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Chapter 4

ELEMENTS OF GROUP 4

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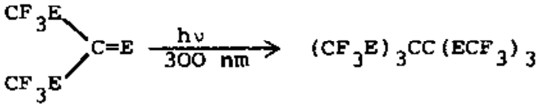
4.1 CARBON

The structure of solid carbon disulphide has been determined between 5 and 150K by the neutron powder profile technique. The general structural features are similar to those at higher temperature, although the C-S bond distance (1.546(2)Å at 5.3K) appears shorter than that in the gas phase.[1] Heating carbon diselenide in methylene chloride or dioxane at 100°C under a pressure of 5000 atmospheres results in conversion to poly(carbon diselenide), a black, highly conducting air- and thermally-stable solid, in 95% yield. Under the same conditions, carbon sulphide selenide is recovered unchanged.[2]

Perfluorinated hexaalkylthia- and hexa-alkylselena ethanes are obtained by photolysis of the corresponding carbonates:



E = S,Se

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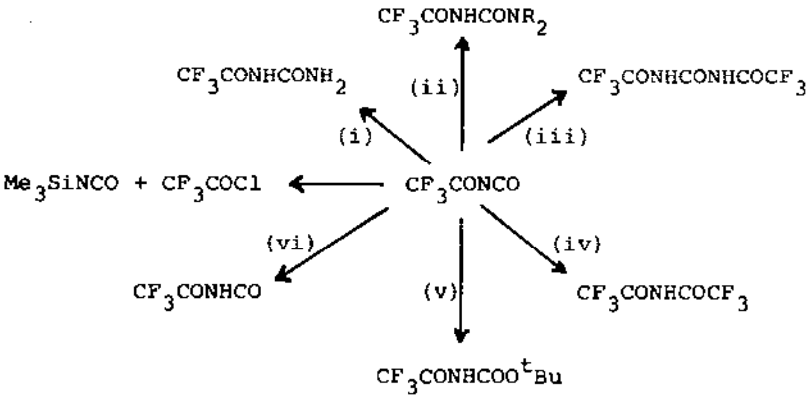
The reactions probably proceed via the formation of $[\cdot CF_3\ CS_2\ \cdot SCF_3]$ species in a solvent cage.[3] Trifluoroacetyl isocyanate is readily prepared by metathesis between Me_3SiNCO and CF_3COCl. Some further reactions are shown in Scheme 1.[4]

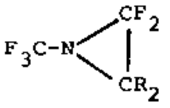


Scheme 1. Reactions of CF_3CONCO, (i) NH_3, (ii) R_2NH, (iii) CF_3CONH_2, (iv) CF_3CO_2H, (v) ^tBuOH, (vi) HN

Trifluorosulphonylamine, CF_3NSO, has been synthesised by the route:

$$CF_3NSF_2 + PCl_5 \longrightarrow CF_3NSCl_2 \xrightarrow{AgO} CF_3NSO$$

and also from the reaction of CF_3NCl_2 and SO_2Cl. It reacts with xenon difluoride and HCl to give CF_3NSOF_2 and CF_3NH_2, respectively.[5] Perfluorinated carbenes such as $[:CF_2]$ and $[:C(CF_3)_2]$ do not react with perfluoro-2-aza-1-propene to yield the expected aziridines(I). Instead, the products are $(CF_3)_2N\text{-}CF{=}N\text{-}CF_3$ and $(F_3C)_2N\text{-}CF_2H$.[6]



R = F,CF_3.

The fluoroformate ion has been isolated for the first time in a condensed phase synthesis by cocondensation of CO_2 with caesium fluoride. The species exists as an ion pair, and exhibits two C-O stretching modes at 1316 and 1749 cm^{-1}. Isotopic labelling confirms the planar C_{2v} structure, whilst normal coordinate analysis is suggestive of strong double-bond character for the C-O bond. Chlorinated acylphosphanes RCO-PPh_2 (R = CF_2Cl, CH_2Cl, CCl_3, CH_3CHCl, CH_3CCl_2) are obtained by the reaction of RCOCl and Me_3SiPPh_2 in ether at -80°C, but decompose eliminating Ph_2PCl and forming the corresponding chloroketene.[8]

Cyanogen does not react with any of the components of the $P_4 \rightleftharpoons P_2$ thermal equilibrium even at 1470K. In contrast, at 950K MeSSMe is quantitatively converted to MeSCN.[9]

4.2 SILICON, GERMANIUM, TIN AND LEAD

4.2.1 Unstable Intermediates

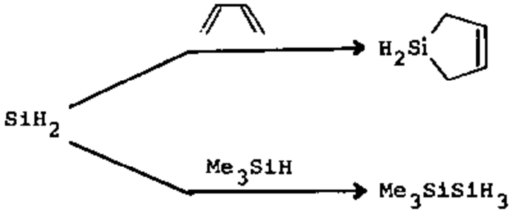
SCF and electron correlation calculations have been performed for the lowest singlet and triple states of Si_2H_4, SiH_3SiH, SiH_2CH_2, SiH_3CH and CH_3SiH, as well as for C_2H_4 and CH_3CH. Of chemical interest is the character of the Si-Si bond in disilene, the distance of which is calculated to be considerably shorter (2.127Å) than in purely single-bonded compounds (cf. SiH_3SiH 2.453Å), and comparable with similar observations C_2H_4 and SiH_2CH_2. In addition, the SiSi force constant in disilene is larger than that in silylsilylene, and hence it appears that the bond does indeed have double-bond character.[10]

Two primary dissociation processes occur in the homogeneous gas-phase decomposition of disilene in the 850-1000K (2300-2700 torr) ranges (single-pulse shock-tube technique:

$$Si_2H_6 \rightarrow SiH_4 + SiH_2$$

$$Si_2H_6 \rightarrow Si_2H_4 + H_2$$

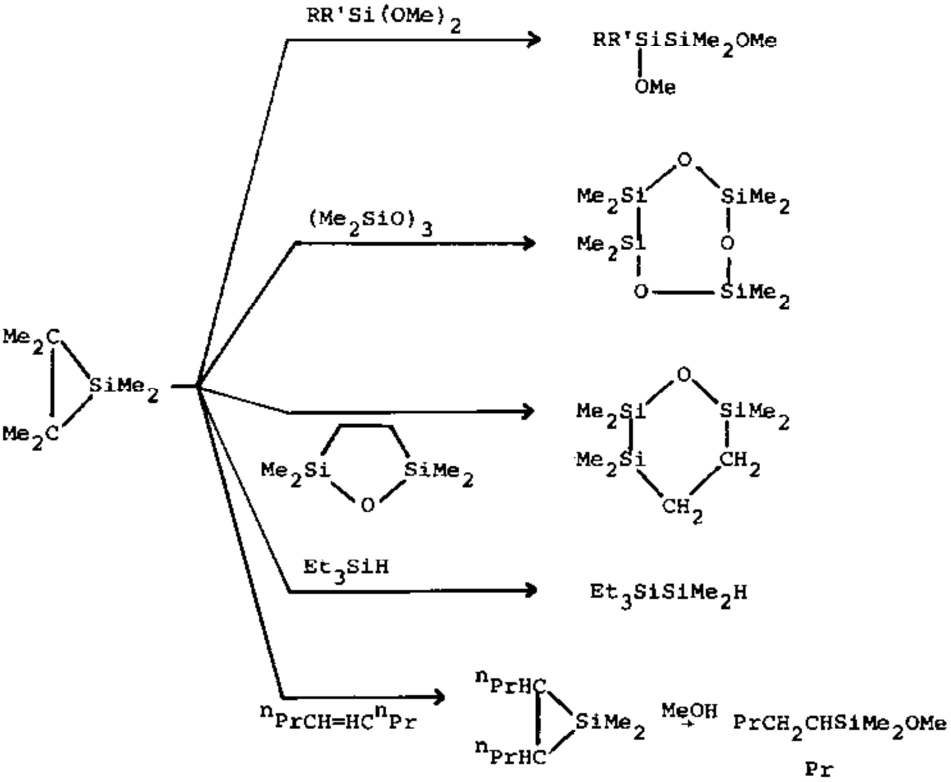
In the presence of butadiene and trimethylsilane, the silylene produced in the former reaction may be effectively trapped by the reactants which have roughly equal rate constants and activation



energies. At temperatures above 950K, in the absence of trapping agents, the yields of hydrogen increase due to subsequent silylene dimerisation/decomposition:[11]

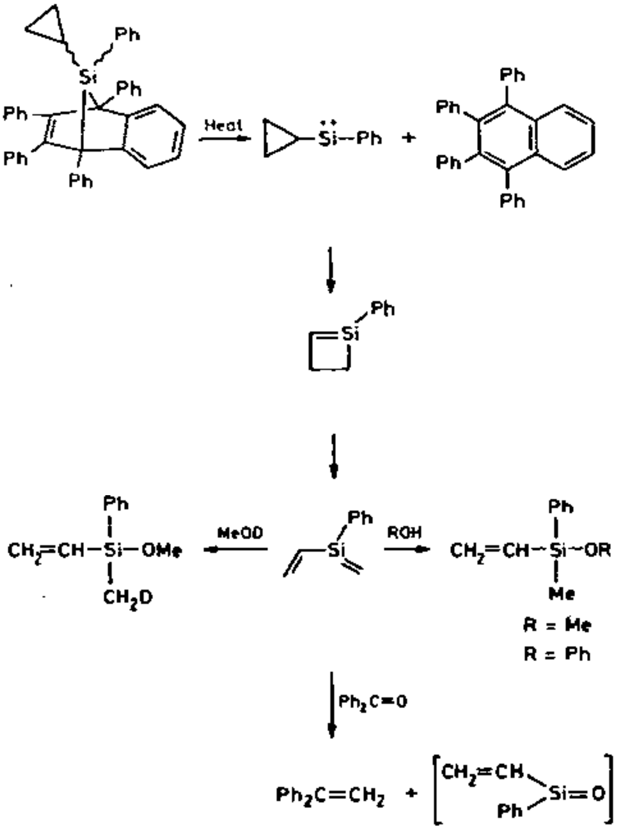
$$2SiH_2 \rightarrow Si_2H_4 \rightarrow Si_2H_2 + H_2$$

The thermolysis of hexamethylsilirane at ca. 65-75° results in the extrusion of trappable dimethylsilylene, which inserts into the Si-H bonds of organosilicon hydrides and into the Si-O bonds of methoxysilanes, hexamethylcyclotrisoloxane, and 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane, and also adds to the C=C bonds of various alkenes to afford novel siliranes:

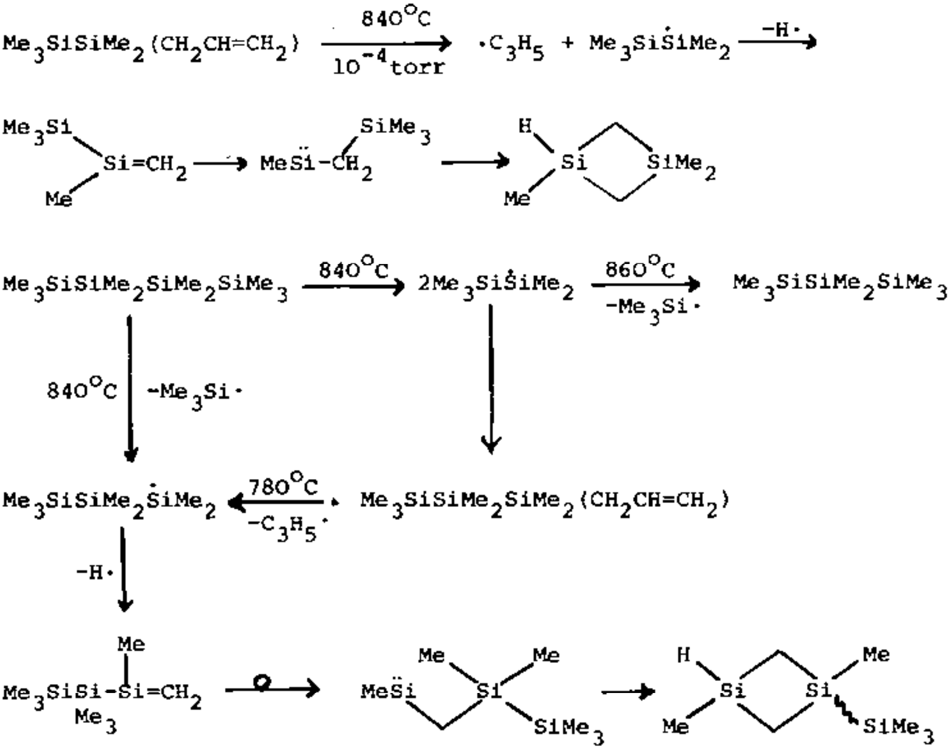


The addition to the C=C bond appears to take place stereospecifically with retention of configuration.[12] Cyclopropylphenylsilylene(cyclopropylphenylsilanediyl), generated by the pyrolysis of the sila-bridged precursor at 540°C, rearranges to

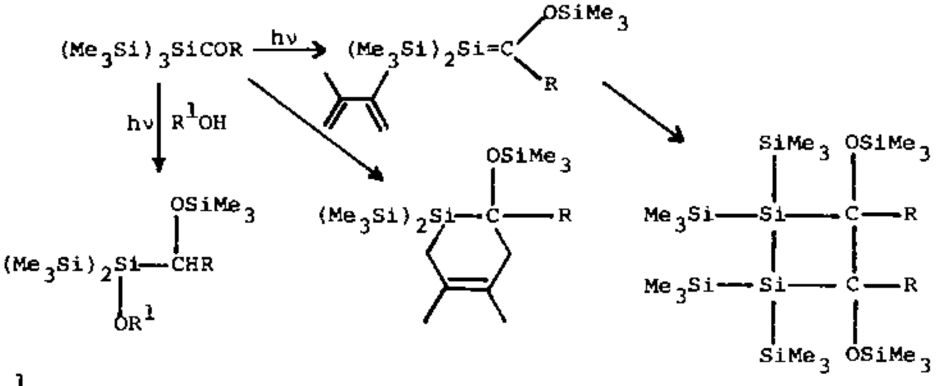
1-phenyl-1-silacyclobutene. Under the conditions of the reaction, the latter compound undergoes subsequent ring-opening to afford 2-phenyl-2-silabutadiene, which can be trapped by the usual type of reagent:[13]



The heats of formation of the metallaalkenes, $Me_2M=CH_2$ (values in kcal mol^{-1}) (M = Si(7), Ge(6), Sn(31) and Pb(59)), have been estimated from pulsed ion cyclotron double resonance spectroscopy.[14] Di- and trisilanyl radicals undergo a thermal sequence of reactions involving an initial disproportionation to the silene, rearrangement to a silylene via a 1,2-silyl migration, and cyclisation via a γ-C-H insertion:[15]



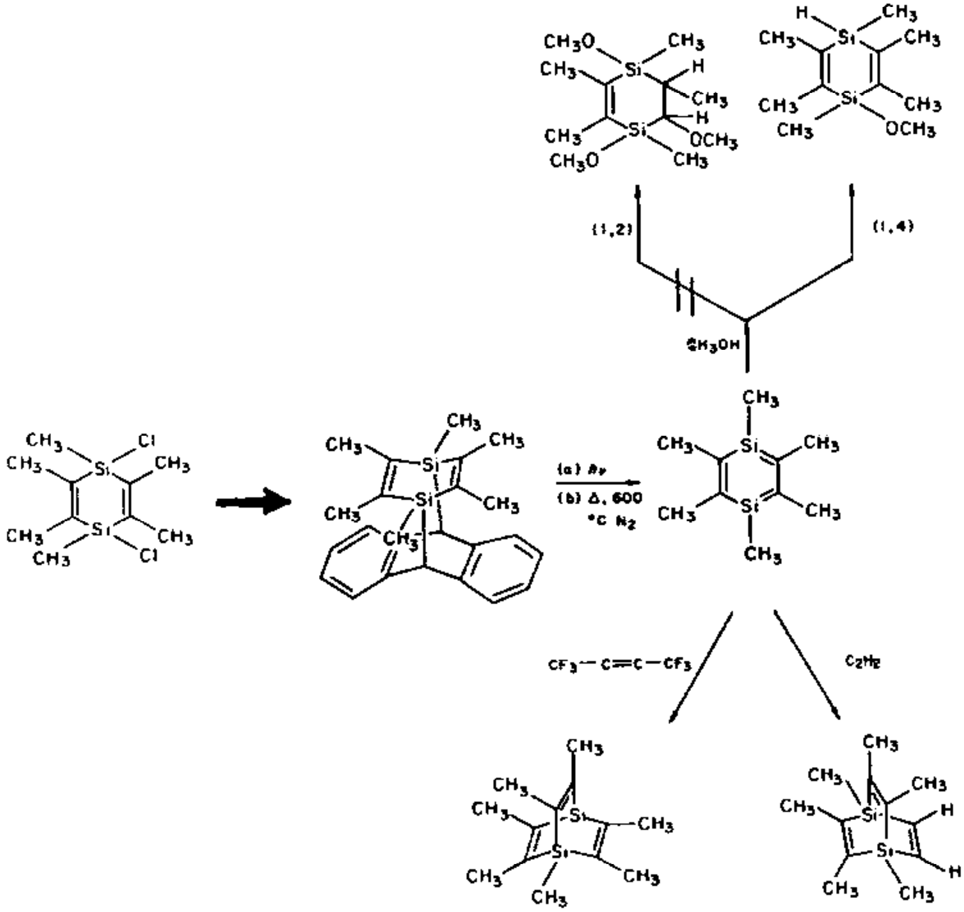
Silaethenes (silaethylenes) are also formed by the photolysis of substitutued branched benzoyl tetrasilanes, $(Me_3Si)_3SiCOC_6H_4Y$ (Y = p-MeO, o-MeO, p-t-Bu, 3,5-Me_2), and the related (trifluoroacetyl)-silane, $(Me_3Si)_3COCF_3$, and can be trapped by reagents such as alcohols or substituted butadienes, or in the absence of trapping agent undergo head-to-tail dimerisation:



$R^1 = CH_3$ or H.

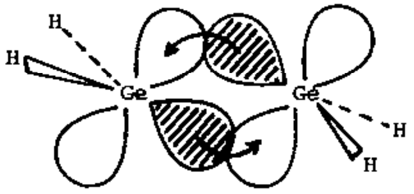
No evidence was found for any significant stabilisation of the silaethenes through conjugative, electronic, or steric effects relative to the protio analogues, and all were found to be less stable than the silaethenes derived from alkoylsilanes containing a bulky alkyl group.[16]

West[17] has reported evidence for the existence of hexamethyl-1,4-disilabenzene, the first example of an aromatic containing two silicon atoms. Its generation, which can be either photochemically or thermally, as well as some trapping reactions are summarised in Scheme 2.

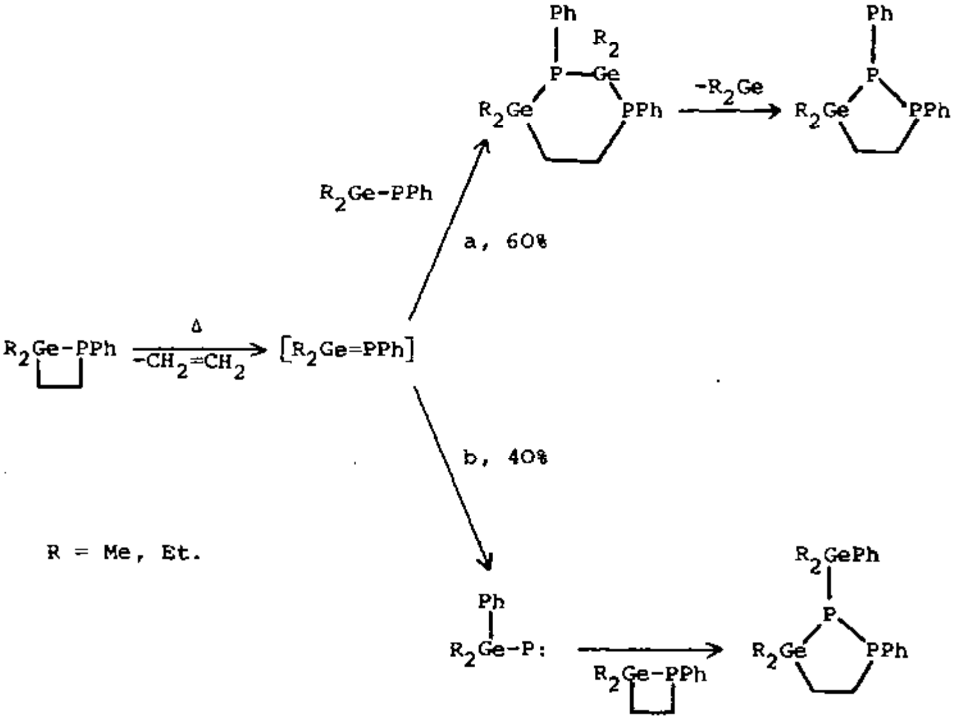


Scheme 2. Generation and Reactions of Hexamethyl-1,4-disilabenzene.

Ab initio MO calculations (with double-ζ plus polarisation basis sets) have been carried out on a number of germylenes and multiply-bonded low-valent germanium intermediates. Calculations for the two singlet isomers of Ge_2H_4 show that digermene ($H_2Ge{=}GeH_2$) is 5 kcal mol^{-1} more stable than germylgermylene ($H\ddot{G}e{-}GeH_3$). The most favourable geometry for the molecule is similar to that of Lappert's compound, $\{[(Me_3Si)_2CH]_2Sn\}_2$ in the solid-state, with a wagging angle for the $[Ge{-}H_2]$ groups of 39°, (although the planar geometry is only 3-4 kcal mol^{-1} higher in energy). The bonding holding together the two germanium atoms is described as two semipolar bent bonds between two singlet germylenes:[18]

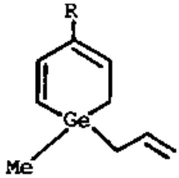


Similar calculations of the lowest singlet and triplet states of germaethylene, $H_2Ge{=}CH_2$, germamimine, $H_2Ge{=}NH$, and germanone, $H_2Ge{=}O$, show them to possess planar structures in the singlet state, whilst the corresponding triplets are both twisted and pyramidalized on germanium. In all three cases the singlet is the ground state. The singlet germylenes, methylgermylene, $HGeCH_3$, aminogermylene, $HGeNH_2$, and hydroxygermylene, HGeOH, are calculated to be more stable than their π-bonded isomers. Relative stabilizations of the two latter germylenes are enhanced by delocalisation of a π-lone pair into the vacant germanium p_π orbital.[19] Germanephosphimines, $R_2Ge{=}PR'$, may be generated by a thermal β-decomposition of 1,2-phosphagermetanes under reduced pressure, and partially rearrange thermally to P-germylated phosphinidines. Both of these intermediates insert into the Ge-P bond of 1,2-phosphagermetanes with the formation of perhydrodiphosphadigermins and P-germylated diphosphagermolanes:[20]



R = Me, Et.

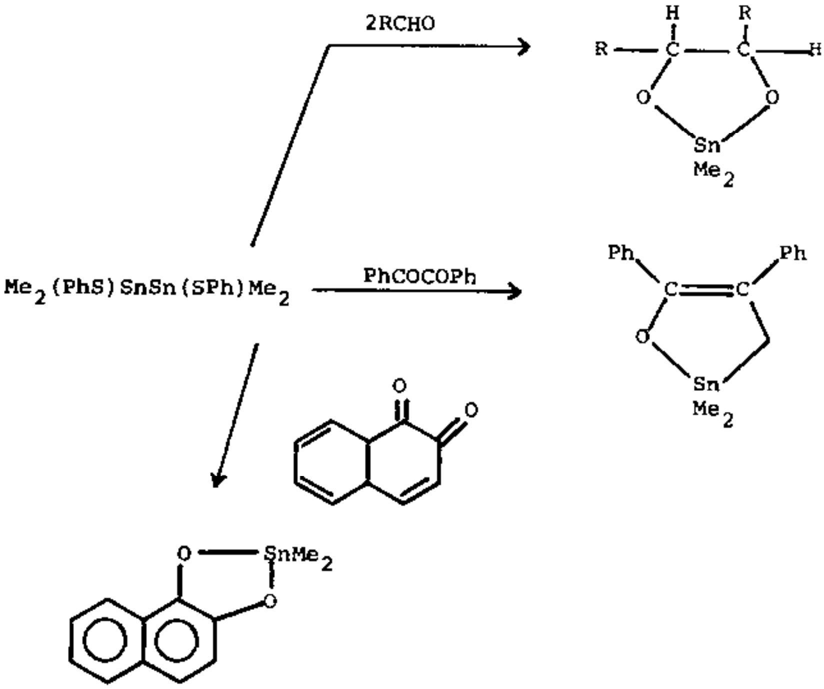
1,4-Dialkylgermabenzenes have been generated by the gas-phase pyrolysis (450-550°, ca. 0.05 mbar) of allylcyclohexadienes:[21]



R = Me, ^{i}Pr, ^{t}Bu.

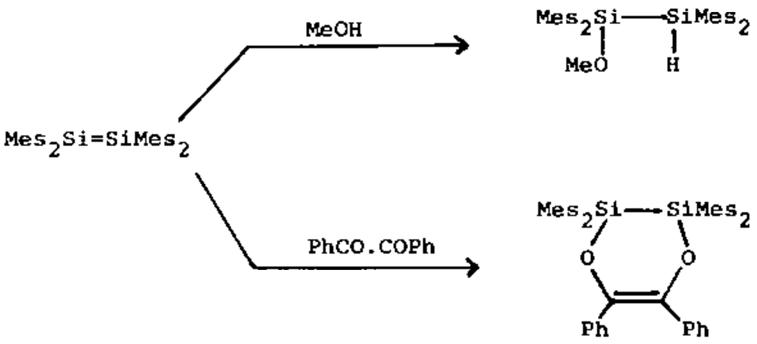
The reaction of $(CF_3)_2Cd$-glyme and tin(II) iodide in thf appears to afford the trifluoromethyltin(II) compounds, CF_3SnI and $Sn(CF_3)_2$, tentatively characterised by ^{19}F n.m.r. and ^{119}Sn Mössbauer spectra.[22]

Neumann[23] has reported a new convenient source of dimethylstannylene, $[Me_2Sn:]$, 1,2-bis(phenylthio)tetramethyldistannane, $Me_2(PhS)Sn-Sn(SPh)Me_2$. This compound undergoes decomposition under mild conditions (photochemically or thermally, 80°, benzene) with the elimination of dimethyltin dibromide. In the absence of a suitable coreactant, the dimethylstannylene polymerises to $(Me_2Sn)_7$, but with two molar equivalents of aldehyde or α-diketenes such as α-naphthoquinone, biacetyl, or benzil, give 1,3,2-dioxastannolanes and 1,3,2-dioxastannolenes, respectively:



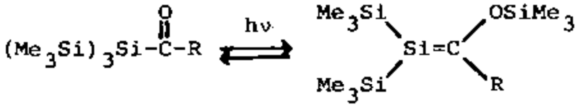
4.2.2 Low Oxidation State Compounds

Perhaps not surprisingly, stable isolable examples of some types of "unstable intermediates" in silicon chemistry have now been synthesised, thus allowing their chemistry to be studied in greater depth. In particular, stable disilenes and silaethylenes are now available. Following its initial synthesis by West, 1,1,2,2-tetramesityldisilene has been obtained in ca. 90% by irradiation of dimesityldichlorosilane with ultrasonic waves in the presence of lithium wire, which is consumed in 20 minutes. Identification of the product was confirmed by trapping with methanol and benzil:[24]



1,1,2,2-Tetrakis(2,6-dimethylphenyl)disilene is produced by the photolysis of the *cyclo*-hexaaryltrisilane at room temperature. It is extremely sensitive to air and moisture, and reacts with bromine to yield the corresponding dibromo-derivative.[25]

The intense research activity directed towards the synthesis of a silaethylene which is stable at room temperature has at last been rewarded. Two such silaethylenes have now been obtained by employing very sterically-demanding substituents, although the method of generation is the same as has been used previously, the photolysis of isomeric acylsilanes:

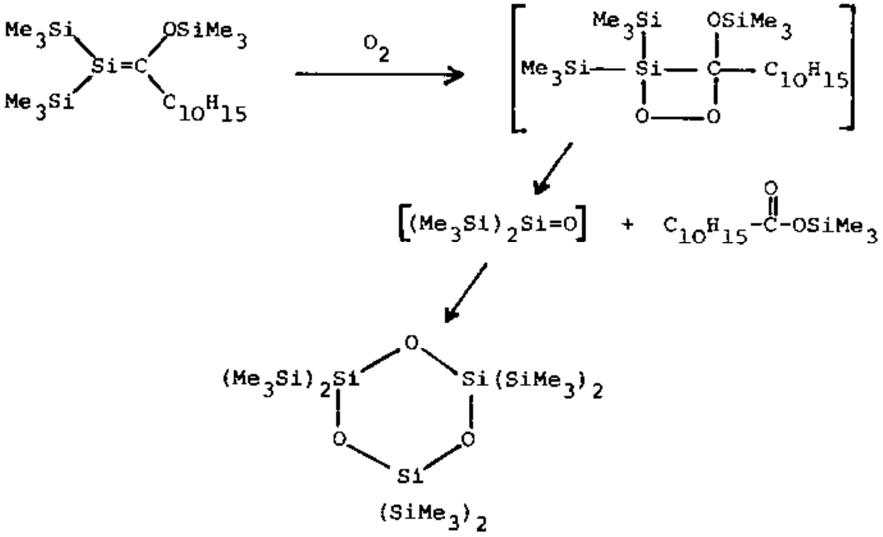


R = CEt_3, 1-adamantyl.

Both silaethylenes are indefinitely stable under argon at room temperature, and the crystal structure of the 1-adamantyl derivative shows a slightly twisted molecule with a silicon-carbon double bond length of 1.764Å. The molecule smokes vigorously in air, yielding a cyclic trisiloxane and the silyl ester of adamantane-1-carboxylic acid (Scheme 3).[26]

^{29}Si n.m.r. chemical shifts for the *sp*^{2}-hybridised silicons in the silaethylenes lies in the range 41-54 ppm. As expected, coupling constants involving *sp*^{2}-hybridised silicon are greater than those involving *sp*^{3}-hybridised silicon.[27]

An alternative preparation of bis(bis(trimethylsilyl)methyl)tin

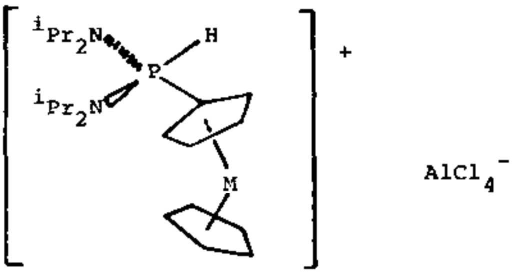


Scheme 3

by the reduction of the corresponding dialkyltin dichloride using Li_2cot in ether. In contrast the dimeric solid-state structure, electron diffraction studies have confirmed the monomeric nature of this compound in the gas phase, confirming the earlier mass spectroscopic data. The Sn-C bond distance (2.24(1)Å) is some 10 pm longer than that in trimethyltin.[28]

SCF Xα scattered wave calculations on dicyclopentadienyltin has shown that the highest occupied molecular orbitals ($6a_2$ and $9b_2$) are of the π type and are highly localised in the cyclopentadienyl rings. In order of decreasing energy, the molecular orbitals associated with the bonding of the cyclopentadienyl to the metal are $11a_1$, $6b_1$, $10a_1$, $8b_2$ and $9a_1$. Of these, the one which exhibits the largest tin lone pair character is $10a_1$. The molecular orbitals $5a_2$, $5b_1$ and $8a_1$ to $2b_2$ inclusive are σ_{CC} and σ_{CH} in character, highly localised on the cyclopentadienyl rings, and comparable in energy to the corresponding molecular orbitals on ferrocene.[29] UV photoelectron spectra have been recorded for both dicylcopentadienyltin and -lead and their pentamethylcyclopentadienyl analogues.[29] Cowley[30] has demonstrated the first electrophilic substitution of a cyclopentadienyl ring in dicylcopentadienyltin and -lead. Using the phosphenium ion, $[(^iPr_2N)_2P]^+$. Addition of $[(^iPr_2N)_2P]^+[AlCl_4]^-$ in dichloromethane cooled to -20° to dicyclopentadienyltin or -lead affords the microcrystalline substitution products in ≥90% yield.

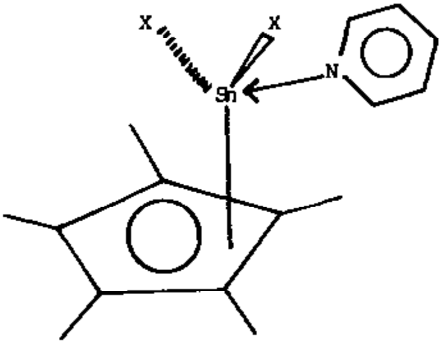
$$(C_5H_5)_2M \quad + \quad [(^iPr_2N)_2P]^+[AlCl_4]^- \longrightarrow$$



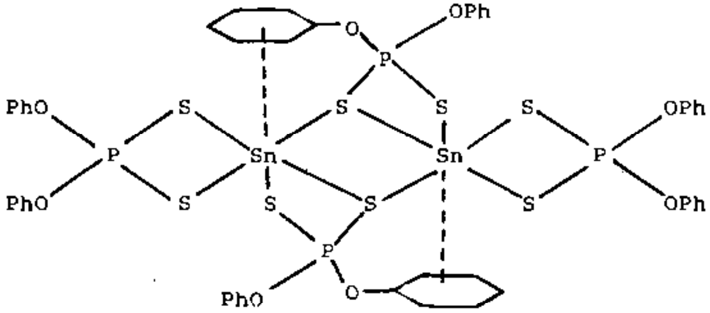
Pyridine forms a 1:1 adduct with the (pentamethylcyclopentadienyl)-stannocenium cation:

$$[(Me_5C_5)Sn]^+[CF_3SO_3]^- \quad + \quad C_5H_5N \quad \rightarrow \quad [(Me_5C_5)Sn{\leftarrow}NC_5H_5]^+[CF_3SO_3]^-$$

X-ray crystallographic studies show that the nitrogen atom of the pyridine is directly coordinated to the tin atom, which is preferentially associated with only two of the five cyclopentadienyl ring carbon atoms. Weaker contacts to two anion oxygen atoms complete the coordination sphere at tin:[31]



An unusual arene ring-metal interaction appears to be present in the centrosymmetric dimeric molecules of tin(II) bis(*O*,*O*'-diphenyldithiophosphate), $\{Sn[S_2P(OPh)_2]_2\}_2$. The molecules are characterised by a central planar $[Sn_2S_2]$ ring, which is circumscribed by an eight-membered $[SnSPS]_2$ ring in a chair conformation:

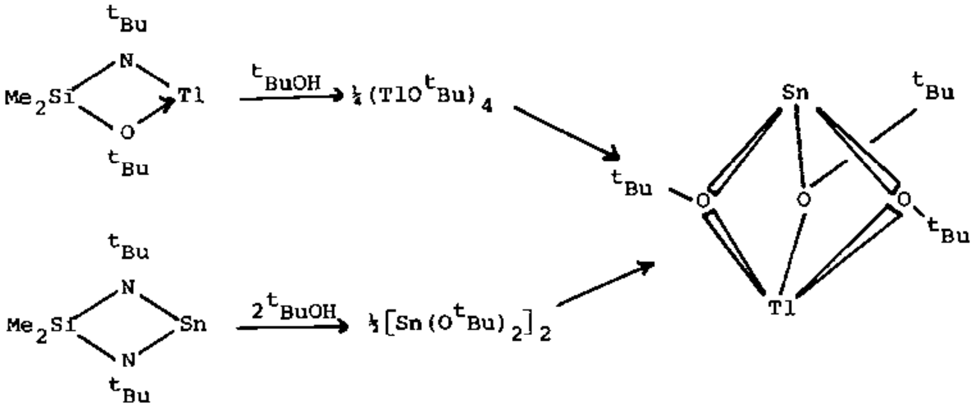


One dithiophosphate ligand chelates the tin atom, whilst the other functiins both as a chelating ligand to one tin atom in an extremely anisobidentate fashion and simultaneously bridges both tin atoms. The coordination sphere of the tin is completed by an η^6-interaction with the phenyl group of the bridging dithiophosphate ligand.[32]

Mössbauer recoil-free fraction temperature coefficient data indicate that bis(aziridinyl)tin and bis(dimethylamino)tin have polymeric associated structures, whilst $Sn[N(SiMe_3)_2]_2$ has a monomeric structure.[33]

Veith has continued his elegant work on the synthesis of tin(II) cage compounds. The monomeric, soluble and easily sublimable thallium/tin cage compound, $Tl(O^tBu)_3Sn$, has been prepared by the route (Scheme 4).[34]

The reaction of the compounds, $Me_2Si(N^tBu)M$ (M = Ge,Pb) with *tert*-butylamine afford the norcubane-like cage, $Ge_3(N^tBu)_4H_2$, and the cubane-like cages, $M_4(N^tBu)_4$ (M = Ge,Pb). The mixed cubane-like cages, $Sn_3(N^tBu)_4M$ (M = Ge,Pb), are obtained by heating $Me_3Si(N^tBu)M$ and $Sn_3(N^tBu)_4H$ at elevated temperatures. $Sn_3(N^tBu)_4Pb$ is less stable than $Sn_3(N^tBu)_4Ge$, and undergoes redistribution to $Sn_4(N^tBu)_4$, $Sn_2Pb_2(N^tBu)_4$, $SnPb_3(N^tBu)_4$ and $Pb_4(N^tBu)_4$ cages at high temperatures.[35] $Me_2Si(N^tBu)_2N$ reacts in

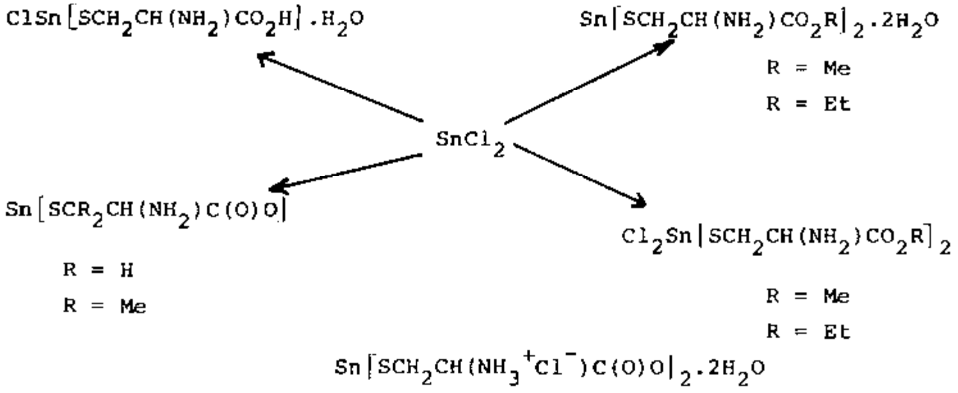


Scheme 4

benzene with N,N-dimethylhydrazine spontaneously and with isopropylamine after warming to afford the cubane cage molecules, $[SnN_2Me_2]_4$ and $[SnN^iPr]_4$, respectively; the structures of which were confirmed by crystallography. In the latter, adjacent molecules are linked by fairly long (3.51Å) contacts.[36]

The structure of germanium(II) bromide has been determined by electron diffraction in the gas phase at 620°. The Ge-Br distance was determined to be 2.337(13)Å with a BrGeBr angle of 101.2(9)°. The presence of another state was suggested by the experimental data.[37] Tetraphenylphosphonium trichlorostannate(II) and tribromostannate(II) have been prepared from the tetraphenylphosphonium halide and tin(II) halide in dihalomethane solvent. The anions are distorted from ideal C_{3v} symmetry (infrared and X-ray diffraction).[38] White, crystalline $(PPh_3)_3AgSnCl_3$ is similarly obtained from tin(II) chloride and $ClAgPPh_3$ in dichloromethane at room temperature. ^{31}P n.m.r. spectra for this product exhibit a single line at room temperature, but at -80° two components, neither of which exhibit P-Ag-Sn coupling, are seen and ascribed to the species $Ag(PPh_3)^+SnCl_3^-$ and $Ag(PPh_3)_4^+SnCl_3^-$.[39] Two products, $SnCl_2.2(glyglyH)$ and ClSn(glygly), have been obtained from the tin(II) chloride-glycyl-glycine system.[40] The nature of the products of the reaction between tin(II) chloride and sulphur-containing amino acids has been investigated. Principal products are illustrated in Scheme 5.[41]

UV spectrophotometric and potentiometric measurements of the formation of lead(II) chloro-complexes at 25° in aqueous sodium chloride and perchlorate mixtures show two complexes ($PbCl^+$ and

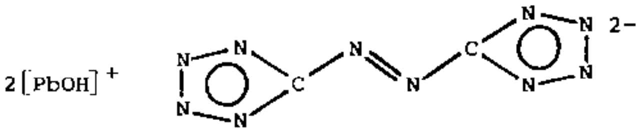


Scheme 5. Synthetic routes to tin(II) and tin(IV) derivatives of sulphur-containing aminoacids.

$PbCl_2$) to exist at ionic strength 0.5M, and the three complexes ($PbCl^+$, $PbCl_2$ and $PbCl_3^-$) at ionic strengths 1M and 2M. Overall thermodynamic stability constants of the three complexes have been determined.[42] The solubility of lead(II) bromide in propylene carbonate is greatly increased by the addition of lithium bromide which facilitates the formation of lead(II) bromo-complexes. Solubility, potentiometric, spectrophotometric data show that two complex species are formed in solutions of LiBr saturated with lead(II) bromide, $PbBr_3^-$, which predominates in dilute (<0.03M) solutions of LiBr saturated with lead(II) bromide and is also formed in propylene carbonate solutions in the absence of LiBr, and the polynuclear complex $Pb_4Br_{11}^{3-}$. In solutions of LiBr which are unsaturated with respect to lead(II) bromide, the major lead(II) species are $PbBr_3^-$ and $PbBr_4^{2-}$.[43]

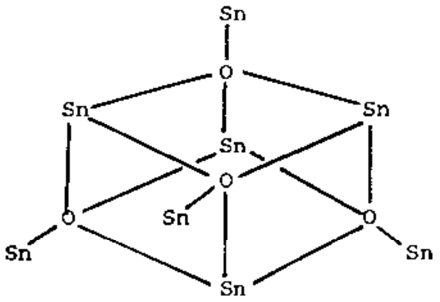
Solvolysis of hexaphenylditin by carboxylic acids leads to the formation of the mixed-valence carboxylates $[Sn^{II}Sn^{IV}O(O_2CR)_4\text{-}O(OCR)_2]_2$. The four-atom tin cluster is held together by two μ_3-oxo bridges and bridging acetato ligands resulting in an octahedral environment for the tin(IV) atoms and a pentagonal pyramidal geometry for the bivalent tin atoms, in which the μ_3-oxo bridge oxygen atom occupies the axial position. The equatorial positions accommodate the four acetato oxygen atoms and an anhydride oxygen. The tin lone pair presumably occupies the second axial site.[44] Crystals of tin(II) ethylene glycolate, prepared from freshly prepared "tin(II) hydroxide" and ethylene glycol under reflux, possess a three-dimensional network of linked five-membered tin(II) ethylene glycolate chelates. The tin(II) atom has ψ-trigonal bipyramidal geometry.[45]

Complex formation between lead(II) and L-α-alanine, L-cysteine and DL-α-aminoadipic acid has been investigated potentiometrically. For all three systems studied, the existence of PbHA, PbA, PbA_2 and $PbH_{-1}A$ species was demonstrated, with the additional species, $PbHA_2$, being present in the Pb(II)-cysteine system.[46] The infrared spectra of the lead(II) salts of fatty acids (C_6-C_{18}) have been measured as a function of temperature from ambient to a few degrees above the melting points. The coordination was deduced to be unsymmetrical bidentate.[47] In bis hydroxylead(II) 5,5'-azotetrazolediide each lead atom is weakly coordinated to two anions,



and closely linked to three oxygen atoms, whilst each oxygen is bonded to three lead atoms resulting in an infinite ladder-like chain of $[PbOH]^+$ ions along the a axis. The lead atoms have a very distorted square pyramidal coodination.[48] In β-lead(II) styphnate monohydrate (2,4,6-trinitro-1,3-benzenediolate), metal cations are linked via oxygen bridges into infinite chains parallel to the c axis. The styphnate ions are aligned in parallel planes. The coordination number of the lead is nine, and the polyhedron may be regarded as a distorted tricapped trigonal prism.[49] Triclinic lead(II) phthalocyanine contains two crystallographically independent molecules, both of which deviate from C_{4v} symmetry, and are arranged in two types of column in the crystal. Both are 'sitting-atop' complexes, with the lead atom 1.28 and 0.91Å, respectively, out of the plane of the four nitrogen atoms.[50]

The three-dimensional structure of ditin(II) oxide sulphate is built up by the linkage of $[Sn_8O_4]^{8+}$ groups, which have the geometry through sulphate ions. The two independent tin atoms have an oxygen coordiante intermediate between three- and four-fold coordination, both having three short and one longer Sn-O bonds:[51]



A similar three short and one longer tin(II)-oxygen coordination is also found in the structure of diammonium tin(II) diphosphite, $(NH_4)_2Sn(HPO_3)_2$, although in this case a fifth, much longer Sn...O contact is also present.[52] The mechanism of the topotactic reaction:

$$Pb(H_2PO_4)_2 \rightarrow PbHPO_4 + H_3PO_4$$

has been studied. Starting from a monocrystal of $Pb(H_2PO_4)_2$, crystallites of $PbHPO_4$ are observed to be found in a unique crystallographic orientation. The phosphoric acid is amorphous and included in these crystallites. The structures of both lead compounds have been determined. In $Pb(H_2PO_4)_2$ the lead is seven-coordinated but only six-coordinated in $PbHPO_4$, both in an irregular fashion.[53]

The electrochemical oxidation of tin or lead into solutions of arenethiols, RSH (R = Ph, C_6H_4Me), leads to the formation of the corresponding tin(II) or lead(II) thiolate, $M(SR)_2$ (M = Sn,Pb).[55] Reaction of tin(II) bromide with tetraethylammoniumcyclopentadienedithiocarboxylate in acetonitrile yields golden brown, air-sensitive crystals of $[NEt_4]^+[Sn(C_5H_4)_3]^-$. The Mössbauer isomer shift of this compound is very low (0.29 mms^{-1}), and is probably due to aerobic oxidation.[56]

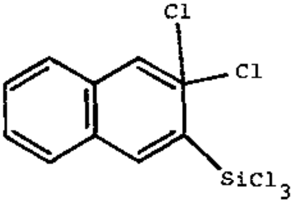
The alloys KSn_2, K_3Bi_2, KSnBi and KTlSn react with 2,2,2-crypt in ethylenediamine at room temperature to afford (from the former three alloys) black crystals of $(2,2,2\text{-crypt-}K^+)_2\ Sn_2Bi_2{}^{2-}\cdot$en, and (from the latter alloy) the complex $(2,2,2\text{-crypt-}K^+)_3(TlSn_9{}^{3-}TlSn_8{}^{3-})_{\frac{1}{2}}\cdot$en. In the former complex, the metal atoms are disordered equally over the four sites, and is the first characterised example of a heteroatomic member of the P_4 family of 20 electron tetrahedral clusters. The $TlSn_9{}^{3-}$ and $TlSn_8{}^{3-}$ anions exhibit an unusual 50-50 occupational disorder in a single anionic site, with seven atoms coincident in both species. $TlSn_9{}^{3-}$ has a bicapped square-antiprismatic geometry, whilst $TlSn_8{}^{3-}$ exhibits a tricapped trigonal prismatic geometry, with thallium in a capped position in each case.[57,58]

4.2.3 Tetravalent Compounds

The microwave spectrum and dipole moment of vinylsilane, $CH_2{=}CHSiH_3$, have been reported.[59] The barrier to internal rotation of the silyl group was determined to be 1488±24 cal.mol^{-1}. A complete microwave and vibrational spectroscopic study, including normal coordiante analysis has been carried out on disilyl iodide, H_3SiSiH_2I, and its perdeuterio analogue (Si-Si = 2.336(7)Å).[60] Gas phase electron diffraction data for the sterically-strained molecule, $(Me_3Si)_3CH$, are compatible with a single conformer of C_3 symmetry. The molecular overcrowding does, however, lead to a slight lengthening of the Si-CH bonds (1.888(6)Å) compared to the Si-CH_3 bonds (1.873(2)Å).[61] Electron diffraction studies of $(SiH_2)_6$ at 130° show that the molecule exists predominantly in a 'chair' form, but the conformational composition could not be determined uniquely since three models fit the experimental data (100% chair, 63% chair + 37% twist, and 62% chair, 25% twist + 13% boat). The bond lengths and angles of the chair conformation from these models are essentially identical (Si-Si = 2.342(5)Å).[62] The crystal structures of disilyl sulphide and selenide have been determined at low temperatures. In both crystals, molecules are aligned with intermolecular Si-E contacts which are 0.35-0.4Å less than the sum of the respective van der Waal's radii, giving [4+1] coordination for silicon and [2+2] coordination for the chalcogenide.[63] The Ge-H and Ge-Ge bond dissociation energies in GeH_4 and H_3GeGeH_3 have been determined as 346 and 276 kJ mol^{-1}, respectively.

Absolute rate constants for the reactions of tert-butoxyl radicals and some ketone triplets with a variety of silanes have been measured by a laser flash technique. At 300K, rate constants for H atom abstraction by tert-butoxyl radicals from, eg, Et_3SiH, n-$C_5H_{11}SiH_3$, $C_6H_5SiH_3$ and Cl_3SiH are 5.7, 10.6, 7.5 and ~40 x 10^6 M^{-1} s^{-1}, respectively, the principal reaction in all three cases being abstraction of an H atom from silicon. With $(EtO)_3SiH$, however, tert-butoxyl radicals abstract hydrogen from the methylene positions rather than from silicon.[65]

The structures of vinyldimethylchlorosilane (electron diffraction),[66] triphenylchlorosilane (X-ray diffraction),[67] $(Cl_3Si)_2CH_2$ and $(Cl_3Si)_2CCl_2$ (electron diffraction),[68] and 2,2-dichloro-8-trichlorosilyl-2-sila-1-oxa-1,2-dihydronaphthalene (1) (X-ray diffraction)[69] have been determined. For vinyldimethylchlorosilane, models with pure syn and a mixture of syn and gauche gave equally good agreement with the diffraction data.[66] The data for both $(Cl_3Si)_2CH_2$ and $(Cl_3Si)_2CCl_2$ may be approximated by models with C_2 symmetry and small tilts of the $SiCl_3$ groups, although some deviation from the staggered conformation is indicated.[68] Crystals of triphenylchlorosilane comprise discrete molecules with tetrahedral coordination of the silicon.[67] The structure of (1) is characterised by a planar conformation of the naphthalene; the intracyclic Si-C distance, however, is somewhat shorter (1.82Å) than usual (1.87Å).

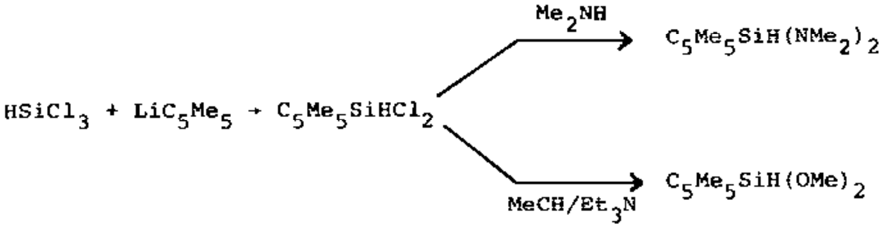


(1)

The vibrational spectra of the perdeuterio trimethylgermanium and tin halides, $(CD_3)_3MX$ (M = Ge,Sn; X = Cl,Br) have been reported; normal coordinate analyses were also carried out.[70] A parallel between ^{29}Si and ^{13}C n.m.r. chemical shifts in analogous compounds has been noted.[71]

Aluminium(III) bromide and trimethylbromosilane form strongly polarised donor-acceptor complexes of the type $Me_3Si^{\delta+}Br\rightarrow^{\delta-}AlBr_3$ in methylene bromide. No free silicenium ion formation could be detected.[71] η^1-Pentamethylcyclopentadienyltrichlorosilane, $C_5Me_5SiCl_3$, has been synthesised from $SiCl_4$ and C_5Me_5Li in diethylether, and can be handled in air for a short time. X-ray analysis shows the C_5 ring to be essentially planar, with monohapto bonding, to silicon. The Si-C distance is quite normal, but the $Cl\widehat{Si}Cl$ angles are 2-5° less than the tetrahedral value due to the steric effect of the ring. Substitution reactions with

Me_2NH and $MeOH/Et_3N$ occur, but give incomplete substitution, in contrast to the corresponding pentamethylcyclopentadienyldichlorosilane:



$$\begin{tikzcd}
 & & C_5Me_5SiH(NMe_2)_2 \\
HSiCl_3 + LiC_5Me_5 \arrow[r] & C_5Me_5SiHCl_2 \arrow[ur, "Me_2NH"] \arrow[dr, "MeCH/Et_3N"'] & \\
 & & C_5Me_5SiH(OMe)_2
\end{tikzcd}$$

The low-temperature direct fluorination of hexamethyldisilane and -digermane results in the cleavage of the metal-metal bond in both cases. From the disilane at -150°, a mixture of partially fluorinated derivatives was obtained:

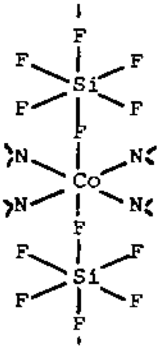
$$Me_6Si_2 \xrightarrow{F_2} \underset{15\%}{(FCH_2)_2MeSiF} + \underset{15\%}{(FH_2C)(CF_2H)MeSiF} + \underset{10\%}{(FH_2C)Me_2SiF}$$

$$+ \underset{8\%}{(FH_2C)_3SiF} + \underset{2\%}{Me(CHF_2)_2SiF}$$

but the reaction with the digermane at -100° afforded $(F_3C)_3GeF$ in 66% yield.[73] The formation of up to 1% of Ge_2OCl_6 in addition to GeO_2 has been observed in the gaseous oxidation of germanium(IV) chloride by molecular oxygen at 1223K, but not above 1273K. The products formed in the hydrolysis of methyltin trichloride have been investigated by ^{119}Sn n.m.r and Mössbauer spectroscopy. The formation of the following species was established: $MeSn(OH)Cl_2.2H_2O$, $MeSn(OH)_2Cl.nH_2O$ and $[MeSn(OH)(H_2O)_4]^{2+}$.[75]

Several matrix-isolation studies of complex formation by silicon(IV) and germanium(IV) fluorides have been reported.[76-78] Both form 1:1 complexes with methyl-substituted amines exhibiting a trigonal bipyramidal geometry with the base on the axial position. Similar complexes are formed with silicon(IV) chloride, but with considerable difficulty.

The GeF_5^- anion ion-paired with Cs^+ is formed when the gas-phase reaction of GeF_4 and CsF diluted with argon is rapidly condensed to 15K. Infrared data again suggest the trigonal bipyramidal geometry perturbed by the Cs^+ cation. At higher concentrations the GeF_6^{2-} is also formed. The ion-pairs $Cs^+GeClF_4^-$ and $Cs^+GeFCl_4^-$ are similarly obtained from the appropriate reactants, but CsCl and $GeCl_4$ did not react. Crystals of $[Co(viz)_4]SiF_6$ (viz = N-vinylimidazole) comprise strictly linear chains with octahedral $[SiF_6^{2-}]$ units bridging the $[Co(viz)_4^{2-}]$ cations as in ($\underline{2}$). All bond angles at silicon and cobalt are close to 90° or 180°.[79]

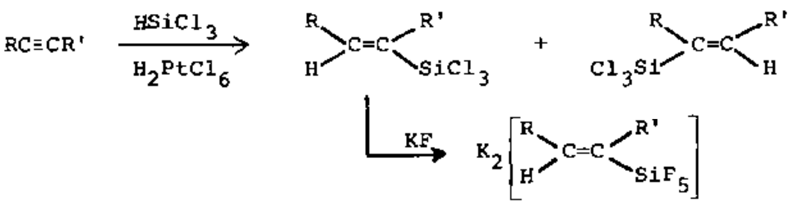


($\underline{2}$)

The final products from the reaction of sodium and potassium hexafluorosilicates and α- or γ-Al_2O_3 are fluoroaluminates and aluminosilicates.[80]

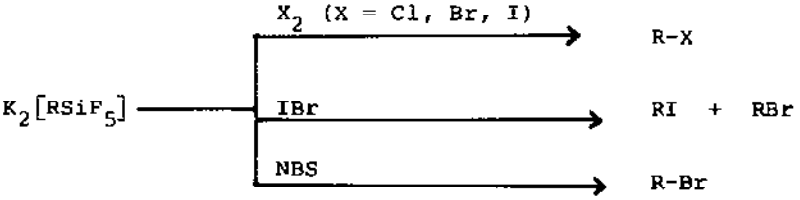
Organopentafluorosilicates have found application as reagents in in organic synthesis. Potassium salts, $K_2[RSiF_5]$, are obtained from the corresponding organotrichlorosilanes (readily accessible by the well-established, highly regio- and stereoselective hydrosilation of alkenes and alkynes with trichlorosilane catalysed by chloroplatinic acid. Treatment of the organotrichlorosilanes with KF in water or ethanol at 0° affords the silicates as white, air-stable powders:

$$\begin{array}{l} RCH=CH_2 \quad \text{or} \\ \text{internal olefins} \end{array} \xrightarrow[H_2PtCl_6]{HSiCl_3} RCH_2CH_2SiCl_3 \xrightarrow{KF} K_2[RSiCH_2CH_2SiF_5]$$

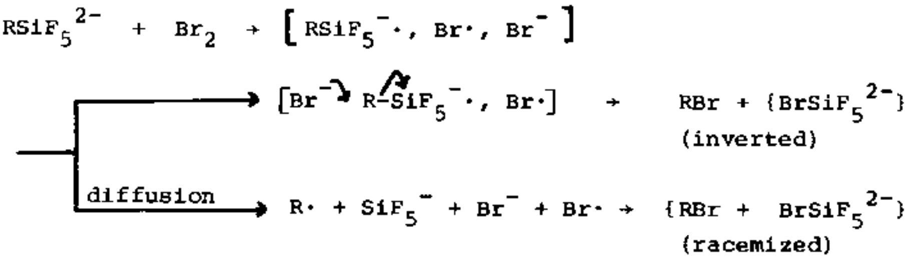


R' = H or R

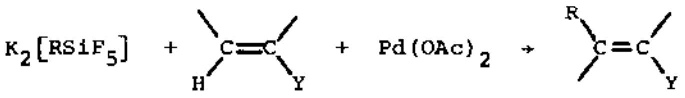
The organosilicates containing other alkali-metal countercations (Na, Rb, and Cs) have also been prepared by the reaction of the corresponding organotrifluorosilanes with NaF, RbF, and CsF, respectively. The silicates have been found to react with Cl_2, Br_2, I_2, IBr and NBS under mild conditions to give the corresponding organic halides.



In both the halogen and NBS cleavage reactions a halogen atom is regioselectively introduced onto the carbon to which the silicon atom has been attached. The present procedure provides a new general method for anti-Markownikoff hydrohalogenation of olefins. The NBS cleavage tolerates some functional groups such as the alkoxycarbonyl, oxo, halo, and alkenyl groups. The reaction of (E)-alkenylsilicates with NBS affords (E)-alkenyl bromides with high stereoselectivity, while stereoselectivity of the bromine cleavage is relatively low. Stereochemistry at the aliphatic carbon in the cleavage reaction of alkylsilicates has also been investigated. Reactions of exo- and endo-2-norbornylpentafluorosilicates with Br_2 and NBS proceed stereospecifically with predominant inversion of configuration. Partial stereochemical scrambling has been observed, however, in the reaction of the exo silicate with Br_2 in nonpolar solvents. On the basis of these experimental results, a mechanism involving the initial one-electron transfer has been proposed for the bromine cleavage reaction of alkylsilicates.

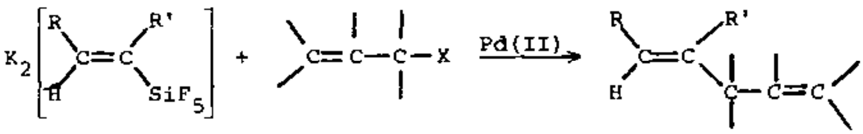


The reaction of alkylsilicates with IBr giving both alkyl iodide and bromide also supports the proposed mechanism. The NBS cleavage of alkylsilicates and all reactions of alkenyl- and arylsilicates, however, seem to proceed by an electrophilic mechanism.[81] The carbon-silicon bond in these organopentafluorosilicates is also cleaved by copper(I) chloride or bromide to give the corresponding organic halides in high yields. The reaction obeys a stoichiometry of $K_2[RSiF_5]/CuX_2 = 1/2$. A halogen atom is regioselectively introduced to the carbon atom to which the silicon atom has been attached. (E)-Alkenyl halides are obtained stereoselectivley from (E)-alkenylsilicates. Since organopentafluorosilicates can readily be prepared from olefins and acetylenes, the present reaction provides a synthetically useful route to organic halides. A two-step mechanism involving initial formation of an organic radical followed by ligand transfer from CuX_2 has been suggested by (1) spin trapping of the alkyl radical intermediate, (2) formation of an aldehyde in the presence of oxygen, and (3) stereochemical scrambling in the reaction of exo- and endo-2-norbornylpentafluorosilicates. Alkylsilicates undergo conjugate addition to α,β-enones in the presence of copper(II) acetate under rather forced conditions. In contrast to the inertness of alkylsilicates, alkenylsilicates react with some copper(II) pseudohalides. The reaction of (E)-alkenylsilicates with copper(II) thiocyanate gives (E)-alkenyl thiocyanates. The reaction with copper(II) selenocyanate prepared from $Cu(OAc)_2$ and KSeCN in situ gives a dialkenyl selenide. Copper(II) acetate induces the oxidative solvolytic cleavage of the carbon-silicon bond in alkenylsilicates. The reaction in the presence of an alcohol or water gives the alkenyl ethers or aldehydes, respectively.[82] The potassium (E)-alkenylpentafluorosilicates undergo palladium-promoted coupling reactions with a number of different reagents, such as activated alkenes:

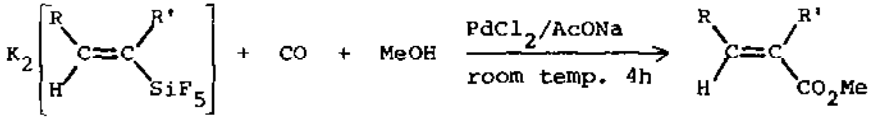


$Y = CO_2R'$, CHO, CN

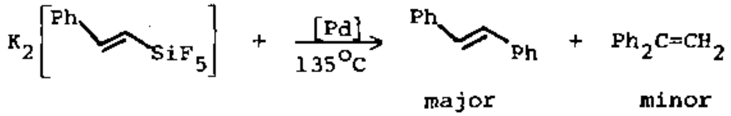
or allylic halides:

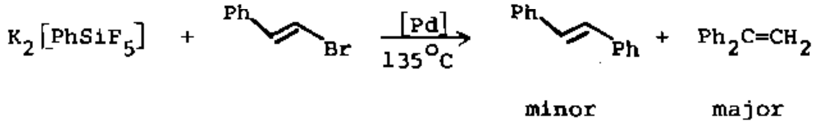


and undergo carbonylation:



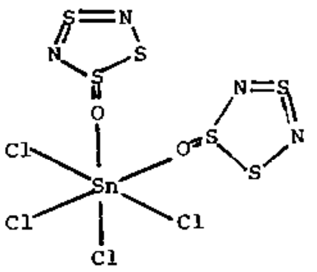
and cross-coupling with C(sp^2) halides, eg:[83]





Several studies reporting complexes of tin(IV) halides have been reported. All possible isomers, $SnCl_xBr_yI_2$ (x + y + z = 4), have been observed by ^{119}Sn n.m.r. in mixtures of the tin(IV) halides. The same technique has been used to study mixtures of SnX_5^- and SnX_6^{2-} (X = Cl,Br), where again all possible species and isomers were detected. ^{31}P and ^{119}Sn spectra for the complexes $SnX_4(PBu_3)_2$ (X = Cl,Br) and a mixture of both show the presence of all six possible trans isomers in statistical distribution. Spectra for the $SnX_5(PBu_3)^-$ (X = Cl,Br) species indicate some disproportionation, although the $SnX_5(PBu_3)^-$ anion is predominant. A mixture of both of these anions gives rise to complex spectra, although all twelve isomers of the $[SnCl_5Br_{5-x}(PBu_3)^-]$ series were identified.[84] X-ray structures of two octahedral tin(IV) chloride adducts, cis-bis(1,2,4λ^4,3,5-trithiadiazole-1-oxide)-tetrachlorotin(IV) (3)[85] and trans-bis(1,5-dithiacyclooctane)-tetrachlorotin(IV) (4),[86] have been determined.

Adducts of tin(IV) chloride and bromide with S_4N_4 of



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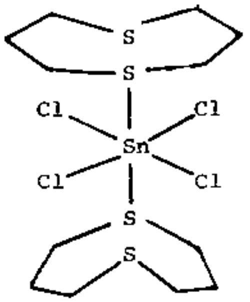
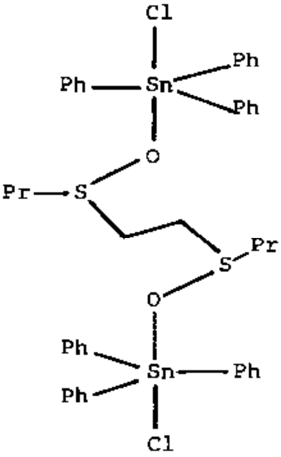


(4)

stoichiometry $SnX_4.2S_4N_4$ are bright red in colour and high melting. Mössbauer spectra of these and also of the adducts with tin(II) compounds, of stoichiometry SnX_2,S_2N_2 (X = Cl,Br,NMe_2,OMe), show them to contain tetravalent tin.[87,88] The electric field gradients in the complexes $[Ph_2PO_2]_2SnBr_2$, $[(Me_2N)_3P]_2SnCl_4$, $[(Me_2N)_3PO]_2SnMe_2Cl_2$, and $[(Et_2N)Me_2PO]_2SnMeCl_3$ have been determined as positive.[89] The CNDO/2 method in a sp-valence basis has been used to calculate the electronic structure and Mössbauer isomer shifts of $SnCl_4$ and its 1:2 adducts with EtOH, Me_2S, MeCN, and $POCl_3$. The decrease in the isomer shift which occurs in 5s electron density on the tin atom.[90]

Analysis of the melting point diagrams of methylhalogenosilane-pyridine systems demonstrated the existence of the stable adducts $MeSiCl_3.2py$, $MeSiBr_3.2py$, $Me_2SiBr_2.py$ and $Me_3SiBr.py$. The complexes $Me_2SiCl_2.py$ and $Me_2SiBr_2.py$ were unstable, whilst Me_3SiCl showed no tendency towards complex formation.[91] The structures of several complexes of organotin(IV) halides have been determined, including μ[rac-1,2-bis(n-propyl-sulphinyl)ethylene]-O,O'-bis-[chloro-cis-triphenyltin(IV)] (5),[92] (2,2':6',2"-terpyridyl)aqua-chlorotriphenyltin (6) (in which the terpyridyl is hydrogen-bonded to the water molecule rather than chelating the metal),[93] chlorotriphenyltin pyridiniumcarboxylate (7) (in which the nitrogen atom is protonated, and symmetry-related molecules are hydrogen-bonded together),[94] dichlorodiethyl[2-(5-methyl-1,2,4-oxadiazol-3-yl)-1,10-phenanthroline]tin(IV) (8) (in which the tin atom is coordinated in a pentagonal bipyramidal fashion with the ethyl groups occupying the two axial sites),[95] trans-dichlorodimethyl-(3,5-dimethylpyrazole-N^2)tin (in which the pyrazole ligands are bonded to tin via the pyridine-like nitrogen atom, and adjacent molecules are held together by intermolecular Cl...H hydrogen-bonds



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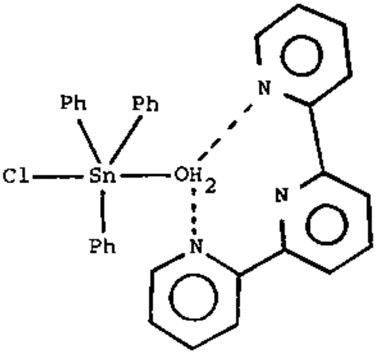

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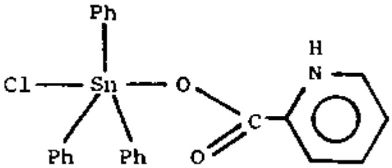

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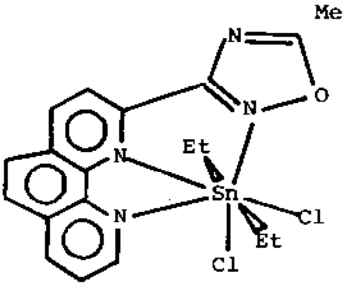

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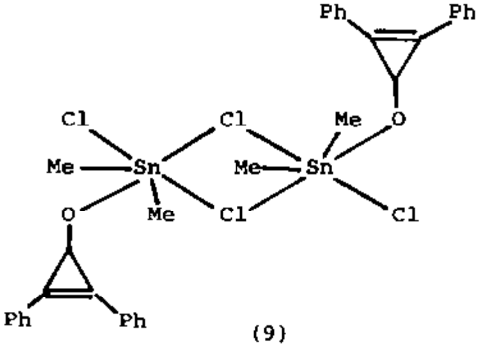


(9)

to form infinite linear chains),[96] and the 1:1 adducts of dimethyltin dichloride with diphenylcyclopropenone and 2,6-dimethylpyridine-*N*-oxide.[97,98] In both the two latter adducts, and most probably also in the 1:1 adduct with salicylaldehyde, association by chlorine-bridging occurs to give six-coordinated tin. The central $[Sn_2Cl_2]$ ring in the dimers of the diphenylcyclopropenone adduct is almost flat, but the bridging Sn...Cl distance is very much longer (3.56Å) than the covalent bonding distance (2.47Å). The MeSnMe framework is distorted substantially from linearity (CSnC = 142.2°). ^1H and ^{13}C n.m.r. data indicate that in their complexes with dimethyltin dichloride, *N*-arylsalicylideneimines behave as unidentate ligands via the oxygen rather than the imine nitrogen atom.[99] N.m.r. measurements have also demonstrated the occurrence of proton scrambling in the phosphazenium ring of the salts $[N_3P_3Me_6H]^+[Me_2SnX_3]^-$ (X = Cl,Br)(from $N_3P_3Me_3$ and Me_2SnX_2).[100]

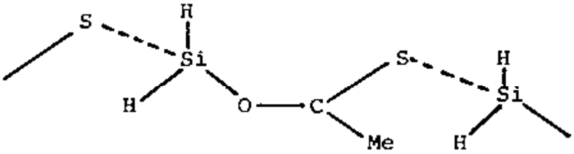
Two structural studies of Me_3SiCN have been reported. The microwave spectrum has been re-examined in an attempt to elucidate the previous conflicting evidence for the existence of the isocyanide isomer, Me_3SiNC, but only evidence for one isomer with the Si-C-N framework was found.[101] The solid-state structure at 140K consists of chains of molecules aligned head-to-tail with an intermolecular Si...N distance of 3.66Å. Crystals appear to be disordered such that the chains may be aligned either parallel or antiparallel to the *c* axis.[102] The first examples of silyl cyanates have been synthesised by treating sterically-hindered iodosilanes with silver cyanate in dichloromethane:

$$[(Me_3Si)_3C]R_2SiI + AgOCN \rightarrow [(Me_3Si)_3C]R_2SiOCN$$

$$R_2 = Me_2, Ph_2, Me(OMe).$$

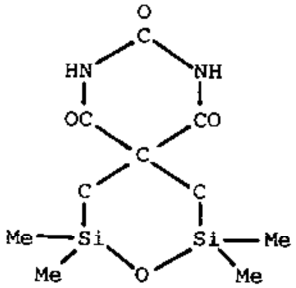
Isomerisation to the corresponding isocyanates occurs on heating in a sealed tube at *ca*. 150° for two hours.[103] (2,2-Bipyridyl)-diisocyanatodiphenyltin has a distorted octahedral structure with *cis* phenyl groups and *trans* isothiocyanates.[104]

The structures of several compounds containing bonds to oxygen have been determined. The molecular structure of silyl monothioacetate has been determined both in the crystal (at 130K) and in the gas phase. In the crystal, adjacent molecules are linked by weak intermolecular Si...S interactions (3.38Å) to give chains (10). The Si-O and C=S bonds are eclipsed in both phases, with the intramolecular Si...S distance in both the gas phase (3.14Å) and in the crystal (3.185Å) being less than the sum of the van der Waal's radii. The Si-O bond distance is slightly shorter in the crystal (1.699Å) than in the gas phase (1.717Å).[105]



(10)

Hexa-*tert*-butyltrisoloxane, $({}^tBu_2SiO)_3$, hexaphenyltrigermoxane, $(Ph_2GeO)_3$,[107] and hexamesityltristannoxane, $(Mes_2SnO)_3$,[108] are all characterised by a $[M_3O_3]$ six-membered ring, which is planar in the former two molecules. The latter adopts a twist conformation, and is the sole example of a non-polymeric diorganotin oxide. Crystals of both $Me_3SiONa.3H_2O$ (11) and $(Me_2SiONa)_2O.4H_2O$ (12) are composed of double layers, each of which contains a hydrophilic and a hydrophobic part, the hydrophilic part consisting of ionized $Si\text{-}O^-$ groups Me_3SiO^- anions in (11) and $^-OMe_2SiOSiMe_2O^-$ dianions in (12) groups turned towards one another, with Na^+ cations and water molecules arranged between them.[109] The ring compounds 8,10-diaza-2,4-disila-3-oxa-7,9,11-trioxo-2,2,4,4-tetramethyl-spiro[5.5]indecane (13),[110] 1,3,7,9-tetramethyl-5,5,11,11-tetrakis(carbethoxy)-1,3,7,9-tetrasila-2,8,13,14-tetraoxatricyclo-$[7.3.1.1^{3,7}]$tetradecane (14),[110] 1,7-diphenyl-3,3,5,5,9,9,11,11-octamethylbicycloheptasiloxane (15),[111] 1,1,7,7,9,9-hexamethyl-3,5,11,13-tetraphenyltricyclononasiloxane (16),[111] 1,1,5,5-tetrakis(hydroxymethylsiloxy)-3,3,7,7-tetraphenylcyclotetrasiloxane (17),[112] and octaethyl- and octaallylsilasesquioxanes (18)[113,114] all have molecular structures, although molecules of (17) are joined by hydrogen-bonds to form layers. Centrosymmetric molecules of (14) have a *trans*-arrangement of the lateral six-membered carbosiloxane rings relative to the central eight-membered tetrasiloxane ring. In contrast, (16) exhibits a *cis*-arrangement. (17) Exists as two crystallographically independent molecules with different conformations of the eight-membered siloxane rings. Structural data for the two new organo-



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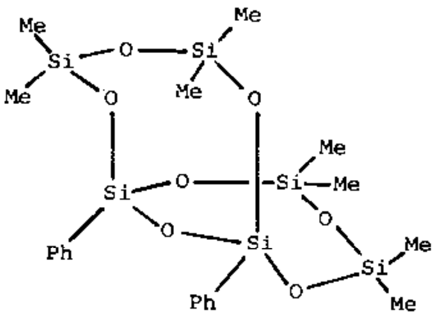

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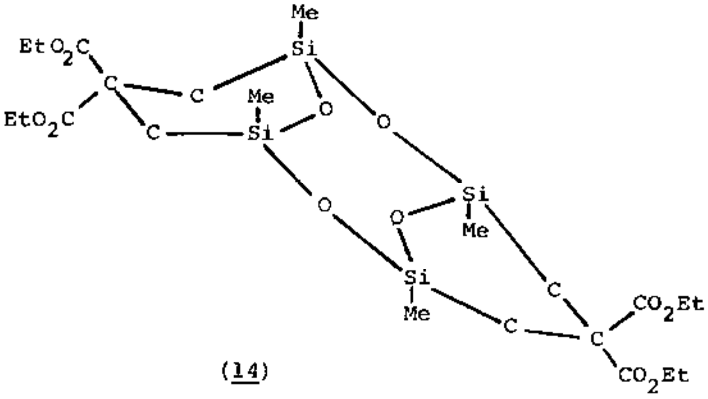

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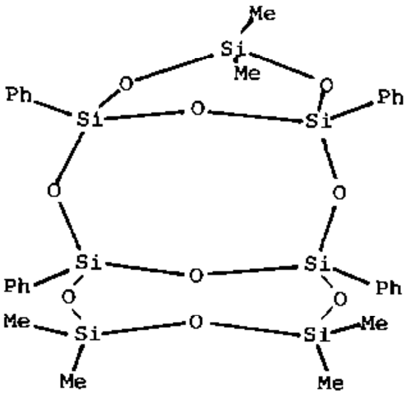

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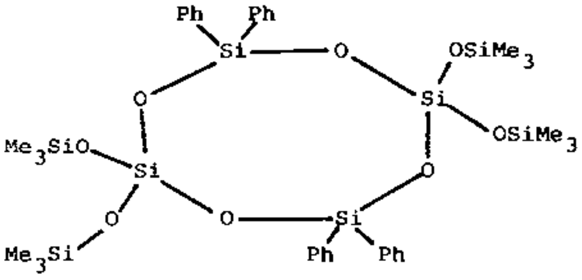

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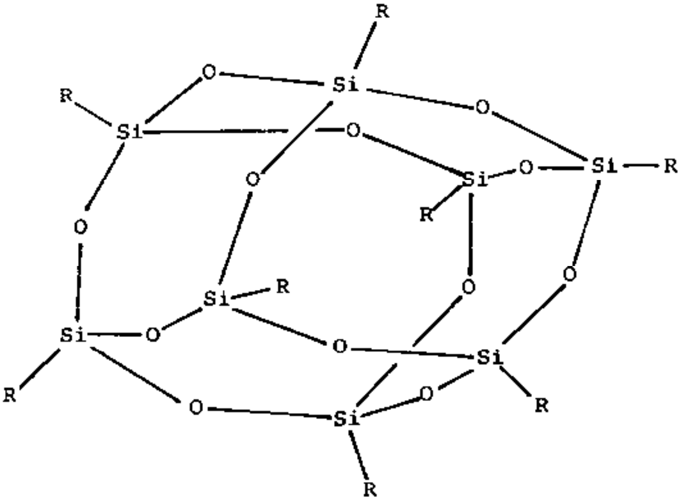
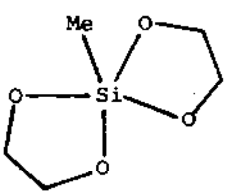


(18) R = Et, CH_2:CH.CH_2



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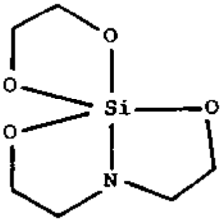


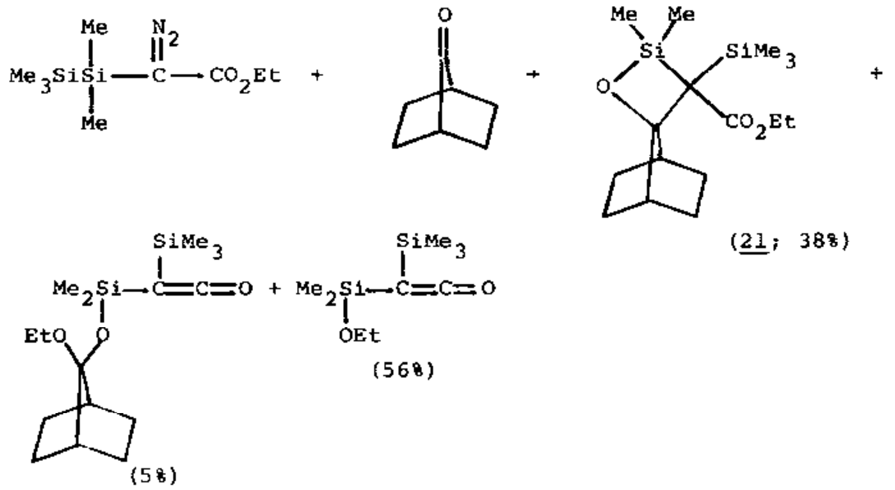
(20)

silasesquioxanes (18) (others previously determined have R = H, Me, $CH=CH_3$ and Ph) confirm that the structure of the $[Si_8O_{12}]$ is not influenced in any way by the nature or size of the substituents. A solid-state ^{13}C and ^{29}Si n.m.r. study of these compounds has established a correspondence between the non-equivalence of the silicon atoms and the distortion of the Si-O framework of the molecule.[115]

Both the bis(ethylenedioxy)methylsilane(1-) anion (19)[116] and minobis(ethyleneoxo)ethylenedioxysilane (20)[117] have five-coordinated silicon. In the former, the geometry is intermediate between trigonal bipyramidal and square pyramidal, with strong NH...O hydrogen bonds connecting the anions and hexamethylenediammonium cations. The latter has almost ideal trigonal bipyramidal geometry, although the silicon atom is displaced 0.101Å from the plane of the three equatorial ligands.

The chemical shifts of the SiK_α and ClK_α X-ray lines have been used to obtain the Pauling changes on the silicon and chlorine atoms in silatrane molecules of the types, $XSi(OCHRCH_2)_{3-n}(OCH_2CH_2)_nN$ (R = H, Me; n = 0-3), $XSi(OEt)_3$ (X = H, Cl, Me, CH_2Cl), $Me_2Si(OCH_2CH_2)Y$ (Y = O, MeN) and $Me_2Si(OEt_2)_2$. Increase in coordination number at silicon leads to an increase in its positive charge, which may be reduced by intramolecular N...Si interaction.[118]

The first stable 1,2-silaoxetane (21) has been isolated from the reaction of ethyl pentamethyldisilanyldiazoacetate with 7-norbornone at 185°:

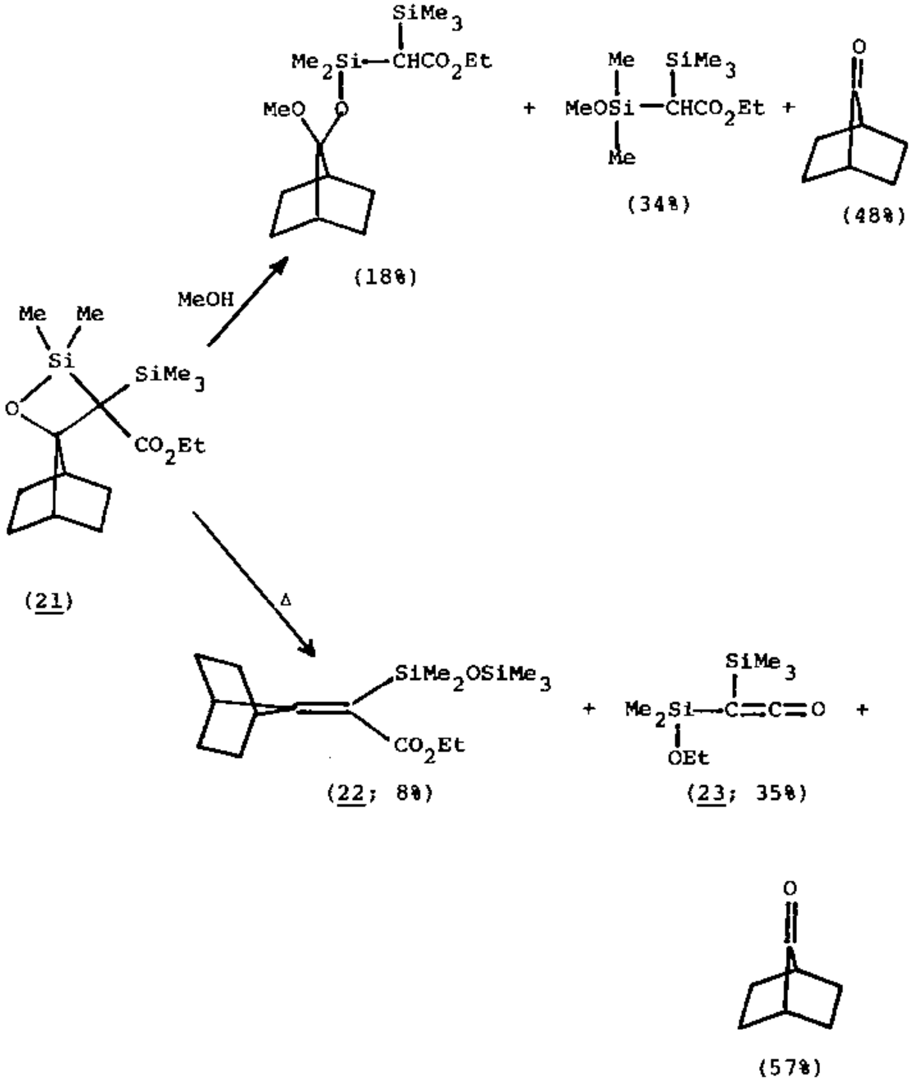


(21; 38%)

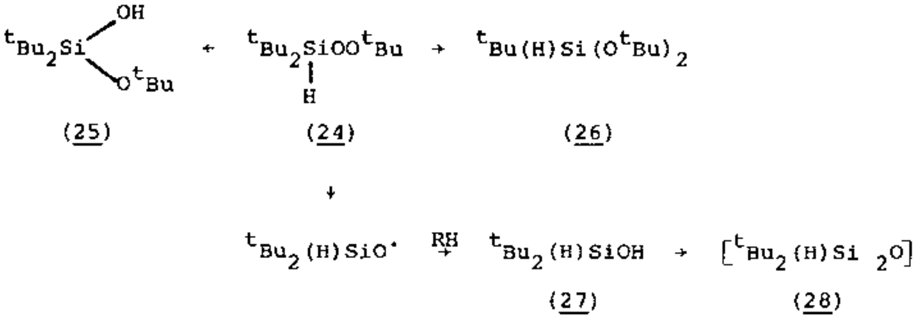
(56%)

(5%)

(21) is attacked by alcohols with cleavage of both the ring Si-O and C-C bonds, whereas thermal decomposition at 185° led to the formation of the vinylsiloxane (22), the silylketene (23) and norbornone:[119]

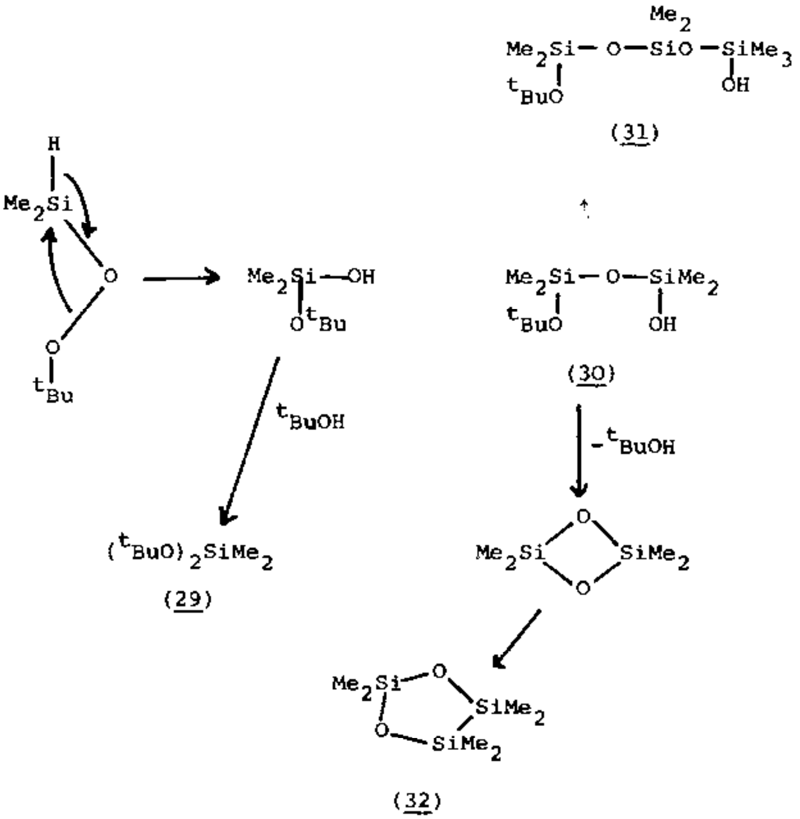


Mechanisms other than silanone formation have been proposed in the condensed-phase thermolysis of hydridosilyl peroxides, $R_2Si(H)OO^tBu$. Thermolysis of $^tBu_2Si(H)OO^tBu_2$ (24) affords (25) and (26) with small amounts of (27) and (28) but no [$^tBuSi=O$]:


(25) (24) (26)

(27) (28)

Similarly, $Me_2Si(O^tBu)(OH)$, expected to be a principal rearrangement product of (24) reacts rapidly at temperatures >100° to give the four products, (29)-(32), the yields of which were dependent upon the concentration of the starting silanol:[120]


(31)

(30)

(29)

(32)

Pentamethyldisiloxane reacts with benzene under catalysis by Vaska's compound to yield phenylsiloxanes and other redistribution products.[121]

Both bis(1,2-benzenediolato)fluorogermanate(1-) and bis(4-methyl-1,2-benzenedithiolato)fluorogermanate(1-) have stereochemistries which lie along the Berry C_{2v} coordinate connecting the idealised trigonal bipyramidal and rectangular pyramidal geometries. The greater displacement of the oxa anion (*ca*. 81% along the coordinate, *cf*. *ca*. 40% for the thia anion) maybe rationalised in terms of reduced electron pair repulsion effects.[122] 1-Phenylgermatrane-3-one (33)[123] and 1-methyl-2-carbagermatrane (34)[124] each have trigonal bipyramidal geometries with fairly short transannular Ge...N distances (2.203Å (33) and 2.436Å (34)). In (33), a flattening of the half-rings with the carbonyl group is accompanied by an increase in the torsional angles of the remaining chains of the atrane bicyclic system, which in solution undergoes rapid (on the n.m.r. time scale) synchronous conversion. Alkylphenyltin oxides react with nitrilotriacetic acid in DMF/toluene to afford 5-alkyltriptychoxazastannolidones (35):

$$^{1}/n(\mathrm{RPhSnO})_n + (\mathrm{HO_2CCH_2})_3\mathrm{N} \xrightarrow[-C_6H_6]{-H_2O} \mathrm{RSn(OCOCH_2)_3N}$$

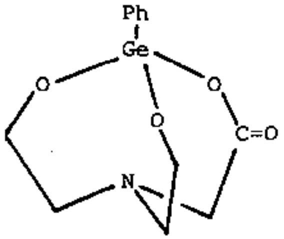
(35)

The reaction of methyltin triethoxide with nitrilotriacetic-N,N',-N"-trimethyltriamide leads to 4,5,6,11-tetramethyltriptychdiazastannolidone (36):

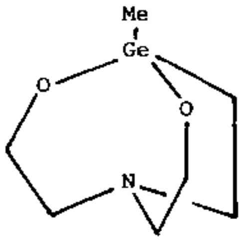
$$\mathrm{MeSn(OEt)_3} + (\mathrm{HNMeCOCH_2})_3\mathrm{N} \rightarrow \mathrm{MeSn(NMeCOCH_2)_3N}$$

(36)

In donor solvents, (35) and (36) achieve six-coordination as in (37).[125] A similar method has been employed to prepare 1,4,6-trimethyl-5,5-dialkyldiptychdiazastannolidones (38).[126]



(33)



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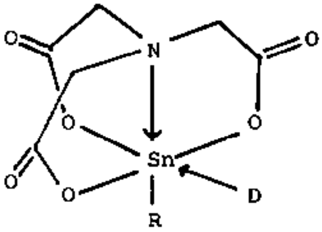
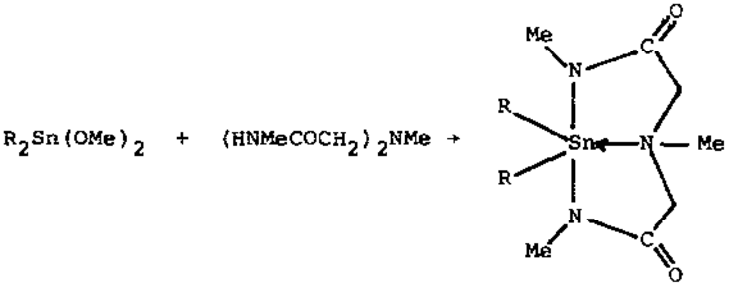


D = H_2O, DMSO

(37)



$R_2Sn(OMe)_2 + (HNMeCOCH_2)_2NMe \rightarrow$

(38)

Depolarised scattering data obtained by the molecular optical anisotropy method for diorganotin tropolonates, oxinates and dibenzoylmethanates, together with observed large positive Kerr constants and non-zero permanent dipole moments, have shown that these molecules adopt predominantly a distorted *trans*-type (skew-trapezoidal bipyramidal) structure.[127,128] [Tris(trimethylsilyl)-methyl]dimethyllead oxinate, $[(Me_3Si)_3C]Me_2Pbox$ (ox = oxinate), is stable in boiling ethanol over short periods, but undergoes redistribution and reductive-elimination reactions affording $Pb(ox)_2$, Me_3Pbox, Hox, and $[(Me_3Si)_3C]Me_3Pb$. Silyl-group cleavage, yielding $[(Me_3Si)_2CH]MePb(ox)_2$, occurs during its preparation from $[(Me_3Si)_3C]MePbCl_2$ and oxine at pH ~10 in methanol, ethanol or aqueous dioxane. Further silyl-group displacement occurs on refluxing in these media leading successively to $(Me_3SiCH_2)MePb(ox)_2$ and $Me_2Pb(ox)_2$. These cleavage reactions occur in competition with disproportionation and reductive-elimination reactions, the final products being $Pb(ox)_2$, Me_4Pb, Me_3Pbox and Hox.[129]

The reaction of bis(trimethylsilyl)amine and sulphur dioxide affords $(Me_3Si)_2O$, Me_3SiNSO and the ammonium salt, $NH_4Me_3SiOSO_2$, which sublimes readily at ambient temperatures, but which still retains ionic properties. The mechanism of yhe reaction is complex, and is probably best described by the sequence:

$$4(Me_3Si)_2NH + 4SO_2 \rightarrow 4(Me_3Si)_2NH.SO_2$$

$$3(Me_3Si)_2NH.SO_2 \rightarrow 3Me_3SiNSO + 3Me_3SiOH$$

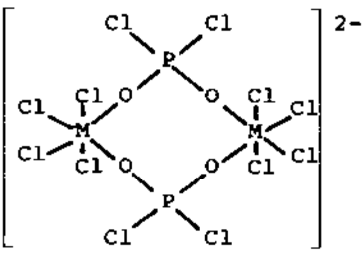
$$Me_3SiOH + (Me_3Si)_2NH.SO_2 \rightarrow (Me_3Si)_2O + Me_3SiNH_2.SO_2$$

$$Me_3SiNH_2.SO_2 + Me_3SiOH \rightarrow (Me_3Si)_2O + NH_3.SO_2$$

$$Me_3SiOH + NH_3.SO_2 \rightarrow NH_4Me_3SiOSO_2$$

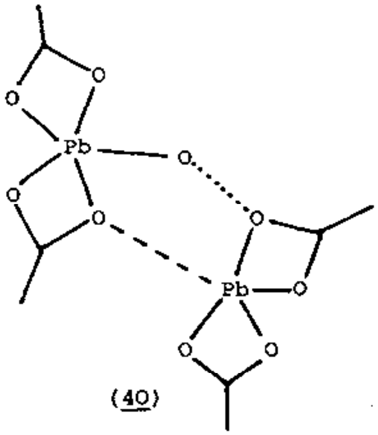
The gas phase inequilibrium with solid $NH_4Me_3SiOSO_2$ has been shown to contain $(Me_3Si)_2O$, NH_3, SO_2 and water, which combine to form ammonium pyrosulphate, $(NH_4)_2S_2O_5$.[130,131]

The dichlorophosphate complex, $(AsPh_4)_2[SnCl_4(O_2PCl_2)]_2$, has been obtained from tin(IV) chloride and $AsPh_4[PO_2Cl_2]$ in dichloromethane. Infrared data suggest the dimeric structure (39).[132]



(39)

Molloy and Zuckerman[133-135] have further continued their studies of tin-substituted phosphate esters. Di- and triorganotin diphenylphosphate esters, $R_2Sn[O_2P(OPh)_2]_2$ and $R_3SnO_2P(OPh)_2$ can be prepared either by elimination of water from the organotin hydr(oxide) and diphenylphosphonic acid or by metathesis between the organotin chloride and the sodium salt. Similar methods were used for the synthesis of organotin phenylphosphonate phenyl esters, $R_2Sn[O_2PPh(OPh)]_2$ and $R_3SnO_2PPh(OPh)$. Spectroscopic data suggest similar associated structures for both series of compounds, with six-coordinated trans-geometries at tin for the diorganotin derivatives, and five-coordination with planar $[SnC_3]$ units in the triorganotin derivatives. The oligomeric nature of the association was confirmed by X-ray studies in the case of $Ph_3SnO_2P(OPh)_2$, in which molecular units associate to form a centrosymmetric cyclic hexamer in which planar $[Ph_3Sn]$ units are axially bridged by the OPO framework of the diphenylphosphate ligand to achieve almost perfect trigonal bipyramidal coordination at tin. The ring is linear at tin but bent at phosphorus with an average OPO angle of 118.5°, and slightly puckered into a chair conformation. Triorganotin(diphenylphosphinyl)- and (diphenylthiophosphinyl)acetates, $R_3SnO_2CCH_2P(E)Ph_2$ (E = O,S), obtained either by metathesis or condensation, are white solids, soluble in common organic solvents. The triphenyltin derivative (E = O) undergoes decarboxylation at its melting point ($180-183^\circ$), and forms a 1:2 complex, $[Ph_2P(O)CH_2CO_2SnPh_3]_2.Ph_3SnCl$ with triphenyltin chloride. Spectroscopic evidence indicates P=O...Sn rather than C=O...Sn bonding, giving rise to weak association or the presence of small oligomers in the solid. The diorganotin derivatives, $R_2Sn[O_2CCH_2P(O)Ph_2]_2$, contain chelated, six-coordinated, trans-R_2Sn octahedra in all phases.[136] Several inorganic tin derivatives of amino acids and amino acid esters[137] and triorganotin and -lead derivatives of acylglycines[138] have been reported. Crystals of $[Ph_2Pb(OAc)_2]_2.H_2O.C_6H_6$ comprise binuclear $\{[Ph_2Pb(OAc)_2]_2.H_2O\}$ units with the benzene molecules occupying a cleft position in the crystal lattice. The geometry at each lead atom is that of a slightly distorted pentagonal bipyramid in which the axial positions are occupied by the phenyl groups. Each lead is chelated in the equatorial plane by two anisobidentate acetato ligands; the fifth equatorial site being occupied on one lead by a triply-bridging acyl oxygen atom, and on the other by the solvating water molecule, which also forms a hydrogen-bond to an acetato oxygen atom coordinated to the second lead. The geometry of the equatorial plane is shown in (<u>40</u>).[139]



(<u>40</u>)

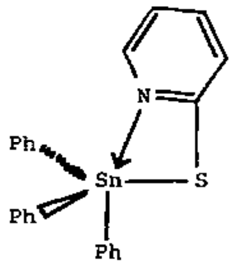
A conformational analysis of methyl dimethylsilylsulphide, $Me_2Si(H)SMe$, has demonstrated the presence of two possible isomers due to rotation about the Si-S bond. Both C_1 and C_s forms exist in the liquid phase, but only the C_1 form is present in the solid. No enthalpy difference was found between the two conformers in the liquid ($\Delta H(C_1 - C_s) = 0 \pm 50$ cal.mol^{-1}).[140] Trimethylsilylthioboranes have been obtained in high yield by the reaction of lithium trimethylsilanethiolate with halogenoboranes:[141]

$$Me_3Si\text{-}SLi + XBRR' \rightarrow Me_3Si\text{-}SBRR' + LiX$$

$$2Me_3Si\text{-}SLi + MeBBr_2 \rightarrow (Me_3SiS)_2BMe + 2LiBr$$

Crystals of tris(p-tolyl)tin pyridine-2-thiolate comprise two crystallographically-independent molecules with identical structures in which the pyridine-2-thiolato ligand chelates the tin atom via axial (N) and equatorial (S) sites of a distorted trigonal bipyramid (<u>41</u>).[142]

The structures of organotin derivatives of 6-thiopurine have been studied by infrared and Mössbauer spectroscopy. The trimethyltin derivative (<u>42</u>) has a polymeric solid-state structure in which planar $[SnC_3]$ units are bridged via the thione tautomer by N^1 and N^3. The dibutyltin bis(6-thiopurine) derivative, however, has a molecular structure in which the ligands function



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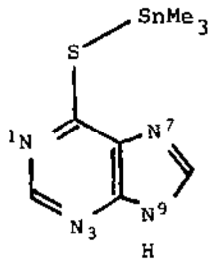


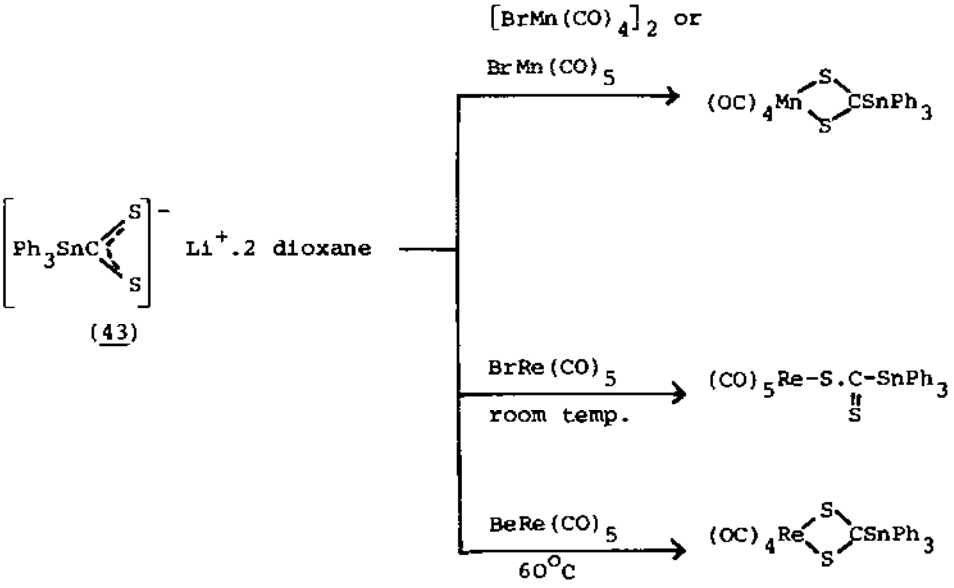
(42)

as [S,N] chelating groups.[143] The dimethyltin compounds, $Me_2SnL_2.H_2O$ (L = SCH_2CO_2H, $-SCH_2CH_2CO_2H$, and $-SCHMeCO_2H$), also contain five-coordinated tin.[144] Barriers to conformer interconversion in dithiastannolanes, RR'Sn[$SCH_2CHR''S$], have been studied by low-temperature n.m.r. At room temperature, the chelate rings exist in the half-chair conformation, with the $-CH_2CHR''-$ moiety in a fully staggered configuration as in the solid state. $\Delta G^{\ddagger}$ values for the interconversion of the two half-chair conformations lie in the range 30-32 kJ mol^{-1}, and are essentially independent of the substituents both on the tin atom and on the ring.[145] The reaction of bis(toluene-3,4-dithiolato)-tin with DMSO, HMPA and Ph_3PO leads to the formation of hexacoordinated spirocyclic neutral adducts, but with hydroxide and halide anions; the anions $[Sn(TDT)(OH)]^{2-}$ and $[Sn(TDT)_2X]^-$ are obtained. Reversible colour changes take place on heating the latter derivatives, which are deduced to possess rectangular pyramidal geometries.[146] Air- and moisture-sensitive golden yellow prisms of the salt $[Ph_3SnCS_2]^-Li^+.2$ dioxane (43) are obtained by the addition of dioxane to the reaction mixture of Ph_3SnLi and CS_2 in THF. With manganese and rhenium carbonyl halides (43) forms complexes in which the $[S_2CSnPh_3]$ group can function either as an uni- or a bidentate ligand as shown in Scheme 6.[147,148]

The synthesis of tetraethylammonium tris(cyclopentadienedithiocarboxylate)stannate(IV), $NEt_4[Sn(S_2C_5H_4)_3]$, has been reported.[56]

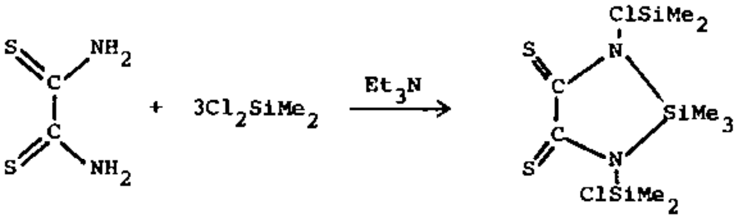
Pyridine and imidazole catalyze the reaction of trialkylsilanethiols with substituted anilines, providing a convenient method for the synthesis of N-(trialkoxysilyl)arylamines

$$(RO)_3SiSH + R'NHC_6H_4X \rightarrow (RO)_3SiNR'C_6H_4X + H_2S$$

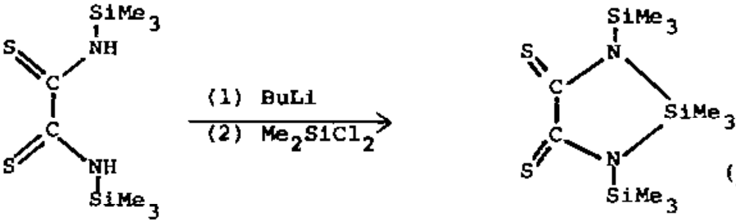


Scheme 6.

The reaction kinetics were also investigated, and rate constants and activation parameters evaluated.[149] The cyclic silyldithiooxamides (44) and (45) have been synthesised by conventional methods. In both, all atoms save for the methyl groups are coplanar:[150]



(44)



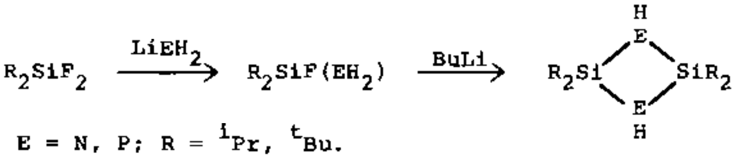
(45)

Silyl- and germylamines react with $N_3S_3Cl_3$ to afford sulphurdiimide derivatives:[151]

$$(Me_3M)_2NY + \tfrac{1}{3}N_3S_3Cl_3 \rightarrow Me_3M{-}N{=}S{=}N{-}MMe_3$$

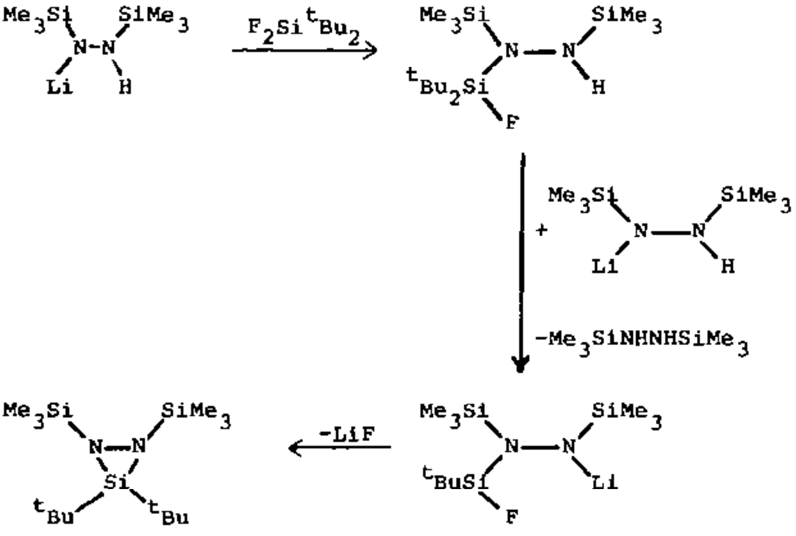
$Y = MMe_3$, H; M = Si, Ge.

1,3-Diaza- and 1,3-diphospha-2,4-disilacyclobutanes have been obtained via the route:[152]



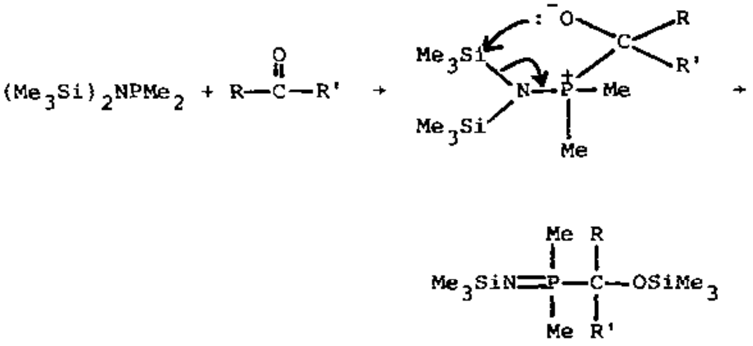
E = N, P; R = ^{i}Pr, ^{t}Bu.

whilst the stable diazasilacyclopropane (46) was prepared according to the Scheme:[153]



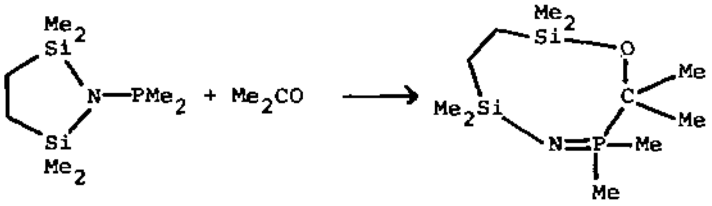
(46)

(Silylamino)phosphines including $(Me_3Si)_2NPMe_2$, $Me_2SiCH_2CH_2SiMe_2NPMe_2$, and $Me_3SiNRPMe_2$ react smoothly with carbonyl compounds in dichloromethane via nucleophilic attack by phosphorus and [1,4]-silyl migration from nitrogen to oxygen.[154] Thus, treatment of $(Me_3Si)_2NPMe_2$ with saturated ketones and aldehydes affords high yields of the new N-silylphosphinimines (47):



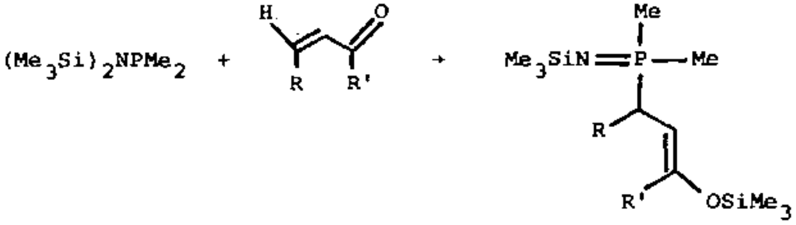
(47)

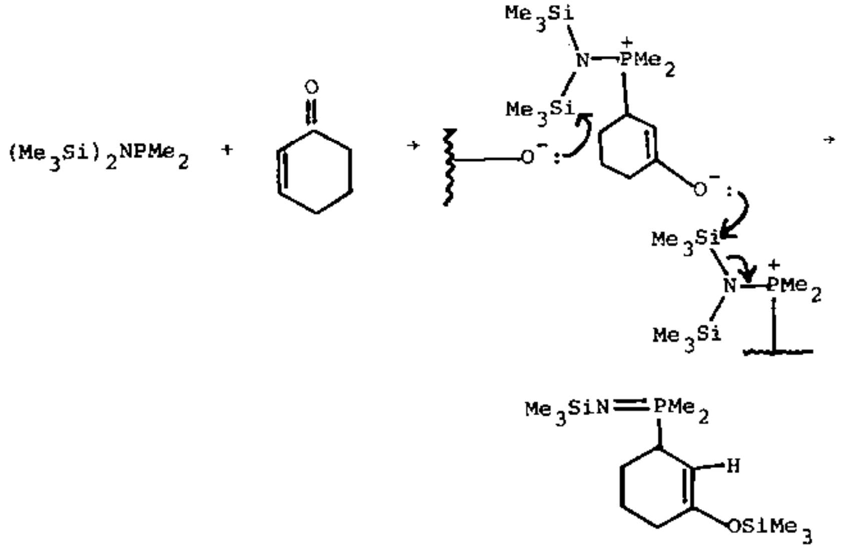
Similarly, $Me_2SiCH_2CH_2SiMe_2NPMe_2$ reacts with acetone to form the eight-membered ring product (48):

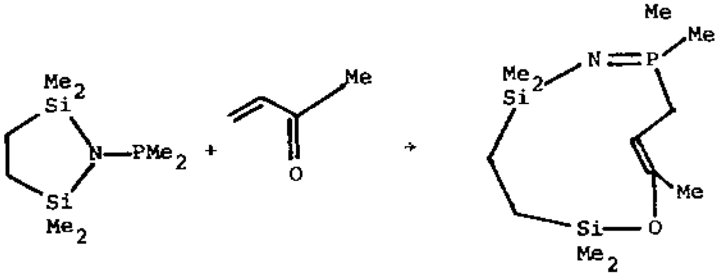


(48)

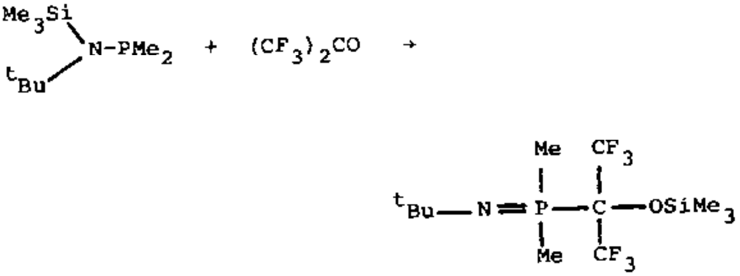
With α,β-unsaturated carbonyl compounds, 1,4-addition occurs to yield acyclic or 10-membered cyclic silyl enol ethers:

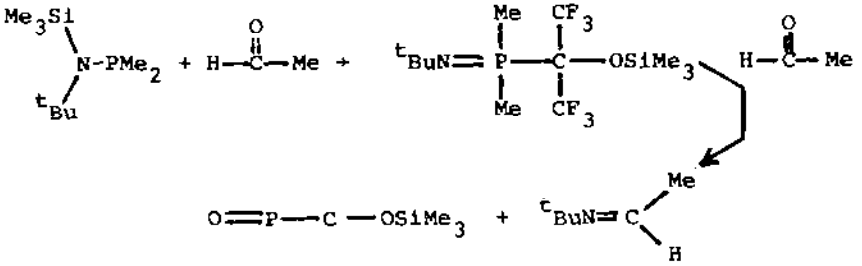


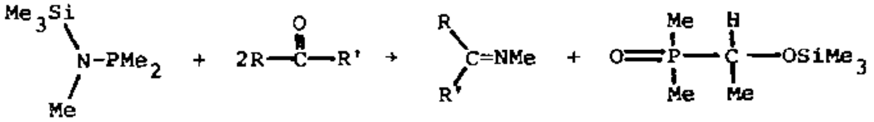




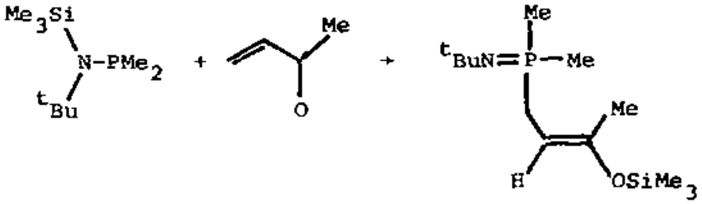
The (N-alkyl-N-silylamino)phosphines also react with carbonyl compounds, but, except for ${}^{t}BuN{=}PMe_2C(CF_3)_2OSiMe_3$, the products are phosphine oxides, $O{=}PMe_2{-}CRR'{-}OSiMe_3$:





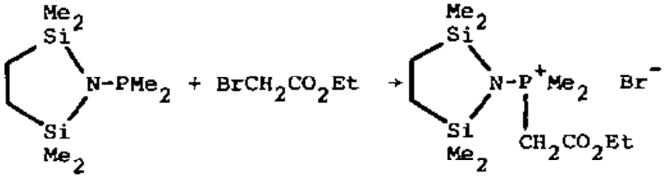


$(Me_3Si)N^tBuPMe_2$ reacts with vinylmethylacetone to afford the unstable phosphinimine (49):

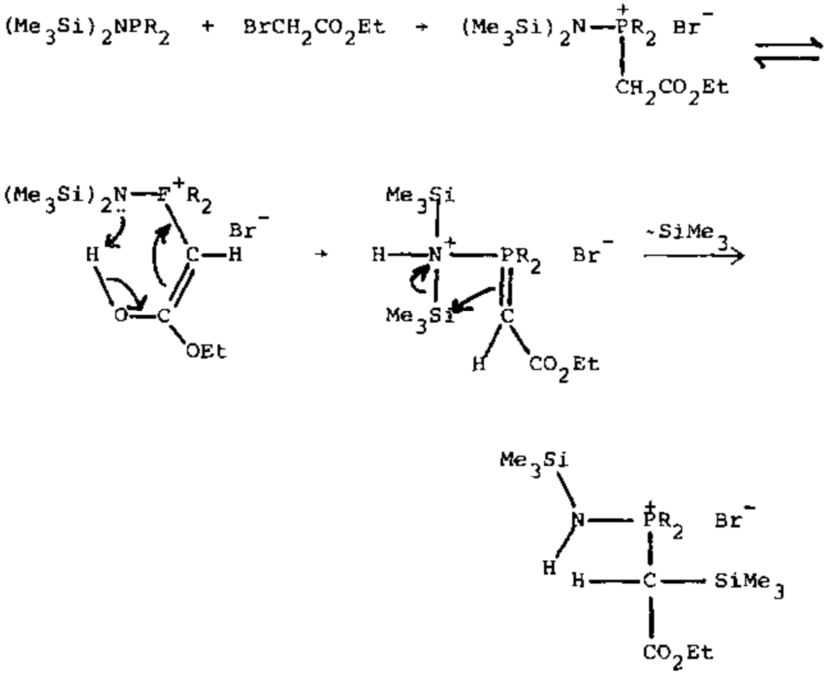


(49)

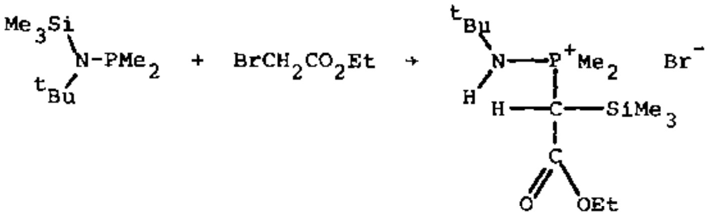
With organic halides, the same types of (silylamino)phosphines react readily to give a variety of products. Reaction with ethylbromoacetate affords either simple (50) or structurally-rearranged (51) and (52) phosphonium salts:



(50)

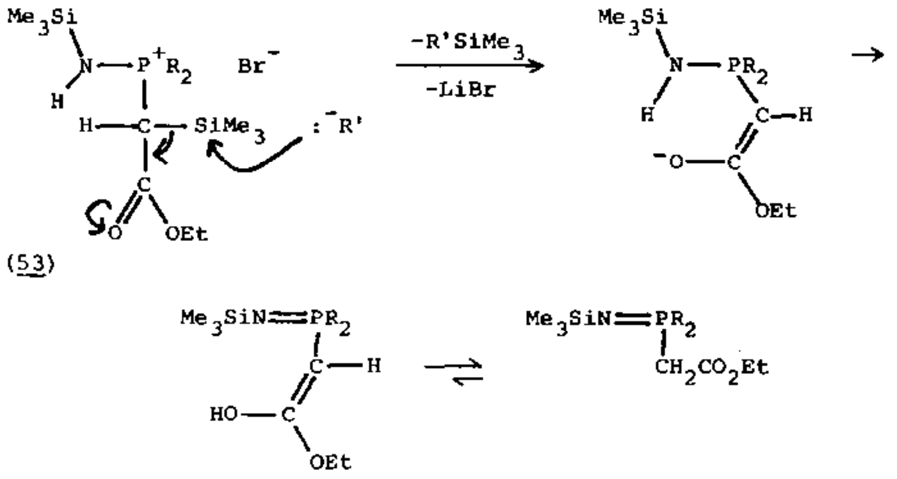


(51)



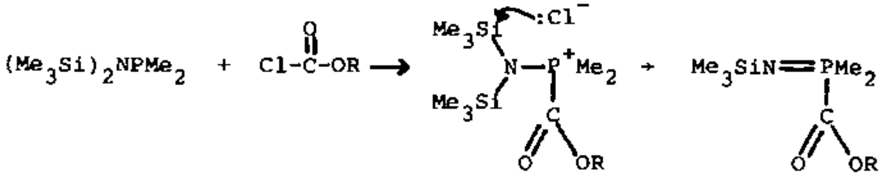
(52)

The salts (53) react with alkyllithium reagents to give N-silylphosphinimines, via attack on the C-bonded silyl group:

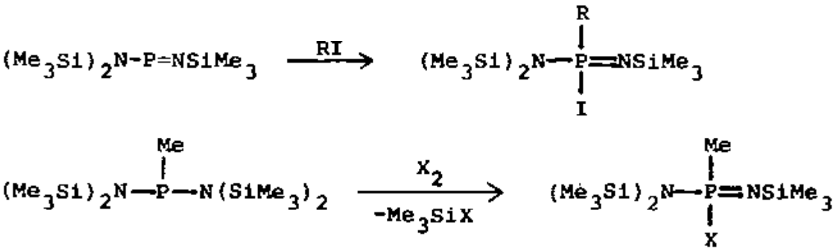


(53)

With allyl bromide, $(Me_3Si)_2NPMe_2$ reacts to form a mixture of the isomeric phosphonium salts, $[(Me_3Si)_2N\text{-}\overset{+}{P}Me_2R]Br^-$, where R = $CH_2CH{=}CH_2$ and CH=CHMe, which readily eliminate Me_3SiBr yielding the ohosphinimines, $Me_3SiN{=}PMe_2R$, but with chloroformates, the alkoxycarbonyl-substituted phosphinimines, $Me_3SiN{=}PMe_2\text{-}CO_2R$ are obtained:[155]



P-Alkyl-P-halo-substituted (silylamino)phosphinimines, $(Me_3Si)_2NP(R)(X){=}NSiMe_3$, may be obtained either by oxidative addition of alkyl iodides to $(Me_3Si)_2NP{=}NSiMe_3$ or by treatment of $[(Me_3Si)_2N]_2PMe$ with I_2 or Br_2:



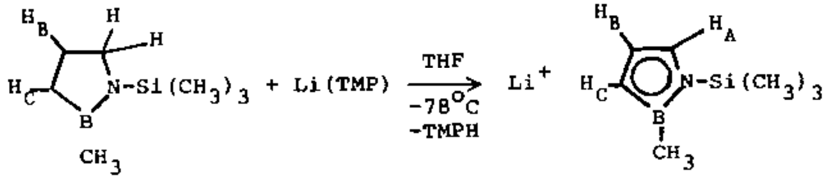
$$(Me_3Si)_2N\text{-}P{=}NSiMe_3 \xrightarrow{RI} (Me_3Si)_2N{-}\overset{R}{\underset{I}{P}}{=}NSiMe_3$$

$$(Me_3Si)_2N{-}\overset{Me}{P}{-}N(SiMe_3)_2 \xrightarrow[-Me_3SiX]{X_2} (Me_3Si)_2N{-}\overset{Me}{\underset{X}{P}}{=}NSiMe_3$$

X = Br, I.

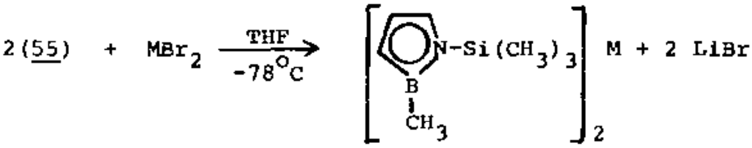
Reaction of the iodophosphinimines with MeLi affords the dialkyl derivatives $(Me_3Si)_2NPRMe{=}NSiMe_3$. Variable temperature ^1H n.m.r. studies of these (silylamino)phosphinimines demonstrate that, depending on the nature of the substituents, fluxional [1,3]-silyl exchange, [1,3]-proton exchange, or hindered rotation about the amino P-N bond may occur.[156]

When the (silylamino)borane, $(Me_3Si)_2NB(Cl)NHSiMe_3$, is allowed to react with $LiBH_4$, the isolated products are $(Me_3Si)_2NBH_2$, $[Me_3SiN(H)BH_2]_3$, and $[Me_3SiNBH]_3$. The reaction of $(Me_3Si)_2NB(H)NHSiMe_3$ with $THF\text{-}BH_3$ gave $(Me_3Si)_2$, $[Me_3SiN(H)BH_2]_3$, $[Me_3SiNBH]_3$, $(Me_3Si)_2HN_3B_3H_3$, and $(Me_3Si)_2NH$. In contrast, $[Me_3SiN(H)BH_2]_3$, $[Me_3SiNBH]_3$, $(Me_3Si)_2HN_3B_3H_3$, and $(Me_3Si)H_2N_3B_3H_3$ were obtained from the reaction of $(Me_3Si)_2NB(Cl)N(H)SiMe_3$ with $THF\text{-}BH_3$. The reaction of $(Me_3Si)_2NH$ and $THF\text{-}BH_3$ produced $[Me_3SiN(H)BH_2]_3$, $(Me_3Si)_2NBH_2$, and $^{n}BuOB(H)N(SiMe_3)_2$ in low yields.[157] A mixture of $^{s}Bu_2NBH_2$ and $(Me_3Si)_2NBH_2$ was obtained from the reaction between $^{s}Bu_2NB(Cl)N(SiMe_3)_2$ and $LiBH_4$, but the reaction of $^{s}Bu_2NB(H)N(SiMe_3)_2$ with $THF\text{-}BH_3$ resulted in the formation of $^{n}BuOB(H)N(SiMe_3)_2$ and $^{s}Bu_2NBH_2$. The compounds $^{s}Bu_2NB(Cl)N(SiMe_3)_2$ and $^{s}Bu_2NB(H)N(SiMe_3)_2$ have been prepared by allowing $(Me_3Si)_2NLi$ to react with $^{s}Bu_2NBCl_2$ and $^{s}Bu_2NBClH$, respectively. In the reaction between $^{s}Bu_2NB(Cl)N(H)SiMe_3$ and $LiBH_4$, $^{s}Bu_2NBH_2$, $(Me_3Si)_2HN_3B_3H_3$ and $[Me_3SiNBH]_3$ were isolated. The same products were obtained from the reaction of $^{s}Bu_2NB(H)N(H)SiMe_3$ with $THF\text{-}BH_3$. However, $^{s}Bu_2NBH_2$, $^{s}Bu_2NBClH$ and $^{s}Bu_2NH_2Cl$ were isolated from the reaction of $^{s}Bu_2NB(Cl)N(H)\text{-}SiMe_3$ with $THF\text{-}BH_3$. The compounds $^{s}Bu_2NB(Cl)N(H)SiMe_3$ and $^{s}Bu_2NB(H)N(H)SiMe_3$ were prepared by allowing $(Me_3Si)_2NH$ to react with $^{s}Bu_2NBCl_2$ and $^{s}Bu_2NBClH$, respectively.[158] 2-Methyl-1-(trimethylsilyl)-Δ^3-1,2-azaboroline (54) reacts with lithium 2,2,6,6-tetramethylpiperidide [Li(TMP)] to give the lithium salt (55) of the 2-methyl-1-(trimethylsilyl)-1,2-azaborolinyl anion:



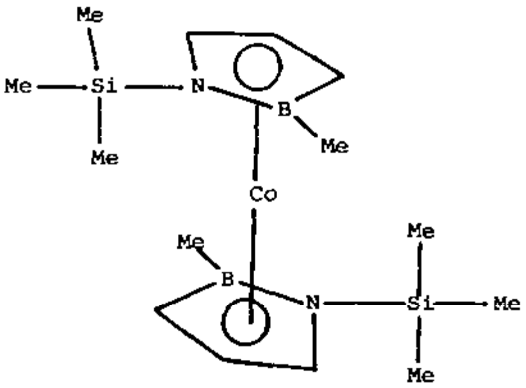
(54) (55)

(55) Reacts with $FeBr_2$ and $CoBr_2$ to yield the sandwich complexes (56). The molecular structure of (56) (M = Co) has a staggered conformation (57).[159]



(M = Fe, Co)

(56)

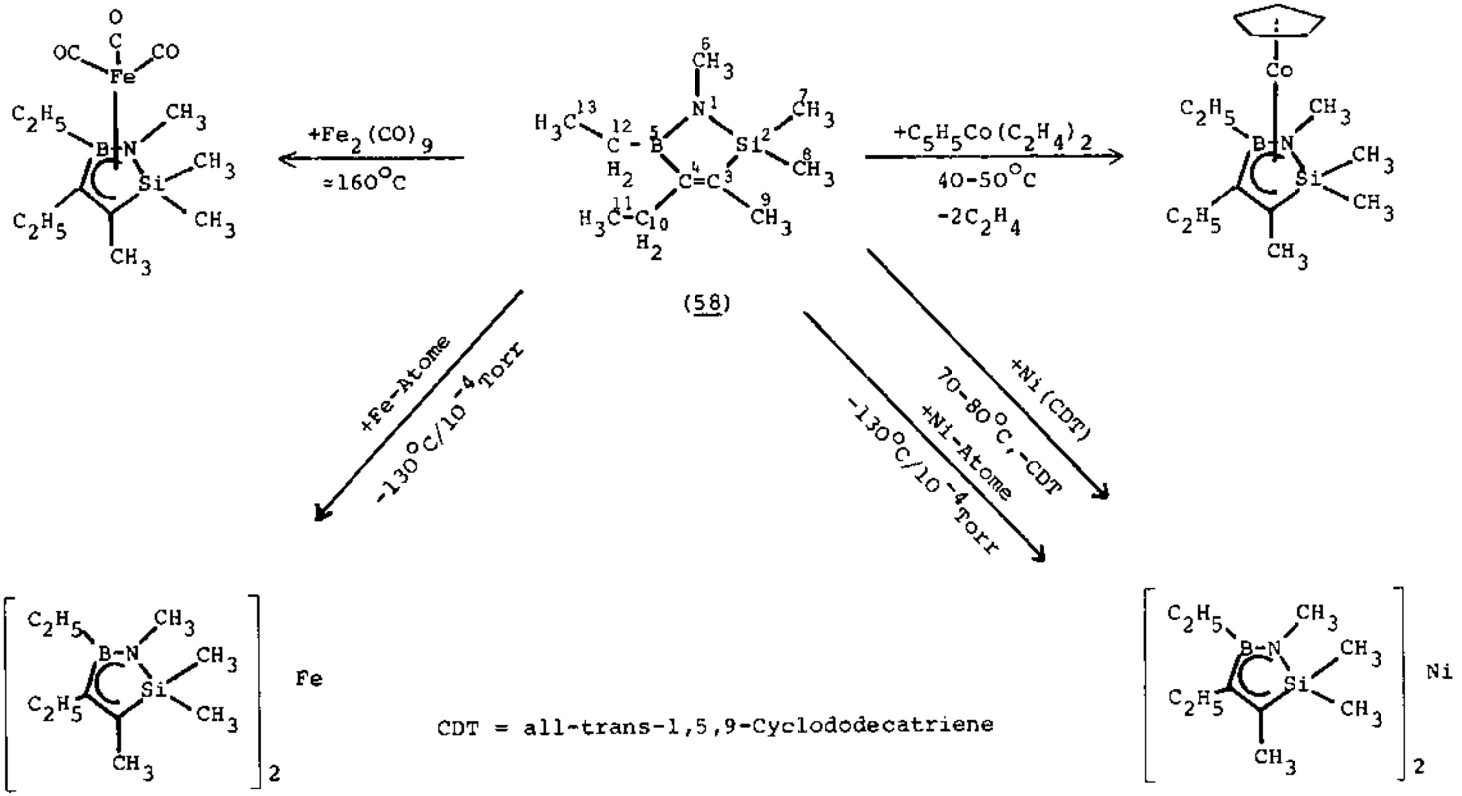


(57)

4,5-Diethyl-1,2,2,3-tetramethyl-Δ^3-1,2,5-azasilaboroline (58) acts as a 4π electron donor in various transition metal complexes. Various syntheses are illustrated in Scheme 7.[160]

The dimeric, benzene-soluble, crystalline compounds, $[RClGaN(H)SiMe_3]_2$, have been obtained by the reaction of $(Me_3Si)_2NH$ with alkylgallium dichlorides. In the crystal, the methyl derivative is characterised by a planar 4-membered $[Ga_2N_2]$ ring in which the equatorial substituents are mutually trans.[161] In $[N(SiMe_3)_2]_3$ forms a 1:1 adduct with Me_3PO which dissociates on heating *in vacuo*. Variable temperature n.m.r. studies showed the occurrence of restricted rotation of the silylamide ligands about the In-N axis.[162] Photoelectron spectra for a number of bis(silyl-amido)metal derivatives have been recorded.[163]

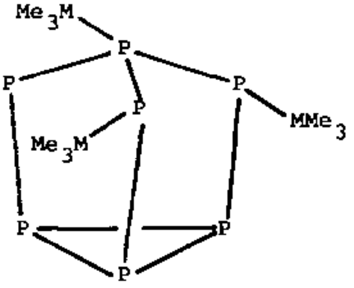
Whereas n-butyllithium cleaves the P-P bond of $(Me_3Si)_2P-P(SiMe_3)_2$ in THF to give $LiP(SiMe_3)_2.2THF$ and $Me_3{}^nBuSi$, tert-butyllithium reacts yielding $(Me_3Si)_3P$, $(Me_3Si)_2PLi$ and Li_3P_7 via the formation of $(Me_3Si)_2P-P(Li)(SiMe_3)$, which decomposes at



CDT = all-trans-1,5,9-Cyclododecatriene

Scheme 7

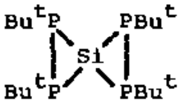
-40°C. The metallation of $(Me_3Si)_3P_2H$ with ^tBuLi leads to the same results. ^{t}Butyllithium with $[(Me_3Si)_2P]_2PH$ in pentane forms $[(Me_3Si)_2P]_2PLi$, which reacts with MeCl or Me_3SiCl to give $[(Me_3Si)_2P]_2PMe$ and $[(Me_3Si)_2P]_2PSiMe_3$, respectively. $(Me_3Si)_2PLi$, Li_3P_7, and $(Me_3Si)_3P$ are also formed on the addition of monoglyme to a suspension of $[(Me_3Si)_2P]_2PLi$ in pentane, or by treating $[(Me_3Si)_2P]_2PH$ in ethers with ^tBuLi. The same compounds are generated by reacting $[(Me_3Si)_2P]_2P{-}SiMe_3$ in ethers with ^tBuLi. The metallation of $(Me_3Si)_3P_7$ in ethers with ^tBuLi yields $(Me_3Si)_2PLi$, $(Me_3Si)_3P$, $^tBu_3P_4(SiMe_3)$, Li_3P_7 and a red solid, via the initial formation of $(Me_3Si)_2P_7Li$.[164] The reaction of $P_7(SiMe_3)_3$ with Me_3PbCl in monoglyme at -50° affords a quantitative yield of $P_7(PbMe_3)_3$. In contrast to the very sensitive silicon derivative, the lead compound can be stored for days in air without any noticeable change. The analogous tin compound may be obtained by similar methods, whilst the corresponding germanium analogue results from the reaction of Na_3P_7 and Me_3GeCl. Structurally, all the compounds have the nortricyclene framework (<u>59</u>), and are chiral in the crystal with only one enantiomer being present.[168]



(<u>59</u>)

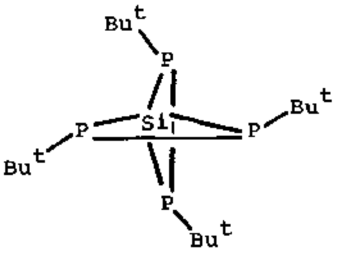
The first spirocyclic phosphorus-silicon three-membered ring compound, 1,2,4,5-tetra-tert-butyl-1,2,4,5-tetraphospha-3-silaspiro[2.2]pentane, $(PBu^t)_2Si(PBu^t)_2$ (<u>60</u>), has been synthesised by cyclocondensation of $K(Bu^t)P{-}P(Bu^t)K$ with $SiCl_4$ in a molar ratio of 2:0.9 :

$2K(Bu^t)P{-}P(Bu^t)K + SiCl_4 \rightarrow$

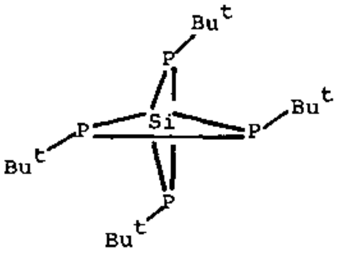


(<u>60</u>)

Spectroscopic data show that (60) is formed as a mixture of the two diastereoisomers (61a) and (61b) which differ in the relative arrangement of the trans oriented organic substituents at the two three-membered rings. Both isomers could be isolated in a pure state, although the sterically less-favoured isomer (61b) rearranges into the comparatively more stable isomer (61a).[166]

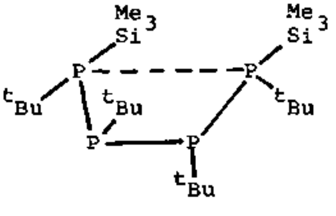


(61a)

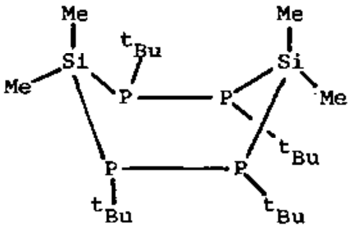


(61b)

The structures of two disilyltetraphosphanes, one linear and the other cyclic, have been determined. Molecules of 1,2,3,4-tetra-tert-butyl-1,4-bis(trimethylsilyl)tetraphosphane, $Me_3Si(^tBuP)_4SiMe_3$, form a twisted [Si-P_4-Si] chain with two types of P-P bond, with the central P-P bond being much longer (2.214Å) than the others (2.188Å). Additionally, a fairly short intramolecular P...P contact of 3.456Å imposes a nearly planar trapezium shape (62) on the molecule.[167] Molecules of $[Me_2Si(^tBuP)_2]_2$ have a nearly ideal boat conformation (63), which appears to result from the repulsion of the all-trans tert-butyl groups and the lone pairs on phosphorus.[168]

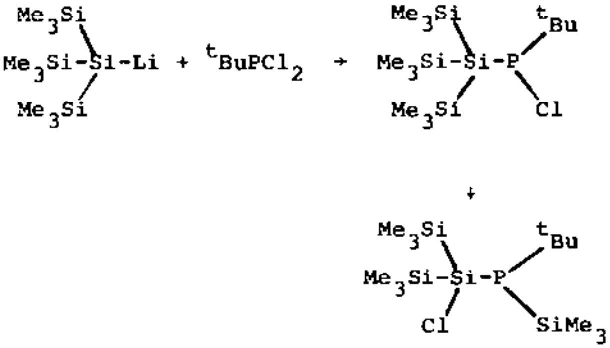


(62)

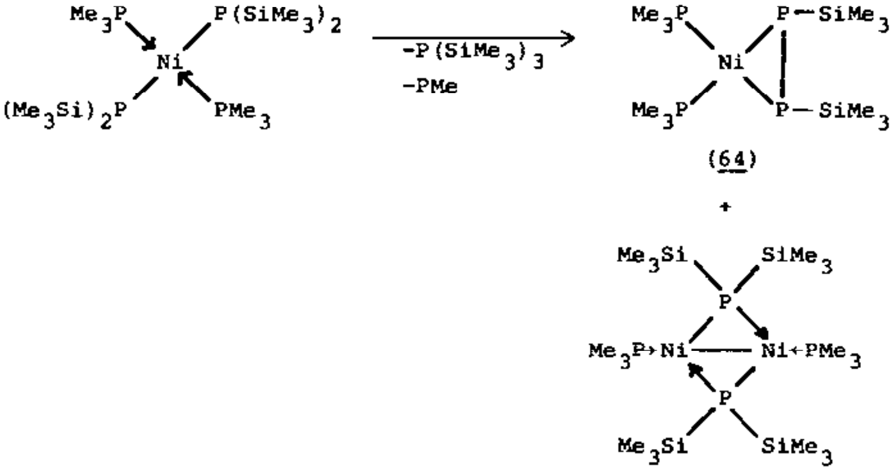


(63)

The reaction of $(Me_3Si)_3SiLi$ with $^tBuPCl_2$ results initially in the formation of $(Me_3Si)_3SiP(Cl)^tBu$, which undergoes thermal rearrangement to $(Me_3Si)_3(Cl)SiP(^tBu)(SiMe_3)$ via a Si-Cl exchange reaction:[169]



Two types of complex (64) and (65) result from the decomposition of $[(Me_3Si)_2P]_2Ni(PMe_3)_2$, the structures of both of which have been determined. Crystals of the diphosphene complex (64) are dark violet and extremely air-sensitive. The coordination at nickel is nearly planar, and the P-P bond distance is quite short (2.149Å).[170] The central four-membered $[Ni_2P_2]$ ring in (65) is planar, with a Ni-Ni distance of 2.38Å.[171]

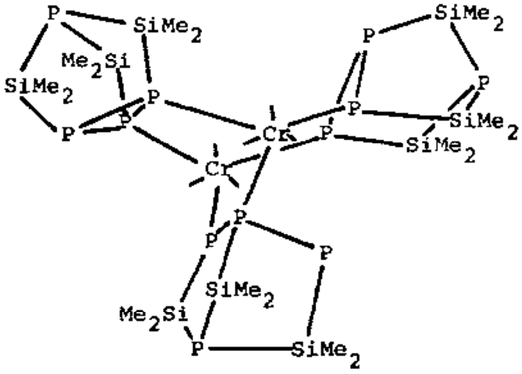


(64)

(65)

Hexamethyl-trisila-tetraphosphanortricyclene, $P_4(SiMe_2)_3$, reacts with $C_6H_6Cr(CO)_3$ or (cycloheptatrienyl)$Cr(CO)_3$ to afford red crystals of the complex, $[P_4(SiMe_2)_3]_3[Cr(CO)_3]_2$. The same complex also results from heating solutions of $[P_4(SiMe_2)_3]Cr(CO)_5$

in benzene or THF at 120-130°. The complex crystallises in two crystal modifications, differing in the packing of the molecules in which the two $Cr(CO)_3$ residues are bridged by three $P_4(SiMe_2)_3$ groups (66).[172]



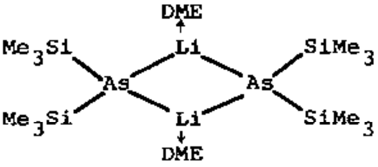
(66)

Dimethoxyethane adducts of lithium bis(trimethylsilyl)arsenide and -stibide (67) are obtained from the alkyllithium cleavage of the corresponding tris(trimethylsilyl)arsine and -stibine in DME:[173,174]

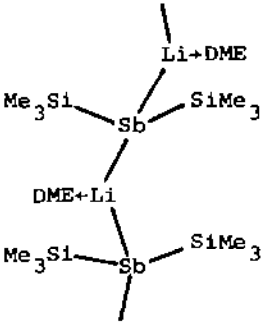
$$(Me_3Si)_3E + MeLi \xrightarrow{DME} Me_4Si + \underset{(67)}{(Me_3Si)_2ELi.DME}$$

E = As,Sb.

The arsenide (67; E = As) is dimeric both in solution and also in the solid (68). The four-membered $[As_2Li_2]$ ring is planar, with carbon atoms statistically occupying positions on both sides of the mirror plane.



(68)



(69)

In contrast, crystals of the analogous antimonide (67; E = Sb) comprise infinite chains of alternating, tetrahedrally-coordinated antimony and lithium atoms (69).[174]

The corresponding bismuth analogue can be obtained as a THF adduct (70) by the following route:[175]

$$\mathrm{Me_3SiCl + Na_xBi/K_xBi \xrightarrow{DME} (Me_3Si)_3Bi}$$

$$\downarrow \mathrm{MeLi/Et_2O\text{-}THF}$$

$$\mathrm{(Me_3Si)_2BiLi.2THF}$$

(70)

(70) reacts with Me_3SnCl to form $(Me_3Sn)_3Bi$. With ethylene dibromide, all three lithium salts are converted into the tetrakis(trimethylsilyl)diarsane, -distibine, or -dibismuthine:

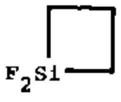
$$\mathrm{2(Me_3Si)_2MLi.L \xrightarrow{BrCH_2CH_2Br} (Me_3Si)_2MM(SiMe_3)_2}$$

M = As,Sb,Bi.

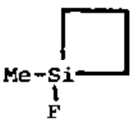
Molecules of both the diarsane and distibane adopt a gauche conformation.[176,177] $(Me_3Si)_2BiBi(SiMe_3)_2$, which can be isolated in preparative amounts as green lustrous crystals, is thermally rather stable, and undergoes colour changes on dissolution (to orange-red) and on melting (red).[175]

Core-level binding energies have been recorded for all atoms in the series of methyl(trifluoromethyl)germanes, $(CF_3)_{4-n}Me_nGe$ (n = 1-3), $(CF_3)_4Ge$, and the (trifluoromethyl)halogermanes, $(CF_3)_{4-n}GeX_n$ (n = 0-3; X = F,Cl,Br,I).[178,179] High resolution HeI and HeII photoelectron spectra have also been reported for $SnCl_4$ and $SnMe_4$.[180]

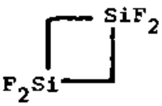
The fluorosilacyclobutanes (71)-(74) have been prepared in moderate to good yields by fluorination of the corresponding chlorine compounds with SbF_3, ZnF_2, AgF or AgF_2.



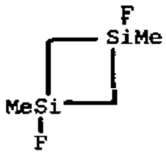
(71)



(72)

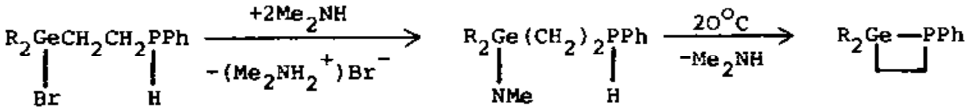


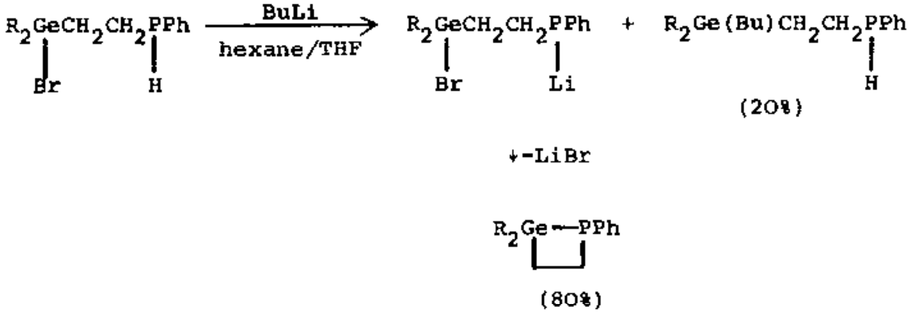
(73)



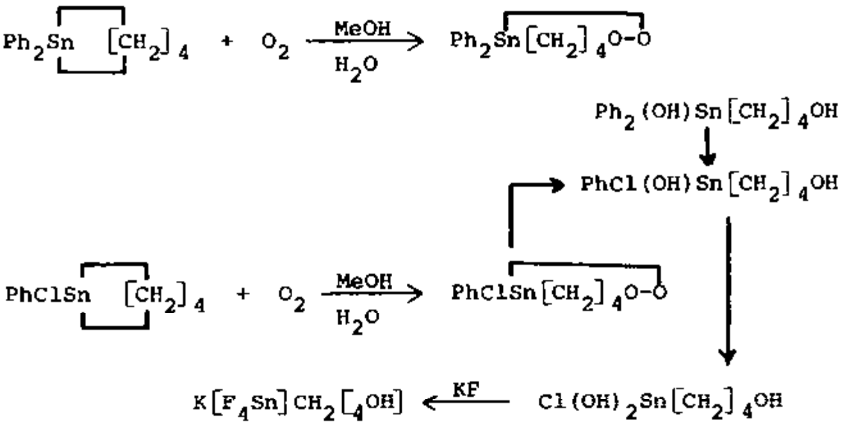
(74)

The disilacyclobutanes, (73) and (74), can also be obtained by the gas-phase pyrolysis of (71) and (72), respectively. Ring-cleavage occurs with SbF_3 and ZnF_2, leading to the generation of $[F_2Si{=}CH_2]$.[181] The first 1,2-phosphagermetanes have been synthesised from bromogermyl phosphines by dehydrohalogenation with amines and reaction with BuLi followed by intramolecular elimination of LiBr:





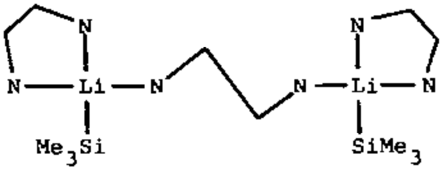
These heterocycles undergo a thermal β-decomposition process under reduced pressure to afford germaphosphimines, $R_2Ge{=}PR'$, which undergo partial thermal rearrangement to P-germylated phosphinidenes. Both of these intermediates insert into the Ge-P bond of 1,2-phosphagermetanes, with the formation of perhydrodiphosphadigermins and P-germylated diphosphagermolanes, respectively.[20] The stannacycloalkanes, $Ph_2Sn(CH_2)_4$ and $PhClSn(CH_2)_4$, are rapidly oxidised via an intermediate peroxide with simultaneous slow cleavage of the Sn-Ph bonds (Scheme 8).[182] Bis(triphenylstannyl)mercury is the main product of the electroreduction of Ph_3SnCl at a mercury electrode in methanolic solutions.[183] The reactions of $Ph_3Sn(CH_2)_nSC_6H_4Me$-p (n = 3,4) with $HgCl_2$, Br_2 and I_2 lead to Ph-Sn bond cleavage. In contrast, reactions with MeI afford $Ph_3Sn(CH_2)_nI$ and $MeSC_6H_4Me$-p. Charge-transfer adducts are formed between $Ph_3Sn(CH_2)_nSC_6H_4Me$-p (n =1-4) and both tetracyanoethylene and p-bromoanil.[184] (Triphenylphosphonium alkylide)triphenylmetal chloride, $[Ph_3\overset{+}{P}CHR\text{-}MPh_3]Cl^-$ (M = Ge,Sn,Pb), and (triphenylphosphonium alkylide)metal chloride,



Scheme 8.

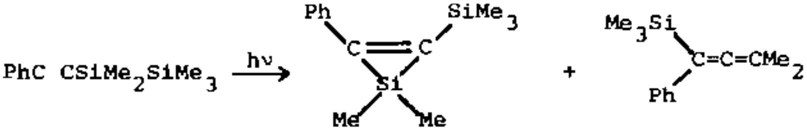
$[Ph_3\overset{+}{P}CHR]_nMCl_n^-$ (M = Ge, n = 4; M = Pb, n = 2), have been isolated from reaction mixtures of alkylidenetriphenylphosphoranes and the appropriate metal chlorides.[185] Complexes of the type $Me_2Sn[ArCr(CO)_3]$, have been studied by cyclic voltametry, and can be made to undergo chemically reversible oxidation upon judicious choice of conditions and nature of the aryl group R. The persistence of the cations appears to be a function of the steric bulk around the phenyl rings. Oxidation involves one electron per $[Cr(CO)_3]$ unit. The same results are found for the bis and tris complexes of methyltriphenyltin, where a dication and a trication are formed,respectively. The structure of one of the complexes, $Me_2Sn[2,4,6\text{-}Me_3C_6H_2Cr(CO)_3]_2$, has been determined. Molecules have a distorted tetrahedral geometry at tin. A $[Cr(CO)_3]$ group is bonded in a hexahapto fashion to each mesityl group with the three carbonyl groups eclipsing the methyl groups.[186] Several other similar mono- and bis-(tricarbonyl)-chromium complexes of dimethyldiaryl-Group IV elements have been synthesised and studied spectroscopically.[187]

The structure of the highly reactive silylating agent, $(LiSiMe_3)_2\cdot(Me_2NCH_2CH_2NMe_2)_3$, has been determined. Two TMEDA ligands chelate the lithium atoms, whilst the third bridges both lithium atoms as in (75). The Li-Si distance is relatively long (2.70Å).[188]

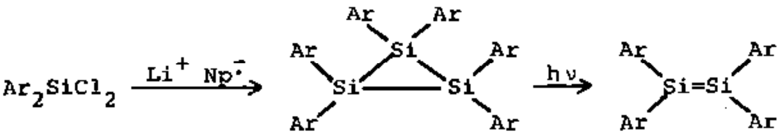


(75)

Silyl borates, $Li[R_{3-n}B]SiMe_3[_{n+1}]$, result from the reaction of Me_3SiLi with nethoxyboranes $R_{3-n}B(OMe)_n$ (n = 1-3) in hexane at 175°.[189] The photolysis of phenyl-ethynylpentamethyldisilane affords 1,1-dimethyl-2-phenyl-3-trimethylsilyl-1-silacyclopropane and 1,1-dimethyl-3-phenyl-3-trimethylsilyl-1-silapropadiene:[190]



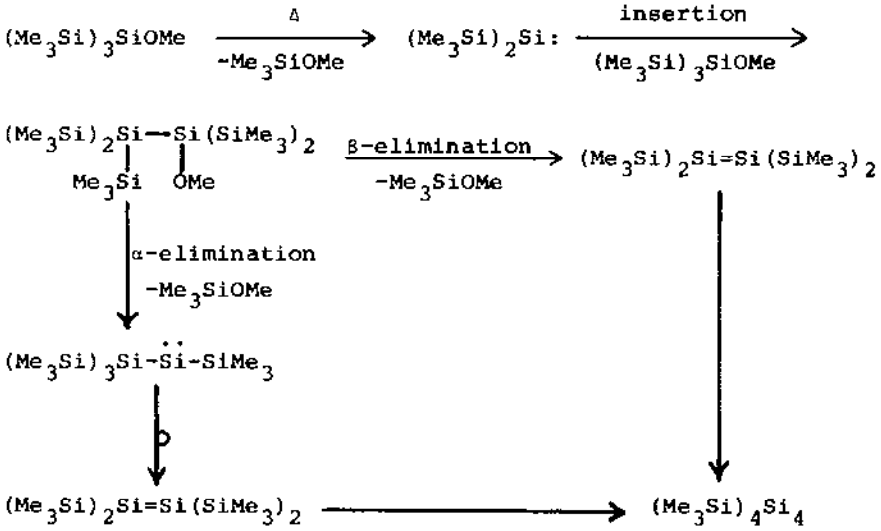
The reduction of bis(2,6-dimethylphenyl)dichlorosilane wi lithium naphthalide at -78° affords the hexaarylcyclotrisilane (76), which can be converted photochemically in near quantitative yield to the disilene (77):[25]



(76) (77)

Ar = $2,6\text{-}Me_2C_6H_3$

The structure of (76)[25] and the analogous cyclotrigermane, $[Ar_2Ge]_3$,[191] have been confirmed crystallographically. Liquid-phase pyrolysis of neat methoxytris(trimethylsilyl)silane leads to the formation of octakis(trimethylsilyl)cyclotetrasilane, which has a planar central $[Si_4]$ ring. The intermediate formation of tetrakis(trimethylsilyl)disilene is strongly indicated, and a mechanism involving the insertion of bis(trimethylsilyl)silylene into its own precursor, followed by direct β-elimination to the disilene or by α-elimination to the silylene $(Me_3Si)_3Si\text{-}\ddot{S}i\text{-}SiMe_3$ followed by rearrangement to the disilene are both suggested:

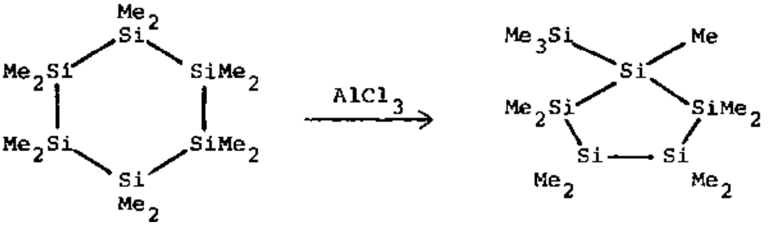


$$\begin{tikzcd}
(Me_3Si)_3SiOMe \arrow[r, "\Delta", "-Me_3SiOMe"'] & (Me_3Si)_2Si: \arrow[r, "insertion", "(Me_3Si)_3SiOMe"'] & {} \\
(Me_3Si)_2\underset{Me_3Si}{Si}\text{—}\underset{OMe}{Si}(SiMe_3)_2 \arrow[r, "\beta\text{-elimination}", "-Me_3SiOMe"'] \arrow[d, "\alpha\text{-elimination}", "-Me_3SiOMe"'] & (Me_3Si)_2Si{=}Si(SiMe_3)_2 \arrow[dd] \\
(Me_3Si)_3Si\text{-}\ddot{S}i\text{-}SiMe_3 \arrow[d] & \\
(Me_3Si)_2Si{=}Si(SiMe_3)_2 \arrow[r] & (Me_3Si)_4Si_4
\end{tikzcd}$$

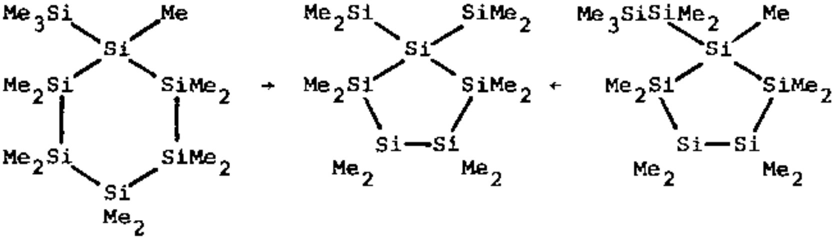
Reductive coupling of tert-butylmethyldichlorosilane with a 10% excess of lithium metal in THF at 0° afforded an 80% yield of 1,2,3,4-tetra-tert-butyltetramethylcyclotetrasilane as a mixture of four geometrical isomers. The five-membered ring product, $(^tBuMeSi)_5$, also present as a mixture of four isomers, was formed in 3% yield. A third product, 1,2,3-tri-tert-butyltrimethylsilane, was formed in 5% yield.[193] The four isomers of $(^tBuMeSi)_4$ are unreactive to air and to concentrated H_2SO_4, but react with meta-chloroperbenzoic acid to give oxygen insertion products $(^tBuMeSi)_4O_n$ (n = 1,2,4):

$$(^tBuMeSi)_4 \xrightarrow[]{\substack{MCPBA \\ CCl_4}} (^tBuMeSi)_4O \rightarrow (^tBuMeSi)_4O_2 \rightarrow (^tBuMeSi)_4O_3 \rightarrow (^tBuMeSiO)_4$$

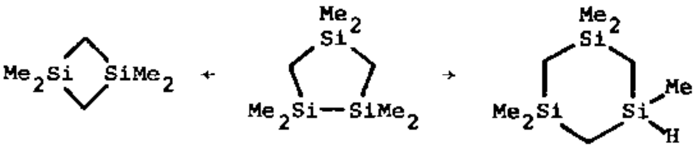
The reactions are stereospecific and regioselective, giving only one of the many possible isomeric products for each oxidation. The structural effects favouring oxidation include ring strain, neighbouring oxygen substitution, and the cis-methyl/cis-t-butyl configuration. The monooxidation product $(^tBuMeSi)_4O$ is an excellent photolytic source of [^{t}BuMeSi:] both in solution and in a hydrocarbon glass matrix.[194] The cleavage of $(Ph_2Si)_4$ and $(Ph_2Sn)_5$ with iodine, phosphorus pentabromide, and bromine, and the successive reaction with $HBr/AlBr_3$ or HI/AlI_3 gives the linear silanes $n\text{-}Si_4Br_{10}$, $n\text{-}Si_5Br_{12}$, $n\text{-}Si_4I_{10}$ and $n\text{-}Si_5I_{12}$.[195] Aluminium chloride catalyses skeletal rearrangements of mono- and bicyclic polysilanes. Thus, in the presence of catalytic amounts od $AlCl_3$ in refluxing cyclohexane, $(Me_2Si)_6$ gives (trimethylsilyl)nonamethylcyclopentasilane:



Isomerisation of both (trimethylsilyl)undecamethylcyclohexasilane and (pentamethyldisilanyl)nonamethylcyclopentasilane in benzene affords 1,1-bis(trimethylsilyl)octamethylcyclopentasilane in high yields:



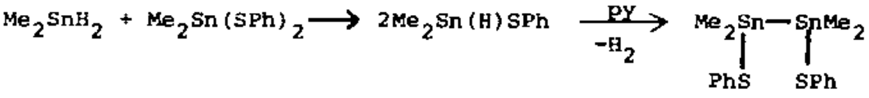
Similar rearrangement of tetradecamethylbicyclo[2.2.2]octasilane gave 1-(trimethylsilyl)undecamethylbicyclo[2.2.1]heptasilane as the sole product. Under identical conditions, trans-octadecamethylbicyclo[4.4.0]decasilane and bi(nonamethylcyclopentasilanyl) were both converted into an equilibrium mixture consisting of 1,4-bis-(trimethylsilyl)dodecamethylbicyclo[2.2.2]octasilane, 1,4,7-tris-(trimethylsilyl)nonamethylbicyclo[2.2.1]heptasilane, and a small amount of an unidentified isomer.[196] At a pressure of <u>ca.</u> 1 atmosphere, pyrolysis of hexamethyl-1,3,4-trisilacyclopentane at 773K gives the ring expansion isomer (<u>78</u>):



(79) (78)

but at low pressure the main product is 1,1,3,3-tetramethyl-1,3-disilacyclobutane (79).[197]

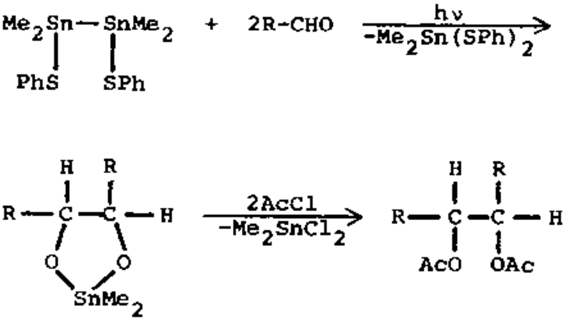
1,2-Bis(phenylthio)tetramethyldistannane, (80), is readily formed by the route:

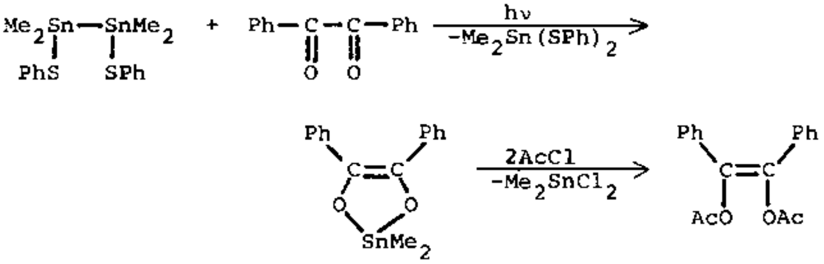


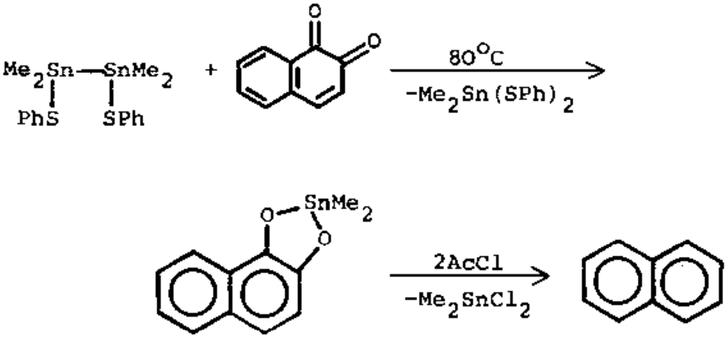
$$Me_2SnH_2 + Me_2Sn(SPh)_2 \longrightarrow 2Me_2Sn(H)SPh \xrightarrow[-H_2]{py} Me_2Sn(SPh)-Sn(SPh)Me_2$$

(80)

and can be isolated as colourless crystals (mp. 89) which are stable at room temperature in air, in the solid state and in benzene solution, but is a convenient thermal and photolytic source of dimethylstannylene $[Me_2Sn:]$. Thus, 1,3,2-dioxastannolanes are formed on reaction with 2 molar equivalents of aldehyde or 1,3,2-dioxastannolenes by reactions with α-diketones. The saturated heterocycles are converted to the corresponding glycol diacetates by acetyl chloride:[23]







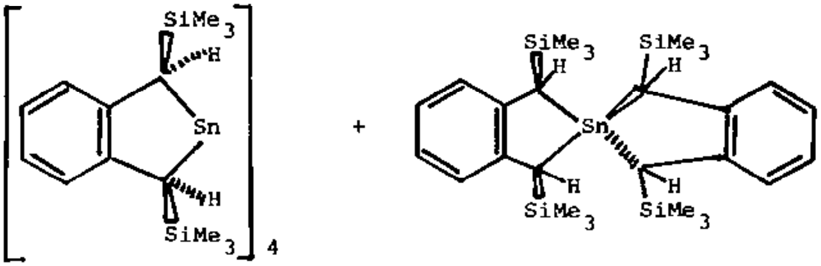
(Pentaalkylditin)lithium compounds have been shown to be present in preparations of trialkyltin lithium reagents from trialkyltin halide and lithium metal in THF by ^{119}Sn n.m.r. and by direct alkylation to R_5Sn_2R' derivatives. The cyclohexylation of $(^{i}Pr)_5Sn_2Li$ proceeds by free-radical route. The R_3Sn_2Li species are considered to be formed by the oxidative-addition of R_3SnLi to R_2Sn species formed by the R_3SnLi R_3Sn/RLi dissociation which is promoted by the R_6Sn_2 scavenging of RLi.[198] The structures of two cyclotetrastannanes (<u>81</u>)[199] and (<u>82</u>),[200] formed by different methods:

$$2(Me_3SiCH_2)_2SnH_2 + 2(Me_3SiCH_2)_2Sn(NEt_2)_2 \rightarrow$$

$$[(Me_3SiCH_2)_2Sn]_4 + 2Et_2NH$$

(<u>81</u>)

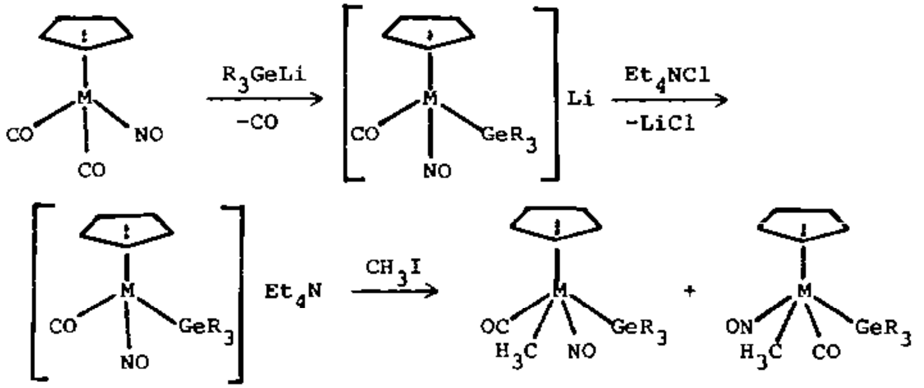
$SnCl_4$ + $2[\{Li(TMEDA)\}_2\{\underline{o}\text{-}C_6H_4(CHSiMe_3)_2\}]$ →



(82)

have been determined. In both, the four-membered $[Sn_4]$ ring is nearly square.

Reactions of optically-active $MePh(1\text{-}C_{10}H_7)GeLi$ with $(\eta^5\text{-}C_5H_5)M(CO)_2NO$ (M = Mo,W) result in the replacement of CO and the formation of anionic species, which can be alkylated with methyl iodide to afford mixtures of the diastereoisomeric complexes, $[(\eta^5\text{-}C_5H_5)M(CO)(NO)(GeR_3)Me]$ (R_3 = $MePh(1\text{-}C_{10}H_7)$):[201]

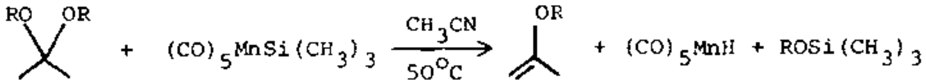


M = Mo,W R_3 = $MePh(1\text{-}C_{10}H_7)$

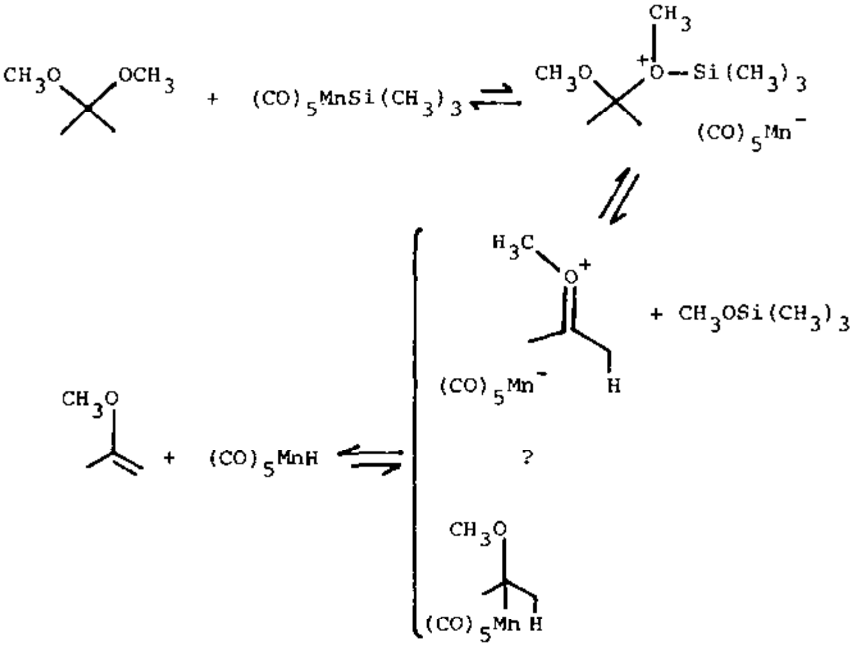
Nucleophilic cleavage of hexacoordinated silyl- and germyl-transition metal complexes such as $R_3SiMn(CO)_5$, $R_3SiMn(CO)_4PPh_3$, $R_3GeMn(CO)_5$, $R_3GeM[C(OEt)Me](CO)_4$ (M = Mn,Re) and $R_3GeW(NO)(CO)_4$ (R_3 as above), by $LiAlH_4$ always takes place with low retention of configuration (stereoselectivity from 55 to 70%).[202] The carbene complex, $[(CO)_5Cr(CNEt_2)]BF_4$, reacts with $LiPbPh_3$ by addition of the $[Ph_3Pb^-]$ ion to the carbyne carbon atom producing the complex

$(CO)_5Cr|C(PbPh_3)NEt_2|$ (83). At room temperature, (83) rearranges by first-order kinetics with loss of CO and |C,Cr| migration of the plumbyl group affording $(Ph_3Pb)(CO)_4Cr(CNEt_2)$.[203]

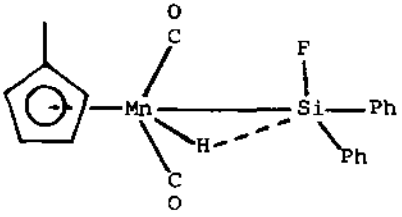
The reaction of $Me_3SiMn(CO)_5$ with ketals in acetonitrile at 50° affords methyl enol ethers in 56 - >95% yields, together with the easily removed byproducts, $MeOSiMe_3$ and $(CO)_5MnH$ (or $Mn_2(CO)_9.MeCN/Mn_2(CO)_{10}$).



When regio- and/or geometric isomers are possible, thermodynamic mixtures are obtained. Reaction with acetals is more complex, but when conducted under 200 psi of CO, manganese acyls, $(CO)_5MnCOCH(OR)R'$, derived from the alkyl intermediates, can be isolated. The general mechanism:



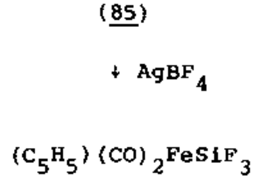
in which a ketal or acetal oxygen atom is initially silylated by the silyl-manganese complex was proposed.[204] N.m.r. stusies on silicon manganese hydride derivatives indicate the possibility of the occurrence of a bonding interaction between silicon and hydrogen.[205] Such an interaction has been shown by neutron diffraction studies to be present in (η^5-MeC_5H_4)$(CO)_2(H)MnSiFPh_2$ (84).[206]



(84)

Although the Mn-H distance is comparable to other examples, notably $HMN(CO)_5$, the Si-H distance in this complex (180.2pm) is distinctly shorter than the sum of the van der Waal's radii (ca. 300 pm), (cf. Si-H single bond distance ca. 148±2 pm). Furthermore, the geometry at silicon is strongly perturbed away from tetrahedral geometry, and is best described as a distorted trigonal bipyramid with hydrogen and fluorine in apical positions. The geometry at tin in $[(Ph_3P)(CO)_4Mn]_3SnBr$ is distorted tetrahedral.[207] Only M-C bonds of the complexes $Ph_{4-n}M[Mn(CO)_5]_n$ (M = Sn,Pb; n = 1, 2), are cleaved by acetic acid affording the acetato complexes, $(AcO)_2M\ Mn(CO)_5$, $(AcO)_3SnMn(CO)_5$ and $(AcO)_2PhPbMn(CO)_5$. $(AcO)_2PhSnMn(CO)_5$ was obtained by metathesis from $Cl_2PhSnMn(CO)_5$ and silver acetate. Infrared data suggest that the acetato groups are chelating in the diacetato complexes, but both uni- and bidentate acetate groups are present in the tris(acetato) complexes.[208]

Dicobalt octacarbonyl reacts with $(C_5H_5)(CO)_2FeSiHCl_2$ to afford the FeSiCo complex (85), which is cleaved by silver tetrafluoroborate:



$$(C_5H_5)(CO)_2FeSiHCl_2 + Co_2(CO)_8 \rightarrow \underset{(85)}{(C_5H_5)(CO)_2FeSiCl_2Co(CO)_8} \xrightarrow{AgBF_4} (C_5H_5)(CO)_2FeSiF_3$$

Similarly, reaction with $(C_5H_5)(CO)_2FeSiH_3$ affords the μ^3-metallosilylidine tricarbonyl cluster (<u>86</u>) which is cleaved by acetic acid:[209]

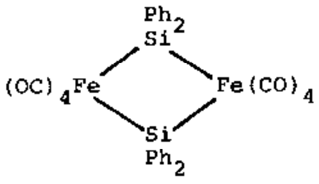
$$(C_5H_5)(CO)_2FeSiH_3 + Co_2(CO)_8 \rightarrow \mu^3\text{-}(C_5H_5)(CO)_2FeSiCo_3(CO)_9$$

(<u>86</u>)

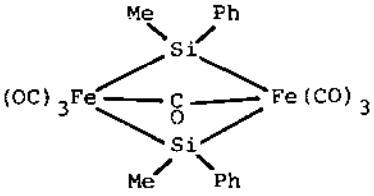
$$\downarrow HOAc$$

$$(C_5H_5)(CO)_2Fe\text{-}Si(OAc)_3$$

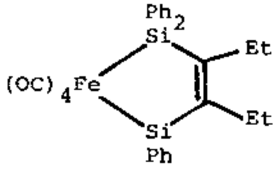
μ-Silanediyl complexes such as (<u>87</u>) and (<u>88</u>) can be obtained by the photolysis of the diorganosilane with $Fe(CO)_5$. (<u>87</u>) reacts readily with alkynes to afford mono- and di-iron carbonyl complexes such as (<u>89</u>) and (<u>90</u>).[210]



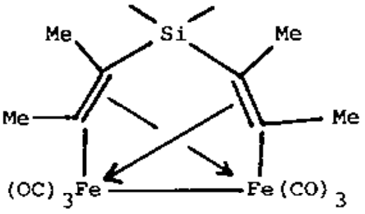
(<u>87</u>)



(<u>88</u>)



(<u>89</u>)

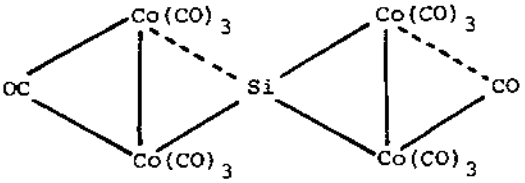


(<u>90</u>)

The reaction between $Fe(CO)_4(H)SiPh_3$ and different nucleophiles (CO, PPh_3, $AsPh_3$, $SbPh_3$, $Ph_2PCH_2CH_2PPh_2$, PEt_3) has been studied. <u>Inter alia</u>, the complexes $Fe(CO)_3(H)(SiPh_3)PPh_3$, $Fe(CO)_2(H)(SiPh_3)(Ph_2PCH_2CH_2PPh_2)$, and $[Et_3PH][Ph_3SiFe(CO)_4]$ were characterised.[211]

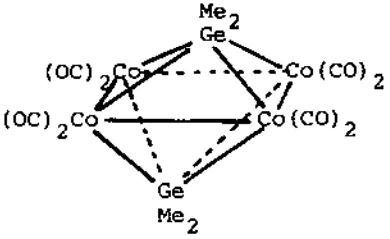
Silane reacts with $Co_2(CO)_8$ to give $Si\{Co_2(CO)_7\}_2$, which loses CO quantitatively to form the known cluster compound $(CO)_4CoSiCo_3(CO)_9$.

$Si\{Co_2(CO)_7\}_2$ has spectroscopic properties almost identical to those of its germanium analogue, and is therefore postulated to have a similar structure (91).[212]



(91)

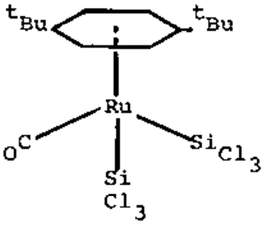
Several new germanium-cobalt cluster compounds have been synthesised and investigated structurally. Methylgermane reacts with $Ge\{Co_2(CO)_7\}_2$ to afford $Co_4(CO)_{11}(GeMe_2)_2$, which has a very irregular square bipyramidal structure (92).[213]



(92)

The anion $[Ge\{Co_5(CO)_{10}\}]^-$ has a metal skeleton consisting of a $[GeCo_2]$ triangle and a $[GeCo_3]$ tetrahedron sharing a common apex at germanium. Three of the carbonyl ligands on the $[GeCo_3]$ unit bridge the three Co-Co bonds, with two terminal carbonyls on each cobalt. On the $[GeCo_2]$ unit there are six terminal and only one bridging carbonyl ligand.[214] In the $[Ge_2Co_7(CO)_{21}]^-$ anion, two $[GeCo_3(CO)_9]$ units are bonded in mutualy <u>trans</u> positions about a trigonal planar $[Co(CO)_3]$ group giving idealised C_{3v} symmetry. The structure of the $[Ge\{Co_7(CO)_{20}\}]^-$ anion may be considered as a derivative of the C_{3v} structure of $Co_4(CO)_{12}$, with the axial carbonyl ligand of one basal cobalt atom replaced by a $[GeCo_3(CO)_9^-]$ fragment.[215] The sole and unexpected products from the reactions of a variety of lead(II) and lead(IV) compounds with $Co_2(CO)_6L_2$ complexes (L = tertiary phosphine, arsine or phosphite) in refluxing benzene are the blue, air-stable percobaltoplumbanes, $Pb\{Co(CO)_3(L)\}_4$. The same complexes are also formed by the reaction of lead(II) acetate and $Na[Co(CO)_3(L)]$. The complex, $Pb\{Fe(CO)_2(NO)[P(OPh)_3]\}$, is obtained similarly.[216] Methyl group transfer from dimethylcobalt(III) complexes to dimethyllead(IV), trimethyllead(II) and lead(II) was rapid in acetonitrile.[217]

The new arene-nickel complex, $(\eta^6\text{-toluene})Ni(SiCl_3)_2$ has been prepared by three methods: by the reaction of (i) nickel vapour, Si_2Cl_6 and toluene, (ii) nickel vapour, $SiHCl_3$, and toluene, and (iii) bis(cyclooctadienyl)nickel, $SiHCl_3$ and toluene. The toluene ligand is very labile, and exchanges with C_6D_6 at room temperature.[218] Polymeric organostannylphosphinyl(tricarbonyl)-nickel complexes are catalysts for the oligomerisation of alkynes.[219]

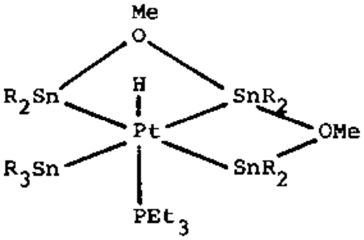


(93)

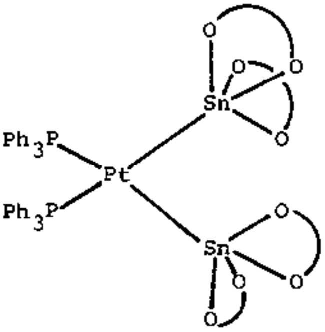
Molecules of $[p\text{-}^tBu_2C_6H_4]Ru(CO)(SiCl_3)_2$ adopt the 'piano-stool' conformation (93).[220] The novel cluster anion, $[HRu_3(CO)_{11}(SiEt_3)_2]^-$ is formed by reacting the anion, $[HRu_3(CO)_{11}]^-$ with triethylsilane in THF. In the presence of CO and H_2 under pressure, the transformation is reversed, but on reduction of pressure the anion is again formed.[221,222] The complexes, $HOs_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)(SnMe_3)$ and $H_2Os_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_7(PMe_2Ph)$ have been isolated from the reaction of Me_3SnH with $Os_3(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)(CO)_8(PMe_2Ph)$. The structure of the former complex contains a $[Me_3Sn]$ group bonded to one of the exterior osmium atoms of the cluster.[223]

Several papers report studies on trichlorostannate complexes. The anion $[Ru(SnCl_3)_6]^{4-}$ is stereochemically rigid (cf. the fluxional behaviour of isoelectronic Rh(III)-Sn(II) complexes), and exhibits very large tin-119—tin-11 coupling constants in the tin-119 n.m.r. spectrum. $[Pt(SnCl_3)_5]^{3-}$ has a regular trigonal bipyramidal geometry in which the average axial Pt-Sn distance is shorter than the equatorial distance consistent with current theoretical predictions. This structure is retained in acetone solution, but is stereochemically non-rigid between 183K and 363K. Throughout this range, spin correlation is preserved, thus establishing that the non-rigidity is due to intramolecular exchange, probably via Berry pseudo rotations. No dissociation products could be discerned in solution.[225] The Pt-Sn bond distance in $[PtCl_2(SnCl_3)_2]^{2-}$ is significantly shorter than in $[Pt(SnCl_3)_5]^{3-}$, consistent with the much larger $J(^{145}Pt-^{119}Sn)$ n.m.r. coupling constants (27,640 vs 16,030 Hz). The data suggest a greater amount of Pt-Sn π-bonding in the four-coordinate than in the five-coordinate complex.[226] $[(Ph_3P)_2N][Pt(SnCl_3)_3(AsMe_3)_2]$ and its triethylarsine analogue are readily prepared by reacting the appropriate cis-$PtCl_2L_2$ complex with tin(II) chloride in a 1:3 molar ratio in acetone. The anion has a trigonal bipyramidal geometry with the arsine ligands in the axial groups. The mean Pt-Sn distance is slightly longer than the mean equatorial Pt-Sn distance in $[Pt(SnCl_3)_5]^{3-}$.[227] The insertion of tin(II) halides into the Pt-Pt bond of tetraalkylammonium salts of the $[Pt_2Cl_4(CO)_2]^{2-}$ anion in dichloromethane has been investigated by n.m.r., which shows that terminal $[SnCl_3]$ groups are not formed. Rather the product is the $[(OC)Cl_2Pt-SnCl_2-PtCl_2(CO)]^{2-}$ anion.[228] ^{31}P n.m.r. has shown that the complexes trans-$Pt(SnCl_3)PhL_2$ (L = PPh_3 or $PMePh_2$) react with CO by an initial rapid displacement of the $[SnCl_3]$ ligand to afford trans-$[PtPh(CO)L_2]^+[SnCl_3]^-$. Further reaction to produce trans-$[Pt(SnCl_3)(COPh)L_2]$ occurs slowly in the absence of free CO by initial nucleophilic attack of $[SnCl_3^-]$, but in the presence of excess CO an alternative route involving phosphine dissociation (PPh_3 only) operates.[229] The reaction of tin(II) chloride with trans-$IrCl(CO)(P)_2$ ((P) = $(p-XC_6H_4)_3P$; X = F,H,Cl,OMe) in dichloromethane affords blue-green complexes of composition $[IrCl(CO)(P)SnCl_2]$, which are suggested to be a mixture of isomers containing bridging chlorine. The tin does not appear to be directly bound to iridium. Solutions, also initially blue-green, undergo a reversible colour change to red at -193°. Reaction of the isomeric mixture with either HCl or H_2 gives the expected products, $Ir(H)(Cl)(SnCl_3)(CO)(P)_2$ and $IrH_2(SnCl_3)(CO)(P)_2$.

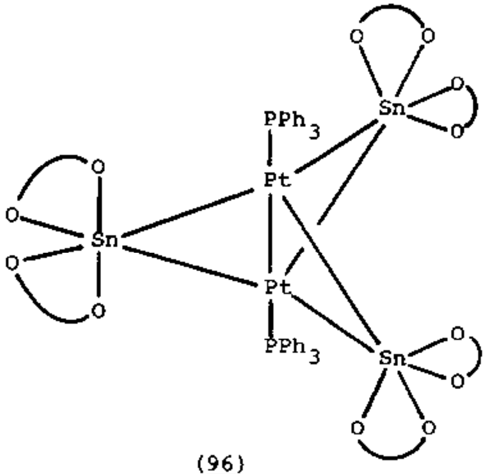
The platinum complex, $Pt(CO)_3(SEt_2)(PEt_3)$, reacts readily with tris(p-tolyl)stannane in methanol to afford the unusual complex (94), which contains four tin-platinum bonds, one involving formally a stannylene species. The four tin and two oxygen atoms lie approximately in a plane with the platinum displaced 0.48Å out of the plane towards the phosphine ligand. The geometry about the formally bivalent tin atom is that of a distorted trigonal bipyramid, with the two oxygen atoms in the apical positions at Sn-O distances longer than the other Sn-O distances of the molecule.[231] The addition of a hexane solution of $Sn(acac)_2$ to $Pt(C_2H_4)(PPh_3)_2$ in benzene affords pale orange crystals of (95), whilst reaction in refluxing toluene gave deep orange crystals of $[(Ph_3P)Pt]_2\{Sn(acac)_2\}_3$.[232]



(94)



(95)



(96)

The rhodium(V) complex, $(\eta^5-C_5Me_5)Rh(H)_2(SiEt_3)_2$, is formed by the reaction of $(\eta^5-C_5Me_5)_2Rh_2Cl_4$ and $HSiEt_3$.[233] Trans-

$Rh(CO)Cl(PEt_3)_2$ and silyl or germyl chloride react at low temperature to afford the complexes $Rh(H)(CO)(Cl)(PEt_3)_2(MH_2Cl)$ (M = Si,Ge), with mutually trans phosphine ligands and the Group IV metal trans to the hydride. Similar reactions occur between trans-$Rh(CO)I(PEt_3)_2$ and MH_3I. Both give analogous adducts with MH_4, MH_3Me, $SiH_3CH_2CH{=}CH_2$ and SiH_2MeX (X = Cl,I), which dissociate reversibly between 200K and 280K.[234] A number of tin-transition metal complexes, $[NMe_4]_3[Pt(SnCl_3)_5]$, $(Ph_4P)_2[PdCl_3SnCl_3]$, and $Cs_4[Rh(Sn_4F_{15})]SnF_2(H_2O)_2)_2$, have been subjected to an infrared, n.m.r. and Mössbauer study.[235]

Triphenylcyclopentadienyllead has a tetrahedral geometry, although the $Pb{-}C(C_5H_5)$ bond distance is somewhat longer (2.30Å) that the $Pb{-}C_6H_5$ distances (mean 2.22Å), consistent with the greater reactivity of that bond. The endocyclic C-C distances of the cyclopentadienyl ring show that electron density is concentrated over the carbon atoms most remote from lead. Reaction of $Ph_3PbC_5H_5$ with acetic acid, thiophenol and imidazole, and of $Ph_2Pb(C_5H_5)_2$ with acetic acid, hydrogen chloride, and imidazole result in the formation of the corresponding Ph_3PbX and Ph_2PbX_2 complexes. However, thermolysis of $Ph_2Pb(C_5H_5)_2$ at $60{-}70^{o}$ affords $Pb(C_5H_5)_2$, and lead(II) thiolates and products of composition $[Ph_2Pb(OR)]_n$ are obtained on reaction with thiols and phenols, respectively.[236] [Tris(trimethylsilyl)methyl]trimethyllead, $[(Me_3Si)_3C]Me_3Pb$, (98) may be mono- or dihalogenated without cleavage of the Pb-R (R = $C(SiMe_3)_3$) bond affording XMe_2PbR and X_2PnMeR (X = Cl,Br). Similarly, electrophilic cleavage of one methyl group from lead occurs when (98) is treated with acetic or halo-substituted acetic acids to give monoester derivatives of the type Me_2RPbO_2CR'. The esters $Me_2RPbO_2CCX_3$ slowly decompose in solution via the route:

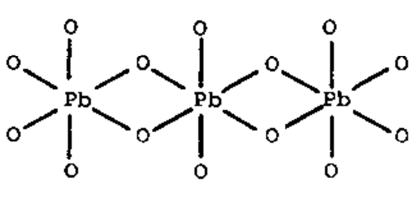
$$Me_2RPbO_2CCX_3 \rightarrow Me_2RPbX + CO_2 + [CX_2]$$

whilst the formate ester, Me_2RPbO_2CH appears to disproportionate in benzene solution to Me_3RPb and products derived from $MeRPb(O_2CH)_2$ (Pb, $Pb(O_2CH)_2$, CO_2, RH, and CH_4). Other esters also were observed to disproportionate to Me_3RPb when heated in aqueous dioxane.[237]

4.2.4 Oxides, Sulphides, Selenides and Tellurides

The trimethylsilylation method together with ^{29}Si n.m.r. have been employed to show that saturated tetramethylammonium (TMA) silicate solutions of TMA:SiO_2 ratios of 0.6 to 20 contain mainly four-ring silicate anions. $Si_8O_{20}^{8-}$. For saturated solutions with TMA:SiO_2 ratios of 1:1 to 3:1, the content of $Si_8O_{20}^{8-}$ anions amounts up to 80% of the total SiO_2 concentration. This preferred formation of only one single type of silicate anion differs from the results found for sodium silicate solutions, and is explained by a clathrate-like structure of the water molecules in the concentrated TMA silicate solutions due to the high concentration of TMA cations. With increasing dilution of the TMA silicate solutions, the concentration of the $Si_8O_{20}^{8-}$ anion decreases, and mainly mono-, di- and trisilicate anions are formed. Oligomeric cyclic and polymeric cyclic silicate anions could be detected in concentrations up to 5%.[238] Crystalline tetramethylammonium aluminosilicates with molar constitutions of $wNMe_4OH.xSiO_2.yAl_2O_3.zH_2O$ (w = 1-1.2; x = 1; y = 0.02-0.5; z = 8.1 -9.7) have been obtained from mixtures of diluted TMA aluminate and TMA silicate solutions with different molar Si/Al ratios by concentration and cooling the mixtures. Trimethylsilylation and ^{29}Si n.m.r. identification show these TMA aluminosilicates to consist of double four-ring units. The arrangement of the aluminium atoms in the double rings agrees in general with Loewenstein's rule, and leads to five distinct types of double four-rings with different Al content and Si-Al distribution. ^{29}Si n.m.r. of the TMA aluminosilicates exhibit up to 4 sharp signals with characteristic chemical shifts which can be assigned to the central silicon atom of $[OSi(OSi)_{3-n}(OAl)_3]$ building units of the double four-ring aluminosilicate anions. These units can exist as monomers or can be connected to polymeric structures by SiOAl bridges. The structure of these aluminosilicates is therefore different from the structure of the crystalline TMA aluminosilicates obtained from the solutions.[240] ^{29}Si n.m.r. has been employed in the study of ultrastabilisation processes in synthetic Faujasite.[241] The new sodium zincosilicate, $Na_2ZnSiO_4.2H_2O$, has been synthesised by adding at 95° with constant stirring to a solution of sodium zincate, Na_2ZnO_2, in water a solution of sodium metasilicate pentahydrate, $Na_2H_2SiO_4.4H_2O$, followed by sodium disilicate, $Na_2Si_2O_5$.[242] The structure of $Na_2Be_2Si_3O_9$ is built up of $[Si_3O_9]$ rings parallel to [010] linked together by $[Be_2O_6]$ groups. Sodium cations occupy cavities in the framework.[243] The lead silicate, $Pb_4Si_3O_{17}$, contains both $[SiO_4]^{4-}$ and $[Si_2O_7]^{6-}$ anions.[244] The rare tube silicate, litidianite, $NaKCuSi_4O_{10}$, has been made by two methods. In one, a 2:1:1:8 mole ratio mixture of CuO:Na_2CO_3, K_2CO_3 and SiO_2 is sintered, and in the other a glass made from a mixture of these reagents in the same ratio is devitrified.[245] $LiNa_2YSi_6O_{15}$ comprises corrugated double silicate chains, which have a six-tetrahedra repeat unit in the c direction, are linked by sodium cations, $[LiO_4]$ and $[YO_6]$ units to form a three-dimensional network.[246] The structure of $K_2Ba_7Si_{16}O_{40}$ consists of infinite $[Si_2O_5]$ sheets parallel to [201] linked together via eight-coordinated potassium and seven and nine coordinated barium.[247]

Crystals of $BaZnGeO_4$ have a structure derived from the stuffed tridymite framework with ordering of germanium and zinc between two tetrahedral sites.[248] The hitherto unknown $Rb_2Sn_2O_3$ has been obtained by heating mixtures of $RbO_{0.48}$ and SnO_2 at 600°. It is isotypic with K_2SnO_2, and extremely sensitive to moisture.[249,250] The structure of the low temperature form of Li_2PbO_3, obtained by the decomposition of $K_2Li_6Pb_2O_8$ at 690° in vacuo, is a variant of the NaCl-type, with alternating layers of $Li(2)^+$ and $Li(1)^+/Pb^{4+}$ cations. All atoms have octahedral coordination.[251] $PbAl_2O_4$ and $PbGa_2O_4$ also belong to the family of stuffed tridymite structures. Lead atoms are coordinated by three oxygens in a trigonal pyramidal fashion.[252] The first example of an oligooxoplumbate, $K_2Li_{14}Pb_3O_{14}$, has been prepared by heating a mixture of K_2PbO_3, "PbO_2", and Li_2O in the ratio K;Li:Pb = 2:14:3 at 560°. The structure is characterised by the triple-octahedron $[Pb_3O_{14}]$ group (97).[253] Crystals of $TlPb_8O_4Br_9$ contain $[Pb_8O_4]$ units.[254]



(97)

The structures of SiS_2 (at 138K) and $SiSe_2$ (at 293K) have been redetermined. Both consist of chains of edge-sharing $[SiE_4]$ tetrahedra.[255] $Cu_5Si_2S_7$ has a compact hexagonal arrangement of sulphur atoms with the silicon and copper atoms in the tetrahedral cavities and the [SiS_4] tetrahedra bound to form [Si_2S_7] groups.[256] The structure of the mixed valence tin sulphide, $Sn^{II}Sn^{IV}S_3$, has been redetermined and confirmed.[257] $Tl_2Sn_2S_3$ has a structure of the defect NaCl type.[258] In both this and in Eu_2SnSr, tin has four-fold sulphur coordination.[259] The structure of $Bi_xSb_{2-x}Sn_2S_5$ ($0.4>x>0.2$) is built up of ribbon-like [$(Bi,Sb,Sn)_8S_{10}$] sheets extending along [100]. The coordination polyhedra of the metals are that of slightly distorted square pyramids. However, for three of the sites, a longer sulphur interaction gives octahedral coordination, whilst for the fourth site two such long interactions give overall [5+2] sulphur coordination.[260]

The anions of $K_4[Si_4Te_{10}]$ have an adamantane-like structure.[261]

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