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Chapter 4

ELEMENTS OF GROUP IV

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4.1 UNSTABLE INTERMEDIATES OF CARBON, SILICON AND GERMANIUM

4.1.1 Carbenes and Related Species

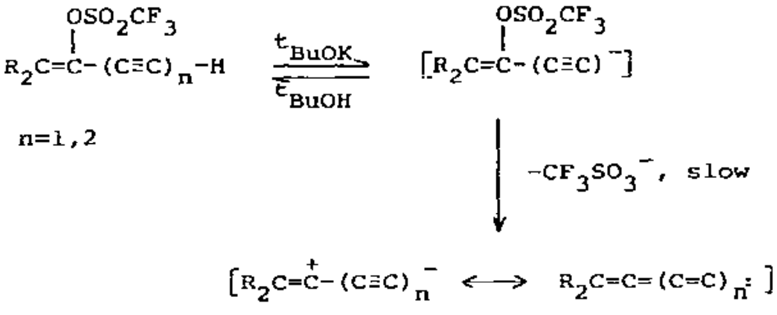
Singlet carbenes $:CX_2$ are linear if X is an element or group less electronegative (Li→B) than the central carbon atom, and are bent if X is more electronegative (N→F) than carbon. Table 1 lists calculated C-X bond distances and XCX valence angles for a variety of groups X.[1]

Table 1. Calculated C-X Bond Distances and XCX Valence Angles For Carbenoid Species.

X	C-X (Å)	XCX (°)
F	1.323	102.8
OH	1.354	101.9
OMe	1.358	101.0
NH_2	1.356	109.2
H	1.127	100.2
BH_2	1.419	180.0
BeH	1.612	180.0
Li	1.842	180.0

The equilibrium constant for the singlet-triplet interconversion of diphenylcarbene has been computed to be 5.4(1) x 10^3, with an associated free energy difference between the two states of 5.1(1) kcal mol^{-1} at 25°.[2] For dibromocarbene the singlet state is computed to be ca. 8 kcal mol^{-1} lower than the triplet. The calculated valence angle for the singlet is in agreement with that derived experimentally (ca. 112°), but the computed value for the triplet state (127°) is 23° smaller than the experimental value (ca. 150°).[3]

The reagent $Cd(CF_3)_2$.glyme is a new low temperature source of difluorocarbene, converting with acyl halides to acyl fluorides via extrusion of CF_2 at -25°. The participation of the carbene in this reaction can be demonstrated by trapping with tetramethylethylene giving the expected difluorocyclopropane in 53% yield.[4] Extended unsaturated carbenes can be generated via base-initiated elimination from alkynyl vinyl triflates.[5,6]



$$R_2C{=}\overset{OSO_2CF_3}{C}-(C{\equiv}C)_n-H \quad \underset{^tBuOH}{\overset{^tBuOK}{\rightleftharpoons}} \quad [R_2C{=}\overset{OSO_2CF_3}{C}-(C{\equiv}C)^-]$$

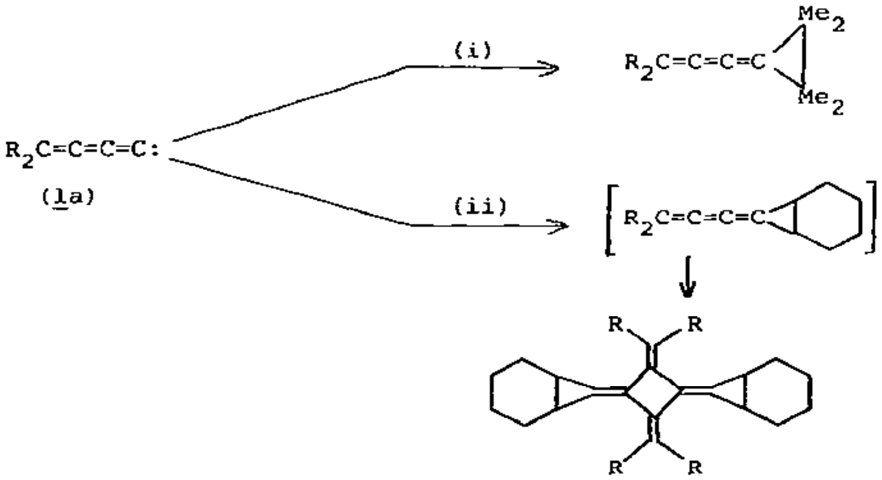
$n=1,2$

$$\xrightarrow{-CF_3SO_3^-,\ slow}$$

$$[R_2C{=}\overset{+}{C}-(C{\equiv}C)_n^- \longleftrightarrow R_2C{=}C{=}(C{=}C)_n\colon]$$

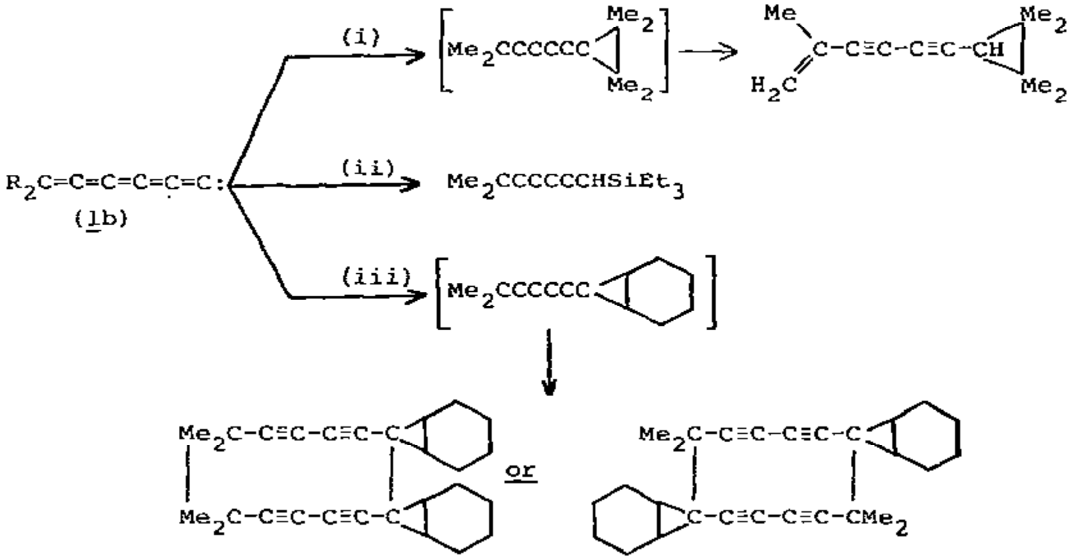
(<u>1</u>)

Both the alkadienylidene- and alkatetraenylidene-carbenes (<u>1</u>a) and (<u>1</u>b) are electrophilic, most likely singlets, and unencumbered, with little or no steric effects on substitution. Typical reactions are summarised in Schemes 1 and 2.



(i) $Me_2C{=}CMe_2$, (ii) cyclohexene.

<u>Scheme 1</u>.



(i) $Me_2C{=}CMe_2$, (ii) Et_3SiH, (iii) cyclohexene.

Scheme 2.

Phosphaethene, $CH_2{=}PH$, has been obtained by the pyrolysis of $Me_3SiCH_2PH_2$ at 700° as well as of methyl- and dimethylphosphines at 1000° though less efficiently. Rotational constants derived from its microwave spectrum indicate that the $\widehat{CPH}$ angle is ca. 97.5°, a much more acute value than the corresponding $\widehat{CNH}$ angle in $CH_2{=}NH$ (110.4°).[7] The monophosphorus analogue of dicyanogen, C-cyanophosphaethyne, $N{\equiv}C{-}C{\equiv}P$, has been detected by microwave spectroscopy in the products of the high temperature (ca. 700°) gas phase reaction between cyanogen azide, NCN_3, and phosphaethyne, $HC{\equiv}P$. The dipole moment was determined to be 5.5D.[8]

4.1.2 Silylenes, Silaethylenes and Other Miscellaneous Species.

The standard method for the generation of diorganosilylenes is by the photolysis of polysilanes. Photolysis of the linear trisilane, $Me_3SiSiMePhSiMe_3$ yields methylphenylsilylene, MePhSi:,[9] whilst photolysis of cyclo-$(Me_2Si)_6$ is the most convenient route to dimethylsilylene, Me_2Si:.[10] The reactions of dimethylsilylene with a wide variety of reagents have been studied. Insertion into HCl requires an activation energy of 28 kJ mol^{-1} affording Me_2SiHCl, whilst insertion into the Si-H bond of Me_3SiH or Me_3SiMe_2SiH occurs with approximately zero activation energy to yield Me_5Si_2H and Me_7Si_3H as the only measurable products consistent with the reaction sequence:[10]

$$(Me_2Si)_6 \xrightarrow{nh\nu} nMe_2Si:$$

$$Me_2Si: + Me_3SiH \longrightarrow Me_5Si_2H$$

$$Me_2Si: + Me_5Si_2H \longrightarrow Me_7Si_3H$$

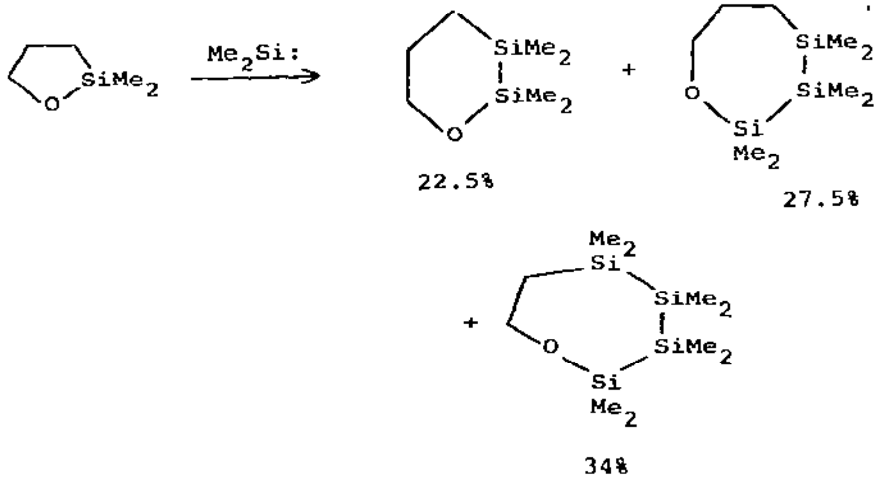
$$Me_2Si: \longrightarrow \text{surface polymer.}$$

Other authors, however, report that sequential insertion upto the tetrasilane, Me_9Si_4H, can occur.[11]

$$Me_3SiH \xrightarrow{Me_2Si:} \underset{28.5\%}{Me_5Si_2H} + \underset{22\%}{Me_7Si_3H} + \underset{11\%}{Me_9Si_3H}$$

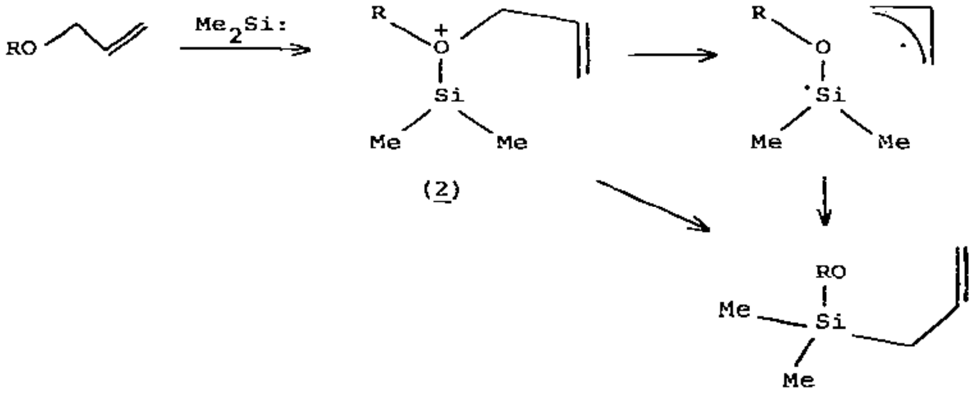
Similar sequential insertion also takes place with both linear and cyclic alkoxysilanes.[11]

$$Me_3SiOEt \xrightarrow{Me_2Si:} \underset{10\%}{Me_5Si_2OEt} + \underset{25\%}{Me_7Si_3OEt} + \underset{32\%}{Me_9Si_4OEt}$$

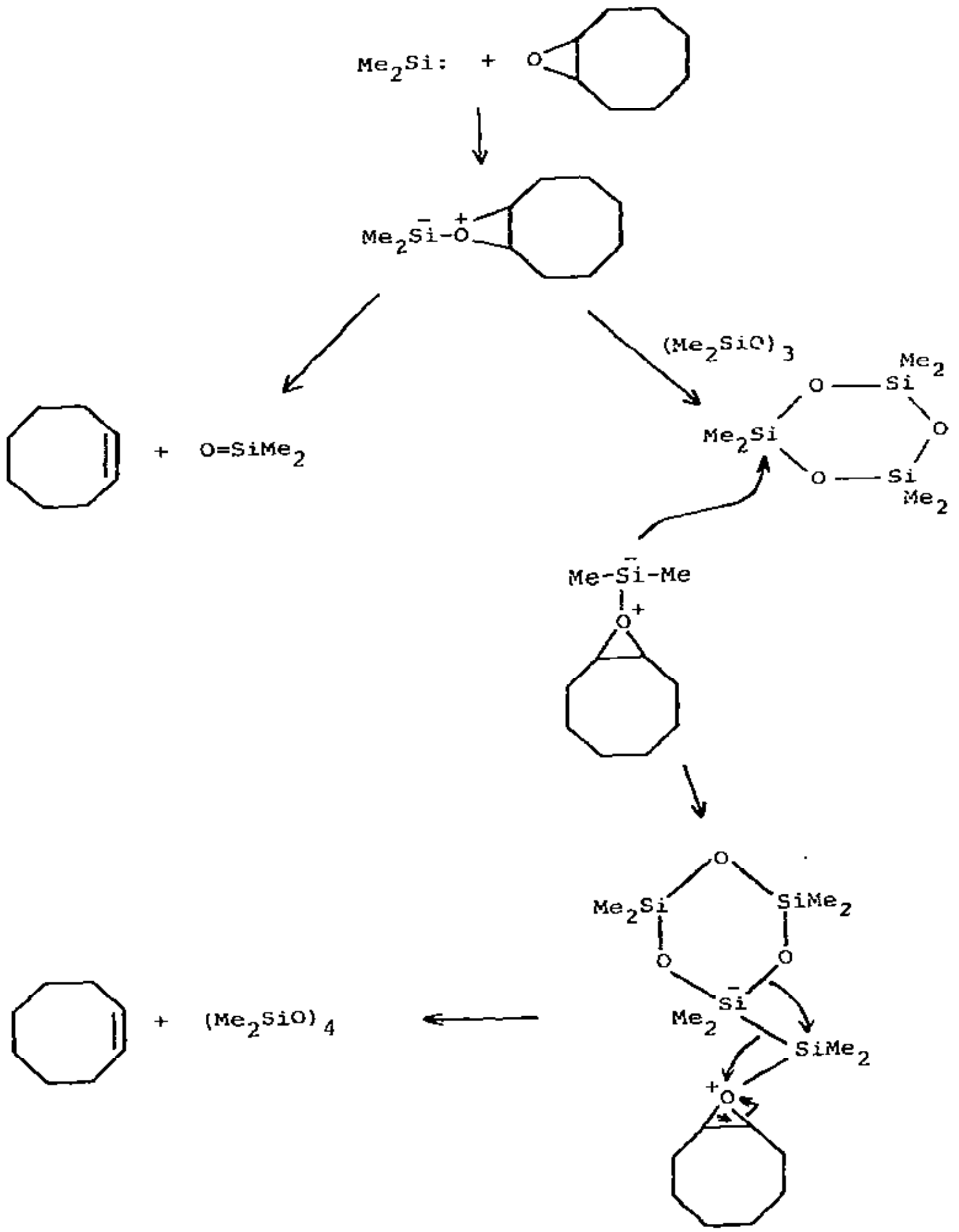


Dimethylsilylene inserts efficiently into the O-H bond of alcohols to yield alkoxydimethylsilanes. The use of EtOD affords $Me_2Si(OEt)D$. Insertion into both bonds of water or D_2O occurs when the products are $HMe_2SiOSiMe_2H$ or $DMe_2SiOSiMe_2D$, respectively. The insertion reaction with primary or secondary amines affords aminodimethyldisilanes, and provides an efficient route to difunctional silanes.[12] The selectivity of dimethylsilylene with pairs of alcohols is influenced by the solvent, and the insertion reaction is more selective when carried out in ether than in hydrocarbon solvents. The difference in reactivity may result from the formation of complexes between donor solvents and the silylene, which can deliver the silylene in a form which is less reactive and more selective than free dimethylsilylene.[13]

The mechanisms of the reactions of dimethylsilylene with a variety of other organic reagents including cis- and trans-2-butene,[14] α,β-unsaturated epoxides,[15,16] oxetanes,[17] and allyl ethers[18] have been reported, but only selected examples will be described here. Reaction with allyl ethers gives (alkoxy)allyldimethylsilanes in a mechanism involving the ylidic intermediate (2), which reacts further either by direct allylic rearrangement or by cleavage into a pair of radicals which subsequently recombine:[18]



Reaction of cyclooctene oxide with both thermally and photochemically generated dimethylsilylene results in deoxygenation to cyclooctene. Again the favoured mechanism involves an intermediate ylide (3), but whether this ylide actually extrudes dimethylsilanone or simply acts as a "silanone transfer agent" (Scheme 3) could not be determined conclusively from the data.[16]


Me$_2$Si: + O
Me$_2$Si-O
+ O=SiMe$_2$
(Me$_2$SiO)$_3$
Me$_2$Si
Me$_2$ Si
O
Me-Si-Me
Me$_2$Si
SiMe$_2$
Me$_2$
SiMe$_2$
+ (Me$_2$SiO)$_4$

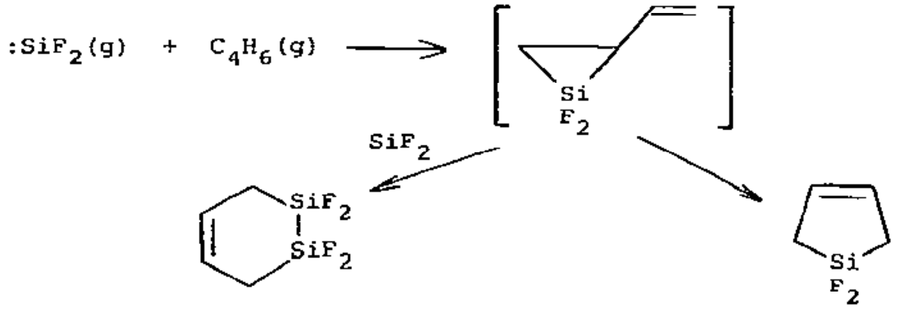
Scheme 3.

The allowed or forbidden nature of silylene insertion reactions has been considered on symmetry grounds together with the consequent energy requirement for such reactions. Calculations show that insertion of silylene and dimethylsilylene into dihydrogen will be limited by symmetry and require excitation to the $^3B_1$ state. The same effect should obtain for all symmetrical substrates in which the lowest lying antibonding orbital is antisymmetric across the central bond. Thus, insertion of SiX_2 into Si_2H_6 and Si_2Me_6 will be forbidden, the lowest unoccupied orbital between the two silicon atoms being strongly antibonding. Allowed silylene insertion reactions will proceed without excitation energy when the antibonding orbital relating to the bond into which insertion occurs is symmetric with respect to the reaction coordinate. So, in the process

$$:SiH_2 \ + \ SiH_4 \longrightarrow Si_2H_6$$

where the reaction is occurring along a path of C_{2v} symmetry, one orbital of the first degenerate set of antibonding molecular orbitals of silane corresponds to the highest bonding orbital of silylene, and the reaction is symmetry allowed.[19]

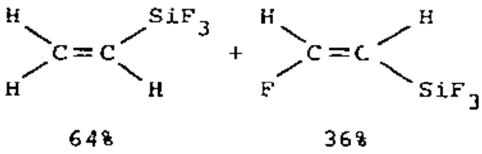
The chemistry of difluorosilylene, $:SiF_2$, also continues to promote interest, and reactions have been carried out both in the gas-phase and in low-temperature matrices. The gas-phase chemistry had sadly been rather neglected, but thermally generated $:SiF_2$ has been found to be reactive towards butadiene in the gas-phase, the major product being 1,1-difluorosilacyclopent-3-ene (4). A small amount of 1,1,2,2-tetrafluoro-1,2-disilacyclohex-4-ene (5) is also produced. The mechanism is thought to proceed via an intermediate silirene species:[20]



(5) (4)

With halogen-substituted ethylenes such as _cis_- and _trans_-difluoroethylene, vinyl chloride or fluoride, only compounds derived by insertion of the silylene into the carbon-halogen bonds are obtained, eg:[21]

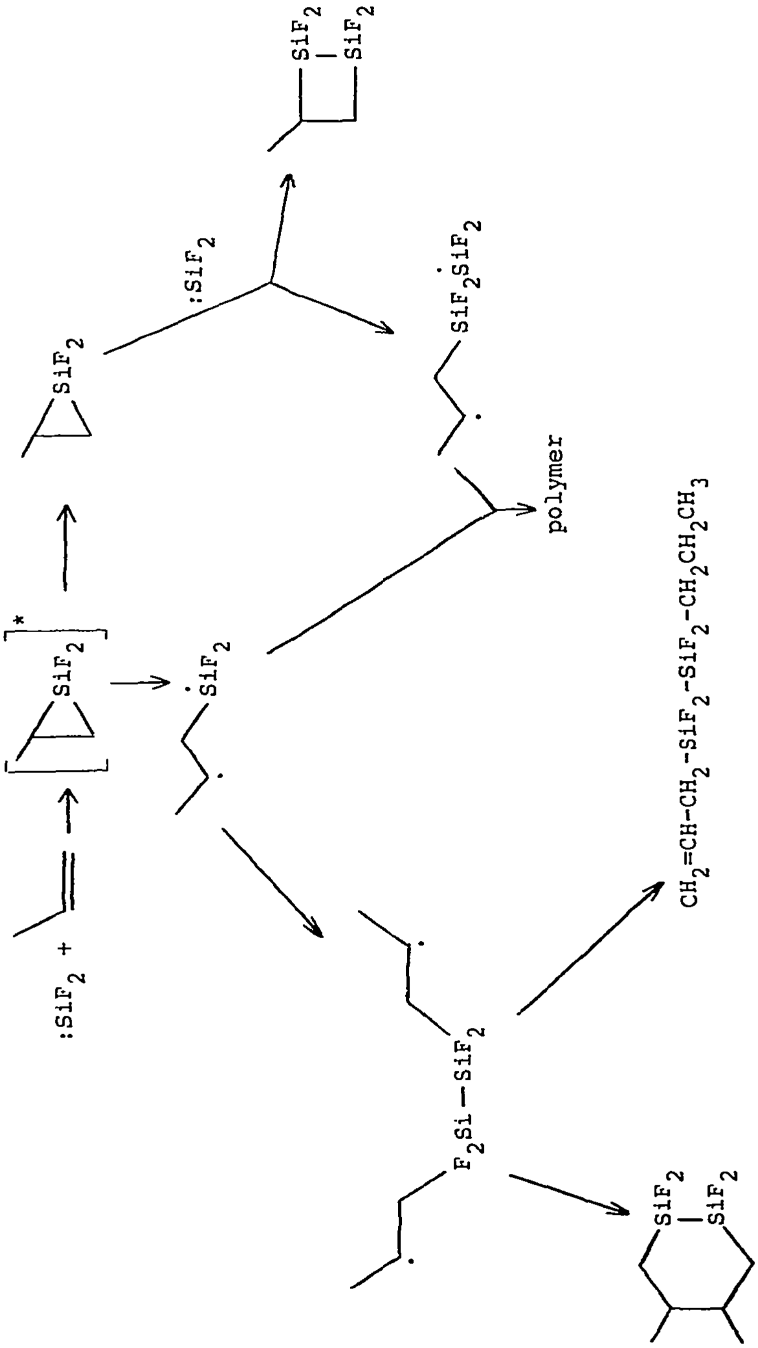
cis- or _trans_-$CHF{=}CHF(g) + SiF_2(g) \longrightarrow$



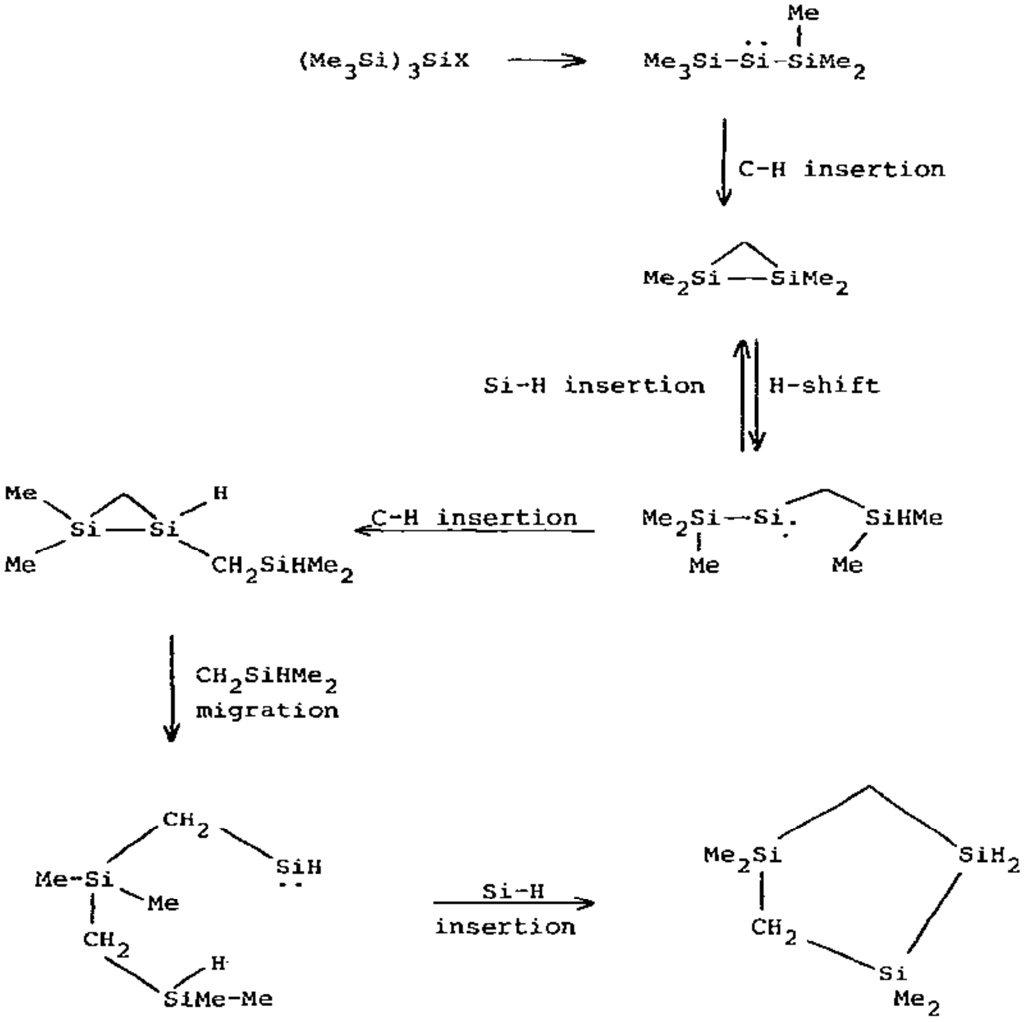
The major products from the reaction of difluorosilylene in a frozen matrix at -196° are polymers, disilacyclobutanes, disilacyclohexanes and open-chain compounds derived from an initially-formed excited silirane intermediate which either ring-opens or relaxes to its ground state, followed in either case by further reaction (Scheme 4). The polymers produced generally have a regular structure with isolated $[SiF_2]$ units between olefin linkages with the latter in a regular head-to-tail fashion, demonstrating that monomeric $:SiF_2$ is the major reactive $\cdot(SiF_2)_n\cdot$ species in this reaction. Unsymmetrical alkenes react with difluorosilylene to yield disilacyclohexanes with greater methyl substitution at C(2), and often more than one disilacyclohexane is produced suggesting that the reaction proceeds by a pathway which allows isomerisation of the alkene.[22]

Bis(trimethylsilyl)silylene, $:Si(SiMe_3)_2$, may be generated in the gas-phase by the flow pyrolysis of tris(trimethylsilyl)methoxy- or -chlorosilane. The major product, produced as a result of a series of rearrangements (Scheme 5) is 1,1,4,4-tetramethyl-1,2,4-trisilacyclopentane (6).[23]

Ab initio calculations on the energy hypersurfaces for $CSiH^-$, $CSiH_2$ and $CSiH_3^+$ reveal one, two and three minima, respectively, with structures in which all the hydrogens are bonded to carbon being the most stable in each case.[24] The energies, structures and unimolecular reactivities of the three isomeric species, methylsilylene, silaethylene and silylmethylene have also been the subject of a theoretical treatment.[25] In the lowest singlet and triplet states of methylsilylene, the CSiH bond angles are 95.9° and 118.9°, respectively, whilst in silylmethylene, the SiCH angles are calculated to be 113.8° in the singlet and 139.5° in the lowest triplet. The transition states for the singlet state 1,2-hydrogen shifts connecting silaethylene to methylsilylene and silylmethylene


:SiF$_2$ +
SiF$_2$
:SiF$_2$
SiF$_2$
SiF$_2$
SiF$_2$SiF$_2$
polymer
F$_2$Si—SiF$_2$
CH$_2$=CH-CH$_2$-SiF$_2$-SiF$_2$-CH$_2$CH$_2$CH$_3$
SiF$_2$—SiF$_2$

Scheme 4.

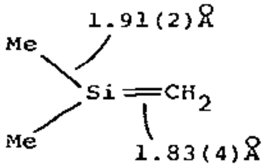


(6)

Scheme 5.

to silaethylene have been rigorously located at the double-ζ SCF level of theory employing gradient methods, and have energy barriers of 13 kcals. However, if carbon and silicon d orbitals are included, this value falls to less than 3 kcals. Hence, it appears that singlet silylmethylene may not be a kinetically stable species relatively to the double-bonded isomer. In contrast, the barrier to the 1,2-hydrogen shift from singlet silaethylene to singlet methylsilylene is indicated to be ca. 40 kcal mol^{-1}. Silylmethylene possesses a triplet ground electronic state with a low-lying singlet state at 25 kcal mol^{-1}, and singlet methylsilylene is predicted to be 11.6 kcal lower in energy than singlet silaethylene. Inclusion of d functions in carbon and silicon in the basis set and configuration interaction decrease this energy separation to only 0.4 kcal. Singlet silylmethyl is calculated to be 69 kcal above singlet silaethylene. For the triplet species, methylsilylene is calculated to be more stable than triplet silaethylene by 19 kcal. Triplet silylmethylene is predicted to be 7 kcal above triplet silaethylene.[25]

Several papers have described more chemistry of silaethylenes. Particularly noteworthy are the studies which report spectroscopic and structural data. The simplest method for the generation of 1,1-dimethylsilaethylene is by the pyrolysis of dimethylsilacyclobutane. Gas-phase electron diffraction yield structural parameters shown in (7), however, the experimental Si=C double bond distance is significantly longer than the range of values derived from theoretical calculations (1.63–1.75Å).[26] Condensation of the pyrolysis product in an argon matrix at 10K has also enabled the vibrational spectrum to be assigned.[27] Although previously considered to be unimportant compared with radical recombination, the disproportionation of trimethylsilyl radicals to yield silaolefins appears to be of quite general occurrence in both the gas-phase and in solution.[28-30] Thus, generation of trimethylsilyl radicals by mercury sensitisation of trimethylsilane (120 torr) in the presence of 0.6–12 torr of perdeuterated methanol affords good yields of $Me_2(CH_2D)SiOCD_3$.

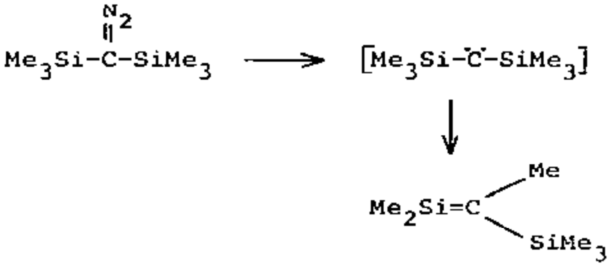


(7)

$$\begin{tikzcd}
2Me_3Si\cdot \arrow[r] & Me_3SiH + CH_2{=}SiMe_2 \arrow[d, "CD_3OD"] \\
 & Me_2(CH_2D)SiOCD_3
\end{tikzcd}$$

Similarly, irradiation of a solution of trimethylsilane in the presence of di-*t*-butylperoxide and excess [^{1}D]-*t*-butanol gives $Me_2(CH_2D)SiOCMe_3$.

Thermolysis or photolysis of trimethylsilyl-substituted diazomethanes also yield sila-olefins via rearrangement of the intermediate carbene:



(7)

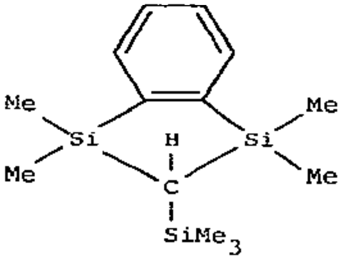
In the absence of other reagents, the sila-olefin (7) dimerises, but can be trapped by the addition of methanol, D_2O, benzaldehyde, butadiene or 2,3-dimethylbutadiene. The germyl-substituted analogues, $Me_3Si-C(N_2)-GeMe_3$ and $Me_3Ge-C(N_2)-GeMe_3$, behave similarly, although on thermolysis the mixed compound gives exclusively a silaolefin, whereas photolysis affords a mixture of silaolefin and germaolefin in a 4:1 ratio.[31]

$(Me_3Si)_3CSiPh_2F$ loses trimethylfluorosilane under reflux or on passage through a hot tube at 450° to give three products which are all isomers of the silaolefin $(Me_3Si)_2C{=}SiPh_2$, which is considered to be the initial product of the elimination reaction after which the equilibrium:

$$(Me_3Si)_2C{=}SiPh_2 \rightleftharpoons (Me_3Si)(Ph_2MeSi)C{=}SiMe_2 \rightleftharpoons$$

$$(Me_3Si)(PhMe_2Si)C{=}SiMePh \rightleftharpoons (Me_2PhSi)_2C{=}SiMe_2$$

is rapidly established. Internal cyclisation reactions involving the addition of aryl C-H bonds across Si=C multiple bonds then yield the observed products, (8), (9) and (10). Consistent with this hypothesis is the production of alkoxysilanes, thought to be $(Me_3Si)_2CHSiPh_2OMe$ and its isomers (formed by addition of methanol across the Si=C bonds of the four silaolefins), when methanol is included in the hot-tube pyrolysis.[32] Similar intermediates have been postulated in the reaction of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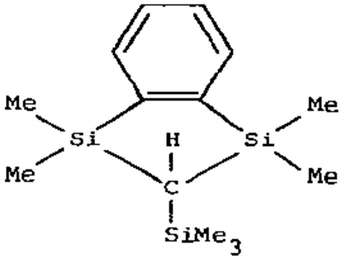
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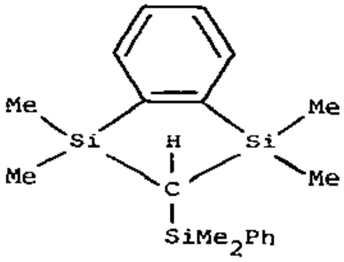

(10)

[tris(trimethylsilyl)methyl]diorgano(halogeno)silanes in boiling 2M MeONa/MeOH, when products of the type $(Me_3Si)_2CHSiR_2(OMe)$ result. The reaction was suggested to proceed by an elimination, analogous to the E_2 eliminations of alkyl halides, involving synchronous attack of methoxide ion at an $[Me_3Si]$ group, liberation of X^-, and the formation of the silaolefin, $(Me_3Si)_2C{=}SiR_2$.[33]

$$MeO^- + Me_3SiC(SiMe_3)_2SiR_2X \longrightarrow [MeO\cdots Me_3Si\cdots C(SiMe_3)_2\cdots SiR_2\cdots X]$$

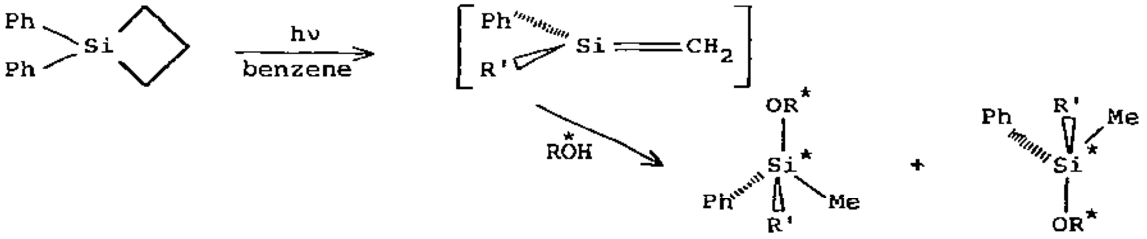
$$\big\downarrow$$

$$MeOSiMe_3 + (Me_3Si)_2C{=}SiR_2 + X^-$$

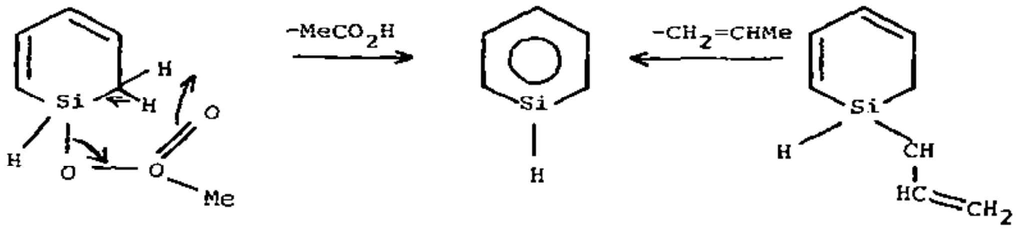
$$\big\downarrow \text{MeOH}$$

$$(Me_3Si)_2CH{-}SiR_2(OMe)$$

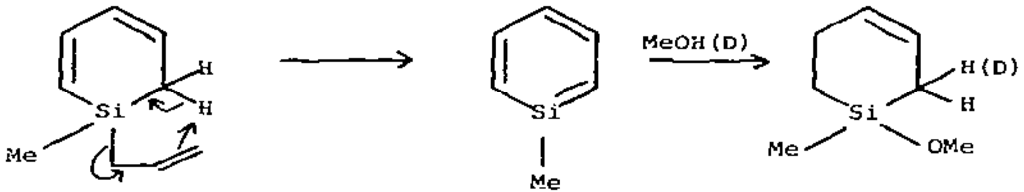
Prochiral silaethylene intermediates react with chiral alcohols to afford unequal amounts of diastereomeric pairs of alkoxysilanes (upto 30% enantiomeric excess), thus providing the first example of asymmetric induction observed in a silicon centre involving a trigonal silicon species.[34]



Silabenzene has been generated both by ester pyrolysis or by a retroene cleavage reaction:[35,36]



and is stable when condensed in an argon matrix at 10K. Its U.V. spectrum exhibits three bands (at 212, 272 and 320nm) expected for a π-perturbed benzene. The photoelectron data has been assigned by help of SCF calculations; the calculated ionisation energies of 8.2, 9.2 and 11.5eV comparing favourably with the experimental values of 8.0, 9.3 and 11.3eV. The thermally-induced retroene extrusion of propene from the silacyclohexadiene (8) similarly yields silatoluene, which again can be trapped in an argon matrix at 23K, when its infrared spectrum was recorded. Conclusive evidence for the presence of silatoluene was obtained by trapping with methanol:[37]



(8)

Both the new molecules, SiOS[38] and $SiOF_2$[39], have been isolated in low-temperature argon matrices. The former was obtained by the reaction of SiS with atomic oxygen generated by microwave excitation, whilst the latter results from the matrix reaction of SiO with difluorine after photolysis with a high-pressure mercury lamp. The respective Si-O and Si-S force constances for SiOS are 4.86(6) and 9.0(1) mdyne $Å^{-1}$, corresponding to bond orders of 1.9 and 2.01, respectively. This molecule, therefore, constitutes the first silicon(IV) compound possessing a Si=S double bond. $SiOF_2$ has a vibrational spectrum consistent with the expected planar structure. Of the four isomeric forms of the "silylenoid"

SiH_2LiF, the two most stable forms have been suggested to be the $SiH_2Li^+F^-$ ion pair and the $H_2Si{=}FLi$ complex analogous to the similar structures found previously for carbenoids.[40]

4.1.3 Germylenes

Valence-only *ab initio* calculations have been carried out on the structure and singlet-triplet separation in the germylenes, GeH_2, GeF_2 and $GeMe_2$.[41] All have singlet ground states; other data is listed in Table 2.

Table 2. Data for Germylenes.

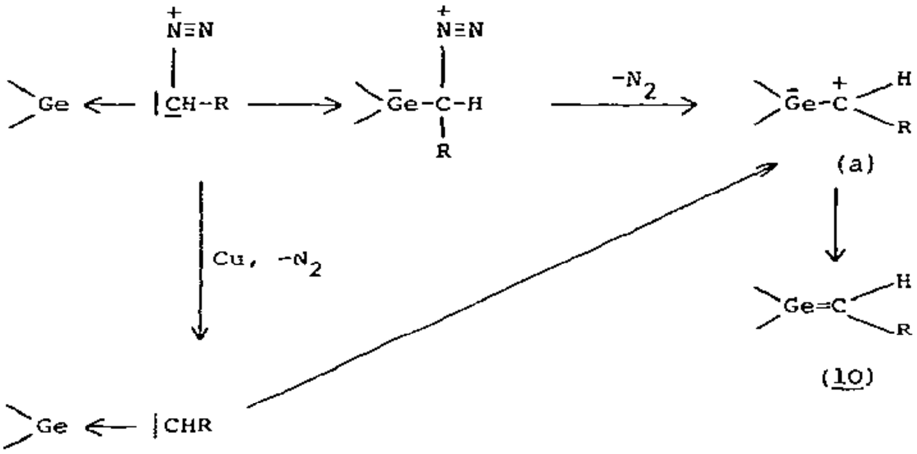
	GeH_2	GeF_2	$GeMe_2$
Singlet-Triplet Gaps (kcal mol^{-1})	10	64	14
Ground State Equilibrium Geometry			
Ge-X (Å)	1.60	1.76	2.02
$\widehat{XGeX}$ (°)	93	97	98

Pyrolysis of pentamethyldigermane, Me_5Ge_2H, leads to the formation of dimethylgermylene as a short-lived intermediate, which inserts into the Ge-H bond of its precursor:

$$\begin{tikzcd}
Me_3GeGeMe_2H \arrow[r, "250^{\circ}"] & Me_3GeH + {:}GeMe_2 \arrow[d, "Me_5Ge_2H"] \\
 & Me_3GeGeMe_2GeMe_2H
\end{tikzcd}$$

Kinetic data support an initial molecular elimination of dimethylgermylene (first-order rate constant -0.075(8) h^{-1}), followed by a rapid attack of Me_2Ge on its precursor. Neither the rate of thermolysis nor the product yields are altered by dilution (x8) with 1-methylnaphthalene.[42] The reactivity of germylenes with diazo compounds such as $PhCHN_2$, and EtO_2CCHN_2 in benzene increases with the relative electrophilic character in the order $Ph_2Ge<PhGeCl<GeF_2$. The reactions were postulated to

proceed via an initial nucleophilic attack at the germylene by the diazo compound leading to an ylide complex (9) and the germene (10), which can be trapped by methanol, and undergoes pseudo-Wittig reactions with aldehydes. With added copper powder, the germene (10) is formed directly by the interaction of the germylene and the generated carbene (scheme 6).[43]



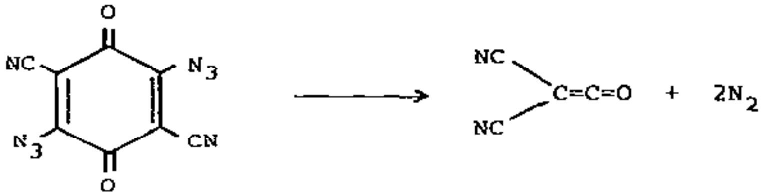
Scheme 6.

4.2 MOLECULAR CARBON COMPOUNDS

Several papers have reported the preparation and properties of substituted ketenes. Dechlorination of trichloroacetyl chloride, CCl_3COCl, at low pressure in the presence of zinc metal leads to the formation of dichloroketene.[44]

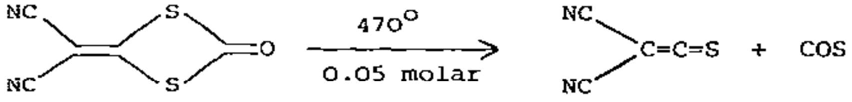
$$Cl_3CCOCl \xrightarrow[\text{ca. 0.1 torr}]{\text{Zn; }500^{\circ}} Cl_2C{=}C{=}O + ZnCl_2$$

Ab initio calculations predict that dicyanoketene is 62.8 kcal mol^{-1} lower in electronic energy than the isomer, dicyanooxirane,[45] and has been obtained by slowly warming the quinone (11) to 60° *in vacuo*. It is stable at low temperatures in the gas phase.[46]

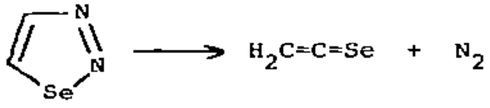


(11)

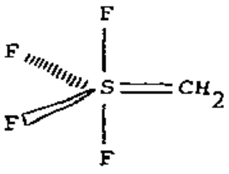
Dicyanothioketene may be similarly obtained by gas phase pyrolysis of 2(4-oxo-1,3-dithietan-2-ylidene)malonitrile, and is also stable under the same conditions:



Unlike dicyanoketene, the sulphur analogue can readily be generated continuously over a prolonged period in a flow system by this method.[47] Selenoketene results from the thermal decomposition of 1,2,3-selenadiazole in the gas phase at temperatures in excess of 720K:[48]



Methylene sulphur tetrafluoride, $H_2C=SF_4$, has an approximate trigonal bipyramidal structure (12), in which the methyl group occupies the same position as the lone pair in sulphur(IV) fluoride. The hydrogen atoms lie in the plane of the sulphur, carbon and axial fluorine atoms.[49]



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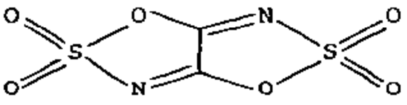


(13)

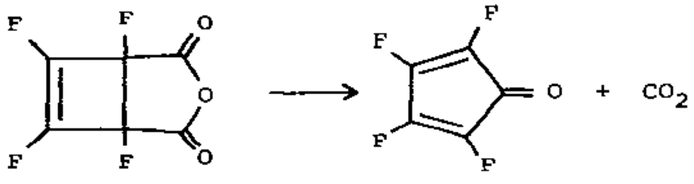
Isomerisation of sulphur dicyanide to cyanogen isothiocyanate, NCNCS, occurs at 850°. From the microwave rotational constants the $\widehat{CNC}$ bond angle was deduced to be 149.4° (cf. NCNCO, 140°).[50] A second conformer (trans,cis) of S-methyl dithiocarbazate has been obtained by low temperature crystallisation. The structure comprises centrosymmetric dimers linked by NH---S hydrogen bonds, in contrast to the cis,trans conformer where NH---N bonds are present. Vibrational spectra of both conformers differ markedly, but change of conformation does not significantly alter the bond distance and angles.[51] The 2:1 addition product of sulphur trioxide to dicyane has the planar bicyclic ring structure (13), which has C_{2h} symmetry.[52] A new strong acid, $HC(SO_2F)_3$, has been obtained by the sequence:

$$\begin{tikzcd}
H_3C\text{-}CONHPh \arrow[r, "(i)"] & HC(SO_3^-K^+)_3 \arrow[r, "(ii)"] & HC(SO_3^-Ba_{\frac{1}{2}}^+)_3 \arrow[d, "(iii)"] \\
 & HC(SO_2F)_3 & HC(SO_3H)_3 \arrow[l, "(iv)"']
\end{tikzcd}$$

(i) SO_3/H_2SO_4; K_2CO_3, (ii) Ba^{2+}, (iii) H_2SO_4, (iv) SF_4

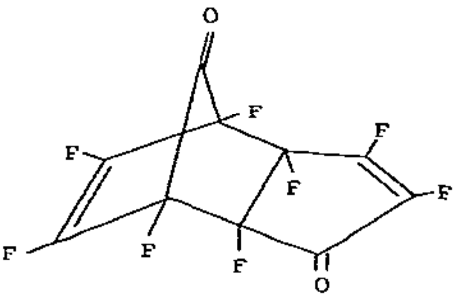
The compound is a colourless, evil-smelling crystalline solid, mp. 44.5-45.5°; with a plane $[CS_3]$ skeleton. Its most striking property is its extreme acid character, which lies between fluorosulphuric and nitric acids, and is most probably due to mesomeric distribution of the negative charge of the anion, $C(SO_3F)_3^-$.[53]

Interest in fluorocarbon derivatives continues. Sublimation *in vacuo* through a vycor tube heated to 585° transforms tetrafluorocyclobutenedicarboxylic anhydride into the dienone (13) cleanly.



(13)

When trapped at -196°, (13) can be preserved neat or as a solution at low temperatures, or sublimed on warming into a gas storage bulb can be stored many hours at low pressure. At room temperature, (13) dimerises very rapidly in the liquid phase to a single isomer, which, remarkably, appears to be the *exo* isomer (14). The bridging carbonyl of (14) readily hydrates to the *gem* dihydroxy derivative (15). Photolysis of (13) at 2537Å in the vapour phase smoothly yields perfluorocyclooctatetraene (16).[54]



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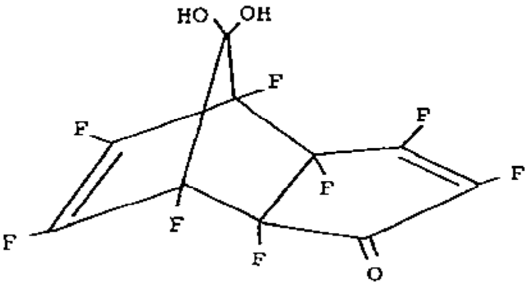

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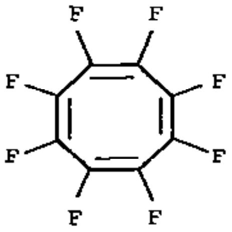


(16)

Perfluoroisobutene reacts with thiazyl fluoride in the presence of caesium fluoride at 130° yielding (17):

$$2(CF_3)_2C{=}CF_2 \quad + \quad 2NSF \longrightarrow \{\,2N{\equiv}S{-}C(CF_3)_3\}$$

$$\downarrow$$

$$(CF_3)_3C{-}N{=}S{=}N{-}S{-}C(CF_3)_3$$

(17)

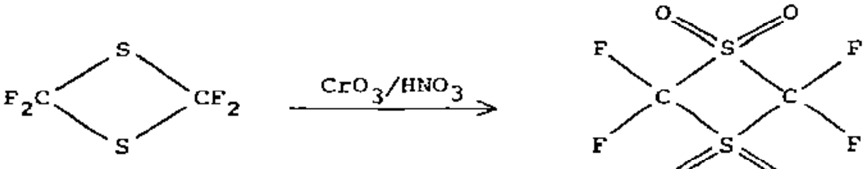
With thiazyl trifluoride, however, $NSF_2C(CF_3)_3$ is obtained which isomerises at temperatures above 110° to $(CF_3)_3CNSF_2$:

$$\begin{tikzcd}(CF_3)_2C{=}CF_2 + NSF_3 \arrow[r] & NSF_2C(CF_3)_3 \arrow[d, ">100^{\circ}"] \\ & (CF_3)_3C\text{-}NSF_2\end{tikzcd}$$

(18)

(19)

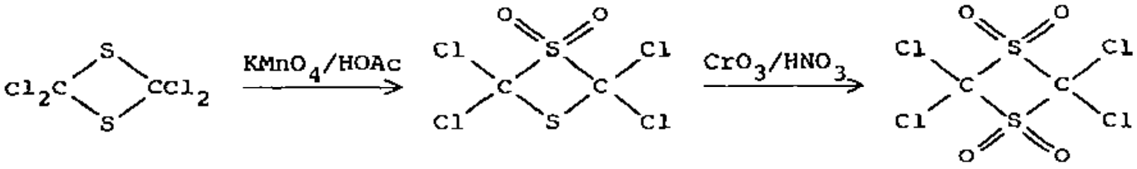
In contrast to (19), the fluoro Lewis acid (18) forms 1:1 adducts with arsenic(V) and antimony(V) fluorides. In 50% aqueous KOH, (19) hydrolyses to the amine $(CF_3)_2CNH_2$.[55] Oxidation of the cyclic disulphide (20) using CrO_3/HNO_3 affords the smallest perfluorinated cyclic disulphone (21) yet obtained:



(20)

(21)

The disulphone has a planar ring, with the oxygen and fluorine atoms in planes orthoganol to each other and the ring plane. This method of oxidation does not work for the corresponding chloro-disulphide (22). However, if the initial oxidation is carried out using $KMnO_4/HOAc$, CrO_3/HNO_3 can be used for the final oxidation to the cyclic disulphone (23):[56]



(22)

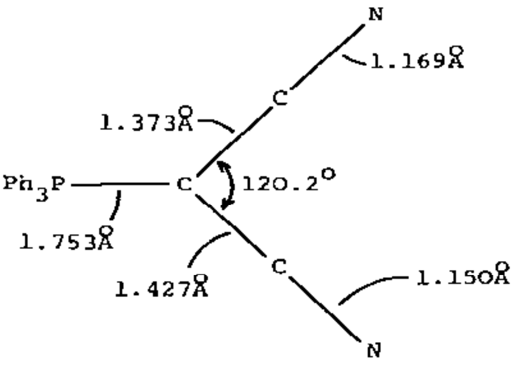
(23)

The reactions of hexafluoroacetone with several sulphur-containing compounds has been investigated. With trimethylene sulphide a concerted addition reaction occurs which results in the formation of the six-membered ring compound, $(CF_3)_2\overline{COSCH_2CH_2CH_2}$, but with tetramethylene sulphide, dimethylsulphide or dimethyldisulphane, insertion into the α-position takes place affording the compounds $\overline{SCH[CH(OH)(CF_3)_2]CH_2CH_2C}HC(OH)(CF_3)_2$, $HO(CF_3)_2CCH_2SCH_2C(CF_3)_2OH$ and $HO(CF_3)_2CCH_2SSCH_2C(CF_3)_2OH$, respectively. With thiophosphoryl chloride, in which no α-hydrogen is present, an oxidative-addition at the sulphur(II) atom takes place yielding $\overline{OC(CF_3)_2C(CF_3)_2OS}{=}PCl_3$. No reaction was observed with fluoroalkyl sulphides under the same conditions, with the exception that those with active functional groups such as NH_2, which behave as primary aliphatic amines in their reactions with hexafluoroacetone. Compounds such as $HO(CF_3)_2CSSSC(CF_3)_2OH$ and $HO(CF_3)_2CSSC(CF_3)_2OH$ are formed when $(CF_3)C(OH)SH$ is mixed with SCl_2 and dichlorine. All three of these perfluorinated derivatives are converted to hexafluoroacetone on treatment with sulphur(IV) fluoride. Reaction of $(CF_3)_2C(OH)(SH)$ with chlorine fluoride in pyrex glassware affords $(CF_3)_2C(OH)_2$.[57]

The structures of several other compounds have been investigated by electron diffraction and/or microwave spectroscopy. These include: 1,1,1,2-tetrafluoroethane,[58] trifluoroethane,[59] 1,1-difluoroethane,[60] bromoacetyl chloride and bromide,[61] chloroacetyl chloride,[62] carbonyl cyanide,[63] carbonyl fluoride,[64] seleno- and thio-carbonyl difluoride,[65] thiocarbonyl bromide,[66] trifluoromethylfluoroperoxide,[67] and trifluoromethylchloroperoxide.[68] A rather interesting paper described an *ab initio* SCF investigation of the model Wittig reaction:

$$PH_3CH_2 + CH_2O \longrightarrow PH_3O + C_2H_4$$

The reaction takes place in an essentially concerted fashion. Starting from PH_3CH_2 and CH_2O, an oxaphosphetane ring is formed via a very small energy barrier. This ring system corresponds to a local minimum in the energy hypersurface. The energy barrier for the dissociation of the ring into the PH_3O and C_2H_4 products is around 25 kcal mol^{-1} with a total reaction energy of ca. -45 - -50 kcal mol^{-1}.[69] The crystal structures of the ylide, triphenylphosphino dicyanomethylide,[70] and the phosphinimine, triphenylphosphino cyanoamide,[71] have been determined. The skeleton of the latter is bent at nitrogen but almost linear at carbon, whilst the former possesses a trigonal carbon. Principal bond data is shown in (24) and (25). The tris(trichlorophosphinimato)carbenium cation, $[C(N{=}PCl_3)_3]^+$, (as the hexachloroantimoniate(V) salt), has approximate C_{3h} symmetry with the carbon, nitrogen, phosphorus and one chlorine per group almost coplanar.[72]



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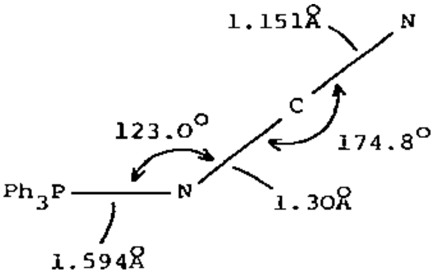
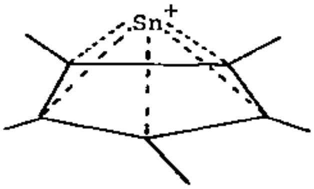


(25)

4.3 BIVALENT COMPOUNDS OF GERMANIUM, TIN AND LEAD.

4.3.1 Bonds to Carbon

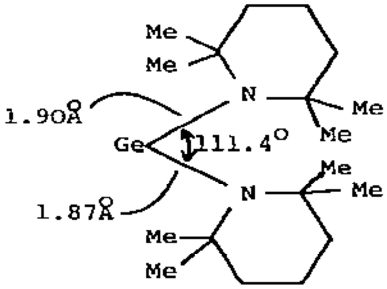
The reaction of pentamethylcyclopentadienyllithium with either germanium(II) chloride, dioxane or tin(II) chloride yields the corresponding bis(pentamethylcyclopentadienyl)metal(II) derivative. The unit cell of the tin compound contains two crystallographically independent molecules both possessing an angular sandwich structure, the angle subtended at the tin by the two C_5 axes being 143.6° and 144.6°. The tin-carbon bond distances vary in the range 2.567 – 2.776Å, with two short and three longer distances. Treatment of $Sn(C_5Me_5)_2$ with fluoroboric acid affords crystals of the salt, $[Sn(C_5Me_5)]^+BF_4^-$, in which the tin is more tightly bound to the remaining cyclopentadienyl ring (Sn–C = 2.46Å) as in (26).[73]



(26)

4.3.2 Bonds to Nitrogen

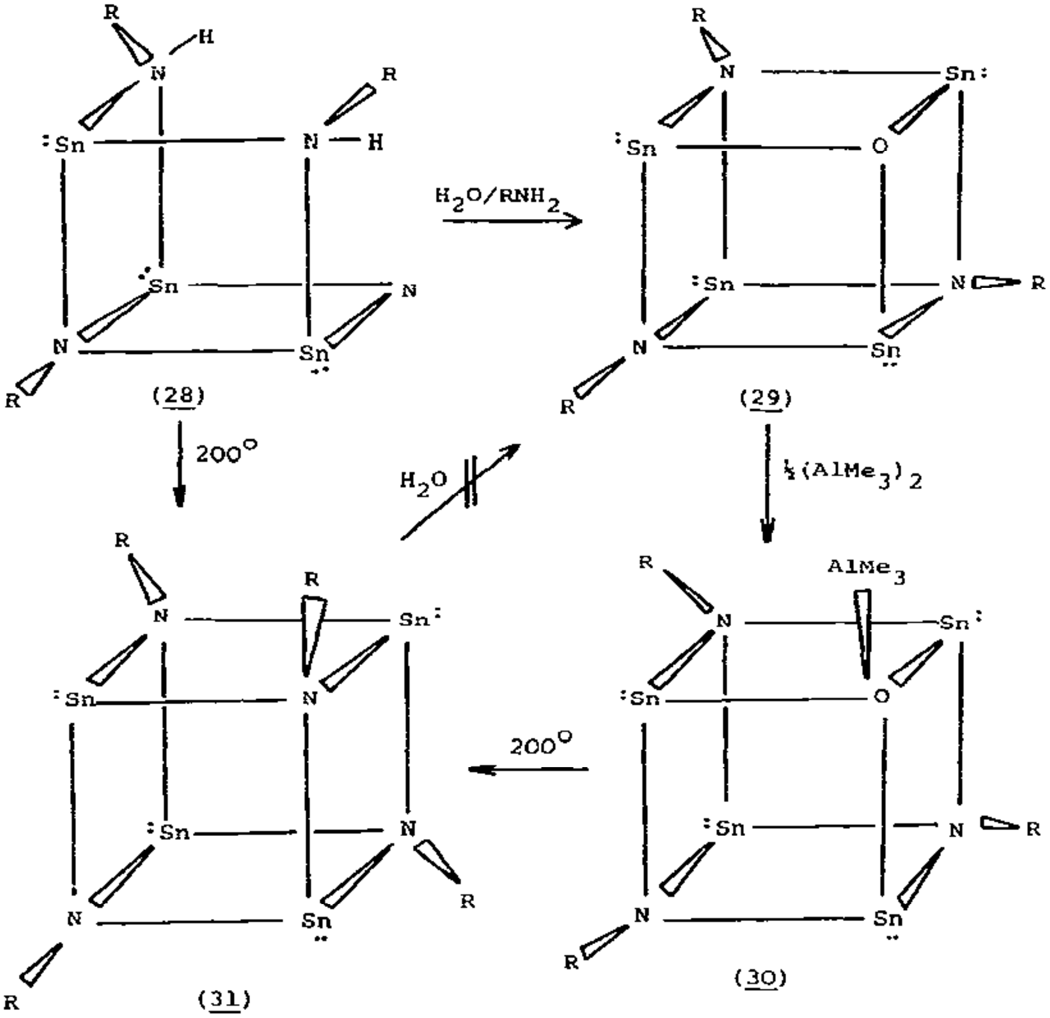
Lappert and his coworkers,[74] continuing their investigations into the chemistry of low-valent heavier Group IV metal amides, have synthesised the monomeric crystalline germanium(II) and tin(II) di-*tert*-butylamides, $M[NCMe_2(CH_2)_3CMe_2]_2$ (M=Ge, Sn) from the appropriate metal halide and the lithium amide in thf. Both derivatives are coloured (orange (Ge) and maroon (Sn)). The germanium compound has the angular structure shown in (27).



(27)

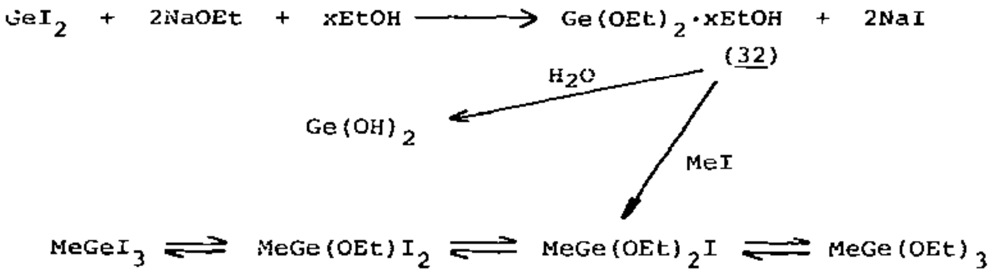
Controlled hydrolysis of the open-cage tin(II) amide (28) affords the cubane-type cage derivative (29) with a $[Sn_4N_3O]$ core. Treatment of (29) with trimethylaluminium yields the adduct (30), which decomposes on heating to the $[Sn_4N_4]$ cubane (31) as does (28). Surprisingly, (29) cannot be obtained by controlled hydrolysis of (31).[75]

The crystal structure of (5,10,15,20-tetra-*n*-propylporphinato)-lead(II) shows it to be a "roof" porphyrin complex. Incorporation of the very large lead(II) atom into the macrocyclic framework principally results in a folding distortion along an axis defined by two opposite methine carbon atoms rather than by a variation in bond distances and angles when compared to the free base. The molecules pack in pairs with a Pb-Pb distance of 4.26Å implying no metal-metal bonding. However, the situation of a pyrrole ring of a neighbouring molecule lying only 3.456Å above the lead is suggestive of a weak π-type interaction. The local bonding environment of the lead is that of a square pyramid, in which the lead atom lies 1.174Å above the $[N_4]$ plane.[76]



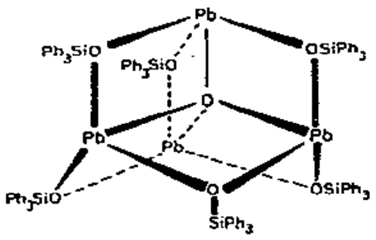
4.3.3 Bonds to Oxygen

The reaction of germanium(II) iodide with sodium ethoxide in ethanol yields the solvated germanium(II) ethoxide (32), which degrades spontaneously to an insoluble, intractable material when stored for several days. Hydrolysis of (32) gives germanium(II) hydroxide, whilst oxidative-addition of methyl iodide gives an equilibrium mixture of methylgermanium(IV) ethoxide iodides:[77]



In solution, (32) is associated, but the ethanolamine derivative, $\overline{Ge(OCH_2CH_2)_2}NMe$, obtained by transalcoholysis, is a monomeric white crystalline solid which can be purified by sublimation. It is stable to dry oxygen, but hydrolyses readily.[78] The germanium(II), tin(II) and lead(II) aryloxides, $M(OC_6H_2M-4-Bu^t{}_2-2,6)_2$ (M=Ge,Sn,Pb), can be obtained either by substitution of the metal(II) chloride or by protolysis of the metal(II) bis(trimethylsilyl)amide. All three compounds are coloured (either yellow (Ge,Sn) or red (Pb)) and air-sensitive. The germanium and tin derivatives are isostructural with angular geometries (M-O=1.806Å (Ge), 2.008Å (Sn); $\widehat{OMO}$=92.0° (Ge), 88.7° (Sn)).[79]

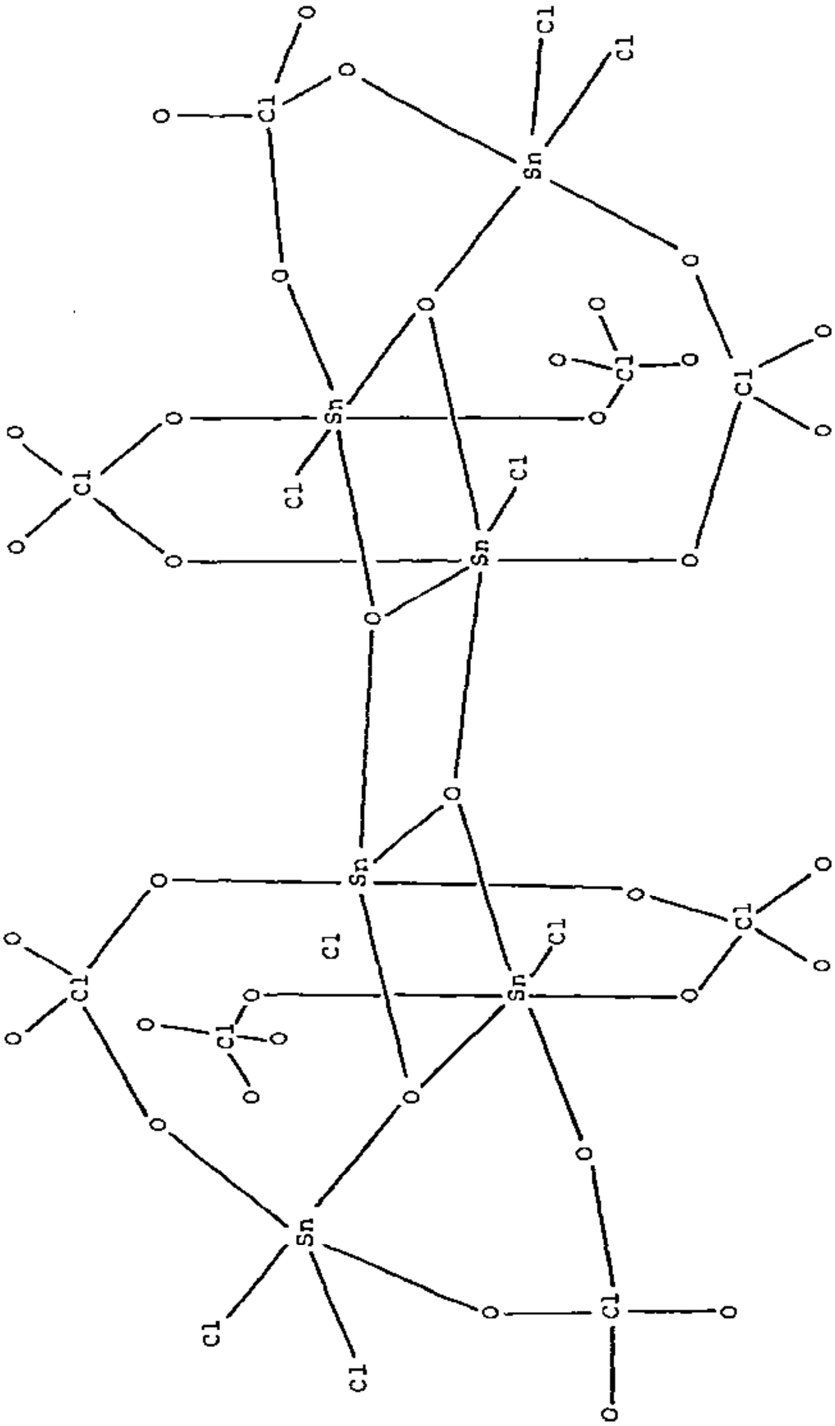
The hydrolysis of lead(II) has been investigated potentiometrically at 25° in 0.1M KNO_3 in the pH range 6.0-8.5.[80] Several species, including $[Pb(OH)]^+$, $[Pb_3(OH)_4]^{2+}$, $[Pb_3(OH)_5]^+$, $[Pb_4(OH)_4]^{4+}$ and $[Pb_6(OH)_8]^{4+}$, occur in complex equilibria depending upon the conditions. Polynuclear species are even formed at low total lead concentrations. Reaction of bis(cyclopentadienyl)lead(II) with triphenylsilanol in benzene yields initially $Pb(OSiPh_3)_2$, which subsequently decomposes to the oxolead cluster, $[Pb_4(OSiPh_3)_6]O$, which possesses the adamantane structure (33). The central oxygen atom is equidistant from and tetrahedrally coordinated by four lead atoms (Pb-O=2.25-2.31Å), whilst in addition each of the lead atoms forms one short (2.28-2.32Å) and two longer bonds (2.36-2.49Å).[81]



(33)

The asymmetric unit of strontium bis tris(monochloroacetato)-stannate(II) comprises one Sr^{2+} cation and two tris(chloroacetato)-stannate(II) complex anions. Both tin atoms have usual pyramid coordination, with the three carboxylate groups functioning as unidentate ligands. The second oxygen atom from each carboxylate group is not bound to the metal, but is involved in contacts to the Sr^{2+} cation ($Sn{-}O = 2.130{-}2.145$Å, $Sn...O = 2.914{-}3.287$Å; $O\widehat{Sn}O = 80.4{-}90.9^{\circ}$).[82] The complex tin(II) perchlorate, $[Sn_3O_2Cl_4(ClO_4)_4]_2$, from the reaction of $(ClO_2)_2Sn(ClO_4)_6$ with excess tin(IV) chloride at 10°, has a dimeric tristannoxane "ladder" structure with a $[Sn_6O_4]$ core and both unidentate and bidentate perchlorate groups (34).[83]

The structures of several tin(II) and lead(IV) phosphates have been determined. Those of tin(II) hydrogen phosphate, $SnHPO_4$, and phosphite, $SnHPO_3$, are quite similar, and consist of $[SnO_3]$ groups fused with $[PO_4]$ groups in the phosphate, and $[SnO_3]$ groups fused with $[HPO_3]$ groups in the phosphite, both giving sheet structures. Hydrogen bonding exists only in the phosphate, and holds the sheets together. The coordination at tin is pyramidal in both.[84] The tritin(II) hydroxide oxide phosphate, $Sn_3O(OH)PO_4$, also crystallises with a layer structure. Each tin is again pyramidally coordinated by three oxygen atoms, but with two additional longer contacts.[85] The complex, $Sn\{Cocp[P(O)(OEt)_2]_3\}_2$, obtained by metathesis from tin(II) chloride and the sodium salt is air-stable, and from spectroscopic evidence appears to be one of the few examples of a bivalent tin compound in which the lone pair is not stereochemically active. All six $P{=}O...Sn$ bonds are equivalent as in (35).[86] Crystals of lead(II) phosphate, $Pb_9(PO_4)_6$, grown from the hydrothermal reaction of lead acetate trihydrate and K_2HPO_4 at 473K, have an apatite structure which is defficient in lead at the Pb(1) site and also has the hydroxyl group missing.[87]



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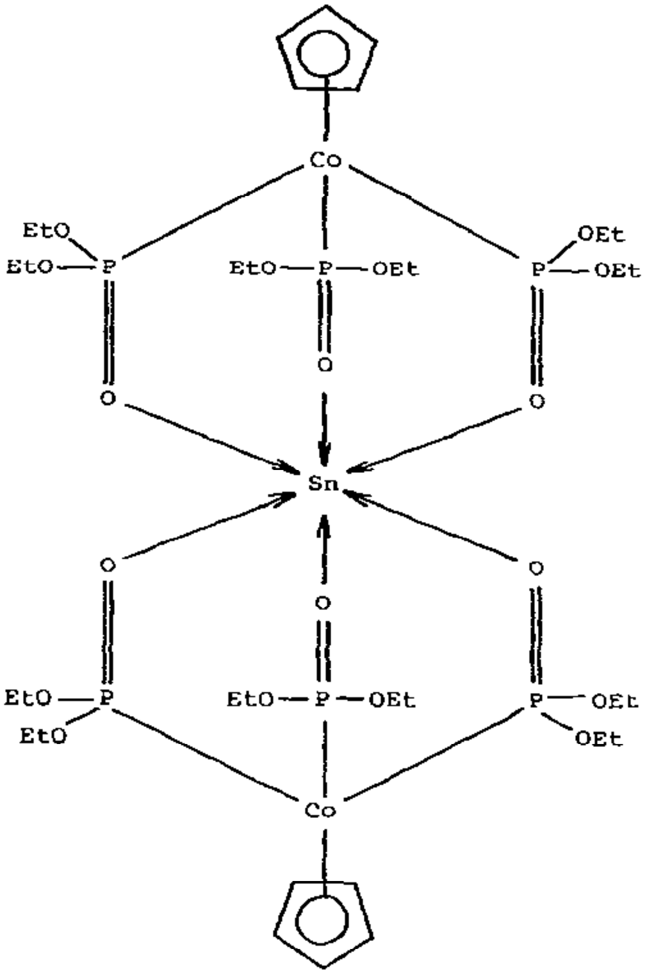
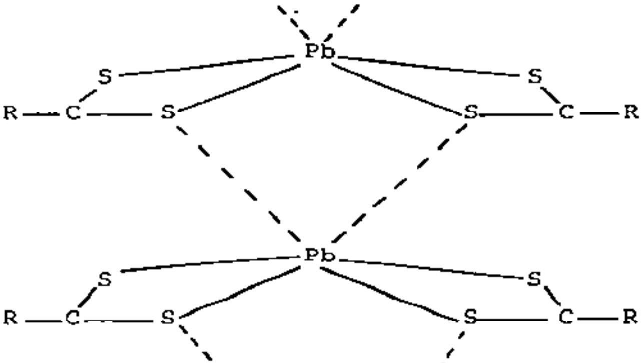


(35)

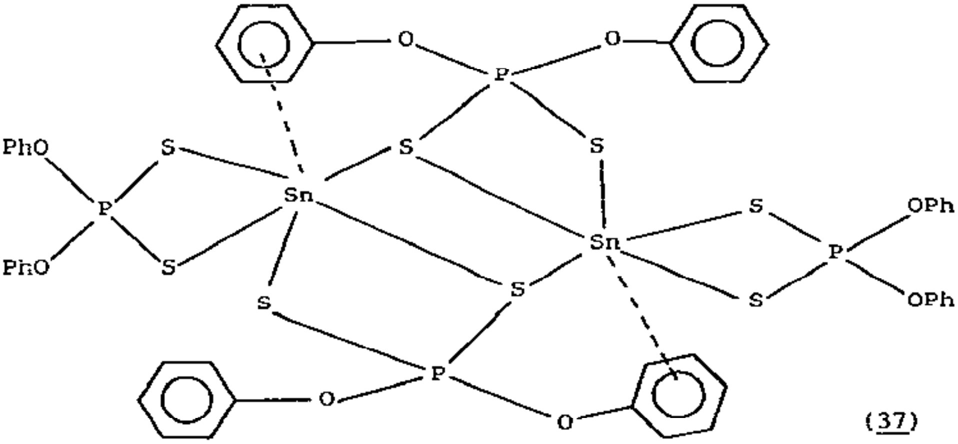
4.3.4 Bonds to Sulphur

Dithiocarbamato complexes of tin(II) and lead(II), prepared from aqueous solutions of $SnCl_2$ or $Pb(NO_3)_2$ and the appropriate sodium salt, exhibit high thermal stability points, usually in excess of 300^o.[88] This behaviour is often associated with a strongly polymeric nature, but the crystal structures of both $Pb[S_2CNMe_2]_2$[89] and $Pb[S_2CNPr^i{}_2]_2$[90] consist of essentially discrete molecules additional intermolecular Pb···S interactions resulting in a distorted octahedral environment for the metal as shown in (36).



(36)

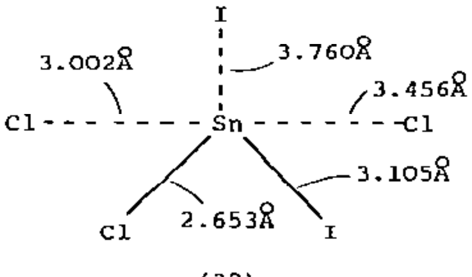
In contrast bis(O,O'-diphenyldithiophosphato)tin(II) has a centrosymmetric dimeric structure (37), in which one ligand bridges the two tin atoms intermolecularly whilst simultaneously chelating one tin atom in an extremely anisobidentate fashion. The second ligand is involved in normal chelation. In addition to the two Sn···S coordinate bonds, the dimer is also held together by a long π-interaction (3.655Å) to the centre of one of the phenyl groups of an ester group of the bridging ligand of the second monomeric unit. The tin atoms are therefore in distorted octahedral coordination by five sulphur atoms and an $^6\eta$-phenyl ring.[91]



(37)

4.3.5 Bonds to Halogen

The heat of formation of PbClF has been determined from the heat of precipitation to be -538.4 kJ mol^{-1}. This value is more negative than the mean of the values for $PbCl_2$ and PbF_2 in agreement with its ready precipitation from them by redistribution in solution or the melt.[92] Tin(II) chloride iodide is isostructure with lead analogue. Additional long contacts result in a distorted trigonal bipyramidal geometry (38).[93] The structure of the mixed tin(II)-antimony(III) sulphoiodide, $Sn_2SbS_2I_3$, consists of parallel ribbon-like $[Sn_2S_2I_2]_n$ units linked together by the coordination polyhedra of antimony. The geometry of tin(II) is similar to the $PbCl_2$-type site in tin(II) iodide itself, in which some of the iodide sites have been replaced by sulphur and one facial site is vacant (39).[94] The complex halides $CsSnI_3$[95], $KPbI_3.2H_2O$, $NH_4PbI_3.2H_2O$ and $RbPbI_3.2H_2O$[96] all comprise double chains of edge-sharing $[MI_6]$ octahedra, which are held together by the cations and, in the case of the hydrates, water molecules. Phase diagrams and enthalpies of mixing have been determined for the $AgCl$-$SnCl_2$ and $AgCl$-$PbCl_2$ systems. Both are of the eutectic type. The latter system exhibits a previously undetected phase transition for $PbCl_2$ at 699K with an enthalpy of 2.1 kJ mol^{-1}.[97]



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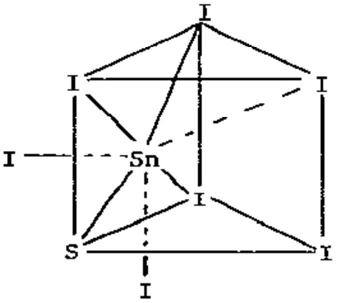
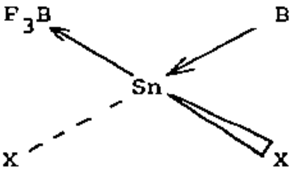


(39)

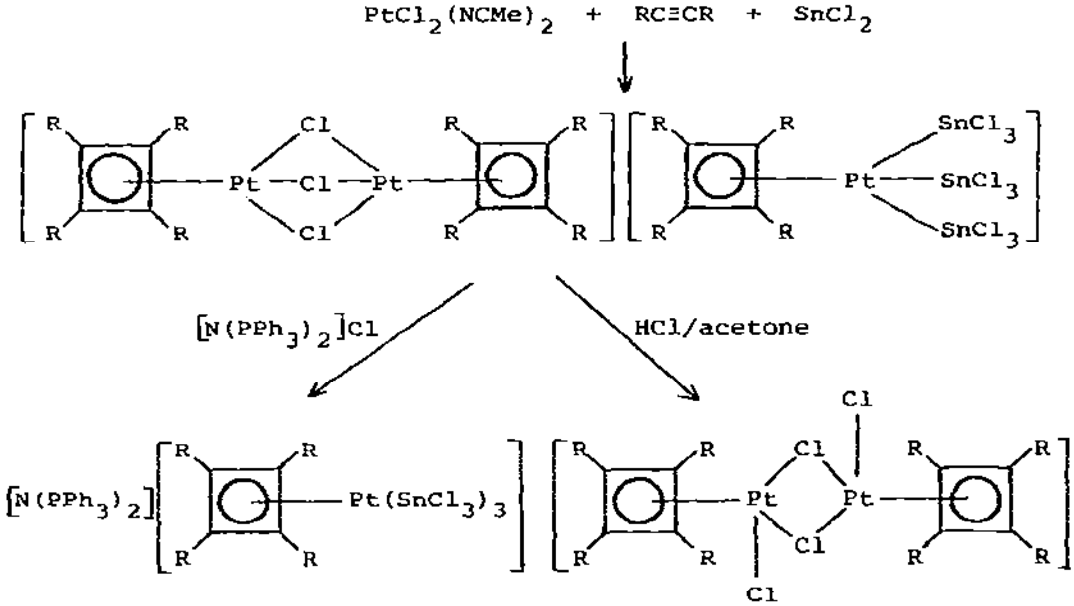
The reaction of 1:1 donor-acceptor complexes of tin(II) halides and bases with boron trifluoride yields 1:1:1 complexes such as $BF_3 \cdot SnX_2 \cdot B$ (X=Cl, Br, I; B=NMe_3, bipy, TMED, DMSO). Spectroscopic evidence supports the diadduct form (40), in which the BF_3 Lewis



(40)

acid complexes the tin lone pair.[98]

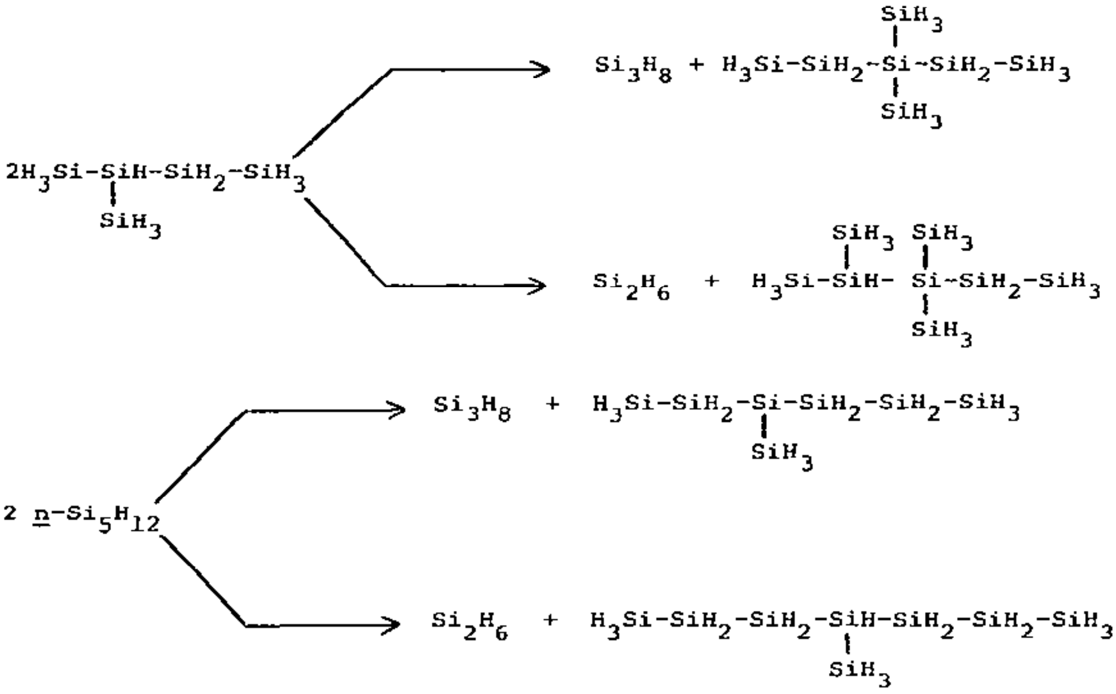
Ligand exchange readily occurs between the stannylene complexes, $M(CO)_5SnCl_2 \cdot thf$ (M=Cr, W), and trimethyl- or triphenyltin hydroxide giving the corresponding complexes of tin(II) hydroxide, $M(CO)_5Sn(OH)_2$. These complexes are highly associated, are involatile, sparingly soluble, and decompose without melting at >ca. 150°.[99] Insertion into only one metal-halogen bond occurs on reaction of tin(II) halides with the cobalt and iron complexes, $[Co(\eta\text{-dienyl})(L)Y_2]$ (η-dienyl = C_5H_5, MeC_5H_4; L = CO, PPh_3; Y = Br, I) and $[Fe(CO)_3(PPh_3)Y_2]$, giving the complexes $[Co(\eta\text{-dienyl})(L)(Y)(SnX_2Y)]$ and $[Fe(CO)_3(PPh_3)(Y)(SnX_2Y)]$. No evidence was apparent for the formation of SnX_3 derivatives, or for di-insertion, and it was suggested that a Lewis acid-Lewis base interaction between the SnX_2Y ligand and the Y ligand cis to it deactivates the second M-Y bond towards attack by further tin(II) halide.[100] Alkynes undergo dimerisation with tin(II) chloride and $PtCl_2(MeCN)_2$ affording ionic (cyclobutadiene)-platinum-tin complexes:[101]



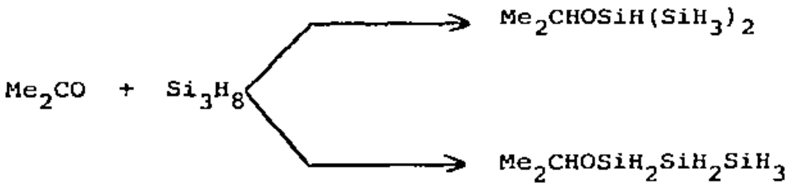
4.4 TETRAVALENT COMPOUNDS OF GERMANIUM, TIN AND LEAD.

4.4.1 Bonds to Hydrogen

U.v. irradiation of solutions of iso- and n-pentasilanes in 2,3-dimethylbutane at room temperature results in decomposition to higher and lower homologues. The main reaction is the disproportionation to trisilane and branched heptasilanes or to disilane and branched octasilanes:[102]



Photolysis of Si_3H_8, n-Si_4H_{10}, iso-Si_4H_{10} and n-Si_5H_{12} in the presence of acetone in dimethylbutane yields new mono- and poly-isopropoxysilanes:[103]



$$Me_2CO + Si_3H_8 \longrightarrow Me_2CHOSiH(SiH_3)_2$$

$$Me_2CO + Si_3H_8 \longrightarrow Me_2CHOSiH_2SiH_2SiH_3$$

$$Me_2CO + n\text{-}Si_4H_{10} \longrightarrow Si_2H_5(SiH_3)SiHOCHMe_2$$

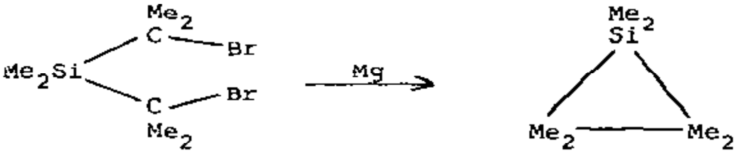
$$Me_2CO + (SiH_3)_3SiH \longrightarrow (SiH_3)_3SiOCHMe_2$$

$$Me_2CO + n\text{-}Si_5H_{12} \longrightarrow (Si_2H_5)_2SiHOCHMe_2$$

An electron diffraction study of the structure of tris(tert-butyl)-silane has shown that this compound is less strained than its carbon analogue, Me_3CH, but somewhat more strained than $(Me_3Si)_3SH$. Bond distance and angle data are normal (Si–C = 1.934Å; HSiC = 105.3°).[104]

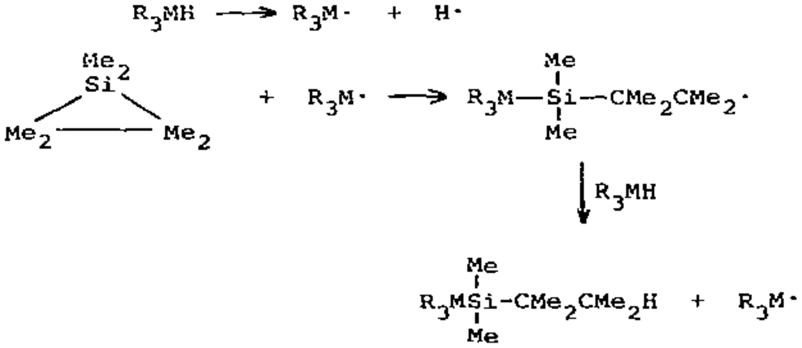
4.4.2 Bonds to Carbon

After having been proposed as intermediates in several reactions, examples of stable siliranes and silirenes have been prepared. Hexamethylsilirane (41) has been obtained by the action of magnesium on bis(α-bromoisopropyl)dimethylsilane in thf:

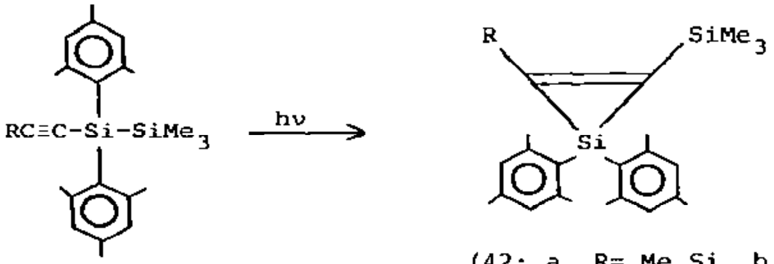


(41)

Not unexpectedly it is highly reactive towards atmospheric oxygen and moisture, and decomposes when heated in solution to 60–75°. This decomposition reaction results in the extrusion of dimethylsilylene, which may either add to the $Me_2C{=}CMe_2$ also produced in the decomposition to regenerate the silirane, or insert into the reactive $[SiC_2]$ three-membered ring to produce octamethyl-1,2-disilacyclobutane, or oligomerize to $(Me_2Si)_n$.[105] Under appropriate conditions, organogermanium and organotin hydrides react with hexamethylsilirane to give ring-opened products of the type $R_3MSiMe_2(CMe_2CMe_2H)$ (M=Ge or Sn) via a radical mechanism of the type:[106]

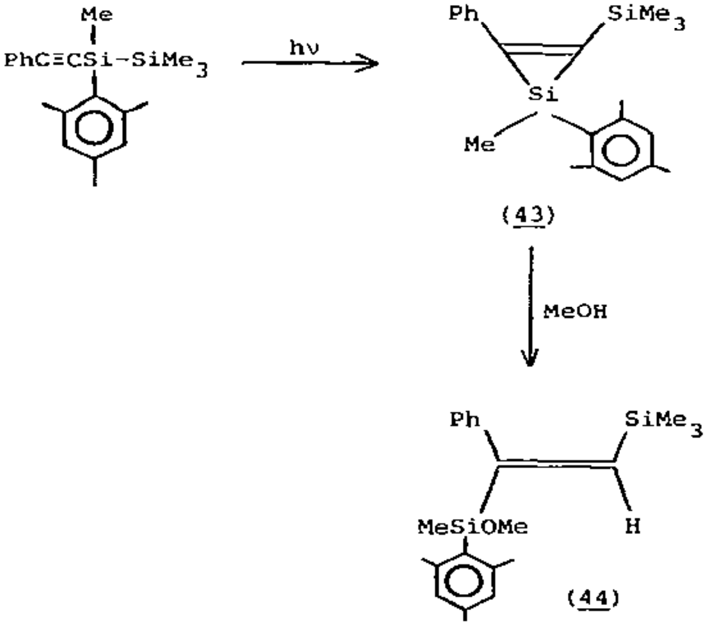


The stable silirenes (silacyclopropenes), 1,1-dimethylsilyl-2,3-bis(trimethylsilyl)-1-silacyclopropene (42a) and 1,1-dimesityl-2-phenyl-3-trimethylsilyl-1-silacyclopropene (42b) have been prepared by the photolysis of 1,1-dimesityl-1-trimethylsilylethynyltrimethyldisilane and 1,1-dimesityl-1-phenylethynyldisilane, respectively:



(42; a, R= Me_3Si b, R= Ph)

In contrast to the silirane above, neither (42a) or (42b) is affected by atmospheric oxygen and moisture or alcohols at room temperature. Photolysis of 1-mesityl-1-phenylethynyltetramethyldisilane yields 1-mesityl-1-methyl-2-phenyl-3-trimethylsilyl-1-silacyclopropene (43) which, although rather stable towards atmospheric oxygen, reacts readily with methanol in benzene to give the ring-opened methoxysilane (44):[107]



(43)

(44)

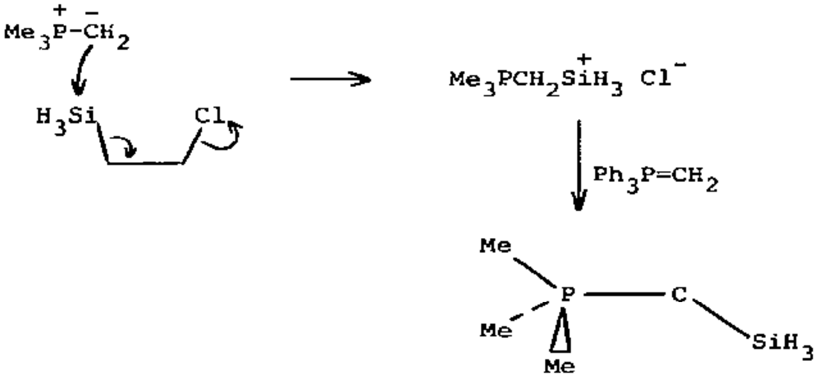
The structure of cyclopentadienylgermane, $Ge(C_5H_5)H_3$, has been determined in the gas phase and also in the crystal at 160K. In both phases, the cyclopentadienyl ring is planar with a diene structure (Table 3).[108]

Table 3. Bond Distance Data (Å) for Cyclopentadienylgermane.[108]

		Ring Distances		
	Ge-C(1)	C(1)-C(2)	C(2)-C(3)	C(3)-C(4)
Gas Phase	1.969	1.478	1.350	1.468
Solid	1.965	1.49,1.46	1.35,1.34	1.44

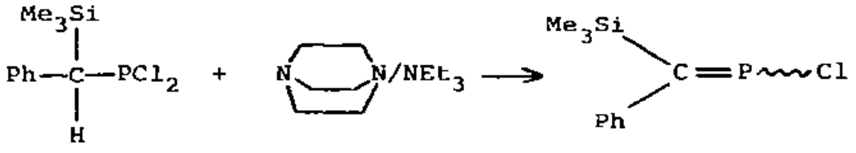
Variable temperature Mössbauer Spectroscopy has been employed to investigate organotin-substituted styrene monomers and polymers. For both bis(p-tolyl)bis(p-styryl)tin and tetrakis(p-styryl)tin, the temperature coefficient of the recoil-free fraction increases on thermal polymerisation due to the added constraint of the polymeric structure on the motion of the tin atoms.[109]

The silylphosphorane (45) has been prepared by the reaction of 2-chloroethylsilane and trimethylphosphorane in a 1:2 molar ratio:

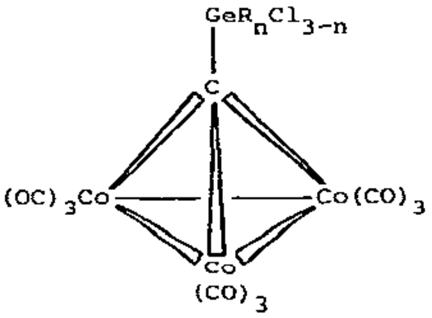


(45)

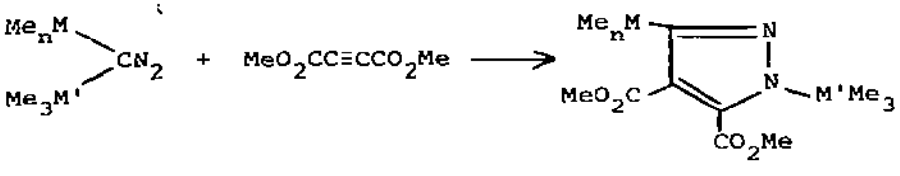
An electron diffraction study of (45) shows that the Si-C bond is twisted 25° from a position in which it eclipses one P-C bond. The $\widehat{PCSi}$ bond angle (123°) is consistent with the expected planarity at the methine carbon.[110] The first P-halogeno functionalised methylene phosphorane (46) has been obtained by dehydrochlorination of (47). It is a yellow-green distillable oil which can be stored in a refrigerator for several weeks.[111]


(47) (46)

The reaction of organochlorogermanes, $GeR_nCl_{3-n}H$ (n=2,3), with $HCCo_3(CO)_9$ in refluxing benzene yields germyl-substituted methylidyne tricobalt nonacarbonyl complexes (48).[112]


(48)

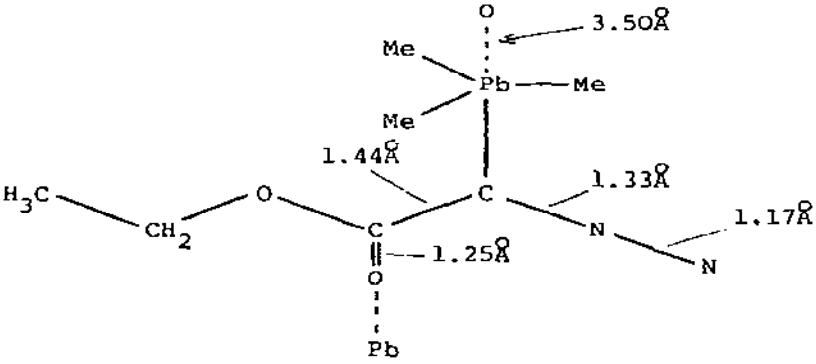
(Stannyl/plumbyl)(silyl/arsenyl)diazoalkanes react with acetylenedicarboxylic acid dimethyl ester yielding the substituted pyrazoles (49) via spontaneous rearrangement of the initially formed substituted isopyrazoles:


(49)

$Me_nM = Me_3Si, Me_2As$

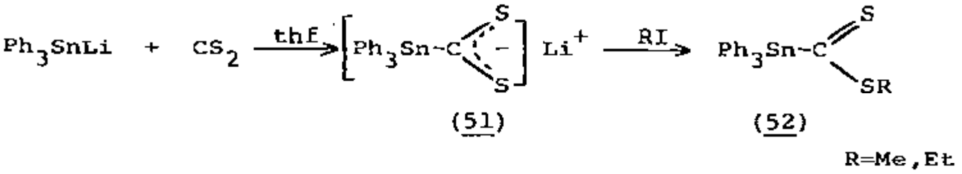
M' = Sn, Pb.

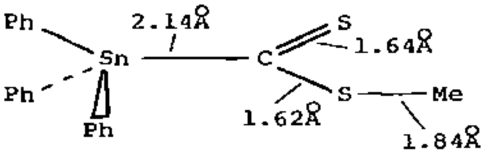
A crystallographic investigation of (49; $Me_nM = Me_2As$, M' = Sn) shows that the pyrazole ring is planar, and intermolecular interaction between a carbonyl group and the tin atom results in a polymeric structure with five-coordinated tin.[113] Trimethylplumbylacetic acid ethyl ester, $Me_3PbC(N_2)CO_2Et$, obtained as yellow crystals from the reaction of $Me_3PbN(SiMe_3)_2$ and $HC(N_2)CO_2Et$, has a similar structure (50), in which the diazoacetic acid ester group is fixed in the E-(1) conformation with an almost linear CNN grouping.[114]



(50)

Treatment of Ph_3SnLi with carbon disulphide yields the adduct (51), which reacts with alkyl iodides to give the air-stable violet crystalline dithioesters (52). The structure of the methylester is shown in (53).[115]



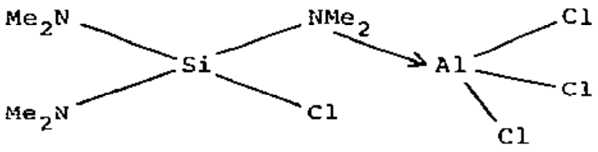


(53)

4.43 Bonds to Nitrogen

Electron diffraction data for tris(trimethylstannyl)amine,

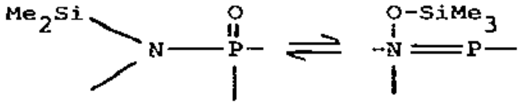
$(Me_3Sn)_3N$, are consistent with a planar configuration at nitrogen, thus confirming the conclusion that lowering the ligand electronegativity weakens the tendency to deviation from planarity.[116] The reaction of bis(trimethylsilyl)amine with sulphur dioxide proceeds smoothly and in very high yield to afford 1,1,1-trimethyl-N-sulphinylsilanamine, $Me_3SiN{=}S{=}O$.[117] Boron trichloride converts the silylaminosilanes, $(Me_3Si)_2NSiMe_2H$ and $Me_3SiN(SiMe_2H)$ in dichloromethane to the corresponding aminochlorosilanes in high yields. Depending upon the reaction conditions, the *tert*-butylaminosilanes, $^tBuN(SiMe_2H)SiMe_3$ and $^tBuN(SiMe_2H)_2$ give either simple H/Cl exchange or the silylaminoboranes, $Me_3Si(Me_2SiCl)NB(Cl)H$ and $(Me_2SiCl)_2NBH_2$, which results from an unexpected C-N bond cleavage. In the case of $Me_3Si(Me_2SiH)NMe$, the $Me_3Si{-}N$ bond is selectively cleaved giving $(Me_2SiCl)(Me)NB(Cl)H$.[118] Ligand exchange also takes place between Me_3SiNPh_2 and $(Ph_2N)_2PCl$ yielding $P(NPh_2)_3$.[119] The reaction of $(Me_2N)_3SiCl$ with Al_2Cl_6 in dichloromethane affords the 1:1 adduct (54). No evidence for the formation of the $[(Me_2N)_3Si]^+$ cation could be deduced.[120]



(54)

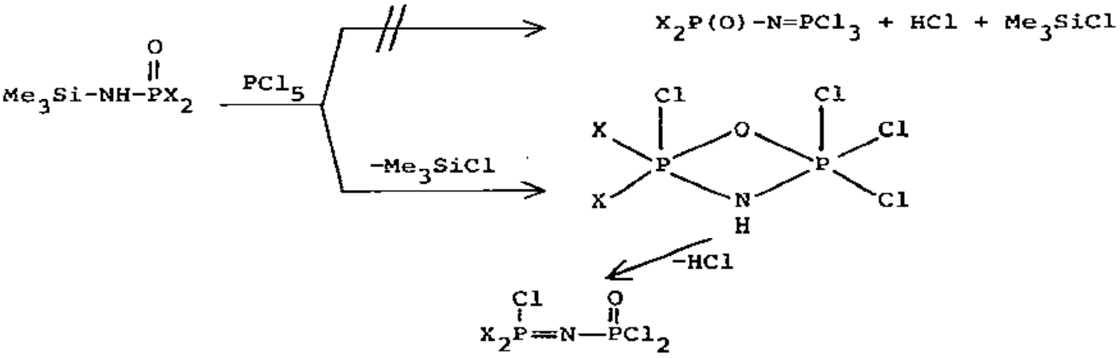
Substitution of the Group IVA metal chlorides, MCl_4 (M = Ti, Zr, Hf), even with excess *N*-lithio bis(trimethylsilylamide) gives only the corresponding tris(silylamino)metal chlorides, $ClM[N(SiMe_3)_2]_3$. All three derivatives are isostructural with a distorted tetrahedral geometry, whilst the fluxional behaviour of the ligands in solution was demonstrated by variable temperature p.m.r. studies.[121] Dimolybdenum tetraacetate reacts with $LiN(SiMe_3)_2$, $LiN(SiMe_2H)_2$ or $LiN(SiMe_3)Me$ in the presence of tertiary phosphines such as PMe_3, PMe_2Ph or PEt_3 yielding complexes of the type $Me_2(OAc)_2(NR_2)_2(PR_3)_2$. When the silylamide group is $[N(SiMe_2H)_2]$, the phosphine and silylamide groups are mutually *trans* relative to the metal-metal bond, but when the silylamide group is $[N(SiMe_3)_2]$ or $[N(SiMe_3)Me]$, the phosphine and silylamide ligands are *trans* to each other on the same molybdenum atom.[122]

Tert-butyl(trimethylsilyl)peroxide is a milder and more generally effective oxidant towards (silylamino)phosphines than molecular dioxygen.[123] Depending on the steric bulk of the substituents on the nitrogen atom on the (silylamino)phosphine, the oxidation products are either the structurally-rearranged siloxyphosphinimines, $Me_3SiN{=}P(R)MeOSiMe_3$ (R=Me,Ph) and $^tBuN{=}PMe_2OSiMe_3$, or the (silylamino)phosphine oxides, $Me_2\overline{SiBH_2CH_2SiMe_2N}P(O)Me_2$ and $RMe_2SiN(Me)P(O)Me_2$ (R = Me, ^tBu). When two different silyl groups were present, the disproportionation products, $RMe_2SiN{=}PMe_2OSiMe_2R$ (R = Me, ^tBu) were obtained. These observations suggest strongly that the presence of sterically bilky groups at nitrogen tend to favour the silyl migration process:

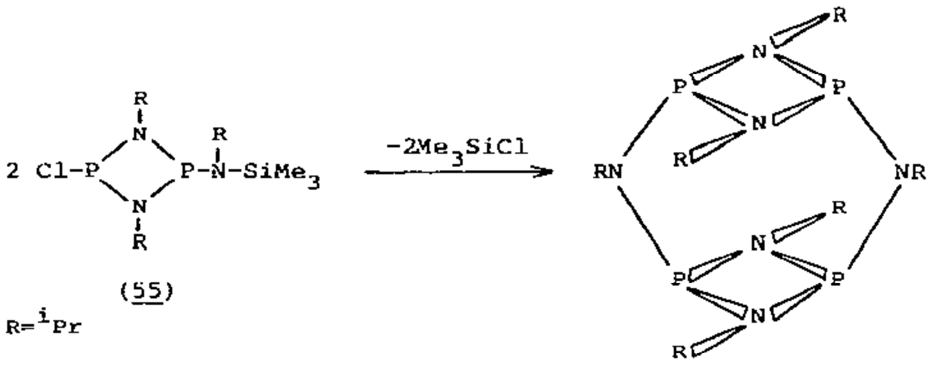


The reaction of bis(trimethylsilyl)aminophosphines with dibromine proceeds with elimination of trimethylbromosilane to give novel *P*-bromo-*N*-silylphosphinimines, $RR'P(Br){=}NSiMe_3$ (RR'=Me_2, MePh, Ph_2, $(OCH_2CF_3)_2$). These derivatives eliminate further trimethylbromosilane on heating yielding the cyclic phosphazenes, $(RR'PN)_n$, with nearly quantitative yields of $(Me_2PN)_n$ (n=3,4,5) resulting from the thermolysis of $Me_2P(Br){=}NSiMe_3$.[124] Elimination of $Me_3SiOCH_2CF_3$ and formation of $(Me_2PN)_n$ from $Me_3Si{-}N{=}PMe_2(OCH_2CF_3)$ is quantitative when heated *in vacuo* at 190° for 40 hours.[125]

The reaction of silylated monoamides, $Me_3SiNHP(O)X_2$ (X=OEt, NEt_2) with phosphorus(V) chloride does not give the expected trichlorophosphazenes, $X_2P(O){-}N{=}PCl_3$, but rather the isomeric *N*-dichlorophosphorylphosphazenes, $Cl_2P(O){-}N{=}PClX_2$:



Similarly, the phosphoryl-P,P-bis(trichlorophosphazene), $(EtO)P(O)(N{=}PCl_3)_2$, and the triphosphazene, $[ClP(N{=}PCl_3)_3]Cl$, are obtained from the silylated diamide, $(EtO)P(O)(NHSiMe_3)_2$, and triamide, $OP(NHSiMe_3)_3$, respectively. The reactivity of silylated amides to P-Cl compounds decreases in the order $PCl_5 > POCl_3 > ClP(O)(OEt)_2 > ClP(O)(NEt_2)_2$.[126] The silylated diazadiphosphetidene (55) decomposes in boiling acetonitrile to the cage phosphazene (56). On heating in a sealed tube at -156-8°, (56) is quantitatively converted into the adamantane isomer.[127]

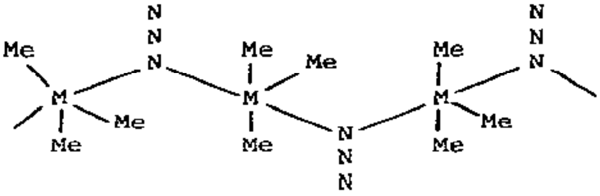


(55)

$R={}^iPr$

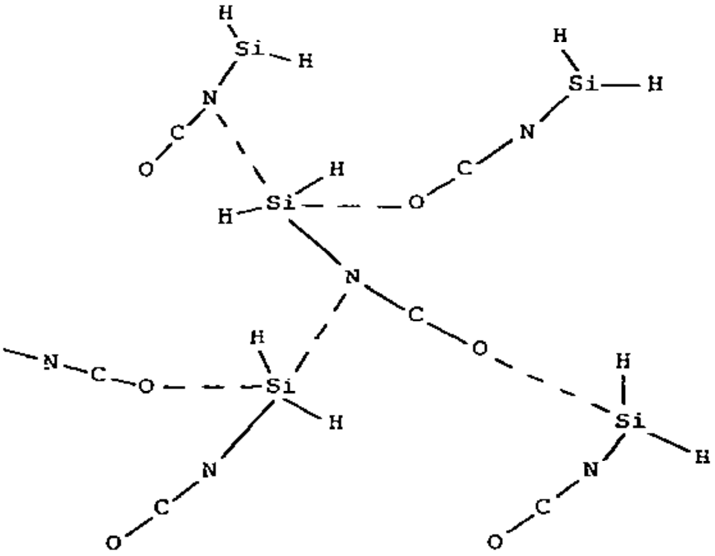
(56)

Trimethylsilyl azide reacts with the phosphazene-phosphanes, $R_3P{=}N{-}P(OR')_2$ ($R{=}Me$, NMe_2; $R'{=}CH_2CF_3$), affording the N-silylated diphosphazenes, $R_3P{=}N{-}P(OR')_2{=}N{-}SiMe_3$, which in air give the corresponding phosphazeno-phosphonamidic acid esters, $R_3P{=}N{-}P(O)(OCH_2CF_3)(NH_2)$. Thermolysis of the diphosphazene, $R_3P{=}N{-}P(OR')_2{=}N{-}SiMe_3$ ($R{=}Me$; $R'{=}CH_2CF_3$) yield the polymeric phosphazenylphosphazenes, $[N{=}P(N{=}PMe_3)OR']_n$.[128] The electrophilic cleavage of $(Me_3Sn)_2CN_2$ with trimethylsilyl azide in ether gives crystalline trimethyltin azide in excellent yield.[129] Trimethyllead azide is similarly obtained from $Me_3PbC(N_2)CO_2Et$ and trimethylgermanium azide.[130] Trimethyltin and -lead azides are isostructural with planar $[Me_3M]$ units α-bridged by azide groups giving almost perfect trigonal bipyramidal coordination for the metal (57).[129,130]



(57)

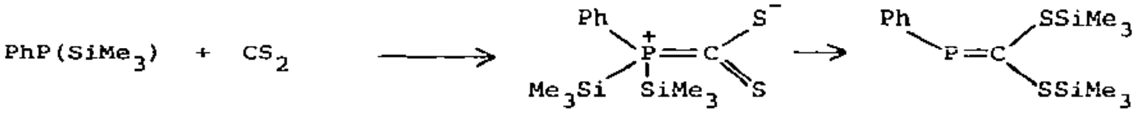
The crystal structures of silyl isocyanate, H_3SiNCO, and germyl isocyanate, H_3GeNCO, have been determined at -135° and -95°, respectively.[131] Both have similar structures involving crystallographic $C_s(m)$ molecular symmetry and heavy atom skeletons bent at nitrogen ($\widehat{SiNC} = 158.4^\circ$; $\widehat{GeNC} = 147.0^\circ$). The isocyanate group is almost linear in both cases. Intermolecular M···N and M···O interactions result in linear N···M-N groupings and distorted trigonal bipyramidal geometry at the metal (58); interactions which were proposed to be responsible for the increased M-N bond distances compared with those observed for isolated molecules in the gas phase.



(58)

4.4.4 Bonds to Phosphorus and Arsenic

Phenylbis(trimethylsilyl)phosphine reacts with carbon disulphide to yield the crystalline (silylsulphano)methylidenephosphine (59) via the red intermediate 1:1 adduct (60):[132]



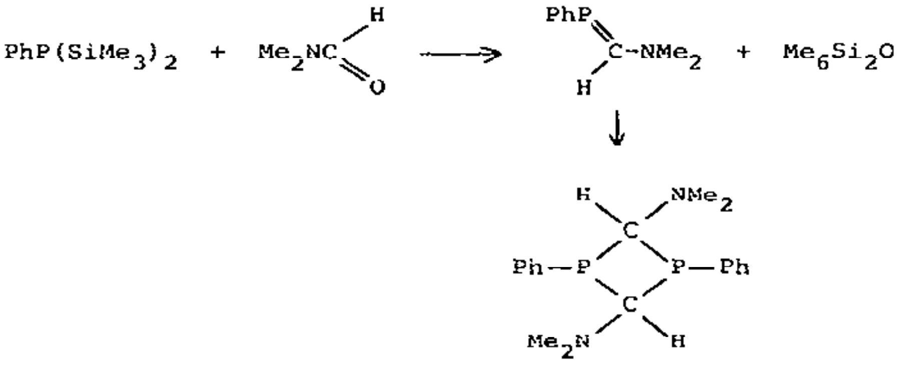
(60) (59)

With formaldehyde, $PhP(SiMe_3)_2$ affords the insertion product (61):

$$PhP(SiMe_3)_2 + 2H_2C{=}O \longrightarrow PhP(CH_2\text{-}O\text{-}SiMe_3)_2$$

(61)

An addition-elimination reaction takes place with dimethylformamide yielding hexamethyldisiloxane and N,N-dimethylaminomethylidenephneylphosphane, some of which undergoes dimerisation:[133]



The reaction of P-lithio bis(trimethylsilyl)phosphine with the complexes $cp(CO)_2FeX$ (X=Cl, Br) to give the complexes $cp(CO)_2Fe[P(SiMe_3)_2]$, which displaces carbon monoxide from $Ni(CO)_4$ and $Fe_2(CO)_9$ yielding the complexes $cp(CO)_2Fe[\mu\text{-}P(SiMe_3)_2]Ni(CO)_3$ and $cp(CO)_2Fe[\mu\text{-}P(SiMe_3)_2]Fe(CO)_4$, respectively. Upon u.v. irradiation, the latter complex is converted to the complex $cp(CO)Fe[\mu\text{-}CO,\mu\text{-}P(SiMe_3)_2]Fe(CO)_3$. Methanolysis of the complex results in cleavage of bridge Si-P bonds and the formation of $[PH_2]$-bridged complexes, which can also be obtained by reacting

$cp(CO)_2FeBr$ with $Me_3SiPH_2Ni(CO)_3$ and $Me_3SiPH_2Fe(CO)_4$.[134]

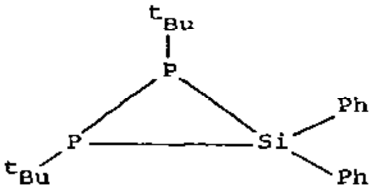
Cyclo-tetrakis(phenylphosphane), $(PPh)_4$, and cyclo-1,2,3-triphenyl-4-tert-butyltetraphosphane are the main products of the [3+1] cyclocondensation of $Me_3Si{-}PPh{-}PPh{-}PPh{-}SiMe_3$ with phenyl- and tert-butyldichlorophosphines, respectively.[135] Reaction of trimethylsilylphosphane with di-tert-butylmercury leads, via the symmetrical diphosphane, $H(Me_3Si)P{-}P(SiMe_3)H$, to the hitherto unknown tetrakis(trimethylsilyl)tetraphosphane (62):

$$\begin{tikzcd} 4Me_3SiPH_2 \;+\; 4\,{}^tBu_2Hg \arrow[r] & H(Me_3Si)P{-}P(SiMe_3)H \arrow[d] \\ & (Me_3Si)_4P_4 \end{tikzcd}$$

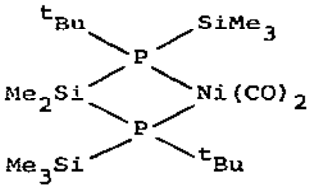
(62)

Additionally, cyclo-pentakis(trimethylsilyl)pentaphosphane can be identified in the reaction products. Solvolysis of (62) by methanol yields cyclo-P_5H_5, whereas thermolysis results in the formation of tris(trimethylsilyl)phosphine and silylphosphanes of higher phosphorus content.[136]

Crystallographic studies of the diphosphasilirane, $Ph_2Si(P^tBu)_2$ (63), show that the three-membered $[P_2Si]$ ring is almost perfectly triangular (P-P = 2.226Å, P-Si = 2.225Å).[137]

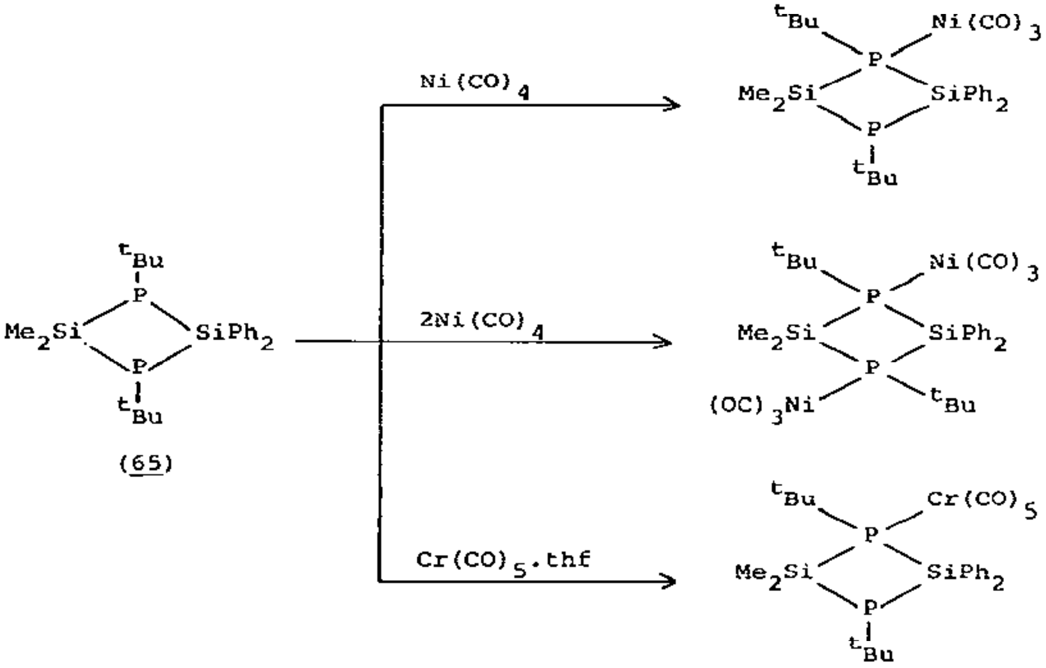


(63)



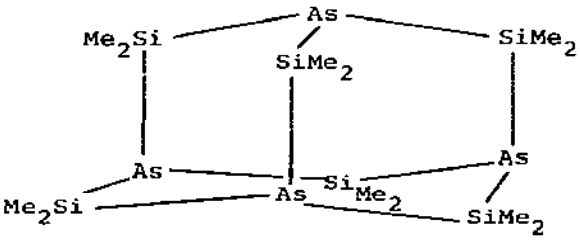
(64)

Linear, cyclic and cage silylphosphanes are good ligands towards transition metals. $Me_2Si[P(SiMe_3)^tBu]_2$ reacts with $Ni(CO)_4$ to yield the four-membered ring complex (64), which exists in two isomeric forms. The four-membered disiladiphosphetane (65) and hexamethyltrisilatetraphosphanortricyclene (66) also form similar complexes in which the skeleton of the ligand remains intact:[138-140]

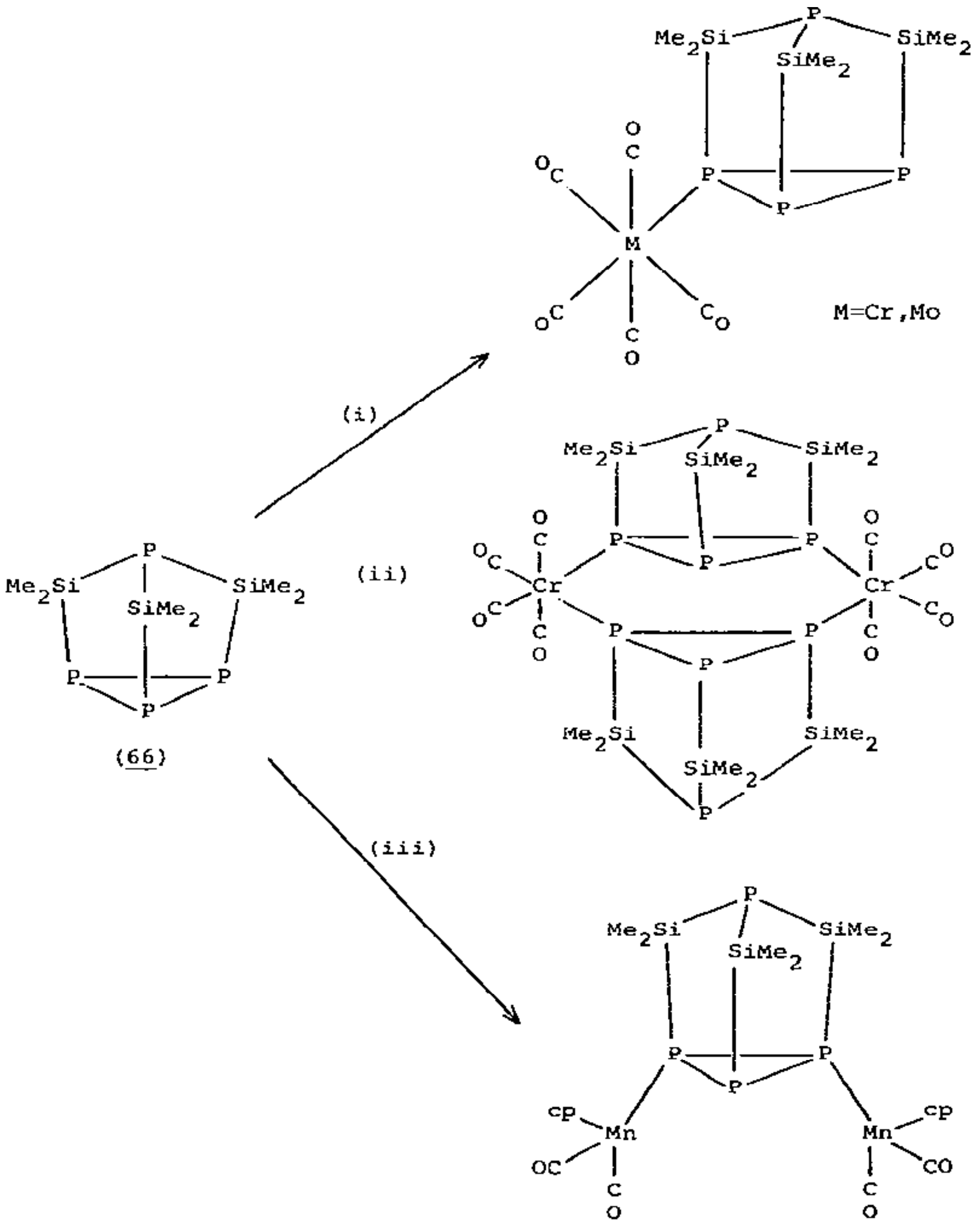


(65)

Tris(trimethylsilyl)arsine, $As(SiMe_3)_3$, can be obtained in 80-90% yield by the reaction of trimethylchlorosilane with "Na_3As/K_3As" (from Na/K and arsenic powder in dimethoxyethane). Treatment of $As(SiMe_3)_3$ with methyllithium in thf or dme affords the lithium salt $LiAs(SiMe_3)_2$, which crystallises with either two molecules of thf or one of dme. Reaction of $LiAs(SiMe_3)_2$ with primary or secondary alkyl halides produces bis(silyl)arsines, $RAs(SiMe_3)_2$, but with diphenylchloromethane and dibromoethane lithium-halogen exchange occurs and the diarsane, $(Me_3Si)_2AsAs(SiMe_3)_2$, is obtained. Treatment of the lithium salt with dimethyldichlorosilane results in the formation of $Me_2Si\ As(SiMe_3)_2\ _2$, which when heated to 240° for several days eliminates $As(SiMe_3)_3$ with the formation of <u>adamanta</u>- $As_4(SiMe_2)_6$ (<u>67</u>).[141]

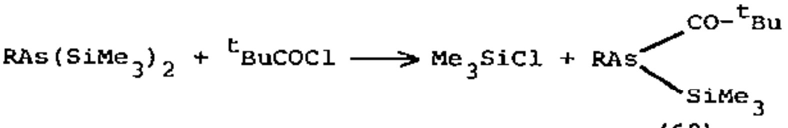


(<u>67</u>)



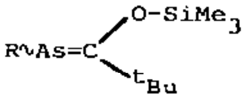
(i) $Mo(CO)_6$ or $Cr(CO)_5thf$, (ii) $Cr(CO)_5thf$, (iii) $Mn(cp)(CO)_2thf$.

Cleavage of one silicon-arsenic bond of the organo-bis(silyl)arsines, $RAs(SiMe_3)_2$, occurs on treatment with pivaloyl chloride giving (68), which isomerises to the enol isomer (69) at high temperatures:[142]



$$RAs(SiMe_3)_2 + {}^tBuCOCl \longrightarrow Me_3SiCl + RAs(CO{-}^tBu)(SiMe_3)$$

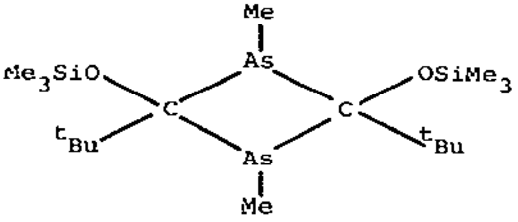
(68)



$$R{\sim}As{=}C(O{-}SiMe_3)({}^tBu)$$

(69)

U.v. irradiation causes the enolates (69) to dimerise to the diarsetanes (70), which contain a strained $[As_2C_2]$ ring with relatively long As-C bond distances.[143,144]



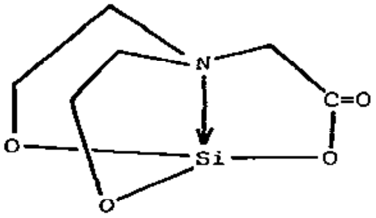
(70)

4.4.5 Bonds to Oxygen

The participation of silicon d orbitals in the siloxane bonds of H_3COSiH_3, $H_3SiOSiH_3$ and $H_3SiOOSiH_3$ has been investigated by *ab initio* termination of geometric and electronic structures of these molecules. $(p{\rightarrow}d)\pi$ bonding in the Si-O bond is of minor importance, whilst the ionic character of the bond is much higher than that estimated from electronegativity considerations.[145] Last year's report of square-planar coordinated silicon (in bis(*O*-phenylenedioxy)silane) has been contested. The principal criticisms were that the chemical identity of the crystal was not established (the cell dimensions reported are suspiciously close to those of catechol), that the space group was incorrectly assigned, and that disorder in the crystal could not be excluded.[146] A reply to these criticisms has also appeared.[147] In the gas-phase structure of silyl formate, the silyl group is twisted away (21°) from the planar cis conformation. However, the non-bonded Si...O contact is still unusually short (2.865Å) (Si-O = 1.695Å).[148]

The structure of octaphenyltetrasiloxane, $(Ph_2SiO)_4$, has been redetermined at room temperature. The eight-membered ring is almost planar, with two types of $\widehat{SiOSi}$ bond angle (153.2° and 167.4°).[149] Molecules of dodeca(phenylsilasesquioxane), $(PhSi)_{12}O_{18}$, contain four ten-membered and four eight-membered siloxane rings, and have crystallographic $\bar{4}$ (S_4) symmetry. The $[Si_{12}O_{18}]$ core approximates to $\bar{4}2m$ (D_{2d}) symmetry.[150] Liquid poly(methylphenylsiloxanes) react at 0° with Ti, V, Cr, Mo and W atoms giving high yields of bis(η^6-arene)metal complexes (arene = -Si(Ph)O- groups). The coloured complexes are very stable thermally, but are all sensitive to air and moisture. Condensation of atomic Fe, Co or Ni under similar conditions yields only a slurry of the metal, although at low temperatures an unstable arene-iron complex was observed.[151] Siloxy-aluminium compounds such as $LAl(O_2SiPh_2)$ and $(L_2Al)_2(O_2SiPh_2)$ (LH = 8-oxine, salicylaldehyde, 2-hydroxy-4-methoxybenzophenone) have been prepared by treating the isopropoxides, $L_nAl(OPr)_{3-n}$ with $Ph_2Si(OH)_2$.[152] The reaction of trimethylsilyl dichlorophosphate with antimony(V) chloride results in the formation of a 1:1 adduct.[153]

The structure of methylsilatrane has been investigated in the gas phase by electron diffraction at 185°. The molecule possesses C_{3v} symmetry with a Si--N distance of 2.45Å indicative of essentially no dative N→Si bonding. These results are quite different from the solid-state structure where dative bonding does occur and the Si-N distance is 2.175Å.[154] Dative N→Si interaction also occurs in crystalline meta-(trifluoromethyl)phenyl- and para-fluorophenylsilatranones (71), where the Si-N distances are 2.106Å and 2.129Å, respectively. Both compounds exhibit long (1.72Å) Si-OCO bond distances.[155] Intramolecularly coordinated pentacoordinated tin esters of N-methyliminodiacetic acid (72) have been obtained by the reaction of dialkyltin oxides or methoxides with the carboxylic acid in DMF. Their temperature dependent ^1H and ^{13}C n.m.r. spectra were interpreted in terms of a dissociative-inversion process. In water, coordination of solvent leads to the six-coordinated species (73).[156] Organostannatranes associate in apolar solvent to relatively stable trimeric units containing six-coordinated tin. 1-Methylstannatrane displays no autoassociation in aqueous solution. In contrast, 1-alkylthiostannatranes are monomeric in all solvents.[157]



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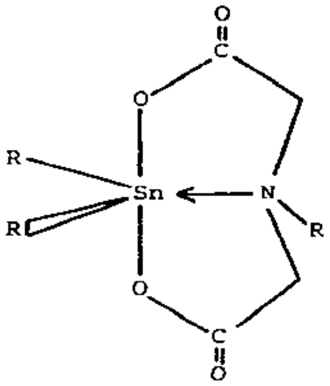

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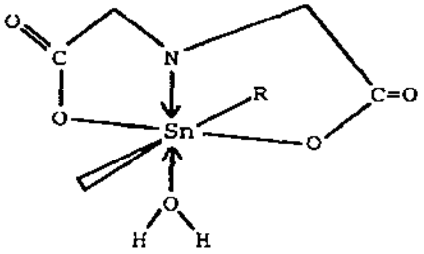
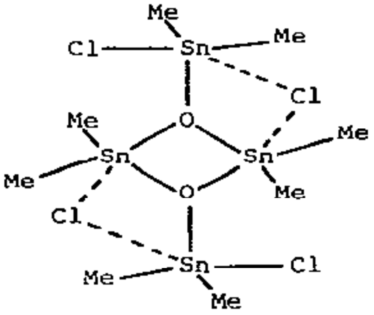


(73)

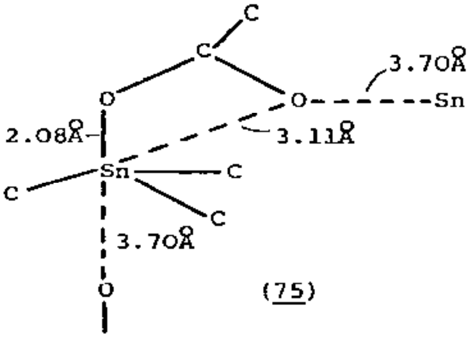
Crystals of dipotassium tris(oxalato)germanate(IV) hydrate contain two crystallographically independent tris-chelated anions with crystallographic C_2 symmetry and approximate D_2 molecular symmetry. The Ge-O bond distances and $\widehat{OGeO}$ angles are all close to the average values of 1.882Å and 85.6°.[158] The absolute configuration of the $(-)_{589}$-tris-(acetylacetonato)germanium(IV) cation has been shown to be Δ. The cation has approximate D_3 symmetry.[159]

The crystal structure and variable temperature Mössbauer data for the two distannoxanes, $[ClR_2SnOSnR_2Cl]_2$ (R=Me,Et) have been reported.[160] The structure of the methyl compound consists of the centrosymmetric dimeric units (74) which are held in a two-dimensional polymeric lattice by anionic chloride bridges. The central four-membered $[Sn_2O_2]$ ring is essentially planar, and the geometry of both endo and exo tin atoms is similar, both forming contacts to six neighbouring atoms in a distorted arrangement midway between trigonal bipyramidal and octahedral. The structure of the ethyl homologue is similar, but was only partially solved due to disorder. The major component (75%) has a similar structure to the methyl compound, but the structure of the second component is best described as a series of alternating $[R_4Sn_2O_2]$ and $[R_2SnX_2]$ units, in which two of the latter type chelate four-membered $[Sn_2O_2]$ rings. The variable temperature Mössbauer data for the ethyl derivative exhibits a discontinuity at ca. 110K attributed to a phase change involving a relaxation of the coordination about one of the two crystallographically independent tin atoms. Reaction of $[ClEt_2SnOSnEt_2Cl]_2$ with bipyridyl results in the extrusion of $Et_2SnCl_2\cdot$(bipyridyl) and the formation of the tristannoxane adduct, $[ClEt_2SnOEt_2SnOSnEt_2Cl]\cdot\frac{1}{2}$(bipyridyl), for which the Mössbauer data indicated similar trigonal bipyramidal geometry for all three tin atoms.[161]



(74)

Crystals of trimethyltin glycinate comprise stacks of linearly polymeric $[Me_3SnO_2CCH_2NH_2]$ molecules bridged axially at tin through the amino nitrogen. Additionally, hydrogen-bonding between the carbonyl oxygen and the amino group along the chains and between adjacent chains result in a perpendicular 'weave' of the one-dimensional polymer threads. The NSnO unit approaches linearity, but the tin atom is distinctly displaced towards oxygen resulting in non-polar $[SnC_3]$ units which are eclipsed in the one-dimensional chain.[162] The coordination at tin in tricylohexyltin trifluoroacetate can be considered as either distorted tetrahedral or trigonal bipyramidal considering the weak intermolecular Sn···O contact (75).[163] The two crystallographically independent molecules in crystals of $Me_3SnONPhCOPh$ have similar five-coordinate geometries (76), although the bond distances vary somewhat. In particular, in one the axial Sn-C bond distance is as expected longer (2.22Å) than the equatorial distances (mean 2.04Å), whereas in the other the equatorial Sn-C distances are marginally longer (2.18Å *versus* 2.16Å). In both molecules, the axial Sn-O distance is longer.[164]



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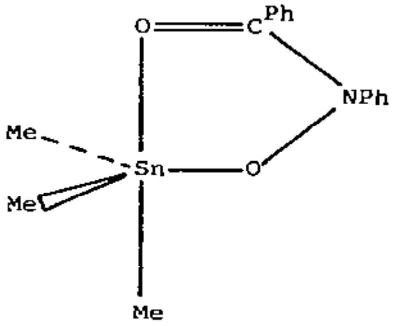
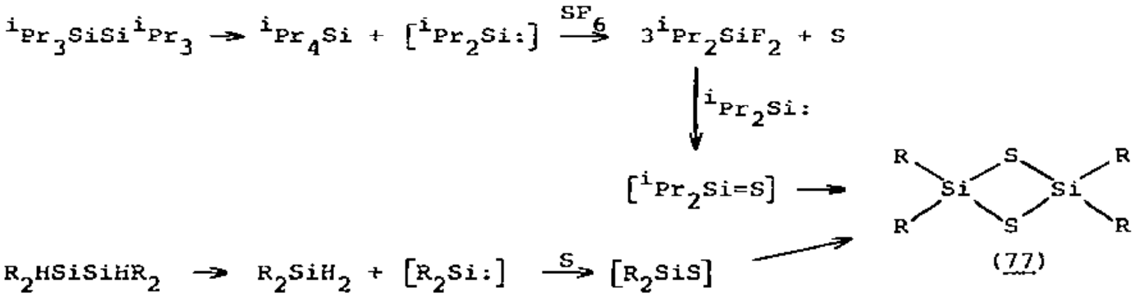


(76)

4.4.6 Bonds to Sulphur and Tellurium

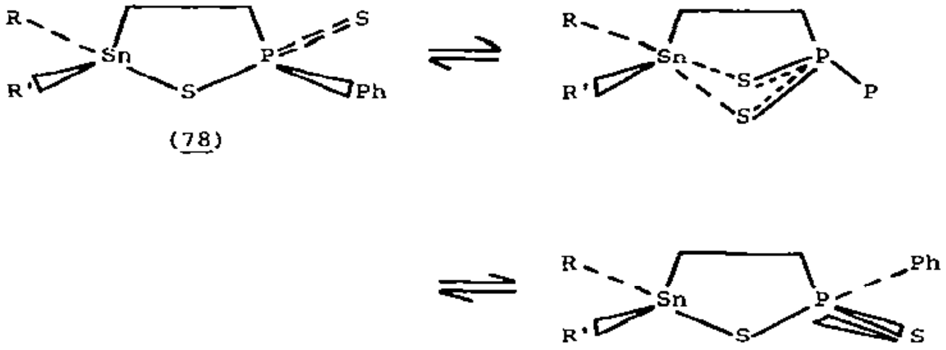
2,2,4,4-Tetraalkyl-1,3,2,4-dithiadisiletanes (77) containing bulky organyl groups may be obtained by copyrolysis of the disilanes R_3SiSiR_3 with sulphur or sulphur(VI) fluoride, or better by the reaction of the disilanes $R_2HSiSiHR_2$ (R=Me, ${}^{t}Pr$, ${}^{cyc}C_6H_{11}$, ${}^{t}Bu$) with sulphur:



$$\begin{tikzcd} {}^{i}Pr_3SiSi{}^{i}Pr_3 \arrow[r] & {}^{i}Pr_4Si + [{}^{i}Pr_2Si:] \arrow[r, "SF_6"] & 3\,{}^{i}Pr_2SiF_2 + S \arrow[d, "{}^{i}Pr_2Si:"] & \\ & & {[{}^{i}Pr_2Si{=}S]} \arrow[r] & (77) \\ R_2HSiSiHR_2 \arrow[r] & R_2SiH_2 + [R_2Si:] \arrow[r, "S"] & {[R_2SiS]} \arrow[ur] & \end{tikzcd}$$

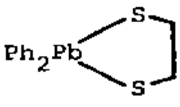
(77)

In the case of the tert-butyl compound, a considerable amount of tert-butyl groups isomerise to less crowded iso-butyl groups. Monomeric silathiones, $R_2Si=S$, are not available by this route.[165] Configuration inversion at phosphorus in 1,1-diorgano-3-phenyl-3-thio-1,2,3-stannathiaphospholanes (78) is indicated by the temperature dependence of the ^1H n.m.r. spectra. The activation parameters of the inversion process are consistent with a pentacoordinated intermediate:[166]



(78)

Triorganotin derivatives of dithiophosphate esters, $R_3SnS_2P(OR')_2$, may be obtained by dehydration of mixtures of the triorganotin hydroxide and $HS(S)P(OR')_2$ or by metathesis between the organotin chloride and the alkali metal salt. The products are crystalline solids except for the trimethyltin derivatives which are oils. Values of the two-bond n.m.r. coupling constant $^2J(Sn-C-H)$ for compounds in the methyltin series are consistent with four-coordinated tin, whilst mass spectra indicate the presence of monomers. Mössbauer data, however, specify five-coordination for the methyltin derivatives in the solid, but four-coordination for the cyclohexyl- and phenyl-tin homologues. Variable-temperature Mössbauer data for the two triphenyltin derivatives, $Ph_3SnS_2P(OR)_2$ ($R=Et, {}^iPr$), are consistent with monomeric molecules packed in a rather tight lattice.[167] The corresponding diorganotin bis(dithiophosphate) esters, $R_2Sn[S_2P(OR')_2]_2$, are available by similar synthetic routes, and are also either oils or crystalline solids soluble in organic solvents.[168] The two-bond coupling constant, $^2J(Sn-C-H)$, for the methyltin derivatives was again employed to demonstrate six-coordination for tin in solution, whilst mass spectra indicated monomers in the gas phase. The Mössbauer quadrupole splitting value was consistent with a six-coordinated trans octahedral solid-state geometry. Variable-temperature Mössbauer data for $SnPh_2[S_2P(O^iPr_2)]_2$ indicate a tightly bound monomeric lattice, which has been confirmed by an X-ray study.[169] The centrosymmetric structure consists of trans $[Ph_2Sn]$ units octahedrally coordinated by symmetrically chelating dithiophosphate ester groups. Metathesis between diphenyllead diacetate and α,ω-disodium dithiolates afford the lead-sulphur bonded heterocycles (79), (80) and (81). All three are hydrolytically stable, but are light sensitive. (81) exists in two modifications, and the X-ray structures of both as well as that of (79) have been determined (at -160°). The five-membered ring of (79) has an envelope conformation, whilst the eight-membered ring in one modification of (81), (81a), has a chair-chair conformation, but in the other modification, (81b), one molecule has a similar chair-chair conformation whilst the other crystallographically independent molecule has a boat-chair conformation. In the crystal, (79) forms infinite chains via intermolecular Pb---S interactions, giving rise to trigonal bipyramidal coordination for the lead with one long (3.55Å) and two short (2.52,2.49Å) Pb-S distances. Crystals of (81a) contain isolated molecules, with a clear [1,5]-transannular Pb---O interaction so that lead is again pentacoordinated (monocapped tetrahedra). Similar [1,5]-transannular interactions also occur in crystals of (81b), but additionally the two independent molecules are coupled via two intermolecular Pb---S bridges to form a dimer in which the lead atoms are hexacoordinated (bicapped tetrahedra). All three derivatives are monomeric in solution.[170]



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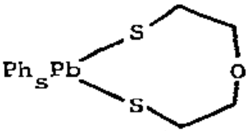

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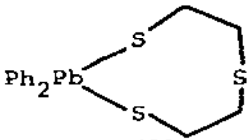


(81)

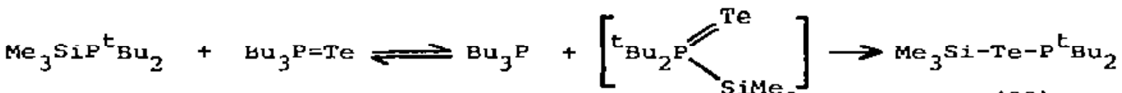
Silyl-, germyl- and stannyl-derivatives of methane and benzene tellurols, H_3MTeR (M=Si,Ge; R=Me,Ph) and Me_3HTeR (M=Si,Ge,Sn) can be synthesised by treatment of the organometal halides with either the lithium or trimethylsilyl arganyltellurol.[171] The products are pale yellow liquids characterised by persistent foul odours. When pure, they are stable for long periods at room temperature in sealed glass tubes. Water, HBr, HI, H_2 and methanol all cleave the Si-Te bond. On prolonged storage or in contact with laser excitation (488nm), the trimethylmetal tellurols undergo some disproportion to the symmetrical tellurides, eg:

$$2Me_3SnTeMe \longrightarrow (Me_3Sn)_2Te + Me_2Te$$

The silyl and germyl tellurides, H_3MTeR (M=Si,Ge), exhibit alternative decomposition routes:

$$H_3MTeMe \begin{cases} \xrightarrow{M=Ge} (H_3M)_2Te + Me_2Te \\ \xrightarrow[M=Si]{} H_2M(TeMe)_2 + MH_4 \end{cases}$$

The phosphane telluride, $Bu_3P{=}Te$, reacts with the silylphosphine, $Me_3SiP^tBu_2$, to yield the silyl tellurophosphane (82):



(82)

Elemental tellurium inserts into the Group IV metal-phosphorus bonds of the trimethylmetal phosphines, $Me_3EP^tBu_2$, yielding the trimethylsilyl-, germyl- and -stannyl-tellurophosphines $Me_3ETeP^tBu_2$ (E=Si,Ge,Sn). The expected intermediates, $^tBu_2P({=}Te)EMe_3$, are not sufficiently long-lived to permit detection. The metal tellurophosphines cannot be obtained pure because their rapid formation is followed within a few hours by the redistribution equilibria:[172]

$$Me_3ETeP^tBu_2 \rightleftharpoons (Me_3E)_2Te + {}^tBu_2PTeP^tBu_2$$

4.4.7 Bonds to Halogen

Silicon(IV) fluoride and $[Bu_4N]^{\cdot}[BH_4]$ react in dichloromethane to yield $[Bu_4N][BH_3SiF_3]$ and $[Bu_4N][BH_2(SiH_3)_2]$. The reaction appears to be unique to SiF_4 and dichloromethane, since only decomposition reactions occur in other solvents and the reaction with germanium(IV) chloride gives only the tetrafluoroborate anion.[173] Pyrolytic graphite is not intercalated by GeF_4 alone, but is by GeF_4-F_2 mixtures to yield at the intercalation limit at 20° a first-stage material $C_{12}GeF_{5-6}$, which is in equilibrium with gaseous fluorine.[174] Tin(IV) chloride forms a 1:2 adduct with S_4N_4, $SnCl_4(S_4N_4)_2$, which is reduced by hydrated tin(II) chloride to $S_4(NH)_4$.[175] ^{35}Cl n.q.r. data has been recorded at various temperatures of a number of other adducts of tin(IV) chloride of the type $SnCl_4 \cdot 2L$ (L=MeCN, CH_2CHCN, ^tBuCN, $CH_2(CN)_2$, 1,2-$C_6H_4(CN)_2$, Me_2O or tetrahydrothiophen), and used to deduce the stereochemistry. All the adducts were *cis* save for the tetrahydrothiophen adduct which was *trans*. The ^{35}Cl n.q.r. frequencies are related to the Sn-Cl bond distance in such systems; higher frequencies tend to be associated with the shorter bonds, although the frequencies also vary markedly with temperature. The formation of CF_3SnBr_3 and $(CF_3)_2SnBr_2$ from the reaction of $Hg(CF_3)_2$ and tin(IV) bromide at 112, 121 and 130° has been followed in a semi-kinetic manner. The data indicate that the trifluoromethyltin bromides are easily formed in reactions that proceed to equilibria, but the decomposition of more fully substituted species, such as $(CF_3)_3SnBr$, is almost immediate, and severely limits the temperature range which can be utilized. Methylation using dimethylcadmium or methyllithium affords the corresponding methyl(trifluoromethyl)tin compounds. Reduction of CF_3SnBr_3 with lithium aluminium hydride gives some evidence for the formation of CF_3SnH_3.[177]

(Chloromethyl)trichlorosilane possesses a staggered conformation in the gas phase with a barrier to internal rotation of *ca*. 10 kJ mol^{-1}.[178] The barriers to internal rotation of the cyclopentadienylgermanium halides, $C_5H_5GeX_3$ (X=Cl,Br,I), determined from their vibrational spectra are very similar in both the solid and gas phases (gas phase: X=Cl (24 cm^{-1}), X=Br (22.5 cm^{-1}), X=I (22 cm^{-1}); solid: X=Cl (27.5 cm^{-1}), X=Br (26 cm^{-1}), X=I (25 cm^{-1}).[179]

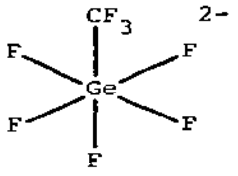
^1H n.m.r. spectra of *o*-$(Me_2NCH_2)C_6H_4SiX_2R$ and *o*-$(Me_2NCH_2)C_6H_4SiXR^1R^2$ indicate that the intramolecular Si←N coordination is controlled by the ability of the Si-X bond to be stretched and substituted with inversion of configuration. The results suggest that a close relationship between the rate of racemisation of halogenosilanes, the substitution of R_3SiX with inversion of configuration, and the ease of pentacoordination at the silicon atom. The pentacoordination and racemisation abilities vary with X in the order

$H \sim OR < F \sim SR < OAc \sim Cl \sim Br$.[180]

A potentiometric method employing solid-state fluoride electrodes has been used to observe the free H^+ and F^- ion concentrations in fluorosilicate equilibria in aqueous solution at 0-60°. In dilute silicic acid solutions, the predominant reaction can be expressed as:

$$Si(OH)_{4\,aq} + 4H^+ + 6F^- \rightleftharpoons SiF_6^{2-} + 4H_2O$$

Evidence was observed for the existence of small amounts of additional species with fewer fluorides under certain conditions, but a regular sequence of $[Si(OH)_{4-x}F_y{}^{x-y}]$ anions does not occur.[181] Readily soluble (trifluoromethyl)fluorogermanate anions of the types $[(CF_3)_nGeF_{6-n}]^{2-}$ (n=1,2) and $[(CF_3)_3GeF_2]^-$ can be obtained by the addition of fluoride anion to the appropriate (trifluoromethyl)germanium halides. In the presence of excess fluoride, intermolecular fluorine exchange is slow enough for coupling between the trifluoromethyl and fluorine ligands to be observable in the ^{19}F n.m.r. spectra, from which it could be shown that the species (83), (84) and (85) exist in solution.



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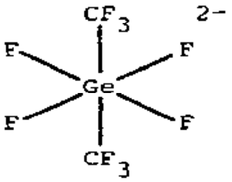

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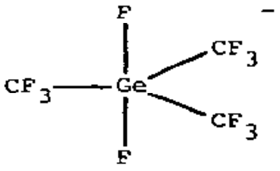
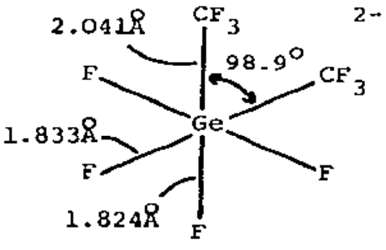


(85)

Although the *trans* isomer (84) exists to >90% extent in solution (unequivocal evidence for the presence of the corresponding *cis* isomer could not be obtained), the potassium salt crystallises as the *cis* isomer (86), which was confirmed by an X-ray analysis. The Ge-C bond distance in the *cis* isomer is somewhat larger than in $Ge(CF_3)_4$, as is the Ge-F bond distance compared to that in K_2GeF_6. Structural data are shown in (86).[182]

An X-ray study of the organotin bromide $SnMePh[C_{10}H_5(OMe\text{-}5)(CH_2NMe_2\text{-}8)]Br$ shows it to possess the five-coordinated structure (87), with a coordinate Sn←N bond distance of 2.410Å. Dynamic ^1H n.m.r. spectra show that the trigonal-bipyramidal structure is retained in solution. In the slow exchange



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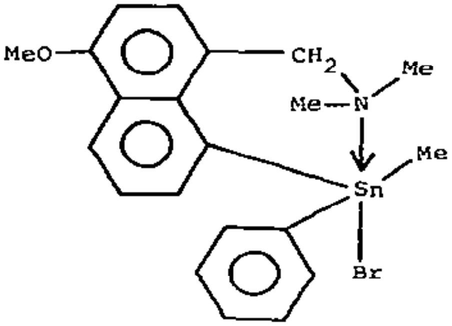
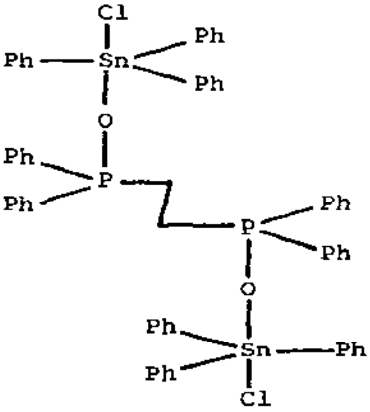


(87)

limit, (87) exists in two diastereomeric forms as a result of the puckering of the chelate ring and the chirality at the tin centre. On raising the temperature, two different processes occur, the first of which involves interconversion between the two ring conformers. The second process (either Berry pseudo-rotation processes in the five-coodinated conformer, or Sn-N bond dissociation followed by combined pyramid inversion at nitrogen and rotation about the C-N bond) is difficult to define because of coincidence of the methylene and methoxyl resonances. Dynamic ^{1}H n.m.r. of MePhSn$[CH_2C_6H_4(CH_2NMe_2\text{-}2)]$Br reveal that the six-membered chelate ring containing two sp^3 hybridised carbon atoms is very flexible compared with the five-membered ring in MePhSn$[C_6H_4(CH_2NMe_2\text{-}2)]$Br.[183] The bis(phosphine oxide) donor functions as a bridging ligand in the adduct $(Ph_3SnCl)_2\cdot OPh_2PCH_2CH_2PPh_2O$. Both tin atoms have usual trigonal bipyramidal coordination (88).[184]



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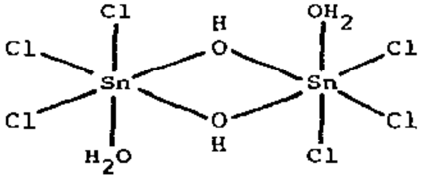


(89)

The crystal structure of several hydroxyhalotin adducts of the general composition $[Sn_2X_6(OH)_2(OH_2)_2]\cdot nL$ have been determined.[185] The Lewis base molecules are hydrogen-bonded to a hydroxo-bridges dimer (*89*) based on *fac*-octahedral coordination. With X=Cl and nL=3 dioxane, all the hydrogen atoms of the dimer participate in bonds to 1,4-dioxane molecules, and each dioxane oxygen atom participates in one hydrogen bond resulting in a layer structure. No such extended structure occurs with X=Cl or Br and $nL=4C_{10}H_{18}O$ (1,f-epoxy-*p*-menthane). With X=Cl and $nL=4H_2O$, hydrogen-bonding to lattice water links the dimers into chains, which are cross-linked by weak $Cl{-}{-}{-}H_2O$ bonds. Tin(IV) chloride pentahydrate is best regarded as $[SnCl_4(OH_2)_2]\cdot 3H_2O$, with *cis* octahedral complexes linked into a three-dimensional network via $H_2O{-}{-}{-}H_2O$ and $Cl{-}{-}{-}H_2O$ hydrogen bonds. The phosphine oxide and arsine oxide complexes of the general formula $Me_2SnCl_2\cdot 2L$ ($L=R_3PO$, R_3AsO, $(RO)_3PO$, $(RO)_3AsO$, $(R'O)_2RPO$ and $(R'O)_2RAsO$) in solution participate in dissociation equilibria which have been studied by n.m.r. According to the initial ratio of Me_2SnCl_2 and L, these equilibria may involve the species $Me_2SnCl_2\cdot nL$ (n=1-4). When $L=Et_3AsO$, all four complexes have been isolated and characterised in the solid-state.[186] Dissociation constants of trimethyllead chloride in water and methanol at 26° have been determined from ^{207}Pb n.m.r. data to be 0.51 mol ℓ^{-1} and 4.65×10^{-4} mol ℓ^{-1}, respectively.[187] Triphenyllead halides form monomeric, trigonal bipyramidal 1:1 adducts, $Ph_3PbX\cdot HMPA$ (X=Cl,Br,I) with hexamethylphosphoramide. The 1:2 complexes, $Ph_2PbX_2\cdot 2HMPA$ (X=Cl,Br,I) are also monomeric, with a *cis* octahedral geometry, but the 1:1 adducts $Ph_2PbX_2\cdot HMPA$ (X=Br,I) are halogen-bridged polymeric materials with six-coordinated lead. The adducts $Ph_3PbX\cdot HMPA$ dissociate in benzene; the degree of dissociation being in the order $NCS \ll Cl < Br < I$.[188]

4.4.8 Bonds to Main Group Metals

Crystals of hexameric trimethylsilyllithium, $(LiSiMe_3)_6$, comprise discrete centrosymmetric hexameric units with a core of lithium atoms surrounded by $[Me_3Si]$ groups. The geometry of the $[Li_6]$ core can either be described in terms of a six-membered ring in a highly folded chair conformation with an acute seat-to-back angle, or, alternatively, as a distorted octahedron severely compressed along a three-fold axis so as to form a shortened trigonal antiprism. The $[Me_3Si]$ groups lie above the six triangular side faces.[189] Hexameric trimethylsilyl lihtium reacts with tetramethylethylenediamine to yield the crystalline complex $(LiSiMe_3)_2(TMED)_3$, and with simple aromatic and unsaturated compounds containing acidic protons in a fashion similar to alkyllithium reagents giving simple metalated products and trimethylsilane. The complex, $(LiSiMe_3)_2(TMED)_3$, reacts similarly also to yield metallated products, but with benzene trimethylphenylsilane and lithium hydride are produced quantitatively. With toluene and other methylbenzenes, the TMED complex attacks the methyl substituent affording (trimethylsilyl)methyl-substituted benzene derivatives.[190] Silicon-hydride and silicon-silicon bonds are quantitatively cleaved by alkali metals either in dimethoxyethane at 40°, HMPA at room temperature, or (for sodium hydride) in THF in the presence of 18-crown-6 at room temperature:

$$R_3SiH + KH \longrightarrow R_3SiK + H_2$$

$$Me_3SiSiMe_3 + KH/NaH \longrightarrow Me_3SiK/Na + Me_3SiH$$

The trialkylsilylsodium and -potassium derivatives undergo coupling reactions with alkyl, allyl and benzyl halides, and with α-enones.[191]

Reaction of trimethylsilyllithium with trimethoxyborane in hexane yields lithium tetrakis(trimethylsilyl)borate as a microcrystalline powder soluble in pentane and hexane:[192]

$$4Me_3SiLi + B(OMe)_3 \longrightarrow Li[B(SiMe_3)_4]$$

Treatment of trimethylchlorosilane with aluminium and lithium metal in THF/benzene or ether in the presence of mercury yields tris(trimethylsilyl)aluminium solvated with either THF or ether. Unsolvated $Al(SiMe_3)_3$ can be obtained by the reaction of $Na[Al(SiMe_3)_4]$ with aluminium(III) chloride in pentane:[193]

$$Al + 3Me_3SiCl + 3Li \longrightarrow (Me_3Si)_3Al \cdot S$$

$$3NaAl(SiMe_3)_4 + AlCl_3 \longrightarrow 4Al(SiMe_3)_3 + 3NaCl.$$

The ether complex, $Al(SiMe_3)_3 \cdot OEt_2$, adds to alkynes in a <u>syn</u> fashion to give vinylsilanes in high yield:[194]

$$(Me_3Si)_3Al\cdot OEt_3 \xrightarrow{HC\equiv CR} (E)\text{-}Me_3SiCH{=}CHR$$

With disubstituted alkynes, addition only occurred with increased concentrations of $Al(SiMe_3)_3\cdot OEt_2$ and with aluminium(III) chloride as catalyst. The silyl-gallium analogue, $Ga(SiMe_3)_3\cdot THF$, has been obtained according to the reaction:

$$GaCl_3 + 6Li + 3Me_3SiCl \xrightarrow{THF} Ga(SiMe_3)_3\cdot THF + 6LiCl$$

The product resembles the indium analogue more closely than the corresponding aluminium derivative.[195]

The photodecomposition of disilane at 147nm affords dihydrogen, SiH_4, Si_3H_8, Si_4H_{10}, Si_5H_{12} and a solid film of an amorphous silicon hydride as products. Three primary processes were proposed to account for the results (quantum yields in parentheses):[196]

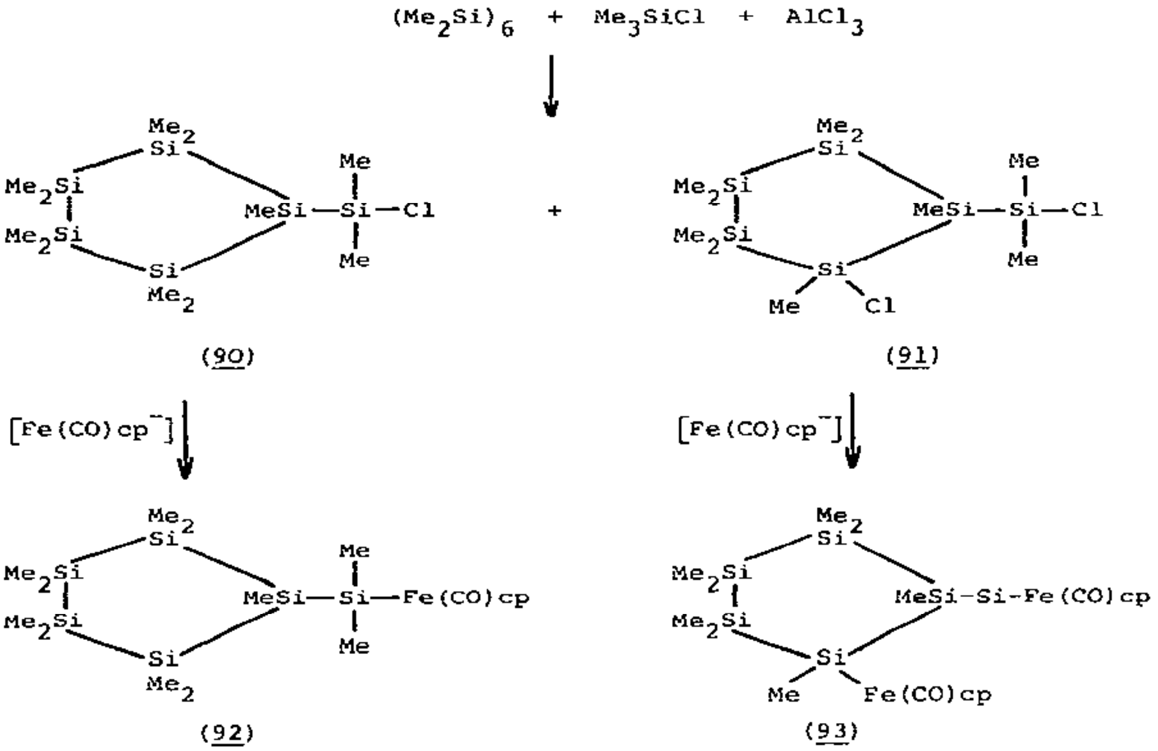
$$\text{(a)}\quad Si_2H_6 + h\nu \longrightarrow SiH_2 + SiH_3 + H \quad (\phi a = 0.61)$$

$$\text{(b)}\quad Si_2H_6 + h\nu \longrightarrow SiH_2{:}SiH_2 + 2H \quad (\phi b = 0.18)$$

$$\text{(c)}\quad Si_2H_6 + h\nu \longrightarrow Si_2H_5 + H \quad (\phi c = 0.21)$$

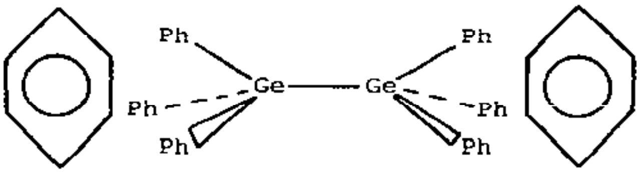
Dimethylzinc is the preferred methylating agent for the conversion of the perchlorocyclosilanes, $(Cl_2Si)_n$ (n=4,5), to the corresponding permethylated compounds.[197] Vibrational data for octachloro- and octabromocyclotetrasilanes indicate that the $[Si_4]$ ring is not planar. The Si-Si stretching force constants are lower than in the corresponding perhalogenated five- and six-membered ring compounds.[198] Elemental sulphur and selenium insert into decamethylcyclopentasilane in decalin at 190° to afford the six-membered ring compounds $(Me_2Si)_5E$ (E=S,Se). Dodecamethylcyclohexasilane is unreactive under the same conditions.[199] Redistribution equilibria between the permethylatedcyclosilanes, $(Me_2Si)_n$ (n=5,6,7), have been studied in the temperature range 30-58°.[200] Enthalpies indicate that the stabilities of the rings increase in the order 5<7<6, but the differences are smaller than the differences between the corresponding cycloalkanes, probably because the silicon compounds are less affected by steric repulsions and angle strain. Reaction of dodecamethylcyclohexasilane with

Me_3SiCl and $AlCl_3$ affords a mixture of the two five-membered ring compounds (90) and (91), the chlorines in which can be substituted by $[Fe(CO)cp^-]$ to afford (92) and (93), respectively:



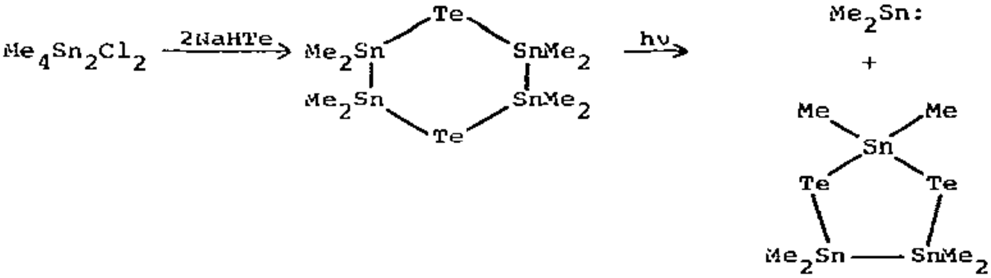
In the $[Si_5]$ fragment of (92), four of the silicon atoms are coplanar, but the fifth is 1.02Å out of the plane. In (93), the second iron atom is attached at the 2 position of the ring, which is in a distorted C_s conformation.[201]

Crystals of the dibenzene solvate of hexaphenyldigermane exhibit an unusual sandwich structure as shown in (94), in which each Ge_2Ph_6 molecule is sandwiched between the two benzene molecules.[202] The four-membered ring in octaphenylcyclotetragermane is nearly planar and square.[203] Several modifications of dodecaphenylcyclohexagermane can be isolated from solution. From benzene, crystals containing either two or seven molecules of solvent may be obtained, whereas from toluene a disolvate crystallises.[204]



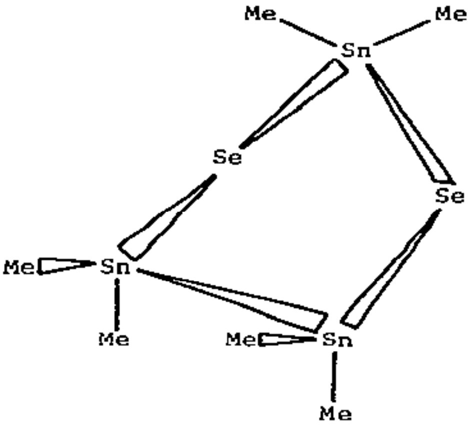
(94)

The preparation and properties of eight distannane derivatives of the type $Me_4Sn_2X_2$ ($X=O_2CR$, S_2CNR_2, $S_2P(OR)_2$) have been described. Their synthesis was accomplished by substitution of $Me_4Sn_2Cl_2$ in aqueous media. In contrast to other tetramethyl distannanes, these derivatives are inert to oxidation by atmospheric oxygen and can be recrystallised without difficulty. Spectroscopic data indicate that the groups X function as isobidentate ligands. The tin-tin coupling constants are extremely large (ca. 11-15kHz), and can be correlated with the pKa values of the corresponding acids HX.[205] Substitution of $Me_4Sn_2Cl_2$ with NaHTe yields the crystalline heterocycle $Me_6Sn_4Te_2$, which undergoes light-induced disproportionation reactions involving the generation of dimethylstannylene:



The stannylene can be trapped either by methyliodide, or by the parent compound itself, when five-membered ring compounds with $[Sn_3Te_2]$ and $[Sn_4Te]$ skeletons are produced.[206]

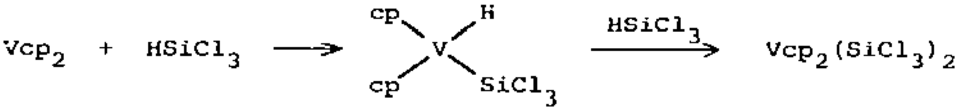
The five-membered ring in 2,2,4,4,5,5-hexamethyl-1,3-diselena-2,4,5-tristannolane (95) is puckered, with short intermolecular Se···Sn contacts (3.76 - 3.98Å).[207]



(95)

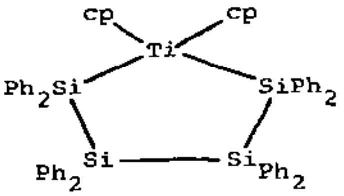
4.4.9 Bonds to Transition Metals

The bis(silyl)vanadium complex, $Vcp_2(SiCl_3)_2$, has been isolated by the treatment of dicyclopentadienylvanadium with trichlorosilane in benzene, presumably via an intermediate oxidative-addition step:



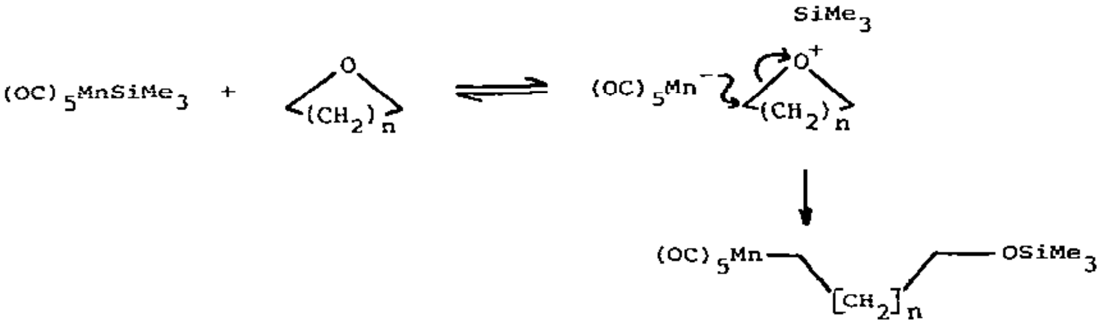
$$Vcp_2 + HSiCl_3 \longrightarrow cp_2V(H)(SiCl_3) \xrightarrow{HSiCl_3} Vcp_2(SiCl_3)_2$$

The analogous tungsten complex, $Wcp_2(H)(SiCl_3)$, can similarly be obtained from Wcp_2H_2 and $SiHCl_3$.[208] Reaction of $Ticp_2Cl_2$ with $Al(SiMe_3)_3$ or $Li\ Al(SiMe_3)_4$ in ether yields the stable silyltitanium complex, $Ticp_2(SiMe_3)Cl$, which has a distorted tetrahedral geometry at titanium and a Ti-Si bond distance of 2.67Å. The corresponding reaction of $Ticp_2Cl_2$ with $Al(GeMe_3)_3{\cdot}OEt$ affords $Ticp_2(GeMe_3)Cl$.[209] Ring-closure occurs on reaction of $Ticp_2Cl_2$ with α,ω-$Li_2Si_4Ph_8$ giving the five-membered ring compound (96) as a green, air-stable solid, which decomposes >140° *in vacuo* to a red-brown tar. The heterocycle is unstable in chloroform solution, and forms bis-solvates with THF, acetone, benzene and toluene.[210]



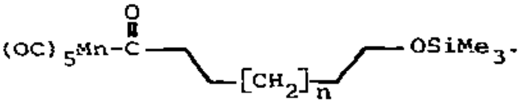
(96)

Ring-opening and metal-carbon bond formation occurs when $(OC)_5MnSiMe_3$ is treated with cyclic ethers with ring size ≤5:



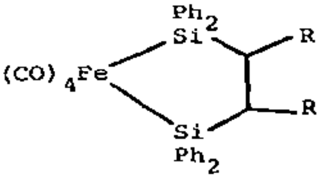
(97)

When the reaction is carried out under a pressure of 200 lb in^{-2} of CO, the ring-opened products (97) are converted in high yield to the corresponding acyl-manganese complexes,

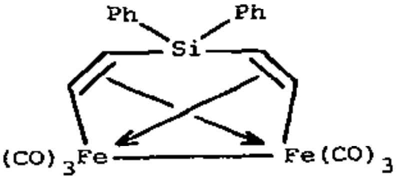


$(OC)_5Mn-C(=O)-CH_2-[CH_2]_n-CH_2-OSiMe_3$. [211]

The silyl-iron complex, $[Fe(CO)_4SiPh_2]_2$, is readily obtained from $Fe(CO)_5$ and diphenylsilane, and reacts under photolysis with alkynes, RC≡CR, to afford two complexes (98) and (99):

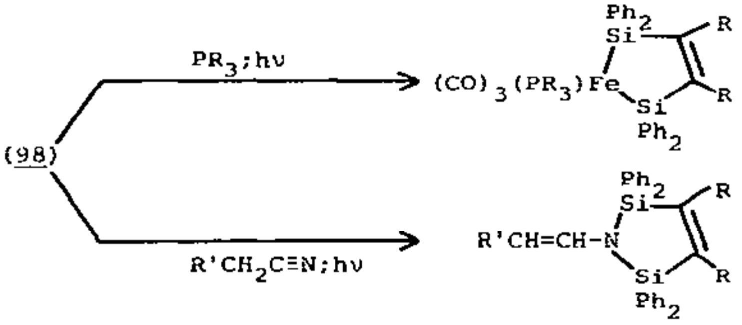


(98)

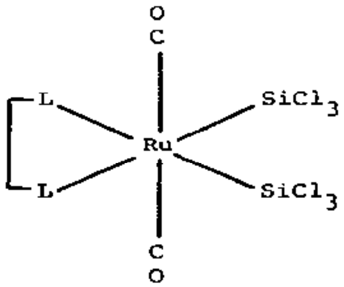


(99)

Reaction of (98) with tertiary phosphines proceeds by displacement of CO, but rather unexpectedly photolysis in the presence of organic cyanides results in cleavage of the Fe-Si bonds:[212]

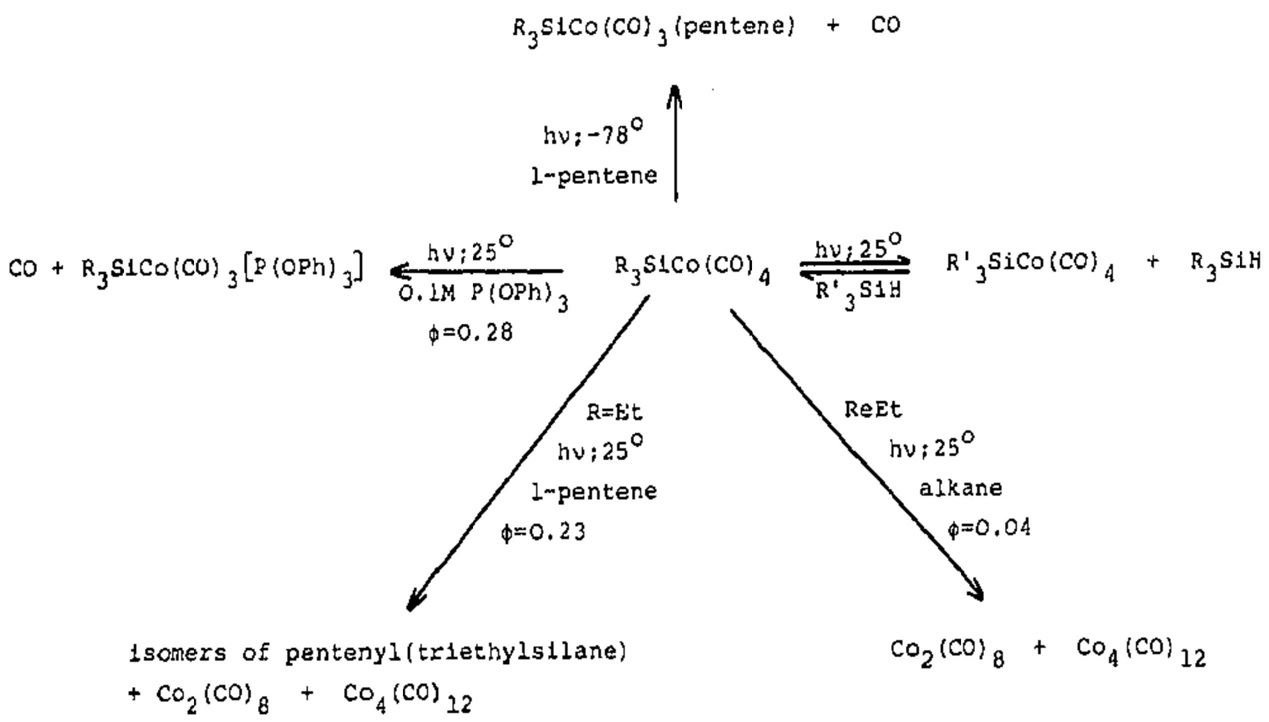


U.v. irradiation of $Ru_3(CO)_{12}$ with excess trichlorosilane in hexane under CO leads to the formation of *cis*-$R(CO)_4(SiCl_3)_2$, which readily undergoes substitution with ligands L at room temperature to yield *mer*-$Ru(CO)_3L(SiCl_3)_2$ complexes. The synthesis of the corresponding *cis*- iron and osmium complexes can be achieved similarly, but substitution reactions with these require much more forcing conditions.[213] With bidentate ligands, *cis*-$Ru(CO)_4(SiCl_3)_2$ affords octahedral substitution products (100). When L-L = $Ph_2ECH_2CH_2EPh_2$ (E = P,As), the bridged derivatives $(Cl_3Si)_2(OC)_3Ru(L-L)Ru(CO)_3(SiCl_3)_2$, can also be isolated.[214]



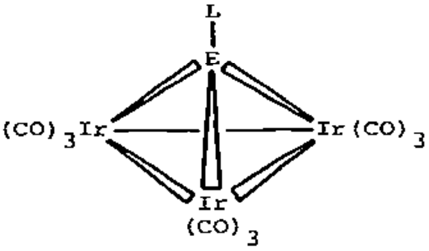
(100)

The photochemistry of trialkylsilyltetracarbonylcobalt has been studied in depth.[215] The major primary photoreaction is dissociative loss of CO. Principal reactions are summarised in Scheme 7. Several silyl-cobalt(I) complexes of the type $[Co(SiR_3)(CO)_nL_{4-n}]$ (R=F, n=1-3; R=Ph,OEt, n=2,3; L=tertiary phosphine


R3SiCo(CO)3(pentene) + CO
hν; -78°
1-pentene
CO + R3SiCo(CO)3[P(OPh)3]
hν;25°
0.1M P(OPh)3
ϕ=0.28
R3SiCo(CO)4
hν;25°
R'3SiH
R'3SiCo(CO)4 + R3SiH
R=Et
hν;25°
1-pentene
ϕ=0.23
ReEt
hν;25°
alkane
ϕ=0.04
isomers of pentenyl(triethylsilane)
+ Co2(CO)8 + Co4(CO)12
Co2(CO)8 + Co4(CO)12

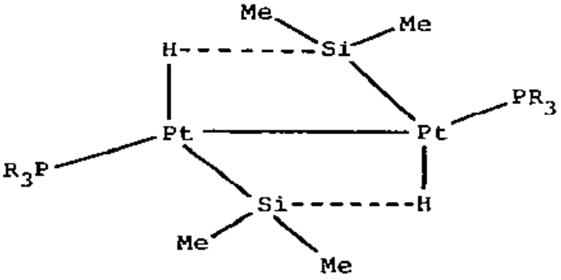
Scheme 7.

or arsine), have been synthesised and studied. For R=Ph, substitution of CO occurs rapidly yielding the unstable *cis*-[$Co(SiPh_3)(CO)_3(PPh_3)$] complexes, which isomerise slowly to the stable *trans* form. When R=Et, however, decomposition occurs to give Si_2Et_6 and [$Co(CO)_3(PPh_3)$]$_2$. Three different geometric isomers of the complexes [$Co(SiR_3)(CO)_2L_2$] were obtained according to the preparative route used.[216] $NaIr(CO)_4$ reacts with Cl_3CL (L=Me,Ph), $SiCl_3Me_3$ or $GeCl_3Me$ to yield the cluster compounds, $(CO)_9Ir_3CL$, $(CO)_9IrSiMe$, and $(CO)_9IrGeMe$, respectively, which by comparison with the well-established methylidene clusters were assigned the structure (101).[217]



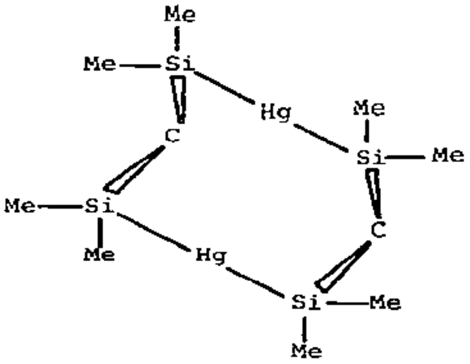
(101)

The silyl-platinum complex {$Pt(\mu-H)(SiMe_2Ph)[P(C_6H_{11})_3]$}$_2$ decomposes in refluxing hexane to afford a low yield of the complex {$PtH(\mu-SiMe_2)[P(C_6H_{11})_3]$}$_2$, which possesses crystallographic C_i symmetry. The two platinum atoms are unsymmetrically bridged by the two dimethylsilyl groups [Pt-Si = 2.420, 2.324Å] as shown in (102). The platinum, silicon and phosphorus atoms are essentially coplanar, and the hydride ligands are located *trans* to the shorter of the Pt-Si bonds at a Pt-H distance of 1.78Å. These sites are also only 1.72Å from the silicon atoms, and so the hydrogen atoms might therefore be considered as bridging the Pt-Si bonds.[218]

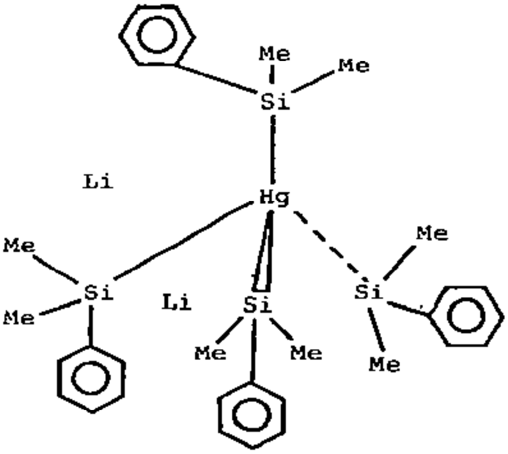


(102)

The structures of four silyl-mercury derivatives have been determined. Both octamethyltetrasila-1,5-dimercuracyclooctane (103) and bis(triphenylsilyl)mercury contain linear [Si-Hg-Si] groups. In the former, these groups are linked by methylene bridges to give the eight-membered heterocycle in a chair conformation.[219] Both the lithium metallates, $Li_2Hg(SiMe_2Ph)_4$ (104) and $Li_2Hg(SiMe_3)_4$ (105), contain mercury in approximately tetrahedral coordination by four silyl groups. Crystals of (104) comprise discrete formula units with mercury on a two-fold axis of symmetry, and with the lithium cations enclosed in a cage of silicon and carbon atoms Zig-zag chains of $[Li_2Hg(SiMe_3)_4]$ units occur in (105), where individual units are held together by lithium atoms which serve as bridges between the $[Hg(SiMe_3)_4]$ moieties of the chains.[220]

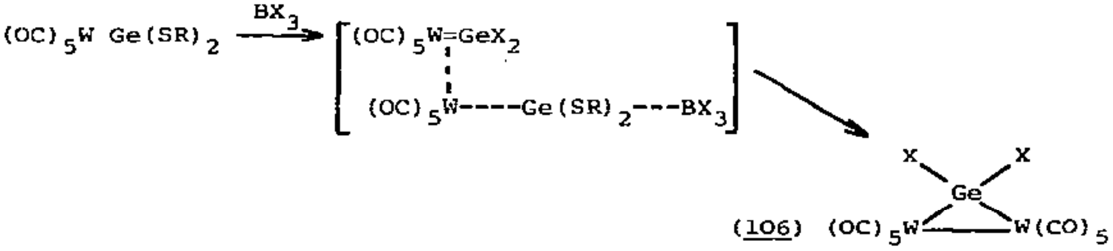


(103)



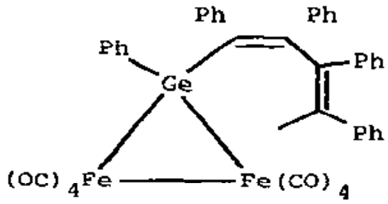
(104)

The reaction of [bis(mesitylthio)germylene]pentacarbonyltungsten with boron trichloride or tribromide affords the (μ-dihalogermylene)-bis(pentacarbonyltungsten) complex (106):[221]



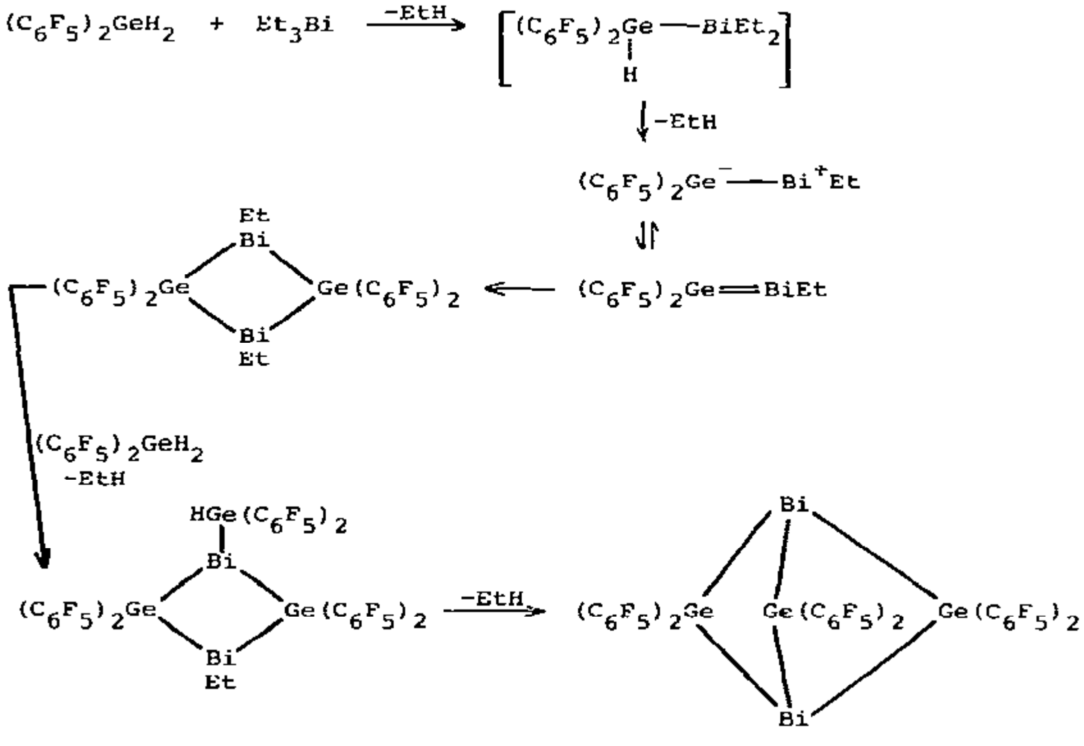
(106)

Pentaphenylgermole reacts with $Fe_2(CO)_9$ to yield an orange crystalline complex, shown by X-ray studies to be (107).[222]



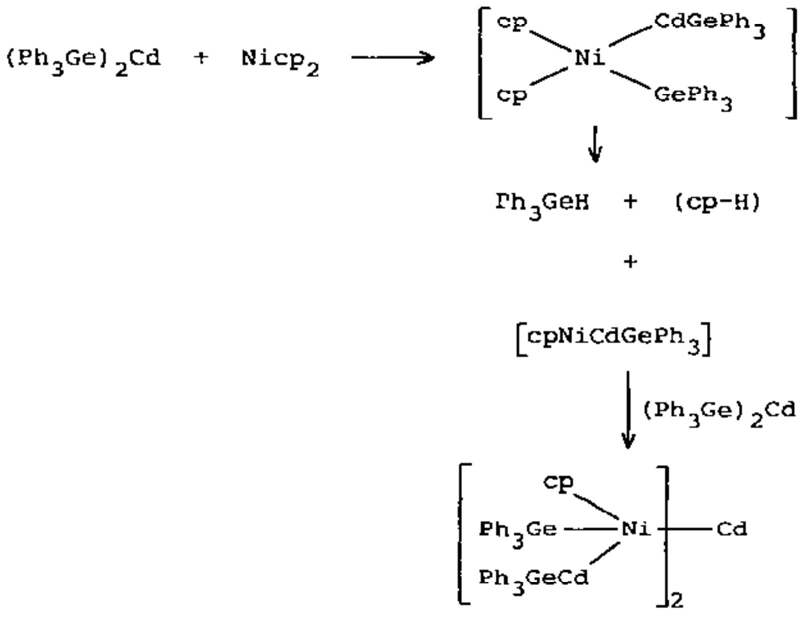
(107)

The structure of the product of interaction of $(C_6F_5)_2GeH_2$ and $BiEt_3$ has also been determined by an X-ray study. The heavy atom skeleton of the product has a trigonal bipyramidal arrangement of three germanium and two bismuth atoms as in (108):[223]



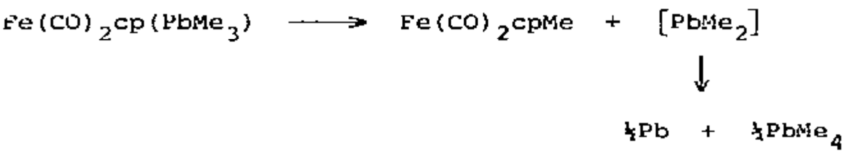
(108)

Bis(triphenylgermylcadmium) reacts with nickelocene to afford red crystals of (109) as a toluene solvate:



(109)

Crystallographic studies show that the metal-metal bonds are not reinforced by bridging ligands. The [Ni-Cd-Ni] framework is linear.[224] The germyl and stannyl complexes, $(\eta^5\text{-}C_9H_7)(CO)_3M(M'R_3)$ (M=Cr,Mo,W; $M'R_3$=$GeEt_3$, $SnMe_3$) have been obtained by normal substitution methods from $(\eta^5\text{-}C_9H_7)(CO)_3M^-K^+$.[225] The organotin-lanthanide derivatives, $[(Me_3SiCH_2)_3Sn]_3Ln.DME$ have been prepared from $(Me_3SiCH_2)_8SnH$ and $[(Me_3Si)_2N]_3Ln$ (Ln=Pr,Nd) in DME. Reactions of the amino-lanthanide compounds with simpler hydrides such as Ph_3GeH or Et_3SnH are complicated by the cleavage of a C-O bond of DME to afford compounds of the type $(R_3M)_nLn(OCH_2CH_2OMe)_{3-n}$.DME (n=1,2; R=Et, Ph; M=Ge,Sn). The compounds are weakly coloured solids which are sensitive to oxygen and moisture. Reagents such as hydrogen chloride, 1,2-dibromoethane, benzoyl peroxide, and silver trifluoroacetate cleave the metal-metal bonds.[226] ^1H and $^{13}C\{^1H\}$ n.m.r. data have provided additional evidence that the product of the reaction between $SiMe_3Cl$ and $[Pt(C_2H_4)(PPh_3)_2]$ is *cis*-$[PtMe(SnMe_2Cl)(PPh_3)_2]$. Similar insertion of platinum into the tin-carbon bonds of a wide range of triorgano tin derivatives, R_3SnX (X=Cl,Br,I,NMe_2,OAc,$\overline{N(CO)(CH_2)_2CO}$,OMe,$OSnPh_3$), and Sn_2Ph_6 takes place, but with $Me_3Sn[N=C(CF_3)_2]$ insertion into the tin-nitrogen bond occurs.[227] $[Pt(C_2H_4)(PPh_3)_2]$ reacts with Pb_2Ph_6 to yield cis-[$PtPh(Pb_2Ph_5)(PPh_3)_2$] which decomposes in solution to cis-[$PtPh(PbPh_3)(PPh_3)_2$]. This latter complex is also obtained by insertion into $PbPh_4$. $PbPhMe_3$ and $PbPh_3Br$ similarly react by insertion into Pb-Ph bonds, but $PbMe_3Cl$ affords cis- and trans-[$PtCl(PbMe_3)(PPh_3)_2$]. The diphosphine $Ph_2PCH_2CH_2PPh_2$, displaces triethylphosphine from trans-[$Pt(PbPh_3)_2(PEt_3)_2$] yielding [$Pt(PbPh_3)_2(DPPE)$], which decomposes readily in solution in the presence of triethylphosphine to a mixture of [$Pt(PbPh_3)(PEt_3)(DPPE)$]Cl and [$PtPh(PEt_3)(DPPE)$]Cl.[228] The plumbyl-iron complex, $Fe(CO)_2cp(PbMe_3)$, synthesised by the standard salt-elimination method, undergoes facile methyl group migration from lead to iron. The reaction is complex in a few hours at only moderately elevated temperatures, and is essentially quantitative according to the scheme:[229]



$$\begin{tikzcd} Fe(CO)_2cp(PbMe_3) \arrow[r] & Fe(CO)_2cpMe + [PbMe_2] \arrow[d] \\ & \tfrac{1}{2}Pb + \tfrac{1}{2}PbMe_4 \end{tikzcd}$$

4.5 OXIDES, SULPHIDES AND SELENIDES

Silicon-29 n.m.r. has been employed for the investigation of the structure of silicates both in solution and also in the solid state. For the latter, high resolution spectra of silicates and aluminosilicates have been obtained with 1ppm resolution using high speed magic angle spinning in combination with high power proton decoupling and wherever possible polarisation transfer. Although ionisation and cation influence are reflected in the ^{29}Si chemical shifts, the isotropic ^{29}Si chemical shifts in solids and solutions are generally the same, and depend mainly on the degree of condensation of the silicate tetrahedra. In solid aluminosilicates, additional paramagnetic shifts appear which correlate well with the degree of substitution by aluminium.[230] Solution studies have demonstrated that essentially only monomeric orthosilicate ions are present at low concentrations (ca. 0.01M in silica) silicate solutions. At higher concentrations, peaks are observed which lack fine structure and indicate the presence of species whose silicon nuclei are all equivalent.[231] Concentrated solutions of tetraethylammonium silicates with a molar ratio of TEA:Si of 2.8:1 contain mainly double three-ring silicate anions.

Besides these, small amounts of mono-, di-, tri-, tetra-, cyclotetra-, double four ring and other polycyclic silicate anions are present. From these solutions a crystalline double three-ring silicate of composition $[NEt_4]_6[Si_6O_{15}].5H_2O$ has been obtained by recrystallisation at low temperature. Concentrated solutions with TEA:Si ratios of 0.8-0.6 contain mainly double three-, double four-, double five- and probably double-six ring silicate anions. From these solutions, the crystallisation product is always the TEA-double four-ring silicate.[232] N.m.r. has been employed in the study of the polymerisation of silicate anions in acidic solutions. The rate of polymerisation of silicic acid (produced from the hydrolysis of $Si(OMe)_4$ is remarkably slow at -10^o) in the pH range 3.5-4.0.[233] The chemical and structural transformations induced by proton-donor catalysts (Amberlyst 15 cation exchange resin and trichloroacetic acid) have been studied using the silicate derivatives $Si_6O_{15}(SiMe_3)_6$ and $Si_6O_{18}(SiMe_3)_{12}$ as model compounds. The transformations tend to produce structures containing only tetrameric siloxane rings when starting from cyclic or polycyclic silicate derivatives containing, trimeric, pentameric or hexameric siloxane rings. Three different types of of reaction were suggested for the interpretation of all the transformations.[234] Trimethylsilylation of $Ag_{10}Si_4O_{13}$ by a modified 'direct method' yields the trimethylsilyl derivative of the linear chain ion $[Si_4O_{13}]^{10-}$ as the major product, although this readily undergoes cyclisation in acidic aqueous media.[235] Such cyclisation side reactions can be reduced to a negligable level by employing DMF as the solvent. Thus, by this method $Ag_{10}Si_4O_{13}$ gives 99.9% of the linear tetramer derivative and only 0.1% of the cyclic tetramer. Only the cyclic tetramer derivatives were observed from $H-Pb_2SiO_4$, confirming the cyclic nature of the silicate in this material.[236]

Changes in the pH or concentration of sodium silicate solutions produce changes in the degree of polymerisation of the silicate species which may be followed by the trimethylsilylation method. However, provided that the pH remains relatively high, above ca. 10 or 11 according to the concentration, equilibrium is rapidly established after such changes. At lower pH, equilibrium is approached much more slowly so that changes in distribution with time can be followed.[237] The following rules have been formulated concerning the structure of the polymeric species in silicate solutions: (i) connectivity is maximised consistent with a lower ring size of four tetrahedra (except possibly in trimeric species), (ii) all tetrahedra in a given species show as nearly as possible the same degree of connectivity. Both these rules are consistent with the idea that the lability of silicate groups in solution decreases with increasing connectivity.[238] The gel time in the polymerisation of the silicate ion is independent of the rate of disappearance of monomeric silicic acid.[239]

The trimethylsilylation technique has been employed to elucidate the structures of calcium orthosilicate, $Ca_2[SiO_4]$, rankinite, $Ca_3[Si_2O_7]$, and ψ-wollastonite, $Ca_3[Si_3O_9]$. With $(Me_3Si)_2O$, isopropanol and Me_3SiCl as the reagents in the absence of added water, $Ca_2[SiO_4]$ gives predominantly $SiO_4(SiMe_3)_x(Pr^i)_{4-x}$ (x=1-4) and a lesser amount of $Si_2O_7(SiMe_3)_x(Pr^i)_{6-x}$ (x=2-6); $Ca_3[Si_2O_7]$ gives predominantly $Si_2O_7(SiMe_3)_x(Pr^i)_{6-x}$ (x=2-6), and $Ca_3[Si_3O_9]$ predominantly $Si_3O_9(SiMe_3)_x(Pr^i)_{6-x}$ (x=2-6) and $Si_3O_{10}(SiMe_3)_x(Pr^i)_{8-x}$ (x=3-8). The mixed trimethylsilyl-isopropyl derivatives may be converted to the fully trimethylsilylated derivatives $SiO_4(SiMe_3)_4$, $Si_2O_7(SiMe_3)_6$ and $Si_3O_{10}(SiMe_3)_8$ on treatment with Amberlyst 15 resin in the presence of $(Me_3Si)_2O$. Side reactions may be suppressed by increasing the proportion of isopropanol and decreasing the calcium silicate. The presence of both isopropanol and Me_3SiCl is necessary for the reaction to occur, although the isopropanol may be replaced by ethanol or water, but at the expense of the yield.[240]

Crystalline silicic acids are strong solid acids with surface acidities ranging from $H_o<-3$ $(H_2Si_{14}O_{29}\cdot5\cdot4H_2O)$ to $H_o\approx2\cdot3$ $(H_2Si_2O_5)$ as measured with Hammett indicators. Thermal dehydration reduces the surface acidity to 2.3-3.3 only. The high acidity probably results from regular extended hydrogen-bonding systems including surface water molecules.[241] The lead silicate, Pb_2SiO_4, has a disordered structure which belongs to a family of OD structures. The member with the maximum degree of order was $Ph_2Si_{0.76}Ge_{0.24}O_4$, which comprised $[(Si,Ge)_4O_{12}]^{8-}$ anions and Pb^{2+} cations arranged in a layer structure.[242] The structured Tinaxite, $Ca_2K_2NaTiO[Si_7O_{18}(OH)]$, has been refined further, and the Si-O bond distances in the fused $[SiO_4]$ tetrahedra vary from 1.566-1.657A.[243]

The structure of tetragonal tin(II) oxide has been redetermined, and the regular square-pyramidal coordination of tin(II) confirmed.[244] The thermal expansion of the cell parameters in the temperature range 273-593K follow the relationships (T in °C):

$$\underline{a}(\text{Å}) = 3.7984(6) + 3.31(36) \times 10^{-5}T + 7.9(16) \times 10^{-8}T^2$$

$$\underline{c}(\text{Å}) = 4.8368(7) + 1.25(4) \times 10^{-4}T + 6.2(19) \times 10^{-8}T^2$$

Pale brown needle crystals of tin(IV) oxide have been grown from a flux of the B_2O_3-V_2O_5 system by soaking mixtures of the flux and Zn_2SnO_4 at 1030-1340° for 10-72 hours, followed by cooling to 900° at a rate of 5° per hour. An increase in the V_2O_5 content of the flux (up to a V_2O_5/B_2O_3 ratio of 2) or an increase in the soaking temperature increases the crystal size; the largest crystal obtained had dimensions of 15.0 x 0.4 x 0.4 mm^3. The electrical resistivity of SnO_2 was determined to be 1.4 x $10^6 \Omega$.cm at 25°.[245] In tetragonal β-lead(IV) oxide, the lead atoms are coordinated by six oxygen atoms in an irregular octahedral arrangement in which the four equatorial Pb-O distances at 2.1689Å and the two axial distances 2.150Å.[246]

The double oxides, $MSnO_3$ (M=Mn, Ca, Cd), crystallise in the ilmenite lattice as well as (for M=Ca and Cd) the perovskite lattice.[247] Crystals of the mixed valence tungsten oxide of bivalent tin, $Sn_{10}W_{16}O_{46}$, are hexagonal, with the tungsten atoms in two types of unit. $[W_2O_9]$ groups are built up from two face-sharing octahedra, whilst $[W_6O_{19}]$ blocks are built up from six almost regular edge-sharing octahedra. The two different tin(II) atoms are coordinated by three and four oxygen atoms, respectively, in the usual geometries for bivalent tin.[248] Catalytically-active mixed tin-antimony oxide phases have been prepared by coprecipitation followed by dehydration at 600°. The single-phase blue solids contain both Sb^{III} and Sb^{V} in oxygen environments. Materials containing >20% Sb and heated for longer periods or at higher temperatures exhibited segregation of an additional antimony oxide phase. Samples with an antimony content of *ca*. <10% contain Sb^{V} replacing Sn^{IV} in the SnO_2 rutile lattice. ^{121}Sb Mössbauer studies indicate an increase in *s*-electron density at both tin and antimony, but no indication of reduction leading to the formation of either Sn^{II} or Sb^{III}. Delocalisation of electrons into a conduction band was proposed to account for charge compensation.[249] The hitherto unknown caesium nesoplumbate, $Cs_4[PbO_4]$, has been obtained as either a yellow powder or yellowish transparent crystals which comprise isolated [PbO_4] tetrahedra connected by caesium cations.[250] Two types of lead coordination are found in crystals of $Pb_3Rh_7O_{15}$. One lead is coordinated by four oxygens at a distance of 2.36Å, whilst the other is six-coordinated by four oxygens at 2.66Å and two at 2.41Å.[251]

The decomposition of solid Sn_2S_3 has been studied by the Knudsen effusion/mass spectrometry/microbalance technique in the temperature range 669-820K yielding pressures from about 10^{-12} - 10 Pa. The results demonstrate that under these conditions, decomposition occurs according to:

$$Sn_2S_3(s) \longrightarrow 2SnS(s) + \tfrac{1}{2}S_2(g)$$

with $\Delta H_f^{\ddagger} = -254.5(6.0)$ kJ mol^{-1} and $\Delta S = 170.5(6.0)$ $JK^{-1}mol^{-1}$.[252] The structure of $BaSn_2S_3$ is a distortion of the NaCl lattice, and can be described in terms of layers parallel to the (100) plane formed by $[Sn_2S_3]_n^{2n-}$ chains, each tin atom having three bonds to sulphur atoms at distances in the range 2.44-2.75Å. These layers are linked by weak Sn-S---Sn and Ba-S-Ba interactions.[253] $Sn_4Sb_6S_{13}$ has a similar ribbon-like structure in which $[X_5S_7]_n$ [X=Sn,Sb] sheets parallel to the b axis are linked together by weak X---S-X and X---E-X interactions (E=lone pair of Sn(II) or Sb(III).[254] The lead atoms in $Pb_2Ga_2S_5$ are in eight-fold coordination by sulphur (Pb-S = 2.79-3.36Å), with the structure built up from alternate sheets of [GaS_4] tetrahedra and $[PbS]_n$.[255]

Crystals of the selenostannate, $Na_4SnSe_4.16H_2O$, have been obtained by reaction of tin(IV) sulphide with alkali selenides with the strict exclusion of oxygen. Crystals contain discrete tetrahedral [$SnSe_4^{4-}$] anions (Sn-Se = 2.504-2.527Å) in contact with octahedral [$Na(OH_2)_6^+$] cations through Se---H-O bridges. From infrared data a value of ca. 1.59mdyne $Å^{-1}$ was determined for the Sn-Se stretching force constant.[256] The germanium atoms in β'-Ag_8GeSe_6 are also tetrahedrally coordinated with a Ge-Se distance of 2.34Å.[257]

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