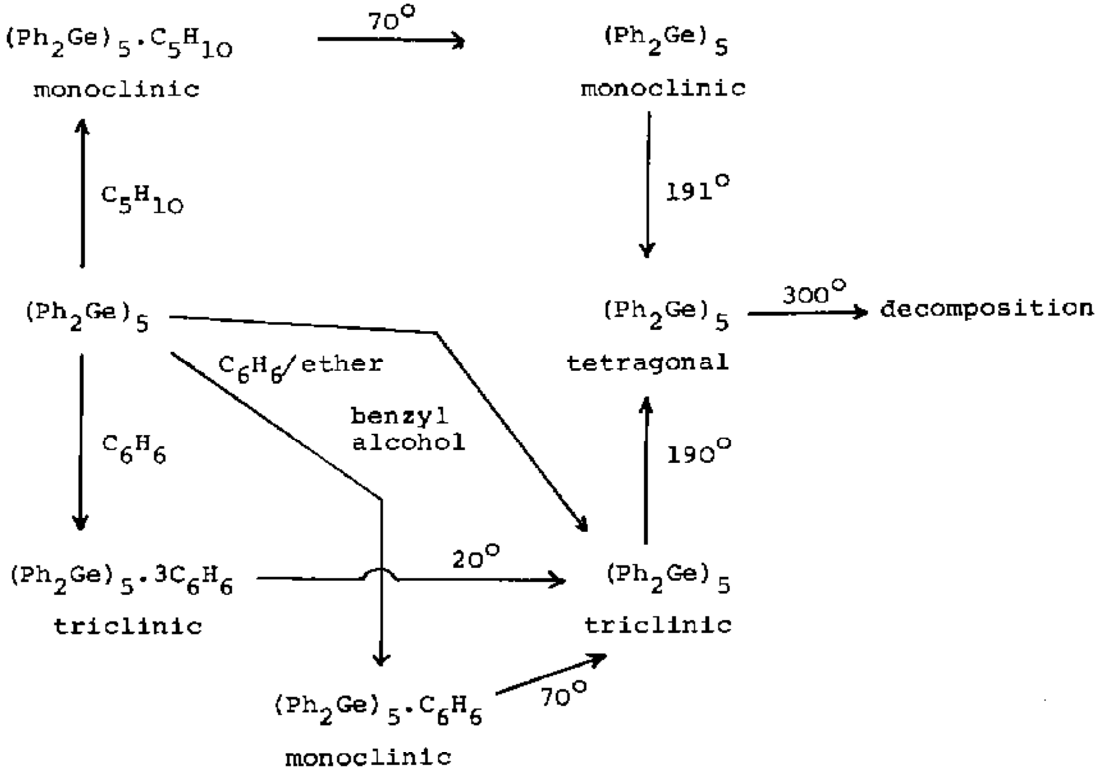


(143)

Five crystalline phases, two pure and three including solvent molecules of crystallisation, have been characterised. Solvent of crystallisation is lost at 70°, and at 190° all phases transform into a plastic crystal phase. The transformations are summarised in Scheme 16.

In the crystal, triclinic $(Ph_2Ge)_5$ has a flexible conformation in accordance with its better solubility than both $(Ph_2Ge)_4$ and $(Ph_2Ge)_6$, both of which contain rigid conformations. $(Ph_2Ge)_6$ attains a plastic crystal state at 346°.[211]

Bis(trimethylsilyl)magnesium is better prepared (as the

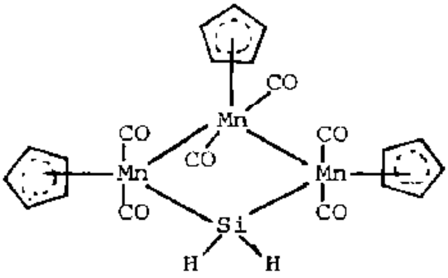


Scheme 16

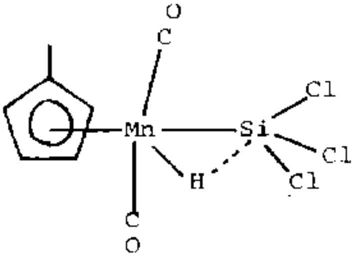
dimethoxyethane solvate) by the reaction of magnesium powder with $Hg(SiMe_3)_2$ in DME in a supersonic bath.[212] The structure of the corresponding tetramethylethylenediamine complex, $(Me_3Si)_2Mg.(Me_2NCH_2CH_2NMe_2)$, has been determined, and shows that the magnesium is four-coordinated by two silicon atoms and the two nitrogen atoms.[213] A number of similar silyl-aluminium compounds have also been investigated. $(Me_3Si)_3Al.Et_2O$ is monomeric in the crystal with four-coordinated aluminium.[214] In bis[tris(trimethylsilyl)aluminium]tetramethylethylenediamine complex, the dinitrogen donor serves as a bridge between the two $[(Me_3Si)_3Al]$ units.[213] Both $Na[Al(SiMe_3)_4]$ and $Na[Al(SiMe_3)_4]$.-2 toluene form linear-chains resulting from contact ion-pair interactions. In the latter, the sodium cation is sandwiched between two arene molecules.[214] Tris(trimethylsilyl)aluminium has found application as a trimethylsilyl-transfer reagent towards unsymmetrical alkynes,[215] α,β-unsaturated carbonyl compounds,[216] and allyl acetates.[217]

Colourless lithium bis(trimethylsilyl)bismuthidedimethoxyethane and green, metallic tetrakisbis(trimethylsilyl)dibismuthane crystallise isotypic to their antimony homologues. Both compounds form chains, which in the case of the former compound are built up as screws of alternating bismuth and lithium atoms. With the latter, the centrosymmetric molecules form nearly linear zig-zag chains with short intermolecular contacts (Bi...Bi = 3.804Å).[218]

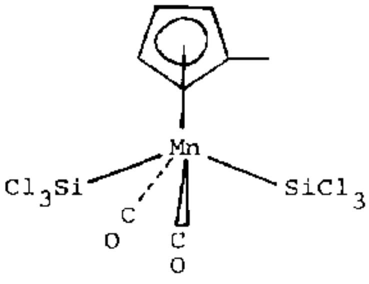
Several notable transition metal derivatives have been described. The main product from the reaction of silane with $(C_5H_5)Mn(CO)_2.THF$ is the heterocycle (<u>144</u>).[219] The main difference between the structures of $MeCp(CO)_2Mn(H)SiCl_3$ (<u>145</u>) and $MeCp(CO)_2Mn(SiCl_3)_2$ (<u>146</u>) is that in (<u>145</u>) the $SiCl_3$ ligand is tilted relative to the Mn-Si vector due to Mn-H-Si three-centre two-electron bonding.[220] The germanium-manganese complex (<u>147</u>)



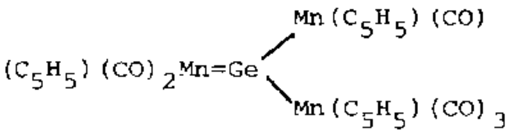
(<u>144</u>)



(<u>145</u>)

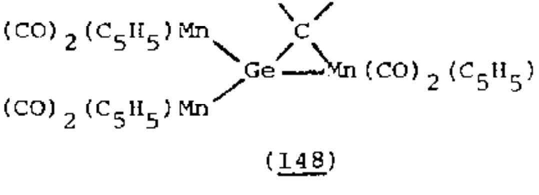


(<u>146</u>)



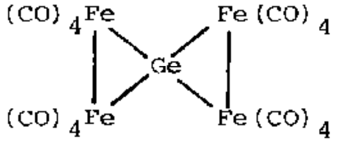
$$(C_5H_5)(CO)_2Mn{=}Ge\begin{matrix} Mn(C_5H_5)(CO) \\ Mn(C_5H_5)(CO)_3 \end{matrix}$$

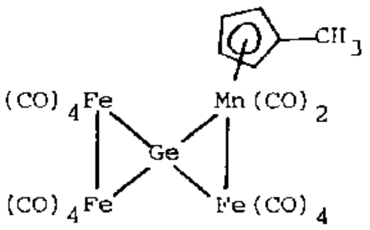
(<u>147</u>)



(<u>148</u>)

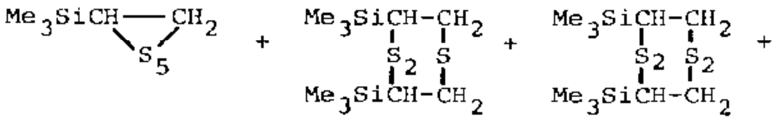
may be prepared in quite high yield by reaction of germane with solvent-stabilised $(C_5H_5)Mn(CO)_2$ in the presence of traces of acid. $(C_5Me_5)Mn(CO)_2$ gives exclusively the orange complex, $(\mu_2\text{-Ge})[(C_5Me_5)Mn(CO)_2]_2$, having a strictly linear Mn-Ge-Mn skeleton. Solutions of (147) react with diazomethane in THF at low temperatures to afford brown air-stable crystals of the μ_3-η^2-methylenegermanediyl complex, (148).[219] The photolysis of $(CF_3)_3GeH$ in the presence of $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ to afford $(CF_3)_3GeMn(CO)_5$ and $(CF_3)_3GeCo(CO)_4$ in high yields. The former compound is also available from $(CF_3)_3GeX$ (X = Cl,I) and $NaMn(CO)_5$. Force constant and ^{55}Mn n.m.r. chemical shift data support the σ-withdrawing nature of the $(CF_3)_3Ge$ group, which is similar to the $GeCl_3$ group. The short Ge-Mn bond and the mean C-Ge-C bond angle imply high Ge 4s character for the metal-metal bond.[221] Two compounds, $Ge[Fe(CO)_4]_4$ and $Ge\{(MeCp)Mn(CO)_2\text{-}[Fe(CO)_4]_3\}$, are formed in the reaction of $(MeCp)(CO)_2MnGe(CO)_2(MeCp)$ with $Fe_2(CO)_9$. $Ge[Fe(CO)_4]_4$ contains a $[GeFe_4]$ skeleton with two Fe-Fe bonds (149). The other product represents the first example of two different transition metal atoms bonded to germanium. Its $GeMnFe_3$ core (150) is structurally similar to the $[GeF_4]$ skeleton with a manganese atom replacing an iron.[222]

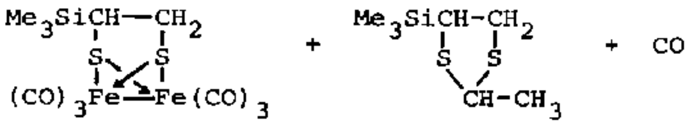

(149)


(150)

(149) has also been synthesised from the reaction between vinylgermanes and iron carbonyls.[223] The reaction of trimethylvinylsilane with S_8 in the presence of $Fe_3(CO)_{12}$ leads to the formation of a number of different products:

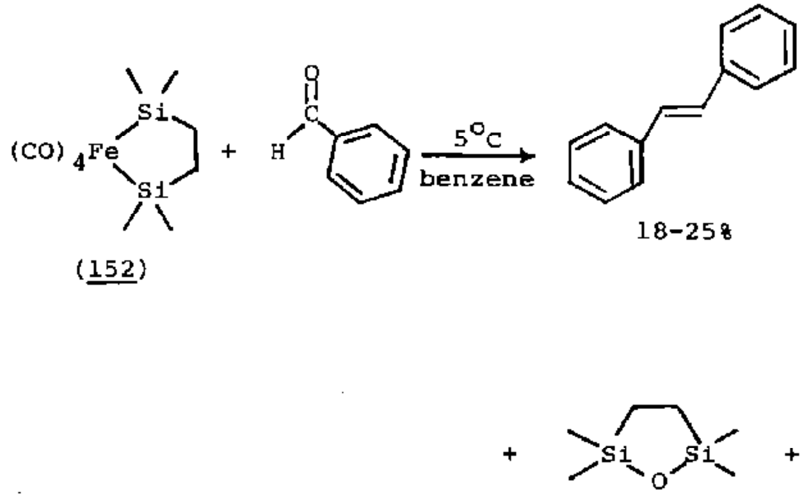
$$Me_3SiCH{=}CH_2 + S_8 + Fe_3(CO)_{12} \rightarrow S_2Fe_2(CO)_6 + S_2Fe_3(CO)_9 +$$





(151)

The structure of (151) was confirmed by a crystal structure determination.[224] The disilanylation complex $(C_5H_5)Fe(CO)_2SiMe_2SiPh_3$ has been synthesised by metathesis between $(C_5H_5)(CO)_2FeNa$ and $ClSiMe_2SiPh_3$. In the complex, the Si-Si bond distance is longer than that found in $Me_3SiSiPh_3$,[225] presumably due to the σ-donor property of the silyl group. When the chelated disilane complex (152) is treated with aromatic or aliphatic aldehydes, the disiloxane (153), iron carbonyls, and, in the case of benzaldehyde, trans-stilbene are formed, eg:

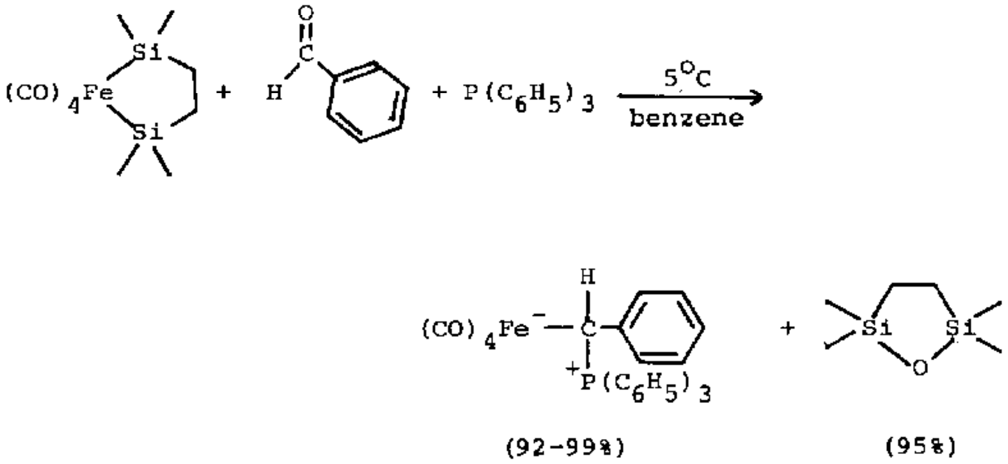


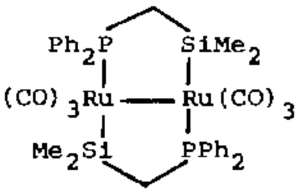
(152)

(153)

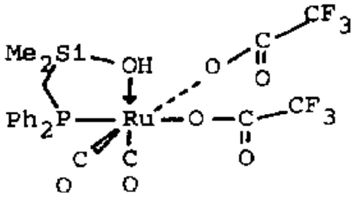
+ $Fe(CO)_5$, $Fe_3(CO)_{12}$, and other organic products.

when, however, these reactions are carried out in the presence of triphenyl- or tritolylphosphine, the ylid complexes $(CO)_4Fe^-CH(R)P^+Ar_3$ are isolated in high yields, eg:





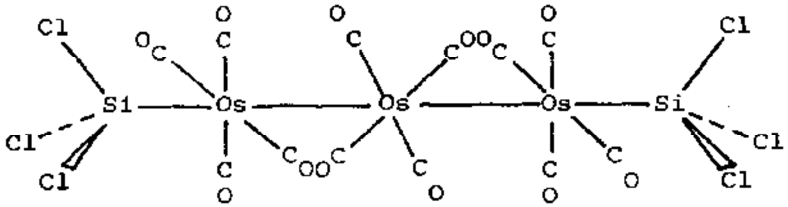
(154)



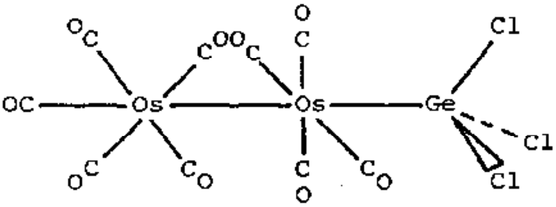
(155)

The symmetrically-bridged diruthenium complex (154) is obtained from the reaction of $Ru_3(CO)_{12}$ and the phosphinomethyl-silane $Ph_2PCH_2SiMe_2H$. On treatment with trifluoroacetic acid, (154), the mononuclear phosphinomethyldimethylsiland complex, (155),[227] is obtained. The reaction of $Na[HRu_3(CO)_{10}(SiR_2R')_2]$ with phosphines leads to the formation of trinuclear cluster anions of the type $[Ru_3(CO)_9(SiR_2R')(PR''_3)_2]^-$.[228] The compounds $Os_3(CO)_{12}(SiXCl_2)_2$ (X = Me,Cl) have been isolated from the reaction of $Os_3(CO)_{12}$ with the appropriate silane Cl_2XSiH at 140° under a carbon monoxide pressure of 80 atmospheres. Xray studies of $Os_3(CO)_{12}(SiCl_3)_2$ shows that the molecule has a crystallographic centre of symmetry with a linear $[SiOs_3Si]$ chain. The carbonyl groups on the terminal osmium atoms are staggered with respect to those on the central osmium as in (156). The structure of the related compound, $Os_3(\mu\text{-}H)_3(CO)_9(SiCl_3)_3$ has also been reported, which has a triangular arrangement of osmium atoms in which each Os-Os bond is presumed to be bridged by a hydrogen atom. The three osmium atoms lie on a crystallographic mirror plane which also includes the silicon atoms.[229] In the germyl-osmium complex,

$(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$, obtained from the reaction of $Os(CO)_5$ and $GeCl_4$, the $[Os(CO)_5]$ unit acts as a donor ligand towards the second osmium atom via an unsupported donor-acceptor Os-Os bond. The framework is shown in (157).[230]



(156)



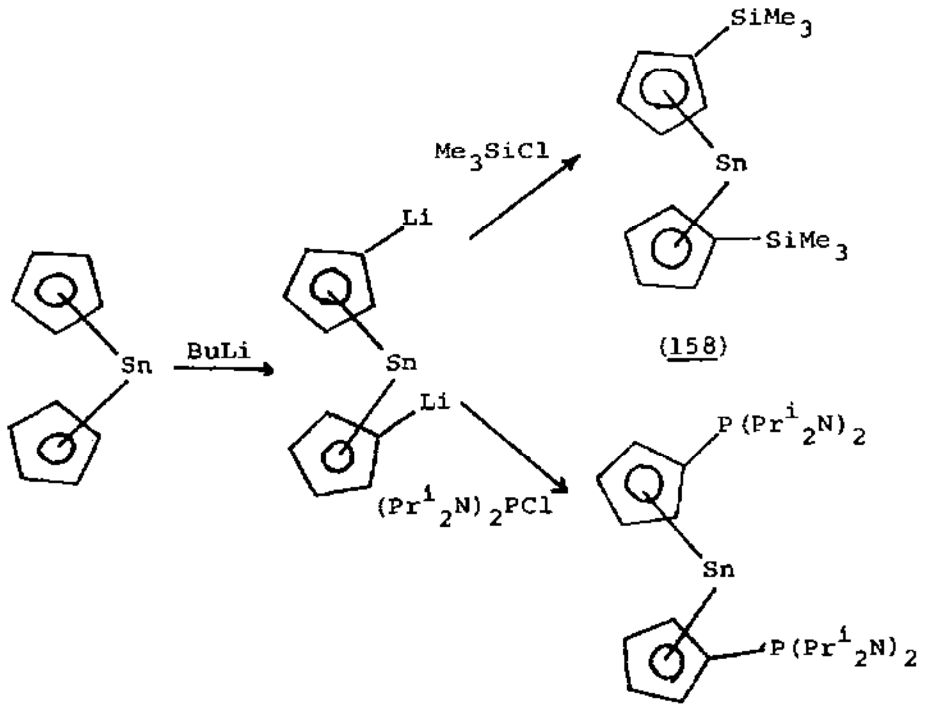
(157)

The reaction of triethylsilane with $(C_5Me_5Ir)_2Cl_4$ gives initially the complex $(C_5Me_5Ir)_2H_2Cl_2$ and then $C_5Me_5Ir(H_2)_2(Cl)SiEt_3$, and finally the silyliridium complex $C_5Me_5Ir(H_2)(SiEt_3)_2$.[231] ^{31}P, ^{195}Pt and ^{199}Hg n.m.r. spectra show that at temperatures below -40°, the complex $(Ph_3P)_2Pt(HgGePh_3)(GePh_3)$ has the cis square-planar geometry at platinum. However, the molecule is fluxional, and experiences a diagonal twist intramolecular rearrangement.[232] Metallic lithium and dibenzenechromium displace thallium from the complex $[(C_6F_5)_3Ge]_3HgTl\cdot1.5DME$ to afford $[(C_6F_5)_3Ge]HgLi\cdot3DME$ and $\{[(C_6F_5)_3Ge]_4Hg\}[Cr(C_6H_6)_2]_2$, respectively.[233]

4.4 TIN AND LEAD

4.4.1 Bivalent Compounds

Metallocene and other metallylene analogues continue to provoke considerable interest. Several ring-substituted metallocenes have been synthesised. Dilithiation of stannocene produces 1,1'-dilithiostannocene, which reacts with Me_3SiCl and $(Pr^i_2N)_2PCl$ to afford (158) and (159), respectively. The X-ray structure of (159) shows it to be a bent sandwich compound, with a ring

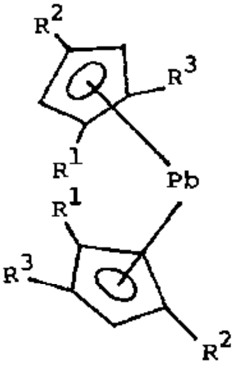


(158)

(159)

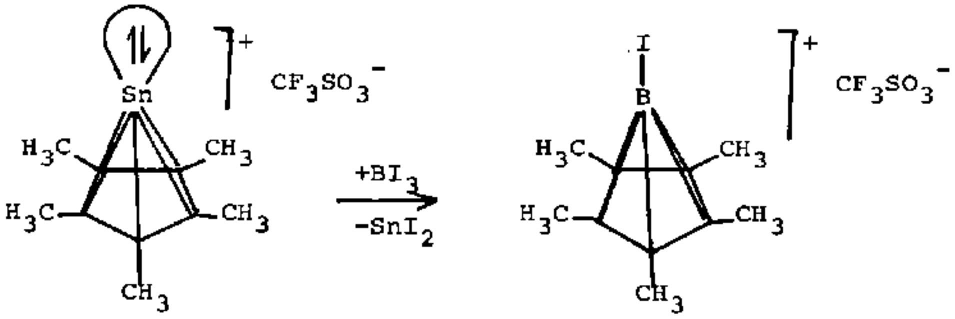
centroid-metal-ring centroid of 150.2°, rather larger than in either of the two crystallographically-independent molecules of stannocene itself.[234] Silylated plumbocenes with two, four or six trimethylsilyl groups in the molecule have also been obtained by the reaction:

$$2C_5\left[(CH_3)_3Si\right]_nH_{5-n}Li + PbCl_2 \xrightarrow{-2LiCl}$$

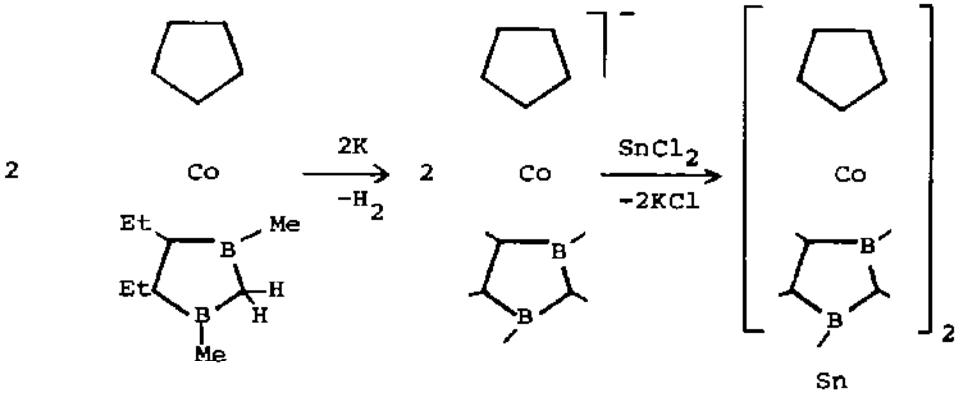


R^1, R^2, R^3 = H or $SiMe_3$; n = 1-3

The stability of these complexes against oxidation and heat increases with increasing number of silyl substituents.[235] Decamethylstannocene reacts with pentakis(methoxycarbonyl)-cyclopentadiene with the elimination of pentamethylcyclopentadiene affording both pentakis(methoxycarbonyl)pentamethylstannocene and pentakis(methoxycarbonyl)stannocene.[236] The reaction of pentamethylcyclopentadienyltin trifluoromethanesulphonate with BI_3 in dichloromethane results in tin-boron exchange and the formation of the $(C_5Me_5)BI^+$ cation:[237]



Related to stannocene is the unusual complex, $[(C_5H_5)Co(C_2B_2C)_2]Sn$ (C_2B_2C) = 4,5-diethyl-1,3-dimethyl-1,3-diborolenyl), prepared from the sandwich anion and $SnCl_2$, which has a 'tetradecker' structure, bent at the central tin atom.[238]



Trimethylsilanol cleaves the cyclopentadienyl groups from stannocene affording bis(trimethylsiloxy)tin, $(Me_3SiO)_2Sn$, which is a dimer exhibiting rapid exchange between terminal and bridging trimethylsilyloxy groups. Contrary to earlier reports, this compound cannot be obtained from $SnCl_2$ or $Sn(OMe)_2$, which instead yield the polynuclear compound (<u>160</u>).[239]

$$\left.\begin{array}{l} 2SnCl_2 + 4NaOSiMe_3 \xrightarrow{-4NaCl} \\ \\ 2Sn(OMe)_2 + 4Me_3SiOH \xrightarrow{-4MeOH} \end{array}\right] \rightarrow \frac{1}{x}[Sn_2O(OSiMe_3)_2]_x + (Me_3Si)_2O$$

(<u>160</u>)

Both bis(trimethylsiloxy)tin and bis(t-butoxy)tin displace carbon monoxide from nickel tetracarbonyl forming 1:1 and 1:2 complexes, respectively. Bis(triphenylsiloxy)tin does not react under similar conditions, but both bis(trimethylsiloxy)tin and bis(triphenylsiloxy)tin react with $\{M(CO)_5thf\}$ ($M = Cr, W$), forming the complexes $M(CO)_5\{Sn(OSiR_3)_2\}$.[240]

Bis(t-butoxy)tin reacts with mercaptans of the type $E(CH_2CH_2SH)_2$ ($E = Bu^tN$, MeN, O, S) at temperatures up to 50° affording 5-aza(oxa, thia)-2,8-dithia-1-stanna-bicyclo$[3.3.0^{1.5}]$-octanes (<u>161</u>):

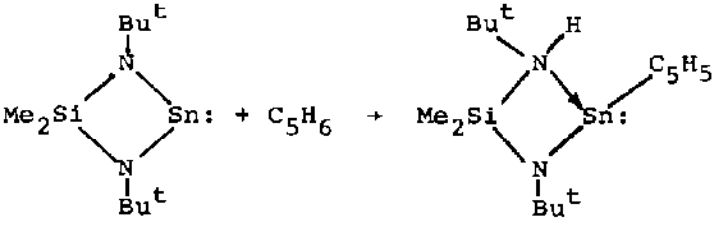
$$Sn(OBu)_2 + E(CH_2CH_2SH)_2 \rightarrow E(CH_2CH_2S)_2Sn + 2BuOH$$

(<u>161</u>)

The compounds are monomeric in solution, and form complexes with BF_3 and $Cr(CO)_6$. When the reactions are carried out at higher temperatures, the spiro derivatives, $[E(CH_2CH_2S)_2]_2Sn$ are formed.[241] The tin bis(arenedithiolate), $Sn(SC_6H_2Bu^t{}_3\text{-}2,4,6)_2$ (<u>162</u>), is 'V'-shaped, but the tin and lead bis(2,6-diisopropylbenzenethiolates) are trimeric with both bridging and terminal thiolate ligands with four coordinated (central) and three coordinated (terminal) metal atoms. The thiolate (<u>162</u>) undergoes the expected reactions of a monomeric stannylene, i.e. oxidative-addition (forms $MeSnI(SAr)_2$ with methyl iodide, adduct formation (forms $[Cr(CO)_5[Sn(SAr)_2]]$ with $Cr(CO)_5thf$), and tin-centred radical $Sn(SAr)_3$, formation on photolysis.[242]

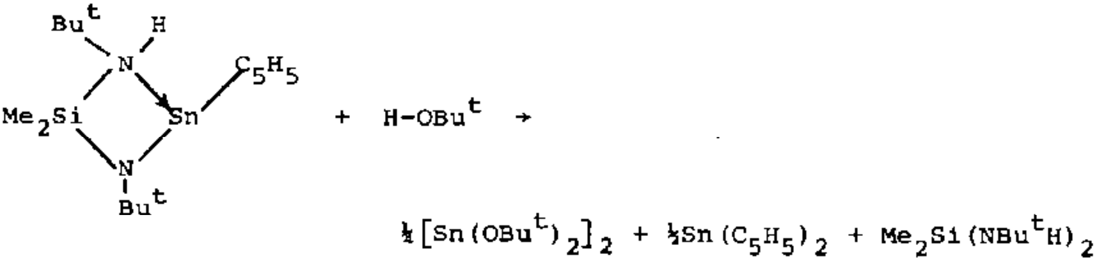
The germanium, tin and lead bis(trimethylsilyl)amides, $M[N(SiMe_3)_2]_2$, ($M = Ge,Sn,Pb$) are also 'V'-shaped monomers both in the crystal (Sn,Pb) at 140K and in the vapour at ca. 380K. The $\widehat{NMN}$ bond angles in the vapour 101(1.5)° (Ge), 96(2)° (Sn), or

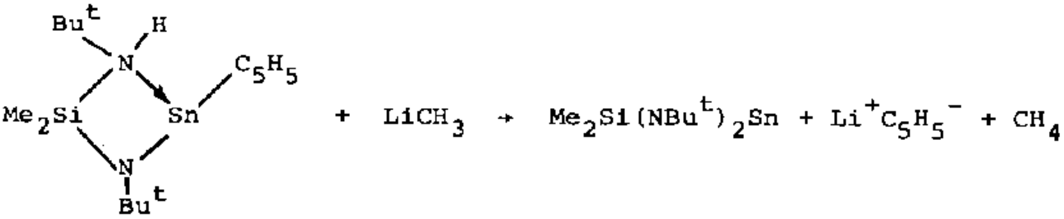
91(2)° (Pb) are smaller than in the solid (104.7(2)° (Sn), 103.6(7)° (Pb).[243] 1,3-Di-tert-butyl-dimethyl-1,3,2,4λ^2-diazasilastannetidine (162') adds cyclopentadiene across one of the Sn-N bonds forming (163); which has fluxional properties in solution:



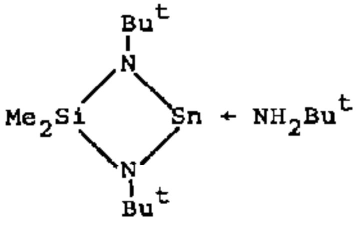
(162') (163)

When two moles of cyclopentadiene are employed in the reaction, stannocene is obtained. (163) also reacts with $BuOH^t$ and MeLi:[244]





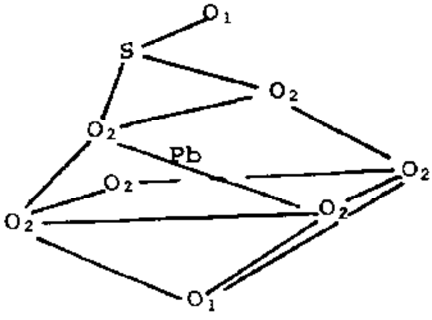
The primary step in the reaction of (162') with tert-butylamine is the formation of the adduct (164), whose structure has been confirmed by X-ray analysis.[245] In crystals of the two cage molecules, $Sn_4(NBu^t)_4$ and $Sn_4(NBu^t)_3O$, molecules of the former are held together only by van der Waal's forces, whereas in the latter, weak intermolecular O→Sn interactions are present forming dimers.[246]



(164)

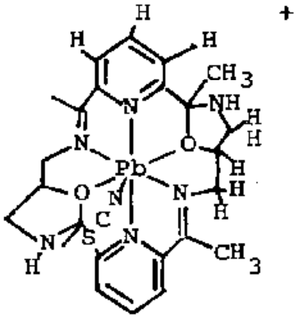
The coordination of the tin atoms in di-ammonium trichlorostannate chloride monohydrate is intermediate between three and four, with three short Sn-Cl distances, and a fourth much longer contact to the chloride anion. Neighbouring $SnCl_3...Cl^-$ units are connected by two longer Sn...Cl bridges forming a chain structure, and completing a severely distorted octahedral environment at tin. The anionic chains, ammonium cations, and the water molecule participate in a three-dimensional network of hydrogen-bonds.[247] The basic unit of the thiourea complex of tin(II) chloride is the formula unit $SnCl_2\{SC(NH_2)_2\}$, which are tightly bound into chains both by chlorine and sulphur bridging. Interchain N-H...Cl hydrogen-bonding again results in a three-dimensional structure.[248] Two complexes, $Oct_3N^+H\ SnCl_3^-$ and $(Oct_3NH...Cl...NHOct_3)^+SnCl_3^-$, have been detected in the extraction system $Oct_3N^+HCl^-$/benzene-$SnCl_2$-HCl.[249] ESCA data support the previously proposed ionic structures for the adducts of tin(II) chloride with aromatic Schiff bases.[250] As an after-effect of the converted isomeric transition in ^{119m}Sn, about 30% yield of the oxidised aliovalent Sn^{4+} species has been observed in Mössbauer spectra of frozen solutions of $^{119m}SnCl_2$ in organic solvents such as dimethylsulphoxide and methanol. Similar large yields of Sn^{4+} are also observed in the emission spectra of the crystalline solid adducts of $^{119m}SnCl_2$ with dimethylsulphoxide, pyridine-N-oxide, and picoline-N-oxides.[251] The gas-phase and solid-state He photoelectron spectra of SnF_2 and PbF_2 are very similar. In the gas-phase spectra of SnF_2, features corresponding to the presence of Sn_2F_2 were identified; no polymeric species were identified in the spectrum of PbF_2.[252] The phases Pb_3GeF_{10}, $Pb_3Ge_3F_{14}$ and $PbMF_6$, as well as a restricted solid-solution domain, have been identified in the PbF_2-MF_4 (M = Sn,Ge) systems.[253] The new compounds Cs_4SnBr_6 and Cs_4SnCl_6 have been synthesised, and phases of the type $Cs_4Sn_{1-n}Pb_nBr_{6-x}Cl_x$ (n = 0-1, x = 0-6) have been examined by XRD, Mössbauer, optical reflectance, and electrical conductivity.[254]

The structures of several oxo-lead compounds have been reported. That of $Pb_2F_2CO_3$ is isotypic with that of Brenkite ($Ca_2F_2CO_3$), and comprise infinite spiral chains of edge-sharing $[FPb_4]$ tetrahedra, with the carbonato groups situated in the funnels formed by this network. The lead atoms are nine-coordinated by four fluorine and five oxygen atoms in a very distorted tri-capped trigonal prism.[255] Crystals of hexalead chloride triorthoborate oxide, $Pb_4O[Pb(BO_3)_3Cl]$, may be regarded as being built up of $[Pb_4O]$ tetrahedra, $[Pb\text{-}Pb]$ dumbells, isolated planar $[BO_3]$ groups, and isolated Cl^- ions.[256] Like the thallium compound, $TlPb_8O_4Br_9$, $Pb_9O_4Br_{10}$ also contains the $[Pb_8O_4]$ group, which may be considered as four $[Pb_4O]$ tetrahedra sharing mutual common edges. The central $[Pb_4O_4]$ cube is reminiscent of the 'cubane' units in the $[Pb_4(OH)_4{}^{4+}]$ cations.[257] In crystals of lead sulphite, $PbSO_3$, the lead atom is seven-coordinated (a distorted mono-capped trigonal prism) as in (165). The structure is closely related to that of $PbSO_4$.[258]



(165)

The reaction of 2,6-diactylpyridine with 1,3-diamino-2-hydroxypropane in methanol in the presence of lead(II) ions affords the lead complex of the ring-contracted oxazolidine-containing Schiff base macrocycle (166). The ligand is hexadentate, with one thiocyanate group N-bonded to lead in the cationic complex.[263] The partially-oxidised tetracyanoplatinate salt, $Pb_{0.77}K_{0.23}[Pt(CN)_4].1{\cdot}5H_2O$, is obtained from aqueous solutions of $Pb(NO_3)_2$ or $Pb(O_2CCH_3)_2$ and $K_2[Pt(CN)_4].3H_2O$ with nitric acid irrespective of the starting K:Pb ratio. The conductivity of single crystals of this material slowly rises with decreasing temperature, passes through a maximum at 215K, and falls rapidly



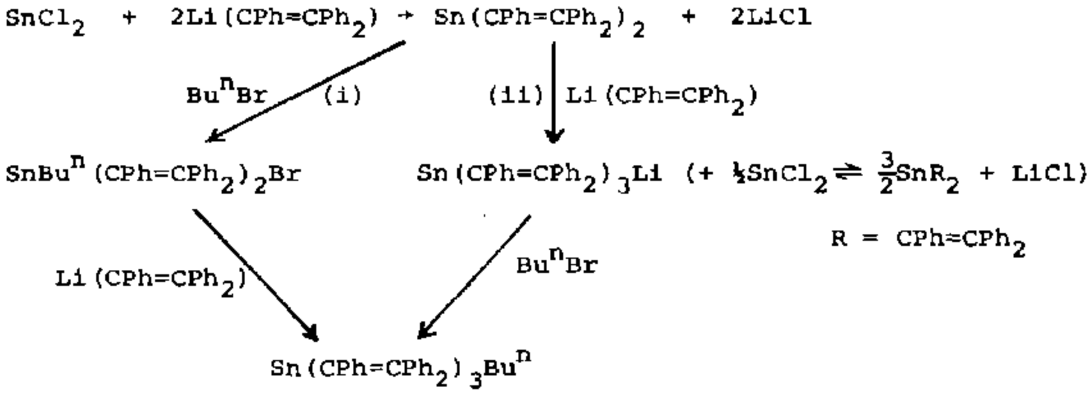
(166)

below 150K indicating a metal to semiconductor transition.[264]

4.4.2 Tetravalent Compounds

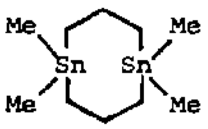
The reaction of tin(II) chloride with the alkenyllithium reagent, $Li(CPh{=}CPh_2)$, in diethylether-hexane-tetrahydrofuran affords what was considered to be the first alkenyl-tin(II) derivative, $Sn(CPh{=}CPh_2)_2$. The deep-red solution is unstable, but the species is sufficiently long-lived to undergo intramolecular oxidative-addition to give ultimately the tetravalent tin compound $Sn(CPh{=}CPh_2)_3Bu^n$, which has been isolated and characterised crystallographically (Scheme 17):[265]

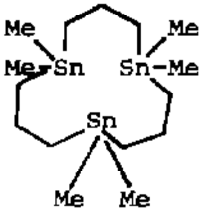
$$Ph_2C{=}CPhBr \quad + \quad LiBu^n \rightarrow Ph_2C{=}CPhLi \quad + \quad Bu^nBr$$

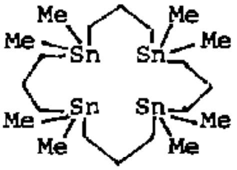


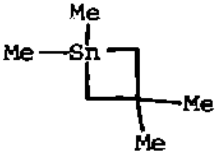
Scheme 17

As expected, the reaction of tin(IV) chloride with $Li(CPh{=}CMe_2)$ yields $Sn(CPh{=}CMe_2)_4$, also characterised crystallographically.[266] The addition of a stoichiometric amount of Me_2SnCl_2 to the di-Grignard reagent $BrMgCH_2CH_2CH_2MgBr$ gives the cyclic oligomers (167)-(169) in ca. 70% yield. Only indirect evidence for the formation of 1,1'-dimethylstannacyclobutane could be obtained due to its high volatility and instability. Nevertheless, 1,1,3,3-tetramethylstannacyclobutane, (170), could be isolated, albeit in only 5% yield.[267]

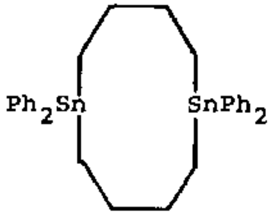

(167)

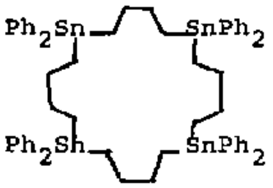

(168)

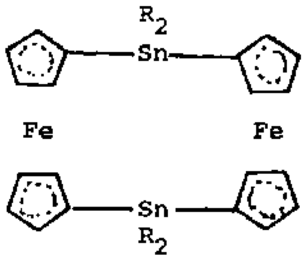

(169)


(170)

Similar methods have been employed to synthesise the macrostannacycloalkanes (171) and (172).[268]


(171)


(172)

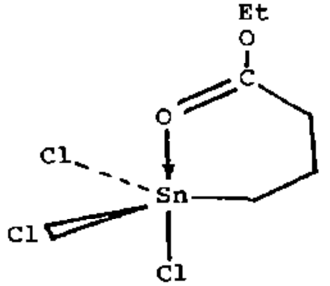

(173)

Treatment of 1,1'-dilithioferrocene-tetramethylethylenediamine with dibutyltin dichloride affords the doubly-bridged derivative (173) ($R = Bu^n$).[269] Bond distances and angles in this molecule are not unusual. However, in tris[(triphenylstannyl)methyl]methane, repulsive interactions involving the bulky $[Ph_3Sn]$ substituents lead to larger $Sn-C(H_2)-CH$ bond angles (mean 117.3°), whereas the $C(H_2)-C(H)-C(H_2)$ bond angles at the tertiary carbon atom average only 111.3°. There is little distortion of the tetrahedral coordination at the tin atoms. The phenyl groups create a pocket in the middle of the molecule which encloses and shields the tertiary hydrogen atom. The resulting inaccessibility of this hydrogen atom partly accounts for the low reactivity of the compound in redox reactions.[270] The structures of tetraphenyltin (a redetermination) and tetra-o-tolytin have been reported. The introduction of a methyl group in the ortho position causes a lengthening of the Sn-C bond.[271]

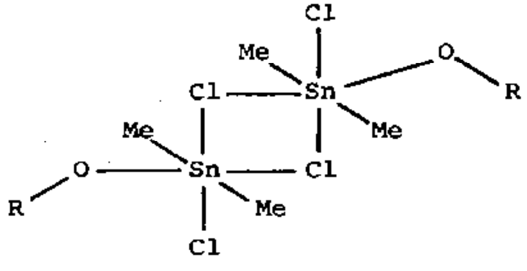
The direct synthesis of dimethyltin dichloride from methyl chloride and molten tin proceeds with a high space-time yield in a $NaAlCl_4$ melt. The reaction proceeds via an addition of CH_3Cl to $SnCl_2$ forming CH_3SnCl_3, which is reduced by the tin metal, followed by another addition of CH_3Cl.[272] The second order rate constants for the redistribution of tetramethyltin with dimethyltin dichloride is proportional to the dielectric constant of the solvent. There is also a weak relationship between the rate constants and the values of the two bond $^2J(^{119}Sn\text{-}C\text{-}^1H)$ coupling constants in several solvents, interpreted as reflecting the coordinating ability of the solvents. The activation entropies of the reactions typically have large negative values, indicating that the processes proceed via a four-centre transition state.[273] Solutions of methyltin chlorides in carbon tetrachloride and water degrade under ultraviolet irradiation to an inorganic tin species via di- and monomethyltin species. In water, the monomethyltin species was not observed.[274] In methanol, triphenyltin chloride undergoes electrochemical alkylation via the corresponding triphenylstannyl-mercury derivatives.[275] A series of 3,3-bis(trimethylstannyl)-, 3,3-bis(halodimethylstannyl)-, and 3,3-bis(dihalomethylstannyl)-propyl derivatives having carboxyl, hydroxy, acetoxy, and sulphoxy functional groups has been synthesised by conventional methods.[276]

X-ray crystallography has been employed widely to characterise a large number of compounds, and is of great assistance in the interpretation of spectroscopic data. The tin atom in $Cl_3SnCH_2CH_2CH_2CO_2Et$ is five coordinated, with the carbon atom occupying an equatorial site and the carbonyl oxygen atom an axial site as in (174). The six-membered ring is slightly boat-shaped. Coordination of the carbonyl group persists in solution, but is broken down when strong nitrogen donors such as 2,2'-bipyridyl, 1,10-phenanthroline and pyridine are added.[277] Six-coordination predominates in complexes of diorganotin dihalides, as in (1,10-phenanthroline)dichlorodibutyltin[278] and [3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine]dichlorodiethyltin.[279]

In both these complexes, the organic groups are mutually trans. The 1:1 2,6-dimethylpyridine N-oxide complex of dimethyltin dichloride is dimeric (175), with a central four-membered $[Sn_2Cl_2]$ ring. The oxygen atoms of the donor ligands are trans to the bridging chlorines.[280] The tin atom in dichlorobis[2-(phenylazo)-phenyl]tin (obtained from the reaction of chloro[2-(phenylazo)-phenyl]mercury with metallic tin) is six-coordinated in a very distorted octahedral fashion. The two carbon atoms of the ortho-metallated phenyl groups are significantly displaced from ideal trans positions (CSnC = 149.7°).[281] 1,2-Bis(diphenylphosphoryl)-ethane (dppoe) and cis-1,2-bis(diphenylphosphoryl)ethylene (dppoet) form 1:1 complexes with diorganotin dichlorides. The structure of Bu_2SnCl_2(dppoe) is polymeric, with the dppoe ligand bridging adjacent tin atoms, which are coordinated in a distorted fashion resulting from the weaker bonding of one of the phosphoryl groups. The CSnC bond angle in this complex is again low (154.3°).[282] In contrast, crystals of the two complexes Bu_2SnCl_2(dppoet) and Pr_2SnCl_2(dppoet) comprise discrete molecules. The major difference between the two structures is associated with the behaviour of the dppoet ligand, which chelates symmetrically in the former, but is predominantly unidentate in the latter.[283] Tin-119 Mössbauer data was reported extensively for both types of complex.[282,283] The coordination polyhedron in the complex of dibutyltin dichloride with 2-(2'-pyridyl)3-(N-2-picolylimino)-4-oxo-1,2,3,4-tetrahydroquinazoline is best described as a distorted pentagonal bipyramide. The ligand functions as a terdentate [ONN] donor, with rather weak equatorial Sn...N interactions.[284]



(174)



R = $NC_5H_3Me_2$

(175)

Trigonal bipyramidal geometry with trans electronegative atoms is found in the 2:1 complex of triphenyltin chloride and

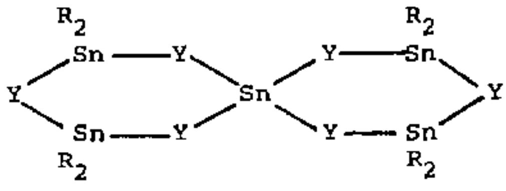
$Ph_2As(O)CH_2CH_2(O)AsPh_2$, which functions as a bridging ligand,[285] and the rather unusual compound $[IrH\{P(OMe)_3\}_4\{P(OMe)_2OSnMe_2Cl_2\}]$-$[SnCl_3Me_2]$.[286]

Several complexes with crown ethers have been reported, including those of the types $SnX_4.L.2H_2O$ (X = Cl,Br; L = 18-crown-6, 15-crown-5, 12-crown-4), $(Ph_3SnCl)_2.L.2H_2O$ (L = 18-crown-6, 15-crown-5), $(R_2SnCl_2)_n$.18-crown-6.$2H_2O$ (R = Me,Ph). Spectroscopic data suggest that the crown ethers function as bridging ligands towards the metal atoms for the larger crowns or as a bidentate chelating ligand for 12-crown-4.[287,288]

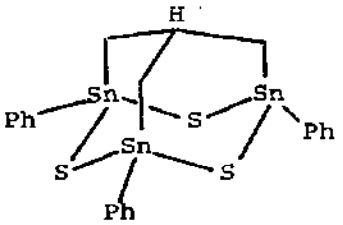
Differences in the two crystalline forms of dihalotin bis(xanthates) have also been investigated by crystallography. The gross molecular structures of the orthorhombic modifications of $SnCl_2(S_2COEt)_2$ and the monoclinic form of $SnBr_2(S_2COEt)_2$ are very similar, with only minor differences in the metal ligand geometries. The major difference between the two forms lies in the conformation of the ethyl groups.[289] The low temperature ^1H n.m.r. spectra of bis(8-quinolinato)tin dichloride, bis(5,7-dichloro-8-quinolinato)tin dichloride, and bis(2-methyl-5,7-dichloro-8-quinolinato)tin dichloride show that only two configurations, the cis-cis-trans and the cis-trans-cis (with respect to Cl, N and O atoms) are appreciably populated, the latter predominating.[290]

Several new complexes of the tin(IV) halides have been reported. A cis-octahedral configuration for the 1:2 complexes of tin(IV) chloride with aliphatic aldehydes such as acetaldehyde, propanol and 2-methylpropanol has been inferred from spectroscopic data,[291] whilst a trans geometry was considered to occur in the complexes of tin(IV) chloride and bromide with N-(dimethylphenyl)-benzaldimines.[292] The question of cis-trans isomerism in complexes of tin(IV) chloride with tetrahydrofuran, tetrahydrothiophen, 1,2-dimethoxyethane, hexamethylphosphoramide and trimethylphosphate has been studied by ^{35}Cl n.q.r; however, this technique could not provide unequivocal conclusions concerning stereochemistry.[293] Tin-119 and phosphorus-31 n.m.r. spectra are more successful in describing the nature and stereochemistry in solution of adducts of tin(IV) halides. The complex $SnCl_4L_2$ (L = tributylphosphine oxide) exists predominantly as the trans isomer, with a small proportion of the cis isomer, whereas the corresponding $SnBr_4L_2$ complex only appears to be present as the trans isomer. In the mixed solution, all the trans $SnCl_nBr_{4-n}L_2$ species are observed. The anionic complexes $[SnCl_5L]^-$ and $[SnBr_5L]^-$ both exhibit slight dissociation in solution to SnX_4L_2 and $[SnX_6]^{2-}$. The tin-119 n.m.r. spectrum of an equimolecular mixture of $[SnCl_5L]^-$ and $[SnBr_5L]^-$ shows the presence of ten of the twelve possible $[SnCl_nBr_{5-n}L]^-$ mixed anions. In contrast, the acetone complexes $SnX_4L'_2$ (L' = acetone; X = Cl,Br) exist predominantly as cis isomers. However, a 1:1 mixture of these complexes in dichloromethane exhibit only time-averaged tin-119 resonances even at -50°, although at -100° the intramolecular processes are slowed sufficiently to distinguish and identify most of the individual component isomers for each stoichiometry of cis-$[SnCl_nBr_{4-n}L'_2]$. The anion complexes $[SnCl_5L']^-$ and $[SnBr_5L']^-$ show no appreciable dissociation in dichloromethane solution, and the tin-119 n.m.r. spectrum of a 1:1 mixture of these compounds at -100° shows only six resonances corresponding to various $[SnCl_nBr_{5-n}L']^-$ species, without distinguishing between individual isomers of each stoichiometry. Some identification was possible, however, at -110°.[294] Polarograms recorded of tin(IV) chloride in acetonitrile in the presence of controlled quantities of substituted pyridine N-oxides demonstrated that stable soluble complexes are formed whose stoichiometry is dependent upon the nature and position of the ring substituent.[295] The complex anions, trans-$(SnF_4Cl_2)^{2-}$, trans-$(SnCl_4Br)^{2-}$, and trans-$(SnF_4Br_2)^{2-}$ are the principal tin anions in the glassy aqueous mixed hydrogen halide solution systems, Sn(IV)-HF-HCl, Sn(IV)-HCl-HBr, and Sn(IV)-HF-HBr, respectively.[296] ^{79}Br n.q.r. studies of $[NH_2Me_2]_2[SnBr_6]$ in the temperature range 77-300K has demonstrated that a phase transition occurs at 253±1K. At room temperature crystals are orthorhombic, and X-ray data show that two of the Sn-Br distances in the anion are slightly longer than the other four, consistent with the high temperature n.q.r. data. Results at low temperatures were interpreted in terms of stronger hydrogen-bonding.[297] Crystals of $[PPh_4]_2[Sn(N_3)_6]$ (from $SnCl_2$ with AgN_3 or NaN_3 in a CH_2Cl_3 suspension in the presence of PPh_4Cl) comprise discrete anions and cations. The symmetry of the anion is C_i, with with the azide groups covalently bonded to tin. The SnNN angle varies between 119° and 126°.[298]

Following the report of a planar $[Sn_3O_3]$ six-membered ring in $(Bu^t{}_2SnO)_3$,[299] hexakis[2,6-diethylphenyl]cyclotristannoxane has also been shown to contain this structural unit.[300] The $[Sn_3Y_3]$ rings in octa-iso-propyl and octa-tert-butylspirobis(cyclotristannathiane) and octa-iso-propylspirobis(cyclotristannaselenane) (176) are, however, non-planar, but exhibit conformational isomerism.[301] 1,3,5-Triphenyl-2,4,6-trithia-1,3,5-tristanna-

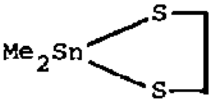


(176)

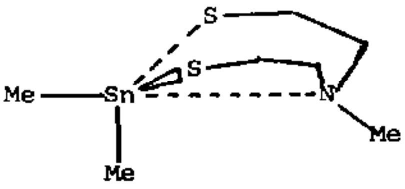


(177)

adamantane, (177), also possesses a non-planar $[Sn_3S_3]$ ring, but is of interest because the bridgehead carbon atom is one of the most flattened carbon atoms known, leading to an increased reactivity of the bridgehead hydrogen.[302] 1,1-Dimethyl-1-stanna-2,5-dithiacyclopentane (178) has an envelope conformation in the crystal. Further short intermolecular Sn...S contacts complete a distorted trigonal bipyramidal geometry at tin.[303] The molecular geometry in 2,2,6-trimethyl-1,3-dithia-6-aza-2-stannocane, (179), is similar. However, in this case, five-coordination is complete by a transannular intramolecular Sn...N interaction.[304]

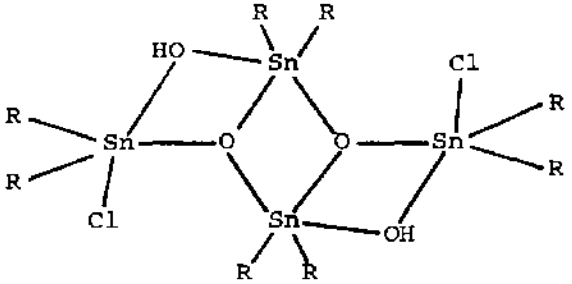


(178)



(179)

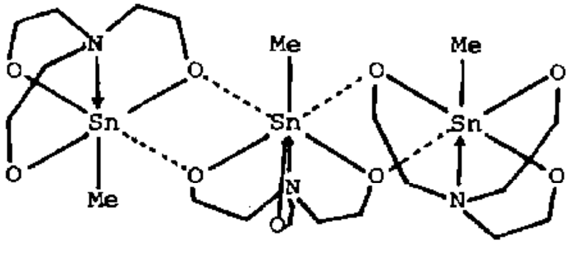
Organotin oxides and sulphides such as $(Bu_2SnE)_n$ and $(Bu_3Sn)_2E$ (E = O,S) can form well defined adducts with transition metals.[305,306] In particular, the cobalt and iron complexes, $(CoCl_2)_n.L.xMeCN$ and $(FeCl_3)_n.L.xTHF$ (n = x = 1; n = 2, x = 3), have been isolated as reddish-brown solids which decompose on heating and are insoluble in common organic solvents suggesting a polymeric structure.[306] Both 1-chloro-3-hydroxo-tetra-iso-propyl-distannoxane and 1-chloro-3-hydroxo-tetra(trimethylsilyl-methylene)-distannoxane are dimeric with a "ladder" type structure, (180).[307] A second study[308] of the structure of $[ClMe_2SnOMe_2SnCl]_2$ has been published, identical to, though without reference to, the first.[309]



R = Pr^i, CH_2SiMe_3

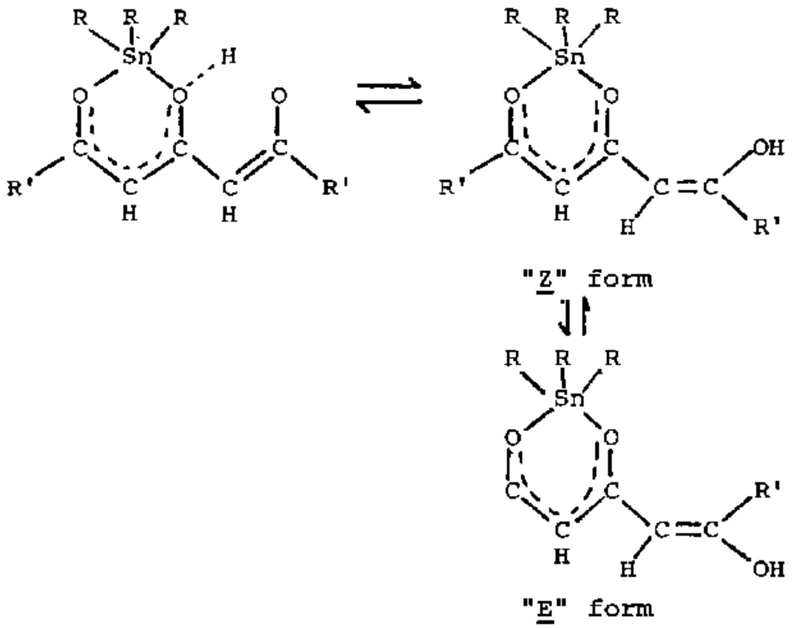
(180)

Attempts to prepare tin derivatives containing Sn-O bonds from inorganic tin(II) or tin(IV) derivatives and methyl 4,6-O-benzylidene-α-D-glucopyranoside have been unsuccessful, although an unstable 1:1 adduct with tin(IV) chloride could be isolated.[310] The first complete structure of a stannatrane has been reported. Methyl(2,2',2"-nitrilotriethoxy)stannane hexahydrate is trimeric as in (181). The trimeric unit is disordered about a two-fold axis, which passes through the central tin atom. This atom has an approximately pentagonal bipyramidal coordination polyhedron; the coordination at the two terminal tin atoms is distorted octahedral. The solid-state structure agrees well with solution n.m.r. data, which indicates three non-equivalent tin centres. The six water molecules are hydrogen-bonded to each other, forming hexagonal rings, and also to the trimeric stannatrane units.[311]

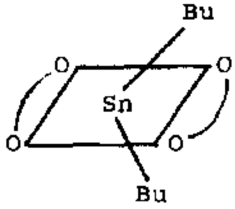


(181)

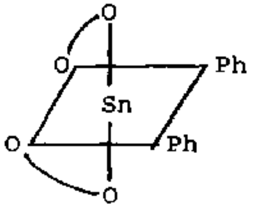
Two papers report tin derivatives of β,δ-triketones.[312,313] Derivatives of the types $R_3Sn(R'COCHCOCH_2COR")$ and $[R_3Sn]_2(R'COCHCOCHCOR")$ have been obtained by the reaction of the triorganotin chloride with the mono- or disodium salt of the triketone (2,4,6-heptanetrione, 1-phenyl-1,3,5-hexanetrione, and 1,5-diphenyl-1,3,5-pentanetrione). Both "Z" and "E" forms have been identified in the 1:1 complexes in equilibrium with the enol form containing five-coordinated tin:



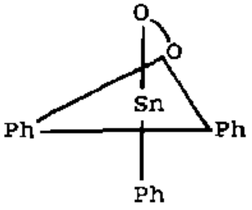
The 2:1 derivatives contain one five- and one four-coordinated tin atoms, except the phenyl analogue where both are five-coordinated.[312] Similar tin(II) and dichlorotin(IV) bis(triketonate) derivatives have also been characterised.[313] Several diorganotin bis(N,N-disubstituted)hydroxylamine and triphenyltin mono(N,N-disubstituted)hydroxylamine derivatives have been synthesised by standard methods. Spectroscopic data indicate that the dibutyltin derivatives have the distorted trans geometry (183), whilst the corresponding diphenyl compounds have the cis octahedral coordination (184). The triphenyltin derivatives are five-coordinated, with the ligand spanning equatorial and axial sites (185).[314] Similar dibutyl- and dioctyltin derivatives of ferrocenyl hydrazones have a structure involving chelation through the azomethine nitrogen atom and amide oxygen atom (186).[315]



(183)

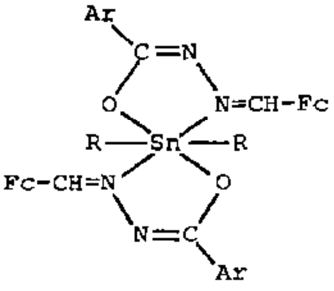


(184)



(185)

Tin-119 n.m.r. has been employed to study the stereochemistry of triorganotin oxinates in solution. Contrary to the previously

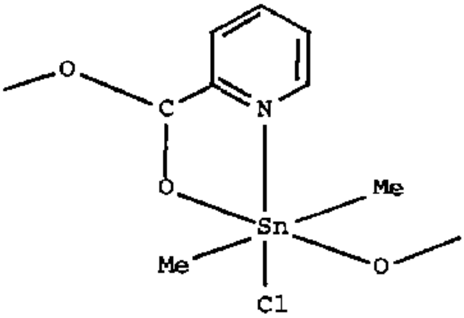


(Where Fc = C_5H_5-Fe-C_5H_4)

(186)

proposed fluxional trigonal bipyramidal structure, the n.m.r. chemical shift data are consistent with tetrahedral, four-coordinate tin. No fluxional processes could be detected in the ^{1}H and ^{13}C n.m.r. spectra of trimethyltin oxinate down to -90°.[316] Tin-119 n.m.r. data for di-tert-butyltin bis(acetylacetonate) bis(tropolonate) and bis(oxinate) indicate a six-coordinated structure, but in the case of the bis(2-methyloxinate) and bis(dialkyldithiocarbamates) a non-chelating structure is also partially involved.[317] 5-Phenylazo-8-quinolinol forms di- and triorganotin derivatives analogous to the well-known classes of these compounds. 5-(2'-Carboxyphenylazo)-8-quinolinol (LHH'), however, forms three classes of derivative, the carboxylates, R_3SnLH, and the quinolinates, $R_2Sn(LSnR'_3)_2$, and $R_3SnLSnR'_3$. The quinolinates $R_2Sn(LH')_2$ can be converted into the water soluble disodium salts $R_2Sn(LNa)_2$ by treatment with $NaHCO_3$.[318]

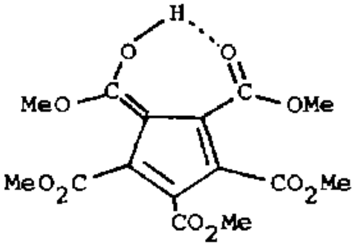
Carbon-13 and tin-119 n.m.r. data have been reported for a large number of triphenyltin compounds,[319] particularly triphenyltin carboxylates.[320] The ^{119}Sn chemical shifts and one-bond coupling constants, $^1J(^{119}Sn-^{13}C)$, depend markedly on the coordination number of the tin atom and on the geometry of the coordination sphere. For four-coordinated compounds, ^{119}Sn chemical shifts fall in the range -40 to -120ppm, whilst $^{1}J(^{119}Sn-^{13}C)$ coupling constants are 550-660 Hz. Five-coordinate compounds with a trigonal bipyramidal geometry have chemical shifts in the range -180 to -260ppm, although the magnitude of the coupling constants depends whether the phenyl groups all occupy equatorial positions (750-850 Hz) or two in equatorial sites and the third in an axial site (600-660 Hz). Data for the triphenyltin carboxylates show chemical shifts in the range -65.1 to -117.7 ppm and coupling constants of 638.7-650.4 Hz indicating a monomeric, four-coordinated structure in solution. Crystals of triphenyltin 2-hydroxy-5-methylphenylazobenzoate comprise monomeric molecules (cf. the chain structures usually encountered for triorganotin carboxylates). However, in this case the carboxylato group chelates the tin atom (Sn-O = 2.070, 2.463Å), resulting in a distorted cis-$[SnC_3O_2]$ geometry at tin. Tin-119 Mössbauer data suggest a molecular structure for the 4-hydroxynaphthyl derivative in which the tin is chelated by one carboxyl oxygen atom and a nitrogen atom with a meridional-$[SnC_3ON]$ geometry, and a weakly carboxylato-bridged chain structure for the tricyclohexyltin compound.[321] Dimethylchlorotin 2-pyridinecarboxylate has a one-dimensional chain structure formed by the usual carboxylate bridging. However, the pyridine nitrogen atom also coordinates to the tin resulting in distorted octahedral coordination as in (<u>187</u>).[322] Several triorganotin and



(<u>187</u>)

triorganolead derivatives of N-acetylamino acids have been synthesised from the acid and triorganotin (hydr)oxide. Spectroscopic data indicate a polymeric structure, with five-coordination at tin resulting from bridging by carboxyl and amido oxygen atoms. In solution in $CHCl_3$, C_6H_6, acetone, thf or pyridine, the compounds are monomeric. Coordination of solvent appears to take place in dmso.[323] Penta(methoxycarbonyl)cyclopentadiene reacts with bis(tributyltin)oxide to give the salt (<u>188</u>), the cation of which is trigonal bipyramidal with apical water molecules.[324] Dihydro-xytin uroporphyrin is highly active in the photoreduction of methylviologen.[325]

$(Bu_3Sn)_2O$ +



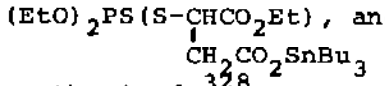
$\rightarrow [Bu_3Sn(OH_2)_2]^+[C_5(CO_2Me)_5]^-$

(<u>188</u>)

In bis[bis(O,O'-diphenylthiophosphato)diphenyltin]hydroxide, an intermediate in the hydrolysis of bis(O,O'-diphenylthiophosphato)-diphenyltin:

$$(C_6H_5)_2Sn[OP(S)(OC_6H_5)_2]_2 + H_2O \rightarrow (C_6H_5)_2Sn[OP(S)(OC_6H_5)_2]OH + HOP(S)(OC_6H_5)_2$$

the molecular units associate through double hydroxide bridges to form centrosymmetric dimers with a central planar $[Sn_2O_2]$ ring. The coordination at the tin atoms is best described as a badly distorted $[Sn_2O_2]$ ring.[326] The phenylphosphonate and phenylarsonate derivatives, $Me_2Sn(O_3PPh)$, $Me_2Sn(O_3AsPh)$ and $Bu_2Sn(O_3AsPh)$, can be isolated in two modifications depending on their method of preparation. The β-modifications and the single modification of $Ph_2Sn(O_3PPh)$ appear to have infinite chain structures, whilst the α-modifications are suggested to have two-dimensional sheet structures.[327] A number of different phosphate derivatives of tin including e.g. $(NH_2CH_2CH_2O)PO(OSnBu_3)_2$,



$(EtO)_2PS(S-\underset{\displaystyle CH_2CO_2SnBu_3}{\underset{|}{C}}HCO_2Et)$, and $(Me_2N)_2PO(OCH_2CH_2SnSnBu_3)$ have been synthesised.[328]

Tin-119 n.m.r. of solutions containing $Sn(S_2COEt)_4$ and $Sn(S_2COPr^i)_4$ has established that ligand exchange occurs with the formation of the mixed species $Sn(S_2COEt)_n(S_2COPr^i)_{4-n}$. Additionally, solutions of mixtures of the tetraxanthates with tin(IV) halides or tin(IV) dihalide bis(xanthates) have been shoen to contain mono-, di, and trihaloxanthate species. The xanthate ligands undergo temperature-dependent monodentate-bidentate exchange about the tin atom.[329]

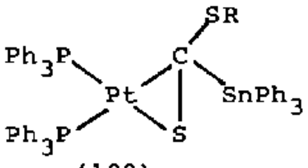
Triorganostannane dithiocarboxylates, formed by the addition of R_3SnLi compounds to carbon disulphide, have been shown to contain four-coordinate tin, with tin-119 n.m.r. chemical shifts in the range -120 to -260ppm.[330] Several complexes of the stannane dithiocarboxylates with transition metal moieties have been reported.[331-334] Such complexation, via a sulphur atom of the ligand, causes a downfield shift due to the higher asymmetry of charge distribution at the tin nucleus.[330] Manganese and rhenium complexes can be obtained by metathesis:[331]

$$R_3SnCS_2Li \ + \ BrM(CO)_5 \rightarrow Ph_3SnCS_2M(CO)_4 \qquad (M = Mn, Re)$$

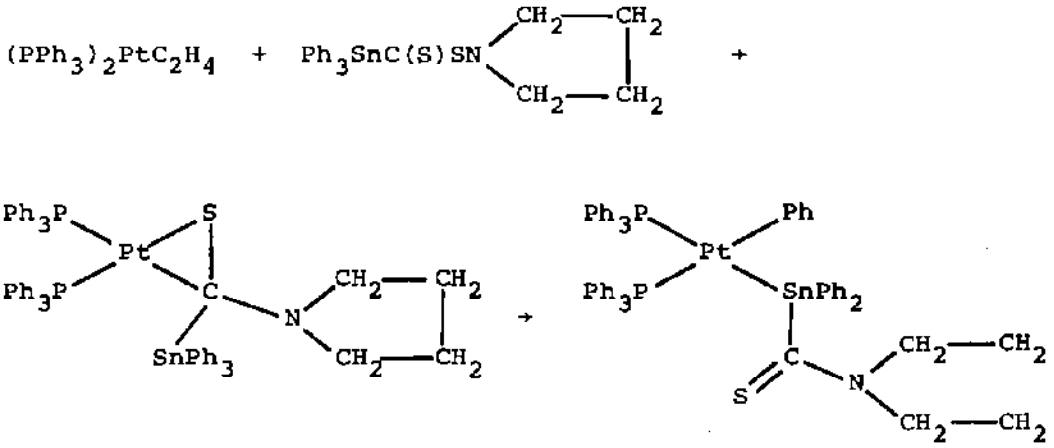
or by ligand displacement:[332]

$$R_3SnCS_2Me + (C_5H_5)Mn(CO)_2.THF \rightarrow R_3SnCS_2Me.Mn(C_5H_5)(CO)_2.$$

The tungsten and dirhenium complexes, $W(CO)_5.L$ and $Re_2(CO)_9.L$ ($L = R_3SnCS_2Me$), are obtained similarly. The complex $Ph_3SnCS_2Mn(CO)_4$ undergoes further substitution with Group $\underline{V}$ donors to afford complexes of the types $Ph_3SnCS_2Mn(CO)_3(L)$.[333] Reaction of the esters Ph_3SnCS_2R with $Pt(C_2H_4)(PPh_3)_2$ results in the displacement of ethylene and the formation of the complex, $(PPh_3)_2Pt[Ph_3SnCS_2R]$. Crystal structure analysis of the methyl ester complex shows η^2 coordination of the ligand via the C=S bond as in (189). The formally platinum(O) centre has approximately planar stereochemistry. The initial products of the reaction between $(PPh_3)_2PtC_2H_4$ and $Ph_3SnC(S)N'$ ($N' = NMeH$ and $NCH_2CH_2CH_2CH_2$) are also η^2-CS coordinated complexes. However, these complexes rearrange by an internal oxidative-addition reaction to afford the Pt-Sn bonded complexes, $(PPh_3)_2Pt(Ph)(Ph_2SnC(S)N')$ (Scheme 18).[334]



(189)



Scheme 18.

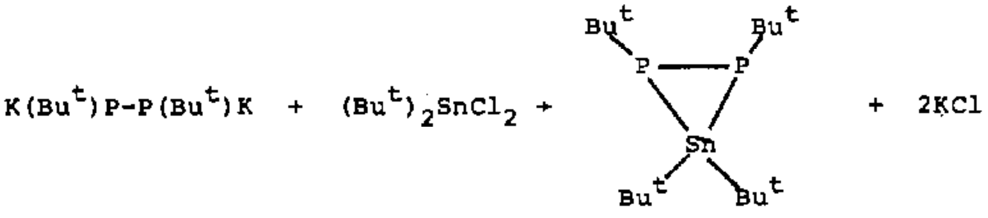
The reaction of $Ph_3SnCS_2^-Li^+$ with 1,n-dibromoalkanes in THF yields stable 1,n-bis(triphenylstannanedithiocarboxylic)alkylene esters (190), whereas when n = 1 or 2, elimination of alkene occurs.[335]

$$2Ph_3SnCS_2^-Li^+ + Br(CH_2)_nBr \xrightarrow[R.T.]{THF} \underset{(190)}{Ph_3SnCS_2(CH_2)_nS_2CSnPh_3} + 2LiBr$$

With irradiated metal carbonyls $Cr(CO)_6$, $(C_5H_5)Mn(CO)_3$) neutral dinuclear complexes similar to those mentioned above are formed.[335]

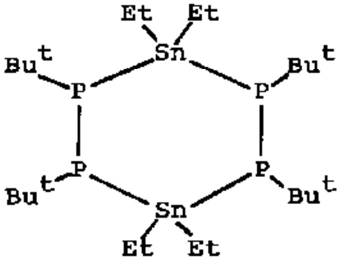
Crystal structure data for trimethyl(tincyanomethanido)tin monohydrate[336] and N-(trimethylstannyl)succinimide[337] have been reported. Both contain five-coordinated tin in a trigonal bipyramidal $[OSnMe_3N]$ geometry. In the former compound, the two nitrogen atoms of the ligand are involved in hydrogen-bonding with the water molecule. In the succinimide derivative, the trimethyltin unit is not planar, the tin atom lying 0.30Å out of the mean plane towards the nitrogen atom. Five-coordination is completed by coordination of one carbonyl oxygen atom of an adjacent molecule resulting in the formation of a one-dimensional helical polymer. The crystal, however, contains two crystallographically independent helices of opposing chirality. Tin-119 chemical shift and $^{2,3}J(SnSn)$ coupling constant data have been reported for the trimethylstannylhydrazines $(Me_3Sn)_{4-n}N_2Me_n$ (n = 0-2) and $(Me_3Sn)_3N_2Ph$. The values of the coupling constants are highly sensitive to lone pair interactions.[338]

The first three-membered $[P_2Sn]$ heterocycle, (191), has been prepared by [2+1] cyclocondensation of $Bu^t{}_2SnCl_2$ with $KBu^tP\text{-}PBu^tK$:



(191)

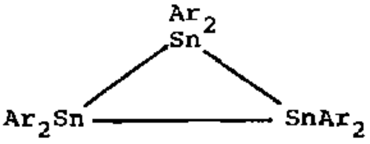
(191) is stable at room temperature. With Et_2SnCl_2, the main reaction product is the six-membered ring compound (192).[339]



(192)

A stable tin colloid in ethanol has been obtained by the chemical reduction of tin(II) chloride with sodium tetrahydroborate in the presence of poly(vinylpyrrolidone) as a protective agent.[340] The polytin anion, $Sn_9{}^{4-}$ has been isolated without the use of a cryptate ligand as the tetrakis(tetramethylammonium) and bis(hexamethylphosphoric triamide)potassium compounds. Both are somewhat thermally unstable at room temperature. The compound K_4SnTe_4 has been isolated by thp aqueous extraction of ternary K/Sn/Te alloys.[341]

The structures of several tin-rich heterocycles have been reported. The Sn-Sn bond distances in the three-membered ring compound (193) and somewhat longer (mean 2.86Å)[300] than those in the six-membered ring of $(Ph_2Sn)_6$.[342]



Ar = mesityl

(193)

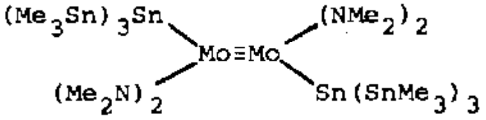
The novel heterocycles $Bu^t_8Sn_4Y$ (Y = S,Se,Te) have been prepared by treatment of $I(Bu^t_2Sn)_4I$ with the corresponding hydrogen chalcogenides. The five-membered rings in these compounds are almost planar.[343] The six-membered $[Sn_4C_2]$ ring in octaphenyl-2,3,5,6-tetrastannacyclohexane has a chair conformation.[344] The first compound containing a direct Si-Pb bond has been synthesised by the reaction:

$$2PbCl_2 \; + \; 2Mg(SiMe_3)_2 \xrightarrow{Et_2O,\ -78^{\circ}C} Pb(SiMe_3)_4 \; + \; Pb \; + \; 2MgCl_2$$

The compound can be isolated as pale yellow, moderately light-sensitive crystals, soluble in hydrocarbon and ether solvents, but decompose at 80°.[345]

The reaction of triphenyltin chloride with the (incompletely characterised) highly reduced carbonyltungsten anion affords the species, $HW(CO)_3(SnPh_3)_3^{2-}$ and $[(Ph_3Sn)_2\{(Ph_2Sn)_2OEt\}W(CO)_3]^-$. The latter results from phenyl-tin cleavage, and the iso-propyl analogue has been characterised by crystallography, which shows that the $[Ph_2SnOPr^iSnPh_2]$ unit chelates the seven-coordinated tungsten atom. The similar species of Group (VI) metals, $HM(CO)_3(SnPh_3)_3^{2-}$ (M = Cr,Mo,W) and $M(CO)_3(SnPh_3)_4^{2-}$ (M = Mo,W) have also been characterised.[346,347] Treatment of $Na_4[M(CO)_4]$ with two moles of Ph_3SnCl gives the salts $[Et_4N]_2[(Ph_3Sn)_2M(CO)_4]$ (M = Cr,Mo,W). The same anions can also be more easily obtained from Ph_3SnLi and $L_2M(CO)_4$ complexes (L = diene or diamine). Further reaction with Ph_3SnCl affords the seven-coordinated complexes $[Et_4N][(Ph_3Sn)_3M(CO)_4]$.[348] The reactions of anhydrous $SnCl_4$ and $SnCl_4.5H_2O$ with $(C_5H_5)_2MoH_2$ afford $[(C_5H_5)_2Mo(H)SnCl_3]_2$-

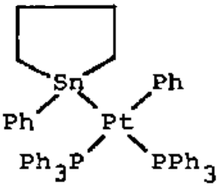
$SnCl_4$ and $(C_5H_5)_2Mo(H)SnCl_3$, respectively, postulated to contain Mo-H-Sn bridges.[349] Orange, air-sensitive crystals of the Mo≡Mo bonded complex (<u>194</u>) have been obtained from the reaction of $Mo_2Cl_2(NMe_2)_4$ with $(Me_3Sn)_3SnLi(THF)_3$. The geometry about each



(<u>194</u>)

tin atom is close to tetrahedral, and the Mo-Sn bond distance is not unusual.[350] The complex anion $[(C_5H_5)Fe(CO)_2Sn]_2W_{10}PO_{38}{}^{5-}$ has been obtained from $(C_5H_5)Fe(CO)SnCl_3$ with aqueous solutions of sodium tungstate and sodium hydrogen phosphate at pH 8-8.6, and characterised by tungsten-183 n.m.r.[351] The photochemical degradation of tin-manganese complexes such as $Me_3SnMn(CO)_3$-$[P(OPh)_3]_2$ appears to proceed via initial homolytic cleavage of the metal-metal bond, with the resulting 15-electron intermediate abstracting hydrogen from the triphenylphosphite ligand giving orthometallated products.[352] The complexes $Ph_3MCo(PMe_3)_3$ (M = Ge, Sn)[353] and $SnBr_2[Re(PPh_3)(CO)_4]_2$ all contain tetrahedrally coordinated Group IV metal.

The complex cis-$PtCl_2(CO)(PPh_3)$ reacts with $SnCl_2.2H_2O$ in acetone to afford solutions which are catalytically active in the hydroformylation of alkenes. N.m.r. data show such solutions to contain the cationic complex, trans-$PtCl(CO)(PPh_3)_2{}^+$ together with four anionic complexes, three of which being $Pt(SnCl_3)_5{}^{3-}$, trans-$PtCl(SnCl_3)_2(PPh_3)^-$ and trans-$Pt(SnCl_3)_2(CO)^-$. Further rearrangement reactions take place upon attempted isolation of these species, and only cis-$PtCl_2(PPh_3)_2$ was isolated. The reaction is extremely solvent dependent. Ligand rearrangement occurs in acetone and acetonitrile, but in chloroform only simple insertion of $SnCl_2$ into one Pt-Cl bond is observed. Comparison of cis-$PtCl_2(L)(PR_3)$ (L = CO, SR'_2, or p-$XCoH_4NH_2$) with cis-$PtCl_2L_2$ and cis-$PtCl_2(PR_3)_2$ shows that the former is the most active catalyst precursor in the presence of tin(II) chloride.[355-357] Phosphorus-31, tin-119 and platinum-195 n.m.r. data have been reported for a large number of Pt-Sn bonded complexes. Platinum-195 chemical shifts cover a range of 450ppm, whilst tin-119 shifts span 300ppm. Plots of $^1J(Pt-P(trans))$ against $^1J(Pt-Sn)$ are approximately linear, indicative of predominantly σ character in the Pt–Sn bond.[358] There also appears to be a qualitative relationship between the ^1J(Pt–Sn) coupling constant and the Pt–Sn bond distance.[359] The reaction of 1,1-diphenyl-1-stannacyclopentane with $Pt(C_2H_4)(PPh_3)_2$ affords the complex (195),

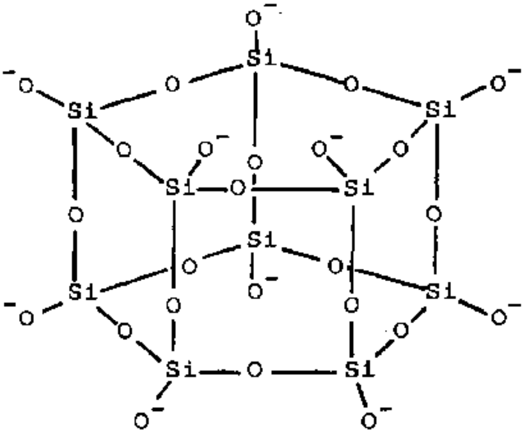


(195)

characterised again by n.m.r.[360] Reaction of sym-trans-$[PtCl(\mu\text{-}Cl)L]_2$ (L = PR_3, $AsEt_3$) with two equivalents of $SnCl_2$ affords dimeric $[Pt(SnCl_3)(\mu\text{-}Cl)L]_2$ complexes. The structure for L = PEt_3, shows that the phosphine and $SnCl_3$ ligand are mutually cis.[359] Red crystals of the complex, $[PPh_4]_2[OsCl_3(NO)(SnCl_3)]_2$ result from the reaction of $OsCl_3(NO)$ and $[PPh_4][SnCl_3]$ in dichloromethane. Crystals comprise discrete anions and cations with octahedrally coordinated osmium.[361]

4.5 CHALCOGENIDE PHASES

Silicon-29 has featured strongly in the characterisation of silicate materials. One study on silica gel prepared at various stages of dehydration showed that the observed spectral changes could not be accounted for by a single structural model of the types previously advanced. However, they are consistent with a heterogeneous silica surface consisting of separate regions resembling the 100 and 111 face of β-cristobalite.[362] The double five-ring silicate, (196), has been identified in ZSM-5 synthesis using silicon-29 n.m.r., attenuated total reflection FT-IR, and mass spectrometry. Redistribution of the silicate species present in the solution phase is observed after the addition of organic solvents to the ZSM-5 synthesis mixture.[363] A correlation between the average Si–O–T (T = tetrahedral atom) bond angle and the associated isotropic silicon-29 chemical shift appears to exist for zeolite materials.[364] Silicon-29 spin lattice relaxation times in some layer aluminosilicates have been found to vary over three orders of magnitude, and demonstrate that, in



(196)

contrast to other reports, T_1 times may be extremely long in such materials.[365] Eight distinct tetrahedral silicon sites have been identified in freshly crystallised (hexagonal) synthetic cordierite, $Mg_2Al_4Si_5O_{18}$, four in the chain manifold and four in the six-membered aluminosilicate rings. In aged (orthorhombic) product, however, there are only two sites (one in the rings and the other in the chains). Si:Al ratios within each manifold can be determined from silicon-29 masnmr spectra, which can also be employed to follow the course of Si,Al ordering as thermodynamic equilibrium is approached.[366] Reaction of synthetic zeolite Na-Y with $SiCl_4$ vapour at 560° yields an essentially aluminium-free faujasite structure, which, as shown by silica-29 masnmr spectroscopy, has regular Si(4Si) lattice ordering. The aluminium-27 masnmr spectrum exhibits two peaks, one due to residual lattice aluminium and the other to $AlCl_4^-$.[367] Alkaline earth chloride silicates have been prepared by heating mixtures of the corresponding carbonates and SiO_2 in different molar ratios in the melt of the alkaline earth chlorides.[368] Trimethylsilylation has been used to examine the distribution in aqueous solutions of alkali metal and tetraalkylammonium silicates.[369]

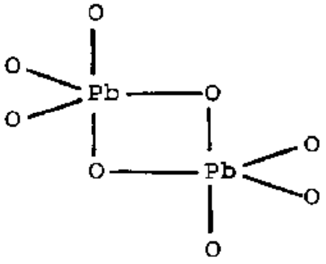
The synthesis and structures of several germanate, stannate and plumbate phases have been reported. A magnesium germanium oxide hydrate of composition, $MgGeO_3.0{\cdot}25H_2O.0{\cdot}nH_2O$, prepared by the simultaneous hydrolysis of magnesium and germanium alkoxides, crystallises slowly at 660-1200° to magnesium metagermanate, $MgGeO_3$. The kinetics show that the initial stage of the dehydration proceeds rapidly, and that the final stages can be expressed in terms of the contracting cube model with an activation energy of 198 kJ mol^{-1}.[370] Orthorhombic $MgGeO_3$ (the high temperature, low pressure phase) is isostructural with orthoenstatile, $MgSiO_3$. Monoclinic $MgGeO_3$ (the low temperature, high pressure phase), however, is different from that of dinenstatile. The transformation from orthorhombic→monoclinic is accompanied by a fairly large volume decrease (3-5%) due to a smaller distortion in the Mg(2) octahedron in the structure of monoclinic $MgGeO_3$.[371] Beta-$BaGeO_3$ (the high temperature form) is formed metastably at 630-660° from an amorphous material prepared by the simultaneous hydrolysis of barium and germanium alkoxides. The transformations of $BaGeO_3$ are summarised as follows:[372]

$$BaGeO_3 \xrightarrow{780-890^{\circ}} \alpha\text{-}BaGeO_3 \underset{1130-1150^{\circ}}{\overset{1180-1200^{\circ}}{\rightleftarrows}} \beta\text{-}BaGeO_3 \xrightarrow{1270^{\circ}} \text{melt}$$

Crystalline amorphous $[GrO_4Al_{12}(OH)_{24}(H_2O)_{12}](SO_4)_4.xH_2O$ is formed by the reaction of aqueous solutions of aluminium chloride and sodium germanate.[373] Single crystals of K_4GeO_4 have been prepared by heating $KO_{0.46}$ and GeO_2, and are isotypic with K_4SnO_4.[374]

Pale yellow barium hydroxostannate(II), which has been assigned different stoichiometries in the past, has now been unequivocally identified as $Ba[SnO(OH)]_2$. This material contains a novel structural unit in tin(II) chemistry, the one-dimensional polyanion, $[SnO(OH)]_{\infty}^{\infty-}$.[375] Two similar sodium hydroxostannates have also been characterised. $Na_2[Sn_2O(OH)_4]$ is identical to the compound previously described as "$Na[Sn(OH)_3]$" and contains $[Sn(OH)_3]^-$ anions. $Na_4[Sn_4O(OH)_{10}]$ contains the oxo-bridged $[(HO)_2SnOSn(OH)_2]^{2-}$ anions, which exhibit a syn configuration with respect to the projection along the Sn-Sn vector.[376] All three compounds crystallise with a layer lattice structure.

The structure of the high temperature phase of Li_2PbO_3 is a variant of the sodium chloride lattice, characterised by alternating layers of Li^+ and Pb^{4+}/Li^+ cations, all of which are octahedrally coordinated.[377] Like K_4GeO_4, K_4PbO_4 and Rb_4PbO_4 are isotypic with K_4SnO_4.[378,379] Annealing mixtures of Na_2PbO_3 and $RbO_{0.81}$ in the ratio Rb:Na:Pb of 4:2:1 affords Rb_3NaPbO_4, which also contains isolated $[PbO_4]$ tetrahedra.[380] Similar methods have been employed for the preparation of rubin red crystals of $Rb_2Pb_4O_7$,[381] a mixed valence compound in which Pb^{2+} has a coordination number of three and Pb^{4+} a coordination number of six, colourless $K_2Li_6[Pb_2O_8]$,[382] nearly colourless $Tb_2Li_{14}[Pb_3O_{14}]$,[383] and pale yellow $Cs_2Li_{14}[Pb_3O_{14}]$.[383] The structure of $K_2Li_6[Pb_2O_8]$ is characterised by the linking of the edge-connected trigonal bipyramidal anion (197). Both the triplumbates are isotypic with $K_2Li_{14}[Pb_3O_{14}]$.



(197)

Experimental values for the heat of formation ($\Delta H^{o}_{298,f}$ = -86.4± 9.9 kJ mol^{-1}) and absolute entropy (S^{o}_{298} = 89.0±7.1 J.K^{-1} mol^{-1}) have been determined for SnSe. The corresponding values for $SnSe_2$ were -118.1±11.8 kJ mol^{-1} and 111.8±11.8 J.K^{-1}mol^{-1}.[384] The structure of $Ga_2S_2S_5$ is essentially built up from two kinds of sheets parallel to [100], alternately sheets of fused $[GaS_4]$ tetrahedra and $[Sn_2Sn]$. The tin atoms are in five- and six-fold coordination.[385] Potentiometric titration of 0.01M solutions of $Na_2M_2X_6$ (M = Si,Ge; X = S,Se) in methanol with bromine has yielded thermodynamic data for these reactions.[386]
$Na_4Ge_2Se_6.16H_2O$ is obtained from the reaction of sodium selenide with $GeSe_2$ in aqueous solution, and crystals contain isolated $Ge_2Se_6{}^{4-}$ anions consisting of two edge-sharing tetrahedra. Adamanta-$Ge_4Se_{10}{}^{4-}$ is obtained when at 1:2 molar ratio of alkali selenide to $GeSe_2$ is employed.[387] Crystals of Na_4SnTe_4 contain isolated $[SnTe_4]^{4-}$ tetrahedra.[388] $Na_8Ge_4Te_{10}$ crystallises in two modifications, one of which has been shown to contain $[Ge_4Te_{10}]^{8-}$ anions in the form of $[(GeTe_2)_4Te_2]^{8-}$ rings.[389] $Ba_6Sn_2P_6$ is isotypic with $K_2Sn_2Te_6$ containing the $[P_3SnSnP_3]^{12-}$ anion (Sn-Sn = 2.891Å).[390]

REFERENCES

1 I.Hargittai and C.Bliefert, Z. Naturforsch., Teil B, 38(1983)1304.

2 S.N.Ahmed, M.L.McKee and P.B.Shevlin, J. Am. Chem. Soc., 105(1983)3942.

3 P.B.Shevlin, D.W.McPherson and P.Melius, J. Am. Chem. Soc., 105(1983)488.

4 M.T.Nguyen and A.F.Hegarty, J. Am. Chem. Soc., 105(1983)3811.

5 J.Mareda, N.G.Rondan, K.N.Houk, T.Clark and P. von R. Schleyer, J. Am. Chem. Soc., 105(1983)6997.

6 P. von R.Schleyer, A.J.Kos and E.Kaufmann, J. Am. Chem. Soc., 105(1983)7617.

7 T.Clark, C.Rohde and P. von R.Schleyer, Organometallics, 2(1983)1344.

8 A.S.Nazran, E.J.Gabe, Y.LePage, D.J.Northcott, J.M.Park and D.Griller, J. Am. Chem. Soc., 105(1983)2912.

9 A.S.Nazran and D.Griller, J. Chem. Soc., Chem. Commun., (1983)850.

10 M.Torres, J.L.Bourdelande, A.Clement and O.P.Strausz, J. Am. Chem. Soc., 105(1983)1698.

11 T.Umenoto and H.Tsutsumi, Bull. Chem. Soc. Jpn., 56(1983)631.

12 A.B.Altabef, E.L.Varetti and P.J.Aymonino, Z. Anorg. Allg. Chem., 506(1983)161.

13 K.Schlosser and H.Willner, Z. Naturforsch., Teil B, 38(1983)161

14 R.C.Kumar and J.M.Sreeve, J. Chem. Soc., Chem. Commun., (1983)658.

15 C.J.Schack and K.O.Christie, Inorg. Chem., 22(1983)22.

16 A.Waterfeld, W.Isenberg, R.Mews, W.Clegg and G.M.Sheldrick, Chem. Ber., 116(1983)724.

17 S.C.Chang and D.D.DesMarteau, Inorg. Chem., 22(1983)805.

18 H.M.Marsden, K.Yasufulai and J.M.Shreeve, Inorg. Chem., 22(1983)1202.

19 H.Bock, R.Dammel and S.Auggen, J. Am. Chem. Soc., 105(1983) 7681.

20 H.Hlawatschek and G.Gattow, Z. Anorg. Allg. Chem., 502(1983)11.

21 R.Appel and M.Siray, Angew. Chem., Int. Ed. Engl., 22(1983)785.

22 R.Appel and W.Paulen, Angew. Chem., Int. Ed. Engl., 22(1983)785.

23 J.C.T.R.Burkett-St.Laurent, M.A.King, H.W.Kroto, J.F.Nixon and R.J.Suffolk, J. Chem. Soc., Dalton Trans., (1983)755.

24 A.H.Cowley, J.E.Kilduff, M.Pakulski and C.A.Stewart, J. Am. Chem. Soc., 105(1983)1655.

25 S.I.Al-Resayes, S.I.Klein, H.W.Kroto, M.F.Meidine and J.F. Nixon, J. Chem. Soc., Chem. Commun., (1983)930.

26 A.H.Cowley, R.A.Jones, C.A.Stewart and A.I.Stuart, J. Am. Chem. Soc., 105(1983)3737.

27 G.Becker, W.A.Hermann, W.Kalcher, G.W.Kriechbaum, C.Pahl, C.T.Wagner and M.L.Ziegler, Angew. Chem., Int. Ed. Engl., 22(1983)413.

28 C.Wentrop, H.Briehl, G.Becker, G.Uhl, H.J.Wessely, A.Maquestiau and R.Flamman, J. Am. Chem. Soc., 105(1983)7194.

29 M.A.Vincent, H.F.Schaeffer, A.Schier and H.Schmidbaur, J. Am. Chem. Soc., 105(1983)3806.

30 A.B.Burg, Inorg. Chem., 22(1983)2 73.

31 H.Schmidbaur, C.Zybill, C.Kruger and H.J.Kraus, Chem. Ber., 116(1983)1955.

32 H.Schmidbaur, A.Schier and D.Neugebauer, Chem. Ber., 116(1983)2173.

33 H.Schmidbaur, U.Deschler and B.Milewski-Mahria, Chem. Ber., 116(1983)1393.

34 R.Appel, U.Baummeister and F.Knock, Chem. Ber., 116(1983)2275.

35 A.Meyer, A.Hartl and W.Matisch, Chem. Ber., 116(1983)348.

36 G.Kleeman and K.Seppelt, Chem. Ber., 116(1983)645.

37 P.A.Chalaner, G.D.Glick and R.A.Moss, J. Chem. Soc., Chem. Commun., (1983)880.

38 G.R.Clark, S.V.Hoskins, T.C.Jones and W.R.Roper, J. Chem. Soc., Chem. Commun., (1983)719.

39 D.T.Cromer, D.Schifel, R.Lesar and R.L.Mills, Acta Crystallogr., C39(1983)1146.

40 T.Ohta, Bull. Chem. Soc. Jpn., 56(1983)869.

41 G.P.Raine, H.F.Schaeffer and R.C.Haddon, J. Am. Chem. Soc., 105(1983)194.

42 P.W.Lednov and P.C.Versloot, J. Chem. Soc., Chem. Commun., (1983)284.

43 R.D.Brown, F.W.Eastwood, P.S.Elmes and P.D.Godfrey, J. Am. Chem. Soc., 105(1983)6496.

44 B.T.Thompson, T.N.Gallaher and T.C.DeVore, Polyhedron, 2(1983)619.

45 B.Sturm and G.Gattow, Z. Anorg. Allg. Chem., 502(1983)7.

46 T.Mallouk and N.Bartlett, J. Chem. Soc., Chem. Commun., (1983)103.

47 I.Palchan, D.Davidov and H.Selig, J. Chem. Soc., Chem. Commun., (1983)657.

48 W.Jones, P.Korgul, R.Schlögl and J.M.Thomas, J. Chem. Soc., Chem. Commun., (1983)468.

49 R.Schlögl, W.Jones and J.M.Thomas, J. Chem. Soc., Chem. Commun., (1983)1330.

50 M.Rabinovitz, H.Selig and J.Levy, Angew. Chem., Int. Ed. Engl., 22(1983)53.

51 R.Setton, F.Beguin, L.Facchini, M.F.Quinton, A.P.Legrand, B.Ruisinger and H.P.Boehm, J. Chem. Soc., Chem. Commun., (1983)36.

52 M.J.Fink, M.J.Michalczyk, K.J.Haller, R.West and J.Michl, J. Chem. Soc., Chem. Commun., (1983)1010.

53 K.W.Zilm, D.M.Grant, J.Michl, M.J.Fink and R.West, Organometallics, 2(1983)193.

54 M.Wiedenbruch, A.Schäfer and K.L.Than, Z. Naturforsch., Teil B., 38(1983)1695.

55 H.Watanabe, T.Okawa, M.Kato and Y.Nagai, J. Chem. Soc., Chem. Commun., (1983)781.

56 S.Masamune, H.Tobita and S.Murakami, J. Am. Chem. Soc., 105(1983)6524.

57 S.Masamune, S.Murakami and H.Tobita, Organometallics, 2(1983)1464.

58 M.J.Fink, D.J.DeYoung, R.West and J.Michl, J. Am. Chem. Soc., 105(1983)1070.

59 S.Masamune, S.Murakami, H.Tobita and D.J.Williams, J. Am. Chem. Soc., 105(1983)7776.

60 M.Ishikawa, H.Sugisawa, M.Kumada, T.Higuchi, K.Matsui, K.Hirotsu and J.Iyoda, Organometallics, 2(1983)174.

61 V.J.Tortorelli, M.Jones, S.Wu, and Z.Li, Organometallics, 2(1983)759.

62 M.Schriewer and W.P.Meumann, J. Am. Chem. Soc., 105(1983)897.

63 A.G.Brook, S.C.Nyburg, F.Abdesaken, B.Gutenkunst, R.Krishna, M.R.Kalluny, Y.C.Poon, Y.M.Chang and W.Wong-Ng, J. Am. Chem. Soc., 104(1982)104.

64 N.Wiberg and G.Wagner, Angew. Chem., Int. Ed. Engl., 22(1983)1005.

65 R.T.Conlin, Y.W.Kwak and H.B.Huffaker, Organometallics, 2(1983)343.

66 T.M.Gentle and E.L.Muetterties, J. Am. Chem. Soc., 105(1983)304.

67 T.J.Barton, G.T.Burns and D.Gschneider, Organometallics, 2(1983)8.

68 R.T.Conlin and R.S.Gill, J. Am. Chem. Soc., 105(1983)618.

69 C.George and R.D.Koob, Organometallics, 2(1983)39.

70 M.Kira, K.Sakamoto and H.Sakurai, J. Am. Chem. Soc., 105(1983)7469.

71 W.Ando, Y.Hamada and A.Sekiguchi, J. Chem. Soc., Chem. Commun., (1983)952.

72 T.J.Barton, S.A.Burns and G.T.Burns, Organometallics, 2(1983)199.

73 G.T.Burns and T.J.Barton, J. Am. Chem. Soc., 105(1983)2006.

74 T.J.Barton and G.T.Burns, Organometallics, 2(1983)1.

75 H.Sakurai, Y.Nakadaira and H.Sakaba, Organometallics, 2(1983)1484.

76 H.Lischka and H.J.Köhler, J. Am. Chem. Soc., 105(1983)6646.

77 R.S.Grev and H.F.Schaeffer, J. Chem. Soc., Chem. Commun., (1983)785.

78 H.Nakatsji, J.Ushio and T.Yonezawa, J. Organomet. Chem., 258(1983)C1.

79 C.F.Pau, W.J.Petro and W.J.Hebre, J. Am. Chem. Soc., 105(1983)16.

80 M.R.Hoffmann, Y.Yoshioka and H.F.Schaeffer, J. Am. Chem. Soc., 105(1983)1084.

81 S.Nagase and T.Kudo, J. Chem. Soc., Chem. Commun., (1983)363.

82 P.R.Jones, M.E.Lee and L.T.Lin, Organometallics, 2(1983)1039.

83 I.Hargittai, G.Schiltz, J.Tremmel, N.D.Kagramanov, A.K.Maltsev and O.M.Nefedov, J. Am. Chem. Soc., 105(1983)2895.

84 A.Castel, P.Riviere, J.Satge, J.J.E.Moreau and R.J.P.Corriu, Organometallics, 2(1983)1498.

85 Y.Kudo and S.Nagase, J. Organomet. Chem., 253(1983)C23.

86 G.Guimon, G.Pfistor-Guillouzo, H.Lavayssiere, G.Dousse, J.Barrau and J.Satgé

87 J.Barrau, M.Bouchaut, H.Lavayssiere, G.Dousse and J.Sargt, J. Organomet. Chem., 243(1983)281.

88 J.Barrau, G.Rima, H.Lavayssiere, G.Dousse and J.Satge, J. Organomet. Chem., 246(1983)227.

89 M.A.Ring, H.E.O'Neal, S.F.Rickborn and B.A.Sawrey, Organometallics, 2(1983)1891.

90 M.Castiglioni and P.Volpe, Polyhedron, 2(1983)225.

91 M.Ishikawa, H.Sugisawa, M.Kumada, H.Kawakami and T.Yamabe, Organometallics, 2(1983)974.

92 S.Masmune, S.Murakami, H.Tobita, D.J.Williams, J. Am. Chem. Soc., 105(1983)7776.

93 K.Peters and H.G. von Schnering, Z. Anorg. Allg. Chem., 502(1983)55.

94 K.Peters, E.M.Peters and H.G. von Schnering, Z. Anorg. Allg. Chem., 502(1983)61.

95 G.Fritz and H.Bauer, Angew. Chem., Int. Ed. Engl., 22(1983)730.

96 G.L.Larson, S.Sandoval, F.Cartledge and F.R.Fronczek, Organometallics, 2(1983)810.

97 N.S.Homane, S.Cradock and E.A.V.Ebsworth, Inorg. Chim. Acta, 72(1983)181.

98 C.Eaborn, Y.Y.El-Kaddar and P.D.Lickiss, J. Chem. Soc., Chem. Commun., (1983)1450.

99 H.H.Karsh and A.Appelt, Z. Naturforsch., Teil B, 38(1983)1399.

100 P.Jutzi, H.Saleske, D.Bühl and H.Grohe, J. Organomet. Chem., 252(1983)29.

101 F.X.Kohl and P.Jutzi, J. Organomet. Chem., 243(1983)31.

102 J.Almlöf, L.Fernholt, K.Faegin, A.Haaland, B.E.R.Schilling, R.Seip and K.Taugbøl, Acta Chem. Scand., Ser. A., 37(1983)131.

103 K.J.Fisher and C.E.Ezeani, Polyhedron, 2(1983)393.

104 P.Livant, M.L.McKee and S.D.Worley, Inorg. Chem., 22(1983)895.

105 A.Szollosy, L.Parkanyi, L.Bihatsi and P.Hencsei, J. Organomet. Chem., 251(1983)159.

106 W.Clegg, U.Klingebiel, J.Neemann and G.M.Sheldrick, J. Organomet. Chem., 249(1983)47.

107 W.Clegg, M.Haase, U.Klingebiel, J.Neemann and G.M. Sheldrick, J. Organomet. Chem., 251(1983)281.

108 W.Clegg, O.Graalmann, M.Haase, U.Klingebiel, G.M.Sheldrick, P.Werner, G.Henkel and B.Krebs, Chem. Ber., 116(1983)282.

109 W.Clegg, M.Haase, H.Hluchy, U.Klingebiel and G.M.Sheldrick, Chem. Ber., 116(1983)290.

110 M.Hesse, U.Klingebiel, J.Heinze and J.Mortensen, Z. Naturforsch., Teil B, 38(1983)953.

111 M.Hesse and U.Klingebiel, Z. Anorg. Allg. Chem., 501(1983)57.

112 H.W.Roesky, H.G.Schmidt, M.Noltemeyer and G.M.Sheldrick, Chem. Ber., 116(1983)1411.

113 R.Hoppenheit, R.Mews, M.Noltemeyer and G.M.Sheldrick, Chem. Ber., 116(1983)874.

114 P.M.Engelhardt, A.S.May, C.L.Raston and A.H.White, J. Chem. Soc., Dalton Trans., (1983)1671.

115 M.F.Lappert, M.J.Slade, A.Singh, J.L.Atwood, R.D.Rogers and R.Shakir, J. Am. Chem. Soc., 105(1983)302.

116 D.J.Brauer, H.Bürger, W.Geschwandtner, G.R.Liewald and C.Krüger, J. Organomet. Chem., 248(1983)1.

117 U.Wannagat, T.Blumenthal, D.J.Brauer and H.Bürger, J. Organomet. Chem., 249(1983)33.

118 H.Bürger, W.Geschwandtner and G.R.Liewald, J. Organomet. Chem., 259(1983)145.

119 R.A.Jones, M.H.Seeberger, J.L.Atwood and W.E.Hunter, J. Organomet. Chem., 247(1983)1.

120 M.D.Fryzuk, H.D.Williams and S.J.Rettig, Inorg. Chem., 22(1983)863.

121 R.P.Planalp, R.A.Andersen and A.Zalkin, Organometallics, 2(1983)16.

122 R.P.Planalp and R.A.Andersen, Organometallics, 2(1983)1675.

123 M.D.Fryzuk and H.D.Williams, Organometallics, 2(1983)162.

124 M.D.Fryzuk and P.A.MacNeil, Organometallics, 2(1983)355.

125 O.J.Scherer, R.Konrad, E.Guggolz and M.L.Ziegler, Chem. Ber., 116(1983)2676.

126 V.D.Romanenko, A.V.Ruban and L.N.Markovski, J. Chem. Soc., Chem. Commun., (1983)187.

127 H.R.O'Neil and R.H.Neilson, Inorg. Chem., 22(1983)814.

128 B.L.Li, J.S.Engenito, R.H.Neilson and P.Wisian-Neilson, Inorg. Chem., 22(1983)575.

129 Z.M.Xie and R.H.Neilson, Organometallics, 2(1983)921.

130 Z.M.Xie and R.H.Neilson, Organometallics, 2(1983)1406.

131 E.Niecke, R.Rüger, B.Krebs and M.Dartmann, Angew. Chem., Int. Ed. Engl., 22(1983)552.

132 O.J.Scherer, J.Kerth and M.L.Ziegler, Angew. Chem., Int. Ed. Engl., 22(1983)503.

133 R.A.Jones and M.H.Seeberger, J. Chem. Soc., Dalton Trans., (1983)181.

134 R.Bohra, H.W.Roesky, J.Lucas, M.Noltemeyer and G.M.Sheldrick, J. Chem. Soc., Dalton Trans., (1983)1011.

135 R.I.Papasergio, C.L.Raston and A.H.White, J. Chem. Soc., Chem. Commun., (1983)1419.

136 C.Eaborn, P.B.Hitchcock, J.D.Smith and A.C.Sullivan, J. Chem. Soc., Chem. Commun., (1983)827.

137 C.Eaborn, P.B.Hitchcock, J.D.Smith and A.C.Sullivan, J. Chem. Soc., Chem. Commun., (1983)1390.

138 C.Eaborn, N.Retta and J.D.Smith, J. Chem. Soc., Dalton Trans., (1983)905.

139 W.Clegg, M.Haase, U.Klingebiel and G.M.Sheldrick, Chem. Ber., 116(1983)146.

140 U.Klingebiel, N.Vater, W.Clegg, M.Haase and G.M.Sheldrick, Z. Naturforsch., Teil B, 38(1983)1557.

141 G.Fritz and J.Härer, Z. Anorg. Allg. Chem., 500(1983)14.

142 G.Fritz, J.Härer and K.Stoll, Z. Anorg. Allg. Chem., 504(1983) 38.

143 G.Fritz, J.Härer and E.Matern, Z. Anorg. Allg. Chem., 504(1983) 38.

144 G.Fritz, K.D.Hoppe, W.Honler, D.Weber, C.Mujica, V.Manriquez and H.G. von Shnering, J. Organomet. Chem., 249(1983)63.

145 M.Baudler, T.Pontzen, U.Schings, K.F.Tebbe and M.Feher, Angew. Chem., Int. Ed. Engl., 22(1983)775.

146 M.Baudler, G.Reuschenbach and J.Hahn, Chem. Ber., 116(1983)847.

147 M.Baudler and S.Esat, Chem. Ber., 116(1983)2711.

148 R.Gleiter, M.C.Böhm, M.Eckert-Maksic, W.Schäfer, M.Baudler, Y.Aktalay, G.Fritz and K.D.Hoppe, Chem. Ber., 116(1983)2972.

149 R.Appel and W.Paulen, Chem. Ber., 116(1983)2371.

150 R.Appel and W.Paulen, Chem. Ber., 116(1983)109.

151 R.Appel, F.Knoch, B.Laubach and R.Sievers, Chem. Ber., 116(1983)1873.

152 M.Baudler and H.Suchomel, Z. Anorg. Allg. Chem., 503(1983)7.

153 M.Baudler and H.Suchomel, Z. Anorg. Allg. Chem., 506(1983)22.

154 K.F.Tebbe and R.Fröhlich, Z. Anorg. Allg. Chem., 506(1983)27.

155 W.W.DuMont, T.Severengiz and B.Meyer, Angew. Chem., Int. Ed. Engl., 22(1983)983.

156 E.Niecke and R.Rüger, Angew. Chem., Int. Ed. Engl., 22(1983)155.

156a E.Niecke, R.Rüger, M.Lysek, S.Pohl and W.Schoeller, Angew. Chem., Int. Ed. Engl., 22(1983)486.

157 A.H.Cowley, J.E.Kilduff, S.K.Mehrotra, N.C.Norman and M.Pakulski, J. Chem. Soc., Chem. Commun., (1983)528.

158 A.H.Cowley, J.G.Lasch, N.C.Norman, M.Pakulski and B.R. Whittlesey, J. Chem. Soc., Chem. Commun., (1983)881.

159 A.H.Cowley, J.G.Lasch, N.C.Norman and M.Pakulski, J. Am. Chem. Soc., 105(1983)5506.

160 A.H.Cowley, J.E.Kilduff, N.C.Norman, M.Pakulski, J.L.Atwood and W.E.Hunter, J. Am. Chem. Soc., 105(1983)4845.

161 J.Borm, L.Zsolnai and G.Hütner, Angew. Chem., Int. Ed. Engl., 22(1983)977.

162 K.M.Flynn, N.M.Olmstead and P.P.Power, J. Am. Chem. Soc., 105(1983)2085.

163 A.H.Cowley, J.E.Kilduff, J.G.Lasch, N.C.Norman, M.Pakulski, F.Ando and T.C.Wright, J. Am. Chem. Soc., 105(1983)7751.

164 K.M.Flynn, H.Hope, B.D.Murray, M.M.Olmstead and P.P.Power, J. Am. Chem. Soc., 105(1983)7750.

165 A.H.Cowley, J.G.Lasch, N.C.Norman and M.Pakulski, Angew. Chem., Int. Ed. Engl., 22(1983)978.

166 K.M.Flynn, B.D.Murray, M.M.Olmstead and P.P.Power, J. Am. Chem. Soc., 105(1983)7460.

167 A.H.Cowley, R.A.Jones, C.A.Stewart and A.I.Stuart, J. Am. Chem. Soc., 105(1983)3737.

168 R.Gooden, Inorg. Chem., 22(1983)2272.

169 D.Seyferth, C.Prud'homme and G.H.Wiseman, Inorg. Chem., 22(1983)2163.

170 L.G.Bell, W.A.Gustavson, S.Thanedar and M.D.Curtis, Organometallics, 2(1983)740.

171 M.D.Curtis, J.J.D'Enrico, D.N.Duffy, P.S.Epstein and L.G.Bell, Organometallics, 2(1983)1808.

172 N.N.Makarova, M.Blazso and E.Jakab, Polyhedron, 2(1983)257.

173 M.Blazso, E.Jakab and N.N.Makarova, Polyhedron, 2(1983)455.

174 D.W.H.Rankin and H.E.Robertson, J. Chem. Soc., Dalton Trans., (1983)265.

175 C.Eaborn, P.B.Hitchcock and P.D.Lickiss, J. Organomet. Chem., 252(1983)281.

176 A.I.Yanovskii, I.L.Dubchak, V.E.Shklover, Yu.T.Struchkov, V.N.Kalinin, B.A.Izmailov, V.D.Myakushov and L.I.Zakharkin, J. Struct. Chem., 23(1983)728.

177 W.Bibber, C.L.Barnes, D. van der Helm and J.J.Zuckerman, Angew. Chem., Int. Ed. Engl., 22(1983)501.

178 D.Schomburg, Angew. Chem., Int. Ed. Engl., 22(1983)65.

179 T.Inoue, Inorg. Chem., 22(1983)2435.

180 B.Arkles, K.King, R.Anderson and W.Peterson, Organometallics, 2(1983)454.

181 C.W.Dirk, T.Inabe, K.F.Schoch and T.J.Marks, J. Am. Chem. Soc., 105(1983)1539.

182 B.N.Diel, T.Inabe, J.W.Lyding, K.F.Schoch, C.R.Kannewurf and T.J.Marks, J. Am. Chem. Soc., 105(1983)1551.

183 H.Puff, S.Franken, W.Schuh and W.Schwab, J. Organomet. Chem., 244(1983)C41.

184 H.Puff, S.Franken, W.Schuh and W.Schwab, J. Organomet. Chem., 254(1983)33.

185 H.Puff, S.Franken and W.Schuh, J. Organomet. Chem., 256(1983)23.

186 W.E.Schlower, Y.T.Strutschkow, L.E.Guselnikow, W.W.Wolkowa and W.G.Awakyan, Z. Anorg. Allg. Chem., 501(1983)153.

187 F.Brisse, M.Vanier, M.J.Olivier, Y.Gareau and K.Steliou, Organometallics, 2(1983)878.

188 E.A.V.Ebsworth, C.M.Huntley and D.W.H.Rankin, J. Chem. Soc., Dalton Trans., (1983)835.

189 T.Halder, W.Schwarz, J.Weidlein and P.Fischer, J. Organomet. Chem., 246(1983)29.

190 C.J.Marsden, Inorg. Chem., 22(1983)3177.

191 G.Glebe, J.W.Bats and K.Hensen, Z. Naturforsch., Teil B, 38(1983)825.

192 G.Glebe, K.Hensen and H.Fuess, Chem. Ber., 116(1983)3125.

193 D.Schomberg, Z. Naturforsch., Teil B, 38(1983)938.

194 K.Hensen, T.Zengerly, P.Pickel and G.Klebe, Angew. Chem., Int. Ed. Engl., 22(1983)725.

195 Yu.L.Frolov, M.G.Voronkov, G.A.Gavrilova, N.N.Chipanina, L.I.Gubanova and V.M.D'Yakov, J. Organomet. Chem., 244(1983)107.

196 B.J.Helmer, R.West, R.J.P.Corriu, M.Poirier, G.Royo and A.De Saxce, J. Organomet. Chem., 251(1983)295.

197 S.N.Gurkova, S.N.Tandura, A.V.Kisin, A.I.Gusev, N.V.Alekseev, T.K.Gar, N.Yu. Kromova and I.R.Segel'man, J. Struct. Chem., 23(1982)101.

198 S.M. van der Kerk, Polyhedron, 2(1983)509.

199 H.Oppermann, D.Schmidt and P.Kleinert, Z. Anorg. Allg. Chem., 506(1983)7.

200 H.Oppermann, Z. Anorg. Allg. Chem., 504(1983)95.

201 M.Dakkouri and H.Kehrer, Chem. Ber., 116(1983)2041.

202 R.H.Baney, J.H.Gaul and T.K.Hilty, Organometallics, 2(1983)859

203 C.W.Carlson and R.West, Organometallics, 2(1983)1792.

204 S.M.Chen, L.D.David, K.J.Haller, C.L.Wadsworth and R.West, Organometallics, 2(1983)409.

205 C.W.Carlson, X.H.Zhang and R.West, Organometallics, 2(1983)453.

206 C.Kratky, H.G.Schuster and E.Hengge, J. Organomet. Chem., 247(1983)253.

207 L.Parkanyi, E.Hengge and H.Stüger, J. Organomet. Chem., 257(1983)167.

208 I.S.Alnaimi and W.P.Weber, Irganometallics, 2(1983)903.

209 C.W.Carlson and R.West, Organometallics, 2(1983)1793.

210 C.W.Carlson and R.West, Organometallics, 2(1983)1801.

211 L.Ross and M.Dräger, Z. Naturforsch., Teil B, 38(1983)665.

212 L.Rösch and U.Starke, Z. Naturforsch., Teil B, 38(1983)1292.

213 D.W.Goebel, J.L.Hencher and J.P.Oliver,Organometallics, 2(1983)746.

214 L.Rösch, G.Altnau, C.Krüger and Y.H.Tsay, Z. Naturforsch., Teil B, 38(1983)34.

215 L.Rösch, G.Altnau and G.Jas, Chem. Ztg., 106(1982)441.

216 G.Altnau, L.Rösch and G.Jas, Tetrahedron Lett., 24(1983)45.

217 B.M.Trost, J.Yoshida and M.Lautens, J. Am. Chem. Soc., 105(1983)4494.

218 O.Mundt, G.Becker, M.Rössler and C.Witthauer, Z. Anorg. Allg. Chem., 506(1983)42.

219 W.A.Hermann, J.Weichmann, U.Kü-sthardt, A.Schäffer, R.Hörlein, C.Hecht, E.Voss and R.Serrano, Angew. Chem., Int. Ed. Engl., 22(1983)979.

220 U.Schubert, K.Ackermann, G.Kraft and B.Wörte, Z. Naturforsch., Teil B, 38(1983)1488.

221 D.J.Brauer and R.Eujen, Organometallics, 2(1983)263.

222 D.Melzer and E.Weiss, J. Organomet. Chem., 255(1983)335.

223 A.S.Batsanov, L.V.Rybin, M.I.Rybinskaya, Yu.T.Struchkov, I.M.Salimgareeva and N.G.Bogatova, J. Organomet. Chem., 249(1983)319.

224 E.A.Chernyshev, O.V.Kuz'min, A.V.Lebedev, A.I.Gusev, M.G.Los, N.V.Alekseev, N.S.Nametkin, V.D.Tyurin, A.M.Krapivin, N.A.Kubasova and V.G.Zaikin, J. Organomet. Chem., 252(1983)143.

225 L.Parkanyi. K.H.Pannell and C.Hernandez, J. Organomet. Chem., 252(1983)127.

226 H.Nakazawa, D.L.Johnson and J.A.Gladysz, Organometallics, 2(1983)1846.

227 M.J.Auburn, R.D.Holmes-Smith, S.R.Stobart, M.J.Zaworotko, T.S.Cameron and A.Kumari, J. Chem. Soc., Chem. Commun., (1983)1523.

228 G.Herrmann and G.Süss-Fink, Chem. Ber., 116(1983)3406.

229 A.C.Willis, G.N. van Buuren, R.K.Pomeroy and F.W.B.Einstein, Inorg. Chem., 22(1983)1162.

230 F.W.B.Einstein, R.K.Pomeroy, P.Rushman and A.C.Willis, J. Chem. Soc., Chem. Commun., (1983)854.

231 M.J.Fernandez and P.M.Maitlis, Organometallics, 2(1983)164.

232 Yu.K.Grishin, V.A.Roznyatovsky, Yu.A.Ustynyuk, S.N.Titova, G.A.Domrachev and G.A.Razuvaev, Polyhedron, 2(1983)895.

233 G.A.Razuvaev, M.N.Bochkarev, and L.V.Pankratov, J. Organomet. Chem., 250(1983)135.

234 A.H.Cowley, J.G.Lasch, N.C.Norman, C.A.Stewart and T.C. Wright, Organometallics, 2(1983)1691.

235 P.Jutzi and E.Schlüter, J. Organomet. Chem., 253(1983)313.

236 F.X.Kohl, E.Schlüter and P.Jutzi, J. Organomet. Chem., 243(1983)C37.

237 F.Kohl and P.Jutzi, Angew. Chem., Int. Ed. Engl., 22(1983)56.

238 H.Wadepohl, H.Pritzkow and W.Siebert, Organometallics, 2(1983)1899.

239 W.W. du Mont and M.Grenz, Z. Naturforsch., Teil B, 38(1983)113.

240 M.Grenz and W.W. du Mont, J. Organomet. Chem., 241(1983)C5.

241 A.Tzschach, M.Scheer, K.Jurkschat, A.Zschunke and C.Mugge, Z. Anorg. Allg. Chem., 502(1983)158.

242 P.B.Hitchcock, M.F.Lappert, B.J.Samways and E.L.Weinberg, J. Chem. Soc., Chem. Commun., (1983)1492.

243 T.Fjeldberg, H.Hope, M.F.Lappert, P.P.Power and A.J.Thorne, J. Chem. Soc., Chem. Commun., (1983)639.

244 M.Vieth and F.Töllner, J. Organomet. Chem., 246(1983)219.

245 M.Vieth, G.Schlemmer and M.L.Sommer, Z. Anorg. Allg. Chem., 497(1983)157.

246 M.Vieth and O.Recktenwald, Z. Naturforsch., Teil B, 38(1983)1054.

247 P.G.Harrison, B.J.Haylett and T.J.King, Inorg. Chim. Acta, 75(1983)265.

248 P.G.Harrison, B.J.Haylett and T.J.King, Inorg. Chim. Acta, 75(1983)259.

249 C.Fischer, H.Wagner and V.V.Bagreev, Polyhedron, 2(1983)917.

250 G.Marletta, P.Finocchiaro, E.Libertini and A.Recca, Polyhedron, 2(1983)995.

251 S.Ichiba and M.Yamada, Polyhedron, 2(1983)499.

252 I.Novak and A.W.Potts, J. Chem. Soc., Dalton Trans., (1983)2211.

253 W.Gramer, M.Gendry, A.El Mansouri, S.Vilminot and L.Cot, Z. Anorg. Allg. Chem., 506(1983)59.

254 R.H.Andrews, S.J.Clark, J.D.Donolson, J.C.Dorran and J.Silver, J. Chem. Soc., Dalton Trans., (1983)767.

255 B.Aurivillius, Acta Chem. Scand., Ser. A, 37(1983)159.

256 H.Behm, Acta Crystallogr., C39(1983)1317.

257 H.L.Keller, Angew. Chem., Int. Ed. Engl., 22(1983)324.

258 H.D.Lutz, W.Buchmeier and B.Engelen, Z. Naturforsch., Teil B, 38(1983)523.

259 H.D.Lutz, W.Buchmeier, W.Eckers and B.Engelen, Z. Anorg. Allg. Chem., 496(1983)21.

260 P.G.Harrison, M.A.Healy and A.T.Steel, J. Chem. Soc., Dalton Trans., (1983)1845.

261 M.J.Willes and D.R.Williams, Inorg. Chim. Acta, 80(1983)L35.

262 P.G.Harrison and M.A.Healy, Inorg. Chim. Acta, 80(1983)279.

263 N.A.Bailey, D.E.Fenton, I.T.Jackson, R.Moody and C.R. de Barbarin, J. Chem. Soc., Chem. Commun., (1983)1463.

264 G.S.V.Coles, A.E.Underhill, J.M.Williams and A.T.Schultz, J. Chem. Soc., Dalton Trans., (1983)2529.

265 C.J.Cardin, D.J.Cardin, R.J.Norton, H.E.Parge and K.W.Muir, J. Chem. Soc., Dalton Trans., (1983)665.

266 C.J.Cardin, D.J.Cardin, J.M.Kelly, R.J.Norton, A.Roy, B.J.Hathaway and T.J.King, J. Chem. Soc., Dalton Trans., (1983)671.

267 J.W.F.L.Seetz, G.Schat, O.S.Akkerman and F.Bickelhaupt, J. Am. Chem. Soc., 105(1983)3336.

268 M.Newcomb, Y.Azuma and A.R.Courtney, Organometallics, 2(1983)175.

269 A.Clearfield, C.J.Simmons, H.P.Withers and D.Seyferth, Inorg. Chim. Acta, 75(1983)139.

270 A.L.Beauchamp, S.Latour, M.J.Olivier and J.D. J. Organomet. Chem., 254(1983)283.

271 V.K.Belsky, A.A.Simonenko, V.O.Reichsfeld and I.E.Saratov, J. Organomet. Chem., 244(1983)125.

272 A. von Rumohr, W.Sunderneyer and W.Towal, Z. Anorg. Allg. Chem., 499(1983)75.

273 Y.Yamashita, K.Aito, A.Yoshino and K.Takahashi, Bull. Chim. Soc. Japan, 56(1983)2555.

274 S.J.Blunden, J. Organomet. Chem., 248(1983)149.

275 C.Feasson and M.Deraud, Bull. Soc. Chim. France, (1983), I-40.

276 H.G.Kuivila, T.J.Karol and K.Swami, Organometallics, 2(1983)909.

277 R.A.Howie, E.S.Paterson, J.L.Wardell and J.W.Burley, J. Organomet. Chem., 259(1983)71.

278 P.Ganis, V.Peruzzo and G.Valle, J. Organomet. Chem., 256(1983)245.

279 L.Prasad, Y. Le Page and F.E.Smith, Inorg. Chim. Acta, 68(1983)45.

280 S.W.Ng, C.L.Barnes, D. van der Helm and J.J.Zuckerman, Organometallics, 2(1983)600.

281 J.L.Brianso, X.Solans and J.Vicente, J. Chem. Soc., Dalton Trans., (1983)169.

282 P.G.Harrison, N.W.Sharpe, C.Pelizzi, G.Pelizzi and P.Tarasconi, J. Chem. Soc., Dalton Trans., (1983)921.

283 P.G.Harrison, N.W.Sharpe, C.Pelizzi, G.Pelizzi and P.Tarasconi, J. Chem. Soc., Dalton Trans., (1983)1687.

284 C.Pelizzi, G.Pelizzi and P.Tarasconi, Polyhedron, 2(1983)145.

285 C.Pelizzi and G.Pelizzi, J. Chem. Soc., Dalton Trans., (1983)847.

286 P.B.Hitchcock, S.I.Klein and J.F.Nixon, J. Organomet. Chem., 241(.983)C9.

287 P.A.Cusack, B.N.Patel and P.J.Smith, Inorg. Chim. Acta, 76(1983)L21.

288 P.J.Smith and B.N.Patel, J. Organomet. Chem., 243(1983)C73.

289 S.W.Cowan, R.W.Gable, B.F.Hoskins and G.Winter, Inorg. Chim. Acta, 77(1983)L225.

290 J.L.Nieto and A.M.Gutierrez, Polyhedron, 2(1983)987.

291 W.Langseth and K.Taugbol, Inorg. Chim. Acta, 72(1983)43.

292 J.A.Garcia-Vazquez, M.Lopez-Becerra and J.R.Masaguer, Polyhedron, 2(1983)1081.

293 J.Rupp-Bensadon and E.A.C.Lucken, J. Chem. Soc., Dalton Trans, (1983)495.

294 R.Colton and D.Dakternieks, Inorg. Chim. Acta, 71(1983)101.

295 A.Drtil, J.Meux, J.W.Meux, R.J.Williams and J.W.Rogers, Polyhedron, 2(1983)479.

296 M.Katada, H.Kanno and H.Sano, Polyhedron, 2(1983)104.

297 K.B.Dillon, J.Halfpenny and A.Marshall, J. Chem. Soc., Dalton Trans., (1983)1091.

298 D.Fenske, H.D.Dorner and K.Dehnicke, Z. Naturforsch., Teil B, 38(1983)1301.

299 H.Puff, R.Sievers, R.Zimmer and W.Schuh, Angew. Chem., Int. Ed. Engl., 20(1983)591.

300 S.Masamune, L.R.Sita and D.J.Williams, J. Am. Chem. Soc., 105(1983)630.

301 H.Puff, E.Friedrichs, R.Hundt and R.Zimmer, J. Organomet. Chem., 259(1983)79.

302 A.L.Beauchamp, S.Latour, M.J.Olivier and J.D.Wuest, J. Am. Chem. Soc., 105(1983)7778.

303 A.Secco and J.Trotter, Acta Crystallogr., C39(1983)451.

304 M.Dräger, J. Organomet. Chem., 251(1983)209.

305 C.M.Mikulski and N.M.Karayannis, Inorg. Chim. Acta, 77(1983)L43.

306 S.P.Narula, H.K.Sharma and R.K.Sharma, Inorg. Chim. Acta, 76(1983)L7.

307 H.Puff, I.Bung, E.Friedrichs and A.Jansen, J. Organomet. Chem., 254(1983)23.

308 R.Graziani, U.Casellato and G.Plazzogna, Acta Crystallogr., C39(1983)1188.

309 P.G.Harrison, M.J.Begley and K.C.Molloy, J. Organomet. Chem., 186(1980)213.

310 S.J.Blunden, P.A.Cusack, P.J.Smith and P.W.C.Barnard, Inorg. Chim. Acta, 72(1983)217.

311 R.G.Swisher, R.O.Day and R.R.Holmes, Inorg. Chem., 22(1983)3692.

312 A.Kumar, B.P.Bachlas and J.C.Maire, Polyhedron, 2(1983)907.

313 B.P.Bachlas, H.Sharma, J.C.Maire and J.J.Zuckerman, Inorg. Chim. Acta, 71(1983)227.

314 M.K.Das, M.N.Nath and J.J.Zuckerman, Inorg. Chim. Acta, 71(1983)49.

315 S.R.Patil, U.N.Kantak and D.N.Sen, Inorg. Chim. Acta, 68(1983)1.

316 H.C.Clark, V.K.Jain, I.J.MaMahon and R.C.Mehrotra, J. Organomet. Chem., 243(1983)299.

317 J.Otera, T.Yano and K.Kusakabe, Bull. Chem. Soc. Jpn., 56(1983)1057.

318 T.S.Basu Baul, T.K.Chattapadhyay and B.Majee, Polyhedron, 2(1983)635.

319 J.Holecek, M.Nadvornik, K.Handlir and A.Lycka, J. Organomet. Chem., 241(1983)177.

320 J.Holecek, K.Handlir, M.Nadvornik and A.Lycka, J. Organomet. Chem., 258(1983)147.

321 P.G.Harrison, K.Lambert, T.J.King and B.Majee, J. Chem. Soc., Dalton Trans., (1983)363.

322 I.W.Nowell, J.S.Brooks, G.Beech and R.Hill, J. Organomet. Chem., 244(1983)119.

323 G.Roge, F.Huber, H.Preut, A.Silvestri and R.Barbieri, J. Chem. Soc., Dalton Trans., (1983)595.

324 A.G.Davies, J.P.Goddard, M.B.Hursthouse, and N.P.C.Walker, J. Chem. Soc., Chem. Commun., (1983)597.

325 J.A.Shelnutt, J. Am. Chem. Soc., 105(1983)7179.

326 F.A.K.Nasser, M.B.Hossain, D. van der Helm and J.J.Zuckerman, Inorg. Chem., 22(1983)3107.

327 D.Cunningham, P.Firtear, K.C.Molloy, and J.J.Zuckerman, J. Chem. Soc., Dalton Trans., (1983)1523.

328 J.L.Lecat and M.Devaud, Polyhedron, 2(1983)1087.

329 D.Dakternieks, R.W.Gable and G.Winter, Inorg. Chim. Acta, 75(1983)185.

330 B.Mathiasch and U.Kunze, Inorg. Chim. Acta, 75(1983)209.

331 Th. Hättich and U.Kunze, Z. Naturforsch., Teil B, 38(1983)655.

332 U.Kunze and P.R.Bolz, Z. Anorg. Allg. Chem., 498(1983)41.

333 U.Kunze and Th. Hättich, Chem. Ber., 116(1983)3071.

334 S.W.Carr, R.Colton, D.Dakternieks, B.F.Hoskins and R.J.Steen, Inorg. Chem., 22(1983)3700.

335 U.Kunze and P.R.Bolz, Z. Anorg. Allg. Chem., 498(1983)50.

336 D.Britton and Y.M.Chau, Acta Crystallogr., C39(1983)1539.

337 F.E.Hahn, T.S.Dory, C.L.Barnes, M.B.Hossain, D. van der Helm and J.J.Zuckerman, Organometallics, 2(1983)969.

338 T.Gasparis-Ebeling, H.Nöth and B.Wrackmeyer, J. Chem. Soc., Dalton Trans., (1983)97.

339 M.Baudler and H.Suchomel, Z. Anorg. Allg. Chem., 505(1983)39.

340 S.Ichiba, H.Ono, S.Kawasaki, S.Nakagawa, and M.Yamada, Bull. Chem. Soc. Jpn., 56(1983)2837.

341 R.G.Teller, L.J.Krause and R.C.Haushalter, Inorg. Chem., 22(1983)1809.

342 M.Dräger, B.Mathiasch, L.Ross and M.Ross, Z. Anorg. Allg. Chem., 506(1983)99.

343 H.Puff, A.Bongartz, W.Schuh and R.Zimmer, J. Organomet. Chem., 248(1983)61.

344 J.Meunier-Piret, M. van Meerssche, M.Gielen and K.Jurkschat, J. Organomet. Chem., 252(1983)289.

345 L.Rösch and U.Starke, Angew. Chem., Int. Ed. Engl., 22(1983)557.

346 G.L.Rochfort and J.E.Ellis, J. Organomet. Chem., 250(1983)265.

347 G.L.Rochfort and J.E.Ellis, J. Organomet. Chem., 250(1983)277.

348 J.T.Lin, G.P.Hagan and J.E.Ellis, Organometallics, 2(1983) 1145.

349 A.N.Protsky, B.M.Bulychev and G.L.Soloveichik, Inorg. Chim. Acta, 71(1983)35.

350 M.J.Chetcuti, M.H.Chisholm, H.T.Chiu and J.C.Huffman, J. Am. Chem. Soc., 105(1983)1060.

351 P.J.Domaille and W.H.Knoth, Inorg. Chem., 22(1983)818.

352 S.Onaka, Y.Kondo, N.Furuichi, K.Toriumi and T.Ho, Bull. Chem. Soc. Jpn., 56(1983)87.

353 H.F.Klein, K.Ellrich, D.Neugebauer, O.Orama and K.Kruger, Z. Naturforsch., Teil B, 38(1983)303.

354 H.Preut and H.J.Haupt, Acta Crystallogr., C39(1983)981.

355 G.K.Anderson, A.C.Clark and J.A.Davies, Inorg. Chem., 22(1983)427.

356 G.K.Anderson, H.C.Clark and J.A.Davies, Inorg. Chem., 22(1983)434.

357 G.K.Anderson, C.Billard, H.C.Clark, J.A.Davies and C.S.Wong, Inorg. Chem., 22(1983)439.

358 S.Clark, R.Colton and D.Dakternieks, J. Organomet. Chem., 249(1983)327.

359 A.Albinati, R.Naegeli, K.H.A.Ostoja Starzewski, P.S.Pregosin and H.Rüegger, Inorg. Chim. Acta, 76(1983)L231.

360 J.D.Koola and U.Kunze, Inorg. Chim. Acta, 76(1983)L283.

361 B.Czeska, F.Weller and K.Dehnicke, Z. Anorg. Allg. Chem., 498(1983)121.

362 D.W.Sindorf and G.E.Maciel, J. Am. Chem. Soc., 105(1983)1487.

363 G.Boxhorn, O.Sudmeijer and P.H.G. van Kasteren, J. Chem. Soc., Chem. Commun., (1983)1416.

364 R.H.Jarman, J. Chem. Soc., Chem. Commun., (1983)512.

365 P.F.Barron, R.L.Frost, J.O.Skjemstad, J. Chem. Soc., Chem. Commun., (1983)581.

366 C.A.Fyfe, G.C.Gobbi, J.Klinowski, A.Putnis and J.M.Thomas, J. Chem. Soc., Chem. Commun., (1983)556.

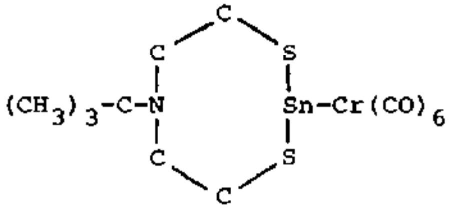
367 J.Klinowski, J.M.Thomas, C.A.Fyfe, G.C.Gobbi and J.S.Hartman, Inorg. Chem., 22(1983)63.

368 A.Winkler, B.Ziemer and W.Wiejer, Z. Anorg. Allg. Chem., 504(1983)89.

369 N.H.Ray and R.J.Plaisted, J. Chem. Soc., Dalton Trans., (1983)475.
370 O.Yamaguchi, K.Kawabe and K.Shimizu, J. Chem. Soc., Dalton Trans., (1983)2139.
371 M.Ozima, Acta Crystallogr., C39(1983)1169.
372 O.Yamaguchi, M.Ki, T.Niimi and K.Shimizu, Polyhedron, 2(1983) 1213.
373 S.Schönherr and H.Görz, Z. Anorg. Allg. Chem., 03(1983)37.
374 B.Nowitzki and R.Hoppe, Z. Anorg. Allg. Chem., 505(1983)105.
375 R.Nesper and H.G. von Schnering, Z. Anorg. Allg. Chem., 499(1983)109.
376 H.G. von Schnering, R.Nesper and H.Pelshenke, Z. Anorg. Allg. Chem., 499(1983)117.
377 B.Brazel and R.Hoppe, Z.Naturforsch., Teil B, 38(1983)661.
378 B.Brazel and R.Hoppe, Z. Anorg. Allg. Chem., 505(1983)99.
379 B.Nowitzki and R.Hoppe, Z. Anorg. Allg. Chem., 505(1983)111.
380 B.Brazel and R.Hoppe, Z. Anorg. Allg. Chem., 499(1983)161.
381 B.Brazel and R.Hoppe, Z. Anorg. Allg. Chem., 499(1983)153.
382 B.Brazel and R.Hoppe, Z. Anorg. Allg. Chem., 497(1983)176.
383 B.Brazel and R.Hoppe, Z. Anorg. Allg. Chem., 498(1983)167.
384 H.Wiedemeier and G.Pultz, Z. Anorg. Allg. Chem., 499(1983)130.
385 A.Mazurier, F.Theuer and S.Jaulmes, Acta Crystallogr., C39(1983)814.
386 A.Feltz and G.Pfaff, Z. Anorg. Allg. Chem., 504(1983)173.
387 B.Krebs and H.Müller, Z. Anorg. Allg. Chem., 496(1983)47.
388 B.Eisenmann, H.Schäfer and H.Schrod, Z. Naturforsch., Teil B, 38(1983)921.
389 B.Eisenmann, H.Schäfer and H.Schwerer, Z. Naturforsch., Teil B, 38(1983)924.
390 B.Eisenmann, H.Jordan and H.Schäfer, Z. Naturforsch., Teil B, 38(1983)404.

ADDENDUM

The crystals of $Ph_3GeO_2CCF_3$ comprise discrete monomeric molecules with a distorted trigonal bipyramidal geometry (C.Glidewell and D.C.Liles, J. Organomet. Chem., 243(1983)291).



(198)

Pentacarbonyl-5-tert-butyl-5-aza-2,8-dithia-1-stannabicyclo-$[3.3.0^{1,5}]$octane chromium(O), (198), has been synthesised from the reaction of $Sn(SCH_2CH_2)_2NBu^t$ with $Cr(CO)_6$ in THF under u.v. irradiation. The eight-membered ring in the complex adopts an asymmetric boat-boat conformation with a Sn-N bond distance of 2.40Å (A.Tzschach, K.Jurkschat, M.Scheer, J.Meunier-Piret and M. van Meerssche, J. Organomet. Chem., 259(1983)165).