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Chapter 4

ELEMENTS OF GROUP 4

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4.1 CARBON

4.1.1 Syntheses and Reactions

Trifluoromethanol and trifluoromethylamine have been made by the reaction of hydrogen chloride with the corresponding chloro compounds, CF_3OCl (at -120°) and CF_3NCl_2 (at -78°), respectively. Both compounds are unstable at room temperature due to elimination of HF. CF_3OH is a typical protonic acid comparable with F_5SOH, F_5SeOH and F_5TeOH. CF_3NH_2 is a base, inspite of the inductive effect of the CF_3 group.[1] An alternative preparation of CF_3NH_2 from CF_3NCO has also been described:

$$\begin{tikzcd}
\mathrm{CF_3NCO} + {}^{t}\mathrm{BuOH} \arrow[r] & \mathrm{CF_3NH{\cdot}COO^{t}Bu} \arrow[r, "(i)"] & \mathrm{F_3CNH_2{\cdot}HCl} \arrow[d, "(ii)"] \\
 & & \mathrm{CF_3NH_2}
\end{tikzcd}$$

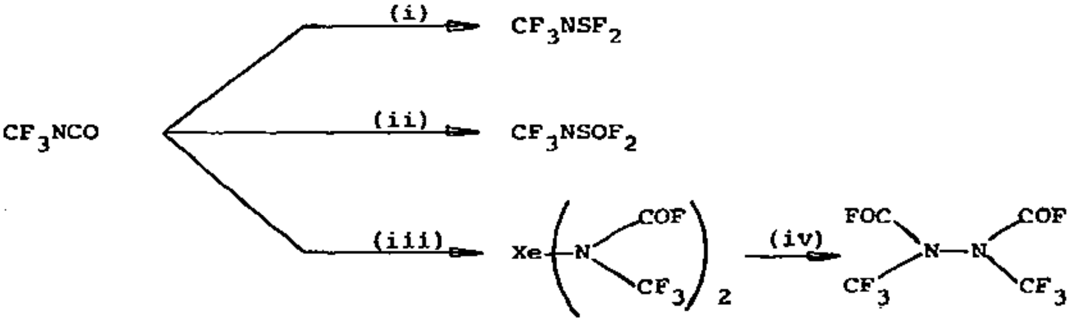
(i) HCl, (ii) pyridine

CF_3NCO itself has been synthesised by a Curtius decomposition of the corresponding azide (from CF_3COCl and trimethylsilylazide):

$$\begin{tikzcd}
\mathrm{CF_3COCl} + \mathrm{Me_3SiN_3} \arrow[r] & \mathrm{CF_3CON_3} \arrow[d, "(i)"] + \mathrm{Me_3SiCl} \\
 & \mathrm{CF_3NCO}
\end{tikzcd}$$

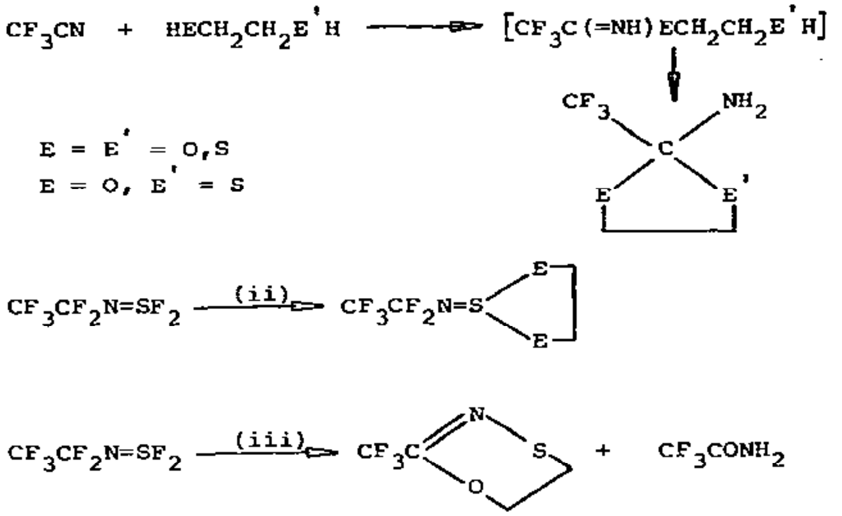
(i) 60°, $-N_2$

With water, CF_3NCO affords $(FCN)_3$, $F_3CNHCOF$ and $F_3CNHCONHCF_3$, whilst reactions with ammonia in $CFCl_3$ at 0° produces $F_3CNH{\cdot}CO{\cdot}NH_2$. Treatment with SF_4, OSF_4 and XeF_2 gives previously characterised products:



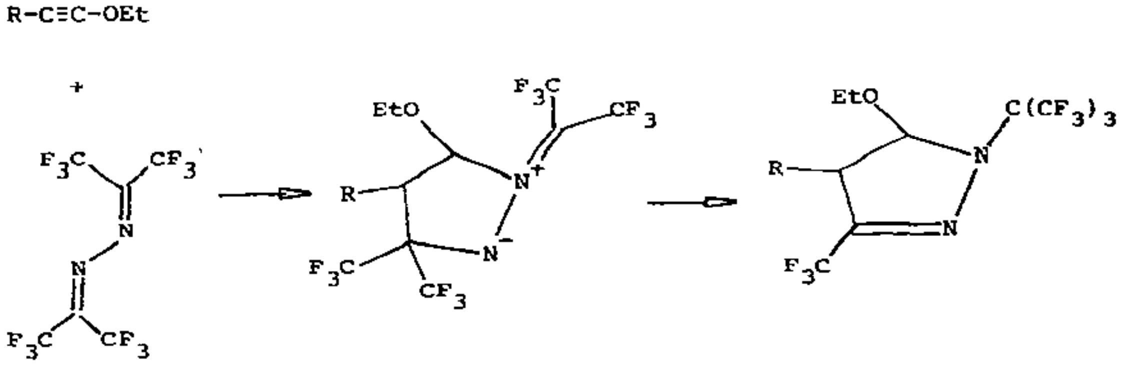
(i) SF_4, DABCO, 100°, (ii) OSF_4, DABCO, 250°, (iii) XeF_2, 20°, (iv) -Xe.

The presence of fluoride ion induces the formation of heterocycles from the reaction of $CF_3C{\equiv}N$ or $CF_3CF_2N{=}SF_2$ with oxygen-, sulphur and nitrogen-containing heterocycles;[3,4]



(i) NaF, (ii) NaF, $HECH_2CH_2EH$ (E=O, NMe), (iii) NaF, $HSCH_2CH_2OH$.

The formation of N-(perfluoro-t-butyl)pyrazoles from the reaction of hexafluoroacetone azine with alkynes involves an azomethine imide intermediate which rearranges by a |1,4| migration of a trifluoromethyl group;[5]



R = H, Me.

Sekiya and Desmarteau[6] have investigated the reactions of metal fluorides with $CF_3OOCF_2NHCF_3$. Lithium and lead fluorides are unreactive, whereas NaF, KF, CsF and KHF_2 react to afford $CF_3\overline{NCF_2O}$, $CF_3NF(CO)F$, $CF_3N(OCF_3)COF$ and COF_2. The preferred method for the synthesis of the acyl chlorides of perfluorinated carboxylic acids, such as CF_3CO_2Cl, $C_2F_5CO_2Cl$, $C_3F_7CO_2Cl$, $ClCF_2CO_2Cl$, HCF_2CO_2Cl and $CF_2(CF_2CO_2Cl)_2$, is by the low-temperature reaction of the sodium salts of the acids with ClF. All the compounds are thermally unstable at 22°, and are explosive in the gas-phase at pressures greater than 20-50 torr.[7]

The only previously characterised sulphur-substituted alkyne, $SF_2C{\equiv}CH$, reacts with SF_5Br in sealed pyrex vessels at 105° to yield the 1:1 addition product, $SF_5CBr{=}CHSF_5$, as a clear liquid which may be readily dehydrobrominated by KOH at ambient temperatures to yield $F_5SC{\equiv}CSF_5$ in 64% yield, a similar series of reactions also occurs with $CF_3C{\equiv}CH$:[8]

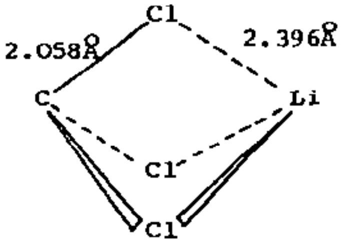
$$CF_3C\ CH \;+\; SF_5Br \longrightarrow CF_3CBr{=}CSF_5 \xrightarrow{(i)} SF_5C\ CCF_3$$

(i) KOH.

4.1.2 Structural and Physico-chemical Studies

The fundamental physical properties of carbon dioxide and its derivatives have been reviewed.[9]

Ab initio M.O. calculations have shown that ClCF has a singlet $^1A'$ ground state with C–Cl = 1.78Å, C–F = 1.344Å and ClCF = 104.63°.[10] Similar examination of the carbene CCl_3Li, for which previous reactivity and matrix-isolation studies suggested the presence of more than one isomeric form, indicate the triply-bonded species (1), with the lithium on the 'wrong' side of the molecule, to be the most stable form.[11] Other geometries, including (2), are less



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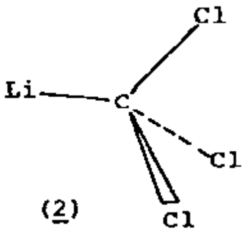
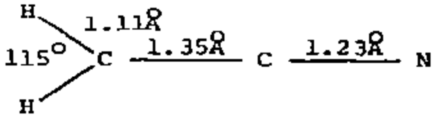


(2)

stable. Such a result, however, is not really unreasonable, since the pyramidal CCl_3^- fragment with negative charge delocalized to the electronegative chlorines, richly endowed with lone pairs of electrons, will preferentially attract the lithium to the chlorine side of the pyramid. Optimized bond distance and angle data for the two radicals $\cdot CH_2CN$ and $\cdot CH_2NC$ have been calculated by the INDO method using a very large Gaussian basis set [(3) and (4)].[12] ΔU^o for the isomerisation $\cdot CH_2CN(g) \rightarrow \cdot CH_2NC(g)$ was also calculated to be 49.6 kJ mol^{-1}.



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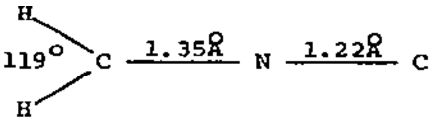
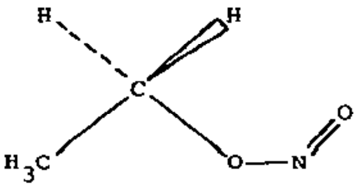


(4)

The structures of several compounds have been determined from electron diffraction and microwave data. A combined study has produced the following parameters for bromoform: $C\text{-}Br_{av}$=1.924(5)Å, C-H = 1.1(5)Å, BrCBr = 111.7(4)°, $HCBr_{av}$ = 107.2(5)°.[13] The structure of 1,1,1-trifluoroethane has been reexamined by electron diffraction in order to resolve the confusion arising from previous contradictory results.[14] The preferred refined yielded a structure with a staggered conformation with C-C = 1.494(8)Å, C-F = 1.340(2)Å, C-H = 1.081(7)Å, CCF = 11.9(2)Å and CCH = 112(1)°. These data agree well with the microwave values obtained by Thomas, Heeks and Slenden,[15] and confirm the very short C-C bond distance. 1,1,2-Trifluoroethane consists of a conformational mixture of rotamers at 265K in the gas phase, with the conformer with the F---F anti distance present in 92% abundance, corresponding to an energy distance between the two conformers of 900 cal.mol^{-1}. [C-C = 1.500(5)Å, $C\text{-}H_{mean}$ = 1.088(11)Å, C-F(CF_2H group) = 1.353(4)Å, C-F(CH_2F group) = 1.387(8)Å, CCF_{mean} = 109.0(5)°, CCH_{mean} = 108.9(14)°, FCF = 106.8(7)°].[16] Electron diffraction, infrared and microwave data for hexafluoropropene show it to be planar except for two of the fluorine atoms of the CF_3 group. The equilibrium conformation of the CF_3 group has one fluorine atom in the molecular plane in the trans position with respect to the fluorine atom bonded to the central carbon. [C=C, $C\text{-}F_{av}$ = 1.329(3)Å, C-C = 1.513(3)Å, C=C-C = 127.8(7)°, F-C=C(CF_2 group) = 123.9(14)°, C=C-F = 120(3)° (for the central F atom) and C-C-F = 110.3(15)° (for the CF_3 group)]. Data obtained at different temperatures indicated a three-fold barrier to internal rotation of the CF_3 group of 1.0-2.0 $kcal.mol^{-1}$.[17] Vibrational data for tris(trifluoromethyl)amine support C_3 rather than C_{3h} symmetry. A normal coordinate analysis of the data showed, however, that the vibrations of the NC_3 skeleton are strongly mixed with the vibrations of the CF_3 group and are entirely non-characteristic. Electron diffraction data confirmed a flattening of the NC_3 pyramid and showed that the C-N bond is shorter and stronger than that in trimethylamine [C-F = 1.323(4)Å, C-N = 1.426(6)Å, FCF = 108.3(4)° and CNC = 117.9(4)Å].[18] 1,1-Difluoroethylene ozonide (3,3-difluoro-1,2,4-trioxolane), isolated from the ozonolysis of 1,1-difluoroethylene, consists of a single ring conformer estimated to be at least 850 $cal.mol.^{-1}$ more stable than any other populated semi-rigid conformation. However, the microwave rational constants do not allow an unequivocal distinction between twisted or envelope ring conformations.[19]

The most striking feature of the molecular structure of hexakis(trifluoromethylthio)ethane, $(CF_3S)_3CC(SCF_3)_3$, is the long C-C bond (1.624(37)Å).[20] In benzene solution at 10-60°, the molecule undergoes reversible homolytic C-C bond cleavage to afford $(CF_3S)_3S\cdot$ radicals (identified by e.s.r.) due to sterically induced destabilisation of the bond. From the temperature dependence of the radical concentration, the C-C bond dissociation energy was determined to be 13.7 $kcal.mol^{-1}$.[21] The kinetics of the thermal dissociation of ethane have been reexamined in the temperature and pressure ranges of 840-913K and 3-700 torr. Rate coefficients for the reaction $C_2H_6 \rightarrow 2\cdot CH_3$ were found to vary with pressure in a manner similar to previous investigations although small temperature discrepancies were noted.[22] The thermal decomposition of 1,1-difluorocyclobutane, studied in the gas phase at 444-516° and 6-8 torr, to yield ethylene and 1,1-difluoroethylene is a homogeneous first-order decomposition pathway and probably a truely unimolecular reaction. Another decomposition pathway to yield HF and 2-fluoro-butadiene takes place largely by a surface reaction which exhibits autocatalysis, and could be largely supressed in the initial stages of the decomposition by "aging" the reaction vessels.[23]

Microwave data for ethyl nitrite shows the presence of three rotational isomers. Two rotamers correspond to cis,trans [τ_1(ON-OC) = 0°, τ_2(CC-ON) = 180°](5) and cis,gauche (τ_1 = 0°, τ_2 = 180°)(6) structures, relative intensity data showing the cis,gauche rotamer to be less stable by 238±50 cm^{-1}. A third rotamer, less stable than the cis,trans by 81±20 cm^{-1}, was assigned a trans,gauche structure [τ_2 = 180°, τ_2 = 90°](7).[24] Electron diffraction data for o-phenylene sulphite reveal an envelope conformation for the five-membered ring with the oxygen



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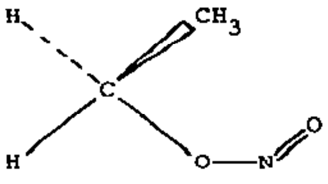

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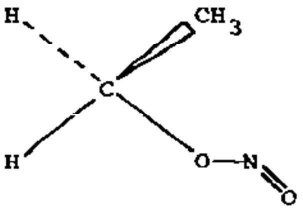


(7)

atoms in the plane of the benzene ring. The S=O bond points towards the axial direction. The analysis also indicated an elongation of the benzene ring skeleton in the direction parallel to the common edge of the two rings.[25] The structure of the molecular ammonium trithiocarbonate has been studied by electron diffraction and shown to have structure (8) with a three-fold axis in the gas-phase [C-S = 1.66(9)Å, N-H = 1.036(20)Å, S-H = 1.532(15)Å, C-N = 1.71(4)Å].[26] Other compounds of interest which have been studied include $HC{\equiv}CPF_4$ (electron diffraction)[$P\text{-}F_{eq}$ = 1.540(4)Å, $P\text{-}F_{ax}$ = 1.599(3)Å, P-C = 1.747(5)Å, C-C = 1.218(7)Å, $F_{eq}\text{-}P\text{-}F_{eq}$ = 114.7(10)°, $F_{ax}\text{-}P\text{-}F_{ax}$ = 179.0(4)°],[27] difluoro(methyl)-borane (microwave)[C-H = 1.102(7)Å, C-B = 1.564(5)Å, B-F = 1.315(5)Å, HCB = 110.4(5)° and FBF = 116.8(5)°],[28] and formylfluoride (electron diffraction and microwave)[planar with, C=O = 1.188(4)Å, C-F = 1.346(3)Å, C-H = 1.11(2)Å, OCF = 122.3(2)° and OCH = 130(4)°].[29]

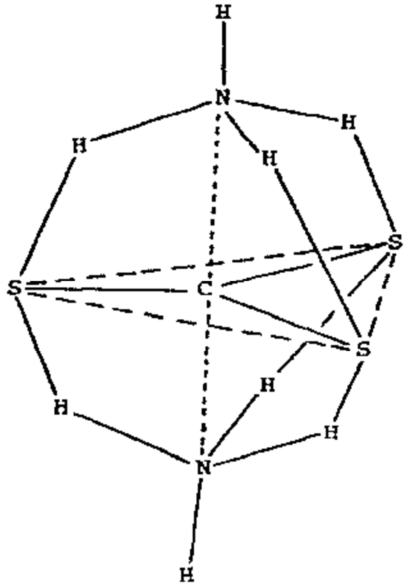
4.2 SILICON, GERMANIUM, TIN and LEAD

4.2.1 Jackson,[30] using known literature values for heats of formation combined with kinetic and appearance potential data, has devised a set of self-consistent values of the bond-dissociation energies, D(Me_3M-X). (M = Si, Ge, Sn, Pb; X = H, Me, MMe_3, OEt, Cl, Br)(Table 1). The double halide ion affinities of several

Table 1. Bond Dissociation Energies, D(Me_3M-X) (in kcal mol^{-1}) of Compounds Me_3MX.

X	M				
	C^a	Si	Ge	Sn	Pb
H	105	90	82	74	(62)
CH_3	90	90	76	65	49
MMe_3	90^b	81	73	56	55
OH	92	126		110	
OEt	82	111	107	84	
Cl	84	111	116	101	
Br	71	94	104	85	

a; Methyl, not t-butyl. b; In ethane.



(8)

metal(IV) halides have been measured, and used to determine both mean homolytic bond strengths, $\overline{E(M-X)}_{hom}$, (i.e. for the process $M(g) + 6X(g) + 2e^- \rightarrow MX_6^{2-}(g)$) and coordinate bond strengths, $\overline{E(M-X)}_{het}$, (i.e. for the process $M^{4+}(g) + 6X^-(g) \rightarrow MX_6^{2-}(g)$) for the hexahalogenometal(IV) anions (Table 2).[31] Glidewell[32] has

Table 2. Homolytic and Coordinate Bond Strengths (kJ mol^{-1}) in some MX_6^{2-} Anions.[31]

Bond	$\overline{E(M-X)}_{hom}$	$\overline{E(M-X)}_{het}$
Si-F	538	1877
Ge-F	471	1821
Ge-Cl	347	1672
Sn-Cl	365	1519
Pb-Cl	310	1518

revised the values for the intramolecular non-bonded atomic radii for carbon (1.25Å), silicon (1.55Å), germanium (1.58Å) and tin (1.82Å).

An ESCA study of 60 tin compounds of many different chemical types has shown that the tin $3d_{5/2}$ binding energy range is very small (3.1eV), and is not suited for the determination of either the degree of oxidation or the coordination number at tin. A quantitative analysis of the data using the cheleq method showed further that besides the partial charge on tin, the potential at the site of the tin atom is also important.[33] Lead $4f_{7/2}$ binding energies of a number of lead compounds have been employed to obtain the order of electron-withdrawing ability of ligands (NO $\sim \frac{1}{2}SO_4 > F \sim Cl \sim \frac{1}{2}C_2O_4 \sim OAc \sim NCO > C(CN)_3 \sim Br \sim \frac{1}{3}PO_4 \geq NCS \sim I \geq \frac{1}{2}NCN \sim \frac{1}{2}O$.[34] The diamagnetic susceptibility of a series of methyl-Group IV metal halides has been measured, and the pure Langerin diamagnetic contribution (χ_m^d) and the temperature independent paramagnetic contribution (χ_m^p) determined separately. Values for the latter were interpreted in terms of steric hindrance, $(p \rightarrow d)\pi$ bonding and polymerisation effects.[35]

A method for the separation and determination of submicrogram levels of tin in sea-water and ordinary water has been described. The analysis involves generation of stannane by sodium borohydride reduction followed by atomic absorption.[36]

4.2.2 Bonds to Hydrogen

Photolysis of silane at 147nm results in the formation of H_2, Si_2H_6, Si_3H_8 and a solid hydride silicon film. Two primary processes

$$SiH_4 + h\nu \longrightarrow SiH_2 + 2H$$

and $$SiH_4 + h\nu \longrightarrow SiH_3 + H$$

are involved in the decomposition.[37]

Doncaster and Walsh[38-40] have studied the kinetics of the gas-phase reactions of iodine with silane,[38] trimethylsilane[39] and trimethylgermane.[40] The reaction with silane, in a well-conditioned quartz vessel at 537.9K with pressures of iodine and silane in the ranges 0.26 - 3.0 torr and 9.4 - 44.4 torr, respectively, follows the rate law

$$-\frac{d}{dt}[I_2] = k[I_2]^{\frac{1}{2}}[SiH_4].$$

with $k = (4.55 \pm 0.28) \times 10^{-5}$ torr$^{-\frac{1}{2}}$ s^{-1} (14nns), suggesting the mechanism

$$I_2 (+M) \rightleftharpoons 2I\cdot (+M)$$

$$I\cdot + SiH_4 \rightleftharpoons \cdot SiH_3 + HI$$

$$\cdot SiH_3 + I_2 \longrightarrow SiH_3I + I\cdot$$

The reaction with trimethylsilane in the range 565 - 599K obeys the rate law

$$-\frac{d}{dt}[I_2] = \frac{k[I_2]^{\frac{1}{2}}[Me_3SiH]}{1 + k'[HI]/[I_2]}$$

over a range of iodine and trimethylsilane pressures provided that the ratio $[Me_3SiH]_0/[I_2]_0 > \approx 25$. The values obtained for the Si-H bond dissociation energy in the two compounds are very similar (376 kJ mol^{-1} for SiH_4 vs. 378 kJ mol^{-1} for Me_3SiH), and show that substitution of methyl groups at silicon has a negligible effect on the bond dissociation energy. The kinetics of the reaction of iodine with trimethylgermane in the temperature range 420 - 474K follow the same rate law as for trimethylsilane, from which the bond dissociation energy, D(Me_3Ge-H), was deduced to be 340 kJ mol^{-1}.

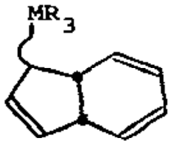
Trimethylsilane, -germane, and -stannane add spontaneously and selectively to tetracyanoethylene to yield 1:1 adducts H(TCNE)MR_3.[41] The insertion shows no deuterium kinetic isotope effect, are not subject to radical-chain initiation or inhibition, but does depend on the metal. Second-order rate constants for the reaction decrease in the order Sn Ge Si (= $10^7:10^3:10^0$). The detection of a transient charge-transfer complexes supports an electron transfer mechanism in which the M-H bond participates as an electron donor in the form of an ion-pair $HMR_3^{+}.TCNE^{\overline{\cdot}}$. The insertion adducts are formed subsequently in a series of fast cage reactions involving fragmentation of this metastable ion pair to a radical pair.

4.2.3 Bonds to Carbon

Tetramethylgermane and -stannane have been prepared by cocondensing the metal vapour with methyl radicals (produced by dissociation of ethane using a radiofrequency) on a cold finger at -196°.[42]

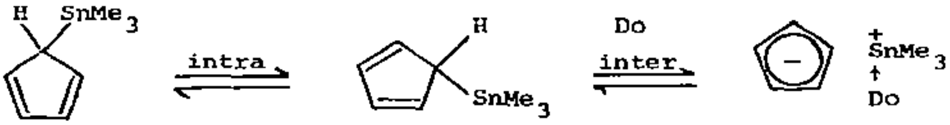
The infrared spectra for $MeSiH_3$, $MeSiD_3$, $MeGeH_3$, CD_3GeH_3 and $MeGeD_3$ measured as polycrystalline samples at 77K are in agreement with previous gas phase studies. The data are consistent with C_5 molecular symmetry for all molecules, and suggest that methylsilane and methylgermane are isostructural.[43] Electron diffraction studies show that the equilibrium configuration of $(CF_3)_4Ge$ has Td symmetry, i.e. the CF_3 groups exactly stagger the Ge-C bonds. The torsional force constant for the CF_3 groups is ca. 0.04 mdyn Å.[44] The trends in the ^{13}C chemical shifts for $(CF_3)_4M$ (M = C, Ge, Sn) are the reverse of that expected on the basis of pure electronegativity effects.[45] 1-Silacyclopent-3-ene, 1,1-difluoro-1-silacyclopent-3-ene, and 1,1-dichloro-1-silacyclopent-3-ene all have C_{2v} symmetry. Apparent deviations from planarity of the rings are caused by ring-puckering vibrations, the amplitudes of which are greatest for the fluoride and smallest for the chloride.[46] The structures of two adamantane cage structures, 1-bromo-3,5,7-trimethyl-1,3,5,7-tetrasila-adamantane[47] (by X-ray diffraction) and 1-methyl-1-germaadamantane[48] (by electron diffraction), have been determined.

A rather elegant variable-temperature ^{13}C n.m.r. study by Bonny and Stobart[49] on the chiral silyl-cyclopentadienes, $RClHSi^*C_5H_5$ (R = Me, n-Bu, Me_3SiCH_2)(obtained from $RHSiCl_2$ and KC_5H_5 at -45°), has provided convincing substantiation for the (1,2) (equivalent to a (1,5)) migration pathway for the metallotropic rearrangements in this type of compound. The 9-metallo-all-cis-cyclonona-1,3,5,7-tetraenes, $C_9H_9GeH_3$, $C_9H_9SnH_3$ and $C_9H_9SnMe_3$ (from H_3GeBr, H_3SnBr and Me_3SnCl, respectively, and $C_9H_9^-$ at -78° - -45°) undergo ring closure on warming to room temperature to the corresponding isomeric 1-metallo-8,9-dihydroindenes (9)



(9)

as a mixture of exo and endo isomers, the former predominating in each case. At temperatures between -90° and +5°, $Me_3SnC_9H_9$ is fluxional, and comparisons with n.m.r. data for $Me_3SnC_5H_5$ and $Ph_3SnC_7H_7$ indicate that successive 1,9 ('least motion') sigmatropic shifts, rather than the alternative symmetry allowed thermal migration (1,5; 'molecular broadjump') are responsible for the metallotropic character. In contrast, the germayl and stannyl derivatives are stereochemically rigid on the n.m.r. timescale at -45°, and isomerisation prevents the observation of fluxional behaviour at higher temperatures.[50] Treatment of $Me_3SnC_5H_5$ in THF at 26° with HMPT causes a broadening of the tin satellites, and when the sample is cooled coalescence occurs at -61° due to the formation of ion-pairs (10):



Do = donor solvent or LiCl.

A similar sequence of events occurs at constant temperature on increasing the concentration of HMPT, DMF or LiCl, and also with $Me_3SnC_9H_9$. However, in the latter case, the addition of DMF, HMPT or DMSO leads to a distinct shift of the ring protons from the olefinic region to that of the |9|-annulene anion, because in this case the equilibrium lies more over to the side of the $[Me_3Sn{\cdot}D_o]^+C_9H_9^-$ ion-pair than in the case of $Me_3SnC_5H_5$.[51]

The reactions of alkyl cations with methyl- and ethylsilanes have been studied in a tandem mass spectrometry apparatus.[52-54] The major reactions are hydride and methide (CH_3^-) or ethide ($C_2H_5^-$) transfer from the silane to the alkyl cation. Isotopic studies show only very minor incorporation of ^{13}C and D atoms in the ionic products when CH_3^+ cations are replaced by $^{13}CH_3^+$ and CD_3^+, which is interpreted as indicating that the reactions do not proceed through pentavalent collision complexes, but rather as a simple interchange of the molecular anion between the reactants.

Two independent studies of the 147nm photolysis of tetramethylsilane have appeared, and are essentially in agreement.[55,56] The principal reaction products are hydrogen, methane, ethane, trimethylsilane and hexamethyldisilane, together with several other minor products and a solid product. The primary decomposition steps were postulated to be:

$$
\begin{array}{lll}
 & \rightarrow \ Me + Me_3Si & (\phi = 0.43) \\
 & \rightarrow \ 2Me + Me_2Si & (\phi = 0.24) \\
 & \rightarrow \ CH_4 + Me_2SiCH_2 & (\phi = 0.17) \\
Me_4Si & \rightarrow \ CH_3 + H + CH_2SiMe_2 & (\phi = 0.10) \\
 & \rightarrow \ H_2 + CHSiMe_3 & (\phi = 0.02) \\
 & \rightarrow \ CH_2 + Me_3SiH & (\phi = 0.04)
\end{array}
$$

followed by combination, disproportionation and abstraction reactions of the radical intermediates. The Me_3Si radical was found to abstract hydrogen from a variety of donors approximately twenty times faster than the methyl radical.

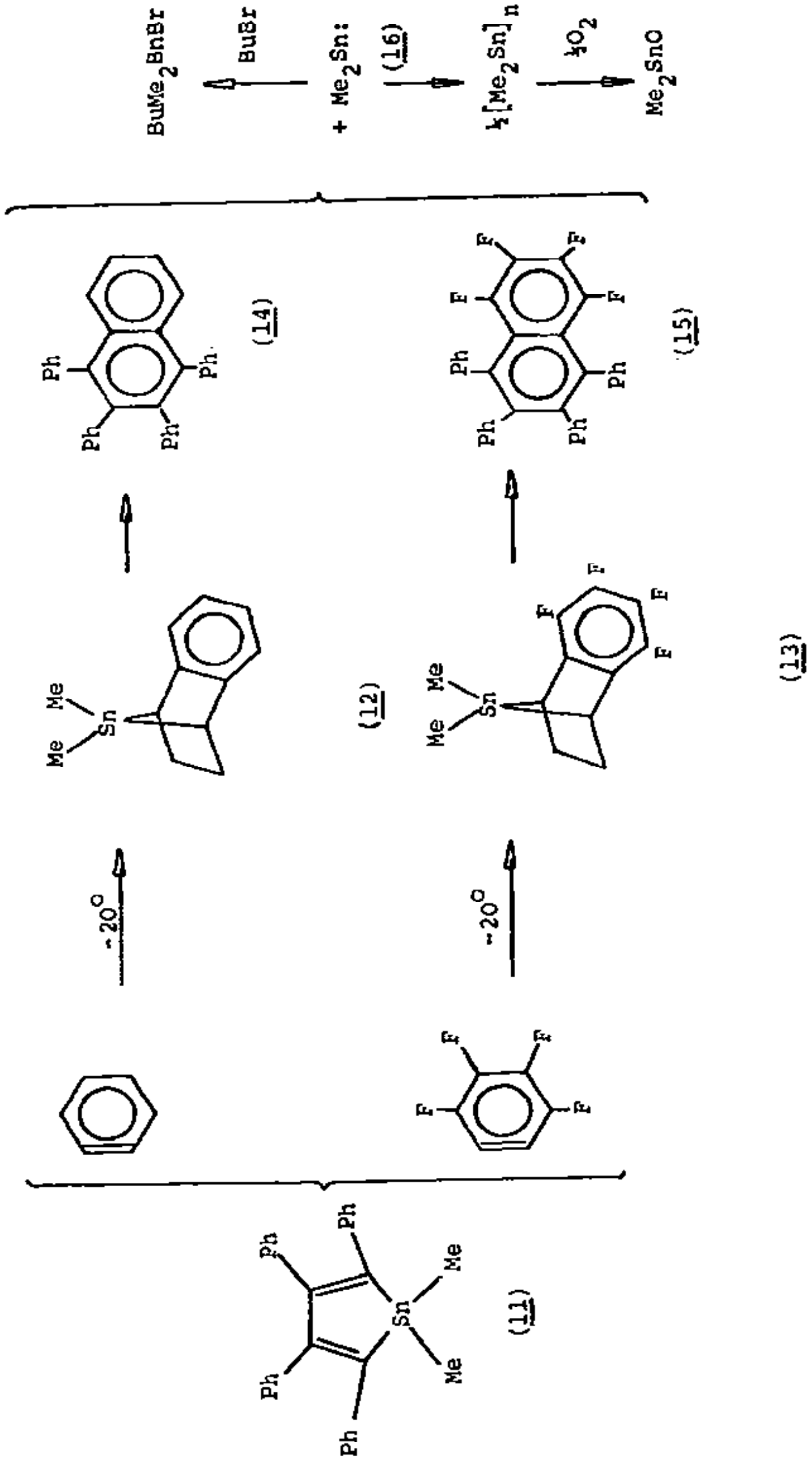
The rates of oxidative-cleavage of homoleptic tetralkylstannanes by iron(III) complexes are highly dependent on the donor properties of the alkyl groups as measured by the ionisation potentials. The rates progressively increase with α-methyl substitution : R = Me< Et< *iso*-Pr approximately $10^0:10^4:10^7$, reflecting an inverse steric effect and counter to any expectation based on a direct bimolecular scission, suggesting that the activation process does not involve cleavage of the alkyl-tin bond itself. Instead, the rate-limiting step involves initial electron transfer from tin to iron, followed by rapid homolytic fragmentation of $[R_4Sn^+]$ and oxidation of the alkyl radical by further iron(III) complex:[57]

$$R_4Sn + Fe^{III} \xrightarrow{k} R_4Sn^+ + Fe^{II}$$

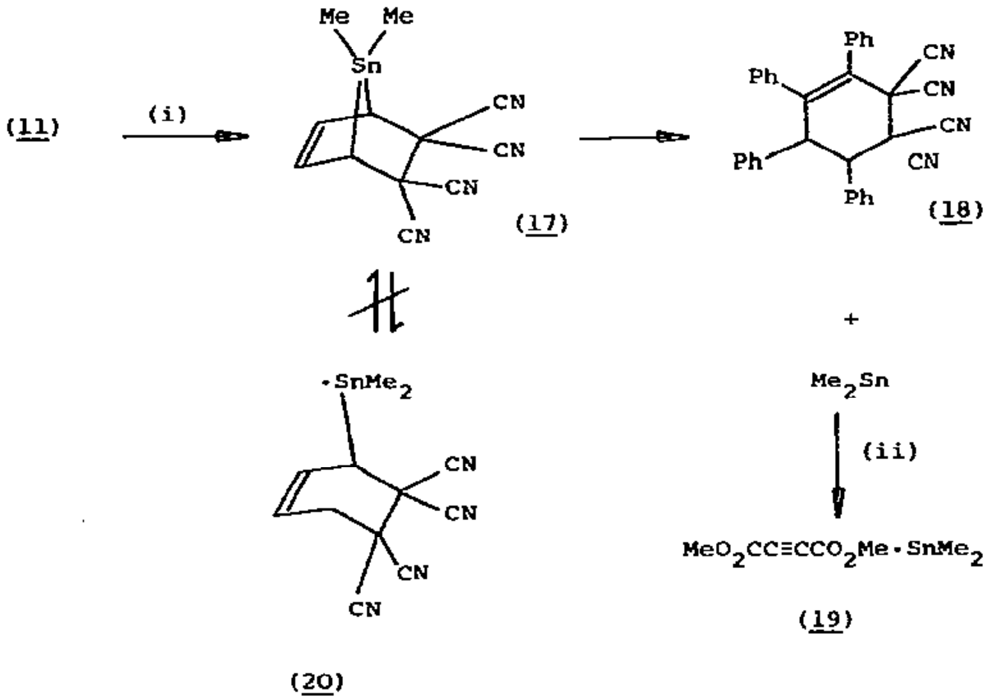
$$R_4Sn^+ \xrightarrow{fast} R_3Sn^+ + R\cdot$$

$$R\cdot + Fe^{III} \xrightarrow{fast} [R^+] + Fe^{II}$$

Attempted Diels-Alder addition of benzene or 2,3,4,5-tetrafluoro-


(11)
Ph
Ph
Ph
Ph
Me
Me
Sn
F
F
F
F
-20°
-20°
Me
Me
Sn
(12)
Me
Me
Sn
F
F
F
F
(13)
Ph
Ph
Ph
Ph
(14)
Ph
Ph
Ph
Ph
F
F
F
F
(15)
BuMe2BnBr
BuBr
+ Me2Sn:
(16)
½[Me2Sn]n
½O2
Me2SnO

benzyne to the stannole (11) did not yield the stannanorbornene derivatives (12) and (13), but rather only the biphenyls (14) and (15), presumably by elimination of dimethylstannylene (16), which may be trapped by butyl bromide. Reaction of the stannole (11) with tetracyanoethylene at -30°, however, proved more successful, and the [4+2] cycloaddition product (17) could be isolated as colourless crystals, stable for several weeks at least at -30°, but decomposing at -20° by a first-order reaction to Me_2Sn: and (18). In the presence of the strong stannylene scavenger, dimethyl acetylene dicarboxylate, the stannylene may be trapped as the adduct (19) of as yet unknown composition. ^{119}Sn CIDNP effects could not be observed in the thermolysis of (17), and hence it was presumed that the formation of the stannylene takes place by a concerted mechanism, rather than via a diradical intermediate such as (20).[58]



Organotin compounds continue to find application as ligand-transfer reagents. $Me_3SnCPh{=}CMe_2$ reacts with the d^0 chlorides of scandium, titanium, zirconium, hafnium, niobium, tantalum and tungsten, as well as molybdenum(V) chloride, smoothly in chloroform to yield the corresponding mono-alkenylmetal chlorides. The reactions show a great variety in rate (Mo ∿ W > Nb ∿ Ta > Ti ∿ Zr ∿ Hf > Sc); the Group VI metal chlorides are essentially alkenylated after 15 minutes, whilst the Group IV metal chlorides require <u>ca</u>. 20h. at 20°.[59] Tributyl(cyanomethyl)tin reacts with phosphorus(III) chloride in acetonitrile at 0° to afford crystalline, air-stable $P(CH_2CN)_3$.[60] Weichmann and Tzschach[61] have prepared several (2-aminoethyl)-triorganostannanes using the two routes:

$$R_3SnCl \xrightarrow{(i)} R_3SnNa \xrightarrow{(ii)} R_3SnCH_2CH_2NH_2$$

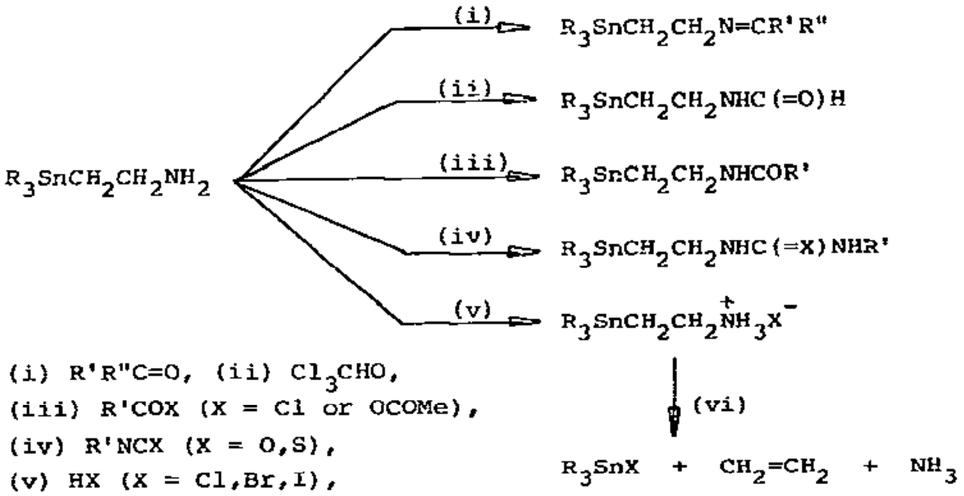
R = Me, Et, Bu, Ph.

(i) Na, (ii) $ClCH_2CH_2NH_2$.

$$(C_6H_{11})_3SnPh \xrightarrow{(i)} KSn(C_6H_{11})_2Ph \xrightarrow{(ii)} Ph(C_6H_{11})_2SnCH_2CH_2NH_2$$

(i) K/liquid NH_3; NH_4Br, (ii) $ClCH_2CH_2NH_2$.

The amine function undergoes typical reactions (Scheme 1).



(i) R'R"C=O, (ii) Cl_3CHO,
(iii) R'COX (X = Cl or OCOMe),
(iv) R'NCX (X = O,S),
(v) HX (X = Cl,Br,I),
(vi) heat.

<u>Scheme 1</u>.

Tris(trimethylsilyl)methyl(trimethyl)germane, $Me_3Ge[C(SiMe_3)_3]$ is slowly but selectively monobrominated to $BrMe_2Ge[C(SiMe_3)_3]$ at room temperature, the remaining methyl groups bound to germanium being strongly deactivated towards further electrophilic attack. Under forcing conditions (150°, $CDCl_3$), further bromination involves cleavage of methyl groups bound to silicon giving $BrMe_2Ge[C(SiBrMe_2)(SiMe_3)_2]$. The tin analogue, $Me_3Sn[C(SiMe_3)_3]$, is more reactive towards bromine, again affording completely selective cleavage of methyl groups from tin:

$$Me_3Sn[C(SiMe_3)_3] \xrightarrow{(i)} BrMe_2Sn[C(SiMe_3)_3] \xrightarrow{(ii)} Br_2MeSn[C(SiMe_3)_3]$$

(i) Br_2, $C_2H_4Br_2$, 20°; (ii) $4Br_2$, $C_2H_4Br_2$, reflux.

Under more drastic conditions upto 10 mole equivalents of bromine reacted, and a tetrabromide, most probably a mixture of $Br_3Sn[C(SiBrMe_2)(SiMe_3)_2]$ and $Br_2MeSn[C(SiBrMe_2)_2(SiMe_3)_3]$ was isolated. Iodine behaved similarly to give initially $IMe_2Sn[C(SiMe_3)_3]$ and then $I_2MeSn[C(SiMe_3)_3]$. Phenyl groups are much more susceptible to electrophilic attack. At room temperature using excess bromine in $CDCl_3$, $Ph_3Sn[C(SiMe_3)_3]$ yields a 1:2 mixture of $BrPh_2Sn[C(SiMe_3)_3]$ and $Br_2PhSn[C(SiMe_3)_3]$ after only 15 minutes; after 19 hours, conversion to $Br_3Sn[C(SiMe_3)_3]$ was complete. Ligand redictribution between $Me_3Ge[C(SiMe_3)_3]$ and $SnCl_4$ (excess) at 50° proceeded slowly but quantitatively to $ClMe_2Ge[C(SiMe_3)_3]$ and $MeSnCl_3$. Further reaction with $SnCl_4$ at 180° over 24 hours gave a mixture of Si-Me cleavage products, $ClMe_2Ge[C(SiClMe_2)(SiMe_3)_2]$ and $ClMe_2Ge[C(SiClMe_2)_2(SiMe_3)_3]$. Exchange between $Me_3Sn[C(SiMe_3)_3]$ and $SnCl_4$ was more facile:

$$\begin{tikzcd}
Me_3Sn[C(SiMe_3)_3] \arrow[r, "(i)"] & ClMe_2Sn[C(SiMe_3)_3] + MeSnCl_3 \arrow[d, "(ii)"'] \\
& \underset{(90\%)}{Cl_2MeSn[C(SiMe_3)_3]} + \underset{(10\%)}{Cl_3Sn[C(SiMe_3)_3]} + MeSnCl_3
\end{tikzcd}$$

(i) $SnCl_4$, 25°; (ii) $SnCl_4$, 150°.

Tin(IV) bromide was less reactive than $SnCl_4$, and effectively gave only $BrMe_2Sn[C(SiMe_3)_3]$. Rather unexpectedly, $SnCl_2$ reacted to afford two tin(IV) products, $ClMe_2Sn[C(SiMe_3)_3]$ and Me_2SnCl_2, together with a deep brown solution and an insoluble, presumably polymeric, tin(II) material.[62]

The ammonolysis of $Ph_2(C_6H_{11})_2Pb$ in liquid ammonia in the presence of KNH_2 at 0° results in the formation of $K[Pb(NH_2)_3]$. Triphenylbenzyllead reacts differently at -35° to give $K_2[Pb(NH_2)_6]$. The organic radicals are eliminated as the corresponding hydrocarbon.[63]

4.2.4 Bonds to Halogen

The stoichiometry of the interaction of ClF_3 with elemental silicon (in excess) in a closed reaction vessel varies with the initial applied pressure of ClF_3.[64] At a pressure of 19,500 Pa, the reaction proceeds according to

$$Si + 2ClF_3 \longrightarrow SiF_4 + 2ClF$$

but at 54,300 Pa, the reaction corresponds to the stoichiometry

$$3Si + 4ClF_3 \longrightarrow 3SiF_4 + 2Cl_2.$$

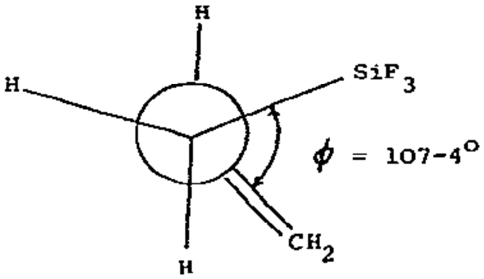
Doncaster and Walsh[65] have studied the system

$$Me_3SiI + HBr \longrightarrow Me_3SiBr + HI$$

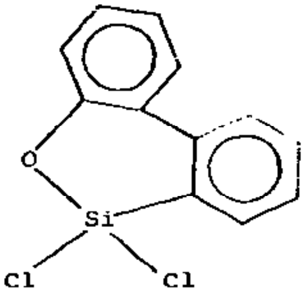
in the temperature range 290-390°. The reaction reaches a steady state and equilibrium is reached. The equilibrium constant at 321° was determined as 12.2±2.4. From the literature value of $\Delta H_f^{\circ}(Me_3SiBr($, a value of -218 ± 4 kJ mol^{-1} was derived for $\Delta H_f^{\circ}{}_{298.2}(Me_3SiI(g))$, and, from an estimated value for $\Delta H_f^{\circ}(Me_3Si\cdot)$, the bond dissociation energy, $D(Me_3Si-I)$, was determined to be approximately 322 kJ $mole^{-1}$.

Kriegsman *et al.*[66] have discussed intramolecular interactions in the trimethyl-Group IV fluorides, Me_3MF (M = C, Si, Ge, Sn), $RC_6H_4(Me)_2SiF$ and $RC_6H_4O(Me)_2SiF$, whilst Dernova *et al.*[67] have made a detailed study of the Raman soectra of the dimethyl-Group IV dibromides, Me_2MBr_2 (M = C, Si, Ge, Sn).

Electron diffraction has shown that allyltrifluorosilane has a conformation (<u>21</u>) intermediate between <u>cis</u>-<u>gauche</u> and <u>trans</u>-<u>gauche</u> in the gas phase.[68]

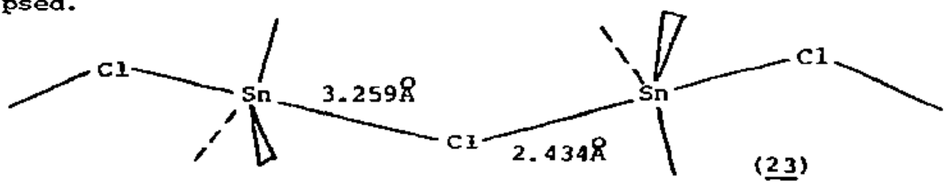


(<u>21</u>)



(<u>22</u>)

Both the orthorhombic and triclinic modifications of 10,10-dichloro-10-sila-9-oxaphenanthrene contain discrete molecules with tetrahedral silicon (<u>22</u>) (Si-C = 1.80, 1.81Å). The almost planar conformation of the silaoxaphenanthrene fragment appears to indicate (p-d)π interactions involving the 3<u>d</u> orbitals of silicon.[69] Crystals of both Ph_3GeBr[70] and Ph_3SnBr[71] contain two crystallographically distinct, but very similar, slightly distorted tetrahedral molecules. The geometry at tin in tricyclohexyltin chloride is also distorted tetrahedral, in spite of the rather large value of the Mossbauer quadrupole splitting (3.49 mm s^{-1}), from which penta coordination at tin was (incorrectly) inferred.[72] Crystals of Me_3SnCl, however, do consist of weakly-intermolecularly coordinated infinite one-dimensional chains with five-coordinated tine (<u>23</u>). The zig-zag chains, which are formed by unsymmetrical chlorine bridging (Sn-Cl = 2.434, 3.259Å), are linear at tin (176.8^o), but bent at chlorine (150.9^o), with the trimethyltin units eclipsed.[73]



(<u>23</u>)

The interaction of phenyl isocyanate with tin(IV) chloride and bromide results in the formation of 1:2 adducts, which possess an octahedral trans-[$SnX_4(PhNCO)_2$] geometry. The reaction of PhNCO with tin(IV) iodide is more complicated, and the solid formed in low yield appears to be a mixture of organic compounds and a tin complex.[74]

Matrix-isolated $M^+SiF_5^-$ ion-pairs have been prepared by reaction of an alkali metal fluoride salt and silicaon(IV) fluoride. Infrared spectra exhibited six bands, three in the silicon-fluorine stretching and three in the deformation regions, observations which are inconsistent with a trigonal bipyramid of D_{3h} symmetry. The data were, however, interpreted by a model in which the cation perturbs the anion axially yielding a C_{3v} species (although C_{2v} and C_{4v} structures were also consistent with the data). Mixed chloride/fluoride anions were also synthesised, but attempts to synthesise $SiCl_5^-$ were not successful.[75] An additional line (at d = 4.07Å), not attributable to crystabolite, occurs in the X-ray powder photographs during the thermal decomposition of K_2SiF_6. The new line was assigned to layers of KF, which act as an active component of the solid in halogen exchange reactions. Crystalline KF is not observed.[76] The novel complex fluorides Rb_3SiF_7, Cs_3SiF_7, Cs_2RbSiF_7, Cs_2KSiF_7, Rb_2CsSiF_7 and Rb_2KSiF_7 have been prepared, and assumed to be isotypic with K_3SiF_7 (space group $P4/_{mbm}$). Raman spectra indicated the presence of [SiF_6]octahedra.[77] The crystal structure of $(MeNH_3)_2SnCl_6$ has been determined by X-ray diffraction at both 298 and 120K, as well as the lattice parameters in the temperature range 113-298K, in order to determine the mechanism of the phase change occurring at 156K. The structure of the high-temperature phase is the same as that determined by Wyckoff except for the discrimination between the carbon and nitrogen atoms. No change in space group nor in the basic structure occurs over the temperature range studied, in spite of strong suggestions from previous ^{35}Cl n.q.r. data. A small but significant anomoly associated with the transition was recognised in the c axis, which retains almost the same length near and below the transition temperature. As a result, the lattice shrinkage below the transition temperature becomes increasingly anisotropic as the temperature is lowered, whereas the thermal expansion above it is relatively isotropic.[78] The structure of K_2SnBr_6 at room temperature has been determined by X-ray diffraction.[79] Sb^{III}-Sb^{V} intervalence transfer excitation is responsible for the intervalence absorption in $Cs_2[Sb^{III}_x\ Sb^{V}_x\ Sn_{1-2x}]Cl_6$. The resonance enhancement in the Raman spectra of the host-Cs_2SnCl_6) reflects the tremendous structural response of the host to inner-sphere ("intramolecular") reorganisations accompanying the Sb^{III}-Sb^{V} electron transfer.[80]

^{31}P chemical-shifts of Ph_3PO complexes of a variety of silicon, germanium and tin compounds recorded in toluene exhibit a downfield shift from the free ligand, interpreted in terms of the formation of adduct complexes in solution. Analysis of the concentration dependency of the chemical shift permitted the determination of the formation constants of the 1:1 complexes (eg. $K(Ph_3PO{:}Me_3SiCl) = 60 \pm 5\ M^{-1}$; $K(Ph_3PO{:}Me_3SnCl) = 100 \pm 5\ M^{-1}$). More complicated spectra for $SiCl_4$-Ph_3PO solutions suggested multiple equilibria in this case.[81] Fujiwara et al.[82] have analysed the concentration dependence of the n.m.r. parameters of the equilibria between Me_2SnCl_2 and 2,2'-bipyridyl or pyridine. With pyridine, both 1:1 and 1:2 complexes coexist, and the equilibrium constants, K_1 and K_2, were determined as ($K_1 = 16.6 \pm 1.9\ dm^3mol^{-1}$, $K_2 = 4.44 \pm 0.24\ dm^3$

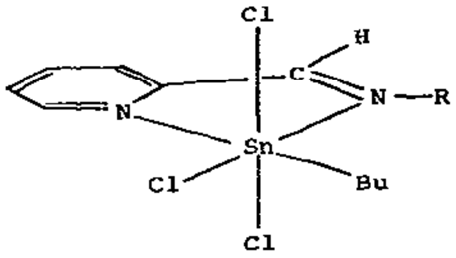
$$Me_2SnCl_2 \ + \ py \xrightleftharpoons{K_1} Me_2SnCl_2{\cdot}py \xrightleftharpoons[py]{K_2} Me_2SnCl_2{\cdot}2py$$

mol^{-1}) using $^2J(Sn\text{-}H)$ data (assuming the value of ^2J for the 1:2 complex to be that of the tin compound in a large excess of pyridine). The formation constant of the 1:1 complex in the bipyridyl system is $4500 \pm 3200\ dm^2mol^{-1}$ in $CHCl_2CHCl_2$, approximately twice that in MeCN, reflecting the much weaker solvation by the chlorocarbon solvent.

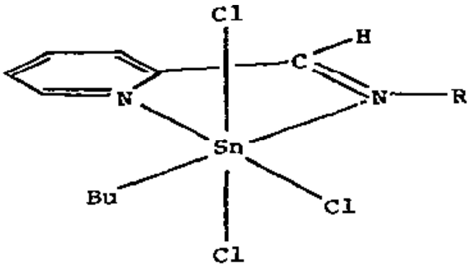
Butyltin trichloride forms six-coordinate adducts with N'-substituted pyridine-2-carbaldimines. When the substituent R on the imine nitrogen is Me, Et or $PhCH_2$, the adduct exists as a mixture of the two isomers (24) and (25), but when R = ^tBu or aryl, only one species exists.

X-ray diffraction studies showed that the complex with R = Ph has structure (24) in the crystal.[83]

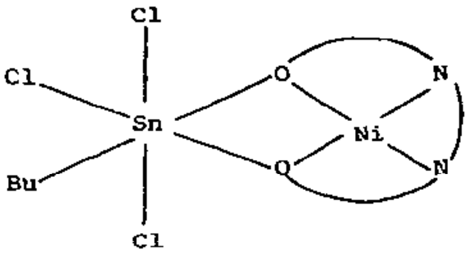
Complexation between $BuSnCl_3$ and nickel(salphen)(28) takes place both in chloroform and acetonitrile, although the products obtained in each case differed in their X-ray powder data, infrared and Mössbauer spectra. Conversion of the chloroform product into the acetonitrile product takes place slowly at room temperature in


Cl
H
C
N
R
Sn
Cl
Bu
Cl

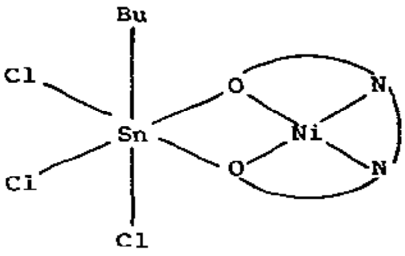
(24)


Cl
H
C
N
N
R
Sn
Bu
Cl
Cl

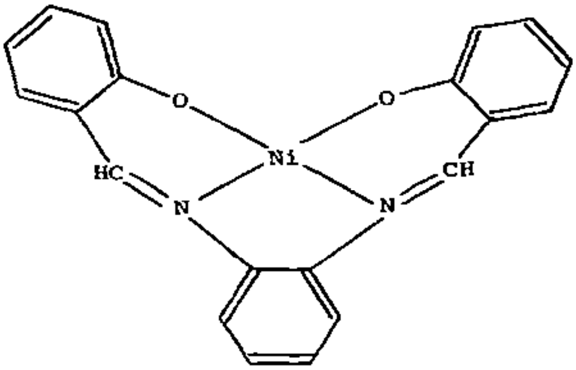
(25)


Cl
Cl
Sn
Bu
Cl
O
N
Ni
O
N

(26)

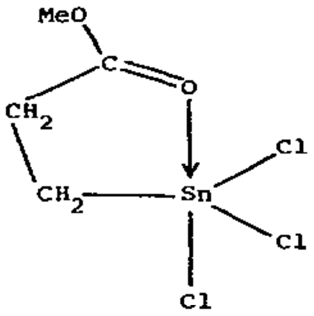

Bu
Cl
Sn
Cl
Cl
O
N
Ni
O
N

(27)


O
O
Ni
HC
CH
N
N

(28)

the solid (partial conversion after six months) but rapidly (complete in 12 hours) when stirred under acetonitrile. The two products were suggested to be the mer and fac isomers.[84] Mössbauer spectra of several diorgano- and dihalogenotin derivatives of the anions of 3,5-diphenyl, 4-methyl, and 1-hydroxy-2-pyrazole N-oxide, 8-hydroxyquinoline N-oxide, 8-quinoline thiol, N,N'-o-phenylenebis(salicylaldimine) and N,N'-o-phenylenebis(pyrroaldimine) have been recorded.[85]



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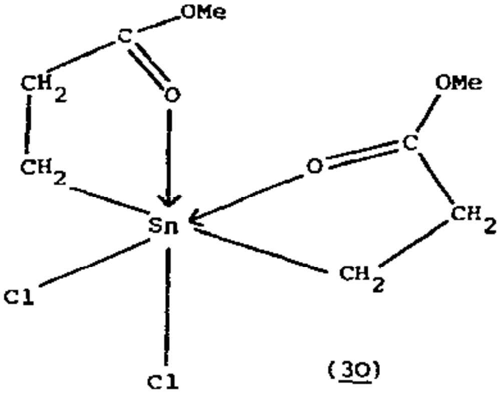

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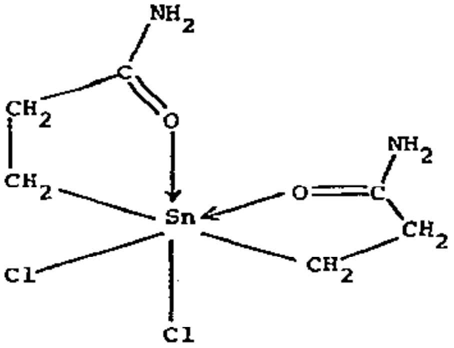

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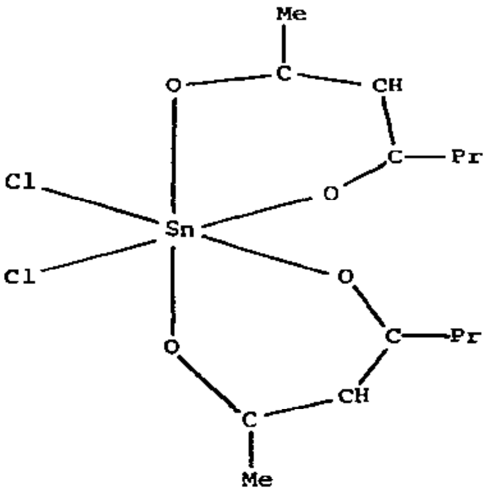


(32)

The structures of three 'estertin' complexes have been determined,

$Cl_3SnCH_2CH_2CO_2Me$ (29), $Cl_2Sn[CH_2CH_2CO_2Me]_2$ (30), and $Cl_2Sn[CH_2CH_2CONH_2]_2$ (31).[86] Intramolecular carbonyl→tin coordination occurs in all three giving rise to discrete molecules in (29) and (30), but in (31) extensive intermolecular hydrogen bonding links adjacent molecules.[86] Like the two latter complexes, dichlorotin bis(ethyl 3-oxobutanoate) has a slightly distorted octahedral geometry with *cis* chlorine atoms (32). The equatorial and axial Sn-O bond distances varied slightly ($Sn-O_{eq}$ = 2.101(15)Å; $Sn-O_{ax}$ = 2.066(15)Å).[87]

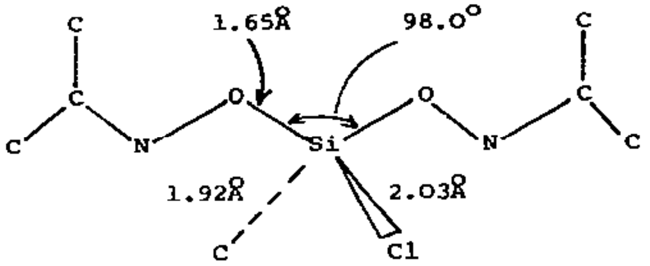
4.2.5 Bonds to Pseudohalogen

Ab initio M.O. calculations for silyl isocyanate, excluding silicon *d* orbitals from the basis set, predict a structure with a Si-N-C bond angle of *ca*. 153°, in good agreement with the most recent experimental estimates, showing that it is quite unnecessary to involve (p-d)π bonding in order to rationalise the geometry of the molecule.[88] The vibrational spectra of the gaseous, liquid and solid germyl and perdeuteriogermyl isocyanates have been recorded and assigned.[89] The rotational fine structure on the GeH_3 modes is believed to be due to the nearly free internal rotation of the germyl group. A normal coordinate analysis utilizing a modified valence force field shows a considerable amount of mixing between the H_3Ge rocking and NCO bending modes. The other normal modes were fairly pure. Me_3SnN_3 and $Me_3SnN_3 \cdot Me_3SnOH$ have been characterised by their physical and chemical properties. Both contain planar Me_3Sn units bridged, in the case of Me_3SnN_3, by azide groups, or, in $Me_3SnN_3 \cdot Me_3SnOH$, by alternately hydroxyl and azide groups. In solution, the azide groups undergo temperature-dependent site exchange.[90]

4.2.6 Bonds to Oxygen

(a) Molecular Compounds

Probably the most interesting report is concerned with bis(*o*-phenyldioxy)silicon(IV). The reaction of $SiCl_4$ with catechol affords polymeric $(C_6H_4O_2)_2Si$, but depolymerisation takes place on the transition to the gas phase, from which condenses a clear, colourless crystalline monomeric modification which is very moisture sensitive. The structure of this latter modification was not determined directly, but inferred from the space group, $P2_{1/c}$ with $\mathrm{Z} = 2$. Hence, if there are two silicon atoms in the unit cell, they must be located on the special, centrosymmetric equivalent positions, the inference from which is that the molecules of monomeric $(C_6H_4O_2)_2Si$ must be planar, is as expected tetrahedral though slightly distorted. M.O. calculations show that for the silicon compound there is only a slight preference for a tetrahedral geometry (6.4 kcal mol^{-1}) over the planar configuration, whilst for the carbon analogue there is a considerable energy difference.[91,92] The structures of several of the silicon-oxygen compounds have been investigated. That of trimethylsilylvinylether has been determined by electron diffraction,[93] whilst the vibrational spectra and rotational isomerism in methylsilylmethylether have been examined.[94] The structure of bis(acetoximato)-methylchlorosilane (33) has been determined by X-ray diffraction.[95] The monoclinic form of cyclo-$(Ph_2SiO)_4$ has an unusually flat eight-membered ring, possibly due to intramolecular crowding. The ring conformation is best described as a shallow, distorted boat. Two determinations of the structure of octa(phenylsilasesquioxane), $(PhSiO_{1.5})_8$, have appeared.[97,98] The cage molecule (34) has four-fold crystal symmetry, and is formed by linking six eight-membered rings. cis-1,1,7,7,9,9,15,15-Octamethyl-3,5,11,13-tetraphenyl-tricyclodecasiloxane is a representative of the class of poly-siloxanes with a cyclic-linear structure. The structural determination confirmed the cis-connection of the tetrasiloxane rings (35), and also showed the presence of conformational disorder in the lateral tetrasiloxane rings leading to the existence of two conformers in the crystal.[99] The isomer of 1,1,7,7-tetramethyl-3,5,9,11-tetraphenyl-tricyclohexasiloxane with melting point 162.5° has a similar cis structure (36), in which the lateral trisiloxane rings are bent away from the central tetrasiloxane ring by 118°. Steric hindrance in the molecule leads to appreciable deformation of its cyclic fragments compared with the corresponding monocyclic compounds.[100] The silaazaoxane ring in 2,2,4,4-tetraphenyl-8,8,10,10-tetramethyl-spiro[5.5]-2,4,6,8,10-penta-sila-7,11-diaza-1,3,5,9-tetraoxane (37) is non-planar with a slightly distorted boat conformation. The siloxane ring is more planar, but the presence of the spiro unit does not lead to a decrease in the endocyclic bond lengths in contrast to other spirosiloxanes.[101] The structure of N,N'-bis(2,2,4,4,6-pentamethyl-cyclotrisiloxanyl-oxadimethylsilyl)tetramethylcyclodisilazane (38) has also been determined.[102]



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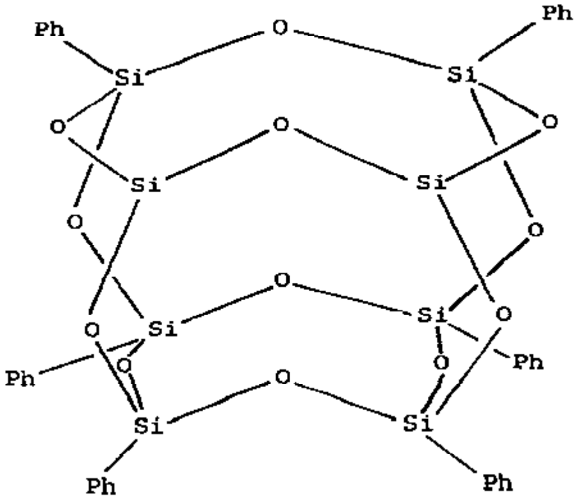

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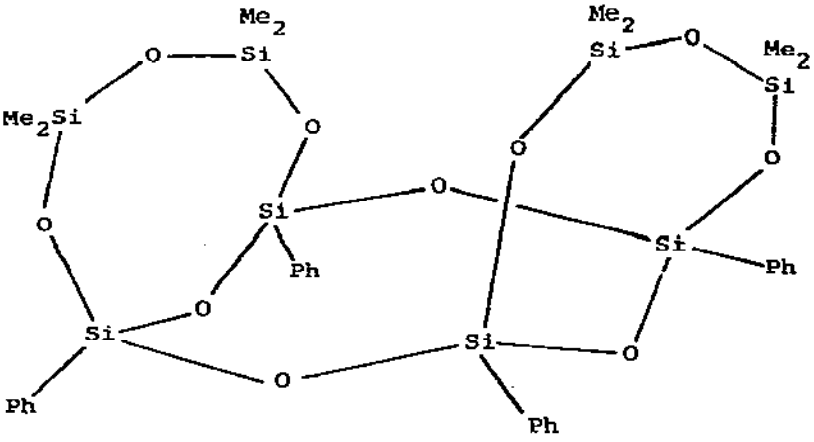
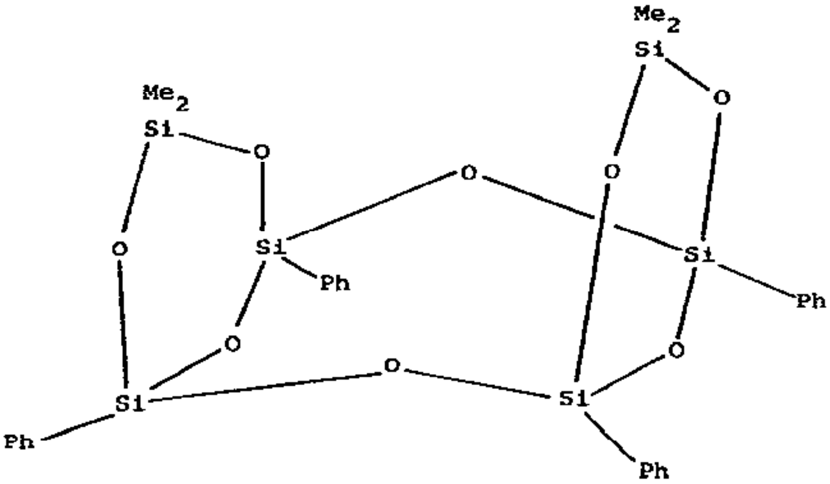
(35)





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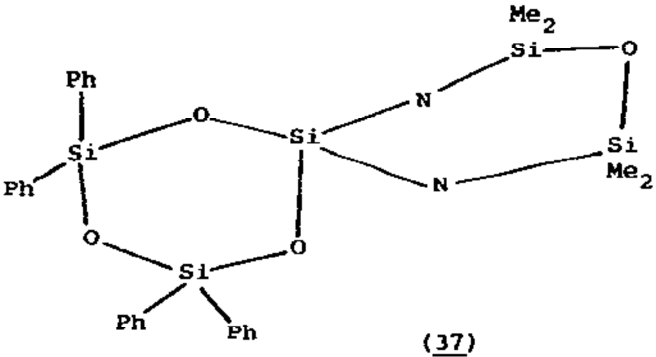

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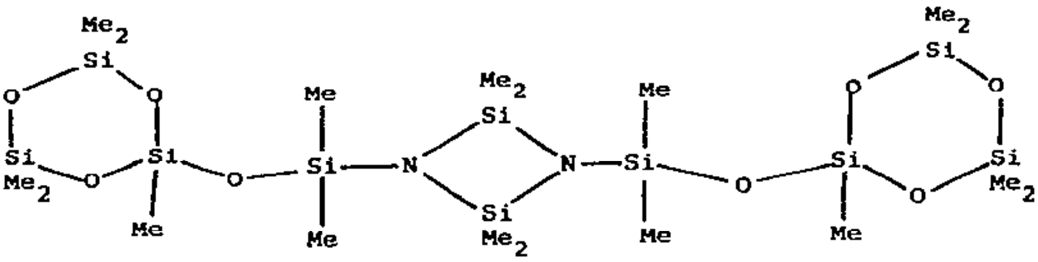


(38)

Hexamethyldisiloxane reacts with $TiCl_4$ with cleavage of the Si-O bonds and the formation of Me_3SiCl and polymeric $[Me_3SiO(Cl)TiO]_n$, whilst with $SnCl_4$ the major product is Me_3SnCl. Hexamethyldisilthiane reacts differently, forming the monomeric complexes $TiCl_2S.2L$ (L = MeCN) and $TiCl_2S.3L$ (L = MeCN or thf) following solvation of the polymeric $[Cl_2TiS]_n$ formed initially. The corresponding tin compound $(Cl_2SnS)_n$ formed with $SnCl_4$ does not give similar lattice degradation with strong donors. The lower halides $MCl_3.3thf$ (M = Ti, V or Cr) do not react with $Me_3SiOSiMe_3$, but with $Me_3SiSSiMe_3$ yield Me_3SiCl and the polymeric complexes MCl(S).nthf (M = Ti or Cr) and $VClS_4$.[103] Tris(silyl)borate has been prepared by the reaction of tris(tributylstannyl)borate and silylbromide:

$$(Bu_3Sn)_2O \;+\; H_3BO_3 \xrightarrow{(i)} (Bu_3SnO)_3B \xrightarrow{(ii)} (H_3SiO)_3B$$

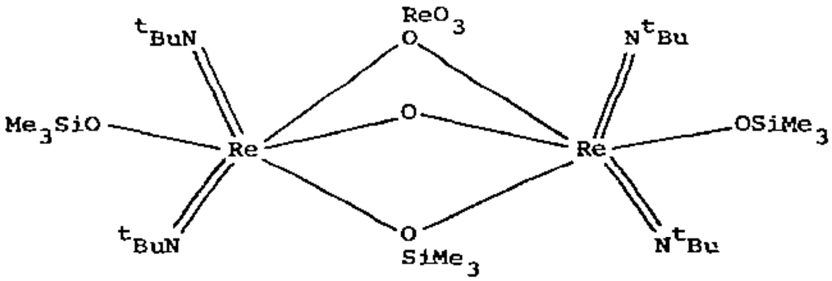
(i) boiling toluene; (ii) H_3SiBr.

The compound is very sensitive to decomposition in the liquid phase, and decomposition appears to be catalysed by the various possible byproducts of the preparation reaction as well as glassware surfaces. The products are hydrogen, silane and disiloxane.[104]

The reaction of trimethylsilylperrhenate with Me_3SiNH^tBu in hexane at 25° affords yellow needles of $Me_3SiORe(N^tBu)_3$, which oxidises trimethylphosphine to the oxide (toluene, 80°) and gradually precipitates $(Bu_4N)(ReO_4)$ on treatment with aqueous Bu_4NOH:

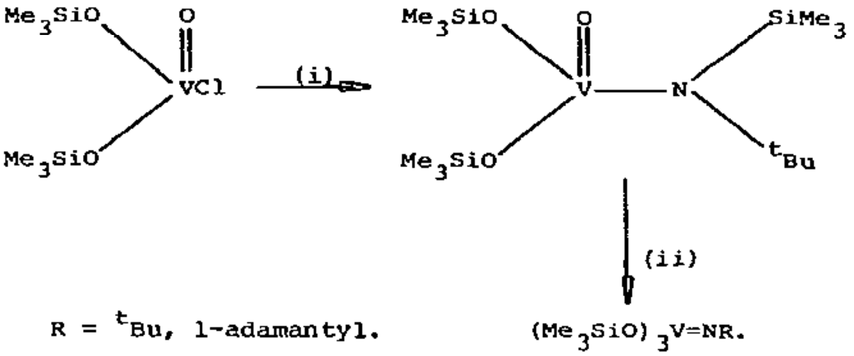
$$Me_3SiOReO_3 \;+\; 3\,{}^tBuNHSiMe_3 \longrightarrow Me_3SiORe(N^tBu)_3 \;+\; Me_3SiOH$$

When an insufficient amount of ${}^tBuNHSiMe_3$ is used in the preparation,



(39)

(<u>39</u>), characterised by X-ray diffraction, is obtained as a yellow, low melting solid.[105] Treatment of $(Me_3SiO)_2V(O)Cl$ with $^tBuNHSiMe_3$ yields (<u>N</u>-alkylimido)tris(trimethylsiloxyl)vanadium derivatives (<u>40</u>) in a reaction which involves a rearrangement:



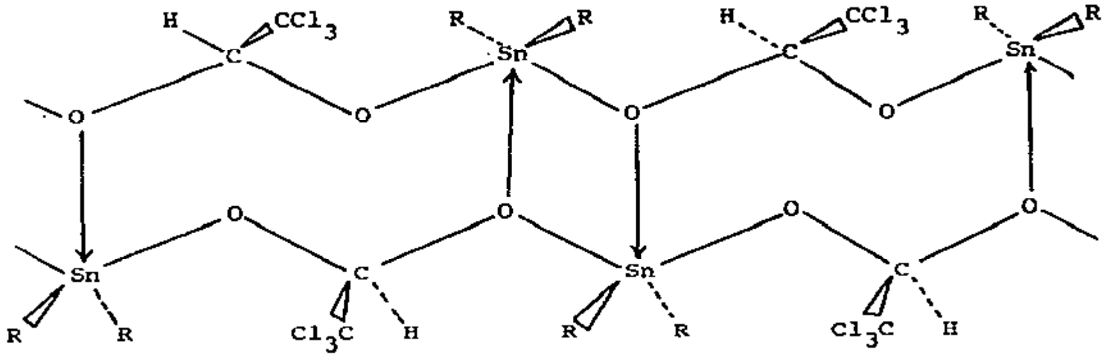
R = ^tBu, 1-adamantyl.

(<u>40</u>)

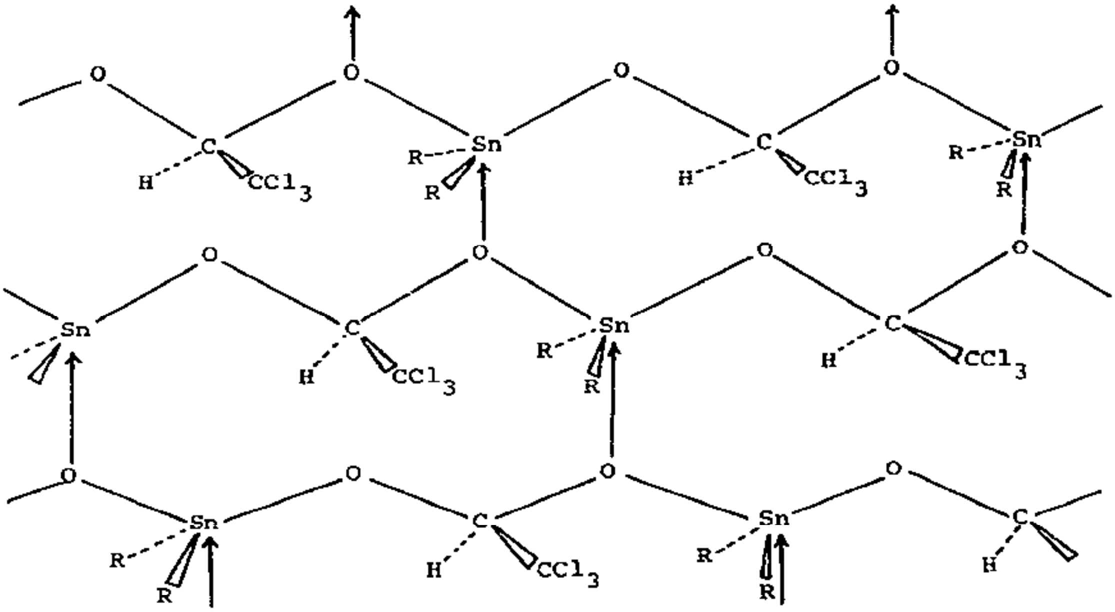
The structure of (<u>40</u>)(R = 1-adamantyl) was determined by X-ray diffraction.[106]

In sharp contrast to $(Ph_3Ge)_2O$ and $(Ph_3Sn)_2O$, in which the bond angles at oxygen are 135.2° and 137.3°, respectively, both $[(PhCH_2)_3Ge]_2O$ and $[(PhCH_2)_3Sn]_2O$ are linear at oxygen. The linearity is crystallographically imposed, and therefore strict, and is interpreted is being due to the low electronegativity of the metal being enhanced by the electron-donating nature of the organic group.[107–109] The reaction of polymeric dialkyltin oxides with chloral yields compounds of elemental formula $[R_2SnOCH(CCl_3)O]$, probably formed by the addition of the Sn-O bond to the carbonyl group. Mössbauer and infrared data suggest polymeric structures such as (<u>41</u>) or (<u>42</u>), with trigonal-bipyramidally coordinated tin atoms and bent CSnC linkages, in the solid-state. In benzene, trimers or tetramers appear to be present.[110]

The crystal structure of trivinyltin trichloroacetate consist of trivinyltin units linked together by <u>syn</u>-<u>anti</u> trichloroacetate bridges, giving five-coordinated tin. A comparison with the data for Me_3SnO_2CMe, $Me_3SnO_2CCF_3$, and $(PhCH_2)_3SnO_2CMe$ shows that distortions in $[SnC_3]$ group and the asymmetry of the two Sn-O distances are in the order $PhCH_2$>vinyl>Me. Mössbauer spectra of the two series of compounds $vinyl_3SnO_2CR'$ and $Buvinyl_2SnO_2CR'$



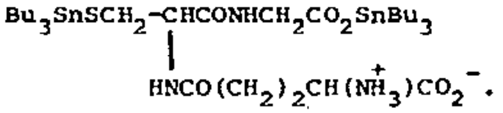
(41)



(42)

(R' = Me, CH_2Br, CH_2Cl, $CHCl_2$, CCl_3 and CF_3) have also been recorded.[111] Tin is also five-coordinated in trimethyltin 2-pyridylcarboxylate monohydrate, which has a structure very similar to those determined previously for $Me_3SnNO_3.H_2O$ and $Me_3SnO_3SPh.H_2O$, with a planar Me_3Sn group and inidentate carboxylate and water occupying the axial sites. The crystal structure, however, differs from the other two in possessing a complex three-dimensional, rather than a one-dimensional network of hydrogen-bonds involving the pyridyl nitrogen and carbonyl oxygen atoms and the water molecule.[112]

Domazetis, Magee and James[113,114] have published further data concerning organotin derivatives of amino acids. Bis(triphenyltin)-oxide reacts with L-cysteine at 70° in water/ethanol as solvent, but after recrystallisation only $(Ph_3Sn)_2S$ was recovered. With L-cysteine ethyl ester hydrochloride at pH 8-11, a product containing Ph_3SnCl, $Ph_3SnSCH_2CH_2(NH_2)CO_2Et$ and $(Ph_3Sn)_2S$ was obtained. $Me_3SnSCH_2CH_2(NH_2)CO_2Et$, together with small amounts of $(Me_3Sn)_2S$, was isolated from the reaction of Me_3SnCl and L-cysteine ethyl ester hydrochloride at pH 9, but decomposes on standing evolving a very pungent odour of NH_3 and H_2S. Under similar conditions, $(Bu_3Sn)_2O$ reacts yielding $Bu_3SnSCH_2CH_2(NH_2)CO_2Et$, which also decomposes, but more slowly. Both Me_3SnCl and $(Bu_3Sn)_2O$ form stable complexes with N-acetyl L-cysteine, whilst $(Bu_3Sn)_2O$ also reacts with glutathione reduced under mild conditions to afford a product which corresponds to



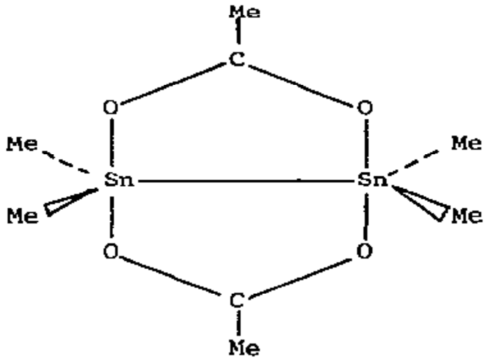
$$\begin{array}{l} Bu_3SnSCH_2-\underset{|}{C}HCONHCH_2CO_2SnBu_3 \\ \qquad\qquad HNCO(CH_2)_2CH(\overset{+}{N}H_3)CO_2^{-}. \end{array}$$

Tributyltin derivatives of α-glutamylcysteinyl glycine were also prepared.

The vibrational spectra of several diorganotin bis(picolinates) have been examined and largely assigned. The materials appeared to be associated in the solid state.[115] All four acetate groups chelate tin in tin(IV) acetate giving a distorted dodecahedral geometry. The Sn-O distances vary (2.13 - 2.29Å, mean 2.22Å) because of steric crowding (cf. $Sn(NO_3)_4$ in which the Sn-O bonds are shorter 2.141 - 2.198Å, mean 2.163Å).[116] The e.p.r. spectra of γ-irradiated germanium(IV), tin(IV), and lead(IV) tetraacetates at 100K are characterised by large hyperfine interactions of the unpaired electron with the Group IV magnetic nuclei (^{73}Ge, $^{117,119}Sn$, ^{207}Pb). In the germanium and tin species, the unpaired electron resides almost entirely in the valence s and p orbitals of the metal atom. In the case of the lead radical, the SOMO again possesses large Pb(6s) character, but negligible 6p character.

The species present were best described as metal tetraacetate radical anions, $M(OAc)_4^{\bar{\cdot}}$, although in the case of lead the species $\cdot Pb(OAc)_3$ also fits the experimental data.[117]

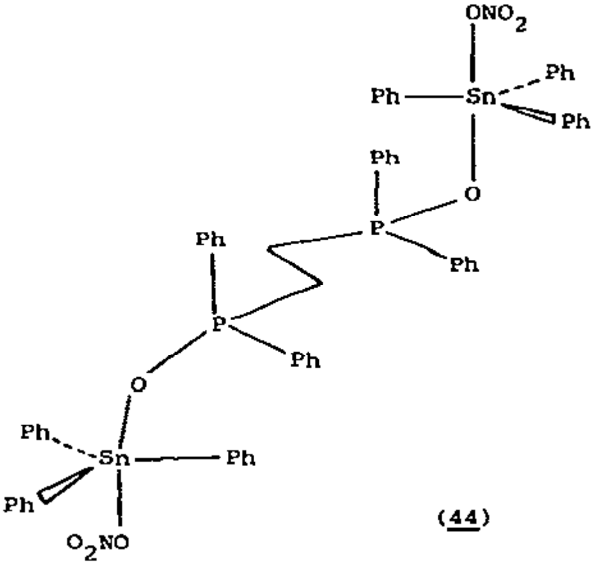
Bis(μ-trifluoroacetato)bis(dimethyltin), $Me_4Sn_2(O_2CCF_3)_2$, is isostructural with $Me_4Sn_2(O_2CCH_2Cl)_2$ with crystallographic 2/m symmetry (43) [Sn-Sn = 2.707(1)Å, Sn-O = 2.319(5), 2.345(4)Å; Sn-C = 2.10(1)Å]. The fluorine atoms are disordered. The molecule possesses almost mmm symmetry; deviations from this being entirely attributable to weak intermolecular C-H···O interactions.[118]



(43)

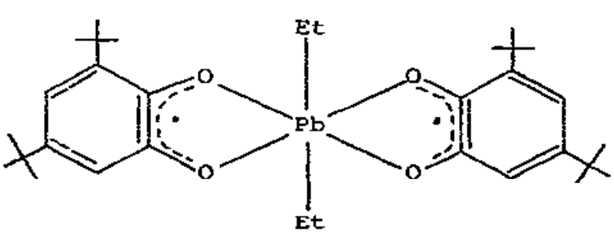
Complexation of triphenyltin nitrate by bis(diphenylphosphino)-ethane results in the formation of a complex of the corresponding phosphine oxide, $\{Ph_3Sn(NO_3)\}_2\{OPPh_2(CH_2)_2Ph_2PO\}$. The adduct has trigonal bipyramidal coordination at tin with the three phenyl groups occupying the equatorial sites, while the unidentate nitrate and the phosphine oxide ligand, which acts as a bridging group between adjacent tin atoms, are mutually trans in the apical sites (44).[119]

Vapour phase He(I) and He(II) excited photoelectron spectra of dichloro- and dimethylbis(pentane-2,4-dianato)tin(IV) have been recorded. The spectra indicate pronounced changes in the bonding depending on the stereochemical conformation of each complex. Natable also is the variation in band intensity patterns going from He(I) to He(II) excitation.[120] Several new addition complexes of organtin halides and Schiff bases of the types $RSnCl_3.2HOC_6H_4CMe{=}NR'$ and $R_2SnCl_2.2HOC_6H_4CMe{=}NR'$ have been synthesised and characterised by molar conductances, infrared and

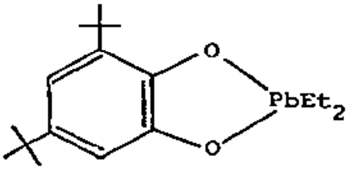


(44)

and Mössbauer.[121] Majima and Kawasaki[122] have investigated the mechanism of the spin-spin coupling dimethyllead(IV) complexes with ONNO quadridentate Schiff base ligands. Both $^3J(^{207}Pb\text{-}N{=}CH)$ and $^2J(^{207}Pb\text{-}CH_3)$, recorded in various solvents, increase with increase in the donor strength of the solvent. The mean excitation energy, the ΔE term in the Fermi contact term, plays a diminishing role for the lead-proton coupling constants. The two proton methyl signals of N,N'-propylenebis(salicylideneaminato)dimethyllead(IV) are magnetically non-equivalent. The reaction of o-quinones with tetramethyllead in thf affords inter alia polymeric lead pyrocatecholate. However, if pentane or hexane is employed as the solvent, the air-stable bis(semiquinolate) complex (45) can be isolated as blue-green crystals. The compound may also be prepared by the reaction of (46) with orthoquinone. Heating benzene solutions of (45) in an evacuated ampoule at 100° for 10 - 15 minutes results in the formation of lead(II) (3,5-di-t-butylpyrocatecholate).[123]



(45)



(46)

(b) Oxides

The effect of pressure on the structure of α-quartz has been studied. The a lattice constant decreases from 4.921(1)Å (at 10^8Pa) to 4.664(2)Å (73 x 10^8Pa) whilst c varies from 5.400(4)Å (at 10^8Pa) to 5.246(3)Å (at 73 x 10^8Pa), giving a c/a ratio change from 1.097 (at 10^8Pa) to 1.125 (at 73 x 10^8Pa). The resulting volume change in this pressure range is ca. 13% (in agreement with elasticity constant data determined by ultrasonic measurements). The effect on the SiO_4 tetrahedra is very small upto 68 x 10^8Pa, and the Si-O bond distance and OSiO bond angle remain constant. The SiOSi bond angle, however, decreases from 142° (at 10^8Pa) to 132° (at 68 x 10^8Pa), and the cross-section of the channels in the structure parallel to the c axis becomes smaller.[124] Hill and Gibbs[125] have assessed the variations in bond data for silica and silicate minerals.

The strontium hydrogen silicates which are precipitated on the addition of sodium silicate solutions to solutions of strontium hydroxide at room temperature are always amorphous and contain silicate anions in various degrees of condensation. Amorphous products are also obtained initially at 100°, but on stnading under the mother liquor at 80° the materials crystallise as the higher anions degrade to monomeric and dimeric anions of compositions such as $1.25SrO.SiO.2H_2O$, $3SrO.2SiO.3H_2O$ and $3SrO.2SiO_2.4H_2O$ (monomeric anions) and $2SrO.2SiO_2.nH_2O$ (n = 1.5, 2, 3)(dimeric anions).[126] The kinetics of formation and transformation of alkyl-derived $SrSiO_3$[127] and β-$CaSiO_3$ (Wollastonite)[128] have been studied. In the former case the crystallisation isotherms are best described by a first-order equation giving an activation energy of 130 kcal mol^{-1}, whilst the

Avrami equation:

$$\ln(1 - \alpha) = -kt^n$$

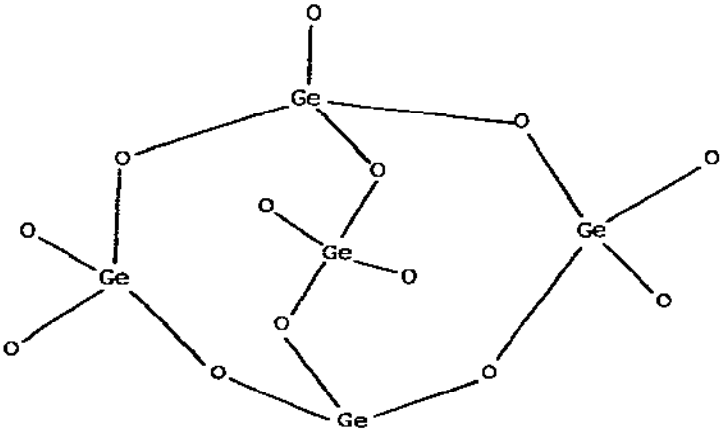
with $n = 3$, giving an activation energy of 284.5 kJ mol^{-1}, describe crystallisation isotherms in the latter system. The kinetics of transformation of α- into β-$CaSiO_3$ are best interpreted by the 'contracting-cube' equation:

$$1-(1 - \alpha)^{1/3} = kt$$

from which the activation energy value 983.2 kJ mol^{-1} was determined. The equilibrium solid phases of the Li_2O-SiO_2-H_2O system at 200° are silica gel, $SiO_2.0.2H_2O$, and the hydrated lithium silicates, $Li_2SiO_3.0.2H_2O$ and $Li_2Si_2O_5.2H_2O$.[129] The substructure of ordered Li_4SiO_4 is identical to that previously refined for Li_4SiO_4. The lithium atoms are ordered, and occupy 19 of the 42 sites of the seven-fold supercell. The ordered nature of the structure is consistent with the low ionic conductivity of pure Li_4SiO_4.[130] The structures of β_{II}-$CoLi_2CoSiO_4$[131] and γ_{II}-$ZnLiSiO_4$[132] have also been determined. All contain tetrahedrally coordinated $[SiO_4]$ units. In $Na_3HSiO_4.2H_2O$, $[HSiO_4]^{3-}$ tetrahedra are arranged linearly along the <u>a</u> axis and connected by Si-O···HOSi hydrogen-bonds. These chains are linked to each other by the sodium ions and by hydrogen bonds from the water molecules. The two crystallographically independent water molecules are also chemically different. One forms two hydrogen bonds to link two chains, whereas the second forms only one hydrogen bond to an $[HSiO_4]^{3-}$ tetrahedron, and has a short OH bond.[133] In the silicon diphosphate, SiP_2O_7, the silicon is octahedrally coordinated by oxygen (mean Si-O = 1.766Å).[134] The bismuth containing silicate apatites, $Ca_{3.2}Bi_{6.8}(SiO_4)_6O_{1.4}\square_{0.6}$ and $Sr_{2.8}Bi_{7.2}(SiO_4)_6O\square_{1.4}$ have been prepared.[135] The organic molecules are regularly ordered in the <u>N</u>-methylformamide intercalate of Dickite ($Al_2Si_2O_5(OH)_4$), but no hydrogen bonds from the amide to the $[SiO_4]$ tetrahedra of neighbouring layers are present.[136] Crystals of the manganese(II) arsenatotrisilicate, $Mn_4[AsSi_3O_{12}(OH)]$, contain the $[AsSi_3O_{12}(OH)]^{8-}$ anions, the conformation of which resembles that of a tetrapolyphosphate, and can be considered to be an extension of the trisilicate $[Si_3O_{10}]^{8-}$ anion.[137] The topology of the framework of the zeolite Amicite, $K_4Na_4[Al_8Si_8O_{32}]\cdot 10H_2O$, is the same as that of garranite, gismondite and synthetic zeolite P. The structure can be described as being formed by two untwisted "double-crankshaft" chains developed in two perpendicular directions.[138] Single-crystal electronic and e.p.r. spectra of $CaCuSi_4O_{10}$, a synthetic silicate containing Cu(II) in a four-coordinate planar environment, have been discussed.[139] The reaction of Ag_2O and low-temperature quartz under oxygen pressure leads to the formation of triclinic $Ag_{10}Si_4O_{13}$ which contains the linear $Si_4O_{13}{}^{10-}$ anion.[140] 1,1-Diphenylethylene and 9,10-dihydroanthracene react smoothly over a synthetic hectorite catalyst to give diphenylethane and anthracene.[141]

The condensation reactions of mono-, di- and trisilicic acids, obtained by the hydrolysis of $Si(OMe)_4$, $(MeO)_3SiOSi(OMe)_3$ and $(MeO)_3SiOSi(OMe)_2OSi(OMe)_3$, respectively, have been quantitatively investigated in acidic aqueous solution. Monosilicic acid reacts via a mixture of di-, tri-, tetra-, cyclotetra- and bicyclohexasilicic acids to higher polymer products. In solutions of di- and trisilicic acids, partial hydrolysis to mono- and di-silicic acids occurs simultaneously with the condensation reactions. In all solutions, no condensation products of uniform structure or molecular weight could be observed, but always mixtures of silicic acids with a wide molecular weight distribution.[142] Trimethylsilylation of tetramethylammonium silicate yields a compound of composition $Si_8O_{11}(OSiMe_3)_{10}$, which ^{29}Si and ^{13}C n.m.r. studies have shown to have a structure related to a double four-membered cage in which one Si-O-Si bridge is replaced by trimethylsiloxy units.[143] Partial trimethylsilyl derivatives have been prepared from the hemimorphite $Zn_4Si_2O_7(OH)_2.H_2O$ by direct trimethylsilylation and analysed by means of combined gas-liquid partition chromatography-mass spectrometry. Silanol groups of the hemimorphite not silylated are esterified by the alcohol solvent.[144] A direct method of trimethylsilylation developed previously has been applied to a glass of composition $3PbO\text{-}PbF_2\text{-}SiO_2$. The major products are the trimethylsilyl derivatives of $[SiO_4]^{4-}$, $[Si_2O_7]^{6-}$ and $[Si_3O_{10}]^{8-}$ together with smaller amounts of the trimethylsilyl derivatives $[FSiO_3]^{3-}$, $[Si_2FO_6]^{5-}$, $[Si_3FO_9]^{7-}$ and $[Si_4FO_{11}]^{7-}$. Trimethylsilyl derivatives of higher silicate and monofluorosilicate ions, and of ions containing more than one fluorine, have also been detected, and provide direct evidence for the presence of Si-F bonds in glasses of this type.[145]

Two studies of the phase equilibria in the PbO-$PbGeO_3$ system have been reported.[146,147] The new stable phases, Pb_5GeO_7 and $Pb_{11}Ge_3O_{17}$, have been found. The former phase melts incongruently at 738° to give PbO and liquid, whereas $Pb_{11}Ge_3O_{17}$ decomposes into Pb_5GeO_7 and Pb_3GeO_5 at 728°. The compounds $PbGeO_3$, $Pb_3Ge_2O_7$, Pb_3GeO_5 and $Pb_5Ge_3O_{11}$ also exist and melt congruently at 810°, 738°, 745° and 743°. Other previously reported phases such as Pb_6GeO_8, Pb_4GeO_6 and $Pb_3Ge_2O_7$ could not be confirmed as stable phases, although one report claimed that $Pb_3Ge_2O_7$ is stable in the narrow temperature range 710 – 725°. The structures of two of the phases, $PbGeO_3$[148] and Pb_5GeO_7,[149] have been determined. A neutron diffraction study of the former shows that crystals comprise infinite chains of diortho-Ge_2O_7 groups, elongated along the $[\bar{1}\bar{1}\bar{1}]$ direction of the unit cell (Pb-O = 2.259 – 2.582Å; Ge-O = 1.681 – 1.776Å). The material is isostructural with the mineral alamosite, $PbSiO_3$. In Pb_5GeO_7, each lead is bonded to four oxygens to form a distorted tetragonal pyramid with the lead at the apex. These $[PbO_4]$ pyramids are connected by common corners and/or edges to form layers which are connected by isolated $[GeO_4]$ groups. Dieurpoium(III) germanate oxide, $Eu_2(GeO_4)O$ (prepared by melting a presintered mix of Eu_2O_3 and GeO_2 in an image furnace using a



(47)

tungsten halogen lamp as a heat source) also contains $[GeO_4]$ tetrahedra.[150] The phase $BaO.GeO_2.5H_2O$ can be formulated structurally as $Ba_2[Ge(OH)_6][GeO_2(OH)_2]6H_2O$, and can be interpreted as an averaged structure of a family of OD structures consisting of two kinds of alternating layers. That containing isolated $[GeO_2(OH)_2]$ tetrahedra randomly occupies one of two possible positions. In the other layer, the germanium is octahedrally coordinated by oxygen.[151] The structure of $Tl_8Ge_5O_{14}$ is composed of isolated $[Ge_5O_{14}]^{8-}$ anions (47) formed by five $[GeO_4]$ tetrahedra linked by shared oxygen atoms.[152] A more accurate remeasurement of $Bi_{12}GeO_{20}$ has been carried out.[153] In

Infrared and Raman studies of the phases M_4SnO_4 (M = Na, K) and Na_4PbO_4 show them to comprise tetrahedral XO_4 groups. Force constant calculations for K_4SnO_4 indicate covalent character for the Sn-O bond.[154] The crystal structure of Li_8PbO_6 is similar to that of Li_8SnO_6 and has the hexagonal Li_8TbO_6 structure.[155] The formation and thermal transformation of polymeric potassium lead phosphates in the system KPO_3-$Pb(PO_3)_2$ have been studied.[156] The polyphosphate $[K_2Pb(PO_3)_4]_2$ and the cyclotriphosphate $[K_4Pb(P_3O_9)]_2$ exist in the system, and are stable at their melting points. The water in hydrated lead trimetaphosphate exhibits a high diffusion mobility ($E_{act} \sim 7$ kcal.mol^{-1}), and its presence stabilises the salt to some extent. Its removal is accompanied by a sudden compaction of the material, and the approach of the structural elements in the crystal facilitates hydrolysis by the water of crystallisation with the formation, predominantly, of the ortho and pyro forms.[157] The hitherto unknown lead silver phosphate $Pb_8Ag_2(PO_4)_6$ has the apatite structure with unoccupied halide positions. At 800° it decomposes to $Pb_3(PO_4)_2$ and $PbAgPO_4$.[158] The reaction of PbO, PbO_2, $PbCO_3$ or $Pb(OAc)_2.3H_2O$ with Sb_2O_3 in a 2:1 molar ratio at 700° yields $PbSb_2O_6$ and a cubic pyrochlore of composition $Pb^{II}_2\,Pb^{IV}_{0.5}Sb^{V}\,O_{6.75}$.[159] After heating at 900°, rhombohedral $Pb_2Sb_2O_7$ is found. The infrared spectra of the phases $4PbO.V_2O_5$ and $8PbO.V_2O_5$ resemble that of lead(II) orthovanadate, and show the presence of tetrahedrally coordinated vanadium.[160] The oxide chromate, $PbO.PbCrO_4$, is precipitated in almost quantitative yield from the $Pb(OAc)_2$-Na_2CrO_4-NaOH-H_2O system.[161] The new lead chromates, isostructural with the known $K_2Pb(CrO_4)_2$, $K_4Pb_4(CrO_4)_6$ and $(NH_4)_4Pb_4(CrO_4)_6$ as well as the solid solutions $(K,NH\ )_{6-2\delta}Pb_{3+\delta}(CrO_4)_6$ ($\delta = 0.3 - 1.2$) have been obtained.[162] In orthorhombic $PbPdO_2$, the palladium atoms enjoy square-planar coordination, whilst the lead atom is at the apex of a square-pyramid)Pb-O = 2.32Å).[163]

4.2.7 Bonds to Sulphur, Selenium and Tellurium

(a) Molecular Compounds.

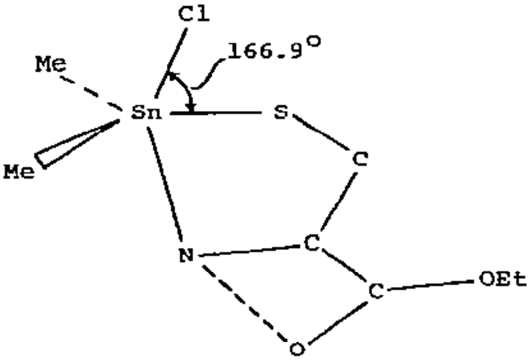
Diodosilane, H_2SiI_2, reacts with mercury(II) sulphide in benzene at 80° to afford primarily oligomeric $(H_2SiS)_y$, which can be depolymerised *in vacuo* at 210° to *cyclo*-trisithiane, $(H_2SiS)_3$. Similarly, the iodosilanes, $H_{4-n}SiI_n$ (n = 1 - 4), react with mercury(II) bis(trifluoromethylsulphide) and bis(trifluoromethylselenide) in hydrocarbon solvents to yield the corresponding silyl derivatives:

$$H_{4-n}SiI_n + n/2\ Hg(XCF_3)_2 \longrightarrow H_{4-n}Si(XCF_3)_n$$

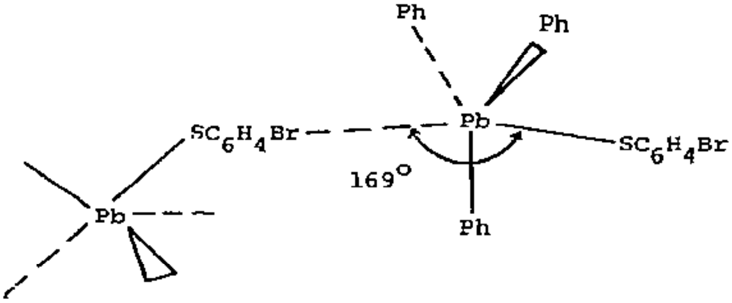
X = S, Se.

In the presence of Al_2S_3, the bis(trifluoromethyl and -seleno)-silane derivatives decompose at 20° to difluorosilane and $F_2C{=}X$ (X = S, Se).[164] The same method has been employed for the synthesis of the germane derivatives, H_3GeECF_3 and $H_2Ge(ECF_3)_2$ (E = S, Se). The latter in particular exhibit unusual thermal stability in comparison with related compounds, as do the digermanyl derivatives, $Ge_2H_5ECF_3$, prepared by the reaction of the mercury(II) salts with Ge_2H_5I *in situ* in ether at -63°.[165]

The structure of ethyl-L-cysteinato-*S*,*N*-(chlorodimethyl)stannate-(IV), $Me_2ClSnCH_2CH(NH_2)CO_2Et$, in which the cysteinato group acts as an *S*,*N*-chelating ligand, has been determined. The tin atom has a distorted trigonal bipyramidal configuration, with the tin lying somewhat out (0.107Å) of the [C,C,S] plane towards the axial chlorine atom (**48**). The Cl-Sn-N bond angle is only 166.9°.[166] Llopiz and Maise[167] have examined the infrared and ESCA spectra of cysteine complexes of germanium, tin and lead (obtained the metal chloride, cysteine and Na_2CO_3 in aqueous media). They concluded that the germanium derivative was bonded via the sulphur and carboxylate groups, the lead via the sulphur and amino residue, whilst all three functions were involved in bonding to tin. The crystal structures of two arylthio-lead derivatives have been published.[168] Crystals of $Ph_3PbSC_6H_3Me_2$-2,6 comprise discrete molecules with tetrahedrally coordinated lead (Pb-C = 2.24(2)Å; Pb-S = 2.512(6)Å), whilst intermolecular interaction between lead and bromine in $Ph_3PbSC_6H_4Br$-2 results in severe distortion to trigonal-bipyramidal geometry (<u>49</u>) (Pb-C = 2.12(5)Å; Pb-S = 2.51(2)Å; Pb····Br = 3.77Å).

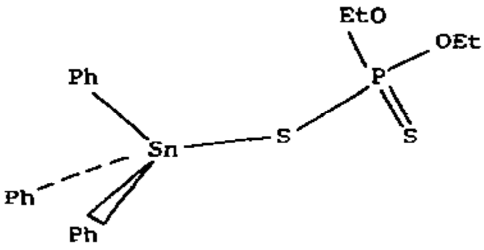


(<u>48</u>)



(<u>49</u>)

Dithiophosphate groups invariably function as chelating or bridging groups, however, in (<u>O</u>,O'-diethyldithiophosphato)triphenyltin, the tin is tetrahedral and the ligand unidentate (<u>50</u>).[169] Several more alkyl- and aryltin dithiocarbamates have been synthesised.[170]



(50)

The structures of both the orthorhombic and monoclinic modifications of $(Ph_3Ge)_2S$ have been determined. The structures differ in the molecular conformation of the Ph_3Ge group around the Ge-S bond.[171] Similarly, the two crystallographically distinct molecules in the monoclinic form of $(Ph_3Sn)_2Se$ differ slightly in conformation, although both have approximate C_2 symmetry.[172] Cyclo-$(Me_2SnTe)_3$ has been synthesised by the reaction of Me_2SnCl_2 and NaHTe in water. The compound crystallises from petroleum ether in the form of yellow needles which are stable for several days at room temperature in the absence of air and light. X-ray diffraction studies at 110K show the presence of both enantiomers of the chiral ring resulting from the two-fold axis through the molecule.[173]

(b) Chalcogenides

A value of $33 kcal\ mol^{-1}$ has been determined for $\Delta H^o(298K)$ for the reaction:[174]

$$Ge + GeS_2 \longrightarrow 2GeS$$

Several thiogermanates and stannates have been synthesised and characterised. Orthorhombic Cu_2SrGeS_4 and Cu_2BaGeS_4 have been obtained by heating stoichiometric amounts of the binary sulphides at 650-750° using molten bromides as solvents. The compounds are isotypic with the corresponding thiostannates(IV).[175] Tetragonal Ag_2BaGeS_4[176] and monoclinic Eu_2GeS_4[177,178] have both been obtained by heating the binary sulphides in evacuated quartz ampoules at >550°. The corresponding europium thiostannate, Eu_2SnS_4, as well as $Eu_3Sn_2S_7$ and $EuSnS_3$, have also been synthesised by heating the appropriate proportions of EuS and SnS_2 at 740-750°.[179] The tin is six-coordinated by two sulphur atoms at 2.576(5)Å and four at 2.575(4)Å in orthorhombic Sm_2SnS_5.[180] The synthetic Rhodostannite, $Cu_2FSn_3S_8$, has a structure similar to that of Fe_2SnS_4, being a disordered spinel structure with tetrahedral sites occupied by Cu^+ ions and the octahedral sites by Sn^{4+} and Fe^{2+} ions in random distribution.[181] Phase equilibria in the Pb-S-Tl system have been studied.[182] Equilibrium diagrams of the Tl_4S_3-PbS, TlS-PbS, Tl_2S-Pb and TlPb-S polythermal sections have been constructed, and the existence of the ternary compound, Tl_4PbS_3 confirmed.

The phase diagram of the Ge-Sn-Se system has been described in detail,[183] and the GaSe-GeTe system equilibrium diagram described.[184] The PbSe-Sm_2Se system is a quasi-binary section of the Pb-Se-Sm system.[185] Two new compounds, Sm_2PbSe_4 and $Sm_2Pb_4Se_7$ were characterised. Similarly, the Ce_2Se_3-PbSe system is a quasi-binary section of the ternary Ce-Pb-Se system in which the two new congruently melting compounds, Ce_2PbSe_4 and $Ce_2Pb_4Se_7$, were detected.[186]

The structure of $Na_3(Al,Si)Te_4$ can be described as a variant of the α-$NaFeO_2$ type. One half of the octahedral sites is occupied by sodium ions, while in the other half of these holes sodium ions and Al-Si dumbbells in a 1:1 ratio are randomly distributed.[187] Both $K_6[Ge_2Te_6]$ and $K_2[Sn_2Te_6]$ comprise discrete X_2Te_6 (X = Ge, Sn) groups with a staggered conformation connected by K atoms (Ge-Ge = 2.492Å; Sn-Sn = 2.814Å; Ge-Te_{av} = 2.579Å; Sn-Te_{av} = 2.724Å).[188]

4.2.8 Bonds to Nitrogen

Tetrakis(trimethylsilyl)tetrazene is formed in almost quantitative yield by the catalytic dimerisation of bis(trimethyl)-diazene with SiF_4. Pyrolysis of the silyltetrazene yields tetrazene, N_4H_4, which reacts with Me_3ENR_2 (E = Ge, Sn) to afford tris(trimethylgermyl)- and tetrakis(trimethylstannyl)-tetrazenes. All three compounds are colourless, crystalline materials possessing the 2-tetrazene geometry with a <u>trans</u> configuration and a planar E_4N_4 skeleton. Thermolysis at temperatures exceeding 100-150° proceeds with evolution of nitrogen to give $(Me_3Si)_2NH$, $(Me_3Ge)_4N_2$, and a mixture of $(Me_3Sn)_3N$ and $(Me_3Sn)_2$. Photolysis of the silyl and germyl derivatives gives $(Me_3E)_3N$ and Me_3EN_3, whereas the tin compound decomposes to $(Me_3Sn)_3N$, $(Me_3Sn)_2$ and nitrogen.[189] The acid-catalysed decomposition of diazene, formed as an intermediate in the reaction of $Me_3Si-N=N-SiMe_3$ with acids, dimerises via tetrazene to finally ammonium azide.[190]

Calculations of the electronic structures of the tris(trimethylmetaila)amines, $(Me_3M)_3N$ (M = C, Si, Ge), by the X_α scattered-wave, SCF method gives a good account of the measured ionisation energies and allows a detailed assessment of the various bond types. Interactions involving d orbitals are most important in the silicon compound, in which the highest occupied ("lone-pair") orbital is stabilised most. Significant $p\pi-p\pi$ bonding is found in deeper orbitals. The planarity of $(SiH_3)_3N$ is ascribed principally to electrostatic, rather than d-orbital, interactions.[191]

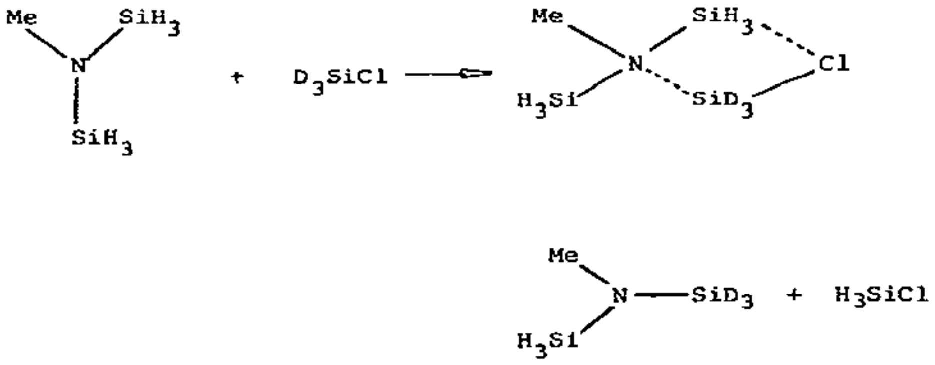
Primary, secondary and tertiary organometallic amines have been synthesised by cleavage of triorganometal halides, or phenyl or vinyl derivative by a Group I metal amide in liquid ammonia:[192]

$$R_3MX \xrightarrow{(i)} R_3MNH_2 \longrightarrow (R_3M)_2NH \longrightarrow (R_3M)_3N$$

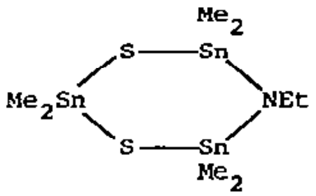
M = Ge, Sn, Pb; M' = Li, Na, K; X = halogen, Ph, vinyl.

(i) $M'NH_2$; liquid NH_3.

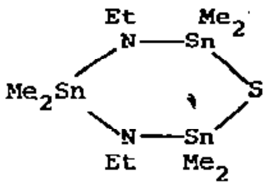
Silyl group exchange between chlorosilane and N-methyl-disilazane is complete within ten minutes at ambient temperature. The favoured mechanism involved a four-centred transition state:[193]



^{119}Sn F.T. n.m.r. has been applied in the study of the exchange between $(Me_2SnS)_3$ and $(Me_2SnNEt)_3$. Both types of mixed-ring compound, (52) and (53), were observed in addition to the two symmetrical compounds.[194]



(52)

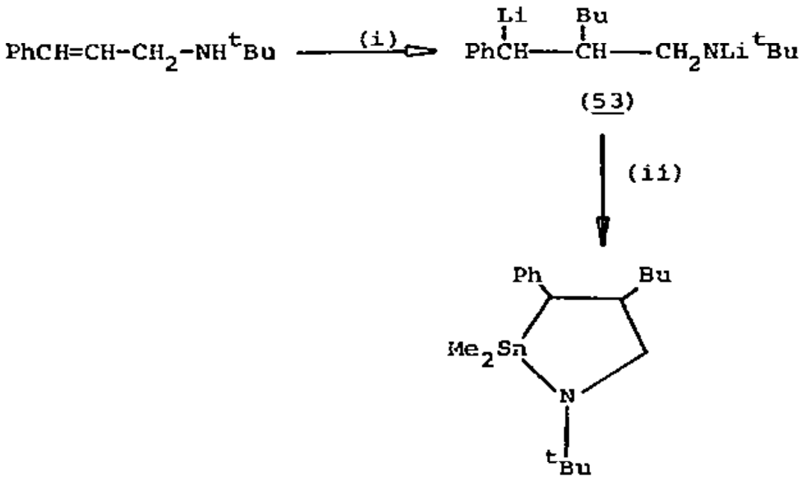


(53)

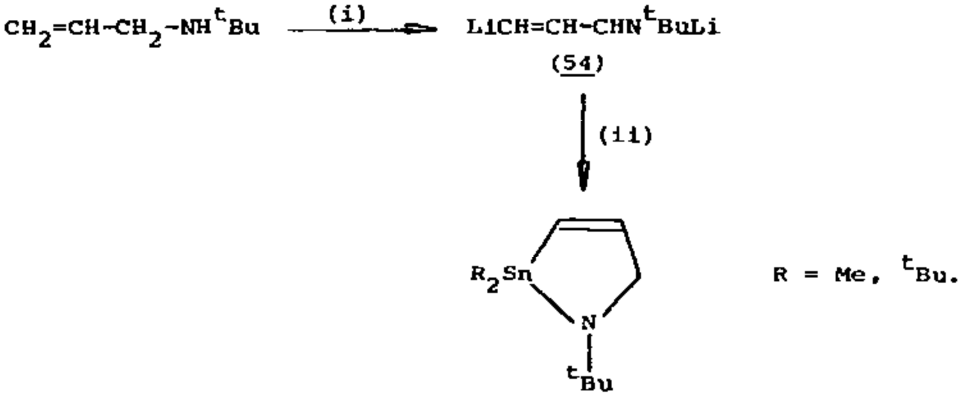
Tin-nitrogen bond cleavage according to the reaction

$$(Me_3Sn)_3N \ + \ 3BCl_3 \longrightarrow N(BCl_2)_3 \ + \ 3Me_3SnCl$$

predominates when the reaction is carried out at low temperatures. Methylation of BCl_3 or $N(BCl_2)_3$ only occurs at high temperatures, and the use of an excess of BCl_3 prevents methylation of $N(BCl_2)_3$. Bis(stannyl)amines, $RN(SnMe_3)_2$ ($R = SiCl_3$, $SiCl_2Me$, $SiClMe_2$ and $SiMe_3$) react analogously.[195] Dilithio compounds such as (54) and (55), derived from the reaction of butyllithium to the alkene in the presence of TMEDA, react with dialkyltin dichlorides to afford 1,2-azastannolines and -stannolidine:[196]

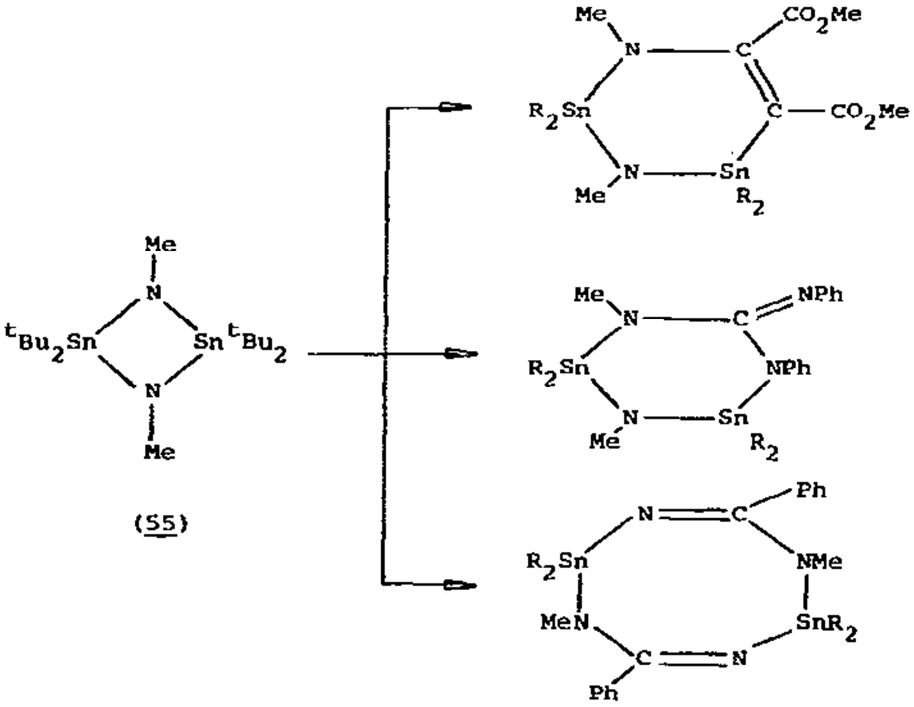


(i) BuLi; (ii) Me_2SnCl_2.



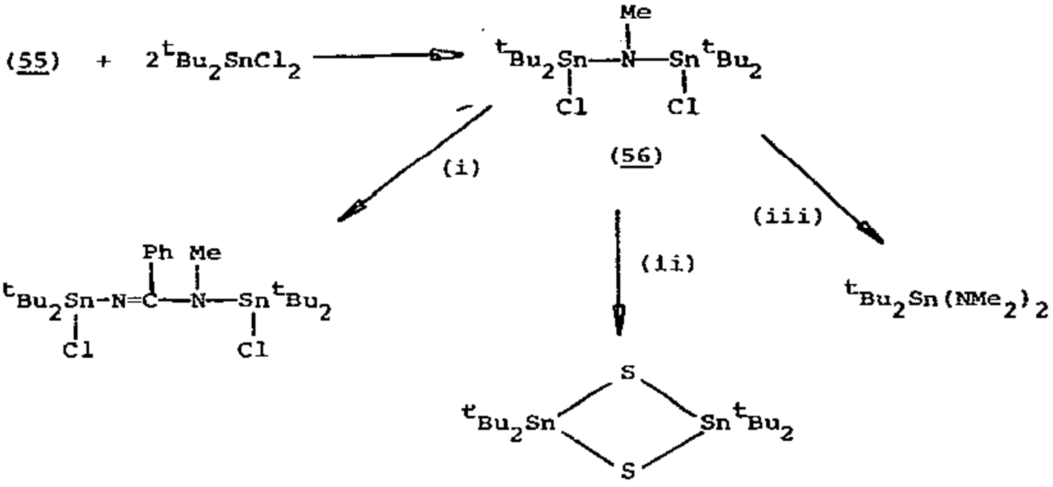
(i) BuLi; (ii) R_2SnCl_2.

The four-membered ring diazadistannetidine (<u>55</u>) undergoes a variety of ring expansion reactions:



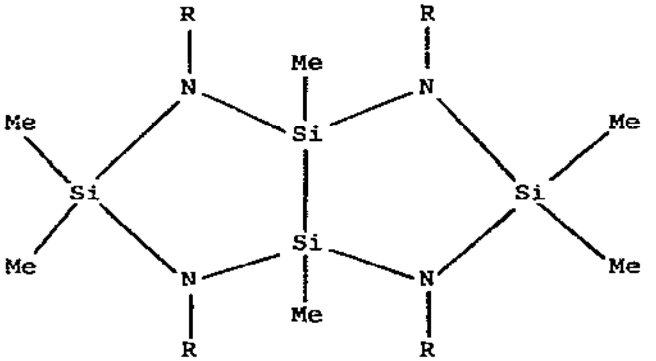
(<u>55</u>)

Reaction with bis(tosyl)sulphurdiimide affords the N-tosyl analogue. With ${}^{t}Bu_2SnCl_2$, the acyclic 1,3-dichlorodistannazane (56) is produced, which also undergoes a variety of reactions:[197]



(i) 2PhCN ; (ii) 2R=C=S (R = S or PhN) ; (iii) $LiNMe_2$.

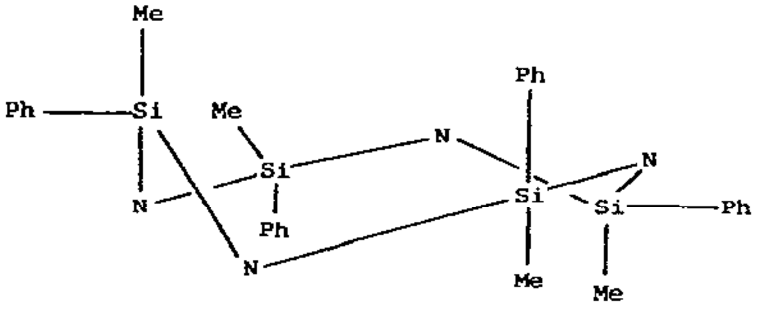
The structures of three cyclic silazanes have been determined: bicyclo[3.3.0]tetrasila-1,3,5,7-tetraazene (57),[198] 1,3,5',7'-tetramethyl-1',3',5,7-tetraphenylcyclotetrasilazane, which has a general "boat" conformation (58),[199] and 2,2,4,4,6,6,8,8,9,9,11,11,-dodecamethylbicyclo-[3.3.3]-hexasilazane[200] (59), in which the



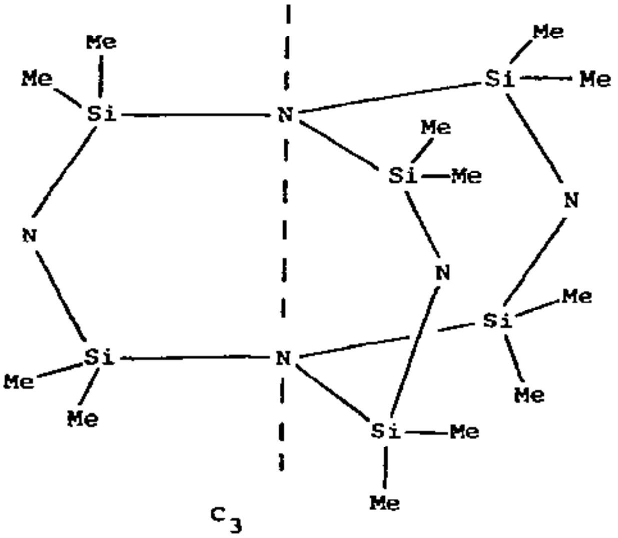
R = tolyl.

(57)

tricyclic silazane core has C_{3h} (non-crystallographic) symmetry, and the axial nitrogen atoms have an almost planar valence configuration.[201]

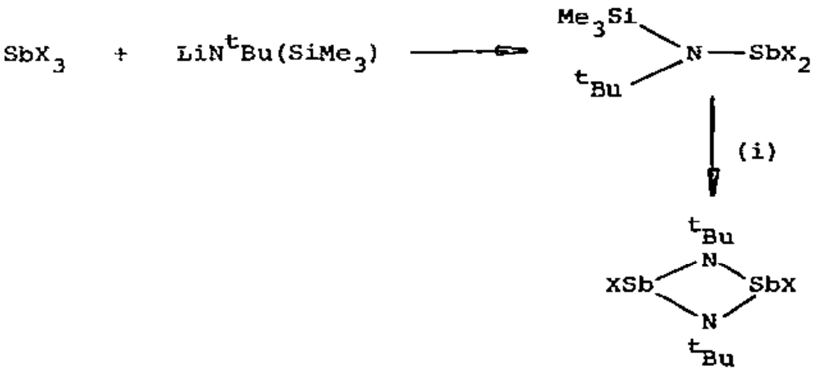


(58)



(59)

The replacement of one halogen on antimony(III) halides by a silylamino group yield a silylaminostibine which eleininates chlorosilane at room temperature:

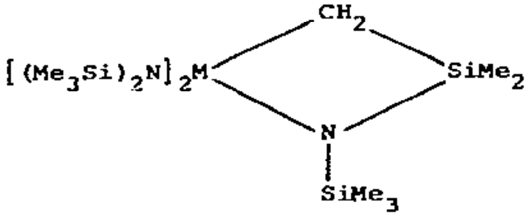


X = Cl, Br.

(i) room temperature ; $-Me_3SiX$.

The bis-derivatives, $[(Me_3Si)(Me_3M)N]_2SbX$ (M = C, Si), however, are stable to elimination even at 200°.[202]

The bis(trimethylsilyl)amino group continues to be widely used as a ligand towards transition metals. Synthesis of the complexes is generally accomplished by reaction of the sodium or lithium silylamide with the transition metal halide, with or without the presence of additional donor ligands. The thermally stable but highly oxygen sensitive manganese(II) and chromium(II) derivatives, $Mn[N(SiMe_3)_2]_2.thf$, $ClCrN(SiMe_3)_2(L)_n$ and $Cr[N(SiMe_3)_2]_2.LL'$ (LL' = aliphatic and cyclic ethers, alkyl cyanides, aromatic amines) have been observed in this way.[203,204] The interaction of oxotetrachlororhenium(IV) with $LiN(SiMe_3)_2$ results in reduction and the formation of $ReO[N(SiMe_3)_2]_2$, which is volatile and very stable in petrol. It is moderately air-stable, and does not react with CO_2, CS_2, PMe_3 or Na/K alloy.[205] Only three of the chlorines of zirconium(IV) and hafnium(IV) chlorides are substituted by $M^{\pm}Na(SiMe_3)_2$ ($M^{\pm}$ = Li, Na) to give hydrocarbon-soluble chlorotris-bis(trimethylsilyl)amino zirconium and -hafnium, $ClM[N(SiMe_3)_2]_3$ (M = Zr, Hf). The fourth chlorine is surprisingly inert, being stable to air and water, and not hydrolysed by mineral acids at pH1. It will, however, react with methyllithium to afford $MeM[N(SiMe_3)_2]_3$, which is also air and water stable, but does undergo hydrolysis with dilute hydrochloric acid reverting to the chloride.[206] The reaction of tantalum(V) chloride with two equivalents of $NaN(SiMe_3)_2$ results in the formation of yellow prisms of $Cl_3Ta[N(SiMe_3)_2]_2$, which reacts further with methyllithium to give monomeric $Me_3Ta[N(SiMe_3)_2]_2$. On reaction with $LiCH_2SiMe_3$, however, instead of the expected compound, $(Me_3SiCH_2)_3Ta[SiMe_3)_2]_2$, the essentially air-stable, yellow, monomeric alkyl-alkylidene complex, $(Me_3SiCH_2)(Me_3SiCH)Ta[N(SiMe_3)_2]_2$, is obtained.[207] Several uranium complexes have been synthesised. Red, monomeric, volatile $[(Me_3Si)_2N]_3U$, from UCl_3 and $NaN(SiMe_3)_2$ in thf, is thought to be pyramidal but does not form complexes.[208] The uranyl derivative, $UO_2[N(SiMe_3)_3]_3.2thf$, is obtained similarly, and is stable in pentane but involatile.[209] Uranium(IV) and thorium(IV) chlorides behave like the zirconium(IV) and hafnium(IV) chlorides substituting only three chlorines giving $ClM[N(SiMe_3)_2]_3$ (M = U, Th) complexes. The fourth chlorine may be substituted using dimethylmagnesium or methyllithium affording the corresponding methyl derivatives, or by lithium borohydride which results in the formation of $BH_4M[N(SiMe_3)_2]_3$ complexes. The crystal structure of the thorium borohydride was determined.[210] Heating the chloro complexes, $ClM[N(SiMe_3)_2]_3$ (M = U, Th), with further $NaN(SiMe_3)_3$ in thf results in the formation of the hydrides, $HM[N(SiMe_3)_2]_3$. Use of thf-d_8 gives the corresponding deuterides, which are also obtained from the hydrides by treatment with butyllithium and CF_3CO_2D. Treatment with carbon tetrachloride regenerates the chlorides.[211] These hydrides undergo a rather surprising facile H-D exchange when stirred under an atmosphere of D_2 (atmospheric pressure) at room temperature. The exchange goes to completion, all hydrogen atoms being replaced by deuterium to give the fully perdeuteriated complex, $DU[N\{Si(CD_3)_3\}_2]_3$. The reaction is reversible, since stirring the perdeuteriated complex under hydrogen regenerates the starting material. Under similar conditions, the thorium analogue also undergoes complete exchange. An insight into the mechanism of the exchange was obtained from the isolation of the four-membered ring metallobutane (60) from the pyrolysis of the hydrides (neat, 180-190°, 1 atmos.) or methyls (neat, 150-160°, 1 atmos.), leading to Scheme 2 for the exchange.[212]



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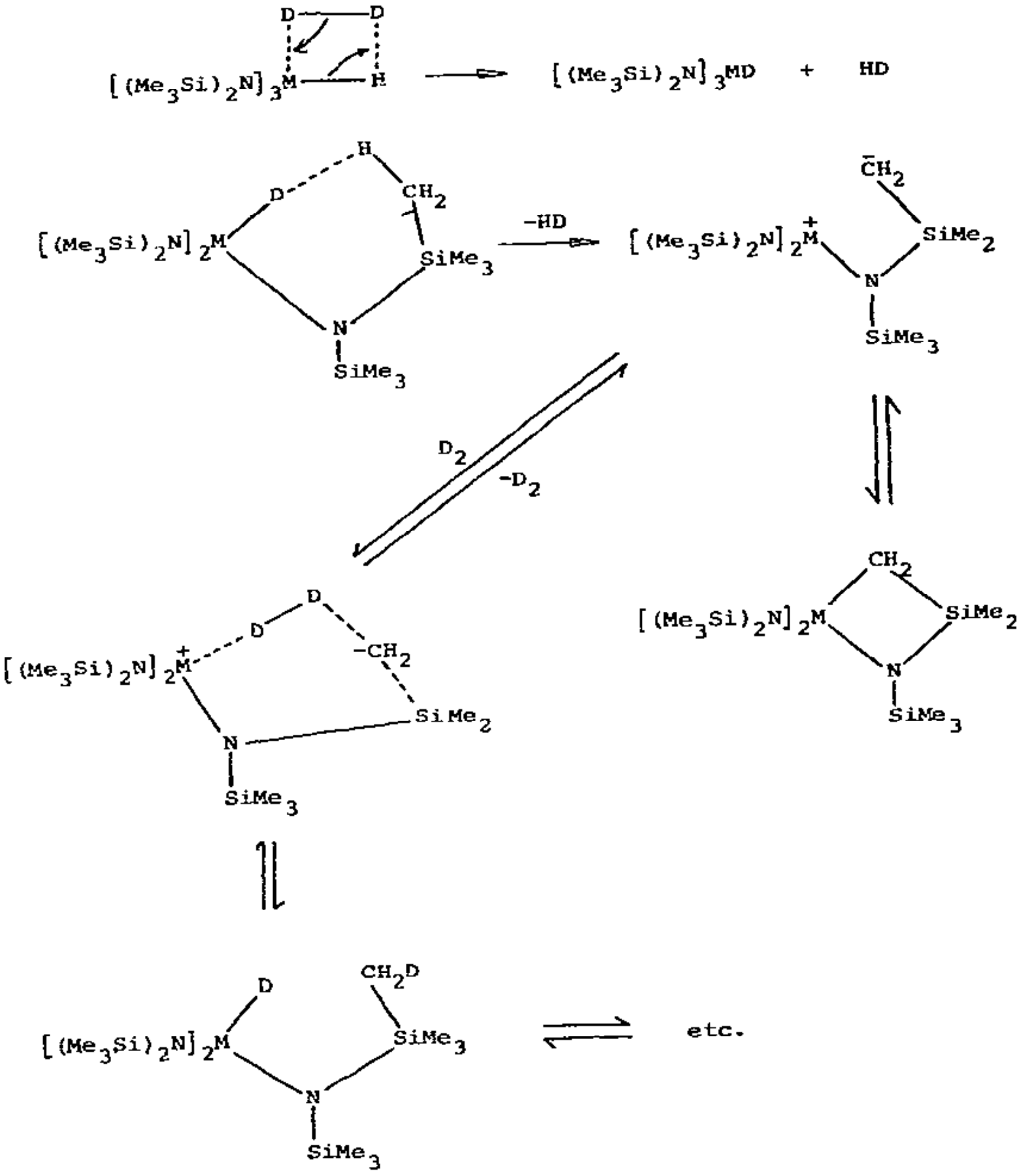
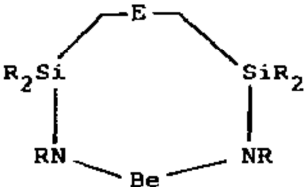

[(Me3Si)2N]3M
D
D
H
[(Me3Si)2N]3MD
+
HD
[(Me3Si)2N]2M
H
D
CH2
SiMe3
N
SiMe3
-HD
[(Me3Si)2N]2M+
CH2−
SiMe2
N
SiMe3
D2
-D2
[(Me3Si)2N]2M+
D
D
-CH2
SiMe2
N
SiMe3
[(Me3Si)2N]2M
CH2
SiMe2
N
SiMe3
[(Me3Si)2N]2M
D
CH2D
SiMe3
N
SiMe3
etc.

Scheme 2

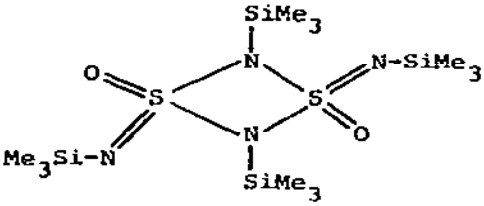
Four novel diaza-disilaberyllacyclohexane (61) have been obtained by the reaction of dimethylberyllium with the appropriate aminosilanes. In solution and in the solid-state, the compounds exist as dimers and probably more highly associated oligomers which, according to their ^1H n.m.r. spectra, interconvert depending on the temperature and solvent. The crystal structure of (61, E = CH_2) comprises dimeric molecules associated via a centrosymmetric BeN-Be'N' ring.[213]



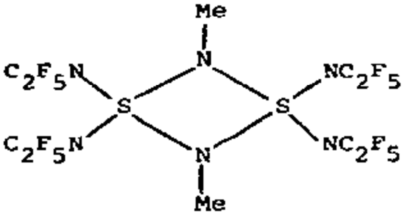
E = ——, CH_2, NR, O.

(61)

The structure of $(Me_3SiN)_3S$ has been determined at -130°. The three-fold coordination of S(IV) is planar, large temperature coefficients perpendicular to the SN_3 plane might be indicative of some disorder due to small deviations from planarity.[214] The silyl-substituted four-membered S_2N_2 ring compound (62) is completely planar (cf. (63) which has a non-planar ring.[215]

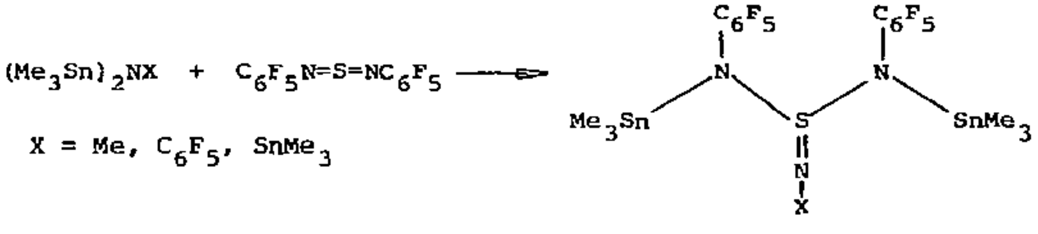


(62)



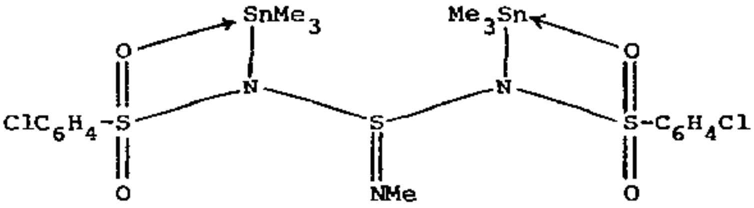
(63)

Roesky and his coworkers have continued their studies of the reactions of silyl- and stannylamines with sulphur compounds. The stannylamines, $(Me_3Sn)_2N{-}X$ ($X = Me, C_6F_5, SnMe_3$), react with $C_6F_5N{=}S{=}NC_6F_5$ to afford the adducts (64):



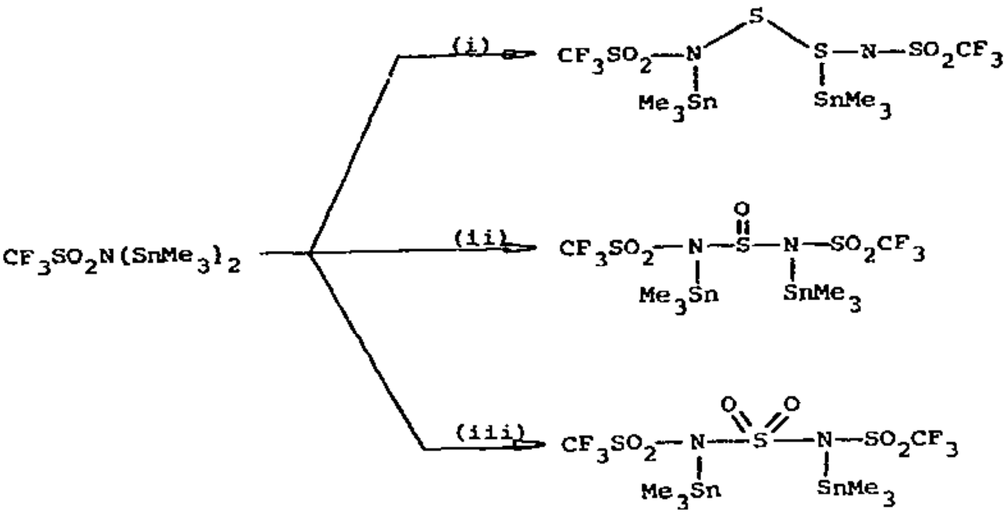
(64)

^1H and ^{19}F n.m.r. data show that the ortho-fluorine atoms interact with the tin atoms. Similarly, in the adduct (65) of $(Me_3Sn)_2NMe_2$ and N,N'-bis(p-chloro-phenylsulphonyl)sulphurdiimide, the sulphonyl oxygen atom is coordinated to the tin.[216]



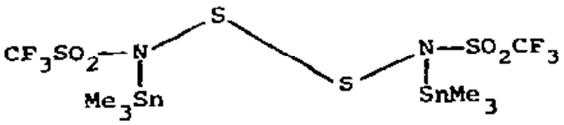
(65)

$CF_3SO_2N(SnMe_3)_2$ reacts with S_2Cl_2, $SOCl_2$ and SO_2Cl_2 with cleavage of one Sn-N bond:

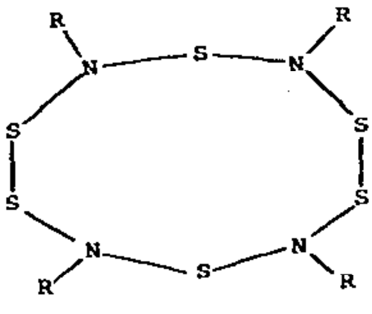


(i) S_2Cl_2; (ii) $SOCl_2$;
(iii) SO_2Cl_2.

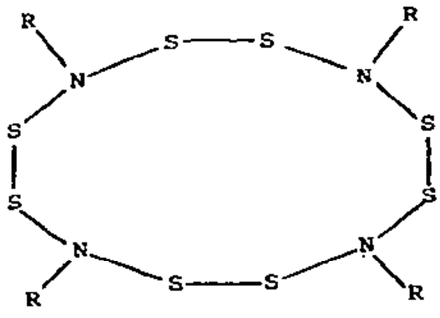
The product with S_2Cl_2 reacts with further S_2Cl_2 or with SCl_2 yielding the twelve- and ten-membered S,N heterocycles (66) and (67):



(i) (ii)



(66)

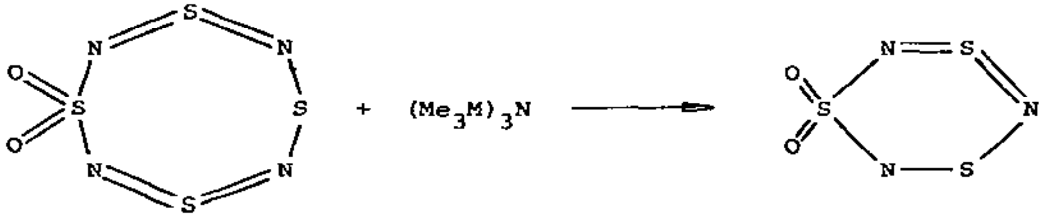


(67)

$R = CF_3SO_2$ (i) SCl_2 ; (ii) S_2Cl_2.

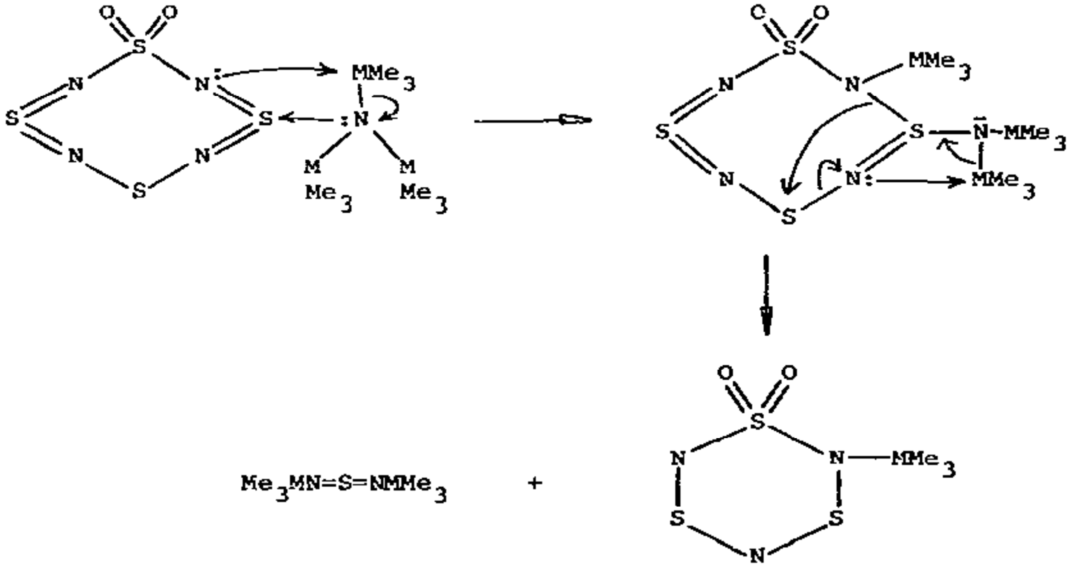
Treatment of $CF_3SO_2N(SnMe_3)_2$ with Me_2GeCl_2 yields (68), whilst heating to 160° causes disproportionation. Reaction with $ClR_2SiOSiR_2Cl$ at room temperature produces (69), which undergoes cyclisation at 40°.[217]

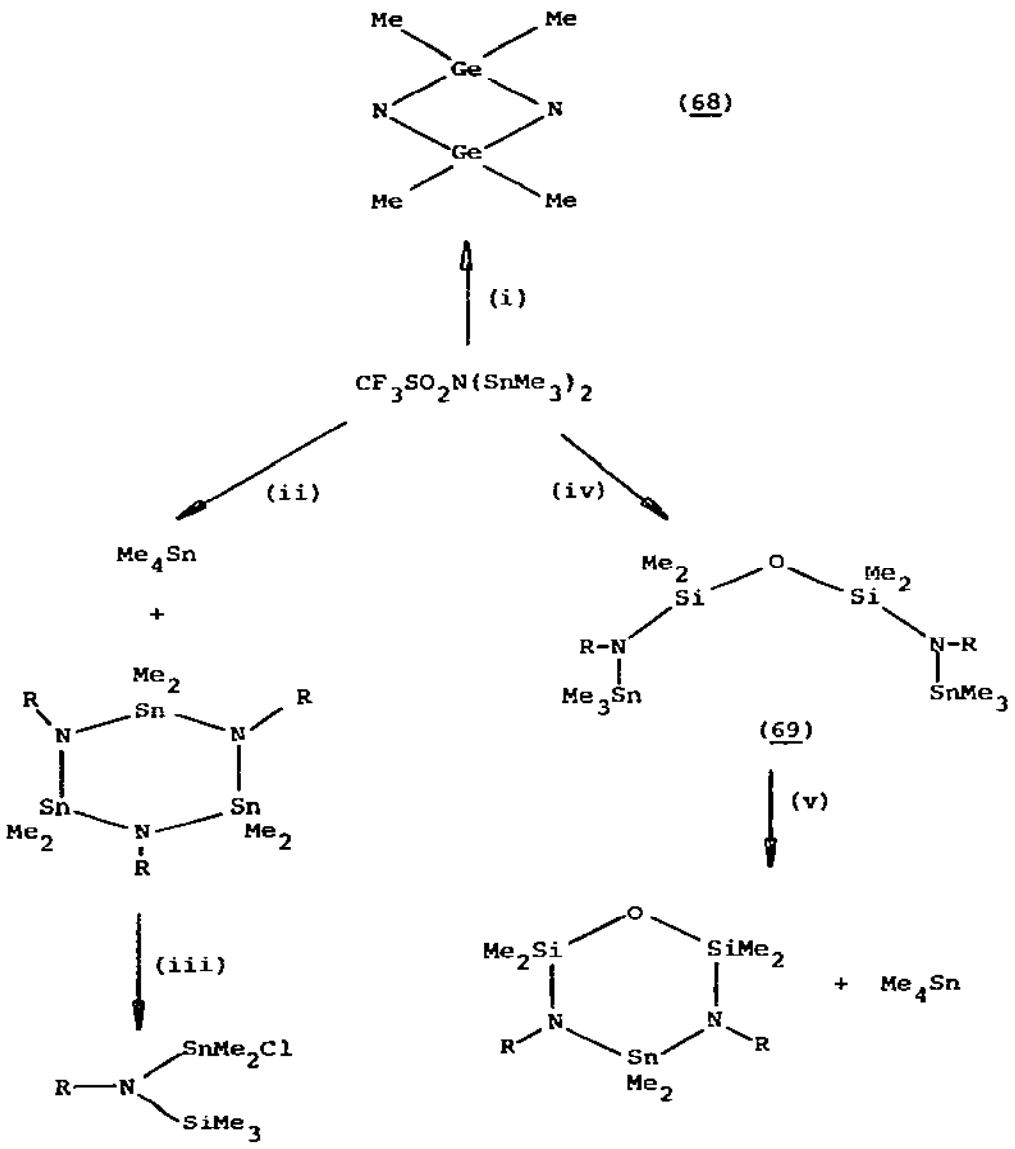
Tris(trimethylsilyl- and -stannyl)amines, $(Me_3M)_3N$ (M = Si, Sn) react with the eight-membered heterocycle, $S_4N_4O_2$, to afford the silyl- or stannyl-substituted six-membered ring compounds (70):



(70)

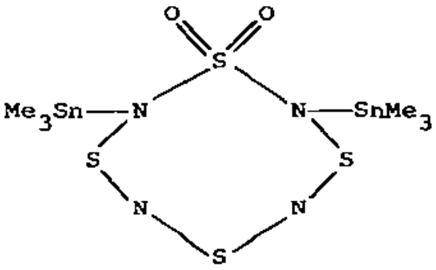
The compounds also arise from the reaction of $FSO_2N{=}S{=}O$ with the sulphurdiimides, $Me_3MN{=}S{=}NMMe_3$ (M = Si, Sn), and also by the reaction of Me_3SnN_3 with $S_4N_4O_2$. The mechanism of the ring-





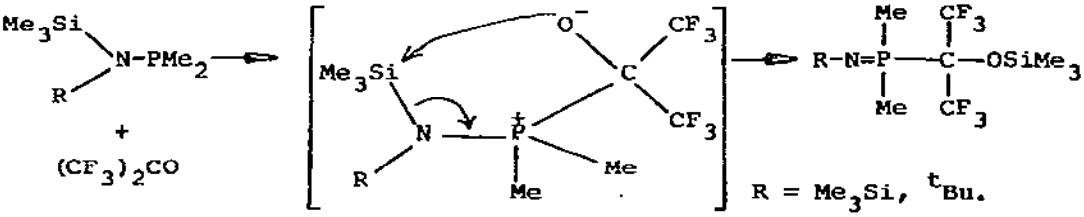
(i) Me_2GeCl_2 ; (ii) 160° ; (iii) Me_3SiCl ; (iv) $ClMe_2SiOSiMe_2Cl$;
(v) 40°.

contraction was considered to involve nucleophilic attack by the metallamine at sulphur, followed by eleimination of the metalsulphurdiimide. When the reaction between $(Me_3Sn)_3N$ and $S_4N_4O_2$ is carried out in a 1:1 molar ratio the bis(trimethylstannyl)-substituted eight-membered ring compound (71) is obtained. X-ray analysis of the hemi-benzene solvate shows the ring to be puckered, with four-coordinated tin. No O→Sn intermolecular coordination is present.[218,219]



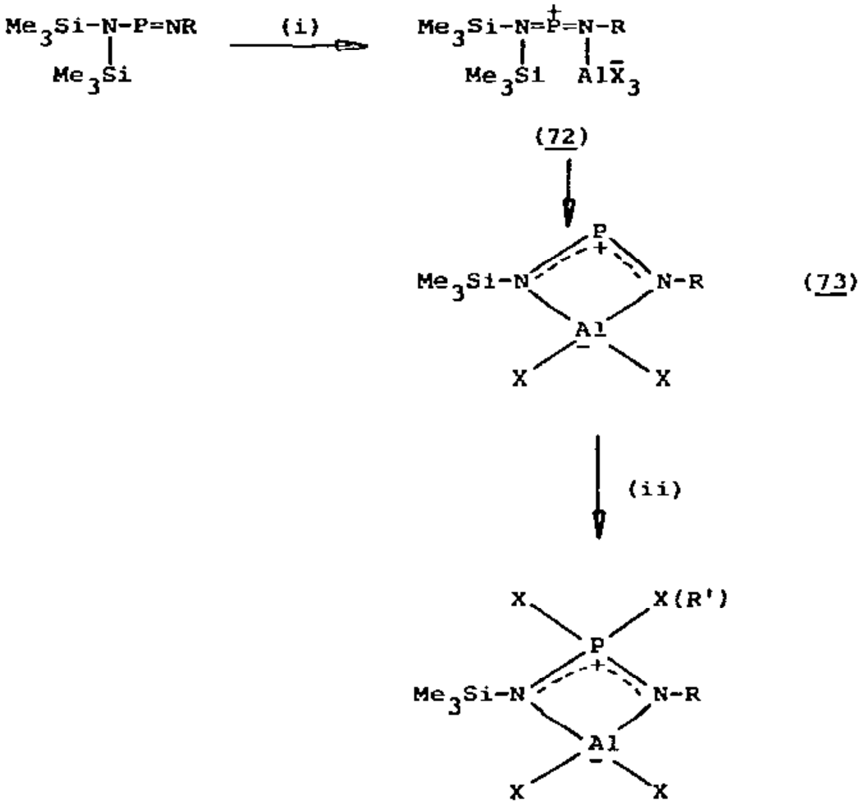
(71)

$Me_3SiN(PF_2)_2$ has been prepared by the reaction of $Me_3SiN(SnMe_3)_2$ and PF_2Cl. With $(Me_3Sn)_3N$, $N(PF_2)_3$ is formed.[220] The similar silyl derivatives, $PF_2[N(SiH_3)_2]$ and $N(PF_2)_2(SiH_3)$, result from the reaction of silyl bromide and trimethylamine with $PF_2[NH(SiH_3)]$ and $NH(PF_2)_2$, respectively. With diborane, $PF_2[N(SiH_3)_2]$ forms an adduct, $PF_2[N(SiH_3)_2].BH_3$, whilst $N(PF_2)_2(SiH_3)$ forms both mono- and bis-borane adducts.[221] $PF_2[NH(SiH_3)]$ reacts with PF_5 to yield the mixed-valence fluorophosphinoamine, $NH(PF_2)(PF_4)$.[222] The novel diphosphorus zwitterion, $F_5\bar{P}CH_2\overset{+}{P}F(NMe_2)_2$, has been obtained from the reaction of Me_3SiNMe_2 and $F_4PCH_2PF_4$.[223] The P,P-dimethylsilylaminophosphines, $Me_3SiNRPMe_2$ react with hexafluoroacetone at 0° in an exothermic reaction involving a [1,5] silyl shift from nitrogen to oxygen:[224]



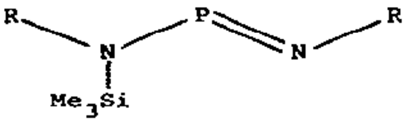
R = Me_3Si, ^tBu.

N-Silylated aminoiminophosphines react with aluminium(III) halides to yield acyclic zwitterionic compounds (72) having two-coordinate phosphorus. At about room temperature, however, the adducts decompose by the elimination of silylhalides to yield 1,3,2λ^2,4-diazaphosphoniaaluminatacyclobutanes (73), which can add halogens or alkyl halides:[225]



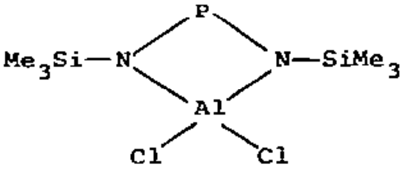
(i) AlX_3 ; (ii) X_2 or R'X.

The crystal structures of two acyclic silylated aminoiminophosphines (74) and the silylated diazaphosphoniaaluminatacyclobutane derivative (75) have been determined.[226]



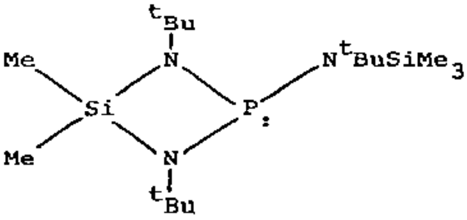
(74)

R = $SiMe_3$, ^tBu

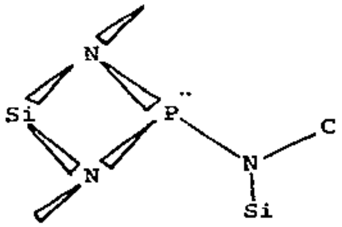


(75)

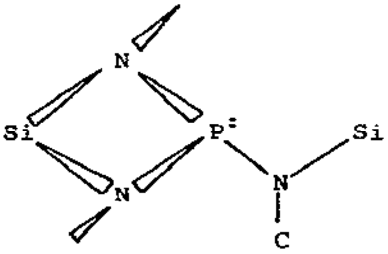
The four-membered ring compound (76), from $Me_2Si[N^tBuLi]_2$ and $Cl_2PN^tBuSiMe_3$, exists as a rotamer (77) and (78) due to hindered rotation about the P-N bond. Isomer (77) predominates initially from the synthesis [(77):(78):: < 6 :1], but is transformed into the more thermodynamically stable isomer (78) on distillation. The two isomers could be separated by fractional crystallisation and fractional distillation. An X-ray analysis of isomer (77) confirmed the spectral assignment of the rotamers.[227]



(76)

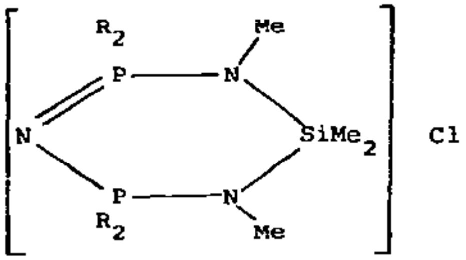


(77)



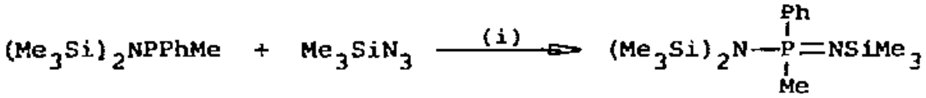
(78)

Cyclo-1-sila-2,4,6-triaza-3,5-diphosph(V)onium chloride (79) does not result from the reaction of $[ClR_2P{=}N{-}PR_2Cl]Cl$ (R = Cl, Ph) with $Me_2Si[HNMe]_2$, but can be prepared, when R = Ph, from $[Ph_2ClP{-}N{=}PClPh_2]Cl$ and $Me_2Si[NMeSiMe_3]_2$.[228]



(79)

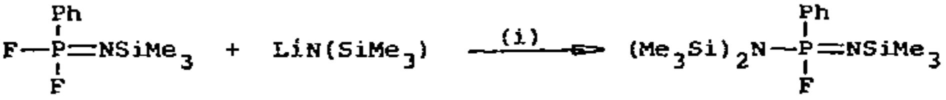
Several methods for the synthesis of N-silylphosphinimines have been described. Trimethylsilylazide reacts with N-silylaminophosphines with the elimination of nitrogen:



$$(Me_3Si)_2NPPhMe \;+\; Me_3SiN_3 \xrightarrow{(i)} (Me_3Si)_2N{-}\overset{Ph}{\underset{Me}{P}}{=}NSiMe_3$$

(i) 100°, 20hr, $-N_2$.

whereas substitution of P-halogenated phosphinimines using N-lithio disilazane allow the preparation of silylphosphinimines bearing a halogen substituent on phosphorus:

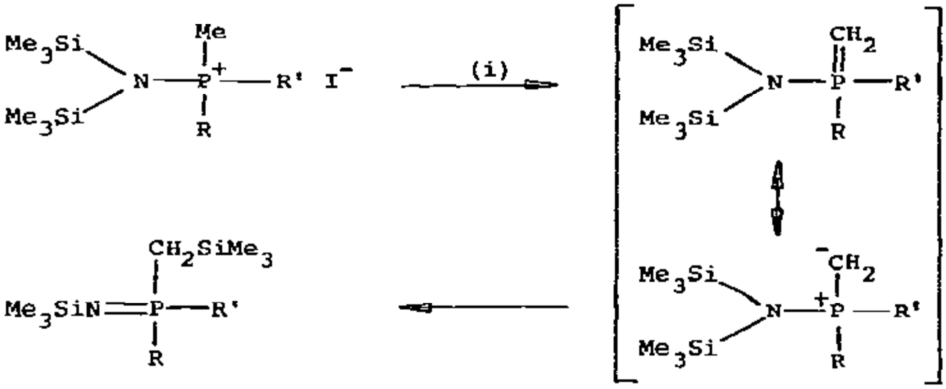


$$F{-}\overset{Ph}{\underset{F}{P}}{=}NSiMe_3 \;+\; LiN(SiMe_3) \xrightarrow{(i)} (Me_3Si)_2N{-}\overset{Ph}{\underset{F}{P}}{=}NSiMe_3$$

(i) $-LiF$.

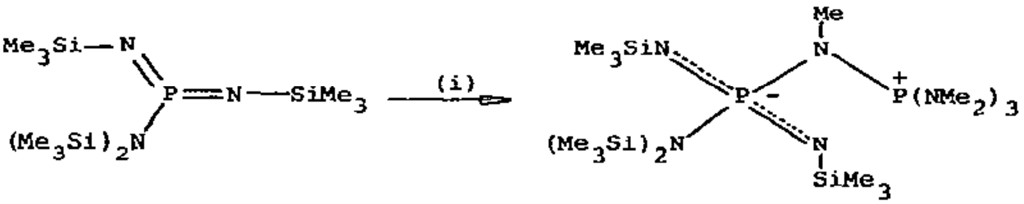
Both complexes exhibit reversible [1,3] silyl group exchange with $\Delta G^{\ddagger}_{1,3}$ values of 14.2 and 18.3 kcal mol^{-1}, respectively.[229] The P-methylsilylaminophosphines, $Me_3Si(R)NPMe_2$ (R = Me_3Si, ^tBu, Me), $(Me_3Si)_2NPPhMe$, $^tBuMe_2Si(R)NPMe_2$ (R = Me_3Si, Me) and $Me_3SiCH_2CH_2SiMe_2NPMe_2$ have also been prepared by substitution from PCl_3 or $PhPCl_2$ and lithium silylamides,followed by methylation using MeMgBr. Treatment with methyl iodide results in the formation of the corresponding (silylamino)-phosphonium iodides which, when allowed to react with butyllithium, usually undergo dehydrohalogenation accompanied by a N→C silyl group migration to afford the (silylmethyl)phosphinimines, $Me_3SiN{=}P(CH_2SiMe_3)RR'$,

$RMe_2SiN{=}P(CH_2SiMe_2R')Me_2$, $^{t}BuN{=}P(CH_2SiMe_3)Me_2$, and $Me_2\overline{SiCH_2CH_2SiMe_2CH_2PMe_2{=}N}$:[230]



(i) BuLi.

The P-N-Si skeleton in $Me_3Si{-}N{=}PMe_3$ is bent (PNSi = 144.6(11)°), and the barrier to inversion is probably only about 10 kJ mol^{-1}.[231] The reaction of N-silylated iminophosphoranes, $Me_3Si{-}N{=}PR_3$ (R = Me, NMe_2, Ph) with phosphites, $P(OR')_3$ (R' = CH_2CF_3, Ph) leads to desilylation and the formation of phosphazeno phosphanes, $R_3P{=}N{-}P(OR')_2$.[232] The addition of $MeN{=}P(NMe_2)_3$ to the silylated aminodiiminophosphorane (80) results in the formation of the acyclic diphosphazane betaine (81), the structure of which has been determined:[233]



(80)

(81)

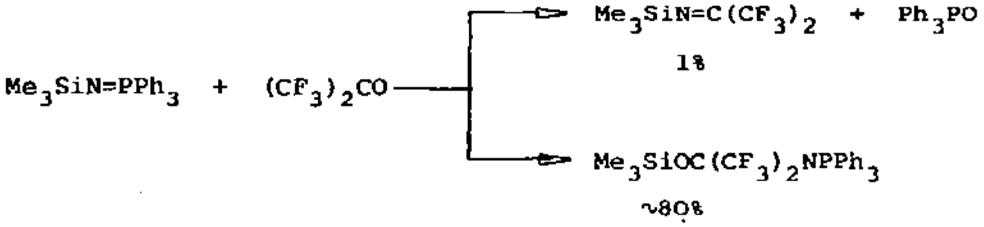
(i) $Me{-}N{=}P(NMe_2)_3$.

Hexafluoroacetone reacts with stannylphosphinimines in a Wittig-type reaction:

$$R_3SnN{=}PPh_3 \quad + \quad (CF_3)_2CO \longrightarrow R_3SnN{=}C(CF_3)_2 \quad + \quad Ph_3PO$$

R = Me, Et.

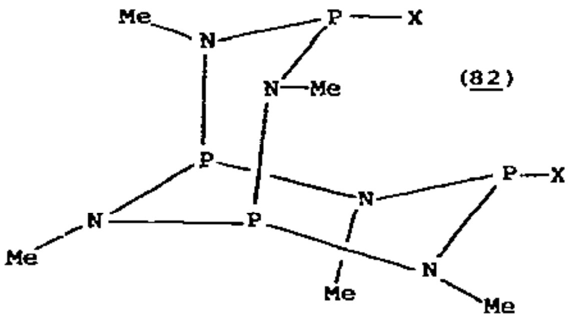
With the corresponding silylphosphinimines, however, only 1% of the reaction follows this pathway, and the bulk of the reaction results in the formation of an insertion product:



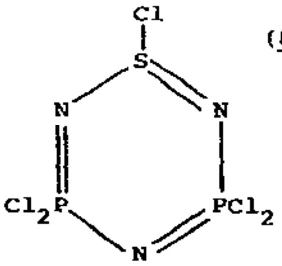
$$Me_3SiN{=}PPh_3 + (CF_3)_2CO \longrightarrow \begin{cases} Me_3SiN{=}C(CF_3)_2 + Ph_3PO & 1\% \\ Me_3SiOC(CF_3)_2NPPh_3 & \sim 80\% \end{cases}$$

Me_3SiN_3 also forms an insertion product, $Me_3SiOC(CF_3)_2N_3$.[234]

Silylamines have been employed extensively in the synthesis of inorganic heterocyclic compounds. P-Perhalogenated cyclo-tri(λ^3)-phosphazanes) have been obtained by the reaction of $(MeNSiMe_2)_3$ or $(Me_3Si)_2NMe$ with excess PX_3 (X = Cl, Br). When the reactions are performed under mild conditions, acyclic silylaminophosphines such as $X_2PNMeSiMe_2X$, $X_2PNMePX_2$, $X_2PNMeSiMe_3$, $Br_2PNMe.PBr.NMeSiMe_3$, and $X_2PNMe.SiMe_2NMe.SiMe_2.NMeSiMe_2X$ are found to be intermediates.[235] Further treatment of cyclo-tri(λ^3)-phosphazanes with $(Me_3Si)_2NMe$ yield symmetrically-bridged, bicyclic cyclotetra(λ^3-phosphazanes) (<u>82</u>).[236] The mixed S,P,N six-membered heterocycle (<u>83</u>) results from the reaction of $Me_3SiN{=}S{=}NSiMe_3$ and PCl_5.[237]

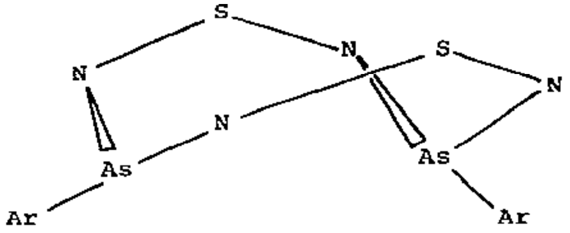


(<u>82</u>)



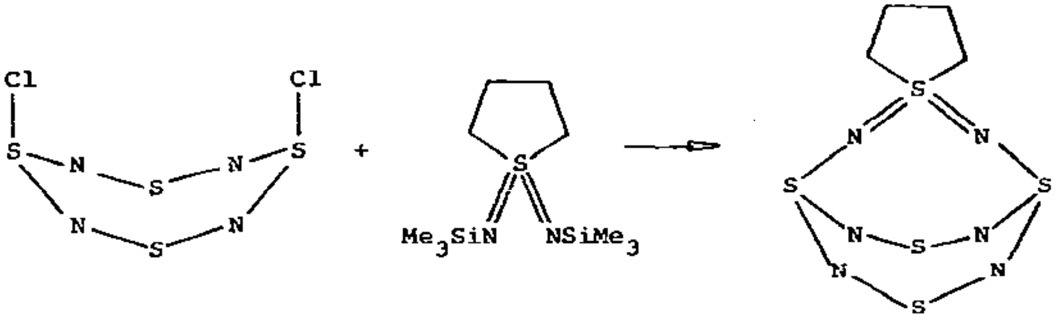
(<u>83</u>)

The reaction of $Me_3SiN{=}S{=}NSiMe_3$ with aryldichloroarsines yields the 3,7-diaryl-3H,7H-1,5,2,4,6,8,3,7-dithia(1,5-S^{IV})tetraazadiarsocins (84). When excess dichloroarsine is used, ArAs(Cl)$NSNSiMe_3$ intermediates are obtained, which in the presence of a large excess of $Me_3SiN{=}S{=}NSiMe_3$ rapidly undergoes further reaction to yield ArAs$(NSNSiMe_3)_2$. Both reactions are followed by a much slower reaction which affords the final diarsocin product.[238] S_4N_5Cl, containing the $S_4N_5^+$ cation, has been prepared in good yield from trithiazyl trichloride, $S_3N_3Cl_3$, and $Me_3SiN{=}S{=}NSiMe_3$ in CCl_4.[239]

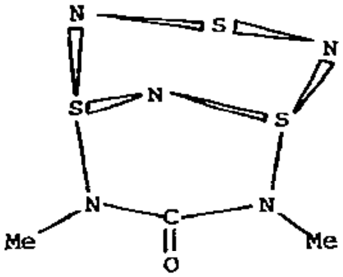


(84)

The spirocyclic 1'λ⁶-thiacyclopentane-sulphur-nitrogen heterocycle (85) has been prepared according to:[240]



(85)

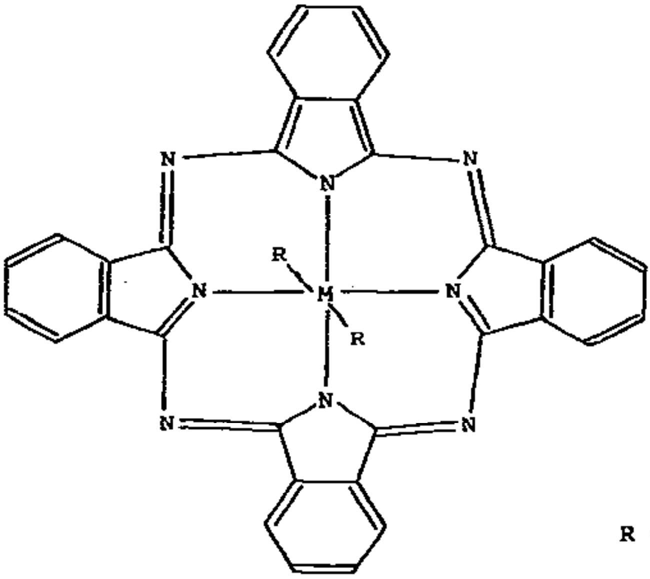


(86)

The similar cage compound (<u>86</u>) results from the reaction of $S_3N_3Cl_3$ or $S_4N_4Cl_2$ with $(Me_3SiNMe)_2CO$ in hexane.[241]

The low-pressure sublimation of tris(2,2'-bipyridyl)-silicon(0) yields bis(2,2'-bipyridyl)silicon(0). Crystals comprise discrete molecules in which both bipyridyl ligands chelate silicon in a distorted tetrahedral fashion.[242]

<u>Trans</u>-bis(1-alkynyl)silicon, -germanium, and -tin phthalocyanines (<u>87</u>) have been isolated in <u>ca</u>. 90% yields by the reaction of the corresponding phthalocyaninatometal dichlorides with Grignard reagents in thf. The tin compounds are rather difficult to isolate in a pure form, since they readily undergo reduction to phthalocyaninatotin(II). Treatment with $HCl/thf/H_2O$ or $NaOH/H_2O$ results in conversion to the phthalocyaninatometal dichloride or dihydroxide, respectively.[242]



R = alkynyl

(<u>87</u>)

Crystals of α,β,γ,δ-tetraphenylporphinatodihydroxytin(IV) bis-chloroform bis-carbon tetrachloride solvate comprise discrete molecules with <u>trans</u> isolated hydroxyl groups. From a combination of sturctural and variable-temperature Mössbauer data, it was deduced that the tin atom vibrates with greater amplitude in the plane of the porphyrin residue, but the temperature coefficient of vibration is significantly larger in the out-of-plane direction (along the OSnO axis) (4.184×10^{14}ÅK^{-1}) than in the in-plane direction (2.618×10^{-4}ÅK^{-1}), reflecting the constraining nature of the porphyrin residue.[244]

The structure of β-Si_3N_4, grown from a silicon melt, is closely related to α-Si_3N_4, although Madelung energy calculations suggest that the β-form is more stable at ca. 293K.[245] Germanium nitride oxide, Ge_2N_2O, has been subjected to a time-of-flight neutron diffraction study.[246]

4.2.9 Bonds to Phosphorus and Arsenic

Two sets of α-type transitions have been observed in the microwave spectrum of methylphosphinosilane. The stronger set of lines were assigned to a trans conformer and the weaker set to the corresponding gauche isomer. The structural parameters indicate a rather short Si-P bond distance of 2.10Å.[247] In the liquid phase, silylphosphine, H_3SiPH_2, and ammonia react to give PH_3, $(H_3Si)_2NH$ and $(H_3Si)_3N$. No evidence was observed for the intermediate formation of H_3SiNH_2. Subsequent ammonia-promoted elimination of silane from the disilazanes yield a series of silazane oligomers and polymers, including the two new condensation oligomers, $(H_3SiNH)_2SiH_2$ and $(H_3Si)_2NSiH_2NHSiH_3$.[248] A number of soluble (chlorosilyl)phosphine complexes of RhI, which are capable of being polymerised into poly(siloxyphosphine)RhI species have been synthesised. Typical examples are $L'_2Rh(CO)Cl$, L'_3RhCl, L''_3RhCl and $L'_4Rh_2Cl_2$ ($L' = Cl_2Si(CH_2)_2PPh_2$; $L'' = Cl_3Si(CH_2)_8PPh_2$). The siloxyphosphine complexes, LPh(NBD)Cl, $L_2Rh(CO)Cl$, L_3RhCl and $L_4Rh_2Cl_2$ ($L = (Me_3SiO)_2MeSi(CH_2)_2PPh_2$; NBD = norbornadiene) were also prepared.[249]

The forst three-membered $[P_2Si]$ heterocycles, diphosphasiliranes, $(^tBuP)_2SiR_2$ (R = Me, Ph), have been synthesised by [2+1] cyclocondensation reactions of $K(^tBu)P$-$P(^tBu)K$ with Me_2SiCl_2 and Ph_2SiCl_2. In addition, the reactions produce the four-, five- and six-membered cyclosilaphosphanes, $(^tBuP)_3SiR_2$, $(^tBuP)_3(SiMe_2)_2$, $(^tBuP)_4(SiMe_2)_2$, as well as $H(^tBu)P$-$P(^tBu)SiR_2Cl$, $^tBuP(SiPh_2Cl)_2$ and $(^tBuP)_4$.[250] Linear and cyclic silylphosphanes have also been prepared using $(Me_3Si)_2PLi.2thf$. The linear triphosphanes obtained from $MePCl_2$ and $PhPCl_2$ rearrange on heating:

$$(Me_3Si)_2PLi.2thf \; + \; MePCl_2 \longrightarrow (Me_3Si)_2P\text{-}PMe\text{-}P(SiMe_3)_2$$

$$\downarrow \text{(i)}$$

$(Me_3Si)_3P$, $P_5(SiMe_3)_4Me$, $P_5(SiMe_3)_3Me_2$, $P_5(SiMe_3)_2Me_3$, and higher compounds including P_9Me_3.

(i) 120°.

$$(Me_3Si)_2PLi.2thf + PhPCl_2 \longrightarrow (Me_3Si)_2P\text{-}PPh\text{-}P(SiMe_3)_2$$

$$\downarrow \text{(i)}$$

$(Me_3Si)_3P$, $(Me_3Si)_2PPPh_2$, $P_5(SiMe_3)_3Ph_2$, $P_5(SiMe_3)_2Ph_3$, $P_5)SiMe_3)P_4$, P_9Ph_3.

With ${}^tBuPCl_2$, in a 1:2 molar ratio, $(Me_3Si)_2PLi.2thf$ forms the four-membering ring compound, $[Me_3SiPP{}^tBu]_2$, which under irradiation rearranges to $(Me_3Si)_3P$, $P_5(SiMe_3)_3{}^tBu_2$, $P_5(Me_3Si)_2{}^tBu_3$, $P_5(Me_3Si){}^tBu_4$, and $P_6(Me_3Si){}^tBu_3$. When the reaction is performed using a 1:1 molar ratio of reactants, the three-membered ring compound, $P_3(Me_3Si){}^tBu_2$, and two isomeric four-membered rings, $P_4(Me_3Si)_2{}^tBu_2$, are obtained. When the central phosphorus atom is substituted by a dimethylamino group, the triphosphane rearranges spontaneously at room temperature:[251]

$$(Me_3Si)_2PLi.2thf \; + \; Cl_2PNMe_2 \xrightarrow{\text{(i)}} (Me_3Si)_2P\text{-}PNMe\text{-}P(SiMe_3)_2$$

$$\downarrow \text{(ii)}$$

$(Me_3Si)_3P$, Me_3SiNMe_2, $P_6(SiMe_3)_6$, $[Me_2SiP\text{-}PNMe_2]_2$

(i) -40° ; (ii) by 20°.

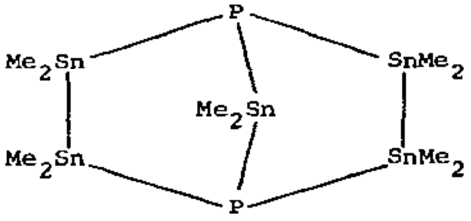
The reaction of $Li_3P_7.3$ solv. (solv. = monoglyme or thf) reacts with Me_3SiCl to afford tris(trimethylsilyl)heptaphosphanortricyclene, $(Me_3Si)_3P_7$, which with methanol yields P_7H_3.[252] The He(I) photoelectron spectrum of $(Me_3Si)_3P_7$ exhibits six distinguishable bands up to 12eV, which were assigned using a quantitative bonding model for P_7H_3.[253] The corresponding arsane, $(Me_3Si)_3As_7$ has been prepared using Rb_3As_7, whilst $P_{11}(SiMe_3)_3$ results from the reaction of excess Me_3SiCl with Na_3P_{11} or Cs_3P_{11} in toluene. The structures of both compounds have been determined.[254]

A convenient method for the preparation of triphenylsilyl- and -stannyldiphenylphosphines has been reported using the procedure:[255]

$$PPhCl \xrightarrow{(i)} PPh_2Li \xrightarrow{(ii)} Ph_3MPPh_3$$

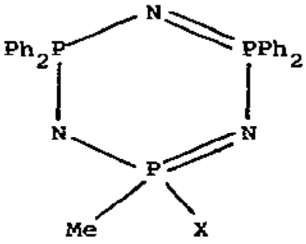
(i) Li, thf ; (ii) Ph_3MCl (M = Si, Sn).

The reaction of dimethylstannane with white phosphorus yields pentakis(dumethylstannyl)diphosphide, a tin-rich heterocycle with the norbornane skeleton (88).[256]



(88)

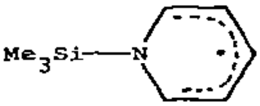
Trimethylsilyl and trimethylstannyl derivatives of the cyclotri(phosphazene) (89; X = Me_3Si, Me_3Sn) have been obtained from the organometal chloride and the lithium derivative of the phosphazene.[257]



(89)

4.2.10 Bonds to Main Group Metals

Pentachlorodisilane reacts with $^tBu_2Hg$ to afford $(Cl_5Si_2)_2Hg$, which on photolysis yields the linear tetrasilane, Si_4Cl_{10}.[258] The cyclic perchlorinated tetrasilane, Si_4Cl_8, has been prepared by cleavage of the phenyl groups from cyclo-Si_4Ph_8 using $HCl/AlCl_3$.[259] Ring-opening occurs with $Cl_2CHCHCl_2$ producing Si_4Cl_{10}. Trimethylchlorosilane reacts with aluminium and lithium in ether in the presence of mercury in ether solvents to give $Li[Al(SiMe_3)_3]$ solvated by ether, thf or DME. The unsolvated complex results from repeated sublimation of the ether solvate.[260] Treatment of $Li[Al(SiMe_3)_4]$ with zinc chloride or cadmium acetate in ether yields bis(trimethylsilyl)zinc and -cadmium, respectively. The zinc compound may be isolated by vacuum sublimation, but ignites spontaneously in air. It is not very stable thermally, and slow decomposition to the metal takes place even at room temperature. The cadmium analogue is in general similar to the zinc compound, but is even less thermally stable and is very light sensitive.[261] A simple synthesis of $(Me_3Si)_2Hg$ has been reported.[262] The method involves the reaction of Me_3SiCl with mercury and aluminium in thf; the desired product is easily separated from the reaction product by sublimation. The photolytic generation of N-trimethylsilylpyridinyls (90), or their 4,4'-dimers, from pyridine or its alkyl derivatives and $(Me_3Si)_2Hg$, surprisingly, does not involve free-radicals, but rather passes through a long-lived photo-excited polar state of $(Me_3Si)_2Hg$. In the mechanism, the excitated state is complexed stepwise by two molecules of pyridine, and only in the last step are free-radicals formed.[263]



(90)

The electrochemical oxidation of zinc, cadmium or mercury in non-aqueous solution containing Ph_3SnCl yields the metal-metal bonded insertion products, Ph_3SnMCl (M = Zn, Cd, Hg). The compounds are easily isolated as either bipyridyl or TMED adducts.

A chain mechanism was postulated:[264]

$$Ph_3SnCl \xrightarrow{e^-} Ph_3Sn\cdot + Cl^-$$

$$2Ph_3Sn\cdot \longrightarrow Ph_6Sn_2$$

$$\text{or} \quad Ph_3SnCl \xrightarrow{e^-} Ph_3Sn^- + Cl\cdot$$

$$Ph_3Sn^- + Ph_3SnCl \longrightarrow Ph_6Sn_2 + Cl\cdot$$

$$Cl^- \longrightarrow Cl\cdot + e^-$$

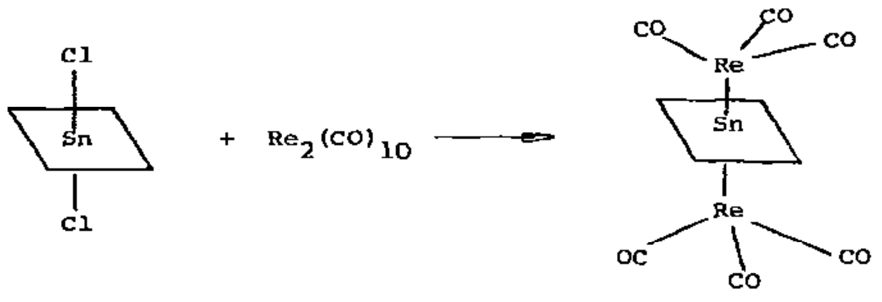
$$Cl\cdot + M \longrightarrow MCl\cdot$$

$$Ph_3SnCl + MCl\cdot \longrightarrow Ph_3SnMCl + Cl\cdot$$

The two latter steps forming the chain-propagating steps.

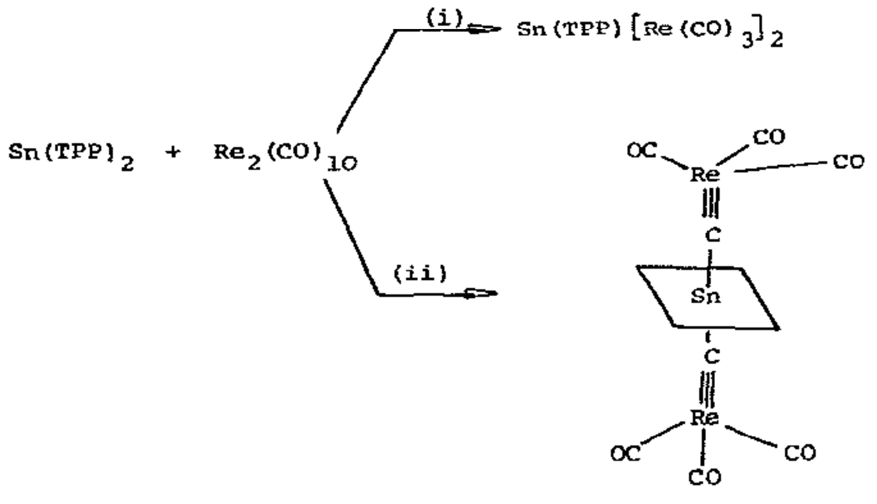
4.2.11 Bonds to Transition Metals

Manganese(II) complexes of the type $(\eta^5\text{-}MeC_5H_4)(CO)_2MnSiPhNpX$ (X = H, Cl, F, MeO) exhibit fice different types of reactions: (i) deinsertion reactions with the formation of PhNpSiHX, (ii) cleavage of the Mn-Si bond with water or methanol, (iii) substitution reactions at silicon without cleavage of the Mn-Si bond, (iv) formation of salts by abstraction of H^+, and (v) reaction with $LiAlH_4$, which leads first to the reduction of the function X, and then to the formation of the anion $[(\eta^5\text{-}MeC_5H_4)(CO)_5MnSiPhNpH]^-$.[264a] The complexes $Cl_3SnMn(CO)_5$, $Cl_3SnMn(CO)_4(PEt\ Ph)$ and $Cl_3SnFe(CO)(C_5H_5)$ react with $TlCo(CO)_4$ and $TlCr(CO)_3(C_5H_5)$ to afford the new, mixed dichlorobis(carbonyl-metallato)tin(IV) complexes, Cl SnXY (X = $Mn(CO)_5$, $Mn(CO)_4PPh_3$, $Fe(CO)(C_5H_5)$; Y = $Co(CO)_4$, $Cr(CO)_3(C_5H_5)$.[265] The reaction of tin(II) halides with $Re_2(CO)_{10}$ leads to the formation of clusters of the type $Re_2(CO)_8[\mu\text{-}SnXRe(CO)_5]_2$ (X = Cl, Br, I). The complexes contain a central four-membered ring which can be opened by reaction with CO under pressure. That the insertion complexes, $X_2Sn[Re(CO)_5]_2$ are also formed during the preparation indicates that insertion of SnX_2 into the Re-Re bond is the primary step. The analogous germanium clusters, $M_2(CO)_8[\mu\text{-}GeXM(CO)_5]_2$ (M = Mn, X = Br, I; M = Re, X = I), were also made.[266] Phthalocyaninato- and porphinatotin(IV) dichlorides react with $Re_2(CO)_{10}$ to afford (91).[267] Bis(tetraphenylporphinato)tin(IV) and $Re_2(CO)_{10}$ also give (91) when the reaction is carried out at 180°, but at 160° the carbyne-like complex (92), shown by an X-ray diffraction to contain a non-linear Sn-C-Re linkage.[268]



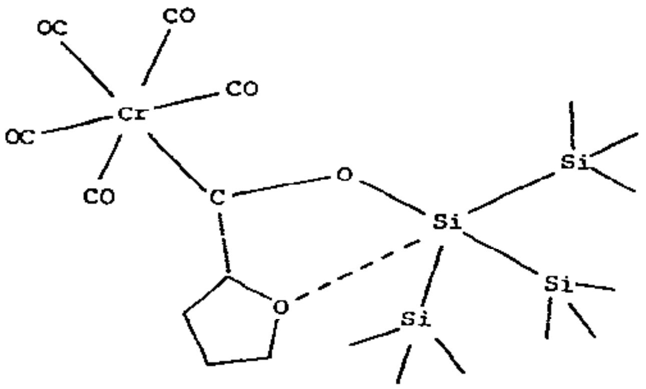
▱ = phthalocyanine,
tetraphenylporphine

(91)



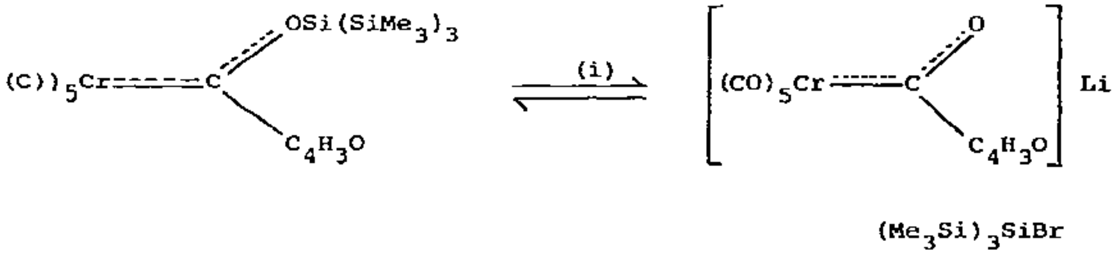
(92)

^{13}C and ^{29}Si n.m.r., as well as X-ray diffraction show that the central silicon atom of the tris(trimethylsiloxy)carbene-chromium(O) complex has a distorted trigonal bipyramidal geometry through interaction with the oxygen of the furyl group (93) both in solution and in the crystal. The Si-O bond in the complex is quite long (1.742(5)Å).



(93)

(93) also reacts with LiBr in ether solution with cleavage of the Si-O bond:[269]

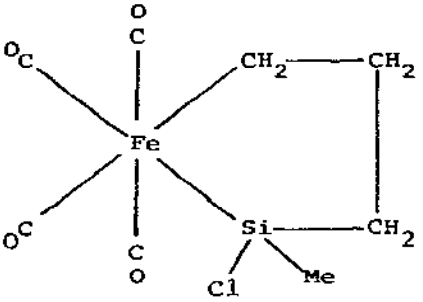


(i) LiBr, ether.

Reaction of $W(CO)_6$ with $LiSiMe_nPh_{3-n}$, followed by subsequent treatment by methylfluorosulphonate, yields the silylcarbene complexes, $(CO)_5W[C(OMe)SiMe_nPh_{3-n}]$ (n = 1 - 3). Aminolysis of the complexes gives the corresponding dimethylamino complexes, $(CO)_5W[C(NMe_2)SiMe_nPh_{3-n}]$ (n = 1, 2). With the Lewis acids Ga_2Cl_2 or Al_2Br_6 at low temperature, the complexes, $(CO)_5M[C(OMe)SiPh_3]$ (M = Cr, W), afford the thermolabile carbyne-complexes trans-$X(CO)_4M{\equiv}CSiMe_nPh_{3-n}$, the halogen of which can be substituted by LiI, $NaRe(CO)_5$, NaC_5H_5 or LiC_9H_7.[270] The stannylcarbene complex, $(CO)_5Cr[C(NEt_2)SnPh_3]$, rearranges spontaneously at room temperature both in the solid state as well as in solution with the loss of CO to yield the yellow crystalline carbyne complex, $Ph_3Sn(CO)_4Cr{\equiv}CNEt_2$. The formation of the complex, whose structure was confirmed by X-ray diffraction (CrCN = 177(1)°), follows a first-order rate law, the rate constant being almost independent of the polarity of the solvent.[271]

The complexes, $(CO)_3(C_5H_5)(R_3Sn)M$ (M = Mo, W), react with liquid SO_2 at 25° by prevailing Sn-C bond cleavage to give di-insertion products, whereas the corresponding chromium complex and the complexes $Ph_2Sn[M(CO)_3(C_5H_5)]_2$ (M = Mo, W) show no reaction. $Me_3SnM(CO)_3(C_5H_5)$ (M = Mo, W), complexes absorb one or two moles of SO_2 by cleavage of the Sn-M bond and the formation of bridged $Me_3Sn(SO_2)_nM(CO)_3(C_5H_5)$ units. Substitution of CO by the stronger σ-donor Ph_3P causes an activation of the Sn-C bond in the complexes $R_3SnMo(CO)_2(PPh_3)(C_5H_5)$ (R = Me, Ph), which at -25° afford monomeric, mono-insertion o-sulphinato adducts.[272]

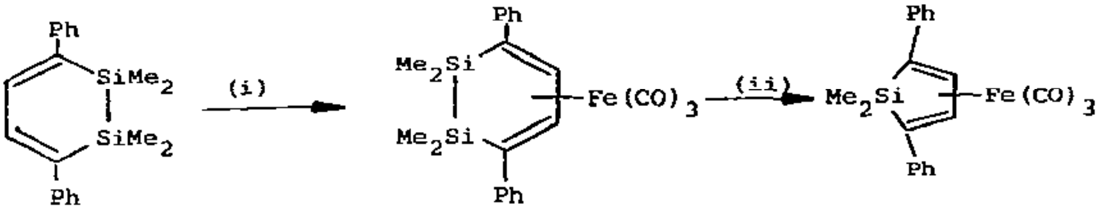
The sila-ferracyclopentane (94) has a ring chair conformation with an Fe-Si bond distance of 2.307(2)Å.[273]



(94)

Parish and Riley[274] have investigated the reactions between tert-phosphine complexes of Fe(O) and Fe(II) and silanes. Only with the bidentate ligand $Ph_2PCH_2CH_2PPh_2$ (dppe) could silyl derivatives be characterised, which were of the types $FeH(SiR_3)(dppe)_2$ and $Fe(SiR_3)_2(dppe)_2$ (R_3 = $(OEt)_3$, Cl_3 or $MeCl_2$). ^{57}Fe Mössbauer spectra indicated a trans configuration. Reaction of either $Fe(H)(SiPh_3)(CO)_4$ or $Fe(SiCl_3)_2(CO)_4$ with PPh_3 resulted in displacement of the silyl group and the formation of $Fe(CO)_4(PPh_3)$. Metallation of $(C_5H_5)(CO)_2FeSiHRCl$ (R = Me, Cl) by $[(C_5H_5)(CO)_2Fe]Na$ in cyclohexane yields the complexes $[(C_5H_5)(CO)_2Fe]_2SiHR$, which are rapidly converted to the chlorides $[(C_5H_5)(CO)_2Fe]_2SiClR$ by CCl_4.

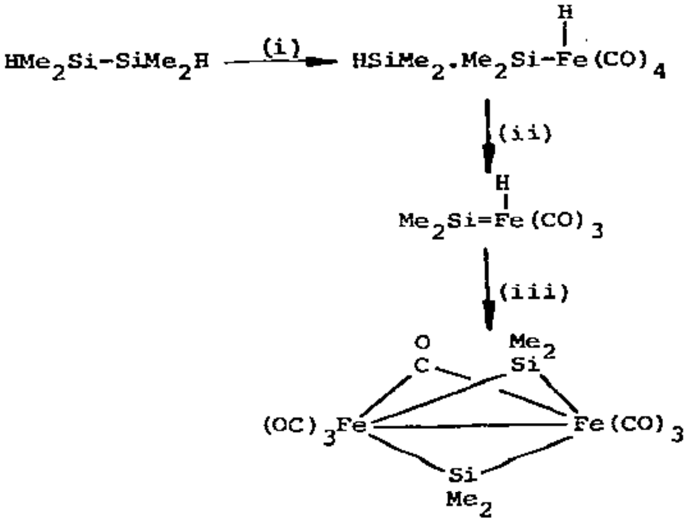
The latter may be transformed into the corresponding fluorides using $AgBF_4$.[275] The photolysis of dimeric $[(CO)_4FeSiRR']_2$ produces $Fe_2(CO)_7(SiRR')_2$ (R_2 = Me_2, ClMe) complexes.[276] The 1,2-disilacyclohexadiene (<u>95</u>) reacts with either $Fe(CO)_5$ or $Fe_2(C))_9$ to afford the corresponding (diene)$Fe(CO)_3$ complex, which undergoes a novel ring-contraction at 160° to produce (<u>96</u>):[277]



(<u>95</u>) (<u>96</u>)

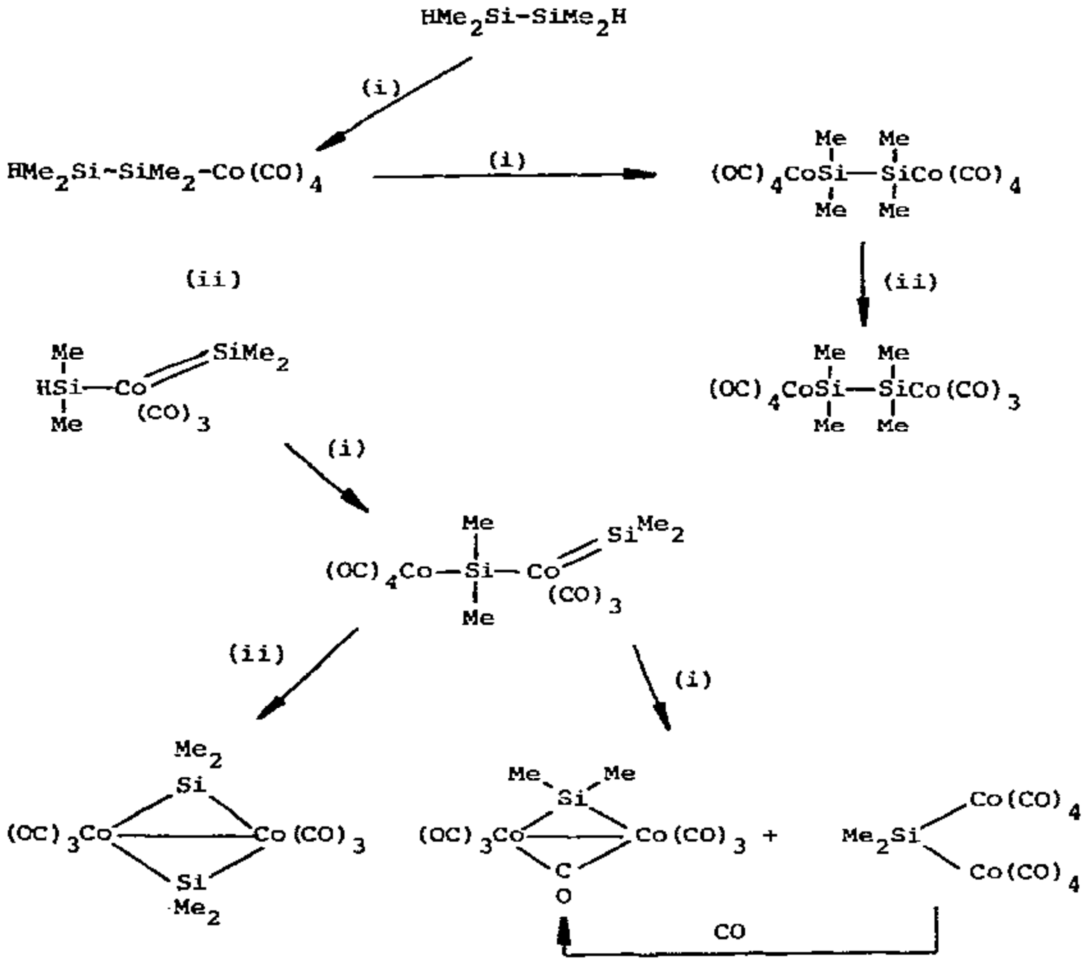
(i) $Fe(CO)_5$ or $Fe_2(CO)_9$; (ii) 160°.

The reaction of $HMe_2SiSiMe_2H$ with $Fe_2(CO)_9$ and $Co_2(CO)_8$ give, respectively, (<u>97</u>) and (<u>98</u>). Spectroscopic data in the latter case indicate <u>inter alia</u> the formation of (tetramethyldisilyl)-tetracarbonylcobalt, μ-(dimethylsilylene)-μ-carbonyl-bis(tri-carbonylcobalt)-(Co-Co) and cobalt cluster compounds.[278]



(<u>97</u>)

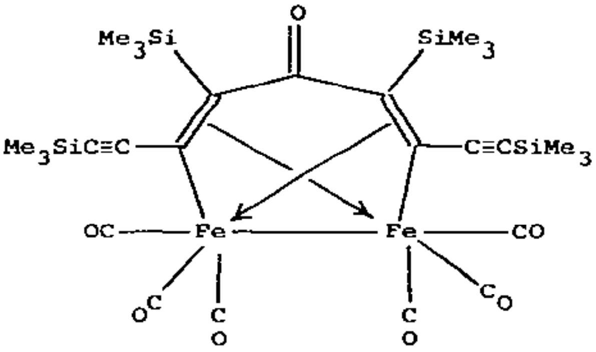
(i) $Fe_2(CO)_9$, $-Fe(CO)_5$; (ii) -CO ; (iii) $HFe(CO)_4$; $-H_2$.



(98)

The photochemical reaction of bis(trimethylsilyl)butadiyne with $Fe(CO)_5$ in benzene affords the red complex (99), whose structure was confirmed by X-ray diffraction.[279]

The 1:1 reaction between $Mn(CO)_5^-$ and $(GeH_3)_2Fe(CO)_4$ gives a near quantitative yield of $(GeH_3)Fe(CO)_4[Mn(CO)_5]$.[280] Complexes of the type $[CoH(X_2)L_3]$ (X = H or N; L = $PPPh_3$) react with silanes to afford the silylcobalt(III) complexes $[Co(H_2)(SiR_3)(L_3)]$ (R_3 = F_3, MeF_2 or $(OEt)_3$). With CO, the cobalt(I) complex $Co(SiF_3)(CO)_2L_2$ is formed. The stability of the silyls to loss of R_3SiH decreases as the electronegativity of R decreases, which



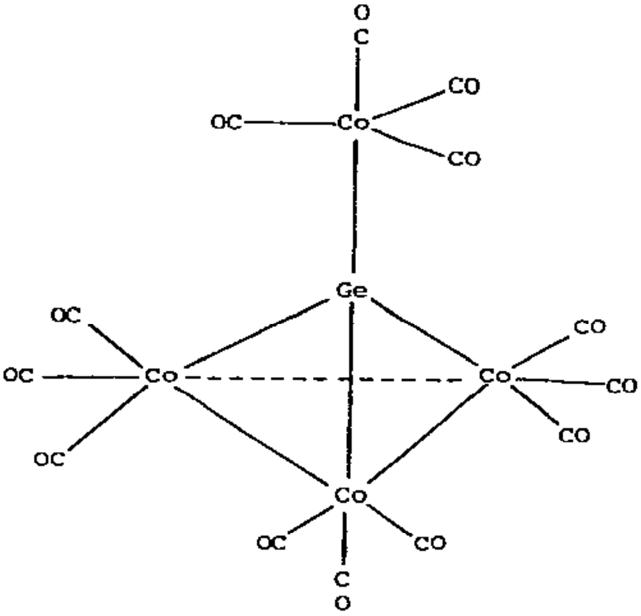
(99)

allows the less stable complexes to participate in catalytic processes. The reactions of R_3SiH with D_2, of $HSi(OEt)_3$ or $Me_3Si[OSi(H)Me]_nOSiMe_3$ with EtOH, and of $HSi(OEt)_3$ with hex-l-ene are catalysed by the complexes $Co(H)(X_2)L_3$ and $Co(H_2)\{Si(OEt)_3\}L_3$.[281]

Methylgermane and $MeGeH_2Co(CO)_4$ each undergo a complex reaction with $Co_2(CO)_8$ to yield $MeGeCo_3(CO)_{11}$ as the principal product. $MeGeCl_3$ and $MeGeBr_3$ react at room temperature with $NaCo(CO)_4$ to give stepwise $MeGeX_2Co(CO)_4$ and $MeGeX[Co(CO)_4]_2$. Further reaction is slight.[282,283] Thermolysis of $MeGeCo_3(CO)_{11}$ at 80° proceeds by loss of CO to the germylidenetricobalt nonacarbonyl cluster, $MeGeCo(CO)_9$.[283] The room temperature reaction of $NaCo(CO)_4$ with halogermanes, or of $Co_2(CO)_8$ with GeH_4, gives $GeCo_4(CO)_{14}$ which was assigned from infrared evidence a $Ge[Co_2(CO)_7]_2$ structure with the germanium acting as a common bridge replacing one CO in each of two $Co_2(CO)_8$ units. This species eliminates one CO at 50° to afford $(CO)_4CoGeCo_3(CO)_9$, and adds a further $Co(CO)_4^-$ to give anionic $[Ge-Co_6(CO)_n]^{2-}$.[284] X-ray diffraction studies of $(CO)_4CoGeCo_3(CO)_9$ show it to have an analogous structure (<u>100</u>) to its methylidene and silylidene analogues,[285] whilst a tin analogue, $MeSnCo_3(CO)_9$, has been obtained from the reaction of Me_2SnCl_2 and $Co_2(CO)_8$ in benzene.[286]

The Group (IV) metal-substituted phosphines, $(Me_3M)_3P$ (M = Si, Ge, Sn), react with $Me_3SnCo(CO)_4$ and $Co_2(CO)_8$ to yield complexes $Me_3SnCo(CO)_3L$ and $Co_2(CO)_6L_2$ (L = $Me_3M)_3P$), respectively.[287,288]

The nickel complexes, $M^INi(PPh_3)_3(EPh_3)$.xthf (E = Ge, Sn, Pb)

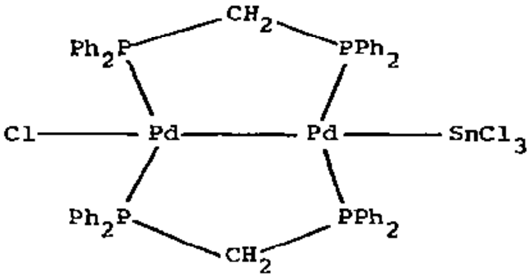


(100)

and $M^{I}{}_3Ni(PPh_3)(EPh_3)_3.xthf$ (E = Ge, Sn) have been formed from $(Ph_3P)_2Ni(C_2H_4)$ by substitution with $M^{I}EPh_3$. The analogous Ph_3Si-compounds could not be prepared because of the reaction of Ph_3SiLi with PPh_3 to give Ph_4Si. Attempts to synthesise triphenylstannylnickel(II) complexes failed also, and only the decomposition products from such syntheses ($Ni^{II}(Pb)Cl(PBu_2Ph)$ and $Na_xNi^{O}(PPh_3)_{4-x}(SnPh_4)_x.ythf$) were isolated. Ph_3SnNa reacted with $(PPh_3)_3CoCl$ to give $NaCo^{I}(PPh_3)_2(SnPh_3)_2.7thf$.[289]

Tin(II) chloride inserts into a Pd-Cl bond of $Pd(Ph_2PCH_2PPh_2)Cl_2$ yielding (101), the crystal structure of which has been determined. The Pd-Pb-Sn unit is nearly linear. Infrared and electronic spectra indicate that CO and SO_2 insert into the Pd-Pb bond of the complex.[290]

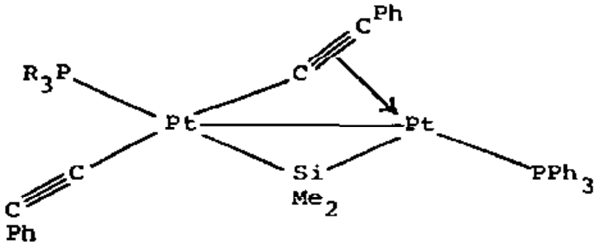
The mutual influence of the ligands in trans-$[HPtX(PPh_3)_2]$ and trans-$[XPt(SnX_3)(PPh_3)_2]$ (X = Cl, Br) has been studied by infrared, n.m.r. and Mössbauer. It was deduced that the order of trans influence increased as $Cl^- < Br^- << SnBr_3^- < SnCl_3^-$, and that



(101)

$SnBr_3^-$ is a strong σ-donor and a slightly stronger π-acceptor than $SnCl_3^-$.[291] The complexes trans-[$PtH(SnCl_3)(PR_3)_2$] (R = Et,Ph) exhibit an exceedingly large two-bond tin-proton coupling of ~1700Hz, the largest ever recorded.[292] The catalytic activity of $PtCl_2$-$SnCl_2$-phosphine complexes is dramatically enhanced when diphosphine ligands, which are capable of forming a strained seven-membered chelate ring, are used. The most active found was trans-1,2-bis(diphenylphosphinomethyl)cyclobutane, which afforded hexanals (n/iso = 99/1) from pent-1-ene with a much higher reaction rate than $HRh(CO)(PPh_3)_3$.[293]

The complexes, trans-[$Ir(CO)X(PEt_3)_2$] (X = Cl, I) form the 1:1 adducts [$Ir(CO)H(X)(PEt_3)_2(MH_2Cl)$] with the silanes and germanes MH_3Q (M = Si, Q = H, Cl, Br, I, Me, SiH_3; M = Ge, Q = H, Cl, Br, I). When M = Si, the major (and in most cases the only) product has H trans to Si, whereas when M = Ge the major (and in some cases only) product has H trans to X. When X = Cl and Q = Br or I, halogen exchange takes place, and the silyl adduct contains chlorine bound to silicon and the heavier halogen bound to indium. When M = Ge, however, the adduct formed initially contains chlorine bound to indium and bromine or iodine bound to germanium, although the latter adduct decomposes in solution at room temperature.[294] The reaction of the triplatinum complex, [$Pt_3(CN^tBu)_6$] with silanes, R_3SiH (R_3 = Me_3, Et_3, Me_2Ph, $MePh_2Si$, Ph_3Si or $(EtO)_3$) leads to the formation of the diplatinum complexes [$Pt(CH{=}N^tBu)(SiR_3)(CN^tBu)$]$_2$, arising from the insertion of an isocyanide ligand into a Pt-H bond formed in an initial oxidative-addition step. Reaction with Ph_3SiH also afforded the bis-silyl complex, $Pt(SiPh_3)_2(CN^tBu)_2$. The structures of the adducts were confirmed by an X-ray diffraction study of $[Pt(CH{=}N^tBu)(SiMePh_2)$-$(CN^tBu)]_2$. Reaction of $[Pt_3(CN^tBu)_6]$ with Me_3GeH yielded the germanium analogue.[295] The dialkynylsilane, $Me_2Si(C{\equiv}CPh)_2$ reacts with $[Pt(C_2H_4)_2(PR_3)]$ ($PR_3 = P(C_6H_{11})_3$, PMe^tBu or PPr_2Ph) to afford the diplatinum complexes (102). Again, the structures were confirmed by an X-ray diffraction study of one example (102; PR_3 $P(C_6H_{11})_3$.[296]

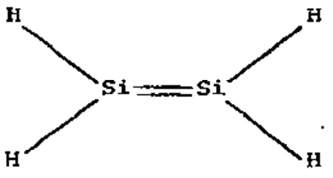


(102)

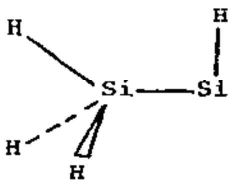
Aryltrimethylstannanes, Me_3RSn (R = aryl), function as arylating agents towards *cis*-$[Pt(O_2CCF_3)_2(PR_3)_2]$ complexes to afford the aryl-platinum complexes, *cis*-$[PtR_2(PR_3)_2]$, except for sterically-hindered trimethyl(mesityl)tin which gives mainly *trans*-$[PtMe(O_2CCF_3)(PR_3)_2]$. The latter complex is also the main product from trimethyl(benzyl)tin. For R = Ph, Me_3PhSn and $Me_3SnC_6H_4Me$-*p*, the principal product is *cis*-$[PtMe(O_2CCF_3)(PPh_3)_2]$. The most reactive tin compound towards aryl-group transfer was trimethyl-(2-thienyl)tin, which readily reacts with *cis*-$[Pt(O_2CCF_3)L_2]$ (L = $PPhMe_2$ or PEt_2Ph) or $Pt(COCl)(O_2CCF_3)$ to give exclusively, *cis*-$[Pt(C_4H_3S\text{-}2)_2L_2]$ or $[Pt(COCl)(C_4H_3S\text{-}2)_2]$.[297]

4.2.12 Unstable Silicon Intermediates

Ab initio M.O. studies of HNSi[298] and Si_2H_4[299,300] have been carried out. That of HNSi have shown the optimum geometry to be linear with Si-N = 1.557Å and N-H = 0.997Å.[298] The two studies of Si_2H_4 are at variance. In one, where the electronic structure of the molecule was discussed in terms of a Mulliken population analysis, describes the geometry as the disilene (103) with a Si-Si bond distance of 2.15Å.[299] In the other, using a 4-31 Gaussian basis set, it was suggested that the electronic ground state structure correspond to a singlet silylsilylene (104), with Si-Si = 2.408Å and Si-Si-H = 92.1°, rather than the planar disilene expected by analogy with ethylene.[300]

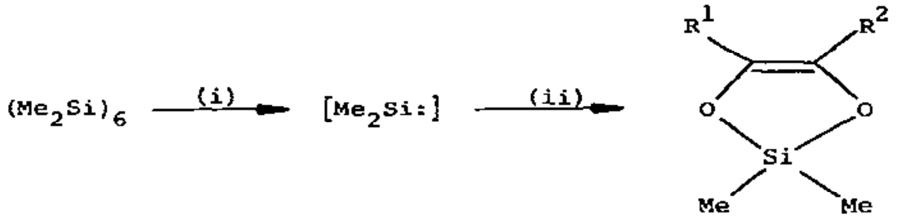


(103)



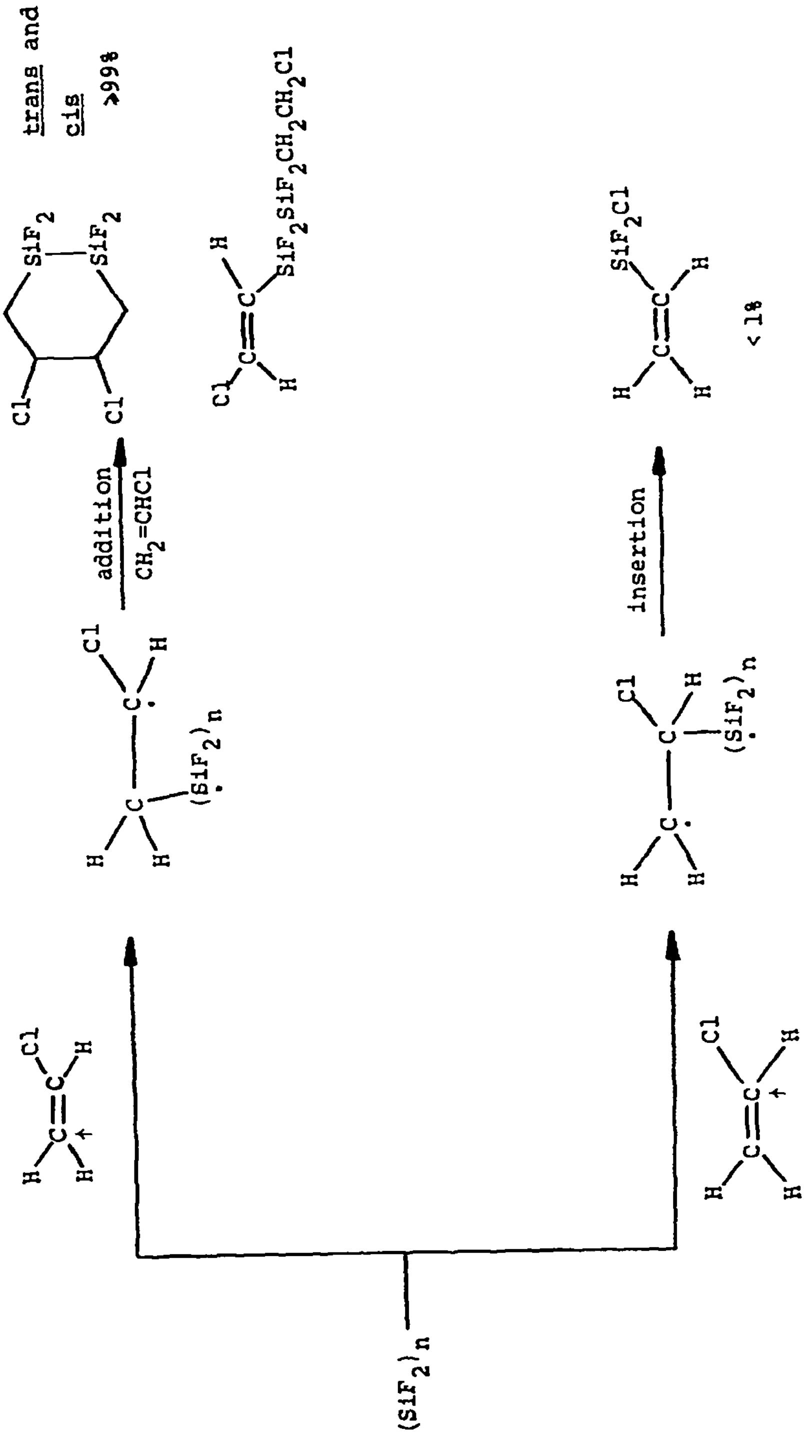
(104)

Irradiation of solutions of dodecamethylcyclohexasilane in rigid hydrocarbon glasses (3-methylpentane, methylcyclohexane, or decalin) at 77K, or in argon at 10K, produces $(Me_2Si)_5$ and bright yellow dimethylsilylene, $Me_2Si:$, which can be trapped by Et_3SiH, bis(trimethylsilyl)ethyne and 1-hexene. It is noteworthy that dimethylsilylene is indefinitely stable in such hydrocarbon glasses at 77K, thus permitting its use as a preformed reagent.[301] Photolysis of $(Me_2Si)_6$ in the presence of biacetyl, penta-2,3-dione, bis-*n*-butyryl, bis-*iso*-butyryl or 3,5-di-*t*-butyl-*o*-benzoquinone results in the formation of substituted 1,3-dioxa-2-silacyclopent-4-enes:[302]



(i) hν ; (ii) $R^1CO.COR^2$.

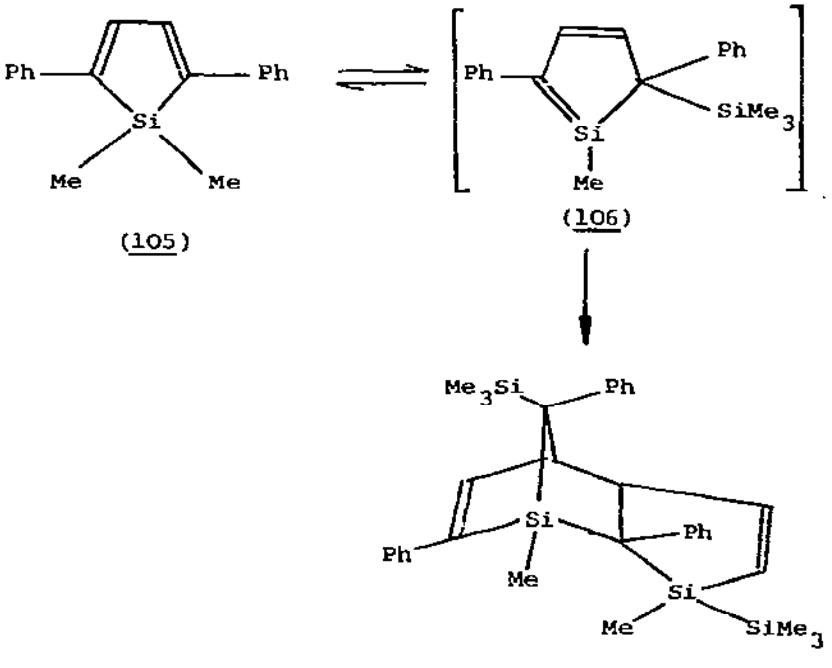
Cocondensation of SiF_2 and vinyl chloride at -196° results in the formation of products of either ring-closure of hydrogen-migration of a diradical intermediate (Scheme 3). The ring-closure process results in *cis* and *trans* isomers of 4,5-dichloro-1,1,2,2-tetrafluoro-1,2-disilacyclohexane. The difference between addition and insertion processes most probably reflects the very large difference in the preference of initial radical attack on the two


(SiF$_2$)$_n$
addition
CH$_2$=CHCl
insertion
trans and
cis
>99%
< 1%
SiF$_2$SiF$_2$CH$_2$CH$_2$Cl
SiF$_2$Cl

Scheme 3.

sides of the double bond. Silirane or silirene intermediates do not have to be invoked to rationalise the mechanism.[303]

Of continuing interest are intermediates in which silicon forms double bonds (or their equivalent) with itself and other elements. Barton and his coworkers[304] have characterised a Si=C double-bonded intermediate formed via a 1,5-sigmatropic migration of a Me_3Si group from silicon to carbon. Heating the silole (105) in a sealed tube for 9 hours at 150° afforded a clean mixture of (105) and (107), rationalised by the formation of (106) which in turn undergoes Diels-Alder addition with (105). That in fact an equilibrium is involved is demonstrated by the observation that heating either (105) or (107) at 150° for more than 20 hours produces essentially the same equilibrium mixture.

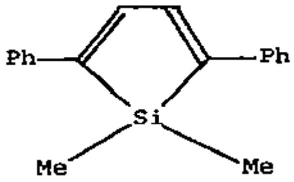


(105)

(106)

(107)

In contrast, the dimethylsilole (108) was unchanged even after heating at 150° for 16 hours.



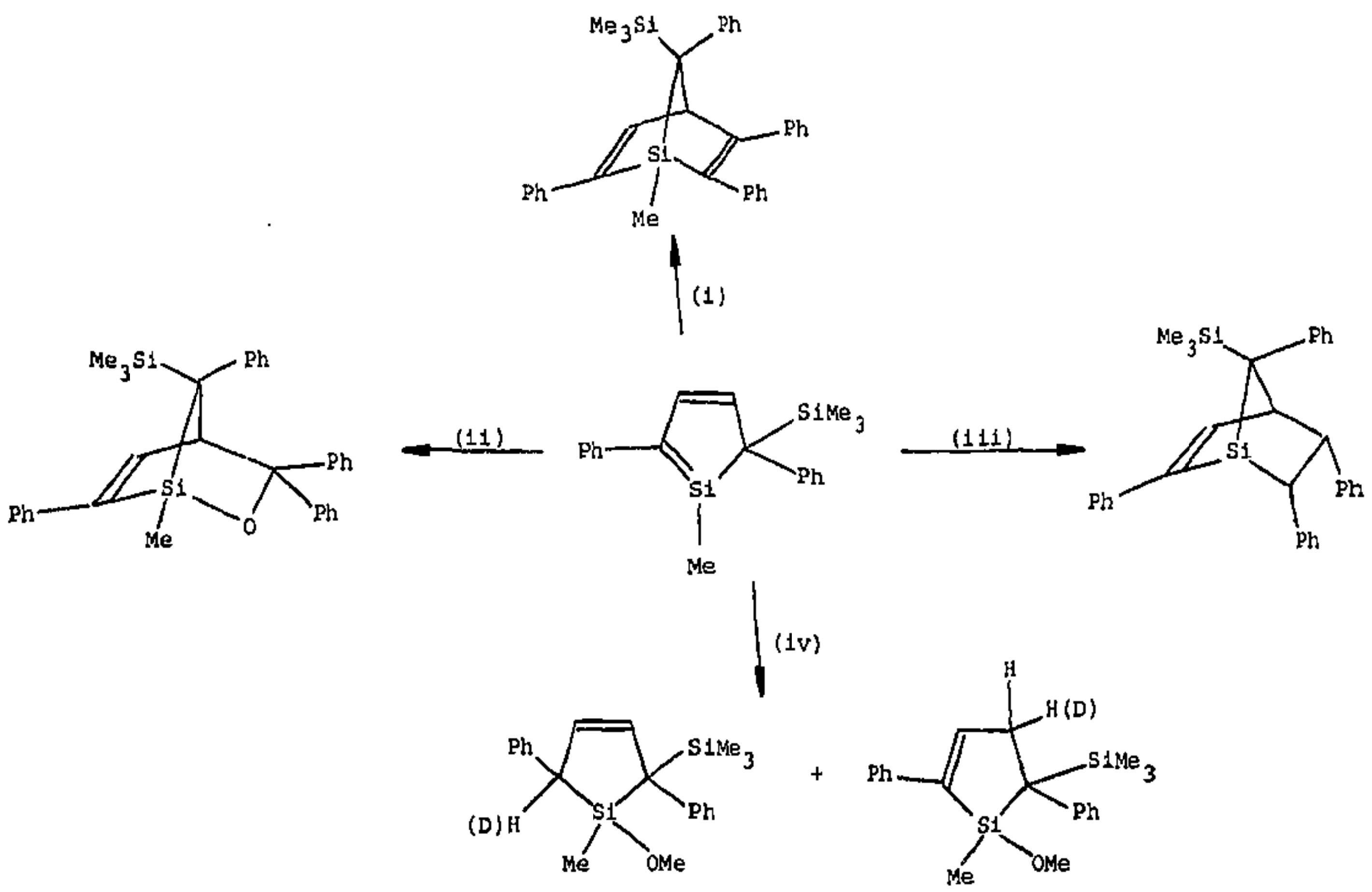
(108)

The Si=C intermediate (106) is present in equilibrium concentration, and can be trapped by the addition of other dienophiles such as diphenylacetylene, benzophenone, cis-stilbene, and methanol (Scheme 4).

The photolysis of acyldi- and acylpolysilanes at about 360nm affords silaethylenes (109) which are relatively stable, and can be trapped with methanol, dienes and alkynes. In the absence of trapping agents, the silaethylenes undergo 'head-to-tail' dimerisation to yield 1,2-disilacyclobutanes (110)(Scheme 5). The silaethylenes (109) have quite moderate lifetimes, especially when the group R is bulky, and can be absorbed using n.m.r. Thus, when R = ^{t}Bu, the silaethylenes could be observed over a two-week period as it slowly reverted to the acylsilane.[305,306]

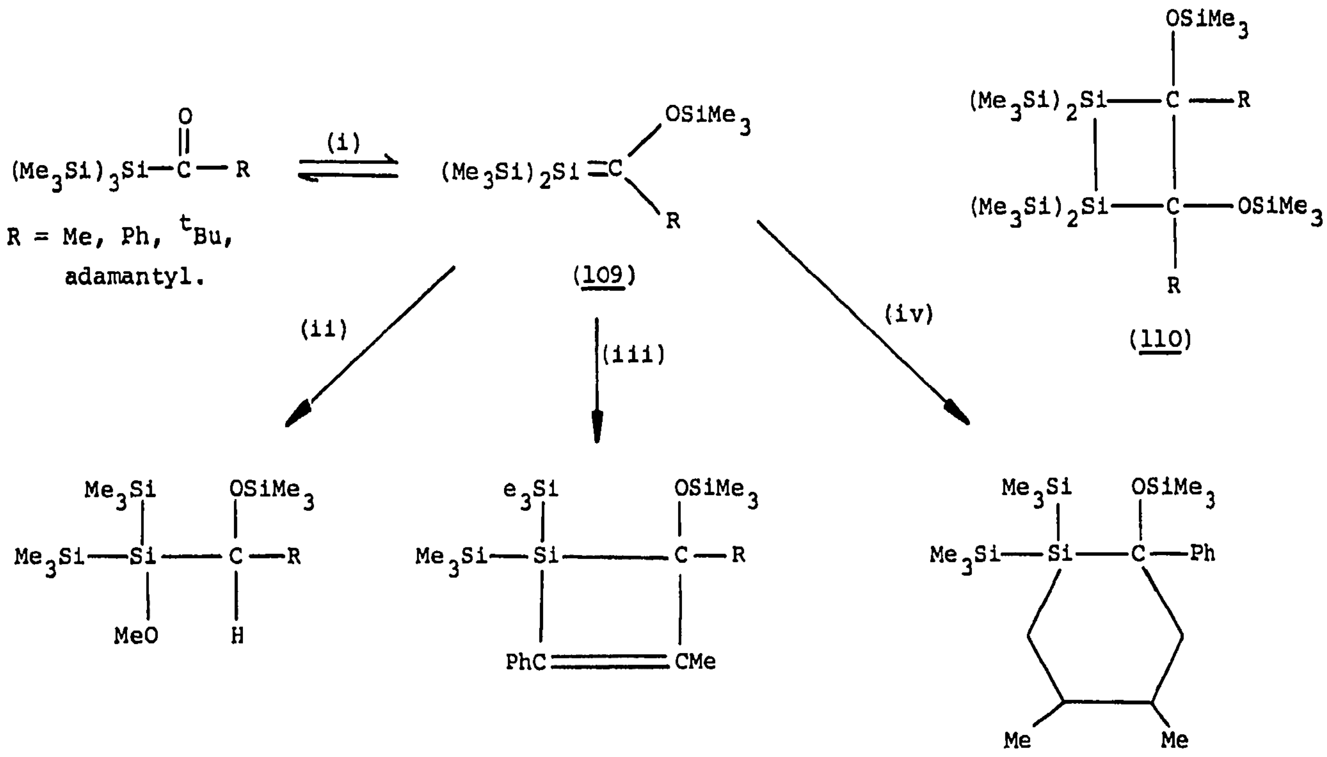
The sila-α-pyran (111) is a convenient precursor for dimethylsilanone, $Me_2Si=O$, generation. When heated at 60° in the presence of hexafluorobut-2-yne, the intermediate (112) is formed, which quickly decompose even at room temperature to bis(trifluoromethyl)benzene and the silanone, which may be trapped by the usual types of trapping agent.[307]

Sakurai and his coworkers[308] have provided aveidence for restricted rotation around (double-bonded nature of) the Si=Si bond in 1,2-dimethyl-1,2-diphenyldisilene. Reaction of the cis- and trans-cyclodisilahexadienes (113) with benzyne yielded the two adducts (114) and (115), which, when pyrolysed in the presence of anthracene, afforded near quantitative(>94%) stereospecificity in the formation of the adducts (116) and (117), indicating restricted rotation around the Si=Si bond in the disilenes (118) and (119). The stereospecificity is quite remarkable since 1,2-diphenyl-1,2-dimethyldisilene produced by the dimerisation of methylphenylsilylene gives a 1:1 mixture of (118) and (119) on reaction with anthracene.



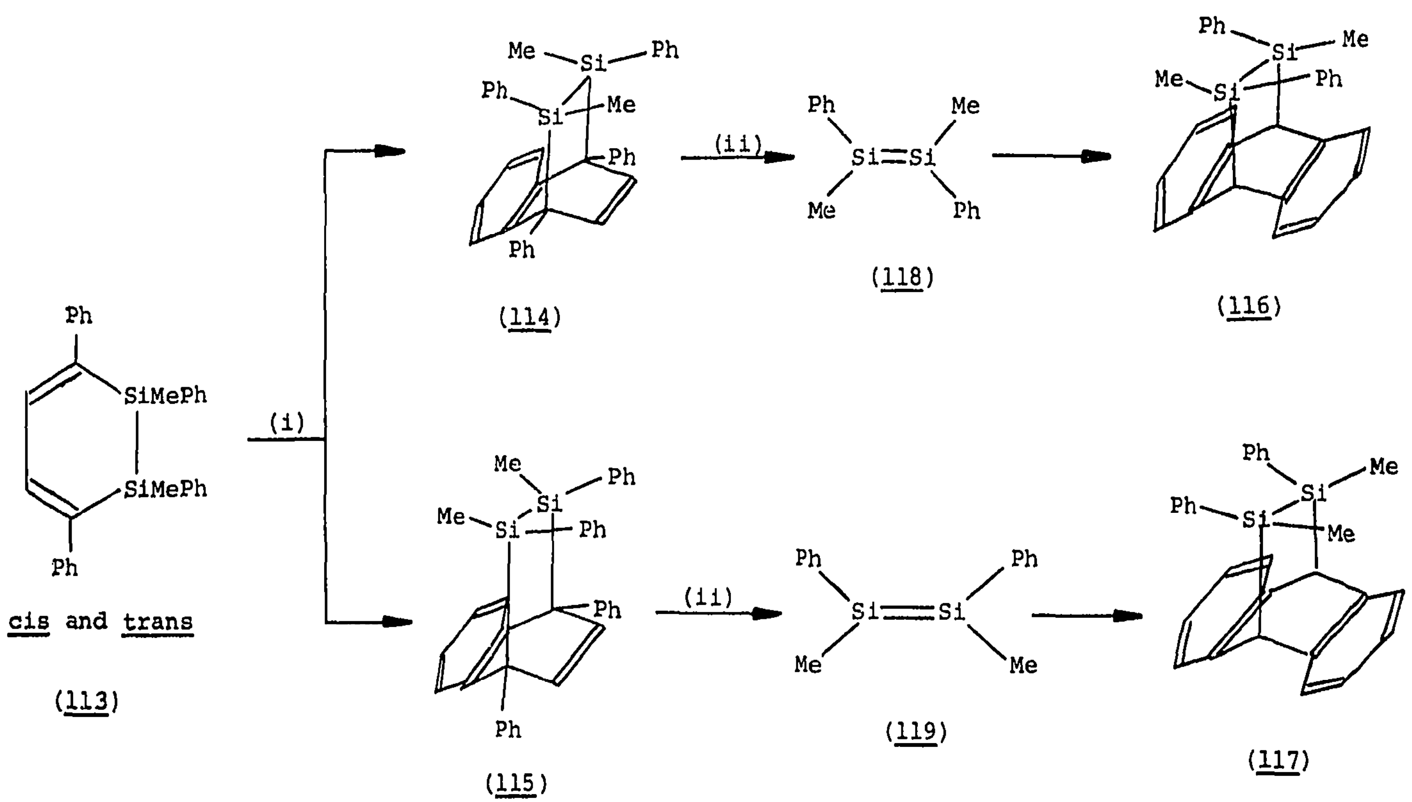
(i) PhC≡CPh, 12hr, 150° ; (ii) $Ph_2C=O$, 10hr, 150° ; (iii) cis-stilbene, 26.5hr, 150°, quantitative ; (iv) MeOH(D), 3hr, 146°, benzene.

Scheme 4.



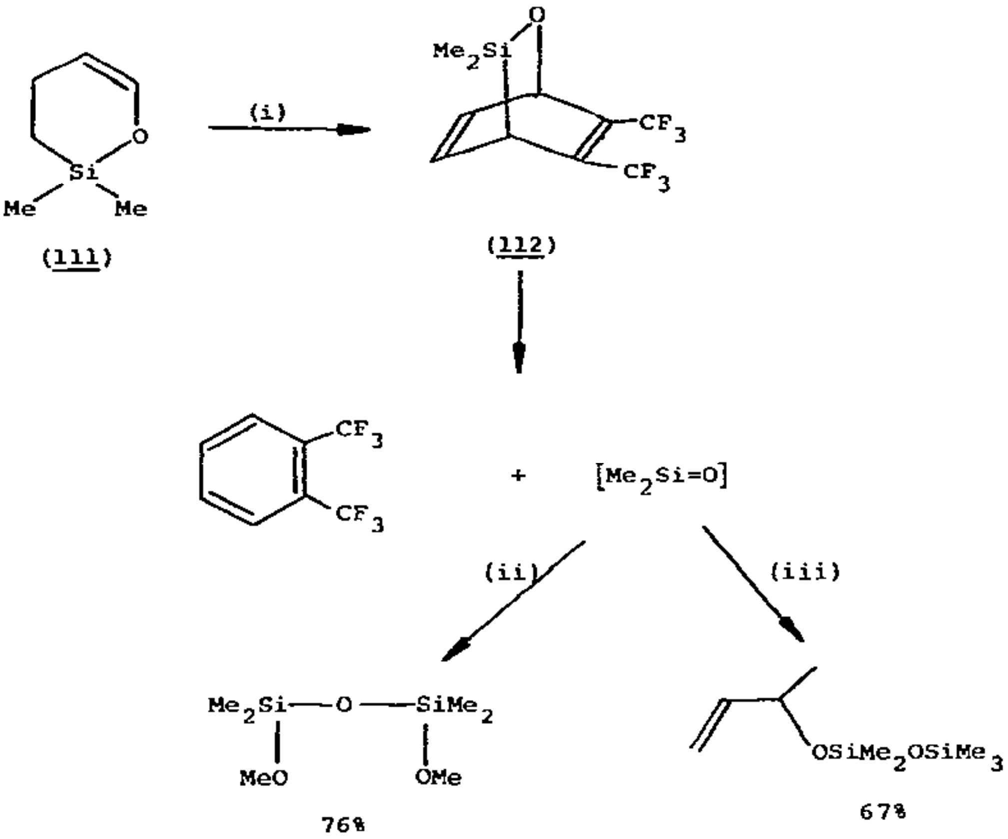
(i) hν ; (ii) MeOH ; (iii) PhC≡CMe ; (iv) 2,3-dimethylbutadiene.

Scheme 5.



(i) benzyne (derived from benzene diazonium-2-carboxylate in thf).
(ii) thermolysis at 300° (sealed tube) in the presence of anthracene.

Scheme 6.



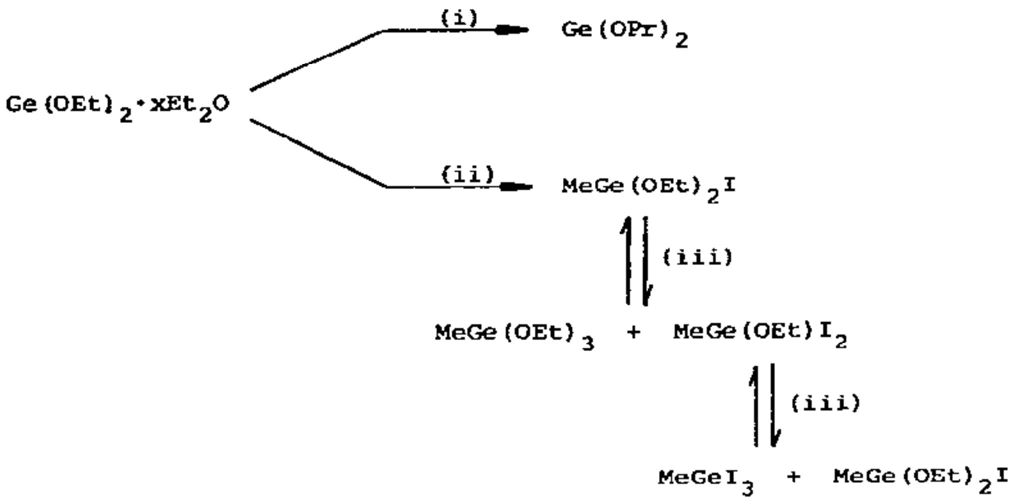
(i) CF_3C CCF_3, 60°, 6hr ; (ii) $Me_2Si(OMe)_2$; (iii) trimethylsiloxy-1-butene.

4.2.13 Bivalent Compounds of Germanium, Tin and Lead

Highly pure SnIBr has been obtained by heating a mixture of $SnBr_2$ and SnI_2 in an evacuated glass ampoule. The compound has a melting point of 252±1°, and has a primitive orthorhombic lattice.[309] The conditions of the formation of PbI_2 from lead metal and gaseous iodine have been studied, and the vapour pressure of PbI_2 determined in the range 627-877°. The enthalpy of volatilisation of liquid PbI_2, ΔH_{vol}, was calculated to be 31.7 kcal mol^{-1}.[310] The structure of gaseous $GeCl_2$, produced by the reaction of Ge and $GeCl_4$ at 660°, has been studied in a combined electron diffraction/mass spectrometry experiment. As expected, isolated molecules are bent (Ge-Cl = 2.183(4)Å; Cl-Ge-Cl = 100.3(4)°).[311] In the structure of $Sn_2Br_{0.65}Cl_{3.35}\cdot 3H_2O$, each tin atom has a pyramidal, three-coordinate environment, and the crystals consist of cationic $[SnBr_{0.15}Cl_{0.85}(H_2O)_3]$ layers and anionic $[SnBr_{0.5}Cl_{2.5}]$ layers parallel to the [100] plane.[312] With the exception of the chloro compounds, the coloured Perovskites $(MeNH_3)[Pb_nSn_{1-n}X_3]$ (X = Cl, Br, I) exhibits electrical conductivity which increases with increasing tin(II) content. Their physical properties may be interpreted in terms of a 'p-resonance' bonding. Replacement ot tin(II) by lead(II) and iodine by chlorine or bromine decreases this bonding effect, which is produced by the interaction of filled halogen p-orbitals with empty p-orbitals on the metal(II) atoms.[313] Crystals of $[Co(NH_3)_6][Pb_4Cl_4]$ contain two crystallographically independent lead atoms, which are both coordinated by six chlorine atoms in a distorted trigonal prismatic fashion with a seventh chlorine above one of the rectangular faces of the prism. Neighbouring prisms share corners thereby forming a three-dimensional network held together by $[Co(NH_3)_6]^{3+}$ cations.[314]

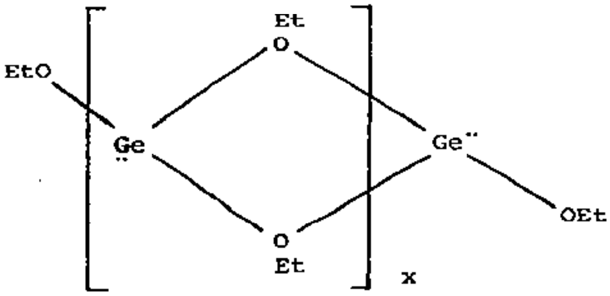
Cocondensation of ethylene and tin vapour in an argon matrix yields species in which tin is bonded to the ethylene via the π-system of the alkene. The analogous experiment with ethylene and SnF_2 is more complicated, with side reactions producing a tin(IV) species, elemental tin and SnF_2-polymerisation products $(SnF_2)_x$. However, bands are also observed in the infrared spectrum assignable to a bent SnF_2 species complex bound to ethylene, again by π-electron donation from ethylene to tin(II).[315] Vicinal dinitro compounds react with $SnCl_2$ in polar solvents to give the corresponding alkenes in good yield.[316] The "1:1 adducts" formed between $^tBu_3P$ and germanium(IV) and tin(IV) bromides have been shown to be ionic $[^tBu_3PBr]^+MBr_3^-$ (M = Ge, Sn) salts.[317]

Germanium(II) bis(ethoxide), generated in solution by the reaction of GeI_2 with sodium ethoxide, may be stabilised in hydrocarbon solution as an ethanolate by the presence of small amounts of the alcohol. As such, it can be used as an intermediate in transesterification and oxidative-addition reactions:



(i) *n*-propanol; (ii) MeI; (iii) redistribution.

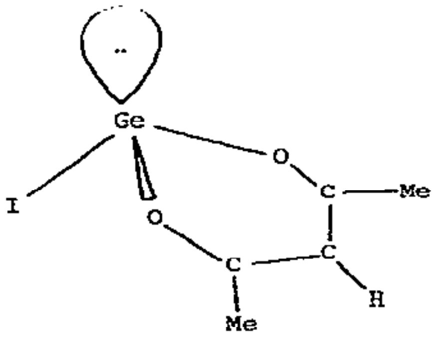
In vacuo, the ethanolate loses ethanol giving a solid which was assigned the polymeric structure (120).[318]



(120)

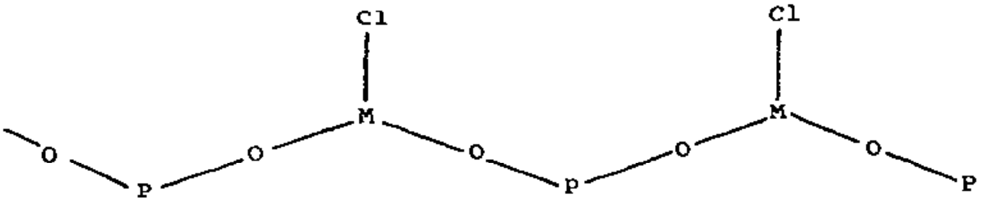
Crystals of Ge(acac)I comprise monomeric units in which the acac ligand chelates germanium rather unsymmetrically (121) (Ge-O = 1.914(5), (1.931(5)Å). The bond angles fall in the range 91.38 - 93.92°.[319]

Chloro(phosphinato)germanium(II) and -tin(II) are isostructural, with the metal atoms lying at the apices of trigonal bipyramids. Each is bonded to one chlorine atom and to two oxygen atoms of



(121)

different $[H_2PO_2^-]$ groups giving infinite chains (122) parallel to the c axis. Weak secondary bonding cross-links the chains.[320]



M = Ge, Sn.

(122)

The decomposition of (isostructural) tin(II) hydrogen phosphate and hydrogen arsenate proceeds according to:[321]

$$2SnPO_4 \xrightarrow{(i)} Sn_2^{II}P_2O_7 \xrightarrow{(ii)} Sn^{IV}P_2O_7 + SnO_2$$

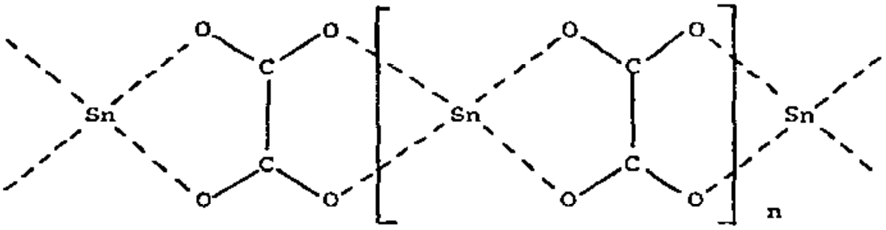
(i) 200-300°, $-H_2O$; (ii) 700-800°.

$$\begin{tikzcd} 2SnHAsO_4 \arrow[r, "(i)"] & 2SnO\cdot As_2O_4 \arrow[r, "(ii)"] & SnO\cdot As_2O_3 \arrow[d, "(iii)"] \\ & & SnO_2 \end{tikzcd}$$

(i) 175-250°, $-H_2O$;

(ii) 460-500°, $-\frac{1}{2}O_2$; (iii) 760-840°, $-As_4O_6$, $+\frac{1}{2}O_2$.

The structures of three carboxylato-tin(II) derivatives have been determined. Tin(II) oxalate forms infinite chains in which tin atoms and oxalato groups alternate (123). Each oxalate group chelates two tins forming five-membered chelate rings in each case; the Sn-oxalate-Sn fragment is essentially planar. Each tin atom in turn is chelated by two oxalate groups, so that its coordination is similar to that in tetragonal, blue-black tin(II) oxide. Weak Sn...O bonds (2.87(1)Å) link neighbouring chains. In dipotassium bis(oxalato)stannate(II) monohydrate, the primary coordination is similar to that found in tin(II) oxalate although the site symmetries differ. Infinite chains are also a feature of the complex oxalate, but in this case the chains contain discrete bis(oxalato)tin(II) anions linked by hydrogen-bonds to water molecules (124).[322] Crystals of potassium tris(monochloroacetato)-stannate(II), $K[Sn(O_2CCH_2Cl)_3]$, comprise discrete $Sn(O_2CCH_2Cl)_3^-$



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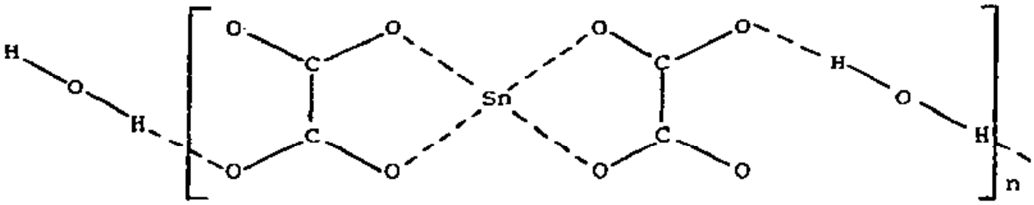
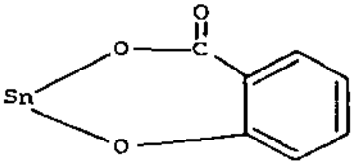


(124)

anions and K^+ cations. The tin atoms are in distorted trigonal bipyramidal sites (Sn-O = 2.14, 2.18, 2.18Å), with distorted octahedral coordination being completed by three further oxygens at 2.92, 2.97 and 3.05Å.[323]

Honnick and Zuckerman[324] have prepared tin(II) heterocycles such as tin(II) salicylate (125) and *o*-biphenylenedioxytin(II) (126) by ligand-exchange between the dibutyltin(IV) derivatives and tin(II) chloride in acetone. The transformation of the room-temperature *N*-form of $PbSO_4$ to the high temperature cubic H-form has been observed using the Guinier technique. The non-quenchable *H*-modification crystallises with the α-$NaClO_4$-type lattice.[325]



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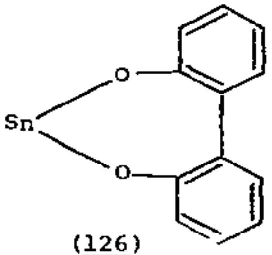
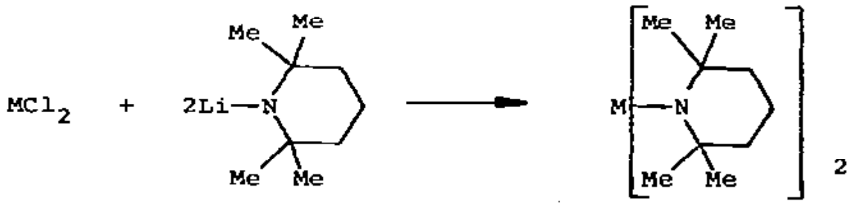


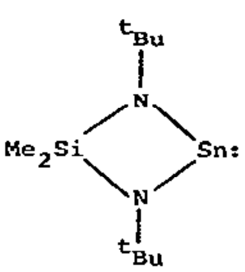
(126)

Electron diffraction studies on gaseous $Sn|N(SiMe_3)_2|_2$ shows only the monomer to be present at *ca.* 100° and 10^{-2} atmos. The molecule has C_{2v} symmetry with a NSnS bond angle of 96.0° and $Sn\text{-}N_{av}$ = 2.09Å. Several new germanium(II)- and tin)II)-nitrogen compounds have been synthesised. Reaction of the lithium derivative of 2,2,6,6-tetramethylpiperidine with $GeCl_2$·dioxan or $SnCl_2$ in pentane yields the coloured, crystalline germanium(II) and tin(II) derivatives (127), which furnish the 2,2,6,6-tetramethylpiperidyl radical on photolysis:[326]



M = Ge, Sn.

1,3-Di-t-butyl-2,2-dimethyl-1,3,2,4λ²-diazasilastannetidine (128) undergoes quantitative cleavage with t-butylamine at 50° in benzene to give, according to the molar ratios, the tricyclic cage, $Me_2Si(N^tBu)_2Sn_2(N^tBu)$ (129), or the seco-norcubane-like molecule $Sn_3[(N^tBu)(NH^tBu)_3]$ (130), plus $Me_2Si[NH^tBu]_2$. (130) can be readily converted tothe complete "cubane", $Sn_4(N^tBu)_4$ (131) (240°, 5 torr).[327]



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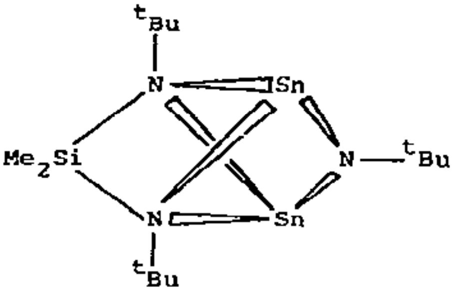

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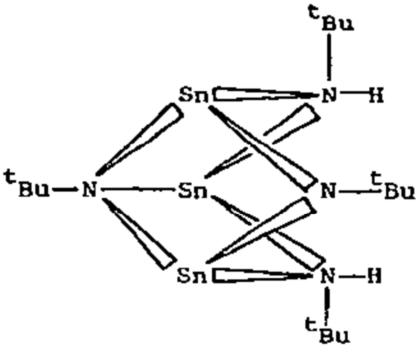

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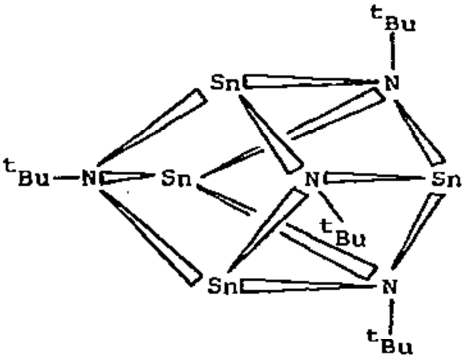


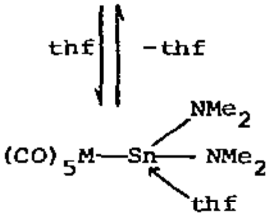
(131)

The presence or otherwise of colour in aminotin(II) compounds has been discussed by Corvan and Zuckerman.[328] The colouration arises when the aminotin(II) compounds are monomeric and two-valent, i.e. when bridging or coordination of solvent is absent. Those compounds which are coloured invariably have bulky substituents on the nitrogen atoms. Thus $\{(Me_3Si)_2N\}_2Si$, $(Me_3SiNC_6H_4Me\text{-}p)_2Sn$, and $(Ph_2N)_2Sn$ are an intense red colour, but the adduct of $\{(Me_3Si)_2N\}_2Si$ with pyridine is colourless, whilst in the cyclic aminotin(II) derivatives, polymeric bis(aziridyl)tin(II) and dimeric $Sn(NMe_2)_2$

are both colourless. A tensimetric titration of $Sn(NMe_2)_2$ with BF_3 has shown that a 1:3 adduct is formed in which the Lewis acid complexes with the lone pairs on both nitrogen atoms and the tin. The adduct is a very air-sensitive white solid which does not melt sharply, but begins to decompose at 190°. Spectra of solutions of 1:1 and 1:2 molar ratios suggest that the initial site of BF_3 coordination is the tin and subsequent coordination occurs at nitrogen.[329] Dimeric $[Sn(NMe_2)_2]_2$ also reacts with photochemically-generated $N(CO)_5{\cdot}thf$ (M = Cr, Mo, W) complexes to afford dimeric nitrogen-tin ylide complexes (132):

$$2M(CO)_5{\cdot}thf \;+\; [Sn(NMe_2)_2]_2 \longrightarrow [(CO)_5MSn(NMe_2)_2]_2$$

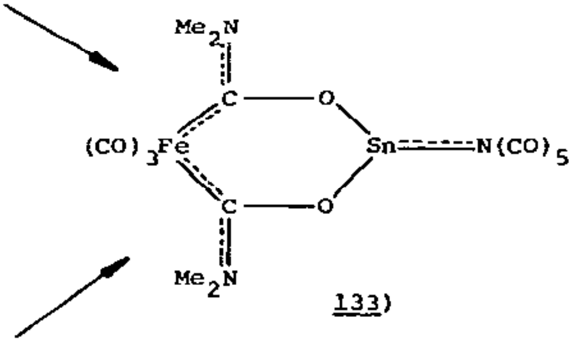
(132)



M = Cr, Mo, W.

With $Fe(CO)_5$, the complex (133) is formed, which may also be obtained from $(CO)_3Fe(CONMe_2)_2Sn$ and $Cr(CO)_5{\cdot}thf$:[330]

$[(CO)_5MSn(NMe_2)_2]_2 \;+\; 2Fe(CO)_5$

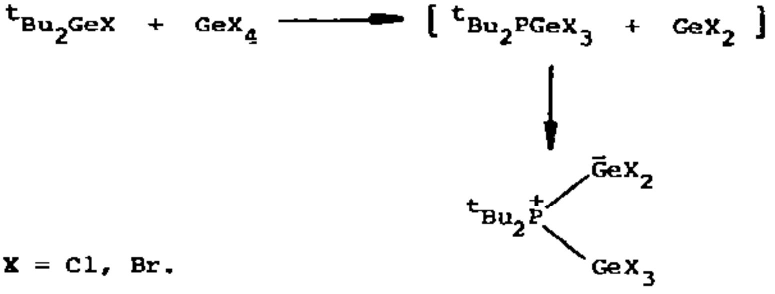


M = Cr, Mo, W.

133)

$(CO)_3Fe(CONMe_2)_2Sn \;+\; Cr(CO)_5{\cdot}thf.$

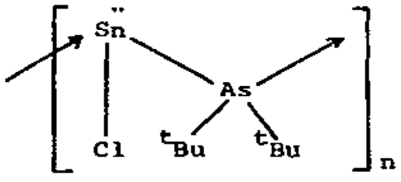
Di-t-butylphosphinogermanium(II) chloride and bromide react with the corresponding germanium(IV) halide in aromatic hydrocarbons with transfer of the phosphino group from germanium(II) to germanium(IV) followed by coordination of the germylene, GeX_2, to phosphorus to give (134):



X = Cl, Br.

(134)

Evidence of coordination came from ^{31}P n.m.r. data. With dioxane, an exothermic reaction produced Bu_2PGeX_3 and $GeX_2 \cdot$dioxane, whilst PPh_3 gave $^tBu_2PX$ and $Ph_3\overset{+}{P}\overset{-}{G}eX_2$.[331] The pentacarbonyl(di-*t*-butylarsinochlorostannio)chromium(0) and -tungsten(0) complexes, $(CO)_5MSnClAs^tBu_2$ (M = Cr, W) have been obtained by the reaction of $(OC)_5M{-}SnCl_2 \cdot$thf and $Me_3SiAs^tBu_2$. The complexes were thought to have an arsino-bridged structure (135) similar to that proposed for the parent compound, $ClSnAs^tBu_2$ (136).[332] The tin-119 Mössbauer spectra for these and the analogous phosphino complexes have been recorded. Coordination at the tin lone pair decreases the isomer to 2.1 0.2 mm s^{-1} and increases the quadrupole splitting, the values of which reflect the highly associated nature of the complexes.[333]



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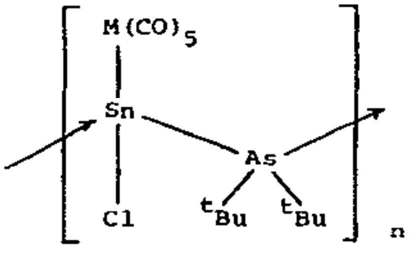
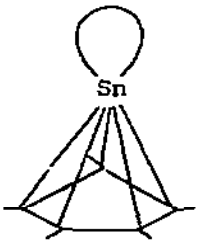


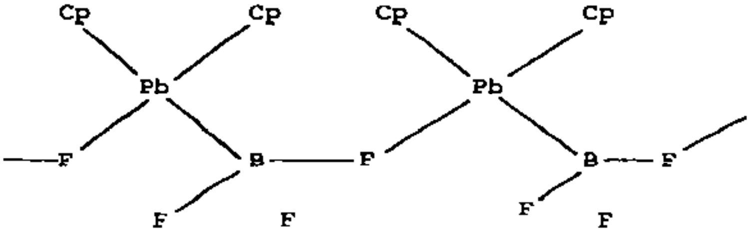
(136)

Although several more reactions of dicyclopentadienyltin(II) and -lead(II) have been reported, the most significant advance in this area is the characterisation of the *nido* cluster, $[Me_5C_5Sn^+]$ (137). This has been obtained as its tetrafluoroborate by the reaction of bis(pentamethylcyclopentadienyl)tin(II) with HBF_4. The colourless crystalline needles are air- and moisture sensitive, and rapidly turn violet on exposure to daylight, but no decomposition took place over several weeks in the dark at -20^o. The tin-carbon bond distance in the cation is significantly shorter (2.462(16)Å) than in either $(C_5H_5)_2Sn$ (2.71Å) or in C_5H_5SnCl (2.61Å).[334,335]



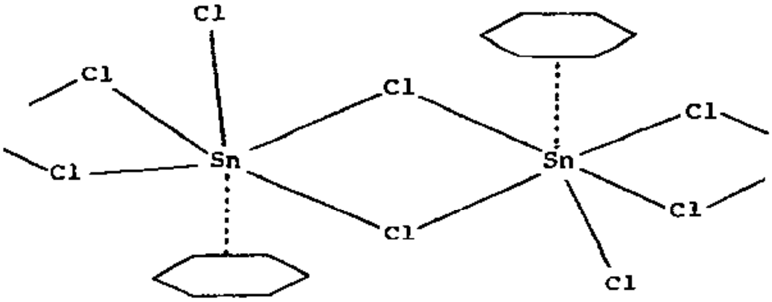
(137)

Dicyclopentadienyltin(II) reacts with pentamethylantimony to afford $2[Me_4Sb^+][(C_5H_5)_4Sn^{2-}]$, - the first example of an anionic organotin(II) species. Me_5Sb and tin(II) chloride do not give similar organotin(II) anions such as $MeSnCl_2^-$ or $Me_2SnCl_2^{2-}$, but rather $[Me_4Sb^+][SnCl_3]$ is formed. ^1H n.m.r. data suggest the occurrence of rapid cyclopentadienyl group exchange between LiC_5H_5 and $Sn(C_5H_5)_2$ in solution, but no evidence for the formation of $Li^+Sn(C_5H_5)_3^-$ was obtained, and $Sn(C_5H_5)_2$ was recovered on remaoval of the solvent.[336] Dicyclopentadienyllead(II) reacts with BF_3 to yield a thermally-stable polymeric 1:1 adduct considered to have structure (138). Weaker Lewis acids such as Me_3B, $(Me_3Al)_2$ or Ph_3B did not react. Other metal chlorides including BCl_3, Al_2Cl_6, $TiCl_3$, VCl_3O and $TaMe_3Cl_2$ reacted by cyclopentadienyl-chlorine ligand exchange. Organic π-acids such as tetracyanoethylene and tetracyanoquinodimethane afforded the complexes $(C_5H_5)_2Pb{\cdot}n$tcne (n = 0.5, 1) and $(C_5H_5)_2Pb{\cdot}$tcnq.[337]



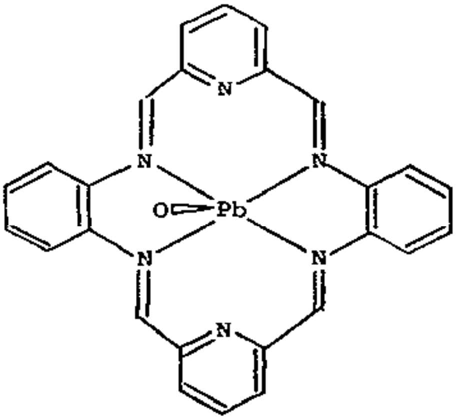
(<u>138</u>)

Full details of the structures of the two chloro(π-aryl)tin(II) tetrachloroaluminates, (π-Ar)ClSn(AlCl$_4$) (Ar = C_6H_6, p-$Me_2C_6H_4$). Both contain the $Sn_2Cl_2^{2+}$ unit as the central feature of the structure, which is composed of these units interconnected by bridging $AlCl_4^-$ groups to give infinite chains extending along the [001] direction. The coordination polyhedron of tin is completed by interaction with adjacent tetrachloroaluminate groups, and with the π-orbitals of the arene to give a distorted octahedron (<u>139</u>). The tin(II) atom lies on a line perpendicular to the arene ring and passing through its centre with approximately equal tin-carbon distances (Ar = C_6H_6: Sn-C = 3.05(2) - 3.30(2)Å; Ar = p-$Me_2C_6H_4$: Sn-C = 2.92(1) -3.27(2)Å).[338]



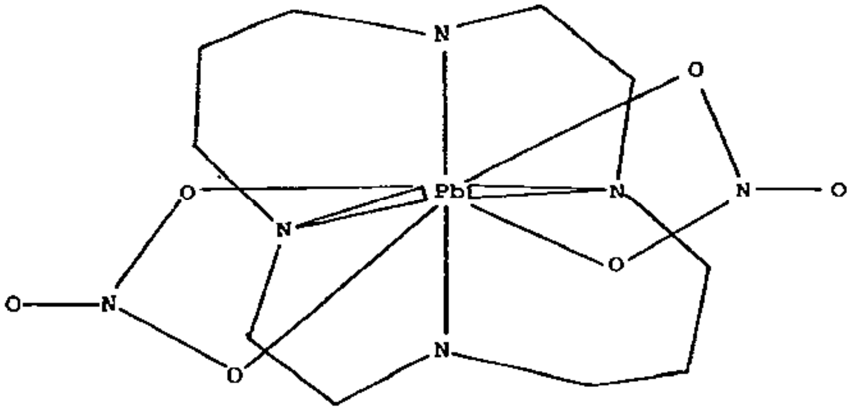
(<u>139</u>)

Electronic and vibrational spectra have been employed to study layers of tin(II) phthalocyanine having different polycrystalline structures and different spectral characteristics. The samples examined were a supported ground powder, a sublimate in a vacuum on a support at room temperature, a sublimate in a vacuum on a support at high temperature, and a sublimate obtained in the presence of air. For the sublimates obtained in a vacuum, the molecules are arranged approximately parallel to the support, whereas in the sublimate obtained in the presence of air and in the ground sample they lie at an angle to the support.[339] Lead(II) salts act as templates for the cyclic condensation of organic dicarbonyl compounds with a variety of polyfunctional diprimary amides to yield macrocyclic Schiff base ligands in moderate-to-good yields. Three types of macrocyclic lead(II) complex have been synthesised by this method: mononuclear complexes of 15- and 17-membered quinquedentate N_5 and N_3S_2 ligands, binuclear complexes of 18-membered sexidentate N_3O_3 and N_2O_4 ligands, and binuclear complexes of a 30-membered decadentate N_6O_4 ligand. The coordination number of lead in the complexes varies between five and eight, and depends on the nature of the anions present as well as the nature of the macrocycle.[340] The lead(II) complex of the nitrogen analogue of [18]-annulene $PbL(ClO_4)_2.2H_2O$, prepared by condensation of two moles of 2,6-diformylpyridine and two moles of o-phenylene diamine in MeOH or MeCN, comprises $[Pb(L)(OH_2)]^{2+}$ cations (140) and perchlorate anions. In the cation the metal is bonded to all six nitrogen atoms, and the water molecule occupies an axial position of a distorted hexagonal pyramid. The macrocycle is not quite planar. The lone pair is probably stereochemically active in the other axial position.[341]



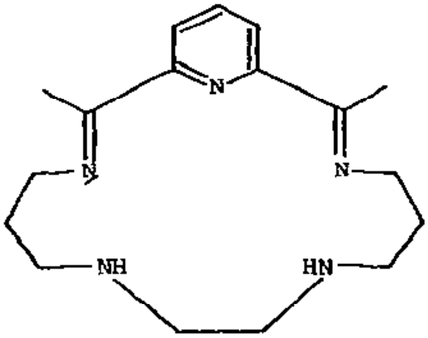
(140)

The two complexes, $[PbL][NO_3]_2$ (L = L_a = 1,4,8,11-tetraazacyclotetradecane; L = L_b = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) have been studied by n.m.r. in DMSO solution. Complex $[PbL_a][NO_3]_2$ adopts a cis-octahedral geometry with a folded macrocyclic ligand, a geometry which was confirmed by an X-ray study and showed the anisobidentate nitrate groups occupied cis positions (141). The asymmetry in the coordination is probably caused by the lone pair on lead. The n.m.r. data also reveal the occurrence of high-temperature dynamic conformational changes. The dynamic process occurring at low temperature is interpreted as an intramolecular rearrangement between two identical cisoid structures, whilst the differing coupling constants observed for axial and equatorial nitrogen atoms ($^1J(^{207}Pb - {}^{15}N)$ = 19.8 and 207.5 Hz) is believed to be a consequence of the axial distortion found in the crystal. When L = L_b, the complex is not very stable in DMSO, and macrocycle exchange occurs at room temperature.[342,343]



(141)

Lead is six-coordinated in the complex $[Pb(L)(SCN)]^+SCN^-$ (L = $C_{17}H_{27}N_5$ (142)), being bonded to five nitrogen atoms of the quinquevalent macrocycle and a sulphur atom of the thiocyanate. Again the geometry of the coordination sphere around lead is indicative of lone pair stereochemical activity.[344]



(142)

The reaction of $Pb(NO_3)_2$ and $K_4[Fe(CN)_6]$ yields $Pb_2[Fe(CN)_6]$ and $K_2Pb[Fe(CN)_6]$ as sparingly soluble products.[345] ^{14}N n.q.r. studies of the complex salts $MPbCu(NO_2)_6$ (M = K, Tl, Rb, NH_4) have been reported.[346]

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