Coordination Chemistry Reviews, 75 (1986) 200—296
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

Chapter 4

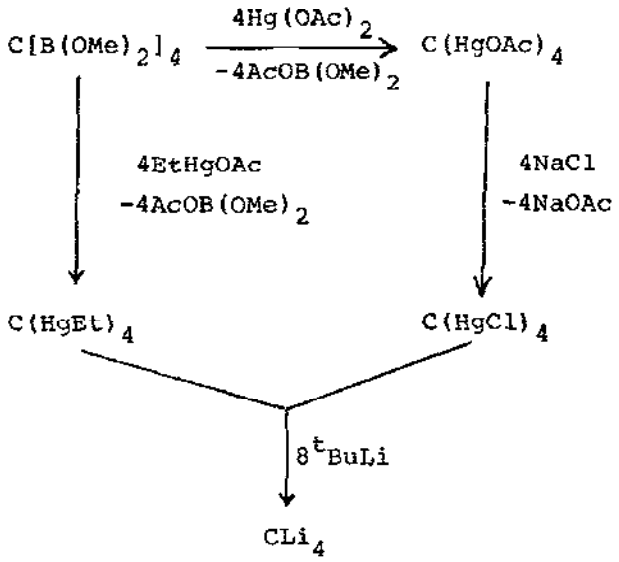
ELEMENTS OF GROUP 4

P.G.Harrison

4.1 CARBON

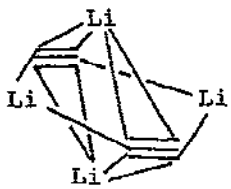
Electron density analysis shows that singlet CH_2Li_2 structures are largely C^-Li^+ in character with a small amount of three-centre bonding. Three centre bonding is, however, less important for triplet structures, which have instead a significant degree of Li-Li bonding. The anomalous reversed dipole moment of the triplet results from decreased positive charge placed on the lithium atoms due to charge transfer into a Li-Li bonding orbital. To a useful approximation, triplet CH_2Li_2 may be modelled in part as a simple summation of triplet methylene and Li_2.[1] Improved methods for the synthesis of tetralithiomethane have been described. The best results are obtained if tetrakis(chloromercurio)methane or tetrakis(ethylmercurio)methane are treated with excess tert-butyllithium. The latter precursor yields a deep red-brown solution in cyclopentane, rather than a suspension, which may be quasi-titrated with dimethyl disulphide in hexane at -50°C yielding tetrakis(methylthio)methane. Perdeuteriomethane is formed on treatment with D_2O (Scheme 1).[2] Bis(trimethyl)dilithio-

0010-8545/86/$33.95



Scheme 1

methane, $(Me_3Si)_2CLi_2$, and (trimethylsilyl)dilithiomethane, $(Me_3Si)CHLi_2$, have been synthesised by the reaction of lithium vapour with $(Me_3Si)_2CCl_2$ and $Me_3SiCHCl_2$, respectively, at 700-720°C.[3] Examination of the potential energy surface of C_4Li_4 using ab initio SCF and RMP_2 calculations has indicated that the most stable isomer is the novel tetralithiodiacetylene, (1), of D_{2h} symmetry, which lies 73.9 kcal mol^{-1} below two molecules of dilithio acetylene.[4]



(1)

Several papers report developments in fluorocarbon chemistry. Halogenoperfluoroalkanes such as CF_3Br and CF_2Cl_2, normally considered rather inert, undergo substitution by potassium arylsulphides in glass apparatus at room temperature when a pressure of about two atmospheres is applied (cf. the little reaction obtained when the reaction is performed in an autoclave

at 80°C). The products are the fluoro(aryl)sulphides, $ArSClF_3$ and $ArSOF_2Cl$ (major). Inhibition experiments with nitrobenzene show that a radical chain mechanism is involved (Scheme 2).[5]

$$ArS^- + CF_3Br \longrightarrow ArS^{\cdot} + [CF_3Br]^{\cdot -}$$

$$[CF_3Br]^{\cdot -} \longrightarrow CF_3^{\cdot} + Br^-$$

$$ArS^- + CF_3^{\cdot} \longrightarrow [ArSCF_3]^{\cdot -}$$

$$[ArSCF_3]^{\cdot -} + CF_3Br \longrightarrow ArSCF_3 + [CF_3Br]^{\cdot -}$$

Scheme 2

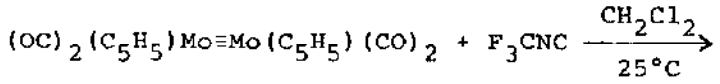
Photoelectron spectroscopic studies show that the thermal isomerisation of CF_3NC to CF_3CN requires temperatures exceeding 750°C, suggesting a considerable kinetic barrier (cf. the rather limited stability of CF_3NC is the liquid phase).[6] Attempts to synthesise N-bromodifluoromethanimine, $CF_2{=}NBr$, have at last been successful. The method involves the fluoride-promoted oxidation of $FC{\equiv}N$ by elemental bromine:[7]

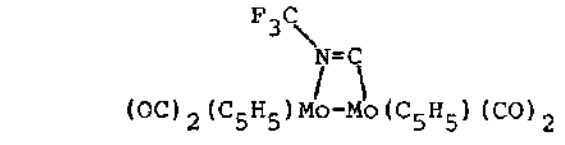
$$FC{\equiv}N + MF \rightarrow F_2C{=}N^-M^+ \xrightarrow{Br_2} F_2C{=}NBr$$

M = K, Rb, Cs.

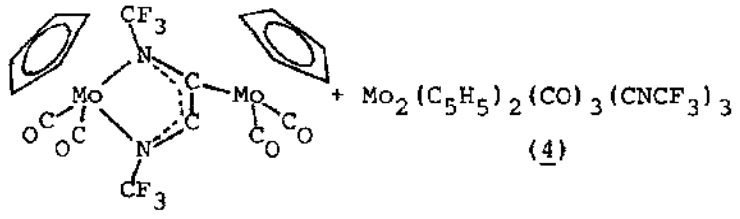
Reaction of $[Mo(\eta\text{-}C_5H_5)_2(CO)_2]_2$ with CF_3NC in a 1:1 molar ratio, leads to the formation of (2), in which the $^2\eta$-bonded isocyanide bridge ligand functions as a four-electron donor. If an excess of CF_3NC is employed, the complexes (3) and (4) are produced, the former of which has been shown to contain the hexafluoro-2,5-diaza-2,3,4-hexatriene, $CF_3N{=}C{=}C{=}NCF_3$, a molecule unknown in the free state.[8]

The heteroalkenes, $CF_3E{=}CF_2$ (E = P, As), may be obtained quite simply by the thermolysis of the stannanes, $Me_3SnE(CF_3)_2$, at 10^{-3} torr at 300-400°C. Although stable at low temperatures, or as 10% solutions in organic solvents, dimerisation, trimerisation or polymerisation can occur leading to the compounds (5)-(8).[9]

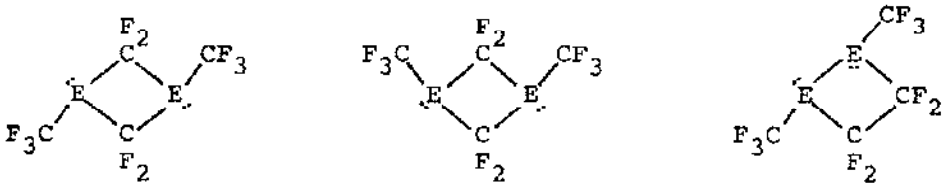




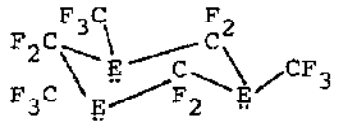
(2)



(3)



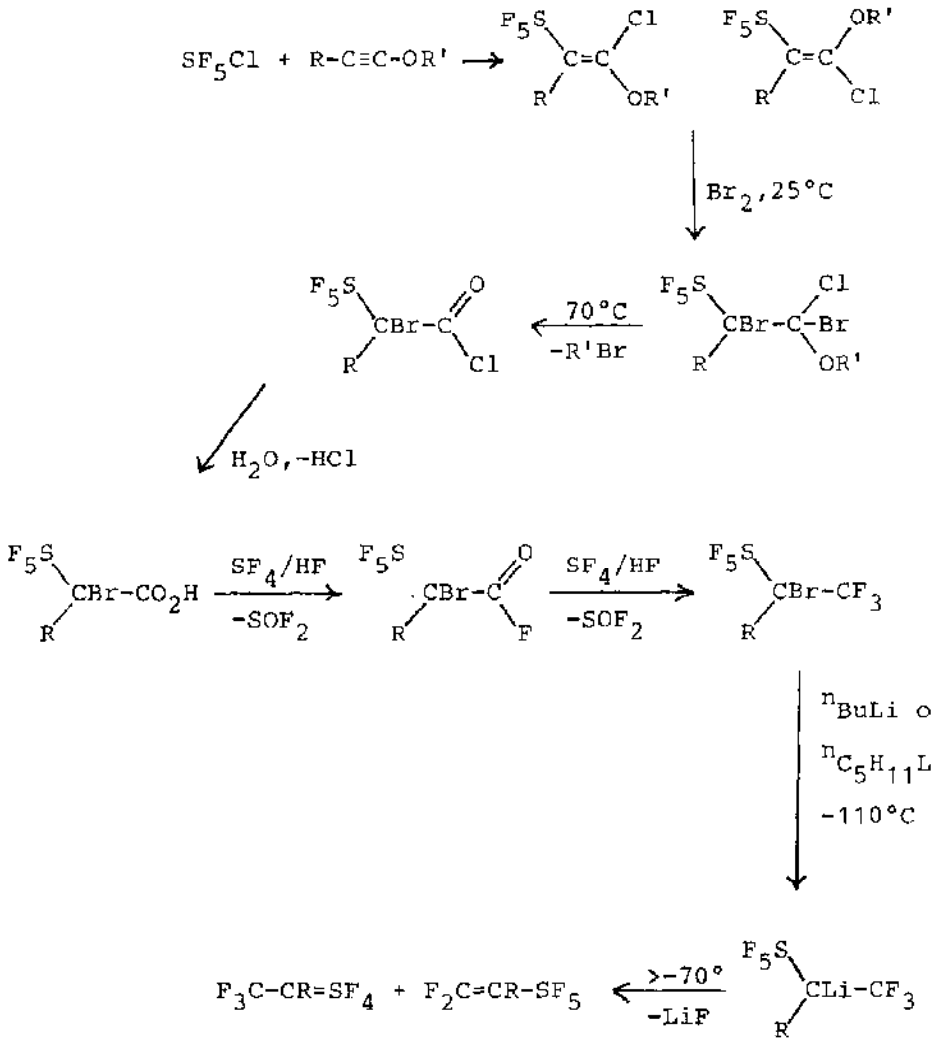
(5) (6) (7)



(8)

E = P,As.

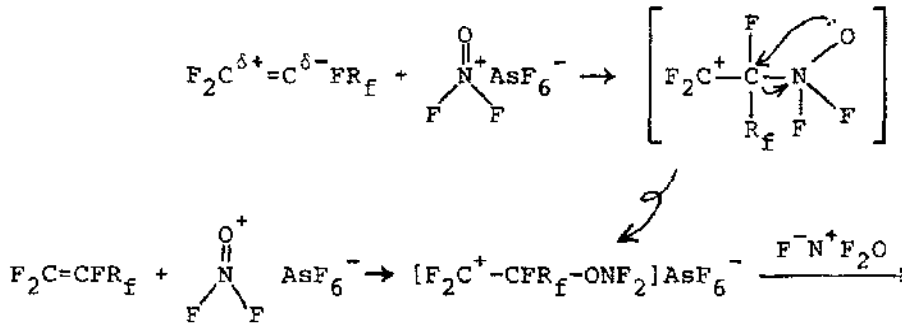
(2,2,2-Trifluoroethylidene)sulphur tetrafluoride, $CF_3CH{=}SF_4$, has been synthesised in a multistep preparation from $HC{\equiv}C{-}OR$ and SF_5Cl (Scheme 3).[10] Elimination of HF from $CF_3{-}CH{=}SF_4$ occurs practically quantitatively affording trifluoroethylidynesulphur trifluoride, $CF_3{-}C{\equiv}SF_3$, when passed through dried KOH at 50-60°C and 10^{-1} mbar. Rapid oligomerisation of the product takes place



Scheme 3

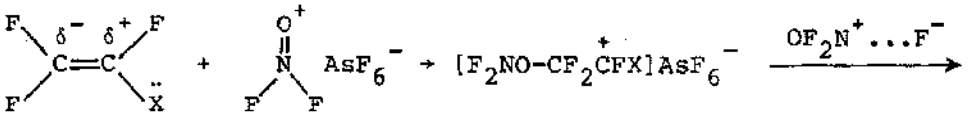
at its boiling point (-15 - -10°C).[11]

The addition of NF_3O to perfluoro-alkenes is catalysed by Lewis acids and yields the novel compounds R_fONF_2 (R_f = perfluorinated organic group). The orientation of the addition can be rationalised by an electrophilic attack of NF_2O^+ on the double bonds, perfluoroalkenes giving Markownikov products whilst perfluorovinyl ethers yield products with the opposite orientation due to the reversed polarity of the double bond:[12]



$$CF_3CFR_fONF_2 + NF_2O^+AsF_6^-$$

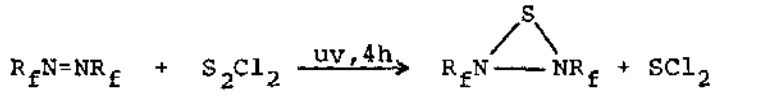
R_f = CF_3, C_5H_{11}, C(O)F, SF_5, $CF_2OCF_2CF(SO_2F)CF_3$,
$CF_2O\overline{CFOCF(CF_3)CF_2O}CF(CF_3)$



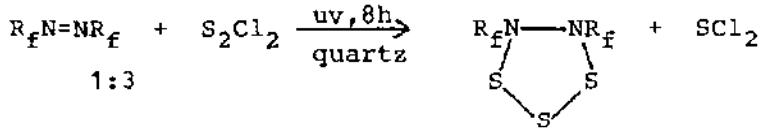
$$F_2NOCF_2CFX + NF_2O^+AsF_6^-$$

X = Cl, Br, OC_2H_5, $OCF_2CF(CF_3)OCF_2CF_2CF_3$

A new class of sulphur-nitrogen heterocycles with the general formula $R_fN\text{-}S_x\text{-}NR_f$ (R_f = CF_2Cl or C_2F_5; x = 1, 3 or 4) results from the photolysis of $R_fN{=}NR_f$ and S_2Cl_2. The products are pale yellow high-boiling liquids which decompose on standing at ambient temperature:[13]

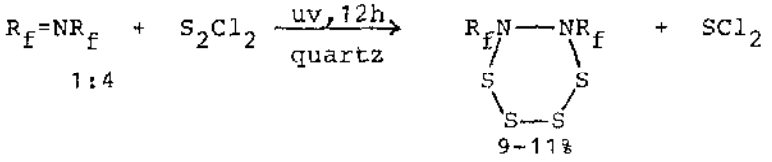


R_f = C_2F_5, CF_2Cl.



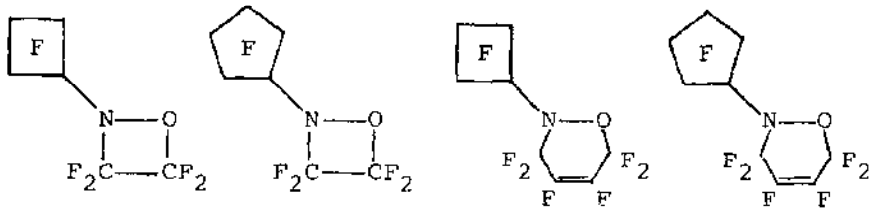
7-9%

R_f = CF_3CF_2, CF_2Cl.

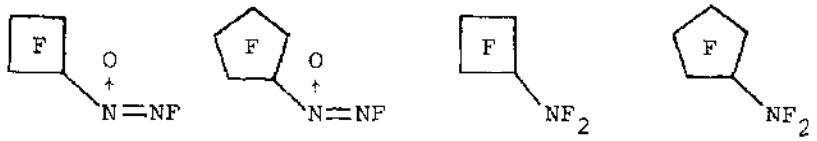


R_f = CF_3CF_2, CF_2Cl

Reaction of hexafluoro-cyclobutene and octafluorocyclopentene with nitrosyl chloride or nitrogen dioxide in the presence of KF in acetonitrile give 80% yields of the blue compounds, heptafluoro-nitrosocyclobutane and nonafluoronitrosocyclopentane, respectively. Thermal decomposition in Pyrex glass results in the formation of the analogous nitro compounds, R_fNO_2. Cycloaddition with C_2F_4 or 1,3-hexafluorobutadiene affords the oxazetidines, (5), and oxazines, (6), respectively. The products resulting from reaction with N_2F_4 depended upon the nature of the reaction vessel. In Pyrex containers, N'-fluorodiimide N-oxides, (7), are obtained, but in metal reaction vessels, the difluoroamines, (8), are produced.[14]

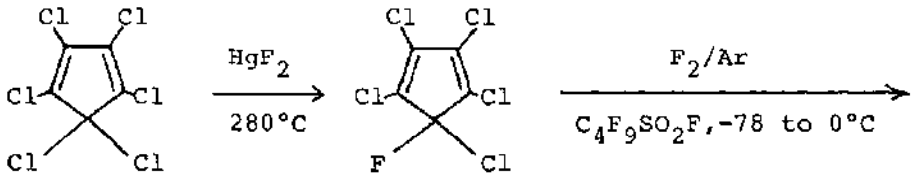


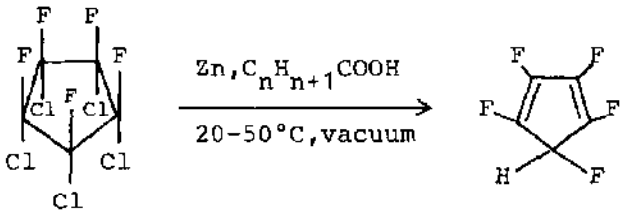
(5) (6)

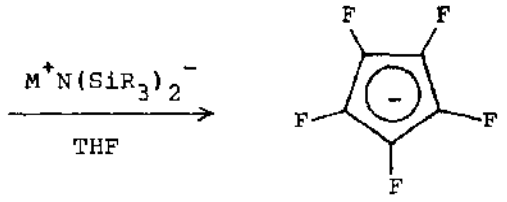


(7) (8)

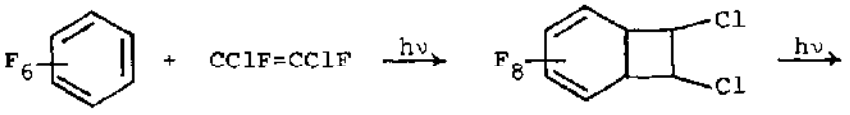
1,2,3,4,5-Pentafluorocyclopentadiene has been obtained in three steps starting from hexachlorocyclopentadiene.

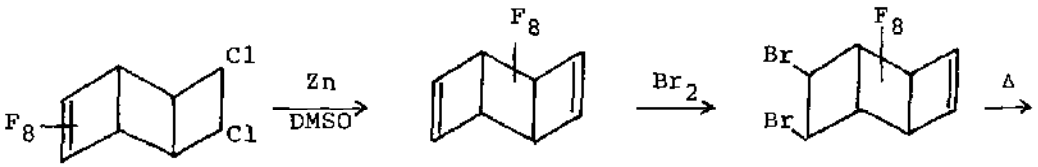


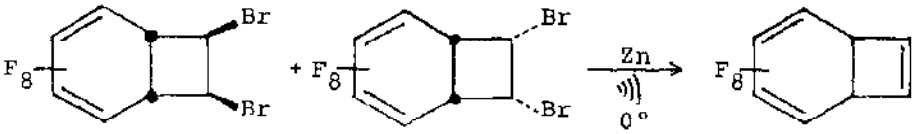




Typically of cyclopentadienes, it dimerises reversibly even at -78°C.[15,16] Metallation of the proton, preferably with $M^+N(SiMe_3)_2^-$ affords the pentafluorocyclopentadienide anion, $C_5F_5^-$, however, THF solutions of the metal salts are unstable via loss of metal fluoride. Acidity measurements show that C_5F_5H is more acidic than C_5H_6 (pK_5 = 15.5) but less than CF_3CH_2OH (pK_5 = 12.8).[16]

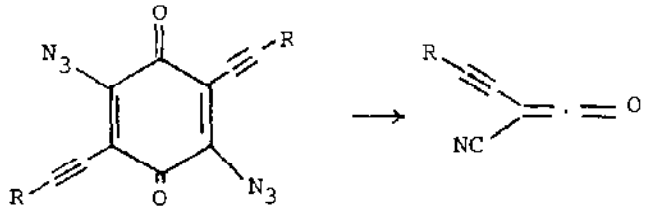






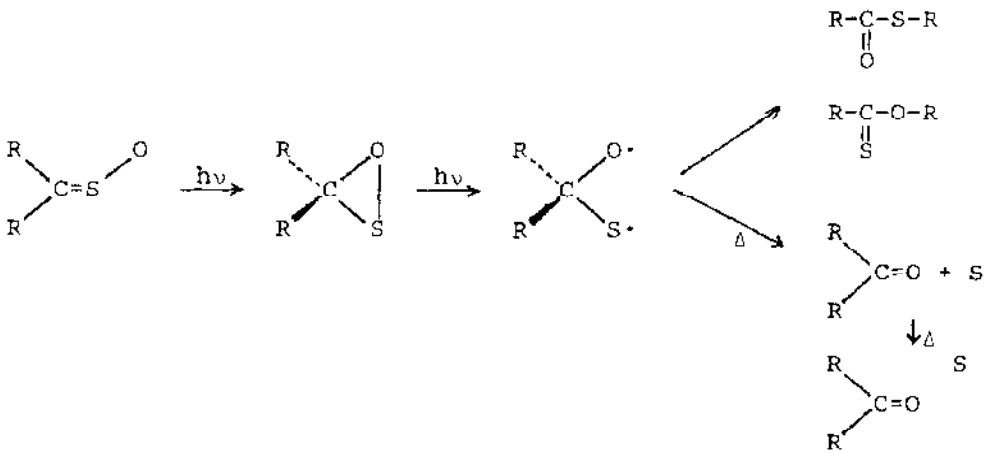
(9)

Hexynylcyanoketene, (10), is found by the thermolysis (80°C) of the 1,4-benzoquinone, (11), in benzene:[18]



(11) (10)

The ketene dication, $CH_2=C=O$,[24] is accessible by charge stripping from $C_2H_2O^{+\cdot}$.[19] Photolysis of thioformaldehyde S-oxide most probably affords rearrangement into the three-membered oxathiirane via an excited singlet state. Further photolysis of oxathiirane apparently leads to a weakened S-O bond, the product being best described as a biradical, whereas no evidence for a possible ring-opening to the corresponding formaldehyde O-sulphide could be obtained (Scheme 4).[20]



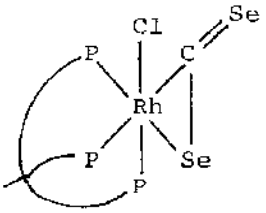
Scheme 4

The structures of a number of compounds have been studied by either microwave spectroscopy, gas-phase electron diffraction, or X-ray diffraction. Ethynamine, $HC{\equiv}C\text{-}NH_2$, has been found to be non-planar with a pyramidal amino group. The calculated barrier to inversion is 6.9 $kJ.mol^{-1}$.[21] Complete structural data for perfluoroethylene oxide has been obtained by assignment of microwave spectra of normal and ^{18}O- and ^{13}C-substituted molecules. The fluorine substituents have a shortening effect on the ring bonds, although the vicinal fluorine-fluorine distance is almost 0.2Å longer than found for other fluorocarbons.[22] A combined electron diffraction and microwave study of azidotrifluoromethane shows the CF_3 group to be in a staggered position with respect to the azide group and tilted away from it by 5.8°.[23] Only the C_s conformer of 1,1,2-trichloro-3,3-difluoro-1-propene, $Cl_2C{=}C(Cl)CF_2H$, is present in the gas phase at 20°C, although the possibility of a small amount (ca. 5%) of another form could not be excluded.[24] Electron diffraction yields a value of 1.475(12)Å for the O-O bond distance and 119(10)° for the dihedral angle in dimethylperoxide.[25] The crystal structure of oxetane, C_3H_6O, m.p. 174K, has been determined at 90K and 140K and shown to have exact C_s symmetry with a non-planar ring. The endocyclic C-O bond distance (1.460(1)Å at 90K) is unusually large for a single bond.[26]

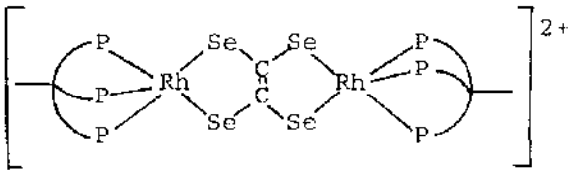
Sophisticated MO calculations have been performed on tricarbon monoxide[26] and butatrienone.[27] The former is predicted to be a stable linear molecule with a singlet ground state lying 168 $kJ.mol^{-1}$ below the lowest triplet state. The fully optimised geometry gives values of the rotational constant and dipole moment which agree well with experimentally determined values. C_3O_2 is predicted to be stable with respect to dissociation into C_2 + CO by 433 $kJ.mol^{-1}$ and to have a ΔH_f° of 282 $kJ.mol^{-1}$. The dipole moment is predicted to be 1.85D (cf. the experimental value of 2.391D). Both the gas-phase dimerisation of C_3O and the $C_3O + C_2H_4$ reaction are predicted not to be rapid. The data imply that the CC bonds are double and the CO bond is of somewhat higher order.[27] An orthogonal-bent structure is predicted for $CH_2{=}C{=}C{=}C{=}O$. Taken with the previous data for propadiene and other results for pentatetraenone and hexapentaenone, the new data suggests that bending of the heavy-atom chain is a general feature of larger cululenones, $CH_2{=}(C)_n{=}O$, with the preferred bending

direction alternating as a function of n between in-plane and orthogonal.[28] The activation energy of CO_2 towards hydration has been calculated to be 15.5 kcal.mol^{-1} by ab initio SCF calculations using the split-valence 3-21G basis set, in good agreement with the experimental value. A quite stable six-membered cyclic complex of CO_2 and the eater dimer was obtained by the calculation. The preferred hydration reaction is with the water dimer, the reaction with the water monomer being for less favoured.[29]

The reaction of CSe_2 with $[RhCl(C_2H_4)]_2$ and the triphosphine, $(Ph_2PCH_2)_3CMe$(triphos), affords the complex, [(triphos)RhCl(η^2-CSe_2)].C_6H_6, (12), which with Lewis acids is converted into the ligand-dimerised cation, [(triphos)Rh(η-C_2Se_4)Rh(triphos)]$^{2+}$, (13).[30]



(12)

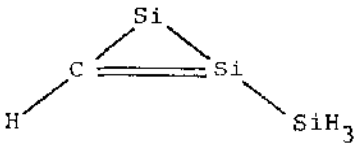


(13)

4.2 SILICON AND GERMANIUM

4.2.1 Reactive Intermediates and Multiply-Bonded Species

The most stable conformation of Si_2H_2 is predicted to be a non-planar bridged structure when polarisation functions are included in the basis set. Electron-correlation effects further stabilise this form relative to silasilene (H_2Si=Si), which is computed to be 11.3kcal.mol^{-1} less stable than bridged disilyne. No stable linear conformation of Si_2H_2 analogous to acetylene was found even when electron correlation was taken into account.[31] Of the thirteen cyclic isomers of $C_2Si_2H_4$ studied, the silyl-substituted silacyclopropenylidene, (14), was found to be the most



(14)

stable. Planar 1,3-disilacyclobutadiene is also a stable structure and exhibits significant diradical character.[32]

A useful review of the gas phase reactions of dichlorosilylene has appeared.[33] Electron diffraction structures of silicon dichloride and dibromide,[34] and of germanium dibromide[35] have been reported. Bond distance and angle data for all the Group 4 AX_2 species are summarised in Table 1. Laser flash photolysis of

Table 1. Bond distances (Å) and angles (°) for Group 4 dihalide species.

M\X	F	Cl	Br
C	1.304;104.8	1.758;108[a]	1.907;109[a]
Si	1.590;100.8	2.083;102.8	2.243;102.7
Ge	1.732; 97.2	2.186;100.3	2.337;101.2
Sn	1.893; 96[a]	2.346; 99	2.497;100.5[a]
Pb	1.989; 95[a]	2.444; 98.3	2.544;100

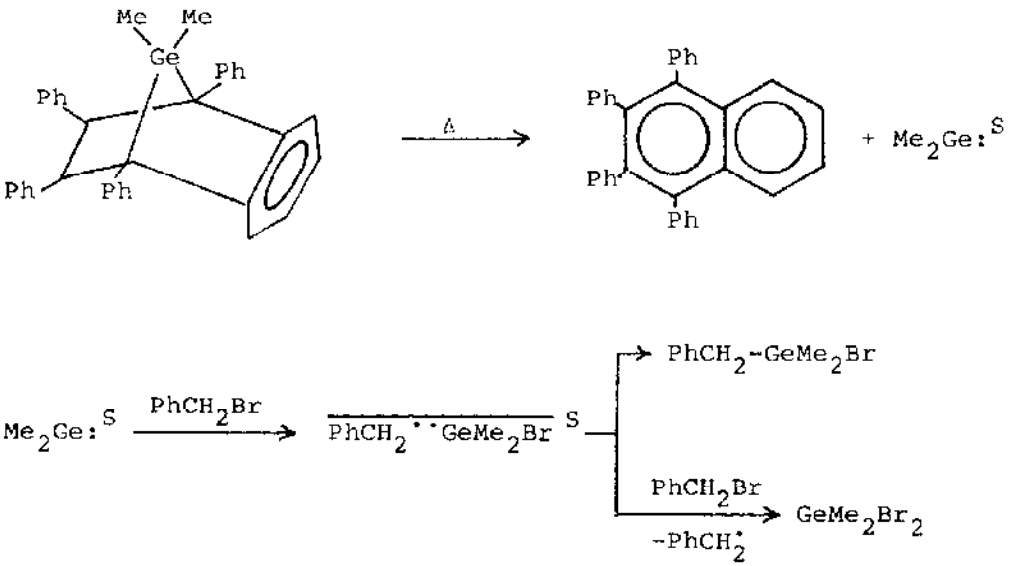
a) Estimated.

dodecamethylsilylene, $(Me_2Si)_6$, in 3-methylpentane or cyclopentane at 293K gives a transient absorption band at 350nm due to dimethylsilylene. The rate constant for the scavenging of Me_2Si: by trimethylsilane to give $Et_3SiSiMe_2H$ was determined to be 2.0×10^6 $M^{-1}s^{-1}$ in cyclopentane. Quenching by methanol also in cyclopentane to give $MeOSiMe_2H$ proceeded at a rate of 3.1×10^7 $M^{-1}s^{-1}$ at concentrations below 0.05M, but at $5.7 \times 10^6 M^{-1}s^{-1}$ at higher concentrations.[36] The insertion of silylene into the CH and SiH bonds of methane and silane have non-zero SCF barriers, but only the insertion into methane retains a non-zero barrier when third-order Møller-Plesser perturbation corrections are included in the 6-31G* basis set.[37] In contrast, the corresponding hydrogen-abstraction reactions from methane and silane by triplet silylene:

$$^3{:}SiH_2 + MH_4 \rightarrow SiH_3 + MH_3$$

M = C, Si.

have significant barriers.[38] The insertion reactions of silylene into NH_3, H_2O, HF, PH_3, H_2S and HCl have been characterised in detail by using ab initio MO theory, including electron correlation and zero-point corrections, and have been shown to involve the initial formation of a donor-acceptor complex followed by a proton shift via an unsymmetrical high-energy transition state. The complex between SiH_2 and NH_3 exists in a deep minimum with a high barrier for rearrangement (38 kcal.mol^{-1}). The complex with PH_3 also involves a fairly deep minimum, but the overall insertion barrier is small. The interaction with water involves a complex with a fairly high rearrangement barrier (22 kcal.mol^{-1}), but those with H_2S, HF, and HCl are fairly weak with lower calculated rearrangement barriers (13, 10 and 8 kcal.mol^{-1}, respectively).[39] The effect of fluorine substitution at silicon on the insertion of silylenes into the hydrogen molecule has also been studied. A dramatic increase in the barrier height is seen with fluorine substitution along the series, SiH_2, SiHF, SiF_2 (51, 130 and 273 kJ mol^{-1}, respectively).[40] The insertion of (thermally-generated) dimethylgermylene into the CBr bond of benzyl bromide has been shown to occur via a cage abstraction-recombination reaction, giving typical ^{1}H ClDNP effects thus proving the singlet state of the germylene (Scheme 5):



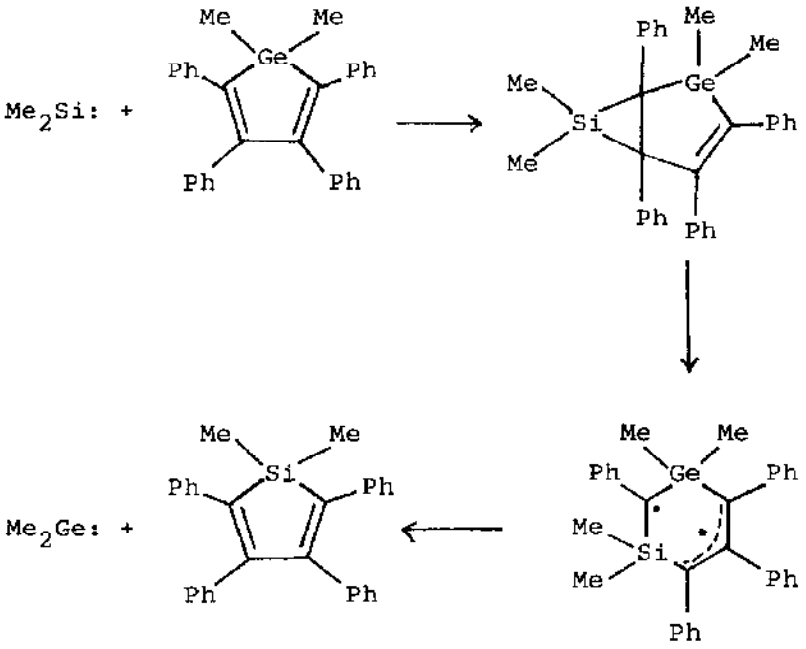
Scheme 5

After the reaction is complete both $PhCH_2Me_2GeBr$ and Me_2GeBr_2 are found as products. The latter, however, is a more effective Me_2Ge scavenger, and yields oligogermanes containing bromine with an average n value of ~2:[44]

$$Me_2GeBr_2 \xrightarrow[k_1]{Me_2Ge:} Me_2Ge(Br)-Ge(Br)Me_2 \xrightarrow[k_2]{nMe_2Ge:} Me_2Ge(Br)-(Me_2Ge-)_nGeMe_2(Br)$$

$k_2 > k_1$, n = 1,2,....

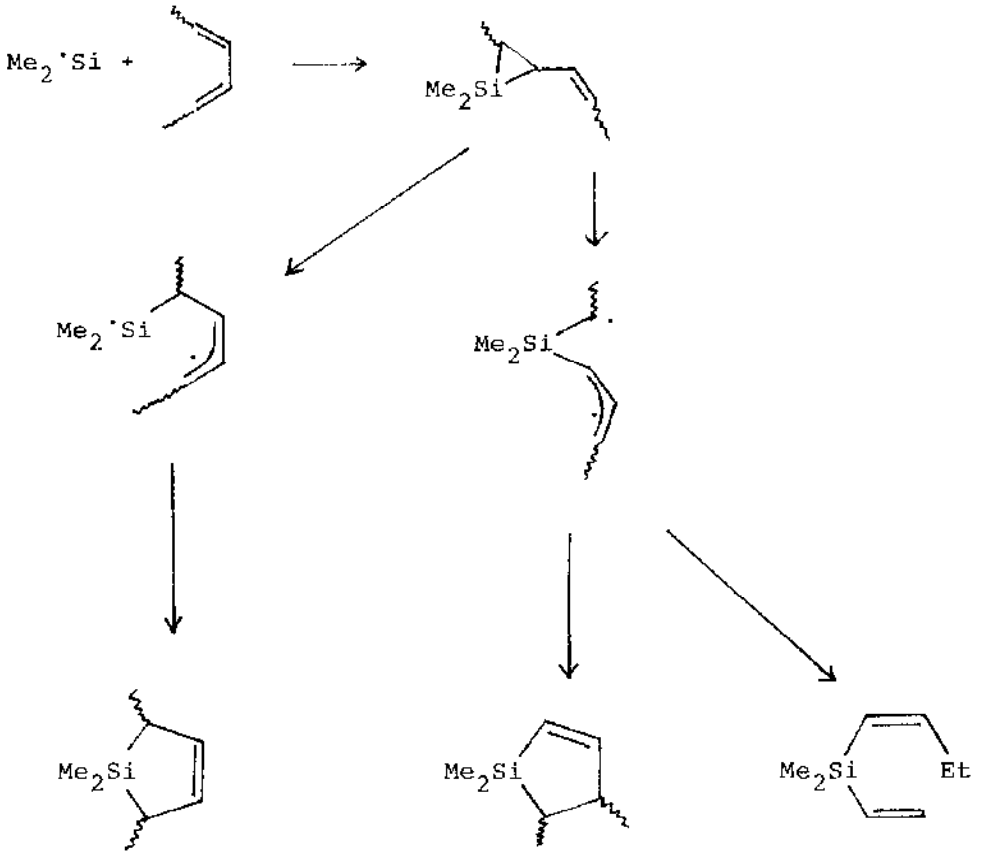
Photochemically-generated dimethylsilylene reacts with 1,1-dimethyl-2,3,4,5-tetraphenyl-1-germacyclopentadiene to bring about a silylene-germylene exchange, presumed to involve an initial formation of a vinylcyclopropane which subsequently rearranges and extrudes dimethylgermylene:



Similar results are obtained when $(Me_2Si)_6$ is used as a photochemical source of dimethylsilylene.[42]

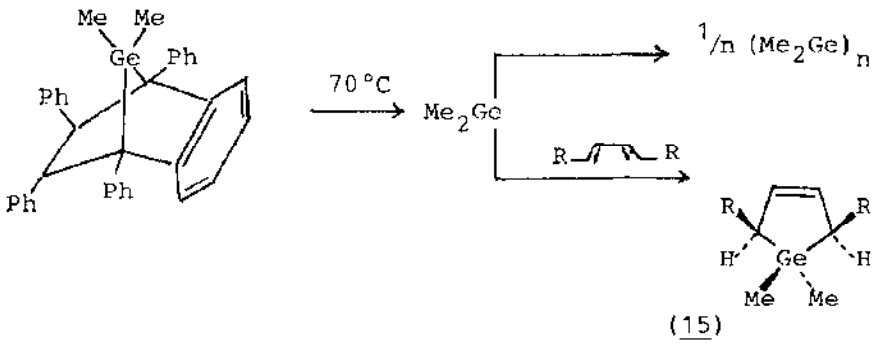
The mechanism for addition of dimethylsilylene to substituted 1,3-butadienes comprises a concerted 1,2-addition followed by ring-opening of vinylsilacyclopropane intermediates to diradicals

which can either cyclize or disproportionate as in Scheme 6.[43] Thermally-generated dimethylgermylene behaves as a nucleophile



Scheme 6

towards 1,3-dienes, reacting faster with more electron-deficient examples to give the desired [2+4] disrotary ring closure product, (15).[44]

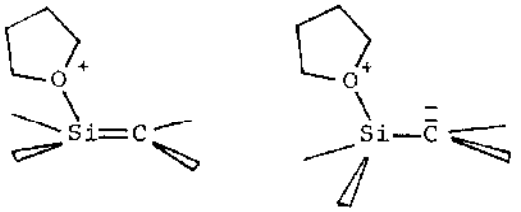


(15)

Photolysis of $(Me_2Si)_6$, the standard method for the generation of dimethylsilylene in solution, appears to be more complex than first thought since both dimethylsilylene and methylsilene, $[(MeCH)Si=CH_2]$ (16), have been identified as products. The mode of formation of (16) is not clear, but isomerisation of initially-formed dimethylsilylene was thought unlikely.[45] However, this isomerisation reaction has been verified by generation of dimethylsilylene (yellow) in an argon matrix (photolysis of $(Me_2Si)_6$ at 254nm), followed conversion to 1-methylsilene (colourless) by irradiation at 450nm. Both species are stable for several hours in the argon matrix temperatures of upto 35K. The infrared spectrum of dimethylsilylene shows considerable resemblance to that of dimethylstannylene and dimethyl sulphide. That of 1-methylsilene is rather similar to that for propene, but with the absorption bands generally shifted to lower frequencies (ν(Si=C) 988cm^{-1}, for propene), although the Si-H stretching mode occurs at about 100cm above that usually found in trialkylsilanes.[46] Infrared spectra have also been recorded for the silenes, $Me_2Si=CD_2$ and $(CD_3)_2Si=CD_2$.[47] In this study, two bands, one around 880cm^{-1} and the other around 1115cm^{-1} contributed to the Si=C stretching mode. Other experimental data also point to the establishment of an equilibrium mixture of dimethylsilylene and 1-methylsilene, irrespective of the direction from which the equilibrium is approached. Such a reversible isomerisation accounts for many of the previous, apparently conflicting, observations.[48] A theoretical study of the barrier heights and transition states for the interconversions of silenes and silylenes via 1,2-hydrogen, 1,2-methyl and 1,2-silyl shifts show that they proceed only at elevated temperatures consistent with experiment observations.[49,51] Methylsilene, generated thermally from three different precursors, 1-methylsilacyclobutane, 2,3-bis(trifluoromethyl)-7-methyl-7-silabicyclo[2.2.2]-octa-2,5-diene, and 1-methoxy-1-methyl-1-[(trimethylsilyl)methyl]-silane, isomerises to dimethylsilylene. With trapping agents such as butadiene and trimethylsilane, products expected from dimethylsilylene are obtained.[51]

The colourless crystalline tetrahydrofuran adduct of the silene, $Me_2Si=C(SiMe_3)(SiMe^tBu_2)$ (17), has been obtained by the room temperature decomposition of $^tBu_2SiF\text{-}CLi(SiMe_3)_2.4thf$ in diethyl ether via the intermediate, $Me_2SiF\text{-}CLi(SiMe_3)(SiMe^tBu_2).\text{-}nthf$. In crystals of (17) the thf molecule is clearly

coordinated to the silicon atom, which adopts a distorted tetrahedral geometry rather than the trigonal planar coordination expected on the basis of sp^2 hybridisation. The latter geometry is found for the carbon atom, whilst the Si-C double bond distance (1.747(5)Å) is the shortest such distance yet observed. The adduct is probably best regarded as a zwitterion, the bonding in which may be described in terms of the resonance formulation.[52]



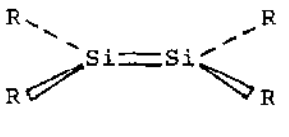
The series of isomeric silenes, $H_2C{=}SiHR$ and $H_2Si{=}CHR$ (R = CH_3, SiH_3, F, OH, $OSiH_3$, CN and NO_2), have been studied at the RHF/3-21G and 6-31G* levels. The two basis sets give similar results. Generally, the C=Si bond distances in the former series are shorter than in the latter. The experimental distance found in $(Me_3Si)_2Si{=}C(adamantyl)(OSiMe_3)$ is electronically elongated and consistent with the calculations. Energy differences between the isomers and for the reaction with silane were a so calculated. Substituent effects on the thermodynamic stability of the Si=C bond are small. A "reversed polarity" of the π-bond, i.e. $C^{\delta+}{=}Si^{\delta-}$, is the most important single electronic factor which reduces the reactivity of silenes. The energies of the π and π* orbitals are less significant.[53] The photolysis of 1-sila-2,5-hexadiene at 1050K leads to the exclusive formulation of hydrogen and silabenzene, for which a valence ionisation energy up to 21eV of its photoelectron spectrum have been observed.[54] Unsaturated silicon and germanium compounds of the types $R_2E{=}C(SiR_3)_2$ and $R_2E{=}N(SiR_3)$ (E = Si, Ge) have been reviewed.[55]

A significant number of papers reporting disilene chemistry have been reported. Ab initio calculations predict that the 1,2-silyl shift in the silylene ⇌ disilene conversion:

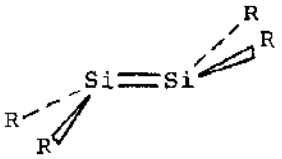
$$HSiSiH_2(SiH_3) \rightleftharpoons (SiH_3)HSi{=}SiH_2$$

proceeds at room temperature, in agreement with experimental

observation. Interestingly, in this study, the equilibrium structures of the two disilenes, $(SiH_3)HSi{=}SiH_2$, are predicted to have C_s symmetry with a planar disilene skeleton, in contrast to predicted trans-bent C_{2h} geometry previously calculated for disilene, $H_2Si{=}SiH_2$.[55] A separate theoretical study of the substituent effects on the bonding in disilenes show that the conformation of the molecule depends strongly on the central π bond and also on the nature of the substituents.[57] Some experimental corroboration of these theoretical studies is found in the crystal structure determinations of the more stable disilenes. The two silicon and four carbon atoms in both tetrakis(2,6-diethylphenyl)-disilene[58] and trans-1,2-di-tert-butyl-1,2-dimesityldisilene[59] are coplanar as in (18) although tetramesityldisilene[59] has a distorted structure with moderate anti-pyramidalisation at the silicon atoms as in (19). The silicon-silicon bond distances in the three



(18)

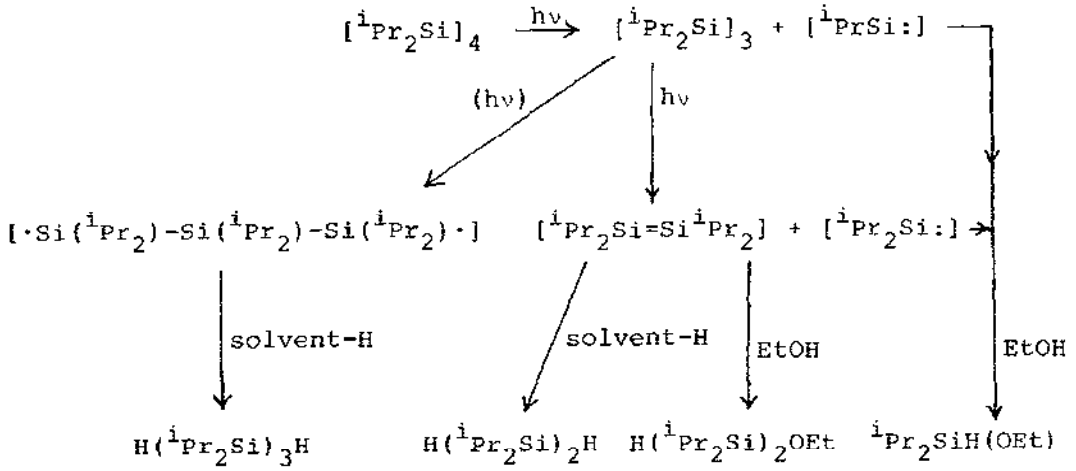


(19)

compounds are 2.140(2)Å, 2.143(1)Å and 2.160(1)Å, respectively. Pyramidalisation in the digermene, R_2GeGeR_2 ($R = CH(SiMe_3)_2$) is more pronounced, but not as much as in the tin analogue. The germanium-germanium bond distance (2.347(2)Å) is ca. 4% shorter than in elemental germanium.[60] Values of the π bond energy of disilenes have been estimated. Experimental data afford a lower bound for H_2SiSiH_2 of 69±11kJ mol^{-1}, whereas ab initio calculations give a value of 93±8 kJ mol^{-1}. A substantial disilene probably has a value of 108±20 kJ mol^{-1}.[61]

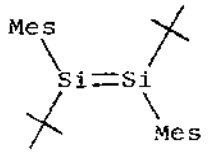
Tetra-iso-propyldisilene has been generated at room temperature in a hydrocarbon solvent by irradiation of the stable cyclotetrasilane, $(^iPr_2Si)_4$, from which di-isopropylsilylene is eliminated in two successive stages (Scheme 7).[62]

Photolysis of 2-tert-butyl-2-mesitylhexamethyltrisilane at -80°C produces >95% of the pale yellow disilene, (20), principally at the trans isomer, (20a). Further irradiation at 350nm leads to a photostationary equilibrium mixture containing 63% of (20a) and 37% of the cis isomer, (20b). The cis isomer is thermally

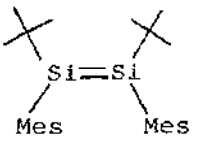


Scheme 7

unstable, reverting back to the equilibrium mixture, which is 25° in benzene contains 98% (20a) and 2% (20b). Similar photolysis

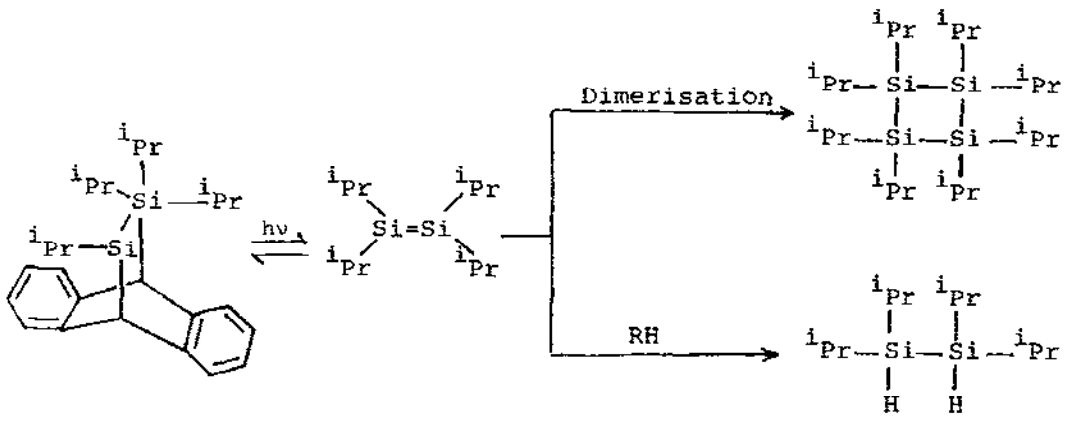


(20a)

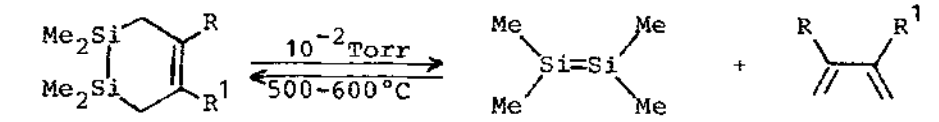


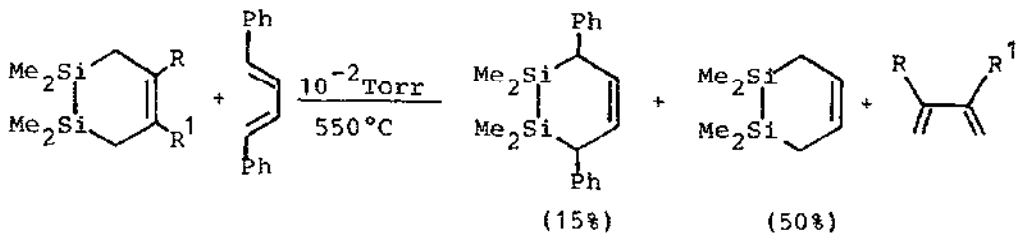
(20b)

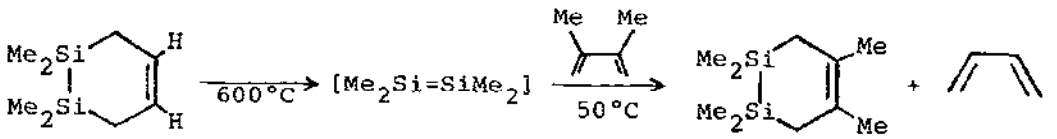
of 2-mesityl-2[bis(trimethylsilyl)amino]hexamethyltrisilane in pentane at -60° gives the corresponding disilene, Mes(R)Si=Si(R)Mes, (R = $N(SiMe_3)_2$), mainly as the unstable cis isomer, which was obtained pure by recrystallisation from pentane at -78°C. Isomerisation of this isomer takes place at 25°C in benzene to an equilibrium mixture of 94% trans and 6% cis.[63] Disilenes also appear to be able to undergo a [2+2] cyclodimerisation. Thus, tetra-iso-propyldisilene in cyclohexane affords octakis-iso-propylcyclotetrasilane (30%) in addition to the hydrogen-abstraction product 1,1,2,2-tetra-iso-propyl-disilane:[64]

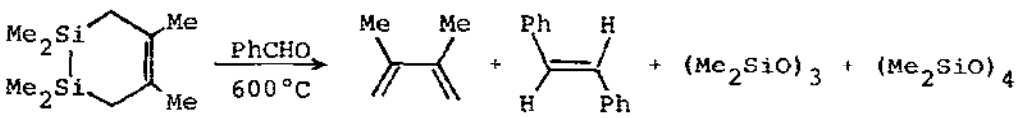


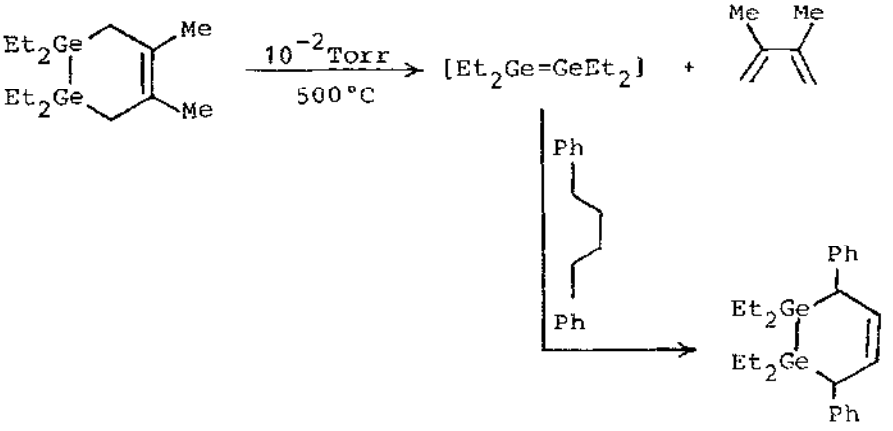
Intermediates with π-bonded silicon or germanium are generated during the gas-phase pyrolysis of 1,2-disila- or 1,2-digermacyclohex-4-enes, and may be trapped by addition or [2+2] and [4+2] cycloaddition reactions, eg.[65]



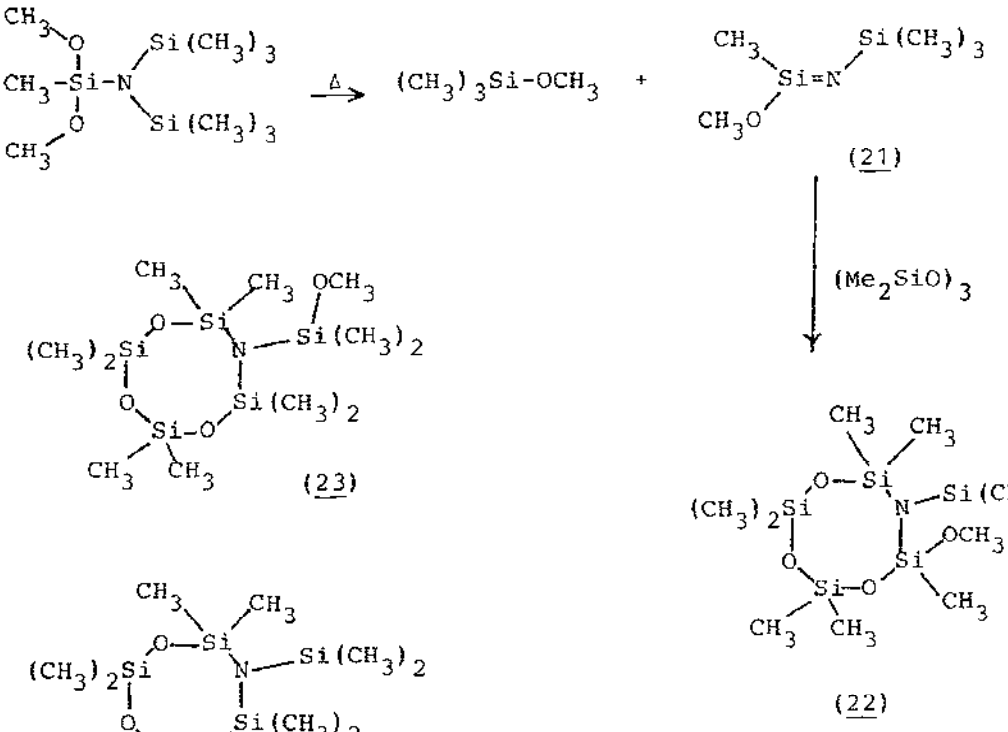






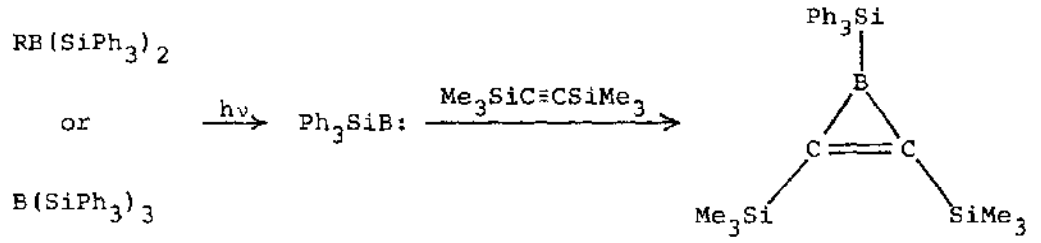


Silaimines have been generated by the flash vacuum pyrolysis of dimethoxymethylsilylbis(trimethylsilyl)amine, (21), and trapped by hexamethyltrisiloxane:



Besides the expected product, (22), arising from $Me(CH_3O)Si{=}NSiMe_3$, (23) (19%) and (24) (3.3%) were also formed in

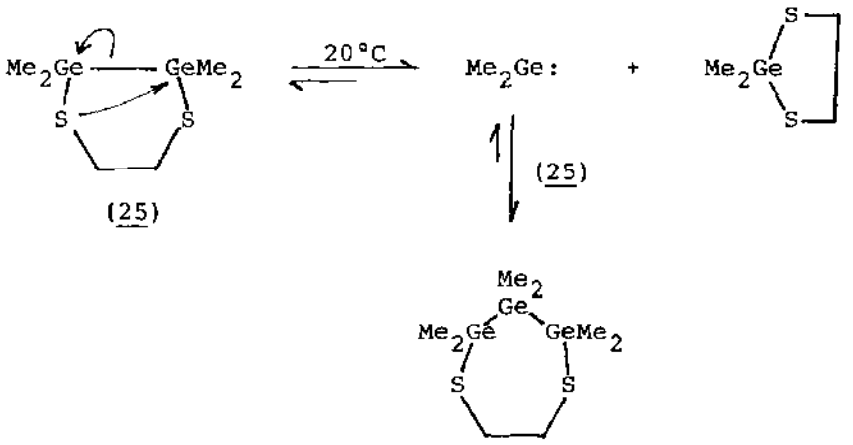
the reaction, indicating that the silaimines, $Me_2Si{=}NSiMe_2(OMe)$ and $Me_2Si{=}NSiMe_2$ are also generated.[66] Irradiation of the silylboranes, $RB(SiPh_3)_2$ (R = Me, C_9H_{11}) or $B(SiPh_3)_3$, affords triphenylsilboranediyl, Ph_3SiB: which may be trapped by typical reagents:[67]



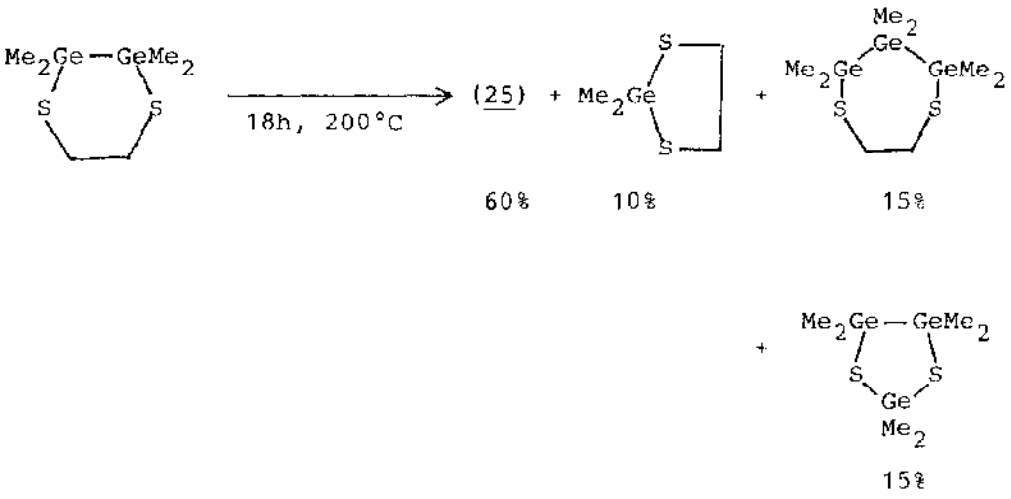
Methylsilanone is predicted to be the more stable than any of its isomers. Using the reaction

$$H_2SiO + C_2H_4 \rightarrow H_2CO + H_2CSiH_4$$

the C=O bond is found to be about to kcal mol^{-1} stronger than the Si=O bond.[68] 2,2,3,3-Tetramethyl-2,3-digerma-1,4-dithiane (25) decomposes slowly at room temperature by α-elimination to afford dimethylgermylene and 2,2-dimethyl-2-germa-1,3-dithiolane. 2,2,3,3,4,4-Hexamethyl-2,3,4-trigerma-1,5-dithiepane is obtained by the further insertion of dimethylgermylene into a germanium-sulphur bond of the digerma-1,4-dithiane:



At 200°C, (25) undergoes thermal fragmentation leading to the same products:



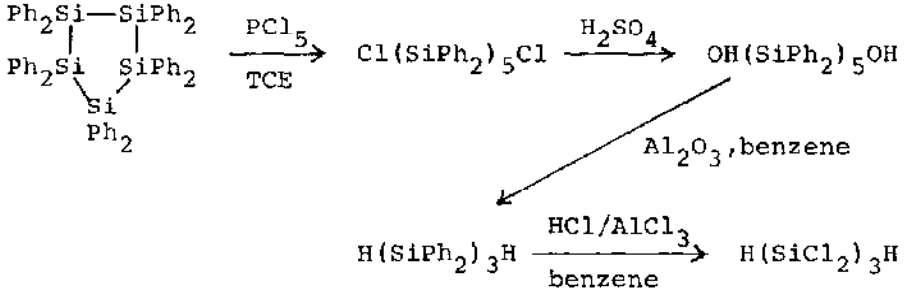
rationalised by the formation of intermediate dimethylgermathione.[69]

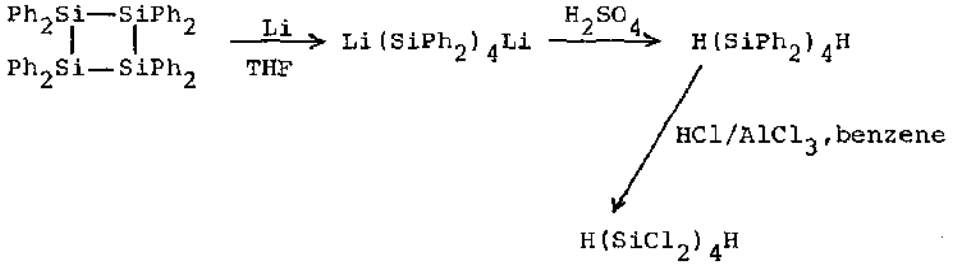
4.2.2 Tetravalent Compounds

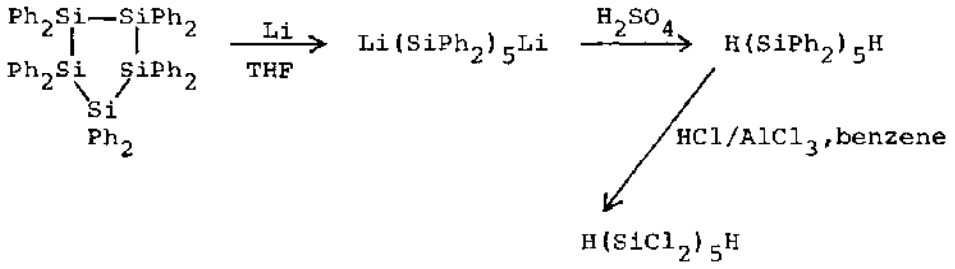
Vibrational spectra and the associated force fields for methylsilane and silane have been calculated using basis sets of double-ζ and double-ζ-plus polarisation quality. The calculations predict that the Si-C bond distance should be ca. 0.03Å longer than the experimentally derived (microwave) value, but support the original assignment of the dipole moment in the sense $^{+}CSi^{-}$. When compared with a similar force field for ethane, the calculations show that a number of vibrations are insensitive to the presence of the silyl group. The calculated force fields for the silyl group are much more sensitive than the corresponding force fields for the methyl group.[70]

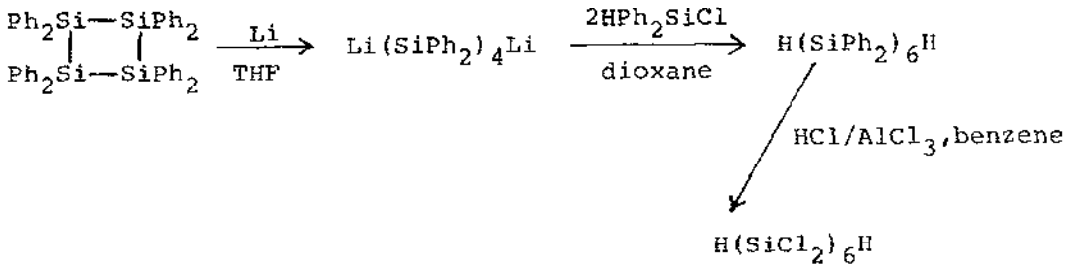
The gaseous products observed in the infrared laser photoreactions of SiH_4-HCl mixtures are H_2, Si_2H_6, SiH_3Cl, SiH_2Cl_2 and $SiHCl_3$, with trace amounts of Si_3H_8 and Si_2H_5Cl. A solid product containing silicon, hydrogen, and perhaps very small amounts of chlorine is also formed. The mechanism is best described by initial decomposition of silane to silylene and H_2 followed by competition of silane and HCl for the SiH_2 molecules. The simultaneous formation of all chlorosilanes suggests that decomposition of the initial product of SiH_2-HCl reaction leads to turn to SiHCl and $SiCl_2$ molecules. Temperature dependance studies indicate a value of <1.3 kcal mol^{-1} for the activation

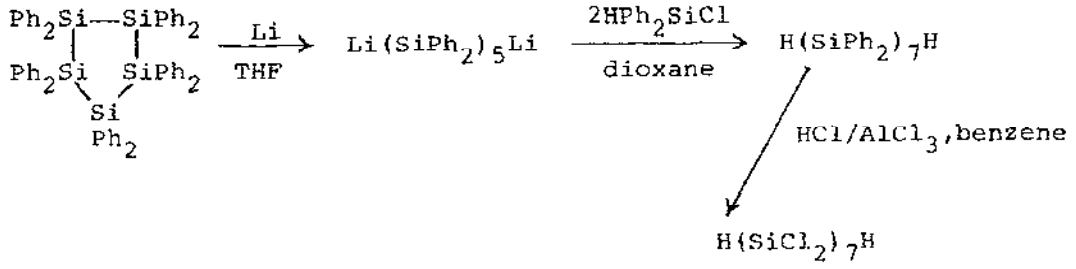
energy for the insertion of SiH_2 into HCl.[71] The reaction time for the preparation of potassium silyl from monosilane in glyme is considerably shortened by employing dispersed Na/K alloy. A simpler (and shorter) preparation uses dispersed pure potassium. Crystalline potassium silyl, free from potassium hydride and glyme, can be obtained by recrystallisation followed by slow crystallisation from a glyme/benzene mixture. Crystals obtained in this way can be stored for 30 months.[72] The novel α,ω-dihydroperchloro silanes, $H(SiCl_2)_nH$ (n = 3-7) and HSi_4Cl_5 have been synthesised starting from perphenylated cyclosilanes:[73]

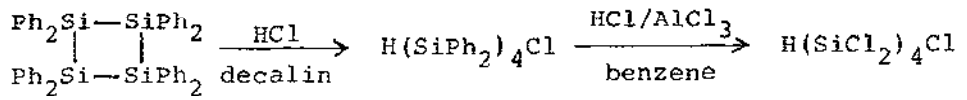






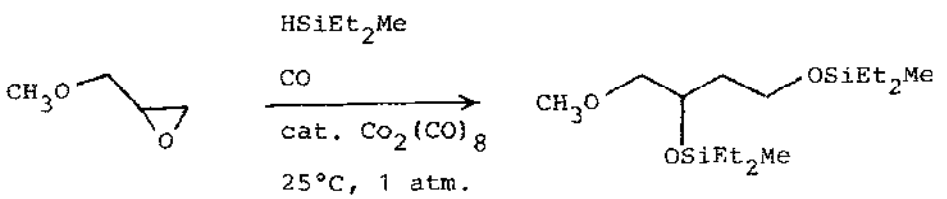




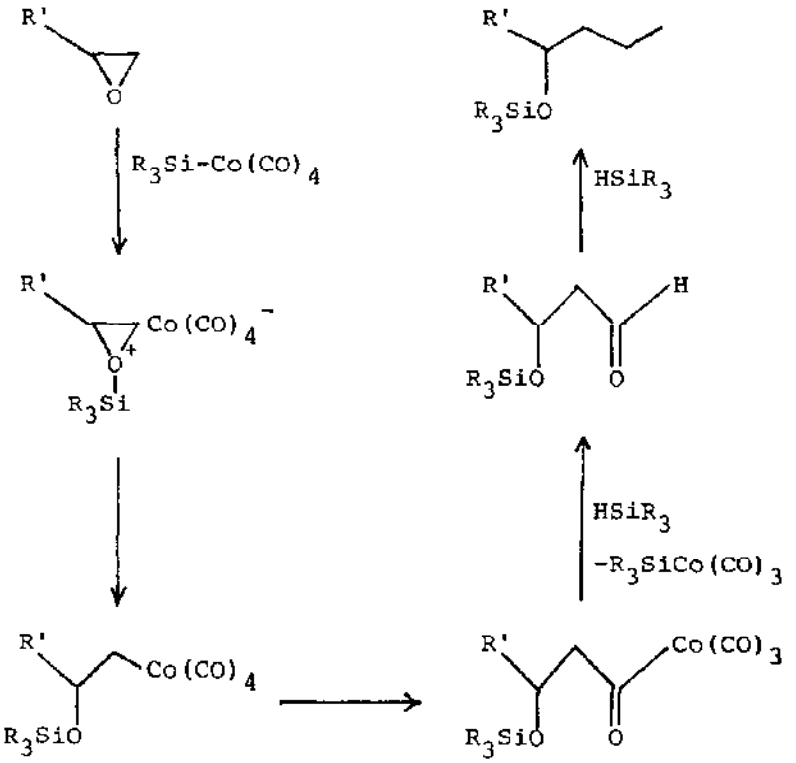


In the mass spectra of these compounds, fragmentation occurs with initial cleavage of Si-Si bonds in the middle of the chains.[74]

The siloxymethylative ring opening of oxiranes leading to 1,3-diol derivatives can be accomplished by using the cobalt carbonyl-catalysed reaction with a hydrosilane and carbon monoxide, eg:

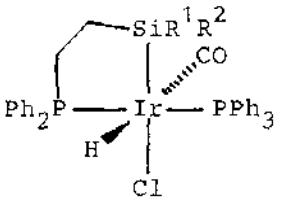


The catalytic transformation may be explained by the processes outlined in Scheme 8:

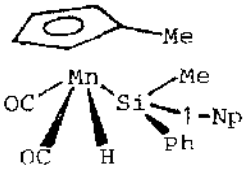


Scheme 8

Irradiation of $R_3SiCo(CO)_4$ in the presence of R'_3SiH affords $R'_3SiCo(CO)_4$ and R_3SiH at 298K in an alkane solvent. At 77K in a rigid alkane matrix, irradiation of $R_3SiCo(CO)_4$ yields dissociative loss of CO to give a 16e complex, $R_3SiCo(CO)_3$. If the matrix contains a sufficiently high concentration of R_3SiH, the light-induced loss of CO occurs, and the metal carbonyl product is $(R_3Si)(R'_3Si)Co(CO)_3H$. The same species is also formed photochemically at 196K in fluid solution. Warming up to 298K results in generation of both $R_3SiCo(CO)_4$ and $R'_3SiCo(CO)_4$.[76] Reaction of trans-$[Ir(PPh_3)_2(CO)Cl]$ with the functionalised silanes, $PPh_2CH_2CH_2SiR^1R^2H$, occur immediately under ambient conditions to give white Ir(III) adducts as single stereoisomers (26) at the octahedral iridium centre.[77] X-ray crystallographic data for the complex (27) shows that the oxidative-addition of (+)-1-NpPhMeSiH on methylcymantrene takes place with

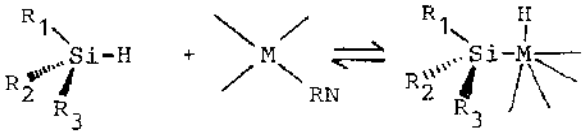


(26)



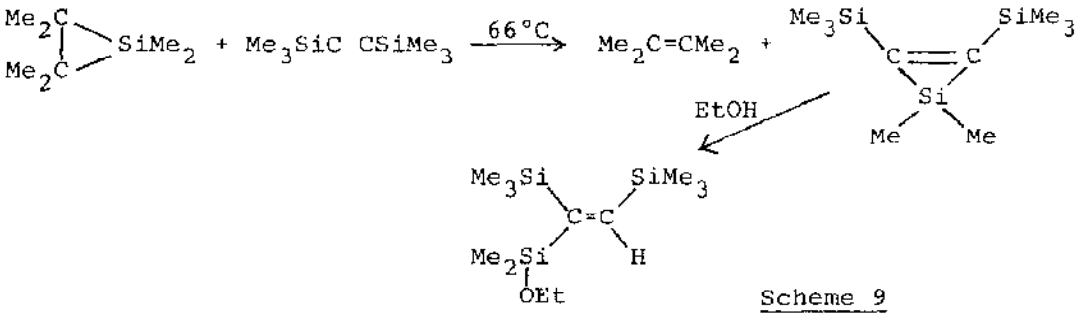
(27)

retention of configuration at silicon, ie:



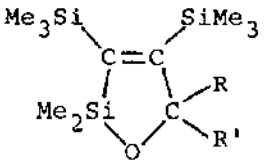
The germyl complexes $(\eta^5\text{-}MeC_5H_4)(CO)_2(R_3Ge)(H)M$ can be prepared either by oxidative-addition of R_3GeH on $(\eta^5\text{-}MeC_5H_4)(CO)_3Mn$ or by protonation of the related anions, $[(\eta^5\text{-}MeC_5H_4)(CO)_2(R_3Ge)Mn]^-$. Only the cis isomers are obtained. Both silyl and germyl complexes undergo facile elimination of silane or germane when treated with PPh_3. The Mn-Ge bond is cleaved by H_2O, MeOH, Cl_2 and CCl_4. The observations are consistent with a two-electron, three-centre bond involving manganese, hydrogen, and silicon or germanium.[78]

The chemistry of ring compounds of all sizes containing silicon- or germanium-carbon bonds has provoked substantial interest. The thermal decomposition of hexamethylsilirane in the presence of selected disubstituted acetylenes, results in the formation of silacyclopropenes via addition of dimethylsilylene to the triple bond. The products are thermally stable, but are extremely reactive towards atmospheric oxygen and methanol or ethanol resulting in Si-C(ring) bond cleavage (Scheme 9). The

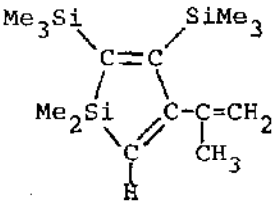


Scheme 9

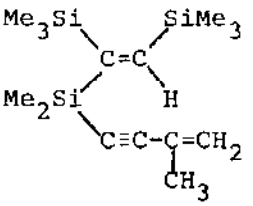
very high field ^{29}Si n.m.r. resonance (-87 to -106ppm) appears to be characteristic of the silacyclopropene ring.[79] 1,1-Dimethyl-2,3-bis(trimethyl)silirene reacts with multiply-bonded organic compounds (aldehydes, ketones, styrenes, conjugated terminal acetylenes, benzene, terminal 1,3-dienes, conjugated imines) undergoing ring-expansions, most probably via radical mechanisms, to give products such as (28)-(31).[80]



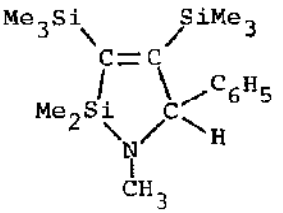
(28)



(29)

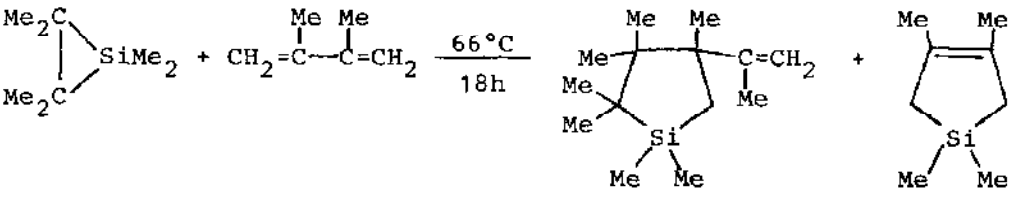


(30)

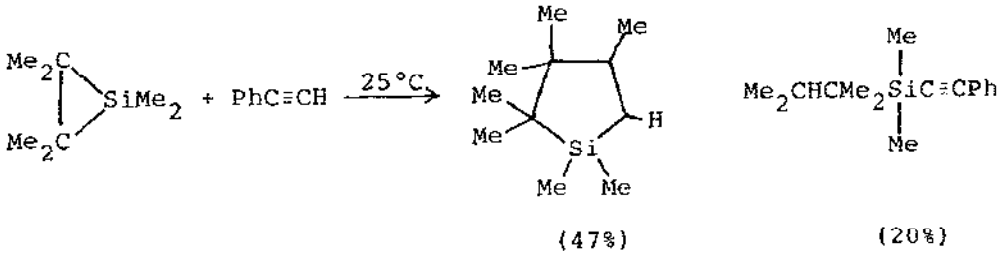


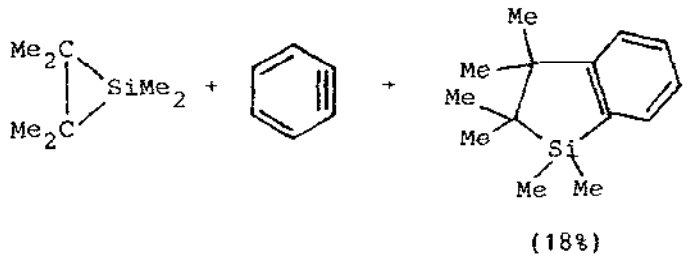
(31)

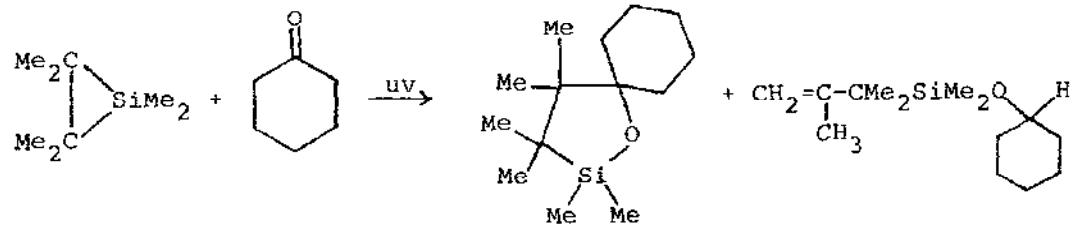
Hexamethylsilirane itself also undergoes similar insertion-ring expansion reactions with the formation of silacyclopentanes, silacyclopentenes, 1-oxa-2-silacyclopentanes, 1-aza-2-silacyclopentanes and 1,2-diaza-3-silacyclopentanes, eg:[81,82]

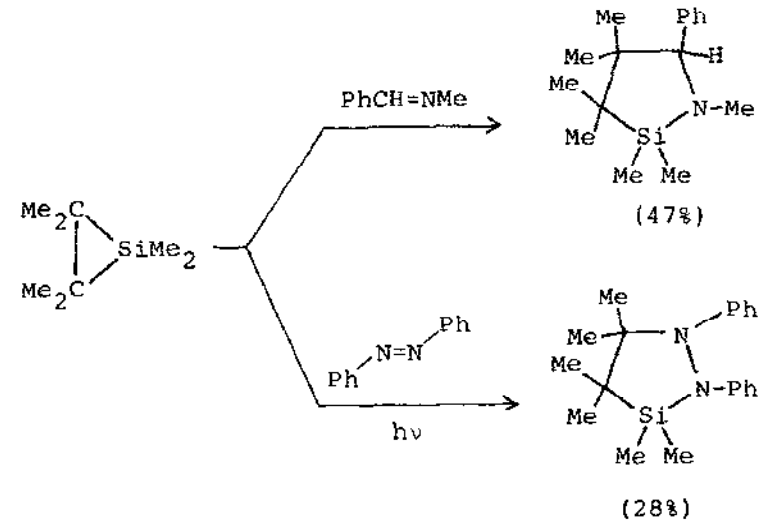


(47%) (15%)

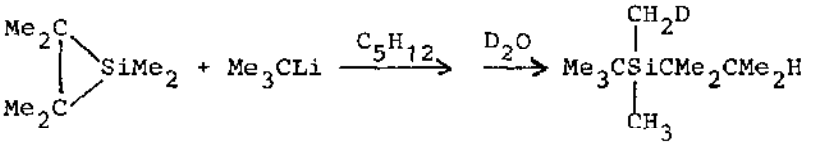

Me2C
SiMe2
Me2C
+ PhC≡CH
25°C
Me
Me
Me
Me
H
Si
Me
Me
(47%)
Me2CHCMe2SiC≡CPh
Me
Me
(20%)


Me2C
SiMe2
Me2C
+
+
Me
Me
Me
Me
Si
Me
Me
(18%)


Me2C
SiMe2
Me2C
+
O
uv
Me
Me
Me
Me
O
Si
Me
Me
+ CH2=C-CMe2SiMe2O
CH3
H

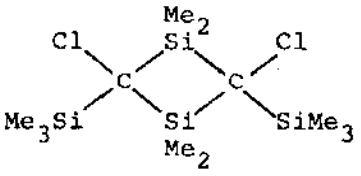

Me2C
SiMe2
Me2C
PhCH=NMe
Me
Ph
Me
H
Me
N-Me
Me
Si
Me
Me
(47%)
Ph
N=N
Ph
hν
Me
Ph
Me
N
Me
N-Ph
Me
Si
Me
Me
(28%)

Alkyllithium reagents, RLi (R = Me, ^{n}Bu, ^{t}Bu) react with hexamethylsilirane at 0°C to afford initially the ring-opened product, $RSiMe_2CMe_2CMe_2Li$, but in a subsequent reaction the reagent metallates the methyl substituents on the silicon atom to give $RSi(CH_3)(CH_2Li)CMe_2CMe_2H$ as the final product, corroborated by deuterolysis, eg.[83]

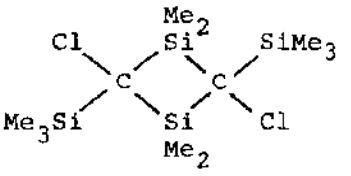


(46%)

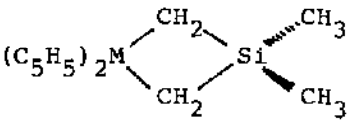
Several novel cyclobutane analogues have been synthesised. The reaction of $Me_3SiCCl_2SiMe_2Cl$ with butyllithium in ether, yields the 1,3-disilacyclobutanes, (32) and (33) (the structure of the former was confirmed crystallographically).[84]



(32)

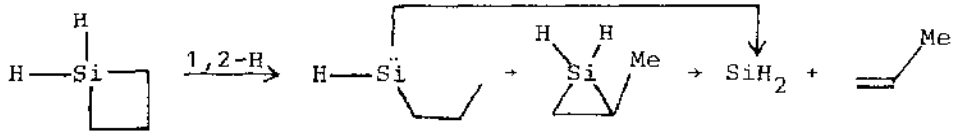


(33)

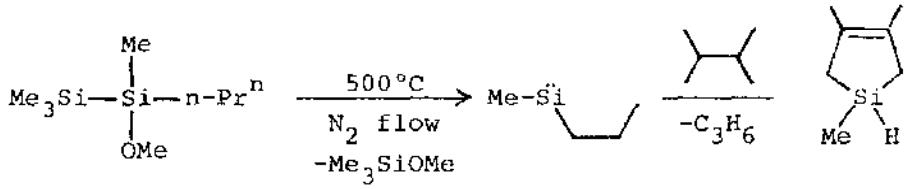


(34)

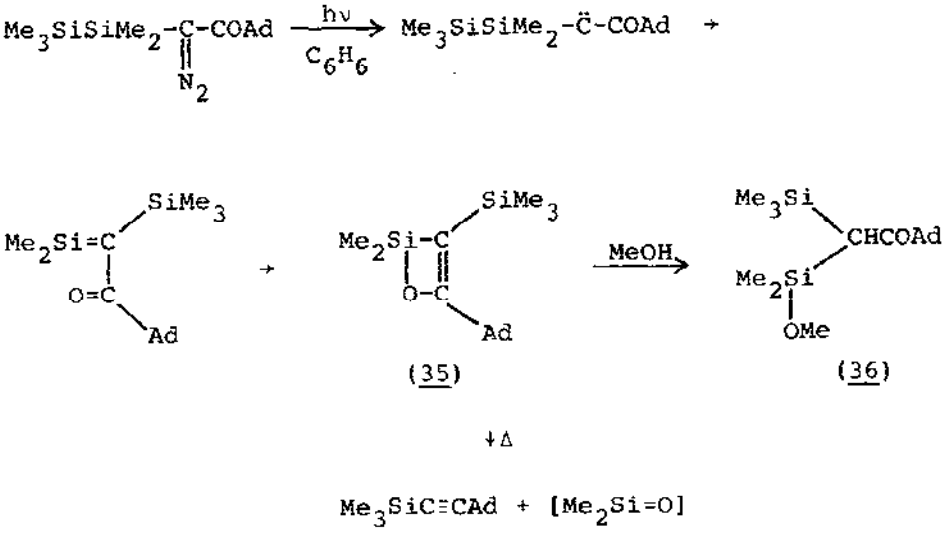
The thermal decomposition of hydridosilacyclobutanes has been examined kinetically by low-pressure pyrolysis and stirred-flow reactor techniques. Proposed intermediates were also generated by independent methods. In contrast to previous reports, which assumed a series of homolytic bond cleavage reactions, the reaction products, RSiH and propene, were considered to arise from an initial rearrangement to n-propylsilylenes, viz:



Support for this mechanism comes from the additional observation that when methylpropylsilylene is generated at 500°C in the presence of 2,3-dimethylbutadiene, the major product is the adduct of methylsilylene:[85]

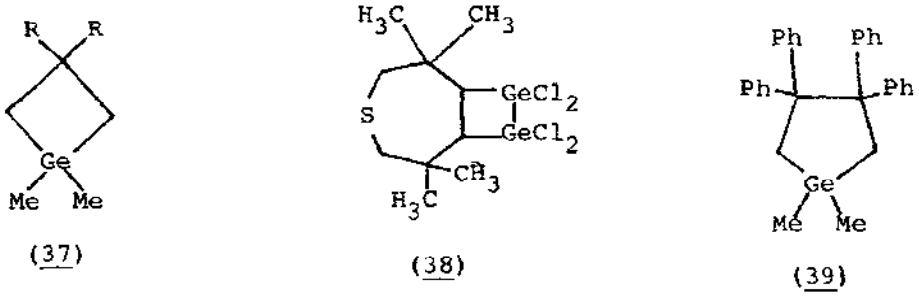


Metathetical reaction of $[Mg(CH_2)_2SiMe_2]_n$ with the metallocene dihalides $(\eta^5\text{-}C_5H_5)MX_2$ (M = Ti, Zr, Nb; X = Cl; M = Mo; X = I) affords the analogous 1-metalla-3-silacyclobutanes, (34). The complexes are thermally stable, and have been characterised spectroscopically and by X-ray crystallography.[86,87] The reaction of the zirconium heterocycle, (34) (M = Zr), with paraformaldehyde proceeds stoichiometrically with the insertion of a formaldehyde into a zirconium-carbon bond with the formation of the 1-oxa-4-sila-6-zirconacyclohexane ring compound, $(\eta^5\text{-}C_5H_5)_2Zr(OCH_2CH_2SiMe_2\text{-}CH_2)$, the conformation of which was again determined by crystallography.[88] A 1,2-silaoxetene, (35), has been produced by photolysis of pentamethyldisilanyladamantyl diazo ketone. (35) is thermally very labile, and attempts at its isolation were unsuccessful. It is, however, more stable in solution (Scheme 10). With methanol, a mildly exothermic reaction occurs resulting in the formation of the β-silyl ketone (36) in 86% yield.[89] The germacyclobutanes, (37), have been obtained by the Grignard method,[90] whilst the first example of a 1,2-digermacyclobutene, (38), was obtained by the reaction of the dioxane complex of $GeCl_2$ with 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne. The structure of (38) has been determined.[91] The structure of 1,1-dimethyl-3,3,4,4-tetraphenylgermacyclobutane, (39), a source of dimethylgermylene, has been determined by X-ray crystallography.[92] Thermolysis of 6-oxa-3-metallabicyclo[3.1.0]-hexanes, (40) (M = Si or Ge), in a flow system at 460°C gives rise

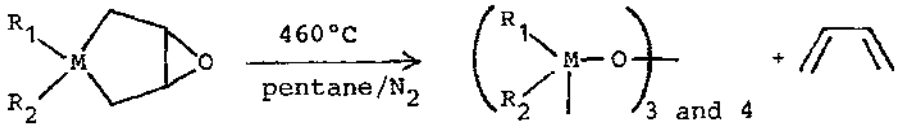


Ad = 1-adamantyl group

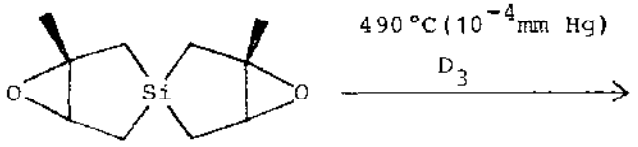
Scheme 10

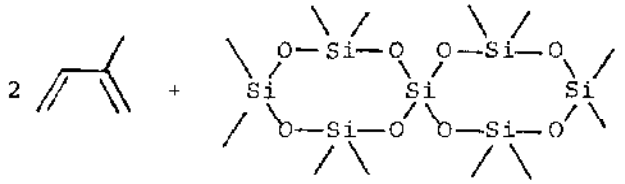


to cyclosiloxanes or -germoxanes on 1,3-butadiene via intermediate silanones or germanones; eg:



The silicon analogue of carbon dioxide was trapped by hexamethylcyclotrisiloxane to yield (41), the expected spiro adduct, in 60% yield:[93]

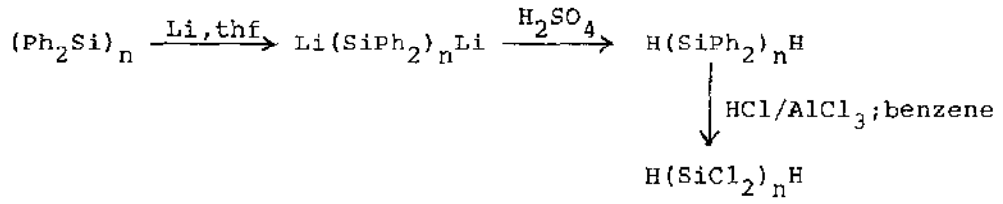




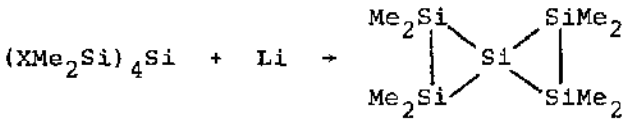
(41)

The 'direct' synthesis of silicon-rich compounds, has been studied by examining the reactions of chloromethnaes, CH_nCl_{4-n} (n = 0,1,2) with elemental silicon (Cu catalyst) in a fluid bed at 320°C. Chlorosilane mixtures obtained were treated with lithium aluminium hydride, and the silanes separated by HPLC. From dichloromethane, the unbranched carbosilanes, $Si_nC_{n-1}H_{4n}$ (n = 4-12, 2 terminal SiH_3 groups) and $Si_nC_nH_{4n+2}$ (n = 4-9, 1 terminal SiH_3 and 1 CH_3 group) as well as 1,3,5-trisilacyclohexanes with carbosilane chains of various length attached either to silicon or carbon, were produced. Branched products were obtained with chloroform and carbon tetrachloride.[94] Germanium vapour reacts with acetylene in a stationary metal atom reactor to form a polymer of the reproducible stoichiometry, $(C_2H_{2.7}Ge_{0.72})_x$.[95] Chlorination of small oligosilanes (Si_3H_8, n- and iso-Si_4H_{10}, n-Si_5H_{12}) by $SnCl_4$ or $HgCl_2$ in 2,3-dimethylbutane at 0°C proceeds mainly by substitution at the primary silicon atom giving monochlorinated products. Further chlorination takes place at other silicon atoms.[96]

α,ω-Dihydroperchlorooligosilanes have been synthesised starting from the perphenylated cyclosilanes according to the general scheme:



In their mass spectra, fragmentation commences with cleavage of Si-Si bonds in the middle of the chains, consistent with infrared data, which indicate that the lowest Si-Si force constants also occur for such bonds.[97,98] As found for sterically crowded hexaorganodistannanes, the metal-metal bonds in hexamesityldisilane and -digermane dissociate reversibly even at low temperatures (-60 to -32°C for the former; -12 to +53°C for digermane), generating the corresponding trimesitylmetal radical. The generated radicals, $Mes_3Si\cdot$ or $Mes_3Ge\cdot$, react irreversibly, for example, by substituting aromatics or abstracting hydrogen. Other hexaaryldigermanes (aryl = 2,6-dimethylphenyl, 2,3,4,6-tetraphenyl, 2,3,4,5,6-pentamethylphenyl and 2,4,6-triethylphenyl) also dissociate reversibly.[99] Reaction of various dialkyldichlorosilanes, $R^1R^2SiCl_2$, with an excess of lithium in tetrahydrofuran gives the corresponding peralkylcyclopolysilanes, $[R^1R^2Si]_n$ (n = 4-7), in reasonable to good yields. Smaller rings, mainly four-membered, were obtained with the more bulky substituents.[100] The structure of the first peralkylcyclotrisilane, $[(^tBuCH_2)_2Si]_3$, which has the longest Si-Si, bond of all known peralkylcyclopolysilanes, and is comparable with that in the perarylcyclotrisilane, $[(2,6\text{-}Me_2C_6H_3)_2Si]_3$,[101] and the synthesis of the first spiropentasilane, octamethylspiropentasilane, (42), are both notable. This latter compound is prepared by the action of lithium metal on tetrakis(dimethylbromo- or -chlorosilyl)silane in thf. Being highly strained (42) undergoes facile cleavage with $LiAlH_4$ (giving $(Me_2SiH)_4Si$), MeMgBr (to $(Me_3Si)_4Si$), and PCl_5 (to $(Me_2SiCl)_4Si$).[102]



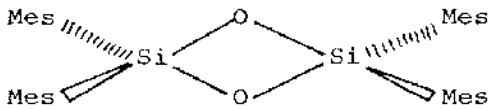
X = Cl,Br. (42)

The vibrational spectra of the homologues, $(Ph_2Ge)_4$, $(Ph_2Ge)_5$, and $(Ph_2Ge)_6$, are nearly identical above $350cm^{-1}$. The $[Ge]_n$ ring vibrations range from 330 to $140cm^{-1}$, and are unspecifically coupled with mass-sensitive phenyl modes.[103]

A novel synthesis of siloxanes has been reported involving the abstraction of oxygen from carbon monoxide by disilanes using a catalyst comprising 50% nickel on Kieselguhr:

$R_3Si\text{-}SiR_3 + CO \rightarrow$ 'C' + $R_3SiOSiR_3$ + $R_3SiOSiR_2OSiR_3$.....

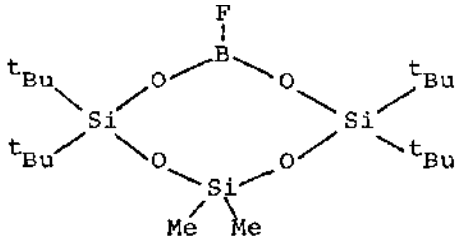
In the presence of hydrogen, the surface-deposited carbon is converted to methane.[104] More traditional methods have been employed for the synthesis of polysiloxanes of the type $RR'R''SiO(SiH_2O)_nSiRR'R''$ (R,R'R" = Me,Me,Me; Me,H,H; Et,Et,Et; Me,Me,H): cohydrolysis of H_2SiCl_2 with Me_3SiCl and Me_2HSiCl using NaH_2PO_4/Na_2HPO_4 - buffered media, H_2SO_4-catalysed equilibrium of cyclic $[H_2SiO]_n$ oligomers with $Me_3SiOSiMe_3$, and the reactions of $ClSH_2O(SiH_2O)_nSiH_2Cl$ with MeMgBr, Me_3SiOH and Et_3SiOH;[105] and cyclic germasiloxanes, $[R_2GeOPh_2SiO]_2$ (R = Me,Ph).[106] Along with the latter compounds, which have puckered eight-membered rings,[106] the structures of several other siloxane ring compounds have also been reported. The most interesting of these is that of tetramesitylcyclodisiloxane, $[Mes_2SiO]_2$, (43), obtained by aerobic oxidation of $Mes_2Si{=}SiMes_2$, and a most stable compound (mp. 215°, survives gas chromatography at 310°C, prolonged heating in refluxing decalin, and lengthy photolysis at 254nm). The presence of the four-membered, nearly planar $[Si_2O_2]$ ring is confirmed by X-ray analysis, but the most striking feature of the molecule is the transannular Si-Si distance (2.31Å) which is



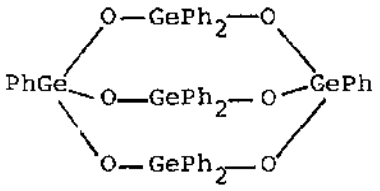
(43)

shorter even than the normal Si-Si single bond distance (2.34Å). The two independent Si-O distances (1.66 and 1.72Å) are somewhat longer than usual (1.61-1.65Å), and the Si-O-Si angle is highly contrained (86°). These data might strongly suggest the retention of some Si-Si bonding on oxidation by oxygen; indeed, treatment of $[Mes_2SiO]_2$ with lithium naphthalide at -78°C followed by quenching with water, affords the disilanediol, $Me_2Si(OH)\text{-}Si(OH)Mes_2$.[107] No similar Si-Si interactions have been observed in other four-membered ring systems of the types $[Si_2X_2]$ (X = CH_2, NPh, $SiPh_2$, S). The $[Si_2S_2]$ ring in $[(^tBuO)_2SiS]_2$ (from alcoholysis of SiS_2 by t-butanol) is rigidly planar.[108]

The silanediol, $^{t}Bu_2Si(OH)_2$, has a crystal structure comprising isolated molecules connected by hydrogen bonds into chains, whereas molecules of $(HO)^{t}Bu_2SiOSiMe_2OSi^{t}Bu_2(OH)$ form dimeric units. In cyclo-$[^{t}Bu_2SiO^{t}Bu(F)SiO]$, the silicon atom bearing the fluorine is displaced from the plane of the $[Si_2O_3]$ fragment.[109] The eight-membered $[Si_3BO_4]$ ring in the cyclo-1-bora-3,5,7-trisiloxane, $[^{t}Bu_2SiOB(F)O^{t}Bu_2SiOSiMe_2O]$, (44), is planar,[110] whilst the



(44)



(45)

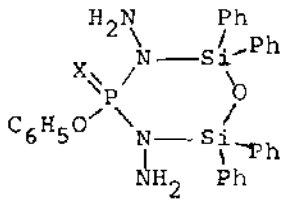
structure of the bicyclo[3.3.3]undecane, (45), from the reaction of a mixture of $PhGeCl_3$ and Ph_2GeCl_2 with silver nitrate in aqueous acetone, has also been reported.[111] Treatment of di-tert-butylchlorosilanol with ammonia affords the stable aminosilanol, $^{t}Bu_2Si(NH_2)OH$, which may be limited at oxygen by butyl lithium producing the lithium aminosilanolate, $^{t}Bu_2SiNH_2)OLi$. This latter compound is tetrameric with a pseudo-cubane $[Li_4O_4]$ core in the solid.[112]

The flowing afterglow technique has been used to study the chemistry of several anionic organosilicon species, such as silyl anions, silicon-stabilised carbanions, and pentacovalent silicon anions. The structures of several of the isomeric (and hence indistinguishable by mass spectrometry) species were determined by chemical reaction with nitrous oxide. For example, the M-1 ion resulting from the reaction of trimethylsilane and H_2N^- was shown not to be Me_3Si^-, but rather $Me_2Si(H)CH_2^-$ (both at m/z = 73) resulting from proton abstraction, since the m/z ion is formed exclusively when nitrous oxide is added to the system:[113]

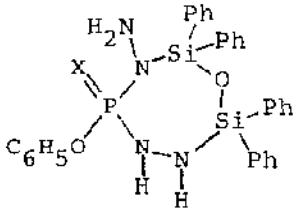
$$(CH_3)_3SiH + H_2N^- \not\longrightarrow \underset{m/z\ 73}{(CH_3)_3Si^-} \xrightarrow{N_2O} \underset{m/z\ 89}{(CH_3)_3SiO^-}$$

$$(CH_3)_3SiH + H_2N^- \rightarrow \underset{m/z\ 73}{(CH_3)_2Si(H)CH_2^-} \xrightarrow{N_2O} \underset{m/z\ 75}{(CH_3)_2Si(H)O^-}$$

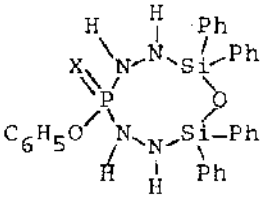
Dihydrazidophosphonic and dihydrazidothiophosphonic acid phenyl ester react with α,ω-dichloro organodisiloxanes and -trisiloxanes in the presence of triethylamine to yield ring compounds, the nature of which depends upon the reactants. With dichlorotetraphenyldisiloxane a six-membered ring with two exocyclic amino groups (46), a seven-membered ring with only one exocyclic amino group (47), and an eight-membered ring (48) are formed. With dichlorohexamethyltrisiloxane corresponding mixtures of eight-, nine-, and ten-membered rings, (49)-(51), respectively, are obtained.[114]



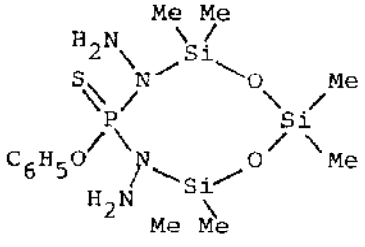
(46)



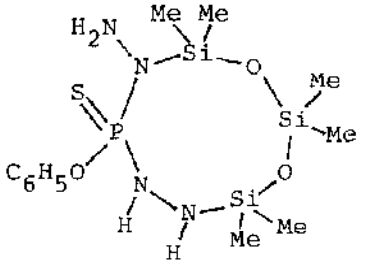
(47)



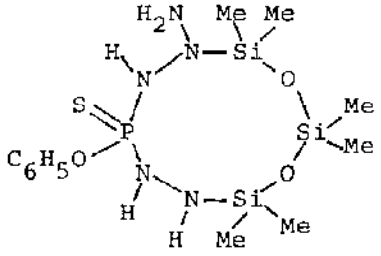
(48)



(49)



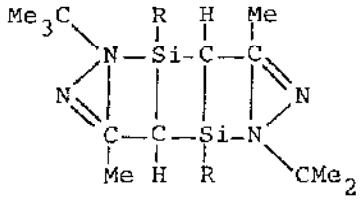
(50)



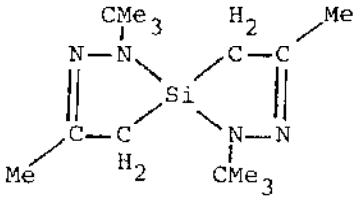
(51)

Trimethyl- and triethylsilyltriflate form strongly polarised donor-acceptor complexes with boron trichloride and tribromide. Deshielding of ^{29}Si n.m.r. chemical shifts and shielding of ^{11}B chemical shifts are consistent with four-coordinated boron and the development of partial positive charge at silicon involving O-coordination of boron halide with the triflates. No ionisation to silicenium ions occurs. Ligand exchange is a competing process, the rate of which increases significantly by incresing the temperature of reaction time. The reaction of tris(alkylthio)silyl triflate with BCl_3 at low temperature only involves ligand exchange. Reaction of the alkoxides Me_3SiOR (R = Me,Et, Ph) with BBr_3 (at -30°) or BCl_3 (at -75°C) gives the trimethylsilyl halide and the corresponding $ROSiX_2$, indicative of initial complexation followed by rapid Si-O bond cleavage. The reaction of $AlCl_3$ and $AlBr_3$ with silyl triflates also results solely in ligand exchange.[115] The first example of a silicon thiocyanate, $(Me_3Si)_2C(SiMe_2OMe)(SiMe_2SCN)$ has been prepared from the analogous chlorosilane and AgSCN. It is much more readily solvolysed than its isothiocyanate isomer.[116]

Trisilylamine, $N(SiH_3)_3$, is planar at nitrogen in the crystal at 115K. There are no short intermolecular contacts.[117] However, in the silylamines, $Me_2SiHNMe_2$, $MeSiH_2NMe_2$, and H_3SiNMe_2, the nitrogen atom has a shallow pyramidal configuration (sum of angles at nitrogen: 352.4°, 355.6° and 354.6°, respectively). The preferred conformations of the two former compounds have one Si-Me bond gauche to the lone pair of electrons on the nitrogen.[118] Three conformational models give excellent agreement with the experimental data for $NH(SiHMe_2)_2$, although one is slightly favoured. In this, the $SiHMe_2$ groups are twisted from the positions in which the Si-H bonds eclipse the N-Si bonds, so that the two $SiHMe_2$ groups are staggered when viewed along the Si...Si direction.[119] The $[Si_3N_3]$ ring in 2,2,4,4,6,6-hexa-tert-butylcyclo-trisilazane is planar, with angles of 104.1° at silicon and 135.9° at nitrogen.[120] The structures of the two heterocyclic compounds (52) and (53) have also been reported.[121] The X-ray crystal structure of $Ph_3SiNHPPh_2$ confirms a trans conformation of the P^{III} lone pair and the N-H bond as a consequence of the minimisation of steric and electronic repulsive interactions.[122] Molecules of $(C_5H_5)_3Zn_2N(SiMe_3)_2$, prepared from $(C_5H_5)_2Zn$ and $Zn[N(SiMe_3)_2]_2$, consist of two zinc atoms bridged by a cyclopenta-

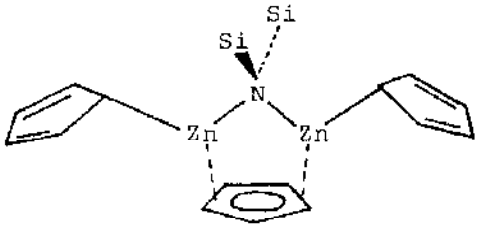


(52)



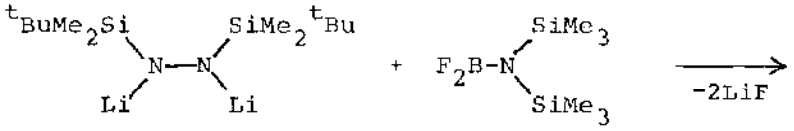
(53)

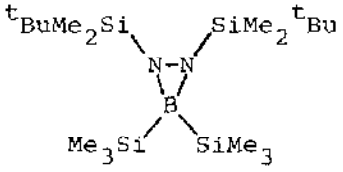
dienyl group and an amido group as in (54).[123]



(54)

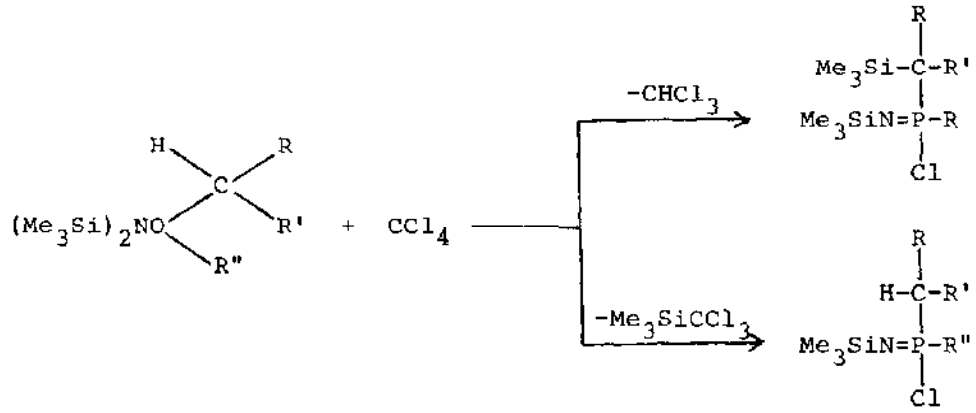
The high steric bulk of silyl groups has been employed to synthesise the stable three-membered [N_2B] heterocycle (55):[124]



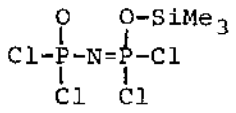


(55)

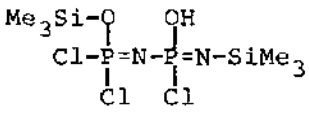
The reactions of several mono(disilylamino)phosphines with either neat carbon tetrachloride or solutions in dichloromethane have been examined. Generally, reactions proceeded with elimination of $CHCl_3$ and/or Me_3SiCCl_3 to form a variety of new P-chloro-N-silylphosphoranimines of general formula $Me_3SiN{=}P(Cl)R'R''$.



The particular course of the reactions is dependent upon such variables as solvent polarity and steric bulk of the substituents at phosphorus and nitrogen.[125] The major components of the liquid phase in the reaction of hexamethyldisilazane and bis(dichlorophosphoryl)imide are (56) and (57), which subsequently condense further to give high polymers.[126]



(56)

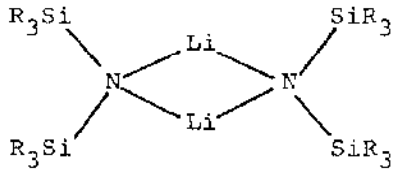


(57)

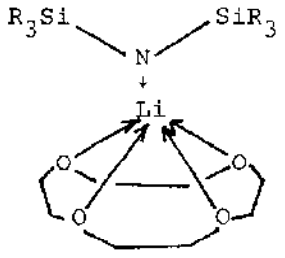
The first stable silylated triazene, $^{t}Bu_3Si-N=N-NH-Si^{t}Bu_3$, has been synthesised by treating $^{t}BuSiN_3$ in thf first with $^{t}Bu_3SiNa$ and then with methanol. Although the pale yellow crystalline solid melts at 139-140°C and can be sublimed at 110°C in vacuo, it decomposed at 150°C with the elimination of nitrogen giving bis(tri-tert-butylsilyl)amine.[127] Partially-substituted tetrazenes, $(Me_3E)N_4H_{4-n}$ (E = Si,Ge) have been prepared by photolysis of more highly substituted tetrazenes, or by metallation of lower substituted tetrazenes. The compounds have the 2-tetrazene constitution with a trans-tetrazene conformation. The tetrazenes, $(Me_3Si)_2N-N=N-NHX$ (X = H,$GeMe_3$) isomerise in dilute solution on heating into $(Me_3Si)XN-N=N-NH(SiMe_3)$. Thermolysis of $(Me_3Si)_2N-N=N-NH(SiMe_3)$ leads principally to Me_3SiN_3 and $(Me_3Si)_2NH$. Similarly, $(Me_3Si)_2N-N=N-NH_2$ gives Me_3SiN_3 and Me_3SiNH_2, and $(Me_3Si)HN-N=N-NH(SiMe_3)$ affords $(Me_3Si)_2N-NH_2$ and N_2 in dilute solution but $(Me_3Si)_2NH$ and HN_3 in

concentrated solution.[128]

Gaseous bis(trimethylsilyl)amidolithium at ca. 403K has the cyclic [LiNLiN]dimeric structure (58) of D_2 symmetry. In the model adopted, the bridging [$N(SiMe_3)_2$] ligands are assumed to be orthogonal to the [Li_2N_2] ring plane.[129] Complexation of the lithium by crown ethers precludes association via LiNLi bridging in the solid state and the 12-crown-4-ether complex of bis(trimethylsilyl)amidolithium, [$LiN(SiMe_3)_2$.12-crown-4] (59) is monomeric.[130]

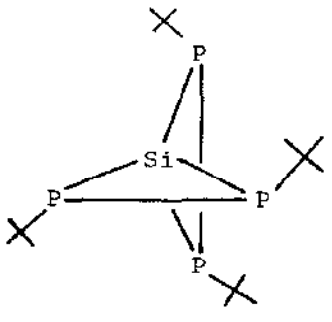


(58)

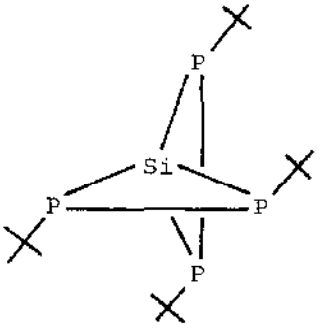


(59)

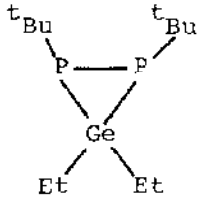
The spirocyclic compound, 1,2,4,5-tetra-tert-butyl-1,2,4,5-tetraphospha-3-silaspiro[2.2]pentane exists in two diastereoisomers of point symmetry $\bar{4}$ and 2 (60a and 60b).[131] The endocyclic P-P distance in both of these isomers (2.255Å and 2.242Å, respectively)[131] and in the related diphosphagermirane, (61), (2.229Å)[132] are rather longer than normal. The same [GeP_2] cyclic unit is present in the novel spirocyclic compound, 1,2,4,5,6,7-hexa-tert-butyl-1,2,4,5,6,7-hexaphospha-3-germaspiro-[2.4]heptane, (62), formed by cyclocondensation of K(^{t}Bu)P-P(^{t}Bu)K with germanium(IV) chloride in the molar ratio 2:1.[133] Tris(tri-



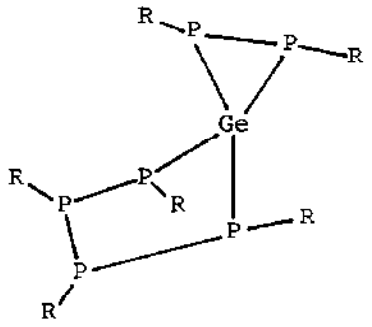
(60a)



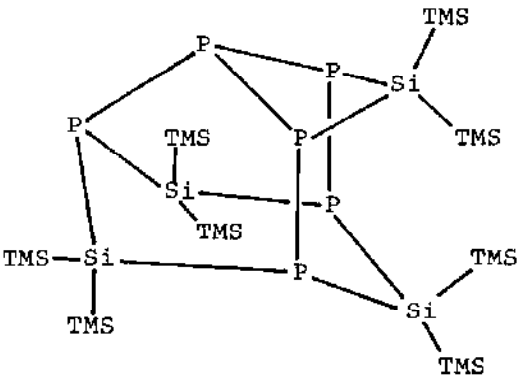
(60b)



(61)



(62)



(TMS = $SiMe_3$)

(63)

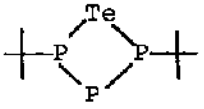
methylsilyl)-tert-butylcyclotetraphosphane, $P_4(SiMe_3)_3{}^tBu$, the previously unknown member of the series, $P_4(SiMe_3)_n({}^tBu)_{4-n}$, has been obtained by the reaction of $P_3(SiMe_3)_5$ with ${}^tBuPCl_2$.[134] A very large polycyclic silylphosphane, $P_6Si_4(SiMe_3)_8$, with probable structure, (63), has been prepared by the reaction of tris(trimethylsilyl)chlorosilane with sodium/potassium phosphide in dme.[135]

Trimethylsilyl(diorgano)phosphines react with elemental tellurium to afford the compounds (65), which readily disproportionate:

$$2R_2PSiMe_3 \xrightarrow{+2Te} 2R_2P\text{-}Te\text{-}SiMe_3 \rightleftharpoons R_2P\text{-}Te\text{-}PR_2 + Me_3Si\text{-}Te\text{-}SiMe_3$$

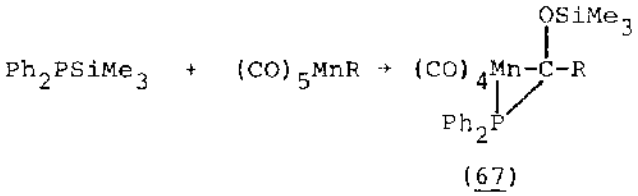
R = ${}^tBu$, Ph (65)

Reaction with ${}^tBuP(SiMe_3)_2$ yields to heterocycle (66):[136]



(66)

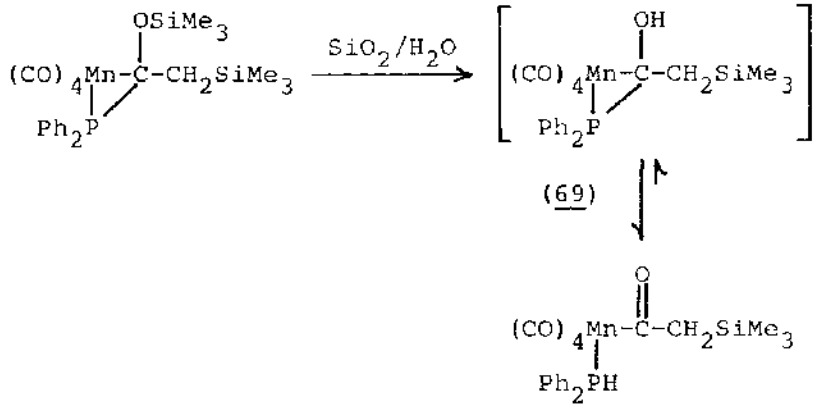
Ph_2PSiMe_3 also interacts with alkyl(pentacarbonyl)manganese complexes giving the ylide complexes (67); a reaction which is favoured by the formation of the strong Si-O bond:



(67)

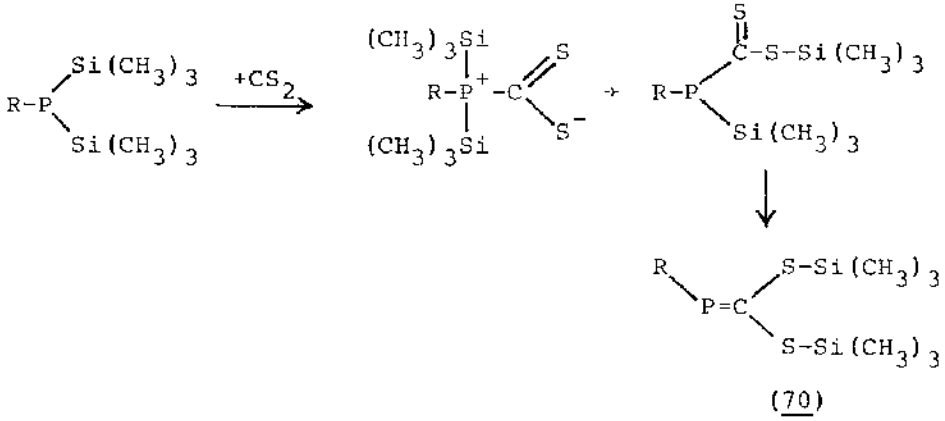
R = Me,Ph,2-Np,CH_2SiMe_3

Passage of the silylmethyl complex (67) (R = CH_2SiMe_3) through wet silica gel gave the acyclic acyl complex (68) via the hydroxy-ylide complex (69):[137]



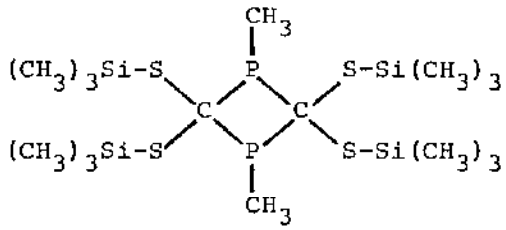
(69) (68)

Alkylbis(trimethylsilyl)phosphines, $RP(SiMe_3)_2$, react with carbon disulphide to afford the corresponding [bis(trimethylsilyl-sulphano)methylidene]phosphines, (70):



(70)

Only when R = mesityl could the two intermediates in the reaction be detected (by n.m.r.). The methyl derivative dimerises rapidly to (71). X-ray structures of this product and also of (70) (R = Ph) have been determined.[138,139]



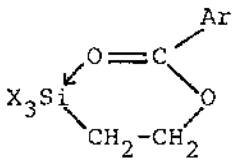
(71)

1,3-Bis(trimethylsilyl)-1,2,3-tri-tert-butyltriphosphane, $Me_3Si(^tBuP)_3SiMe_3$, has been obtained by reaction of $Li(^tBuP)_3Li$ and Me_3SiCl, and exists predominantly as the threo,erythro diastereoisomer.[140]

Compounds of silicon and germanium with coordination numbers greater than four continue to provoke interest, and the X-ray structures of several neutral and anionic species, have been determined. Both the $[SiF_5]^-$ and $[Ph_2SiF_3]^-$ anions have trigonal bipyramidal geometry, with two phenyl groups occupying equatorial positions in the latter.[141] In contrast to these isolated species, the corresponding germanium anion is a fluorine-bridged polymer with six-coordinated metal atoms. Two bridging modes have been characterised depending upon the nature of the cation. The $[XeF_5]^+$ salt contains infinite chains of [GeFe] octahedra sharing trans vertices, and the cations are arranged alternately to either side of the chain along the chain so that each cation approaches symmetrically two of the μ-fluoro-bridged $[GeF_6]$ units. In the $[ClO_2]^+$ salt, infinite helical chains of approximately octahedral $[GeF_6]$ units are joined by sharing cis vertices. The anion chains are held together by interactions with the cations.[142] Each SF_3^+ cation in the hexafluorogermanate salt, $[SF_3]_2^+[GeF_6]^{2-}$, makes close contact with one fluorine from each of three $[GeF_6]^{2-}$ anions to give distorted octahedral coordination about germanium and sulphur.[143] The 1:1 complexes $GeF_4.L$ (L = H_2O, MeOH, Me_2O, CD_2O, Me_2CO) have been formed by codeposition in an argon matrix. Infrared data indicate a trigonal bipyramidal geometry.[144] A finely-grained glass soot is formed of composition $Si_{1-x}Ge_xO_2$

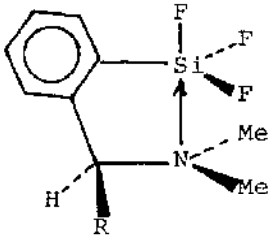
($0 \leq x \leq 1$) by the oxidation of gaseous mixtures of $SiCl_4$ and $GeCl_4$ at temperatures of 2023K.[145]

Silicon-substituted 2-benzoyloxyethylsilanes, $PhCO_2CH_2CH_2SiX_3$ (X = F or Cl), may exist in solution as either an acyclic form with four-coordinated silicon, or as in intramolecularly coordinated five-coordinated form, (72), depending on the concentration and nature of the solvent.[146] Silicon-29 n.m.r. has been employed in the characterisation of the cation five-coordinated silicon species $[Nu_2SiMe_2H]^+X^-$ (73) (Nu = 3-methyl-1-imidazolio, N,N-dimethylamino-pyridinio, or pyridinio; X = Cl, I, SO_3C_3).[147] Fluorine-19 and proton n.m.r. spectra for the pentacoordinated fluorosilanes containing an intramolecular Si-N coordinative bond, (74a) and (74b), indicate the presence of distinct pseudorotation and ring-opening processes.[148]

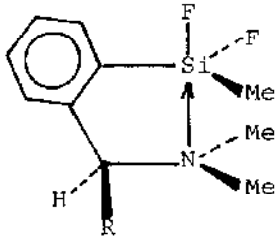


X = F,Cl

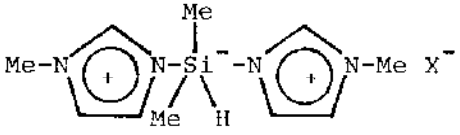
(72)



(74a)

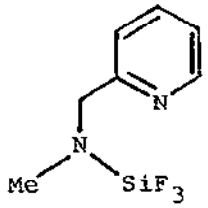


(74b)

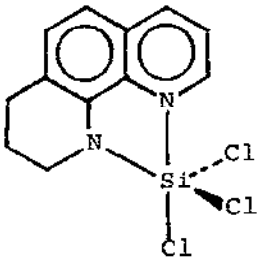


(73)

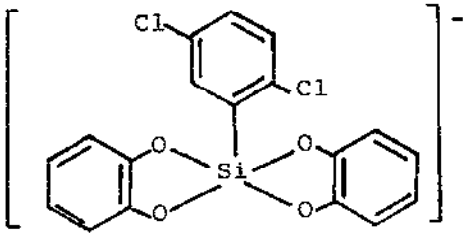
The similar compounds, (75)[149] and (76)[150] possess trigonal bipyramidal geometries. However, when the silicon atom is part of an unsaturated five-membered ring system, the geometry at silicon is distorted away from trigonal bipyramidal towards a square-based pyramid along the Berry pseudorotation coordinate. Thus, whilst the geometry of the anion, (77), is not far distorted from a trigonal bipyramid, the similar anions, (78) and (79), have square based pyramidal geometries, and (80) and (81) geometries midway between the two extremes.[151,152] The intramolecularly-coordinated structure determined by X-ray crystallography for (75)



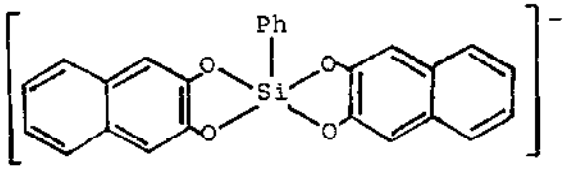
(75)



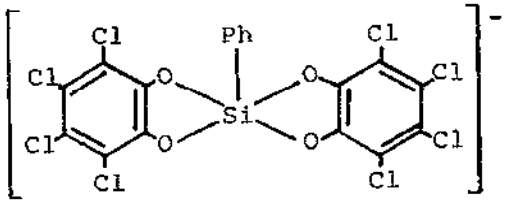
(76)



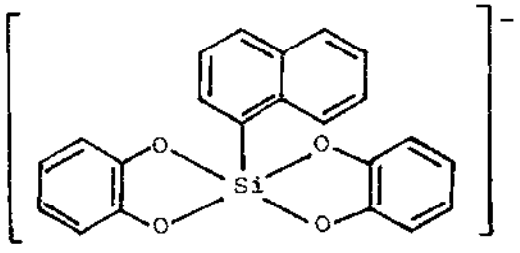
(77)



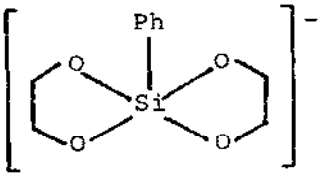
(78)



(79)

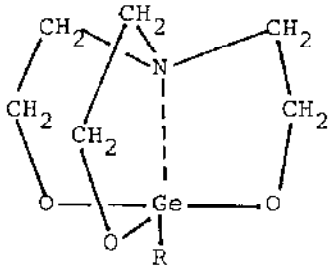


(80)

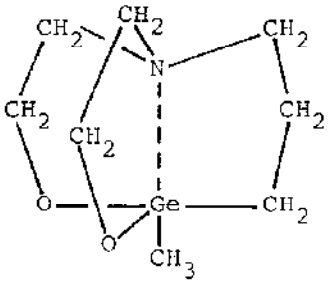


(81)

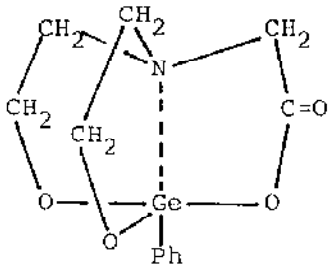
in the crystal is also present in solution below -10°C (n.m.r.). At higher temperatures, however, intramolecular ligand rearrangements occur involving rupture of the Si-N bond.[149] The structures of seven germatranes of the types (82), (83) and (84) have been determined. The intramolecular Ge...N distance falls in the range 2.1-2.4Å, the shortest would be for 1-bromogermatrane (82, R = Br) and the longest, 2.44Å, for 1-methyl-2-carbagermatrane (83).[153]



(82)



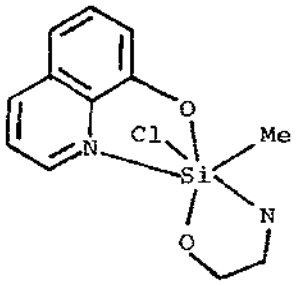
(83)



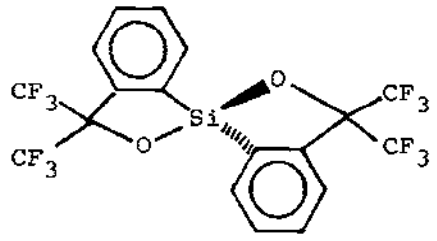
(84)

Dissolution of SiI_4 in dmf results in ionisation of all Si-I bonds and the formation of the salt $[Si(dmf)_6]^{4+}4I^-$, in which the silicon atom is octahedrally coordinated.[154] Crystals of (85) comprise both possible enantiomers,[155] whilst the spiro silane, (86), forms the 1,10-phenanthroline adduct, (87), which undergoes enantiomerisation and diastereomerisation (interconversion with two isomers in solution) by dissociation of the phenanthroline ligand.[156]

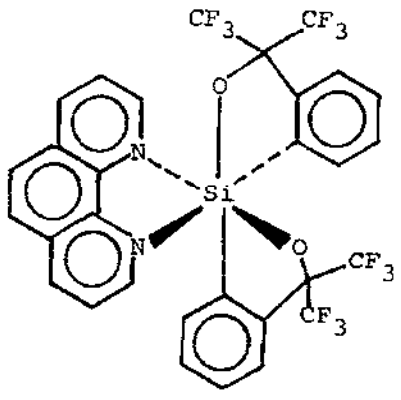
The direct, one-step, high-yield fusion of nido-2,3-$[Me_3Si]_2$-2,3-$C_2B_4H_6$ to give nido-$[Me_3Si]_2C_4B_8H_{10}$, without the need of a metal catalyst, has been reported. The conversion takes place at 210°C over a period of 3 days in a sealed reactor tube. Trimethylsilane



(85)



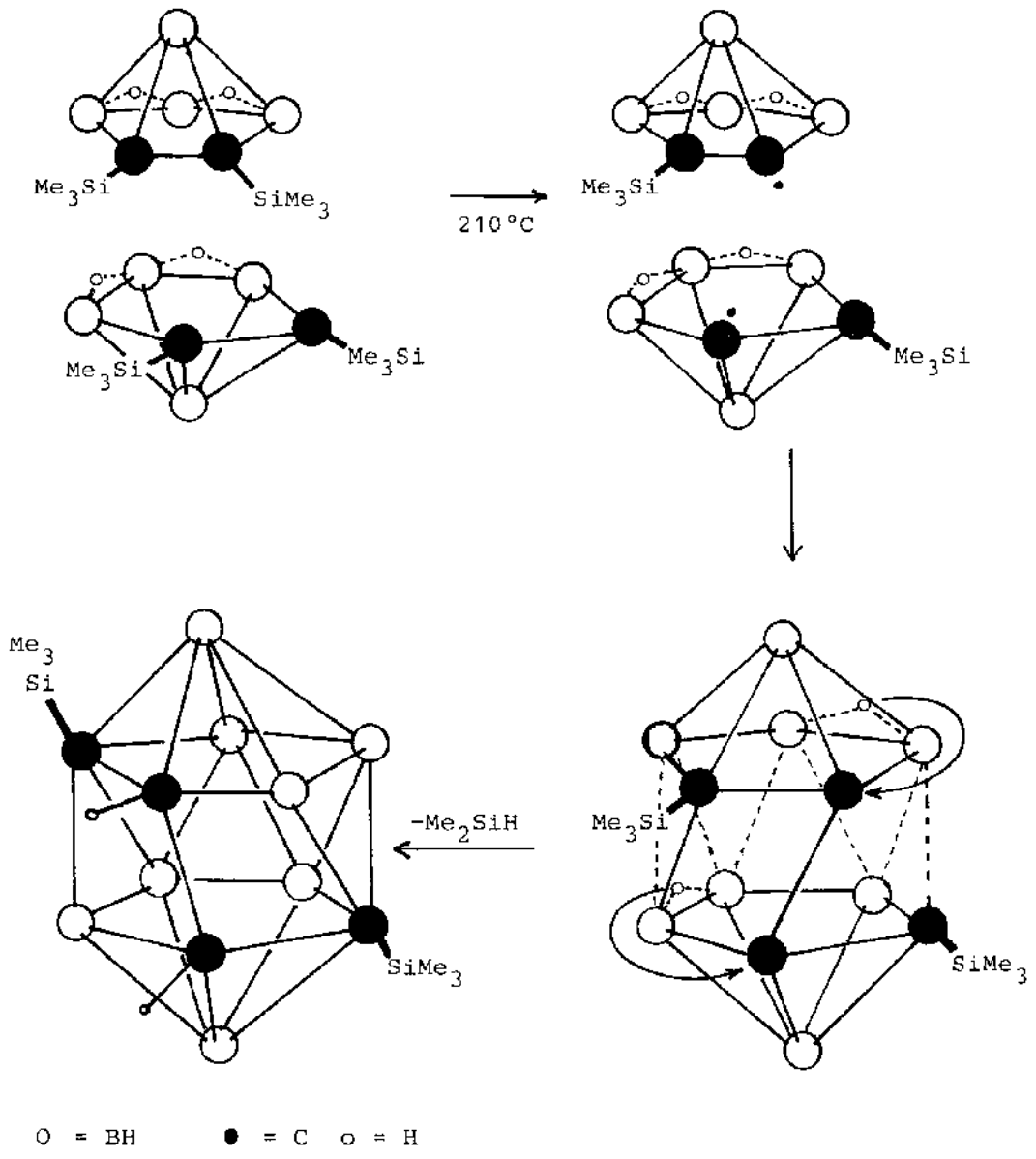
(86)



(87)

is also formed. The exact mechanism of the fusion process is not known, but a plausible scheme is outlined in Scheme 11. Such a scheme involves the high-temperature formation of a trimethylsilyl radical, which could then extract one of the carborane bridge-hydrogen atoms forming Me_3SiH and a reactive carborane fragment that could condense with another such fragment.[157] The closo-osmacarborane, 1-$Os(CO)_3$-2,3-$[Me_3Si]_2$-2,3-$C_2B_4H_4$, has been synthesised by the reaction of $Os_3(CO)_{12}$ with either closo-$Sn[Me_3Si]_2C_2B_4H_4$ or nido-$[Me_3Si]_2C_2B_4H_6$. The former is the preferred method giving almost quantitative yields.[158]

Several improvements in the preparation and use of [tris(trimethylsilyl)methyllithium have been described. The pertinent features may be summarised as follows: preparation of methyllithium using MeCl (rather than MeBr) (although in reactions with metal or metalloid halides, it is advisable to employ the same methyl halide); determination of yield can be accompanied using ^1H n.m.r. to measure the $(Me_3Si)_4C/(Me_3Si)_3CH$ ratio in the

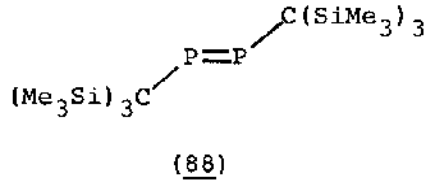


Scheme 11

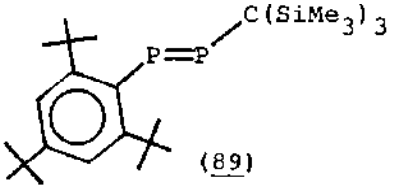
mixture obtained by treatment of the solution with Me_3SiCl; excess MeLi can be destroyed using Me_3SiOMe or Me_3SiOEt, which do not affect $(Me_3Si)_3CLi$.[154] The structures of several compounds containing trimethylsilylmethyl groups have been determined. In the gas phase at ca. 413K, bis(trimethylsilyl)methyllithium, $(Me_3Si)_2CHLi$, is monomeric, but it is polymeric in the solid with

bridging lithium atoms.[160] The related silylmethylphosphido-lithium compound, $[Li(\mu\text{-}PR_2)]_2$ ($R = CHCSiMe_3)_2$], prepared from $PClR_2$ and lithium shot in diethyl ether at 25°C, is dimeric and has a planar central $[Li_2P_2]$ ring.[161] The molecular structure of $(Me_3Si)_3CPH_2$ has been determined in the gas-phase by electron diffraction. Steric strain within the $[(Me_3Si)_3C]$ group is relieved in three ways: compression of the methyl groups within each trimethyl silyl group (the Me-Si-Me angles are only 104.3(4)°), tilting of the trimethylsilyl groups by 7.3° away from each other, and twisting of the trimethylsilyl groups by 21.2° away from the fully staggered conformation.[162]

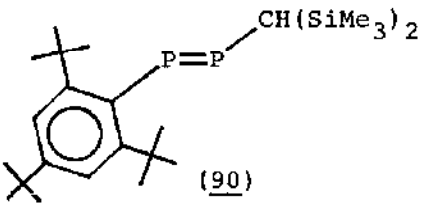
The sterically-crowded nature of bis- and tris-trimethylsilyl-methyl groups has been used to synthesise stable diphosphenes, phosphaarsenes, phosphastibenes and diarsenes such as (88)-(94).[163] The preferred method for the synthesis of the symmetrical diphosphene (88) is by sodium naphthalenide reduction of the corresponding organodichlorophosphine. Reduction of an equimolar mixture of the two organodichlorophosphines affords a moderate yield of the unsymmetrical diphosphene (89). A more general preparation for unsymmetrical compounds, including phosphaarsenes and phosphastibines, is by the dehydrochlorination of a mixture of $[2,4,6\text{-}(^tBu)_3C_6H_2\text{-}PH_2$ with $(Me_3Si)_2CHCl_2$ using DBU in thf, by which method compounds (90), (91) and (93) were obtained. The same methodology was employed to synthesise the diarsenes, (92) and (94). In a separate study, the diphosphene, $(Me_3Si)_2CH\text{-}P{=}P\text{-}CH(SiMe_3)_2$, has been prepared by the reaction of $(Me_3Si)CH\text{-}P(H)GeCl_3$ with DBU. Structural data have been obtained for (88), (91) and (94).[163]



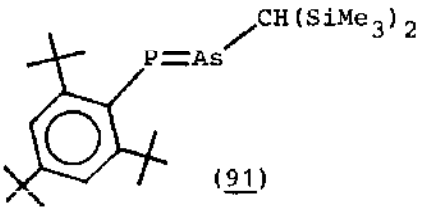
(88)



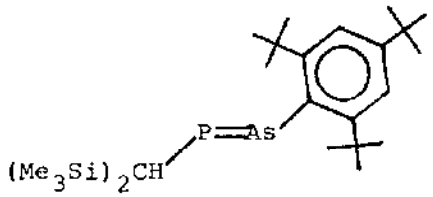
(89)



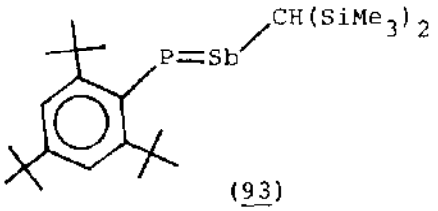
(90)



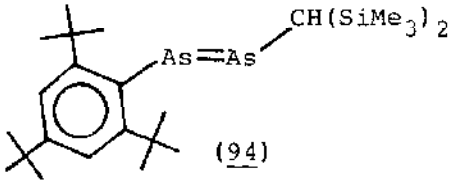
(91)



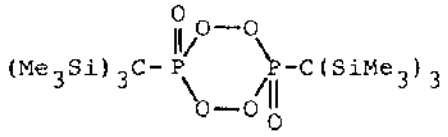
(92)



(93)

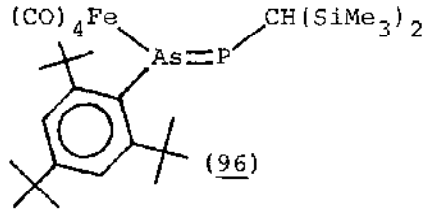


(94)

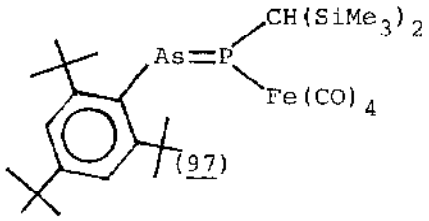


(95)

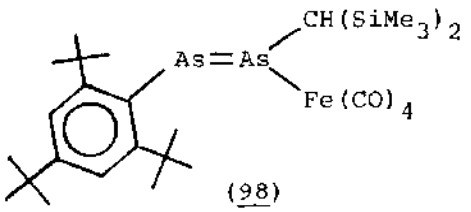
Ozonolysis of (88) takes place in a 2:1 stoichiometry to give, at low temperature, the relatively stable cyclic diperoxide (95).[165] Several complexes of these compounds with transition metal carbonyl fragments have been described. The phosphaarsene, (91), reacts with $Fe_2(CO)_9$ to afford both (96) and (97), whilst the diarsene, (94), reacts with $Fe_2(CO)_9$ and $Cr(CO)_5$.thf to afford the complexes, (98) and (99), respectively.[166] A larger diphosphene-nickel cluster, $[Ni_5(CO)_6[(Me_3Si)_2CHP{=}PCH(SiMe_3)_2]Cl]$, has been obtained by the reaction of $(Me_3Si)_2CHPCl_2$ with $Na_2[Ni_6(CO)_{12}]$, and has a structure in which the diphosphenes function as η^2 bridging ligands.[167]



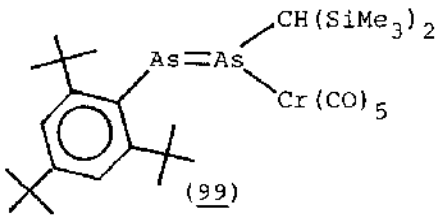
(96)



(97)

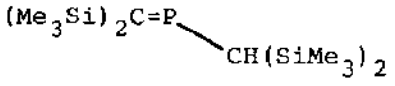


(98)

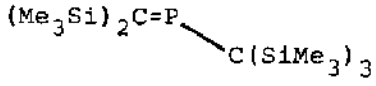


(99)

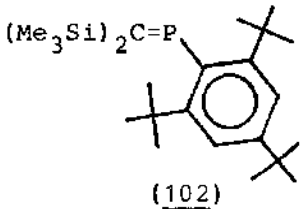
Several similar highly sterically hindered doubly bonded compounds have been synthesised. The phosphaalkenes, (100), (101) and (102) have been prepared by reaction of $(Me_3Si)_2C{=}PCl$ (from $(Me_3Si)_2CHPCl_2$ and DABCO) with the appropriate organolithium reagent; (101) adopts a planar conformation about the P=C bond, with a C=P=C bond angle of 110.7°. Treatment of $(Me_3P)_2NiCl_2$ with $[(Me_3Si)_2CH]_2PNa$ affords the η^2-phosphaalkene complex, (103), which has a square-planar arrangement about nickel.[168] Addition of $(Me_3Si)_2C{=}PCl$ to $K[Mo(CO)_3(\eta\text{-}C_5H_5)]$ in thf, yields bright orange crystals of $[Mo(CO)_2(\eta^1\text{-}P{=}C\text{-}(SiMe_3)_2(\eta\text{-}C_5H_5)]$, whose electronic structure can be described in terms of the two canonical forms, (104) and (105):[169]



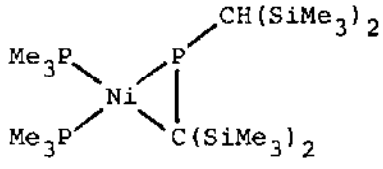
(100)



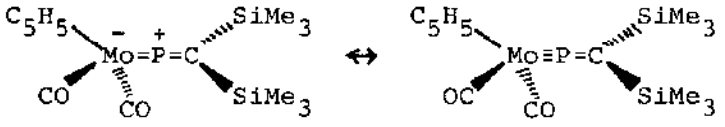
(101)



(102)

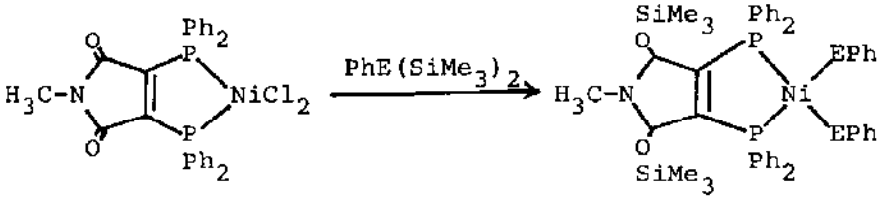


(103)



(104) (105)

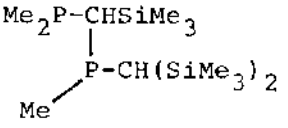
The nickel complex (106) reacts with $PhE(SiMe_3)_2$ (E = P,As) to afford the complexes (107):[170]



(106) (107)

Treatment of [bis(trimethylsilyl)amino][(trimethylsilyl)-methylene]phosphine in ether at -78°C with methyllithium followed by quenching with Me_3SiCl does not yield the expected phosphine, $(Me_3Si)_2NP(Me)CH(SiMe_3)_2$. Instead, the reaction follows a much more complicated course forming the bis(phosphino)methane derivative (108):[171]

$$2(Me_3Si)_2NP{=}CHSiMe_3 + 3MeLi + 3Me_3SiCl \rightarrow$$

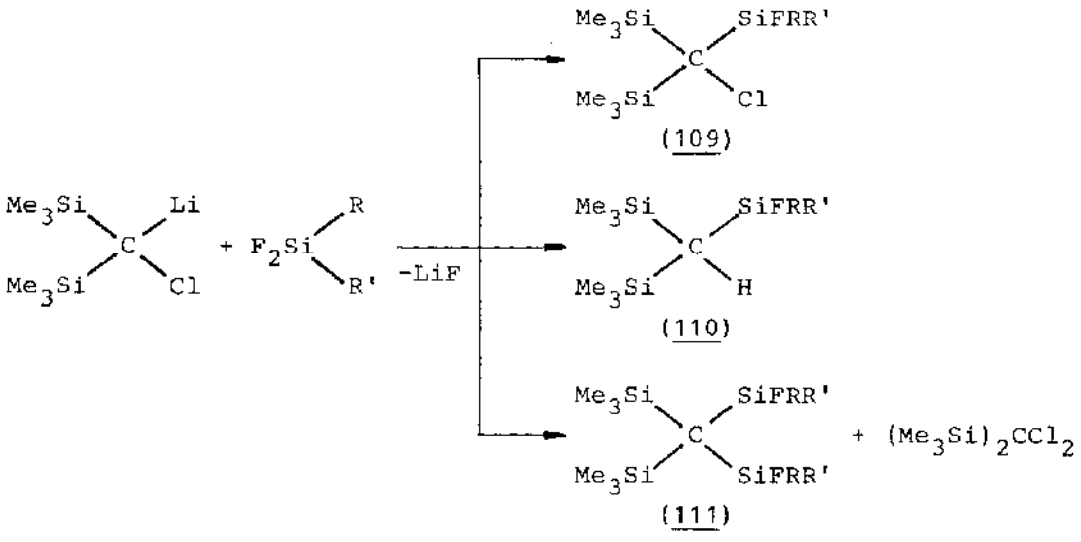


$$+ 3LiCl + 2(Me_3Si)_3N$$

(108)

The reaction of $(Me_3Si)_2CHSbCl_2$ with magnesium in thf affords $[(Me_3Si)_2CHSb]_n$ trimers and tetramers.[172]

The compounds $MH_3C{\equiv}CCF_3$ (M = Si,Ge) and their fully deuterium-substituted analogues have been prepared by reaction of silyl or germyl halides with the Grignard reagent derived from $CF_3C{\equiv}CH$. The silyl compound, as expected, has a linear [SiCCC] skeleton (electron diffraction). Lithium tris(trimethylsilyl)methane and the lithium salt of chlorobis(trimethylsilyl)methane reacts with fluorosilanes to afford mono- and di-substituted products such as (109), (110), (111) and (112).[174,175]

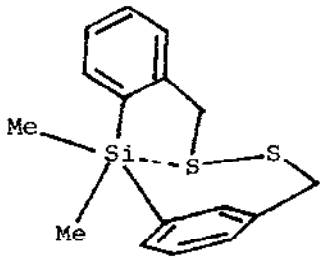


(109) (110) (111)

$$(Me_3Si)_3CLi + F_3Si\text{-}R \xrightarrow[-LiF]{} (Me_3Si)_3C\text{-}SiF_2R$$

(112)

One intramolecular transannular Si...S interaction (3.438(3)Å) is present in 13,13-dimethyl-8,13-dihydro-5H-dibenzo[d,g][1,2,6]-dithiasilonine (113). The second silicon-sulphur distance is much longer (4.190Å).[176]

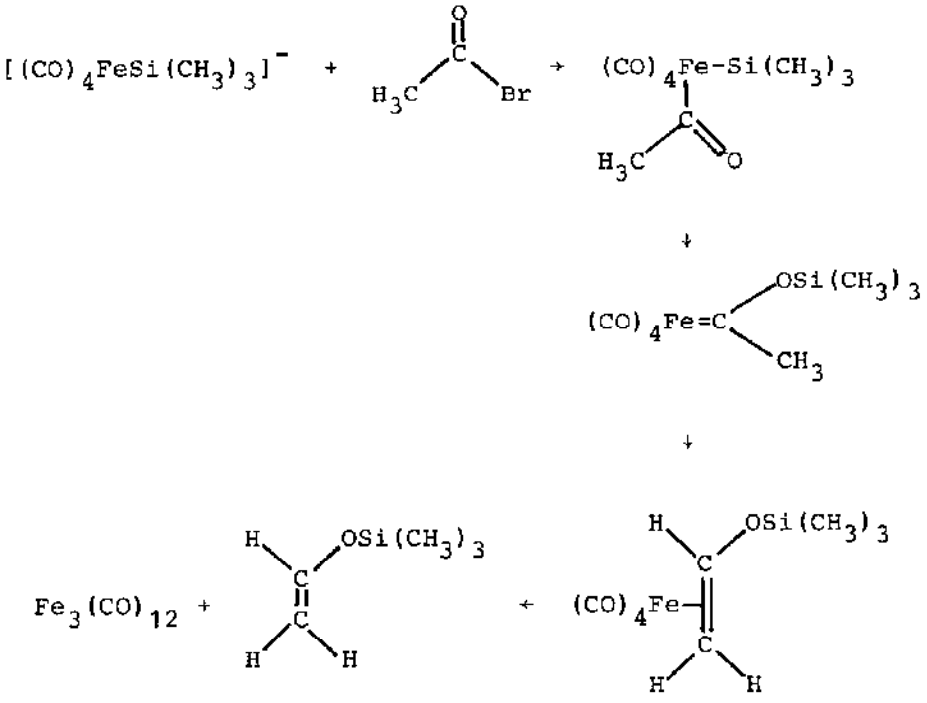


(113)

Reaction of Et_3SiH with $[\{(C_5Me_5)Ir\}_2Cl_4]$ gives the complex $[(C_5Me_5)Ir(H)_2Cl(SiEt_3)]$, which reacts further under more drastic conditions, to form $[(C_5Me_5)Ir(H)_2(SiEt_3)_2]$. Reaction with Ph_3SiH affords the analogous triphenylsilyl complex, but with $[\{(C_5Me_5)Ir\}_2Cl_4]$ the complexes, $[(C_5Me_5)Rh(H)_2(SiPh_3)_2]$ and $[(C_5Me_5)Rh(H)_2(SiPh_3)(SiPh_2Cl)]$, are formed.[177] The oxidative-addition of (+)-1-NpPhMeSiH to methylcymantrene to give the complex, (-)-$(\eta^5\text{-}MeC_5H_4)(CO)_2$(1-NpPhMeSi)(H)Mn, occurs with retention of configuration at silicon. The similar germyl complexes, $(\eta^5\text{-}MeC_5H_4(CO)_2(R_3Ge)(H)Mn$, may be prepared either by oxidative-addition of R_3GeH (R = Ph) to $(\eta^5\text{-}MeC_5H_4)(CO)_3Mn$ or by protonation of the related anions $[(\eta^5\text{-}MeC_5H_4(CO)_2(R_3Ge)Mn]^-$ (R_3 = Ph_3, 1-NpPhMe, Cl_3), although only the cis isomers are obtained. The acidity of the hydrides is close to that of HCl.[178] In these complexes, and the related complexes, $[(\eta^5\text{-}MeC_5H_4(CO)_2Mn(H)SiFPh_2]$ and $[(\eta^5\text{-}MeC_5H_4Mn(H)SiCl_3]$,[179] contains two-electron, three-centre bonds between manganese, hydrogen and the Group IV metalloid. The complexes, $(C_5H_5)(CO)_2FeSiFPh_2$ and $(C_5H_5)(CO)_2FeSiCl_3$, contain 'normal' Fe-Si bonds. The former complex assumes a gauche conformation with respect to the Fe-Si bond, whereas in the

latter, the silyl ligand is rotated 12° about the Fe-Si axis from a staggered conformation.[179] In the complex, $(Me_3Ge)(Ph_3P)Ir(H)(CO)$, the germyl group is trans to a phosphine ligand, both of which are mutually cis. One hydride is trans to the second phosphine, whilst the other is trans to the carbonyl group.[180] The short Ni-Ge bond distance in the complex, $(C_5H_5)(Ph_3P)(Cl_3Ge)Ni$, suggests the presence of appreciable d_π-d_π interaction.[181]

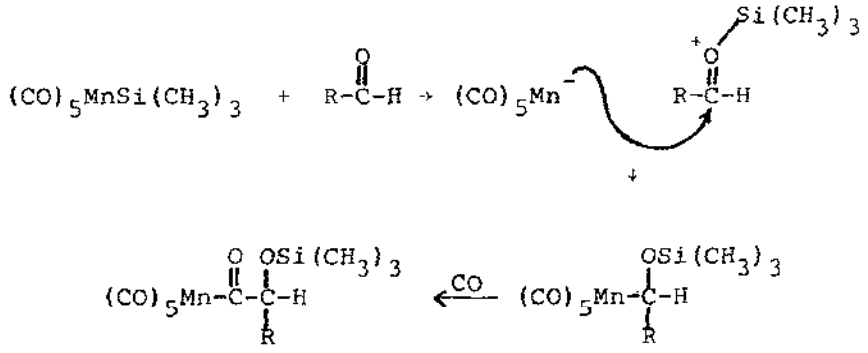
Studies of the reactions between $HFe(CO)_4SiCl_3$ and conjugated dienes (kinetic data, diene reactivity patterns, observation of ClDNP effects) demonstrate that a hydrogen atom transfer free-radical type mechanism operates in all cases. In most cases the reaction is clearly first-order in each reagent.[182] The reaction of $(C_5H_5)(CO)_2Fe\text{-}SiCl(NMe_2)_2$ with $LiNMe_2$ yields $(C_5H_5)(CO)_2Fe\text{-}Si(NMe_2)_3$ in minor quantities. However, high yields are obtained from the reaction of $(C_5H_5)(CO)_2Fe\text{-}SiBr_3$ with diethylamine. Irradiation in the presence of Me_3P affords the complex $(C_5H_5)(Me_3P)_2Fe\text{-}Si(NMe_2)_3$, which reacts with methyl iodide to give $(C_5H_5)(Me_3P)_2FeI$.[183] The labile, air-sensitive alkyls, $cis\text{-}(CO)_4Fe(R)SiMe_3$ (R = Me, Et, $PhCH_2$, $CH_2CH{=}CH_2$), have been isolated from the reaction between $M[(CO)_4FeSiMe_3]$ (M = Na,K) salts and the fluorosulphonates, $MeOSO_2F$, $MeOSO_2CF_3$ or $EtOSO_2F$, or the bromides, $PhCH_2Br$ or $CH_2{=}CHCH_2Br$. When R = Me or $PhCH_2$, reductive-elimination of Me_3RSi occurs at room temperature. Reactions of the salts with acylating agents such as MeCOBr, EtCOBr and $PhCH_2COBr$ give $H_2C{=}CHOSiMe_3$, $CH_3CH{=}CHOSiMe_3$, and $PhCH{=}CHOSiMe_3$, respectively, via a mechanism (Scheme 12) involving initial acylation, a rapid 1,3-silatropic shift to give the observable (silyloxy)carbene complex, $(CO)_4Fe{=}C(CH_2R)OSiMe_3$, and a 1,2-hydride shift to give the olefine complex, $(CO)_4Fe(RCH{=}CHOSiMe_3)$, which dissociates $RCH{=}CHOSiMe_3$.[184] The iron and ruthenium complexes, $HM(SiEt_3)(CO)_3(PPh_3)$ (M = Fe,Ru), have a meridional structure with hydrogen cis to both the phosphine and silyl ligands (the cis-mer)isomer). The $fac\text{-}HM(SiEt_3)(CO)_3(PPh_3)$ complexes undergo thermal isomerisation to the cis-mer isomer upon warming to 298K. Near-u.v. excitation of the cis-mer complexes at ca. 100K in an organic glass gives evidence for both the loss of CO and elimination of Et_2SiH. Similar results are obtained at 298K in fluid solution. Irradiation of the cis-mer complexes in a hydrocarbon solution of Ph_3SiH at 298K results in the formation of $cis\text{-}mer\text{-}HM(SiPh_3)(CO)_3$-



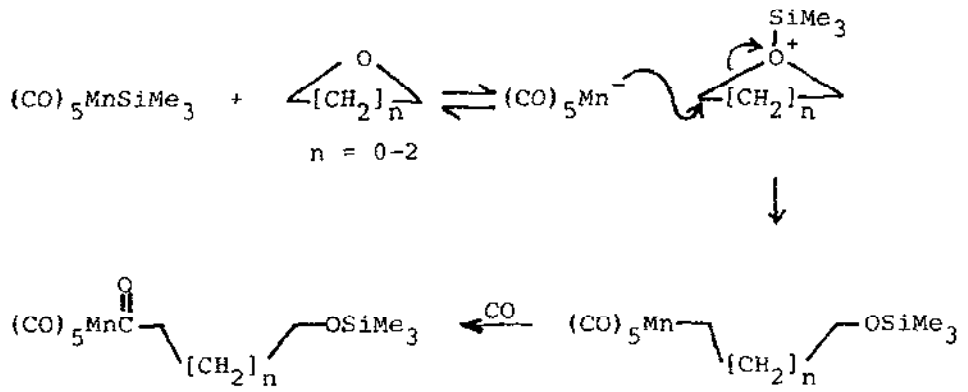
Scheme 12

(PPh_3) and Et_3SiH with a 313-nm quantum yield of ca. 0.6. The process is photochemically reversed if the cis-mer-$HM(SiPh_3)(CO)_3(PPh_3)$ complex is irradiated in the presence of excess Et_3SiH. Irradiation of cis-mer-$HM(SiEt_3)(CO)_3(PPh_3)$ in a hydrocarbon solution at 298K in the presence of ^{13}CO yields both ^{13}CO-enriched $M(CO)_4PPh_3$ and ^{13}CO-enriched cis-mer-$HM(SiEt_3)(CO)_3(PPh_3)$. Irradiation of cis-mer-$HM(SiR_3)(CO)_3(PPh_3)$ (R = OMe, OEt) or cis-mer-$HRu(SiMeCl_2)(CO)_3(PPh_3)$ at 298K in the presence of Et_3SiH yields cis-mer-$HM(SiEt_3)(CO)_3(PPh_3)$, establishing that the light-induced reductive-elimination of R_3SiH occurs for a wide variety of groups R attached to silicon.[185] The reactions of $(CO)_5MnSiMe_3$ and CO with aldehydes, RCHO, and cyclic ethers, $OCH_2(CH_2)_nCH_2$ (n = 0-2), give the acyl manganese complexes, $(CO)_5MnCOCH(R)OSiMe_3$ and $(CO)_5MnCOCH_2(CH_2)_nCH_2OSiMe_3$, respectively. Experiments in the absence of CO show that these transformations proceed via the labile alkyl intermediates, $(CO)_5MnCH(R)OSiMe_3$ an $(CO)_5MnCH_2(CH_2)_nCH_2OSiMe_3$. When the reactions are carried out in the presence of $(CO)_5MnH$ under careful conditions, the homologated aldehydes, $Me_3SiOCHRCHO$, are

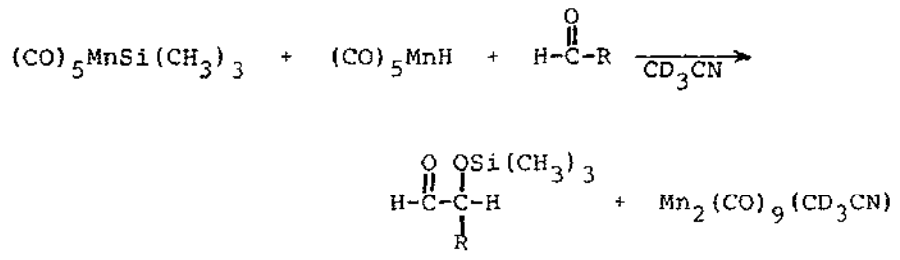
obtained. Reaction of $(CO)_5MnCOCH_2(CH_2)_nCH_2OSiMe_3$ (n = 1 or 2) with $[Et_2N]_3S^+SiMe_3F_2^-$ affords γ-butyrolactone and δ-valerolactone, respectively. Proposed mechanisms are shown in Schemes 13-17.[186]



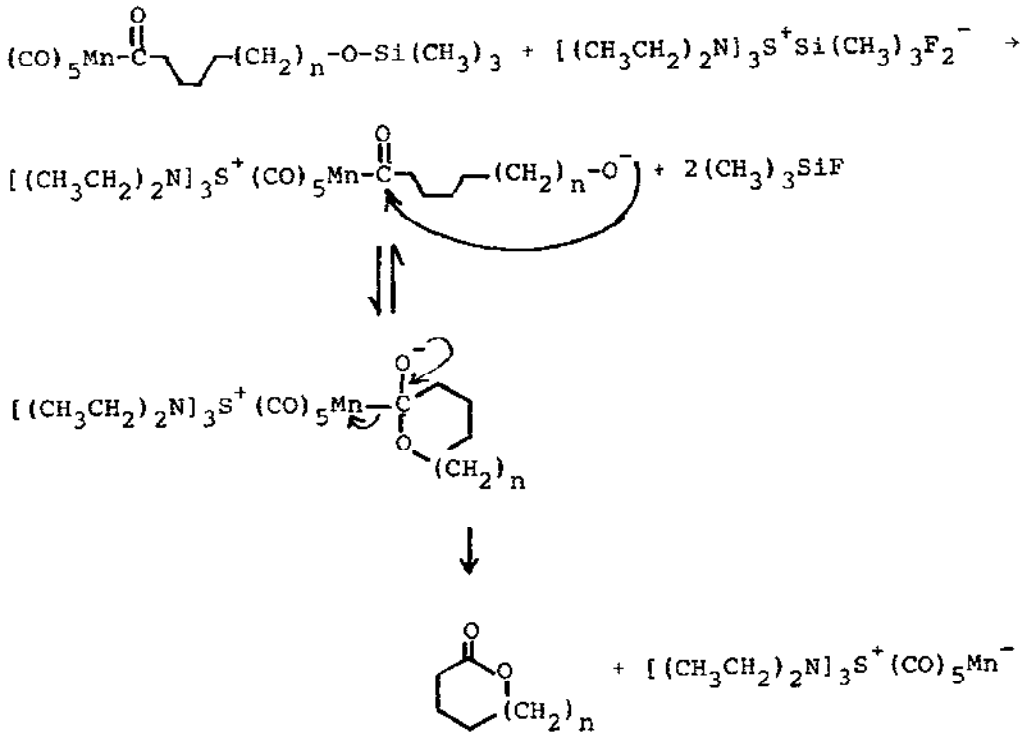
Scheme 13



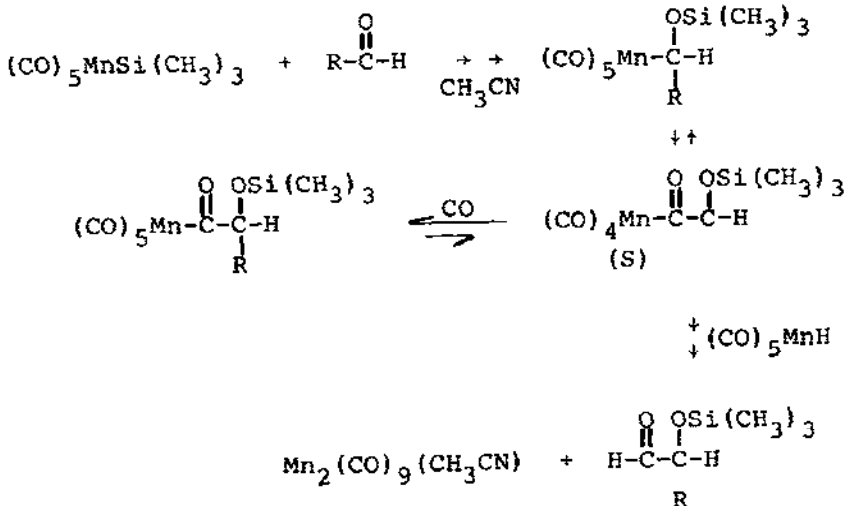
Scheme 14



Scheme 15



Scheme 16



(S) = CH_3CN or vacant coordination site.

Scheme 17

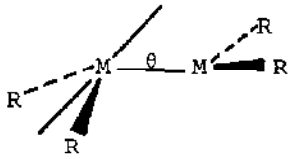
The reaction of GeH_3K with $Cr(CO)_6$ or $W(CO)_6$ affords the salts $K[M(CO)_5GeH_3]$ (M = Cr, W), which may be converted into tetraphenylphosphonium salts using $[PPh_4]Cl$. Similar methods have been employed to synthesise $K[(C_5H_5)Mn(CO)_2GeH_3]$, $K[Co_2(CO)_7GeH_3]$, and $[PPh_4][Co_2(CO)_7GeH_3]$.[187] The X-ray structures of a number of complexes including $[PPh_4][Cr(CO)_5GeH_3]$[187] have been determined. That of $(\eta^5\text{-}C_5H_5)(Cl_3Ge)(Ph_3P)Ni(II)$ (as a hemibenzene solvate) exhibits a short Ni-Ge bond (2.248(1)Å) suggestive of an appreciable $d_\pi - d_\pi$ interaction.[188] The iridium(III) complex, $(CO)(H)(Me_3Ge)(Ph_3P)Ir$, (also as a hemibenzene solvate) has a distorted octahedral arrangement, with mutually cis phosphine groups, and the hydrido and germyl ligand trans to the phosphine ligands.[189] The structures of the complexes $(C_5H_5)(CO)_2FeSiFPh_2$ and $(C_5H_5)(CO)_2FeSiCl_3$ containing 'normal' metal-silicon bonds have been compared with the known structures of the complexes $(MeC_5H_4)(CO)_2Mn(H)SiFPh_2$ and $(MeC_5H_4)(CO)_2Mn(H)SiCl_3$, which contain Mn-H-Si three-centre bonds.[190] Anions of the type $[(C_5H_5)(CO)(L)(MPh_3)M']^-$ (L = CO,NO; M = Si,Ge,Sn; M' = Mn,Mo,W) react with allyl halides affording neutral σ-bonded alkenyl derivatives, which can rearrange to η^3-allyl complexes and lose (allyl)M to give η^2-allyl complexes. Butenyl and hexenyl iodides also react with the anions, giving η^1-complexes which can eliminate CO and rearrange to a η^3-ligand, as exemplified by the crystal structure of $(C_5H_5)(Ph_3Ge)(\eta^3\text{-hexenyl})(NO)Mo$.[191] Reaction of $\{(C_5Me_5)Ir\}_2Cl_4$ with methylsilane affords $(C_5Me_5)Ir(H)_2Cl(SiEt_3)$, which under more drastic conditions, reacts further to give $(C_5Me_5)Ir(H)_2(SiEt_3)_2$. The analogous rhodium complex reacts with Ph_3SiH to give $(C_5Me_5)Rh(H)_2(SiPh_3)_2$ and $(C_5Me_5)Rh(H)_2(SiPh_3)(SiPh_2Cl)$.[192] Reaction between $\mu_4\text{-}Si[Co_2(CO)_7]_2$ and $[Co(CO)_4]^-$ affords the paramagnetic cobalt carbonyl cluster anion, $[\mu_8\text{-}SiCo_9(CO)_{21}]$, in which the silicon atom is encapsulated in a capped square anti-prismatic array of cobalt atoms.[193] The reaction of $Pt(PPh_3)_n$ (n = 3 or 4) with $[(CF_3)_3Ge]_2Hg$ or $(CF_3)_3GeHgPt(PPh_3)_2Ge(CF_3)_3$ affords the stable diplatinum complex, $[(CF_3)_3GePt(PPh_3)_2]_2Hg$, which contains a Ge-Pt-Hg-Pt-Ge chain of C_2 symmetry.[194]

X-ray photoelectron and X-ray emission spectra for the tris(tropolonate) complex $[Si(C_7H_5O_2)_3][PF_6]$ show that the silicon-ligand bonding has both σ and π components, and can be rationalised using simple molecular orbital theory.[195] Proton

polarisation transfer has been successfully applied to germanium-73 n.m.r. Despite relatively short relaxation times, quadrupole moment, and long, inhomogeneous radio frequency pulses, enhancements ranging from 2- to 6-fold for proton-decoupled spectra and upto 20-fold for coupled spectra could be obtained for compounds with hydrogen, methyl, or ethyl groups bonded to germanium. Aquisition times are reduced from 3- to 10-fold for a decoupled spectrum to a 100-fold for a coupled spectrum.[196]

4.3 BIVALENT COMPOUNDS OF GERMANIUM, TIN AND LEAD

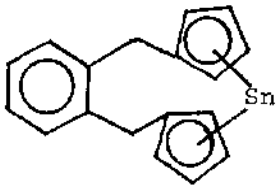
The structure of monomeric $Ge[CH(SiMe_3)_2]_2$ has been determined in the gas phase at 430K by electron diffraction, and has the expected angular structure, with a Ge-C bond distance of 204(2)Å and a CGe valence angle of 107(2)°.[197] However, in the crystal like the tin analogue the same compound is dimeric having the trans-folded structure (114, (R = $CH(SiMe_3)_2$, M = Ge)) with a fold angle (θ) of 32°. Each germanium environment is intermediate between pyramidal and planar (sum of angles at germanium = 348°). The germanium-germanium bond distance is 2.347(2)Å (ca. 4% shorter than in elemental germanium.[198] Ab initio molecular orbital calculations with a better than double-ζ



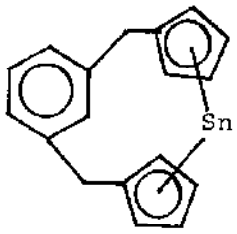
(114)

basis indicate that a similar non-planar trans-folded structure (114) (M = Sn, R = H) is more stable than a planar structure for distannene, Sn_2H_4, by 26 kJ mol^{-1}, with a fold-angle (θ) of 46°.[197] It is interesting to note that the material prepared nearly three decades ago[199] from 9-phenanthrylmagnesium bromide and $SnCl_2$ and described than as 'di-(9-phenanthryl)tin' (implicitly a bivalent compound), has been shown to be a mixture of at least seven compounds, including the cyclostannanes, $(Phen_2Sn)_n$ (n = 3, 4, 6) and $Phen_3Sn(SnPhen_2)_nSnPhen_3$ (n = 0, 1).[200] Synthetically, two reports are of note. Zuckerman[201] has described the preparation of a new class of stannocene derivatives in which the η^5-cyclopentadienyl rings are linked through methylene bridges to

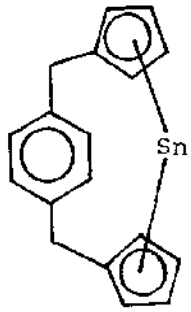
a phenyl system. The ortho-, meta-, and para-xylene derivatives (115)-(117) were synthesised from the disodium salt of



(115)

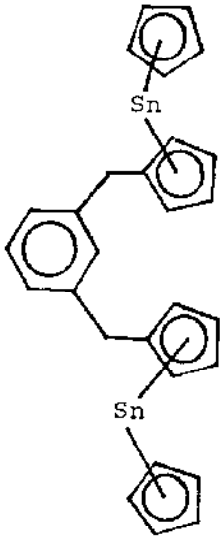


(116)

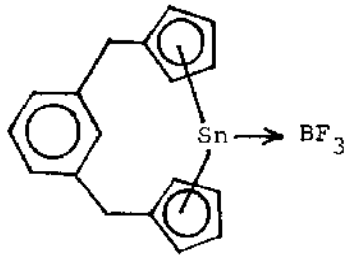


(117)

(phenylenedimethylene)dicyclopentadienide with tin(II) chloride in thf. The products are air-stable, off-white powders, soluble in organic solvents, which have no definite melting points. Reaction of cyclopentadienyltin(II) chloride on the disodium salt affords (118). The meta-derivative (117) gives the infusible adduct (119) with boron trifluoride:



(118)



(119)

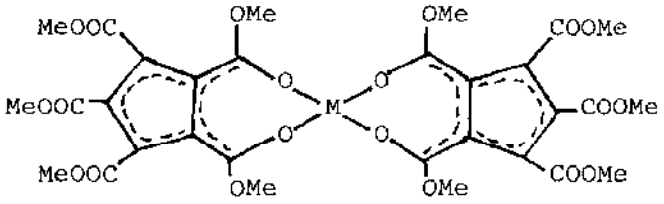
In the other, Cowley and Jutzi have shown that stannocene itself can undergo sequential lithium and silylation leading to polysilylated stannocenes:[202]

$$(C_5H_5)_2Sn \xrightarrow[2)\ 2Me_3SiCl]{1)\ 2nBuLi} (Me_3SiC_5H_4)_2Sn \xrightarrow[2)\ 2Me_3SiCl]{1)\ 2nBuLi}$$

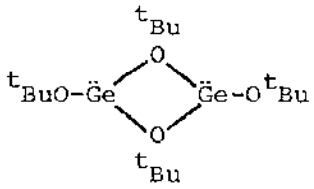
$$[(Me_3Si)_2C_5H_3]_2Sn \xrightarrow[2)\ 2Me_3SiCl]{1)\ 2nBuLi} [(Me_3Si)_3C_5H_2]_2Sn$$

One of these products, $[(Me_3Si)_3C_5H_2]_2Sn$,[202] along with several other germanocene and stannocene derivatives, has been characterised crystallographically. Significantly in the silylstannocene, the ring centroid-Sn-ring centroid angle is opened out to 162°, from the (average) values of 145.8° and 144.1° observed for $(\eta^5\text{-}C_5H_5)_2Sn$ and $(\eta^5\text{-}MeC_5H_4)_2Sn$, whilst in decaphenylstannocene, the rings are planar, staggered, exactly parallel and equidistant from the tin atom.[203] Germanocene[204] and decamethylgermanocene[205] are also angular sandwich compounds, with the angle between the planes being less for the latter compound (22(2)°) than for the former (50.4°). The angle between the Ge-Cl bond and the ring normal through germanium in $(\eta^5\text{-}MeC_5H_5)GeCl$) is 110(2)°, (cf. calculated 115°), whilst the Ge-Cl distance is significantly longer than the gaseous $GeCl_2$.[205,206] Cationic (η^5-pentamethylcyclopentadienyl)-germanium and -tin units (gegenion $CF_3SO_3^-$ or BF_4^-) react with bases such as pyridine, pyrazine or 2,2'-bipyridine to form adducts. In both of the cations, $[(C_5H_5)Sn.L]^{2+}$ (L = pyridine, 2,2'-bipyridine), the bonding of the tin to the ring relaxes from η^5 towards η^2/η^3. The gross structure of the pyridine complex, $[(C_5H_5N)Sn(C_5Me_5)]^+(O_3SCF_3^-]$ is a chain structure in which the $[CF_3SO_3^-]$ anions link adjacent $[(C_5H_5N)Sn(C_5H_5N)Sn(C_5Me_5)]^+$ cations. In contrast, crystals of the corresponding bipyridine salt comprise isolated $[(C_{10}H_8N_2)Sn(C_5Me_5)]^+$ and $[CF_3SO_3]^-$ ions.[207] Reaction of decamethylgermanocene or -stannocene with penta(methoxycarbonyl)cyclopentadiene in a 1:1 molar ratio, leads to the formation of the ionic compounds $[(C_5Me_5)M]^+[(MeO_2C)_5C_5]^-$. Reaction in a 1:2 ratio affords covalent $[(MeO_2C)_5C_5]_2M$ (M = Ge, Sn) compounds (120), which are fluxional in solution. Crystallographic studies of the tin compound show that the metal has four-fold oxygen coordination from the two ligands, with a further two long intermolecular contacts resulting in a distorted octahedral geometry.[208] Tert-butanol cleaves the cyclopenta-

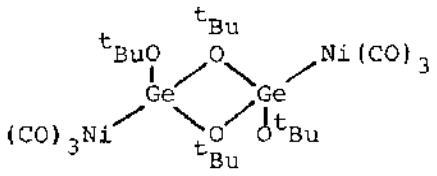
dienyl groups from germanocene to afford dimeric di-t-butoxygermanium (121), which with nickel carbonyl forms the complex (122).[204]



(120)



(121)



(122)

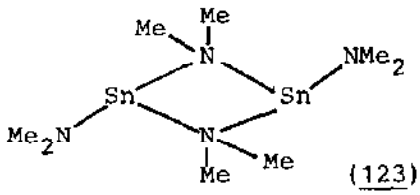
C-trimethylsilyl-substituted stannacarboranes of composition $Sn[Me_3Si][R]C_2B_4H_4$ (R = H, Me, $SiMe_3$) have been obtained as white sublimable solids from the reaction of tin(II) chloride with the corresponding sodium carborane salts in thf. These stannacarboranes do not react with either BH_3.thf or BF_3 to form donor-acceptor complexes, and spectroscopic data are consistent with a pentagonal-bipyramidal structure in which the tin occupying an apical position.[209] Indeed, that with R = Me has been corroborated crystallographically.[210] The reaction of closo-$Sn[Me_3Si]_2C_2B_4H_4$ with $Os_3(CO)_{12}$ gives the closo-osmacarborane, $1\text{-}Os(CO)_3\text{-}2,3\text{-}[Me_3Si]_2\text{-}2,3\text{-}C_2B_4H_4$, in almost quantitative yield.[211] The structure of another stannacarborane, the bipyridine complex of $Sn(Me_2)C_2B_9H_9$, has also been determined. As with the metallocene adducts reported above, complexation is accompanied by a 'slippage' from η^5-bonding, and this complex can be regarded as a η^3-borallyl complex.[210]

MNDO M.O. calculations have been applied to the structures of sandwich and half-sandwich cyclopentadienyltin(II) compounds, and to the possibility of multiple bonding by tin in distannene or dimethylmethylenestannane.[212]

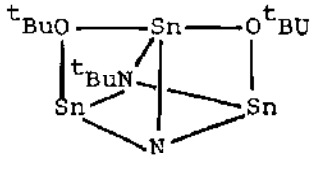
Material of composition $Sn(SbF_6)_2(AsF_3)_2$ is obtained when

$Sn(SbF_6)_2$ is recrystallised from AsF_3. In this compound, the tin is nine-coordinated, with six fluorine from $[SbF_6]^-$ units at the corners of trigonal prism and three from $[AsF_3]$ units capping the rectangular faces. The distortion from regular geometry is compatible with stereochemical-activity of the tin lone pair. The Mössbauer isomer shift (single narrow line) of 4.66 $mm.s^{-1}$ is the highest yet observed.[213] The structure of phyllo-nonafluoropentatintetrafluoroborate, $[Sn_5F_9][BF_4]$, consists of two-dimensional nets, built up from interconnected $[SnF_3]$ and $[SnF_4]$ pyramids, with the $[BF_4]$ groups located between the nets.[214] The compounds $SnCl_2Br_2(MeCN)_2$, $Sn_3Cl_8Br_4(thf)_6$, and $Sn_3Cl_{10}Br_2(OEt_2)_6$ have been obtained from the reaction of $SnCl_2$ and Br_2 in MeCN, thf and diethyl ether. The two latter compounds are solid solutions of $SnCl_4.L_2$ and $SnCl_2Br_2.L_2$ (L = thf, OEt_2) in the proportions of 1:2 and 2:1, respectively. The reaction between $SnCl_2$ and I_2 in the same solvents afforded $SnCl_4.L_2$, SnI_4, and a small amount of SnI_3Cl.[215]

The structures of several amino-tin(II) and lead(II) compounds have been determined. That of $[Sn(NMe_2)_2]_2$ is a centrosymmetric dimer with the tin atoms bridged by two dimethylamido groups as in (123). The lead analogue is both thermally and photolytically unstable, and decomposed rapidly at ambient temperature, although variable temperature n.m.r. data show that the solution structure of both tin and lead compounds are similar.[216] The tin(II) and lead(II) bis(trimethylsilyl)amides, $M[N(SiMe_3)_2]_2$ (M = Sn, Pb), are 'V'-shaped monomers both in the crystal at 140K and in the vapour at ca. 380K (M = Ge, Sn, Pb). The NMN angle varies with the metal and the phase [vapour phase: 101° (Ge), 96° (Sn), 91° (Pb); crystal: 104.7° (Sn), 103.6° (Pb)].[217] The novel cage compound (124) has a crystallographic plane of symmetry and may be regarded as being made up of two $[SnN_2OSn]$ trigonal bipyramids with a common $[SnN_2]$ face.[218] Both PbN_2S_2,NH_3 contain planar five-membered $[PbN_2S_2]$ rings. In the ammonia adduct, the NH_3 molecule is bound to lead in a perpendicular orientation with respect to the plane of the ring.[219] The cyclic bis(amino)-

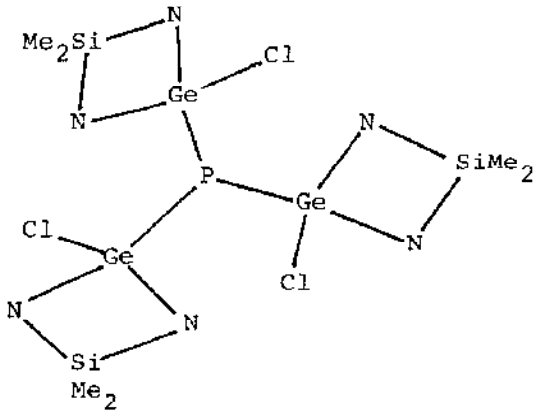


(123)



(124)

germylene, $Me_2Si(N^tBu)_2Ge$, reacts with PCl_3 by a three-fold insertion into the P-Cl bonds forming $[Me_2Si(N^tBu)_2Ge(Cl)_3]P$, (125), which has approximate C_{3h} symmetry with the germanium, chlorine and silicon atoms of each group coplanar and perpendicular to the $[GeN_2Si]$ ring. The coordination at phosphorus is a rather flat pyramid. The unusual nearly planar coordination of the phosphorus atom is rationalised by the steric



(125)

requirements of the substituents. PCl_3 oxidises the tin analogue, whilst ligand-exchange occurs with the lead compound:[220]

$$Me_2Si(N^tBu)_2Sn + PCl_3 \rightarrow Me_2Si(N^tBu)_2SnCl_2 + 1/n(PCl)_n$$

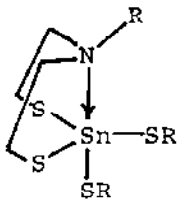
$$Me_2Si(N^tBu)_2Pb + PCl_3 \rightarrow Me_2Si(N^tBu)_2PCl + PbCl_2.$$

Several intramolecularly base-stabilised tin(II) compounds have been synthesised. Transamination of bis(dimethylamido)tin(II) or substitution of tin(II) chloride has been employed to obtain compounds of the type $S(CH_2CH_2NR)_2Sn$:

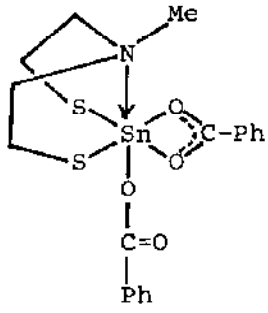
$$Sn(NMe_2)_2 + S(CH_2CH_2N(R)H)_2 \xrightarrow{-2Me_2NH} S(CH_2CH_2NR)_2Sn$$

$$SnCl_2 + S(CH_2CH_2N(R)Li)_2 \xrightarrow{-2LiCl} S(CH_2CH_2NR)_2Sn$$

The products are monomeric in nature.[221] Reaction of $E(CH_2CH_2S)_2Sn$ (E = NMe, S) with mercaptans (or disulphides) and dibenzoylperoxide leads to the formation of (126) and (127) respectively:[222]



(126)



(127)

Analogous intromolecularly base-stabilised compounds of the type, $RN(CH_2CH_2Y)_2Sn$ (Y = O,S; R = Me, ^tBu), react with halogens, tin(IV) chloride, and chloroform by oxidative-addition, eg.[223]

$$RN(CH_2CH_2Y)_2Sn + X_2 \rightarrow RN(CH_2CH_2Y)_2SnX_2$$

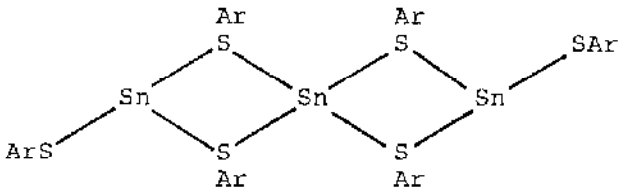
$$^tBuN(CH_2CH_2S)_2Sn + SnCl_4 \rightarrow {}^tBuN(CH_2CH_2S)_2SnCl_2 + SnCl_2$$

$$MeN(CH_2CH_2S)_2Sn + CHCl_3 \rightarrow MeN(CH_2CH_2S)_2Sn(Cl)CHCl_2$$

Mössbauer data for oxalatostannates(II) of the composition $M_2Sn(C_2Sn(C_2O_4)_2.xH_2O$ have been rationalised for the tin atom. In the analogous malonate compound, $K_2Sn_2[CH_2(CO_2)_2]_3.H_2O$, the malonate groups function as bridging rather than chelating ligands, and the tin atoms are three- rather than four-coordinated.[224] Both $K_2Sn_2(CO_4)_3x$ (x = Cl, Br) salts consists of three-dimensional networks of tin atoms and bridging sulphate groups with discrete potassium and halide ions in holes in the networks. The tin atoms have distorted six-fold oxygen coordination.[225] The metal is also six-coordinated by oxygen atoms from four ligands in lead(II) D-gluconate, $Pb[C_6H_{11}O_7]_2$ resulting in a two-dimensional polymeric structure,[226] whilst in the lead(II) salt of 2,4,6-trinitro-1,3-benzenediol, α-$Pb[C_6HN_3O_8].H_2O$, the lead atoms are seven-coordinated, and adjacent formula units are paired via oxygen bridges. The water molecule is coordinated to the metal

and also hydrogen-bonded to the anion.[227] Lead(II) acetate trihydrate undergoes solid-state transformations at room temperature, resulting in anomalous and variable peaks in the ^{13}C cross-polarisation magic-angle spinning n.m.r. spectra of powder samples. As a result isotropic chemical shift differences of upto 12ppm were observed for the carboxyl carbon atoms and 2ppm differences for the methyl atoms. The X-ray structure was also reported, confirming the previous conclusions.[228]

The tin(II) thiolate, $Sn[SC_6H_2{}^tBu\text{-}2,4,6]_2$ is a 'V'-shaped monomer in the solid, whilst the less sterically-hindered thiolate, $Sn[SC_6H_3{}^iPr_2\text{-}2,6]_2$, has the ternuclear structure, (129), in which the central tin atom is four-coordinated and the two terminal tin atoms three-coordinated.[229] The tetraphenylarsonium



(129)

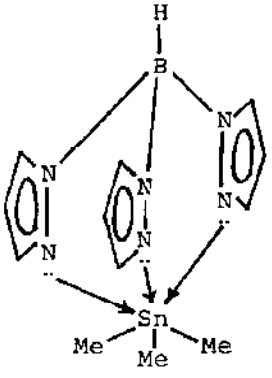
salts, $[Pb_4As][Pb(EPh)_3]$ (E = S,Se), have been obtained by adding >3 moles of NaEPh to lead(II) nitrate, and are isomorphous containing discrete $[Pb(EPh)_3]^-$ anions which have a trigonal pyramidal geometry. In both anions all three phenyl groups adopt a propeller-like conformation, and are disposed in equatorial positions above the basal plane of the chalcogen atoms.[230]

Lead(II) complexes of 16-membered, tetra-aza macrocyclic ligands, 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane and 1,5,9,13-tetra-azacyclohexadecane, have been synthesised and studied by ^{13}C n.m.r. For the latter ligand, (L), all four N-H groups point to the same side of the macrocycle. In the complex with lead(II) chloride, which comprises $[Pb(L)Cl]^+$ cations and chloride anions, the chlorine and the lone pair occupy adjacent positions on one side of the lead atom. Crystals of the lead(II) nitrate complex contain five independent molecules, one of which have two bidentate nitrate groups, two have one bidentate and one unidentate, and two in which the nitrate groups are bridging.[231,232]

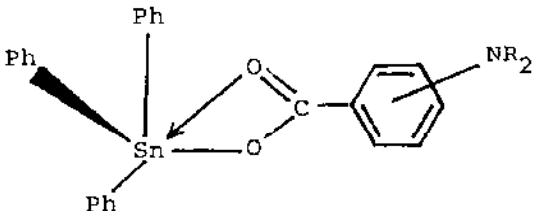
Tin and germanium vapours, react with acetylene to form copolymers with the reproducible stoichiometries, $(C_2H_{2.6}Sn_{0.70})_x$ and $(C_2H_{2.7}Ge_{0.72})_x$. The metal is incorporated as both bivalent and tetravalent metal, and the resultant materials are air-sensitive and possess moderate free-radical concentrations, but are non-conducting under normal pressed powder conditions.[233]

4.4 TETRAVALENT COMPOUNDS OF TIN AND LEAD

The major effort in studies of tetravalent compounds of tin and lead has been directed towards structural elucidation. A truly six-coordinated trimethyltin complex, $Me_3Sn[(pz)_3BH]$ (pz = 1-pyrazolyl), (130), with a fac-$[SnC_3N_3]$ geometry, has at last been characterised. Both the Sn-C and Sn-N bond distances are not unusual, although the NSnN bond angles are closed to 74.8° and the CSnC angles are opened to 105.2°.[234] The tin environment in triphenyltin acetate has also been described in terms of distorted mer-$[SnC_3O_3]$ six-coordination, but this description relies upon a very long (3.206Å) third tin-oxygen interaction. The gross structure is that of one-dimensional helical polymer.[235] The structures of three other triphenyltin carboxylates, triphenyltin salicylate, O-anisate, and p-methylthiobenzoate, have also been determined. Crystals of all three comprise discrete molecules, with a highly anisobidentate carboxylate group as in (131). The structural distortion in each is a displacement from a tetrahedron towards a trigonal bipyramid. Infrared data confirm that carboxylate coordination also occurs in solution.[236]

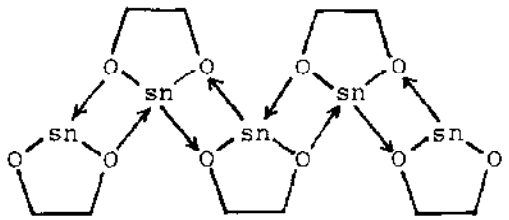


(130)



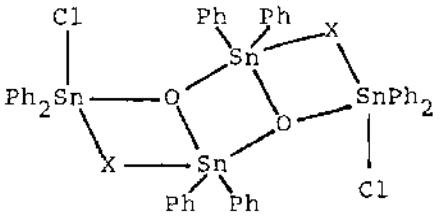
(131)

Unlike typical diorganotin oxides, the sterically-crowded compounds, di-t-butyl- and di-t-amyltin oxide, are cyclic trimers with planar $[Sn_3O_3]$ rings.[237] 2,2-Dibutyl-1,3,2-dioxastannolane exists as an infinite ribbon coordination polymer, (132), contain highly distorted octahedrally coordinated tin.[238] These crystallographic results are, however, at variance with Mössbauer data for a series of such compounds, which have been interpreted in terms of dimeric species with pentacoordinated metal centres.[239] Both of the dimeric distannoxanes, $[ClPh_2SnOSSnPh_2(OH)]_2$ (as a bis acetone solvate) and $[ClPh_2SnOSnPh_2Cl]_2$, possess ladder structures as in (133) with tin atoms in a trigonal-bipyramidal conformation.[240]



sn = Bu_2Sn

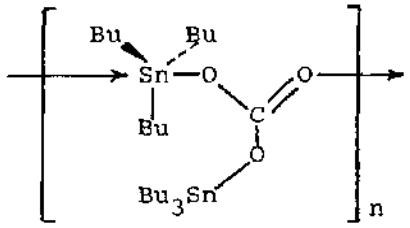
(132)



X = Cl,OH.

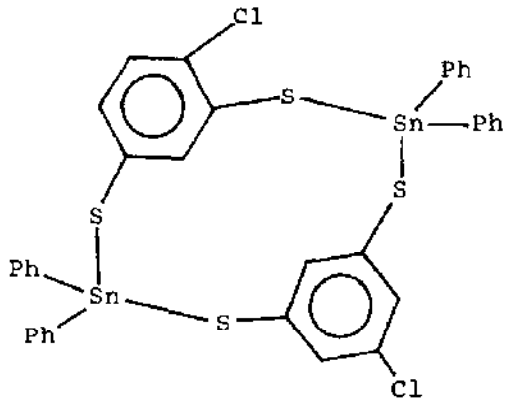
(133)

Polymeric structures are present in trimethyltin dimethylthiophosphinate, $Me_3SnO(S)PMe_2$, (in which planar (Me_3Sn) units are [O,S]-bridged by the tetrahedral phosphinate,[241] and dimethyltin tetraoxomolybdate, Me_2SnMoO_4, where tetrahedral $[MoO_4]$ units and trans-$[SnMe_2O_4]$ octahedra link to form a three-dimensional lattice.[242] In contrast to dimethylbis(8-quinolato)tin, in which the two methyl groups are mutually cis in an octahedral coordination about tin, in ethylpropylbis(2-methyl-8-quinolato)tin the geometry is closer to trans-octahedral (CSnC = 145°).[243] Tin-119 Mössbauer data indicate the presence of both four- and five-coordinated tin sites in the bis(trialkyltin) carbonate, $(R_3SnO)_2CO$, corresponding to the polymeric structure, (134).[244] Hitherto unknown salts of the hemiesters of carbonic acid, $Li[O_2C\text{-}OMMe_3]$ (M = Ge, Sn), have been synthesised by the reaction of $Li[OMMe_3]$ with carbon dioxide at 0°C.[245]



(134)

Structural data for oxy- and thiophosphorus acid derivatives of tin have been reviewed.[246] Methylthiotriphenylmethane, -silicon, -germanium, -tin, and -lead all have a distorted tetrahedral coordination. Only the propeller shape orientation of the phenyl rings seems to be determined by differences in the electronic nature of the central atoms, as well as by steric effects.[247] Tetrahedral four-coordination is also found in $Me_2Sn[S_2AsMe_2]_2$[248] and in $[Ph_2SnSC_6H_3ClS]_2$.[249] Unusually the latter compound is dimeric (135) and contains a twelve-membered $[Sn_2S_4C_6]$ ring.



(135)

Crystallographic analysis of the anionic monocyclic five-coordinated stannoles, $[(C_6H_4OS)SnMe_2F][Et_4N]$, $[(C_6H_4CO_2S)SnMe_2Cl][Et_4N]$, and $[(C_6H_4OS)SnMe_2I][Ph_4P]$, shows that the trigonal bipyramidal geometry becomes increasingly distorted as the size of the halogen increases. The iodo compound is also weakly associated into dimers by intermolecular oxygen bridging.[250] Crystals of $[Ag(PPh_3)_4][SnPh_2(NO_3)_2(Cl_9NO_3)]$ comprise discrete $[Ag(PPh_3)_4]^+$ cations and $(Ph_2Sn(NO_3)_2(Cl,NO_3)]^-$

anions. In the tin anion, the two phenyl groups occupy axial positions and the three bidentate nitrate groups (or two bidentate nitrate groups and the chlorine) the equatorial sites of a distorted hexagonal (or pentagonal) bipyramid.[251] In the tin-crown ether complex, $[Sn(OH_2)_2Cl_4.(18\text{-crown-}6).2H_2O.CHCl_3]$, the crown ether is not coordinated to tin. Rather, the lattice comprises octahedral $[Sn(OH_2)_2Cl_4]$ units, in which the two water molecules are cis, which are linked together with the crown ether molecules, and uncoordinated water to give hydrogen-bonded chains.[252] A number of other crown ether complexes have also been synthesised.[252,253] Both 1:1 and 1:2 complexes are formed with 18-crown-6 and $SnCl_4$ and $MeSnCl_3$, but with Me_2SnCl_2, only a 1:2 complex is obtained. Mössbauer and infrared data indicate octahedral coordination at tin in all cases.

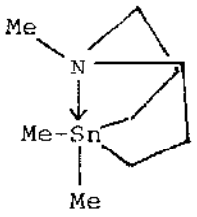
Several tin derivatives with transannular Sn...N interactions have been studied. (136) and (137) have been synthesised by the Grignard method, and can be converted into the methyltin analogues (138) and (139) by treatment with methyllithium.[254]

$$MeN(CH_2CH_2CH_2MgCl)_2 + SnCl_4 \xrightarrow[-MgCl_2]{thf/Toluene} Cl_2Sn(CH_2CH_2CH_2)_2NMe$$

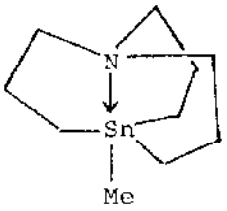
(136)

$$N(CH_2CH_2CH_2MgCl)_3 + SnCl_4 \xrightarrow[-MgCl_2]{thf/Toluene} ClSn(CH_2CH_2CH_2)_3N$$

(137)



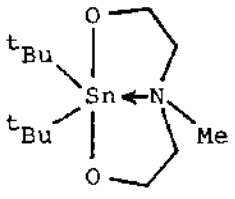
(138)



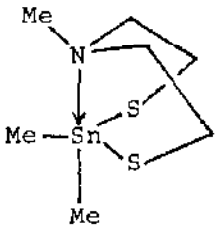
(139)

Sn...N transannular interactions have been confirmed crystallographically for (140),[255] (141)[255] and (142).[256] For (142), n.m.r. data show the occurance of a slow exchange between three isomers in solution, which are assigned to those in which

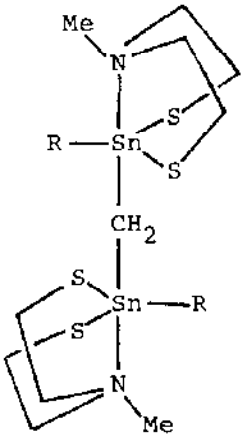
the phenyl groups occupy either both equatorial positions, both axial positions, or one axial and one equatorial position in the trigonal bipyramidal coordination about tin. The latter isomer is the one observed in the solid state, and is also the major component in solution. Tin-119 Mössbauer isomer shifts have been



(140)



(141)



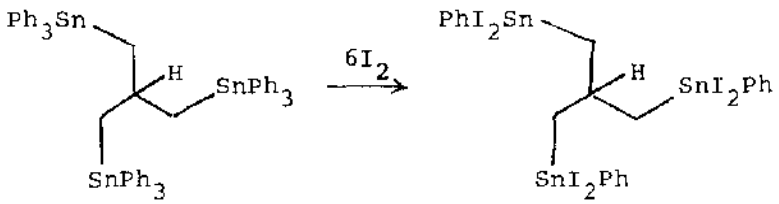
(142)

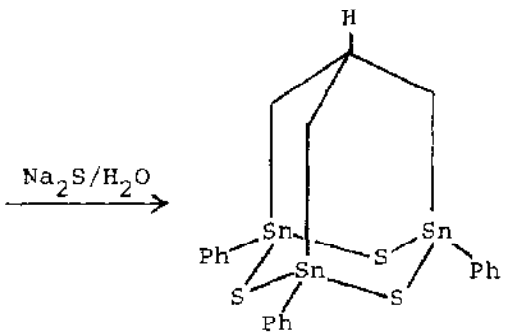
correlated to partial atomic changes on tin, calculated through a valence state electronegativity equalisation procedure, for a number of homologous five-coordinated tin compounds.[257]

Crystals of the tri-3-thienyltin bromide-triphenylphosphine oxide comprise discrete $Br(C_4H_3S)_3Sn.OPPh_3$ molecules, in which their are no intermolecular Sn...S interactions. Each tin atom is in a trigonal-bipyramidal environment, with the sulphur atoms occupying equatorial positions.[258] Whereas the adducts, $Ph_3SnCl(tme)$ (tme = tetramethylurea) and $R_2SnCl_2.2(dmtu)$ (R = Me, Ph; dmtu = 1,3-dimethylthiourea), have the expected trigonal bipyramidal and trans-octahedral geometries, respectively,[259] the structure of the adduct, $Ph_2SnCl_2.3/4(pyz)$ (pyz = pyrazine), (previously thought to have the composition $Ph_2SnC_2.pyz$) is quite unusual. Crystals are composed of layers which are packed in zig-zag $[Ph_2SnCl_2.(pyz)]_n$ polymeric chains with hexacoordinated tin, alternating with layers which contain non-interacting $[Ph_2SnCl_2.(pyz)]$ molecules with pentacoordinated tin. In both, the pyrazine ligand is a bridging group.[260] 2,6-Dimethylpyridine N-oxide forms 1:1 complexes with both diphenyltin dichloride and trimethyltin chloride. Both have the expected trigonal-

bipyramidal geometries.[261] The interaction of $Cl_3SnCH_2CH_2CO_2H$ with aniline bases in dichloromethane solution has been studied by u.v.-visible spectroscopy. As measured by the extents of complexation with the bases, $Cl_3SnCH_2CH_2CO_2H$ is a stronger Lewis acid than the esters, $Cl_3SnCH_2CH_2CO_2R$ and also a very much stronger Brønsted acid than $CH_3CH_2CO_2H$. The enhanced Brønsted acidity arises from the stabilisation of the anion, $Cl_3SnCH_2CH_2CO_2^-$, by intramolecular coordination.[262] Surprisingly, a reaction takes place between methyl iodide and tin(II) sulphide in water at room temperature giving methyltin triiodide, a facile reaction which may have significance in the biological methylation of tin.[263] Phenylhalogenoplumbate salts of the types $[Et_4N][Ph_3Ph_3PbXY]$ (X,Y = Cl,Br,I), $[Et_4N][Ph_6Pb_2X_2Y]$ (X,Y = Cl, Br), $[Et_4N][Ph_2PbX_3]$ (X = Cl,Br,I), and $[Me_4N]_2[Ph_2PbX_4]$ (X = Cl, Br) have been synthesised and characterised spectroscopically. The data are consistent with five- or six-coordination at lead, with halogen-bridging in same cases.[264]

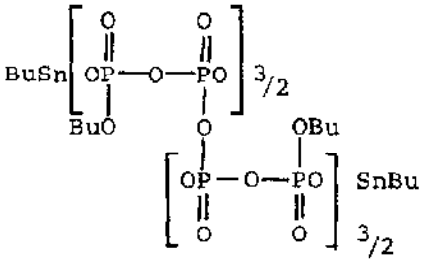
The synthesis of 1,3,5-triphenyl-2,4,6-trithia-1,3,5-tristanna-adamantane, (143), has been accomplished according to the reaction sequence:





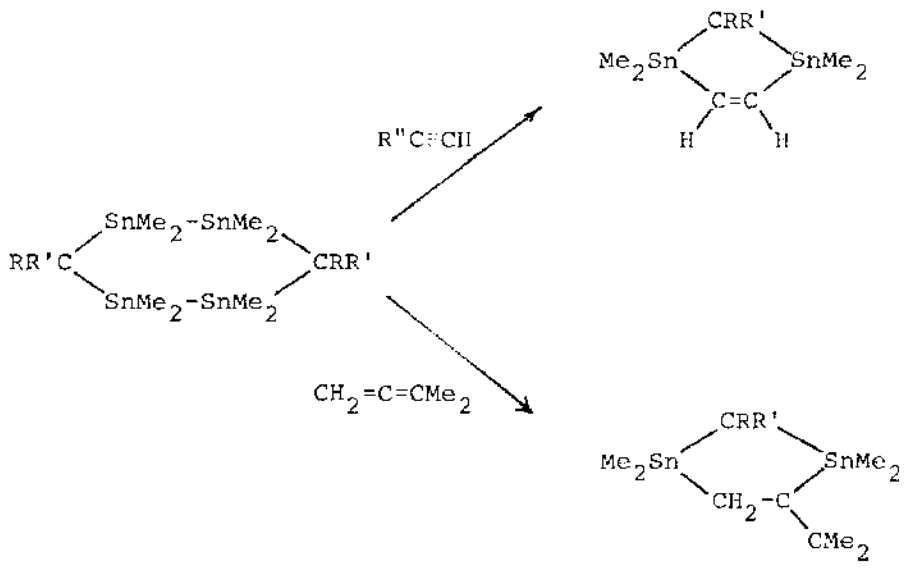
(143)

(143) is unusual in having a severely flattened bridgehead carbon atom, and reduces $Ph_3C^+PF_6^-$ to Ph_3CH almost instantaneously and alkyl halides to the corresponding hydrocarbons. These reactions appear to be radical in nature and are accelerated by AIBN.[265] The desulphurisation of trialkyl- and dialkyl sulphides by peroxides, copper metal, and halogenoalkanes has been investigated.[266] Various organotin phosphates and pyrophosphates have been studied as model catalysts in the polymerisation. Pyrolysis studies either neat or in the presence of dibutyl phosphate show that the phosphato ligands easily condense to give P-O-P linkages and also that dibutyl phosphate cleaves Sn-C bonds. However, the last butyl group attached to tin is resistant to cleavage, and thus monobutyltin compounds are always the ultimate products. With excess dibutyl phosphate, condensation of this compound with pyrophosphato ligands takes place. Polymerisation studies with epichlorohydrin indicates that the monobutyltin pyrophosphate (144) is associated with an actual active species.[267]

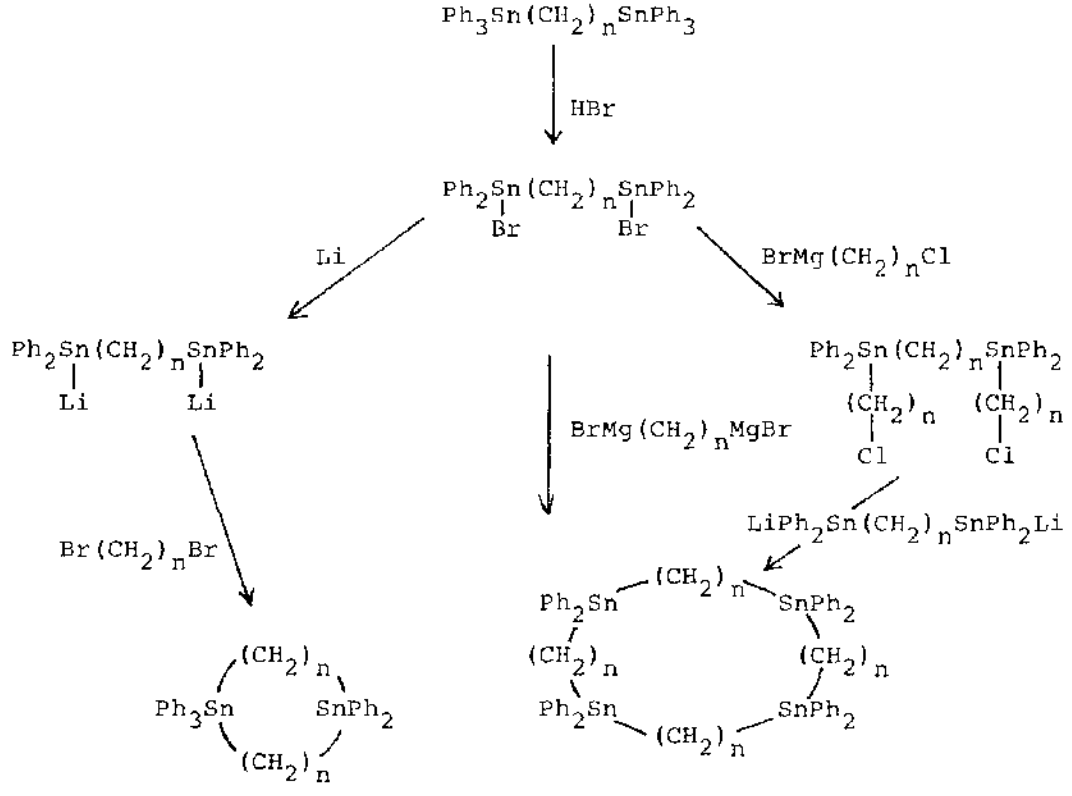


(144)

Crystals of tetrakis(η^1-indenyl)tin contain molecules of the meso diastereoisomer of point group S_4. Diastereotopic effects observed in the ^{13}C n.m.r. spectra of this compound and also n-butyltris(1-indenyl)tin are temperature dependent in a manner which clearly establishes that nondegenerate intramolecular metallotropism in the compounds provides a mechanism for intraconversion between all possible stereoisomers.[268] A number of new carbocyclic tin compounds have been synthesised. 1,2,4,5-Tetrastannacyclohexanes react with 1-alkynes and 1,1-dimethylallene in the presence of $Pd(PPh_3)_4$ to give 4-substituted 1,3-distannacyclopentenes and 4-methylene-1,3-distannacyclopentanes, respectively:[269]

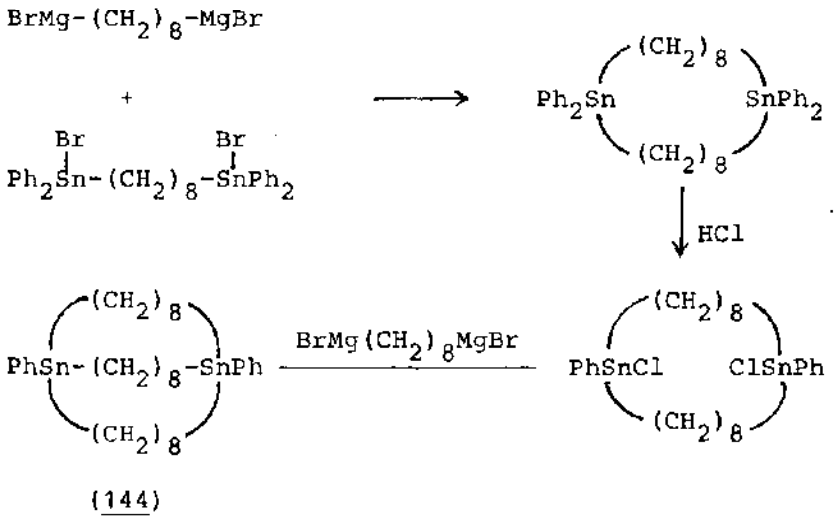


Larger macrocycles have been synthesised according to Schemes 18 and 19:[270,271]



n = 4,5,6,8,10,12

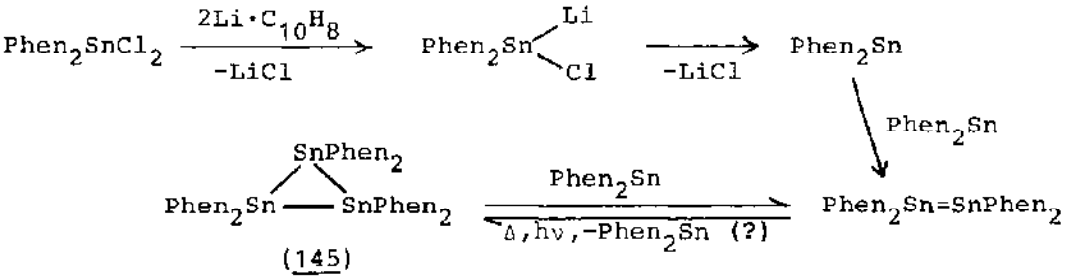
Scheme 18



(144)

Scheme 19

The X-ray crystal structure of (144) has been determined. The compound crystallises in a cylindrical form with a tin-tin distance of 8.45Å. The interior of the cylinder cavity is filled with the hydrogen atoms of the polymethylene chains.[271] The reaction of Ph_3PbLi with Ph_3SnCl or Ph_3GeCl gives $Ph_3Pb\text{-}SnPh_3$ and $Ph_3Pb\text{-}GePh_3$, respectively. There is no reaction with Ph_3SiCl. Ph_3SiLi reacts with Ph_3PbCl to form a regular 1:1 $Pb_2Ph_6 \cdot Si_2Ph_6$ phase. The crystal structures of all the products have been determined ($Ph_3Pb\text{-}SnPh_3$, -40°C), 0.053 ($Ph_3Pb\text{-}GePh_3$, -50°C), 0.068 ($Pb_2Ph_6 \cdot Si_2Ph_6$, 20°C); bond lengths 285 (Pb-Pb), 283 (Pb-Sn), 262pm (Pb-Ge).[272] Hexa-9-phenanthyl-cyclotristannane (145) has been synthesised by four different methods, the best being the reduction of $Phen_2SnCl_2$ (Phen = 9-phenanthyl) by lithium naphthelide at -78°C, for which a mechanism involving the stannylene $Phen_2Sn$ (at the corresponding stannylenoid, eg. $Phen_2Sn(Cl)Li$) and its dimer was proposed (Scheme 20).[273]

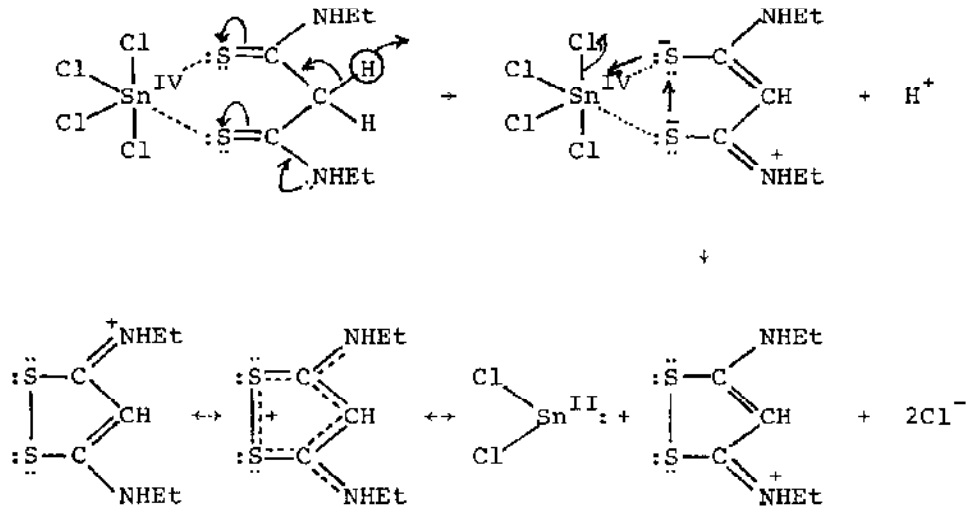


(145)

Scheme 20

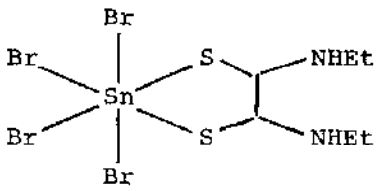
The crystal structures of dodecaphenyl-cyclohexastannane $(Ph_2Sn)_6$ and dodecabenzyl-cyclohexastannanedimethylformamide $(Bz_2Sn)_6$.DMF have been determined. The molecules of $(Ph_2Sn)_6$ show, in contrast to those of $(Ph_2Sn)_6$.2toluene and $(Bz_2Sn)_6$.DMF, remarkable differences in the chair conformation. The tin-tin bonds of $(Bz_2Sn)_6$.DMF are somewhat longer than those of the phenyl compounds.[274] Trifluoroacetolyses of cis- and trans-(4-methylcyclohexyl)- and cis- and trans-(4-tert-butylcyclohexyl)triisopropylstannanes proceed stereospecifically with retention of configuration at carbon. Electrophilic brominolysis in methanol is characterised by a fine energetic balance between inversion and retention pathways, with the former favoured for equatorial and the latter for axial carbon-tin bonds. Free-radical brominolysis yields a stabilised mixture of the cis- and trans-4-alkylcyclohexyl bromides, expected for bromine atom transfer to a 4-alkylcyclohexyl free radical.[275]

Tetrathiafulvalene (ttf) reacts with tin(IV) chloride or bromide in acetonitrile to afford the salt $[ttf]_2[SnX_6]$. The corresponding tetramethyltetraselenafulvalene (tmtsf) salt, $[(tmtsf)_2[SnCl_6]$, salt can be prepared similarly. In contrast, electrocrystallisation of ttf or tmtsf in the presence of SnX_6^{2-} or $[SnMe_2Cl_3]$ in MeCN or $CHCl_2CH_2Cl$ affords $[ttf]_3[SnX_6]$, $[ttf]_3[SnMe_2Cl_4]$, or $[tmtsf][SnMe_2Cl_3]$. A single crystal study of $[ttf]_3[SnCl_6]$ show it to possess a layer structure consisting of ttf trimers.[276] The salt, $[EtNHC(S)CHC(S)NHEt]_2[SnCl_6]$, is obtained unexpectedly following benzene recrystallisation of the product isolated from the reaction of $SnCl_4$ with N,N'-diethyldithiomalonamide. The proposed mechanism involves initial 1:1 adduct formation with a subsequent chelotropic rearrangement (Scheme 21). The structure of the salt in the crystal comprises independent cations and anions connected by hydrogen-bonds.[277] The tin(IV) bromide N,N-di-n-butyldithiooxamide complex (146) is octahedral.[278] Fluorine-19 n.m.r. has been employed to identify species of the types $[SnCl_nF_{6-n}]^{2-1}$ and $[SnCl_nBr_{6-n}]^{2-}$ and their isomeric configurations present in solution.[279] Tin-119 n.m.r. magnetisation transfer has been employed in the determination of the rate of cis/trans isomerisation in the complex $SnCl_4.2SnMe_2$. A comparison of the megnetisation transfer results with line-broadening data shows that the cis/trans isomerisation rate is much greater than that of



Scheme 21

bound ligand-free ligand exchange at the trans site.[280] The MNDO parametric SCF-MO treatment has been applied to a number of tin compounds.[281] Calculated ionisation energies are



(146)

systematically too large, but dipole moments agree well. Bond angles are predicted quite well, although the errors in bond lengths are large.

N.m.r. studies of the reaction of $SnCl_2$ with dichlorobis(1-R-3,4-dimethylphosphole)platinum(II) (R = various organic substituents) (L_2PtCl_2) show that the addition of solid anhydrous $SnCl_2$ to solutions of the phosphole complexes labilizes such phosphate complexes toward complete ligand exchange, producing a solution containing several species invluding, inter alia, cis- and trans-$L_2Pt(SnCl_3)Cl$, trans-$L_2Pt(SnCl_3)_2$, cis-L_2PtCl_2, and L_3PtCl_2. The latter L_3PtCl_2 species are significant as their presence demonstrates that addition of the chloride acceptor $SnCl_2$ to a solution of a noble metal complex not only labilizes the metal-

chloride bond as anticipated, but also labilizes the other metal-ligand bonds as well.[282] Several similar trichlorostannate-platinum complexes, $PtCl_n(SnCl_3)_{2-n}[P(OR)_3]_2$ (n = 0,1), $[Pt(SnCl_3)_3[P(OR)_3]_2]^-$, $[PtCl_2(SnCl_3)L]^-$ (L = PR_3, AsR_3), $[PtCl(SnCl_3)_2L]^-$, $[Pt(SnCl_3)_3(AsEt_3)]^-$, and $[Pt(SnCl_3)_4(PEt_3)]^{2-}$, have also been reported. The complex, $Pt(SnCl_3)_2[P(OPh)_3]_2$, adopts a square-planar geometry with trans $[SnCl_3]$ ligands.[283] That of the $[Pt(SnCl_3)_3(1,5\text{-cod})]^-$ anion is a distorted square pyramid in which one $[SnCl_3]$ group occupies the axial position, apparently the first characterised example of this geometry. This and other olefin complexes may be prepared according to the processes:[284]

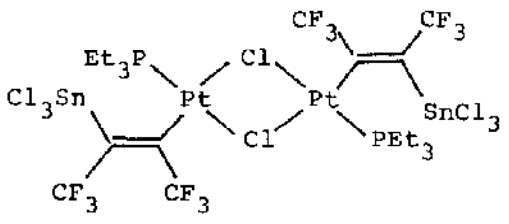
$$[PtCl_3(olefin)]^- + SnCl_2 \xrightarrow{CH_2Cl_2} cis\text{-}[PtCl_2(SnCl_3)(olefin)]^-$$

and

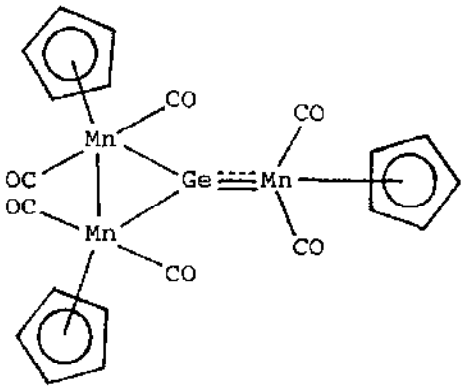
$$[PtCl_2(diolefin)] + 2SnCl_2 + SnCl_3^- \rightarrow [Pt(SnCl_3)_3(diolefin)]^-$$

The chlorine-bridged dimer, $[Pt_2(\mu\text{-}Cl)_2(SnCl_3)_2(PEt_3)_2]$ reacts with two moles of hexafluorobut-2-yne by insertion into the Pt-Sn bonds to give the complex (148), in which the dichloro bridge is preserved and which contains two [Pt-C=C-Sn] moieties.[285] In solution, trans-$[PPh_4]_3[IrCl_2(SnCl_3)_4]$ slowly isomerises to the cis isomer (Sn-119 n.m.r. data).[286] The photoinduced reaction of $PtCl_6^{2-}$ with Me_4Sn affords $MePtCl_5^-$, whereas with Me_2Et_2Sn, $[(CH_2{=}CH_2)PtCl_2]_2$ is also produced. The thermal reaction with Me_4Sn is catalysed by $PtCl_4^-$; reaction of this species with Me_4Sn affords σ-methyl complexes of platinum(IV). The platinum-ethylene complex also appears to be formed by β-elimination from $EtPtCl_5^{2-}$ upon light irradiation.[287] A purple species, believed to be $[Rh(SnCl_3)_5]^{4-}$ is formed from $[Me_4N]_3[RhCl_n(SnCl_3)_{6-n}]$ (n = 2,3,4) and tin(II) in hydrochloric acid.[288] The complex $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)]$ (dppm = bis(diphenylphosphino)methane) reacts with tin(II) chloride to give $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}SnCl_2)(\mu\text{-}dppm)]$.[289] Complexes of both types, $X_{4-n}[SnM(CO)_4PPh_3]_n$ (n = 3; M = Mn; X = F,Cl,Br,I. n = 2; M = Mn,Re; X = Cl,Br,I) and $M_2(CO)_8[\mu\text{-}Sn(X)M(CO)_4PPh_3]_2$ (M = Mn; X = Cl,I. M = Re; X = Cl,Br, I) are obtained by the reaction of the appropriate tin(II) halide and $M_2(CO)_8(PPh_3)_2$. In the rhenium complex, $Re_2(CO)_8[\mu\text{-}Sn(Cl)Re$-

$(CO)_4PPh_3]_2$, the central fragment contains a planar $[Re_2Sn_2]$ rhombus with a transannular Re-Re bond.[290]



(148)



(149)

Other structures worthy of note include the seven-coordinate chromium species, $[Et_4N][(Ph_3Sn)_3Cr(CO)_4]$,[291] $[(Ph_3P)Re(CO)_4]Sn[\mu\text{-}Re(CO)_4]_2Sn[(CO)_4Re(PPh_3)]$, (which contains a central $[Sn_2Re_2]$ four-membered ring with a short (bonding) Re-Re distance of 3.176Å.[292] The novel anion $[Sn_2Co_5Cl_2(CO)_{19}]^-$ (counterion $Co[HB(pz)_3]^+$ (pz = pyrazolyl), (which has two $[ClSn[Co(CO)_4]_2]$ groups mutually trans about a planar $[Co(CO)_3]$ fragment,[293] the Mn-Ge multiply-bonded complex, (149),[294] the niobium-tin bonded complexes, $[Et_4N][Nb(C_5H_5)(SnPh_3(CO)_3]$[295] and $[(C_5H_5)_2Nb(SnPh_3)(CO)]$,[296] the first 'closed' triosmium-main group metal cluster compound, $[Os_3SnH_2(CO)_{10}R_2]$ [R = $CH(SiMe_3)_2$] (obtained by reaction of $Os_3H_2(CO)_{10}$ with the stannylene SnR_2, and which contains a bridging hydride spanning the tin and one osmium atom),[297] and the molybdenum-lead bonded complex, $[(C_5H_5)_2Mo]Pb(O_2CMe)_2$.[298]

The electrochemical reduction of the tin complexes $[Co(CO)_4]_n[Fe(CO)_2(C_5H_5)]_{3-n}SnCl$ (n = 1-3) proceeds via the formation of the radical anion derived from tin-cobalt rather than tin-chloride bond rupture.[299] Similarly, the radical anion is formed following rupture of the iron-Group IV metal bond in the electrochemical reduction of the complexes $(C_5H_5)(CO)_2FeMR_3$ (M = Si,Ge,Sn). Exhaustive electrolysis of complexes of the types $[(C_5H_5)(CO)_2Fe]_nPh_{3-n}SnCl$ (n = 0-3) and $[(C_5H_5)(CO)_2Fe]_2SnCl_2$ affords distannanes stabilised by $[(C_5H_5)(CO)_2Fe]$ groups.[300]

4.5 OXIDE AND RELATED PHASES

A novel synthetic procedure has been devised for the preparation of silicon sesquioxide, Si_2O_3, which involves the reaction of hexabromodisilane with sulphur trioxide at room temperature. Yields are almost quantitative and the only by-products are bromine and sulphur dioxide.[301] The influence of NaF and Na_2SiF_6 on SiO_2 and sodium silicates has been investigated. Silicon tetrafluoride is also formed and influences the reactions as well. With low pressures of SiF_4 the reactions of NaF or Na_2SiF_6 with certain SiO_2 modifications leads to sodium silicates, whilst with higher pressures of SiF_4 to cristabolite and tridymite as well as low-quartz. Sodium silicates react with NaF to give principally Na_2SiO_3. $Na_6Si_8O_{19}$ is only obtained from Na_2SiO_3 when NaF was replaced by Na_2SiF_6. In this case additional low-quartz is formed. The formation of tridymite, which is only possible in the presence of certain foreign ions, is attainable at 1150°C if HF is added together with an alkali metal fluoride. The amount of added fluoride is critical for the size of the crystals of tridymite obtained.[302] The crystalline silicic acid, $H_2Si_{20}O_{41}.xH_2O$, has been obtained from its alkali metal and alkaline earth salts by cation exchange. Both the silicic acid and its salts form layered host lattices which can intercalate many organic compounds. Thermal dehydration at about 150°C gives silica-X, a partially dehydrated form (about $SiO_2.0{\cdot}09H_2O$).[303] The polymerisation of silicic acid adsorbed on iorn(III) hydroxide from dilute monosilicic acid solutions in the concentration range 5-40ppm SiO_2 has been studied over the pH range 6-12, and the nature of the adsorbed species examined by trimethylsilylation-gas chromatography. Dimeric ($Si_2O_7^{6-}$), linear trimeric ($Si_3O_{10}^{8-}$) and tetrameric ($Si_4O_{13}^{10-}$), and cyclic tetrameric ($Si_4O_{12}^{8-}$) species were found.[304] When monosilicic acid is adsorbed on aluminium(III) hydroxide, an allophane-like compound is rapidly formed, and the monosilicic acid adsorbed is consumed until the Si/Al mole ratio of the sample reaches 0.33-0.39. Above these ratios, the formation of polysilicic acid occurs.[305] Only double four-ring silicate anions are observed in trimethyl-2-hydroxyethylammonium silicate solutions with molar N:Si ratios of 1:1 to 2:1, whilst in triethyl-2-hydroxyethylammonium silicate solutions with the same N:Si ratios, varying quantities of double three-ring and double

four-ring silicate anions are detectable.[306] A similar constitution is also present in N-(2)hydroxyethyl- and N-(2)hydroxypropylpyridinium silicate solutions, where the amount of double four-ring silicate increases, and the amount of low-condensed silicates decreases, with increasing concentration.[307] Another novel class of crystalline microporous framework oxide molecular sieves, the silicoaluminophosphates, has been synthesised. Members of the new class (of which some thirteen three-dimensional microporous framework structures are known to date) are synthesised hydrothermally. The materials crystallise at 100-200°C from reactive mixtures containing organic amine or quaternary ammonium templates (R) which are retained within the products. The silicoaluminophosphates have a wide range of composition of $0\text{-}0.3R\text{-}(Si_xAl_yPz)O_2$ in the anhydrous form, where x,y, and z, represent the mole fractions of silicon, aluminium, and phosphorus, and range from 0.01-0.98, 0.01-0.60, and 0.01-0.52, respectively, with $x + y + z = 1$.[308] X-ray diffraction has been employed to demonstrate that the framework symmetry change between monoclinic and orthorhombic nature exhibited in ZSM-5 zeolite depends not only on the aluminium concentration and on the presence of sorbate molecules, but also on the temperature of the sample.[309] The composition of the (Na,TPA) (TPA = tetrapropyl-ammonium) precursor to silicalite-1 is determined by the base content of the reaction mixture, and for both low and high base contents the crystallisation is accompanied by apparently anomalous pH changes.[310] Potassium aluminosilicate solutions with low Si:Al ratios form gels more slowly with increasing KOH content, but at higher Si:Al ratios the reverse is true.[311] Changing the cation has a profound effect on the behaviour of such solutions. With sodium, reaction times increase with increasing alkali regardless of how much silica is present. The highly alkaline solutions put down a white amorphous precipitate rather than gelling, and reaction times are in most cases faster than for the equivalent potassium solutions. Opposite behaviour seems to be observed in the case of caesium, in which case gelation times are generally much longer than for the corresponding potassium solutions, and are particularly retarded in solutions with the highest silica content. For tetramethylammonium solutions, it is the low alkali solutions which are particularly inert, but in this case the pattern is complicated by the formation of crystalline

aluminosilicate compounds from high silica, high alkali solutions. No smooth trend in behaviour with cation size is apparent.[312] KLi_3SiO_4 is isotypic with KLi_3GeO_4, whose crystal structure has been determined.[313] The technique of trimethylsilylation has been used to determine the distribution of aluminium in the tetrahedral layers of a muscovite, a margarite, and a phlogopite.[314] The ion-exchange resin Amberlyst-15 is a powerful proton donor for SiO bond cleavages and rearrangements of trimethylsiloxysiloxanes. In the presence of hexamethyldisiloxane, transformations of trimethylsiloxysiloxanes of different structures exhibit two effects: (i) highly caged structures become loosened, and (ii) very loose structures become more rigid. Tetrameric ring structures predominate in the reaction products. In the absence of hexamethyldisiloxane, trimethylsiloxysiloxanes are highly degraded.[315] Line-broadening in the ^{29}Si n.m.r. spectra of sodium silicate solutions indicate dynamic exchange of SiO_4^{4-} groups between different silicate anion species with the free SiO_4^{4-} anion lifetime in the order of milliseconds.[316] A variable-temperature study using selective inversion-recovery ^{29}Si n.m.r. has also afforded information concerning exchange phenomena in alkaline solutions of potassium silicate. Rate constants of the order of 0.5Kg $mol^{-1}s^{-1}$ and a free energy of activation of 93 kJ mol^{-1} for the dimerisation of the orthosilicate anion were derived.[317] Magic angle spinning ^{29}Si and ^{27}Al n.m.r. has been employed extensively to study solid-state structure. Applied to highly siliceous ZSM-5 (silicalite), mas spectra reveal that changes in the zeolite-structure occur when sorbate molecules are present, and that these changes occur at low loading levels and are characteristic of the nature of the sorbed molecules. XRD demonstrate that the effect is a perturbation of the whole zeolite structure.[318] Introduction of both four- and six-coordinated aluminium occurs during treatment of highly siliceous ZSM-5 silicalite with $AlCl_3$ vapour at high temperatures.[319] A separate paper describes a similar process for the 'alumination' of high silica zeolite frameworks. However, in this report only four-coordinated aluminium was incorporated into the framework.[320] High resolution ^{27}Al mas-nmr spectra for polycrystalline 2:1 phyllosilicates distinguish clearly between tetrahedral and octahedral aluminium coordination. Chemical shifts of the two types fall in the ranges 60-70ppm (four-coordinate Al) and 0-10ppm

(six-coordinated Al). In the ^{29}Si spectra, components associated with silicon surrounded by 3Si, 2Si+Al, Si+2Al and 3Al were identified, allowing an estimation of tetrahedral Si/Al ratios.[321] ^{29}Si mas/nmr analysis of zeolite ZSM-39 has resolved the number of tetrahedral sites and the deviation from ideal symmetry.[322] Only a single sharp resonance is observed in the ^{29}Si mas/nmr spectrum of the completely siliceous analogue of zeolite A, prepared by hydrothermally dealuminating zeolite ZK-4, indicating the removal of the lattice aluminium whilst retaining the crystalline framework.[323] The contributions to ^{29}Si line widths have been systematically discussed and relative importance evaluated. Limiting line widths are determined by long-range chemical shift effects resulting from the distribution of aluminium in second and further nearest neighbour coordination spheres, with the additional line-broadening mechanism in many cases being a chemical-shift distribution due to crystallographic inequivalences.[324] ^{29}Si mas/nmr spectra of twelve glasses in the Li_2O-SiO_2 system ($15<Li_2O<40$ mole%) have been interpreted in terms of Q_m distribution theory. The principal silica species found in such glasses are Q_2, Q_3 and Q_4.[325] ^{29}Si mas/nmr has been used to follow the kinetics of the hydration of tricalcium silicate, and also to ascertain the course of reaction.[326]

The formation of GeO_2 (tetr.), which is kinetically hindered, is catalysed by all sodium-containing materials which react with GeO_2 to give $Na_4Ge_9O_{20}$. In the presence of chlorine, which reacts with sodium germanates and silicates to produce sodium chloride, the formation of GeO_2(tetr.) is catalysed by sodium chloride. The phase transition temperature for the transformation of GeO_2(tetr.) into the hexagonal phase is lowered by the presence of small amounts of SiO_2. The precipitates obtained by the addition of a solution of $NaHCO_3$ to a solution of tin(II) chloride have been identified as $2SnO.SnCl_2.H_2O$ or $Sn_3O(OH)_2Cl_2$ in the pH range 1.9-2.5 and $3SnO.2H_2O$ or $Sn_3(OH)_4O$ in the pH range 7.0-7.7. In the intermediate pH range, the chloride ions are gradually replaced by hydroxide ions. The dehydration of the hydroxide oxide to SnO occurs in two stages, and the disproportionation reaction to give SnO_2 and β-tin proceeds via the formation of Sn_2O_3.[328] Electron microscopy has been employed to show that molybdenum-doped tin(IV) oxide contains many planar defects, including twin boundaries. The segregation of molybdenum at these twin boundaries is

associated with the thermally induced migration of molybdenum to more favourable sites within the rutile-type lattice.[329] Controlled oxidation of the alloys $M^{I}M^{IV}$ (M^{I} - K,Rb,Cs; M^{IV} - Sn, Pb) leads to the formation of the new ternary oxides, $M^{I}{}_{2}M^{IV}{}_{2}O_{3}$. Oxidation of KGe leads to the formation of $K_2Ge_2O_3$ together with $K_6Ge_2O_7$.[330] The ternary oxide, Na_4SnO_3, is unusual in that it contains isolated $[SnO_3]$ groups.[331] The ternary digermanate, $Ag_2Ge_2O_5$, has been obtained from the binary oxides at high oxygen pressures. In the $Ge_2O_5^{2-}$ network structure, both tetrahedrally- and octahedrally-coordinated germanium atoms. These polyhedra share both vertices and edges forming a three-dimensional channel system in which are found Ag^{+} ions. Some Ag-Ag interaction occurs.[332] Heating mixtures of Na_2PbO_3 and Li_2O affords single crystals of Li_8PbO_6, whose structure contains essentially hexagonal-close packed oxygen atoms with lead in the octahedral holes.[333]

Germanium bis(monohydrogenphosphate), $Ge(HPO_4)_2.H_2O$, can be prepared in crystalline form by refluxing the precipitate obtained from $GeCl_4$ and H_3PO_4 in the molar ratio 1:10. Three GeP_2O_7 phases have been characterised on heating to 1300°C. At lower temperatures (600-800°C) a layered phase is obtained, which then gives a monoclinic (slow heating rate) or cubic (fast heating rate) phase in the range 900-1050°C. The two latter phases then slightly decompose above 1000°C to give materials having P:Ge ratios <2:1. Above 1050°C, decomposition to P_2O_5 and GeO_2 occurs.[334] Whereas $Ge(HPO_4)_2.H_2O$ is hydrolysable, $Sn_3PO_4F_3$ possesses a high hydrolytic stability. Thermal decomposition of this material has also been described.[335]

The thermal decomposition of SnS_2 in a nitrogen gas flow proceeds via Sn_2S_3 to SnS. The non-stoichiometric compound, $Sn_{1-x}S$ is also formed in the decomposition.[336] The structure of the synthetic phase, $TlInSiS_4$, has been determined, and is characterised by a sheet structure built up from alternating infinite $(InS_3)_n$ chains and dimeric $[Si_2S_6]$ groups, comprising two edge-sharing $[SiS_4]$ tetrahedra.[337] The compounds, $Na_8Si_4X_{10}$ and $Na_8Ge_4X_{10}$ (X = S,Se) have been obtained by reaction of Ge_2X_3 with Na_2X in a mole ratio 1:2 in methanol. The silicon compounds can also be synthesised from the elements.[338] The phase, $In_5Sn_{0.5}S_7$, has a similar structure to that of In_6S_7 in which one indium atom is replaced by $\frac{1}{2}Sn^{2+}$. The tin atoms are coordinated

by a monocapped trigonal prism of sulphur atoms.[339] $K_6Ge_2S_6$ and $K_6Ge_2Se_6$ are monoclinic and isotypic, forming the $K_6Si_2Te_6$ structure. $Na_6Ge_2Te_6$ crystallises with the $K_6Sn_2Te_6$ structure.[340] $Ba_2Ge_2Te_5$ is orthorhombic, and contains distorted $[Ge_2Te_6]$ trigonal prisms connected by common corners to give infinite chains.[341] The reaction of KSn with tellurium at high temperature gives congruently melting K_4SnTe_4 and Sn. Depending upon the cation and solvent used, a variety of products may be isolated from solutions containing $SnTe_4^{4-}$, including Te_4^{2-} and $Sn_2Te_6^{4-}$. The structure of the salt $(Me_4N)_4\ Sn_2Te_6$ has been determined, and the anion has a diborane-type structure with effective D_{2h} symmetry.[342] The compounds M_2SnTe_4 (M = Cr,Mn,Fe, Co) have been obtained by mixing the appropriate M^{2+} and $SnTe_4^{4-}$ anions in methanol. Pressed powder samples of Fe_2SnTe_4 and Co_2SnTe_4 appear metallic and have low resistivities. Heating to 600°C for 24h. leads to decomposition to $FeTe_2$, FeTe and SnTe.[343]

REFERENCES

1 S.M.Bachrach and A.Streitweiser, J. Am. Chem. Soc., 106(1984)5818.
2 A.Maercker and M.Theis, Angew. Chem., Int. Ed. Engl., 23(1984)995.
3 H.Kawa, J.W.Chinn and R.J.Lagow, J. Chem. Soc., Chem. Commun., (1984)1664.
4 R.L.Disch, J.M.Schulman and J.P.Ritchie, J. Am. Chem. Soc., 106(1984)6246.
5 C.Wakselman and M.Tordeux, J. Chem. Soc., Chem. Commun., (1984)793.
6 H.Bock, R.Dammel and D.Lentz, Inorg. Chem., 23(1984)1535.
7 B.A.O'Brien, J.S.Thrasher, C.W.Baukright, M.L.Robin and D.D.DesMarteau, J. Am. Chem. Soc., 106(1984)4266.
8 D.Lentz, I.Brudgam and H.Harth, Angew. Chem., Int. Ed. Engl., 23(1984)525.
9 J.Brobe and D. Le Van, Angew. Chem., Int. Ed. Engl., 23(1984)710.
10 B.Potter, G.Kleemann and K.Seppelt, Chem. Ber., 117(1984)3255.
11 B.Potter and K.Seppelt, Angew. Chem., Int. Ed. Engl., 23(1984)150.
12 S.A.Kinkead and J.M.Shreeve, Inorg. Chem., 23(1984)3109.
13 R.C.Kumar and J.M.Shreeve, Inorg. Chem., 23(1984)238.
14 H.M.Marsden and J.M.Shreeve, Inorg. Chem., 23(1984)3654.
15 G.Paprott, D.Lentz and K.Seppelt, Chem. Ber., 117(1984)1153.
16 G.Paprott and K.Seppelt, J. Am. Chem. Soc., 106(1984)4060.
17 R.F.Waldron, A.C.Barefoot and D.M.Lemal, J. Am. Chem. Soc., 106(1984)8301.
18 N.V.Nguyen and H.W.Moore, J. Chem. Soc., Chem. Commun., (1984)1066.
19 W.Koch, F.Maquin, D.Stahl and H.Schwartz, J. Chem. Soc., Chem. Commun., (1984)1679.
20 G.Karlstrom, B.O.Ross and L.Carlsen, J. Am. Chem. Soc., 106(1984)1557.
21 S.Saebo, L.Farnell, N.V.Riggs and L.Radom, J. Am. Chem. Soc., 106(1984)5048.
22 J.W.Agopovich, J.Alexander, C.W.Gillies and T.T.Raw, J. Am. Chem. Soc., 106(1984)2250.
23 K.O.Christie, D.Christen, H.Oberhammer and C.J.Schack, Inorg. Chem., 23(1984)4283.
24 S.H.Schei and R.Seip, Acta Chem. Scand., Ser. A, 38(1984)345.
25 B.Haas and H.Oberhammer, J. Am. Chem. Soc., 106(1984)6146.
26 P.Luger and J.Buschmann, J. Am. Chem. Soc., 106(1984)7118.
27 R.D.Brown and E.H.N.Rice, J. Am. Chem. Soc., 106(1984)6475.
28 L.Farnell and L.R. Adam, J. Am. Chem. Soc., 106(1984)25.
29 M.T.Nguyen and T.K.Ha, J. Am. Chem. Soc., 106(1984)599.
30 C.Biancini, C.Meali, A.Meli and M.Sabat, J. Chem. Soc., (1984)1647.
31 J.S.Binkley, J. Am. Chem. Soc., 106(1984)603.
32 T.A.Holme, M.S.Gordon, S.Yabushita and M.W.Schmidt, Organometallics, 3(1984)583.
33 E.A.Chernyshev, N.G.Komalenkova and S.V.Bashkirov, J. Organomet. Chem., 271(1984)129.
34 I.Hargittai, G.Y.Schultz, J.Tremmel, N.D.Kagrammov, A.K.Maltsev and O.M.Nefedov, J. Am. Chem. Soc., 105(1983)2895.
35 G.Y.Schultz, J.Tremmel, I.Hargittai, N.D.Kagrammov, A.K.Maltsev and O.M.Nefedov, J. Mol. Struct., 82(1982)107.
36 A.S.Nazran, J.A.Hawari, D.Griller, I.S.Alnaimi and W.P.Weber, J. Am. Chem. Soc., 106(1984)7267.

37 M.S.Gordon and D.R.Gano, J. Am. Chem. Soc., 106(1984)5421.
38 M.S.Gordon, J. Am. Chem. Soc., 106(1984)4054.
39 K.Raghavachari, J.Chandrasekhar, M.S.Gordon and K.J.Dykema, J. Am. Chem. Soc., 106(1984)5853.
40 C.Sosa and H.B.Schlegel, J. Am. Chem. Soc., 106(1984)5847.
41 J.Köcher and M.Lehnig, Organometallics, 3(1984)937.
42 J.A.Hawari and D.Griller, J. Chem. Soc., Chem. Commun., (1984)1160.
43 D.Lei, R.J.Hwang and P.P.Gaspar, J. Organomet. Chem., 271(1984)1.
44 J.Kocher and W.P.Neumann, J. Am. Chem. Soc., 106(1984)3861.
45 I.S.Alnaimi, W.P.Weber, A.S.Nazran and D.Griller, J. Organomet. Chem., 272(1984)C10.
46 C.A.Arrington, K.A.Klingensmith, R.West and J.Michl, J. Am. Chem. Soc., 106(1984)525.
47 A.K.Maltsev, V.N.Khabasheskuy and O.M.Nefedov, J. Organomet. Chem., 271(1984)55.
48 I.M.T.Davidson, S.Ijadi-Maghsoodi, T.J.Barton and N.Tillman, J. Chem. Soc., Chem. Commun., (1984)478.
49 S.Nagase and T.Kudo, J. Chem. Soc., Chem. Commun., (1984)141.
50 S.Nagase and T.Kudo, J. Chem. Soc., Chem. Commun., (1984)1392.
51 R.J.Conlin and Y.W.Kwak, Organometallics, 3(1984)918.
52 N.Wiberg, G.Wagner, G.Muller and J.Riede, J. Organomet. Chem., 271(1984)381.
53 Y.Apeloig and M.Karni, J. Am. Chem. Soc., 106(1984)6676.
54 H.Bock, P.Rosmus, B.Solouki and G.Maier, J. Organomet. Chem., 271(1984)145.
55 N.Wiberg, J. Organomet. Chem., 273(1984)141.
56 S.Nagase and T.Kudo, Organometallics, 3(1984)1320.
57 W.W.Schoeller and V.Staemmler, Inorg. Chem., 23(1984)3369.
58 M.J.Fink, M.J.Michalczyk, K.J.Haller, R.West and J.Michl, Organometallics, 3(1984)793.
59 S.Masamune, S.Murakami, J.T.Snow, H.Tobita and D.J.Williams, Organometallics, 3(1984)333.
60 P.B.Hitchcock, M.F.Lappert, S.J.Miles and A.J.Thorne, J. Chem. Soc., Chem. Commun., (1984)480.
61 G.Olbrich, P.Potzinger, B.Riemann and R.Walsh, Organometallics, 3(1984)1267.
62 H.Watanabe, Y.Kougo and Y.Nagai, J. Chem. Soc., Chem. Commun., (1984)66.
63 M.J.Michalczyk, R.West and J.Michl, J. Am. Chem. Soc., 106(1984)821.
64 H.Matsumoto, T.Arai, H.Watanabe and Y.Nagai, J. Chem. Soc., Chem. Commun., (1984)724.
65 A.Marchand, P.Gewal, F.Duboudin, M.H.Gaufryau, M.Joanny and P.Mazerolles, J. Organomet. Chem., 267(1984)93.
66 S.A.Kazoura and W.P.Weber, J. Organomet. Chem., 271(1984)47.
67 B.Pachaly and R.West, Angew. Chem., Int. Ed. Engl., 23(1984)454.
68 M.S.Gordon and C.George, J. Am. Chem. Soc., 106(1984)609.
69 J.Barrau, M.El Amine, G.Rima and J.Satgé, J. Organomet. Chem., 277(1984)323.
70 A.Komornicki, J. Am. Chem. Soc., 106(1984)3114.
71 C.B.Moore, J.Biedrzycki and F.W.Lampe, J. Am. Chem. Soc., 106(1984)7761.
72 F.Feher and M.Krancher, Z. Anorg. Allg. Chem., 509(1984)95.
73 E.Hengge and G.Miklau, Z. Anorg. Allg. Chem., 508(1984)33.
74 E.Hengge and G.Miklau, Z. Anorg. Allg. Chem., 508(1984)43.
75 T.Murai, S.Kato, S.Murai, T.Toki, S.Suzuki and N.Sonoda, J. Am. Chem. Soc., 106(1984)6093.

76 F.R.Anderson and M.S.Wrighton, J. Am. Chem. Soc., 106(1984)995.
77 M.J.Auburn, R.D.Holmes-Smith and S.R.Stobart, J. Am. Chem. Soc., 106(1984)1314.
78 F.Carré, E.Colomer, R.J.P.Corriu and A.Vioux, Organometallics, 3(1984)1272.
79 D.Seyferth, D.C.Annarelli and S.C.Vick, J. Organomet. Chem., 272(1984)123.
80 D.Seyferth, S.C.Vick and M.L.Shannon, Organometallics, 3(1984)1897.
81 D.Seyferth, D.P.Duncan, M.L.Shannon and E.W.Goldman, Organometallics, 3(1984)574.
82 D.Seyferth, D.P.Duncan and M.L.Shannon, Organometallics, 3(1984)579.
83 D.Seyferth, G.H.Wiseman, D.C.Annarelli and M.L.Shannon, J. Organomet. Chem., 264(1984)149.
84 G.Fritz, J.Thomas, K.Peters, E.M.Peters and H.G. van Schmering Z. Anorg. Allg. Chem., 514(1984)61.
85 I.M.T.Davidson, A.Fenton, S.Ijadi-Maghsoodi, R.J.Scampton, N.Auner, J.Grobe, N.Tillman and T.J.Barton, Organometallics, 3(1984)1593.
86 W.R.Tikkanen, J.Z.Liu, J.W.Egan and J.L.Petersen, Organometallics, 3(1984)828.
87 W.R.Tikkanen, J.W.Egan and J.L.Petersen, Organometallics, 3(1984)1646.
88 W.R.Tikkanen, J.L.Petersen, Organometallics, 3(1984)1651.
89 A.Sekiguchi and W.Ando, J. Am. Chem. Soc., 106(1984)1486.
90 J.W.F.L.Seetz, B.J.J. van de Heisteeg, G.Schat, O.S.Akkerman and F.Bickelhaupt, J. Organomet. Chem., 277(1984)319.
91 A.A.Espenbetov, Yu. T. Struchkov, S.P.Kolesnikov and O.M.Nefedov, J. Organomet. Chem., 275(1984)33.
92 H.Preut, J.Köcher and W.P.Neumann, Acta Crystallogr., C41(1984)912.
93 G.Manuel, G.Bertrand, W.P.Weber and S.A.Kazoura, Organometallics, 3(1984)1340.
94 G.Fritz and A.Worsching, Z. Anorg. Allg. Chem., 512(1984)131.
95 R.W.Zoellner and K.J.Klabunde, Inorg. Chem., 23(1984)3241.
96 F.Feher and F.Ocklenburg, Z. Anorg. Allg. Chem., 515(1984)36.
97 E.Hengge and G.Miklau, Z. Anorg. Allg. Chem., 508(1984)33.
98 E.Hengge and G.Miklau, Z. Anorg. Allg. Chem., 508(1984)43.
99 W.P.Neumann, K.D.Schultz and R.Vieler, J. Organomet. Chem., 264(1984)179.
100 H.Watanabe, T.Muraoka, M.Kageyama, K.Yoshizumi and Y.Nagai, Organometallics, 3(1984)141.
101 H.Watanabe, M.Kato, T.Okawa, Y.Nagai and M.Goto, J. Organomet. Chem., 271(1984)225.
102 P.Boudjouk and R.Sooriyakumaran, J. Chem. Soc., Chem. Commun., (1984)777.
103 L.Ross and M.Dräger, Z. Anorg. Allg. Chem., 515(1984)141.
104 K.P.C.Vollhardt and Z.Y.Yang, Angew. Chem., Int. Ed. Engl., 23(1984)460.
105 D.Seyferth and C.D.Prud'homme, Inorg- Chem., 23(1984)4412.
106 H.Puff, M.P.Bockmann, T.R.Kok and W.Schuh, J. Organomet. Chem., 168(1984)197.
107 M.J.Fink, K.J.Haller, R.West and J.Michl, J. Am. Chem. Soc., 106(1984)822.
108 W.Wojnowski, K.Peters, D.Weber and H.G. von Schnering, Z. Anorg. Allg. Chem., 519(1984)134.
109 O.Graalman, U.Klingebiel, W.Clegg, M.Haase and G.M.Sheldrick, Chem. Ber., 117(1984)2988.

110 O.Graalmann, U.Klingebiel, W.Clegg, M.Haase and G.M.Sheldrick, Z. Anorg. Allg. Chem., 519(1984)87.
111 K.Häberle and M.Dräger, Z. Naturforsch., Teil B, 39(1984)1541.
112 O.Graalmann, U.Klingebiel, W.Clegg, M.Haase and G.M.Sheldrick, Angew. Chem., Int. Ed. Engl., 23(1984)891.
113 C.H.DePuy and R.Damrouer, Organometallics, 3(1984)362.
114 U.Engelhardt and T.Bünger, Z. Anorg. Allg. Chem., 517(1984)177.
115 G.A.Olah, K.Laali and O.Faroog, Organometallics, 3(1984)1337.
116 C.Eaborn and M.N.Romanelli, J. Chem. Soc., Chem. Commun., (1984)1616.
117 M.J.Barrow and E.A.V.Ebsworth, J. Chem. Soc., Dalton Trans., (1984)563.
118 G.Gundersen, R.A.Mayo and D.W.H.Rankin, Acta Chem. Scand., Ser. A, 38(1984)579.
119 G.Gundersen and D.W.H.Rankin, Acta Chem. Scand., Ser. A, 38(1984)647.
120 W.Clegg, G.M.Sheldrick and D.Stalke, Acta Crystallogr., C40(1984)433.
121 O.Graalmann, M.Hesse, U.Klingebiel, W.Clegg, M.Haase and G.M.Sheldrick, Z. Anorg. Allg. Chem., 514(1984)49.
122 H.Schmidbaur, A.Schier, S.Lauteschläger, J.Riede and G.Muller, Organometallics, 3(1984)1906.
123 P.H.M.Budzekar, J.Boersma, G.J.M. van der Kerk and A.L.Spek, Organometallics, 3(1984)1187.
124 U.Klingebiel, Angew. Chem., Int. Ed. Engl., 23(1984)815.
125 R.R.Ford, M.A.Goodman, R.H.Neilson, A.K.Roy, U.G.Wettermark and P.Wisian-Neilson, Inorg. Chem., 23(1984)2063.
126 J.Heubel, T.Abouchakra, E.Puskaric and R. de Jaeger, Z. Anorg. Allg. Chem., 511(1984)212.
127 N.Wiberg, G.Fischer and P.Karampatses, Angew. Chem., Int. Ed. Engl., 23(1984)2063.
128 N.Wiberg, R.Meyers, S.K.Vasisht and H.Bayer, Chem. Ber., 117(1984)2886.
129 T.Fjeldberg, P.B.Hitchcock, M.F.Lappert and A.J.Thorne, J. Chem. Soc., Chem. Commun., (1984)822.
130 P.P.Power and K.Xiaojie, J. Chem. Soc., Chem. Commun., (1984)358.
131 K.F.Tebbe and T.Heinlein, Z. Anorg. Allg. Chem., 575(1984)7.
132 K.F.Tebbe and B.Freckmann, Acta Crystallogr., C40(1984)254.
133 M.Baudler, L. de Riese-Meyer and U.Schings, Z. Anorg. Allg. Chem., 519(1984)24.
134 G.Fritz and K.Stoll, Z. Anorg. Allg. Chem., 514(1984)69.
135 K.Hassler, J. Organomet. Chem., 266(1984)C1.
136 W.W.du Mont, T.Severengiz and B.Meyer, Angew. Chem., Int. Ed. Engl., 95(1983)1025.
137 G.D.Vaughn, K.A.Krein and J.A.Gladysz, Angew. Chem., Int. Ed. Engl., 23(1984)245.
138 G.Becker, W.Massa, R.E.Schmidt and G.Uhl, Z. Anorg. Allg. Chem., 517(1984)75.
139 G.Becker, O.Mundt and G.Uhl, Z. Anorg. Allg. Chem., 517(1984)89.
140 M.Baudler, J.Hellmann and G.Reuschenbach, Z. Anorg. Allg. Chem., 509(1984)38.
141 D.Schumburg and R.Krebs, Inorg. Chem., 23(1984)1378.
142 T.E.Mallouk, B.Desbat and N.Bartlett, Inorg. Chem., 23(1984)3160.
143 T.E.Mallouk, G.L.Rosenthal, G.Müller, R.Brusasco and N.Bartlett, Inorg. Chem., 23(1984)3167.

144 A.M.Walther and B.S.Ault, Inorg. Chem., 23(1984)3892.
145 P.Kleinert, D.Schmidt, J.Kirchof, H.J.Laukner and B.Knappe, Z. Anorg. Allg. Chem., 508(1984)176.
146 M.G.Voronkor, L.I.Gubanova, Y.L.Frolov, N.F.Chernov, G.A. Gavrilova and N.N.Chipanina, J. Organomet. Chem., 271(1984)169.
147 A.R.Bassindale and T.Stout, J. Chem. Soc., Chem. Commun., (1984)1387.
148 R.J.P.Corriu, A.Kpoton, M.Poirier, G.Royo and J.Y.Corey, J. Organomet. Chem., 277(1984)C25.
149 G.Klebe, M.Nix and K.Hensen, Chem. Ber., 117(1984)797.
150 G.Klebe, J.W.Bats and H.Fuess, J. Am. Chem. Soc., 106(1984)5202.
151 R.R.Holmes, R.O.Day, J.J.Harland, A.C.Sau and J.M.Holmes, Organometallics, 3(1984)341.
152 R.R.Holmes, R.O.Day, J.J.Harland and J.M.Holmes, Organometallics, 3(1984)347.
153 S.N.Gurkova, A.I.Gusev, V.A.Sharapov, N.V.Alekseev, T.K.Gar and N.J.Chromova, J. Organomet. Chem., 268(1984)119.
154 B.Deppisch, B.Gladrow and D.Kummer, Z. Anorg. Allg. Chem., 519(1984)42.
155 G.Klebe and D.T.Qui, Acta Crystallogr., C40(1984)476.
156 W.B.Farnham and J.F.Whitney, J. Am. Chem. Soc., 106(1984)3992.
157 N.S.Hosmane, M.Dehghan and S.Davies, J. Am. Chem. Soc., 106(1984)6435.
158 N.S.Hosmane and N.N.Sirmokadam, Organometallics, 3(1984)1119.
159 Z.H.Aiube and C.Eaborn, J. Organomet. Chem., 269(1984)217.
160 J.L.Atwood, T.Fjeldberg, M.F.Lappert, N.T.Luong-Thi, R.Shakir and A.J.Thorne, J. Chem. Soc., Chem. Commun., (1984)1163.
161 P.B.Hitchcock, M.F.Lappert, P.P.Power and S.J.Smith, J. Chem. Soc., Chem. Commun., (1984)1669.
162 A.H.Cowley, J.E.Kilduff, E.A.V.Ebsworth, D.W.H.Rankin, H.E.Robertson and K.Seip, J. Chem. Soc., Dalton Trans., (1984)689.
163 A.H.Cowley, J.E.Kilduff, J.G.Lasch, S.K.Mehrotra, N.C.Norman, M.Pakulski, B.R.Whittlesey, J.L.Atwood and W.E.Hunter, Inorg. Chem., 23(1984)2582.
164 J.Escudié, C.Couret, H.Ranaivonjatoro and J.Satgé, J. Chem. Soc., Chem. Commun., (1984)1621.
165 A.M.Caminade, C.Couret, J.Escudié and M.Koenig, J. Chem. Soc., Chem. Commun., (1984)1622.
166 A.H.Cowley, J.E.Kilduff, J.G.Lasch, N.C.Norman, M.Pakulski, F.Ando and T.C.Wright, Organometallics, 3(1984)1044.
167 M.M.Olmstead and P.P.Power, J. Am. Chem. Soc., 106(1984)1495.
168 A.H.Cowley, R.A.Jones, J.G.Lasch, N.C.Norman, C.A.Stewart, A.L.Stuart, J.L.Atwood, W.E.Hunter and H.M.Zhang, J. Am. Chem. Soc., 106(1984)7015.
169 A.H.Cowley, N.C.Norman and S.Quashie, J. Am. Chem. Soc., 106(1984)5007.
170 D.Fenske and K.Merzweiler, Angew. Chem., Int. Ed. Engl., 23(1984)635.
171 B.L.Li and R.H.Neilson, Inorg. Chem., 23(1984)3665.
172 H.J.Brennig and A.Soltani-Neshan, J. Organomet. Chem., 262(1984)C27.
173 D.W.W.Anderson, S.Cradock, E.A.V.Ebsworth, A.R.Green, D.W.H.Rankin and A.G.Robiette, J. Organomet. Chem., 271(1984)235.
174 S.Pöhlmann and U.Klingebiel, Z. Anorg. Allg. Chem., 510(1984)169.

175 U.Klingebiel and L.Skoda, Z. Anorg. Allg. Chem., 510(1984)175.
176 V.E.Shklover, Yu.T.Struchkov, O.G.Rodin, V.F.Traven and B.I.Stepanov, J. Organomet. Chem., 266(1984)117.
177 M.J.Fernandez and P.M.Maitlis, J. Chem. Soc., Dalton Trans., (1984)2063.
178 F.Carré, E.Colomer, R.J.P.Corriu and A.Vioux, Organometallics, 3(1984)1272.
179 U.Schubert, G.Kraft and E.Walther, Z. Anorg. Allg. Chem., 519(1984)96.
180 N.A.Bell, F.Glockling, M.L.Schneider, H.M.M.Shearer and M.D.Wilbey, Acta Crystallogr., C40(1984)625.
181 N.A.Bell, F.Glockling, A.McGregor, M.L.Schneider and H.M.M. Shearer, Acta Crystallogr., C40(1984)623.
182 J.W.Connolly, Organometallics, 3(1984)1333.
183 G.Thum and W.Malisch, J. Organomet. Chem., 264(1984)C5.
184 K.C.Brinkman, A.J.Blakeney, W.Krone-Schmidt, and J.A.Gladysz, Organometallics, 3(1984)1326.
185 D.K.Liu, C.G.Brinkley and M.S.Wrighton, Organometallics, 3(1984)1450.
186 K.C.Brinkman and J.A.Gladysz, Organometallics, 3(1984)147.
187 D.Metzer and E.Weiss, Chem. Ber., 117(1984)2464.
188 N.A.Bell, F.Glockling, A.McGregor, M.L.Schneider and H.M.M. Shearer, Acta Crystallogr., C40(1984)623.
189 N.A.Bell, F.Glockling, M.L.Schneider, H.M.M.Shearer, Acta Crystallogr., C40(1984)625.
190 U.Schubert, G.Kraft and E.Walther, Z. Anorg. Allg. Chem., 519(1984)96.
191 F.Carré, E.Colomer, R.J.P.Corriu and A.Vioux, Organometallics, 3(1984)970.
192 M.J.Fernandez and P.M.Maitlis, J. Chem. Soc., Dalton Trans., (1984)2063.
193 K.M.Mackay, B.K.Nicholson, W.T.Robinson and A.W.Sims, J. Chem. Soc., Chem. Commun., (1984)1276.
194 M.N.Bochkarev, N.L.Ermolaev, L.N.Zakharov, Y.N.Saf'yanov, G.A.Razuvaev and Y.T.Struchkov, J. Organomet. Chem., 270(1984)289.
195 M.A.Al-Kadier and D.S.Urch, J. Chem. Soc., Dalton Trans., (1984)263.
196 K.M.Mackay, P.J.Watkinson and A.L.Wilkins, J. Chem. Soc., Dalton Trans., (1984)133.
197 T.Fjeldberg, A.Haaland, B.E.R.Schilling, H.V.Volden, M.F.Lappert and A.J.Thorne, J. Organomet. Chem., 276(1984)C1.
198 P.B.Hitchcock, M.F.Lappert, S.J.Miles and A.J.Thorne, J. Chem. Soc., Chem. Commun., (1984)480.
199 G.Bähr and R.Gelius, Chem. Ber., 91(1984)829.
200 W.P.Neuman and J.Fu, J. Organomet. Chem., 273(1984)295.
201 T.S.Dory and J.J.Zuckerman, J. Organomet. Chem., 263(1984)295.
202 A.H.Cowley, P.Jutzi, F.X.Kohl, J.G.Lasch, N.C.Norman and E.Schlüter, Angew. Chem., Int. Ed. Engl., 23(1984)616.
203 M.J.Heeg, C.Janiak and J.J.Zuckerman, J. Am. Chem. Soc., 106(1984)4259.
204 M.Grenz, E.Hahn, W.W. de Mont and J.Pickardt, Angew. Chem., Int. Ed. Engl., 23(1984)61.
205 L.Fernholt, A.Haaland, P.Jutzi, F.X.Kohl and R.Seip, Acta Chem. Scand., Ser. A, 38(1984)211.
206 A.Haaland and B.E.R.Schilling, Acta Chem. Scand., Ser. A, 38(1984)217.
207 F.X.Kohl, E.Schlüter, P.Jutzi, C.Kniger, G.Wolmershaüser, P.Hofmann and P.Stauffert, Chem. Ber., 117(1984)1178.

208 P.Jutzi, F.X.Kohl, E.Schlüter, M.B.Hursthouse and N.P.C.Walker, J. Organomet. Chem., 271(1984)393.
209 N.S.Hosmane, N.N.Sirmokadam and R.H.Herber, Organometallics, 3(1984)1665.
210 A.H.Cowley, P.Galow, N.S.Hosmane, P.Jutzi and N.C.Norman, J. Chem. Soc., Chem. Commun., (1984)1564.
211 N.S.Hosmane and N.N.Sirmokadam, Organometallics, 3(1984)1119.
212 M.J.S.Dewar, G.L.Grady, D.R.Kuhn and K.M.Merz, J. Am. Chem. Soc., 106(1984)6773.
213 A.J.Edwards and K.I.Khallow, J. Chem. Soc., Chem. Commun., (1984)50.
214 J.Bönisch and G.Bergerhoff, Acta Crystallogr., C40(1984)2005.
215 D.Tudela, U.Fernandez and J.Tornero, Z. Anorg. Allg. Chem., 509(1984)174.
216 M.M.Olmstead and P.P.Power, Inorg. Chem., 23(1984)413.
217 T.Fjeldberg, H.Hope, M.F.Lappert, P.P.Power and A.J.Thorne, J. Chem. Soc., Chem. Commun., (1983)639.
218 M.Veith and W.Frank, Angew. Chem., Int. Ed. Engl., 23(1984)158.
219 H.Martan and J.Weiss, Z. Anorg. Allg. Chem., 514(1984)107.
220 M.Veith, M.Grosser and V.Huch, Z. Anorg. Allg. Chem., 513(1984)89.
221 A.Tzschach, M.Scheer and K.Jurkschat, Z. Anorg. Allg. Chem., 515(1984)147.
222 A.Tzschach, M.Scheer and K.Jurkschat, Z. Anorg. Allg. Chem., 508(1984)73.
223 A.Tzschach, M.Scheer and K.Jurkschat, Z. Anorg. Allg. Chem., 512(1984)177.
224 Z.Arifin, E.J.Filmore, J.D.Donaldson and S.M.Grimes, J. Chem. Soc., Dalton Trans., (1984)1965.
225 J.D.Donaldson and S.M.Grimes, J. Chem. Soc., Dalton Trans., (1984)1301.
226 T.Lis, Acta Crystallogr., C40(1984)374.
227 M.A.Pierce-Butler, Acta Crystallogr., C40(1984)63.
228 R.G.Bryant, V.P.Chacko and M.C.Etter, Inorg. Chem., 23(1984)3580.
229 P.B.Hitchcock, M.F.Lappert, B.J.Samways and E.L.Weinberg, J. Chem. Soc., Chem. Commun., (1983)1492.
230 P.A.W.Dean, J.J.Vittal and N.C.Payne, Inorg. Chem., 23(1984)4232.
231 N.W.Alcock, E.H.Curzon, P.Moore and C.Pierpoint, J. Chem. Soc., Dalton Trans., (1984)605.
232 N.W.Alcock, E.H.Curzon and P.Moore, J. Chem. Soc., Dalton Trans., (1984)2813.
233 R.W.Zoellner and K.J.Klabunde, Inorg. Chem., 23(1984)3241.
234 B.K.Nicholson, J. Organomet. Chem., 265(1984)153.
235 K.C.Molloy, T.G.Purcell, K.Quill and I.W.Nowell, J. Organomet. Chem., 267(1984)237.
236 J.F.Vollano, R.O.Day, D.N.Rau, V.Chandrasekhar and R.R.Holmes, Inorg. Chem., 23(1984)3153.
237 H.Puff, W.Schuh, R.Sievers, W.Wald and R.Zimmer, J. Organomet. Chem., 260(1984)271.
238 A.G.Davies, A.J.Price, H.M.Dawes and M.B.Hursthouse, J. Organomet. Chem., 270(1984)C1.
239 R.H.Herber, A.Shanzer and J.Libman, Organometallics, 3(1984)586.
240 J.F.Vollano, R.O'Day and R.R.Holmes, Organometallics, 3(1984)745.
241 A.F.Shihada, I.A.A.Jassim and F.Weller, J. Organomet. Chem., 268(1984)125.

242 Y.Sasaki, H.Imoto and O.Nagano, Bull. Chem. Soc. Jpn., 57(1984)1417.
243 V.G.Kumar Das, C.Wei, Y.C.Keang and E.Sinn, J. Chem. Soc., Chem. Commun., (1984)1418.
244 S.J.Blunden, R.Hill and J.N.R.Ruddick, J. Organomet. Chem., 267(1984)C5.
245 H.Yildrimyan and G.Gattow, Z. Anorg. Allg. Chem., 519(1984)213.
246 K.C.Molloy and J.J.Zuckerman, Acc. Chem. Res., 16(1983)386.
247 G.D.Andreetti, G.Bocelli, G.Galestani and P.Sgarabotto, J. Organomet. Chem., 273(1984)31.
248 L.S.Dumitrescu, I.Haiduc and J.Weiss, J. Organomet. Chem., 263(1984)159.
249 H.Preut, K.Gratz and F.Huber, Acta Crystallogr., C40(1984)941.
250 J.F.Vollano, R.O.Day and R.R.Holmes, Organometallics, 3(1984)750.
251 C.Pelizzi, G.Pelizzi and P.Tarasconi, J. Organomet. Chem., 277(1984)29.
252 P.A.Cusack, B.N.Patel, P.J.Smith, D.W.Allen and I.W.Nowell, J. Chem. Soc., Dalton Trans., (1984)1239.
253 U.Russo, A.Cassol and A.Silvestri, J. Organomet. Chem., 260(1984)69.
254 K.Jurkschat and A.Tzschack, J. Organomet. Chem., 272(1984)C13.
255 R.G.Swisher and R.R.Holmes, Organometallics, 3(1984)365.
256 R.Willen, M.Gielen, J.Meunier-Piret, M. van Meerssche, K.Jurkschat and A.Tzschach, J. Organomet. Chem., 277(1984)335.
257 R.Barbieri and A.Silvestri, J. Chem. Soc., Dalton Trans., (1984)1019.
258 D.W.Allen, D.J.Derbyshire, I.W.Nowell and J.S.Brooks, J. Organomet. Chem., 260(1984)263.
259 S.Calogero, G.Valle and U.Russo, Organometallics, 3(1984)1205.
260 D.Cunningham, T.Higgins and P.McArdle, J. Chem. Soc., Chem. Commun., (1984)833.
261 A.L.Rheingold, S.W.Ng and J.J.Zuckerman, Organomet. Chem., 3(1984)233.
262 E.S.Paterson, J.L.Wardell and J.W.Burley, J. Organomet. Chem., 273(1984)313.
263 W.F.Manders, G.J.Olson, F.E.Brinckman and J.M.Bellama, J. Chem. Soc., Chem. Commun., (1984)538.
264 I.Wharf, R.Cuenca, E.Besso and M.Onyszchuk, J. Organomet. Chem., 277(1984)245.
265 Y.Ducharme, S.Latour and J.D.Wuest, J. Am. Chem. Soc., 196(1984)1499.
266 G.A.Razuvaev, V.I.Shcherbakov and I.K.Grigor'eva, J. Organomet. Chem., 264(1984)245.
267 J.Otera, T.Yano, E.Kunimato and T.Nakata, Organometallics, 3(1984)426.
268 J.L.Atwood, A.D.McMaster, R.D.Rogers and S.R.Stobart, Organometallics, 3(1984)1500.
269 H.Killing and T.N.Mitchell, Organometallics, 3(1984)1917.
270 Y.Azuma and M.Newcomb, Organometallics, 3(1984)9.
271 M.Newcomb, M.T.Blanda, Y.Azuma and T.J.Delord, J. Chem. Soc., Dalton Trans., (1984)1159.
272 N.Kleiner and M.Dräger, J. Organomet. Chem., 279(9184)151.
273 J.Fu and W.P.Neumann, J. Organomet. Chem., 272(1984)C5.
274 H.Puff, C.Bach, H.Reuter and W.Schuch, J. Organomet. Chem., 277(1984)17.

275 H.A.Olszowy and W.Kitching, Organometallics, 3(1984)1676.
276 K.Kondo, G.Matsubayashi, T.Tanaka, H.Yoshioka and K.Nakatsu, J. Chem. Soc., Dalton Trans., (1984)379.
277 M.G.B.Drew, J.M.Kisenyi and G.R.Willey, J. Chem. Soc., Dalton Trans., (1984)1727.
278 M.G.B.Drew, J.M.Kisenyi and G.R.Willey, J. Chem. Soc., Dalton Trans., (1984)1723.
279 K.B.Dillon and A.Marshall, J. Chem. Soc., Dalton Trans., (1984)1245.
280 C.T.G.Knight and A.E.Merbach, J. Am. Chem. Soc., 106(1984)804.
281 M.J.S.Dewar, G.L.Grady and J.J.P.Stewart, J. Am. Chem. Soc., 106(1984)6771.
282 M.S.Holt, J.J.MacDougall, F.Mathey and J.H.Nelson, Inorg. Chem., 23(1984)449.
283 A.Albinati, P.S.Pregosin and H.Rüegger, Inorg. Chem., 23(1984)3223.
284 A.Albinati, P.S.Pregosin and H.Rüegger, Angew. Chem., Int. Ed. Engl., 23(1984)78.
285 H.C.Clark, G.F.Ferguson, A.B.Goel and L.Ruhl, Organometallics, 3(1984)15.
286 H.Moriyana, P.S.Pregosin, Y.Saito and T.Yamakawa, J. Chem. Soc., Dalton Trans., (1984)2329.
287 G.B.Shuyl'pin, G.V.Nizova, A.N.Kitaigorodslaii and M.V.Serdobar, J. Organomet. Chem., 275(1984)273.
288 S.Iwasaki, T.Nagai, E.Miki, K.Mizumachi and T.Ishimari, Bull. Chem. Soc. Jpn., 57(1984)386.
289 F.Faraone, G.Bruno, S.Lo Schiaro and G.Bombieri, J. Chem. Soc., Dalton Trans., (1984)533.
290 H.J.Haupt, P.Balsaa, B.Schwab, U.Flörke and H.Pteut, Z. Anorg. Allg. Chem., 513(1984)22.
291 J.T.Lin, G.P.Hagen and J.E.Ellis, Organometallics, 3(1984)1288.
292 H.Preut, H.J.Haupt and U.Flörke, Acta Crystallogr., C40(1984)600.
293 O.J.Curnow and B.K.Nicholson, J. Organomet. Chem., 267(1984)257.
294 D.Melzer and E.Weiss, J. Organomet. Chem., 263(1984)67.
295 F.Näumann, J.Kopf and D.Rehder, J. Organomet. Chem., 267(1984)249.
296 Y.V.Skripkin, O.G.Volkov, A.A.Pasynskii, A.S.Artsyshkina, L.M.Dikareva, V.N.Ostrikova, M.A.Porai-Kostrits, S.L.Davydova and S.G.Sakharov, J. Organomet. Chem., 263(1984)345.
297 C.J.Cardin, D.J.Cardin, H.E.Parge and J.M.Power, J. Chem. Soc., Chem. Commun., (1984)609.
298 M.M.Kubicki, R.Kergoat, J.E.Guerchais and P.L'Haridan, J. Chem. Soc., Dalton Trans., (1984)1791.
299 C.Combes, R.J.P.Corriu, G.Dabosi, B.J.L.Henner and M.Martineau, J. Organomet. Chem., 270(1984)131.
300 C.Combes, R.J.P.Corriu, G.Dabosi, B.J.L.Henner and M.Martineau, J. Organomet. Chem., 270(1984)141.
301 B.S.Suresh and D.K.Padma, J. Chem. Soc., Dalton Trans., (1984)1779.
302 B.Krug, W.Legat and R.Gruehn, Z. Anorg. Allg. Chem., 515(1984)159.
303 K.Beneke, H.H.Kruse and G.Lagaly, Z. Anorg. Allg. Chem., 518(1984)65.
304 T.Yokoyama, T.Shimono and T.Tarutani, Bull. Chem. Soc. Jpn., 57(1984)2315.
305 T.Yokoyama, O.Nakamura and T.Tarutani, Bull. Chem. Soc. Jpn., 57(1984)2989.

306 F.Schlenkrich, E.Beil, O.Rademacher and H.Scheler, Z. Anorg. Allg. Chem., 511(1984)41.
307 O.Rademacher, O.Ziemens and H.Scheler, Z. Anorg. Allg. Chem., 519(1984)165.
308 B.M.Lok, C.A.Messina, R.L.Patton, R.T.Gajek, T.R.Cannan and E.M.Flanigen, J. Am. Chem. Soc., 106(1984)6092.
309 D.G.Hay and H.Jaeger, J. Chem. Soc., Chem. Commun., (1984) 1433.
310 S.G.Fegan and B.M.Lowe, J. Chem. Soc., Chem. Commun., (1984) 437.
311 L.S.Dent Glasser and G.Harvey, J. Chem. Soc., Chem. Commun., (1984)664.
312 L.S.Dent Glasser and G.Harvey, J. Chem. Soc., Chem. Commun., (1984)1250.
313 R.We thmann and R.Hoppe, Z. Anorg. Allg. Chem., 509(1984)7.
314 B.R.Currell, H.G.Midgley, B.J.Mingham, J.R.Parsonage and E.A.Vidgeon, J. Chem. Soc., Dalton Trans., (1984)757.
315 G.Garzo, D.Hoebbel, A.Vargha and K.Ujszaszi, J. Chem. Soc., Dalton Trans., (1984)1857.
316 G.Engelhardt and D.Hoebbel, J. Chem. Soc., Chem. Commun., (1984)514.
317 C.J.Greswell, R.K.Harris and P.T.Jageland, J. Chem. Soc., Chem. Commun., (1984)1261.
318 C.A.Fyfe, G.J.Kennedy, C.T. de Schutter and G.T.Kokotailo, J. Chem. Soc., Chem. Commun., (1984)541.
319 M.W.Anderson, T.Klinowski and L.Xinsheng, J. Chem. Soc., Chem. Commun., (1984)1596.
320 C.D.Chang, C.T.W.Chu, J.N.Miale, R.F.Bridger and R.B.Calvert, J. Am. Chem. Soc., 106(1984)8143.
321 J.Sanz and J.M.Serratosa, J. Am. Chem. Soc., 106(1984)4790.
322 G.T.Kokotailo, C.A.Fyfe, G.C.Gobbi, G.J.Kennedy and C.T. de Schutter, J. Chem. Soc., Chem. Commun., (1984)1208.
323 C.A.Fyfe, G.J.Kennedy, G.T.Kokotailo and C.T. de Schutter, J. Chem. Soc., Chem. Commun., (1984)1093.
324 C.A.Fyfe, G.C.Gobbi, W.J.Murphy, R.S.Ozubko and D.A.Slack, J. Am. Chem. Soc., 106(1984)4435.
325 C.M.Schramm, B.H.W.S. de Jong and V.E.Parziale, J. Am. Chem. Soc., 106(1984)4396.
326 N.J.Clayden, C.M.Dobson, C.J.Hayes and S.A.Rodger, J. Chem. Soc., Chem. Commun., (1984)1396.
327 G.Schmidt and R.Gruehn, Z. Anorg. Allg. Chem., 512(1984)193.
328 S.Ichiba and M.Takeshita, Bull. Chem. Soc. Jpn., 57(1984)1087.
329 F.J.Berry, C.Hallett, M.H.Loretto and D.J.Smith, J. Chem. Soc., Chem. Commun., (1984)1483.
330 R.Hoppe and B.Nowitzki, Z. Anorg. Allg. Chem., 509(1984)145.
331 B.Nowitzki and R.Hoppe, Z. Anorg. Allg. Chem., 515(1984)114.
332 M.Jansen and B.Standke, Z. Anorg. Allg. Chem., 510(1984)143.
333 B.Brazel and R.Hoppe, Z. Anorg. Allg. Chem., 515(1984)81.
334 A.La Ginestra, P.Galli, M.L.Berardelli and M.A.Massucci, J. Chem. Soc., Dalton Trans., (1984)527.
335 G.E.Narda, M.C.Apella, S.B.Etchevemy and E.J.Baran, Z. Anorg. Allg. Chem., 515(1984)207.
336 S.Ichiba and K.Kunita, Bull. Chem. Soc. Jpn., 57(1984)51.
337 Y.Nakamura, A.Amga, I.Nakai and K.Nagashima, Bull. Chem. Soc. Jpn., 57(1984)1718.
338 A.Feltz and G.Pfaff, Z. Anorg. Allg. Chem., 517(1984)136.
339 A.Likforman, M.Guittard and S.Jaulmes, Acta Crystallogr., C40(1984)917.
340 B.Eisenmann, E,Kieselbach, H.Schäfer and H.Schrod, Z. Anorg. Allg. Chem., 516(1984)49

341 C.Brinkmann, B.Eisenmann and H.Schäfer, Z. Anorg. Allg. Chem., 517(1984)143.
342 J.C.Huffmann, J.P.Huashalter, A.M.Umarji, G.K.Shenoy and R.C.Haushalter, Inorg. Chem., 23(1984)2312.
343 R.C.Haushalter, C.M.O'Connor, J.P.Haushalter, A.M.Umarji and G.K.Shenoy, Angew. Chem., Int. Ed. Engl., 23(1984)169.