

Chapter 4

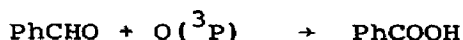
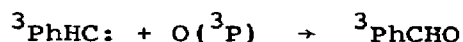
ELEMENTS OF GROUP 4

P.G. Harrison

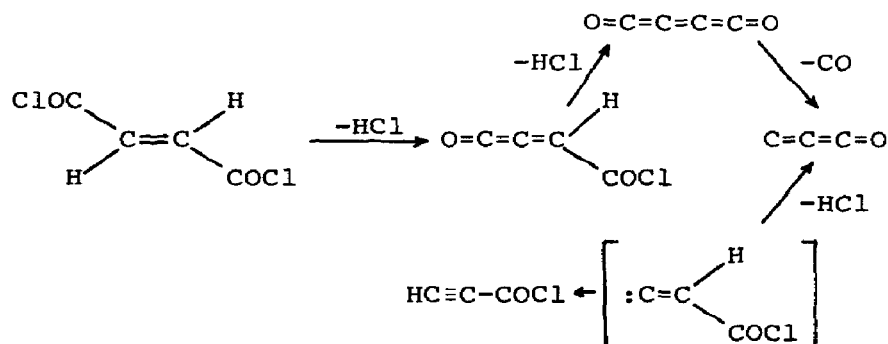
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4.1 CARBON

The infrared-matrix isolation technique has been applied in the study of several carbon systems. The reaction of oxygen with phenylcarbene, produced by irradiation of phenyldiazomethane, PhCHN_2 , in an argon matrix affords both benzaldehyde and benzoic acid. The ratio of these products depends on the oxygen content of the matrix and on the thermal treatment of the matrix. Short irradiation times and at low (8K) temperatures, benzaldehyde is the sole product. Benzoic acid is produced at higher temperatures. Reaction proceeds via the diffusion of atomic oxygen:



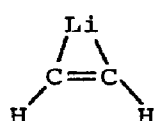
Diffusion of O_2 only occurs at higher temperatures.¹ Matrix-isolated tricarbon monoxide has been produced by pyrolyzing fumaroyl dichloride seeded in excess argon. Two possible reaction pathways were postulated (Scheme 1):



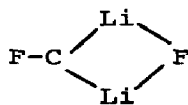
Scheme 1

The ν_1 (2242.6 cm^{-1}), ν_2 (1907.2 cm^{-1}) and ν_4 (579.6 cm^{-1}) bands were observed, and a normal coordinate analysis yielded a general harmonic force field.² The microwave spectra of the same molecule isotopically substituted with ^{13}C or ^{18}O at each of its four atoms have yielded accurate geometrical parameters ($\text{C}_1\text{-O}$ 115.0 pm , $\text{C}_1\text{-C}_2$ 130.6 pm , $\text{C}_2\text{-C}_3$ 125.4 pm). Discrepancies with ab initio MO calculations are somewhat larger than usual, attributed to the effect of a low-frequency bending vibration.³ Codeposition of CF_3I and ozone in excess argon on a CsI window at 17 K gives a $\text{CF}_3\text{I-O}_3$ molecular complex, which photodissociates upon irradiation yielding CF_3IO . Further photolysis produces CF_3OI and two $\text{CF}_2\text{O--IF}$ molecular complexes.⁴ The oxide-transfer technique, involving transfer of O^{2-} from Tl_2O to a suitable acceptor, coupled with matrix-isolation has been employed to synthesise and characterise the mono- and dithiocarbonate anions, CO_2S^{2-} and COS_2^{2-} , and the $\text{CO}_2\text{F}_2^{2-}$, all as triple ions with two Tl^+ cations.⁵ The CO_2S^{2-} anion was characterised by sharp, intense C-O stretching bands at 1445 and 1202 cm^{-1} , and a C-S stretching mode at 603 cm^{-1} . The two most intense bands of the COS_2^{2-} anion occurred at 1506 cm^{-1} (C-O stretch) and 606 cm^{-1} (antistymmetric C-S stretch). The calculated force constants suggest increased localization of the π bonding on the carbon-

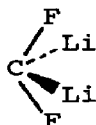
oxygen bonds as the number of sulphur atoms in the anion is increased. On warming, the matrix-isolated $\text{Ti}_2^+\text{CO}_2\text{F}_2^{2-}$ triple ion eliminates TiF giving $\text{Ti}^+\text{CO}_2\text{F}^-$. The simultaneous matrix deposition of lithium atoms and acetylene molecules at high dilution in argon at 15K yields infrared spectra due to four species. The major product (1) has a LiC_2H_2 stoichiometry which is most likely to be planar, with the lithium bridging the π system and cis C-H groups and CCH angles estimated to be $140 \pm 10^\circ$. The C-C stretching mode is reduced to 1655 cm^{-1} , near to that of ethylene, and rationalised by the sharing of electron density between the π system of acetylene and lithium rather than lithium valence electron transfer into an antibonding π^* orbital of acetylene. The minor reaction products have different stoichiometries. Conclusions from the propyne-lithium reaction were similar. All the observed species were unstable above 30K.⁶ The three minima (2)-(4) have been isolated on the potential



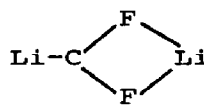
(1)



(2)

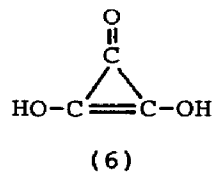
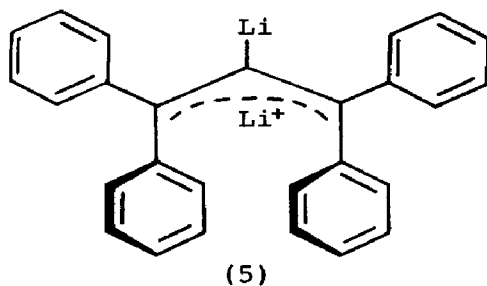


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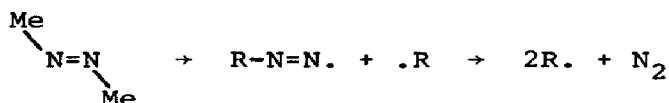
(4)

surface of CLi_2F_2 , of which the most stable is the lithium-bridged species (2).⁷ Only one type of low-binding-energy carbon and lithium environment has been observed for both methyllithium and dilithiomethane, in accord from previous structural (MeLi) and spectroscopic data. In addition, the direction of the carbon 1s core level shifts and the ^{13}C chemical shifts suggest an increased charge density of the methylene carbon in the latter compound. The data also indicate a single lithium environment for CH_2Li_2 strongly suggesting a highly symmetrical structure.⁸ ^1H , ^7Li and ^{13}C n.m.r. have demonstrated that lithium 2-lithio-1,1,3,3-tetraphenylpropenide adopts the ionic allyl-lithium structure (5) with C_{2v} symmetry. The second lithium is covalently bonded to the central carbon atom.⁹ Deltic acid molecules (6) probably form infinite chains linked by two very strong unsymmetrical $\text{OH}\dots\text{O}$ hydrogen bonds. All fundamentals of the vibrational spectra in the range $4000\text{--}20 \text{ cm}^{-1}$ have been assigned.¹⁰ Attempts to record the microwave spectrum of dichloroketene, $\text{Cl}_2\text{C}=\text{C}=\text{O}$, were unsuccessful, probably



due to the near zero dipole moment. However, the Fourier Transform infrared spectrum was able to be recorded under the same conditions.¹¹ Theoretical calculations on fluoroacetones and their conjugate acids exhibit an inverse dependence of the proton affinity on the number of fluorine substituents. The good correlation found between increasing proton affinity and decreasing ionization potential is attributed to the observation that the ionization of a non-bonding electron is essentially localized at a single atom which is also the site of protonation.¹²

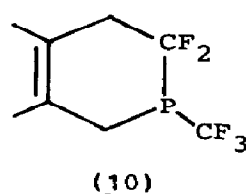
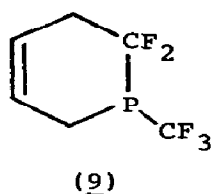
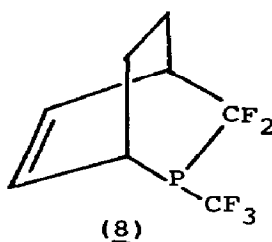
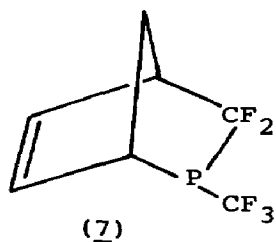
The CARS (Coherent Anti-stokes Raman Spectroscopy) technique has been employed to study the photodissociation of trans-azomethane, $\text{CH}_3\text{N}=\text{NCH}_3$, vapour.¹³ The dissociation is complete within 2 ns, and the nascent N_2 vibrational distribution appears to be consistent with the theoretical prediction of sequential bond cleavage mechanism:



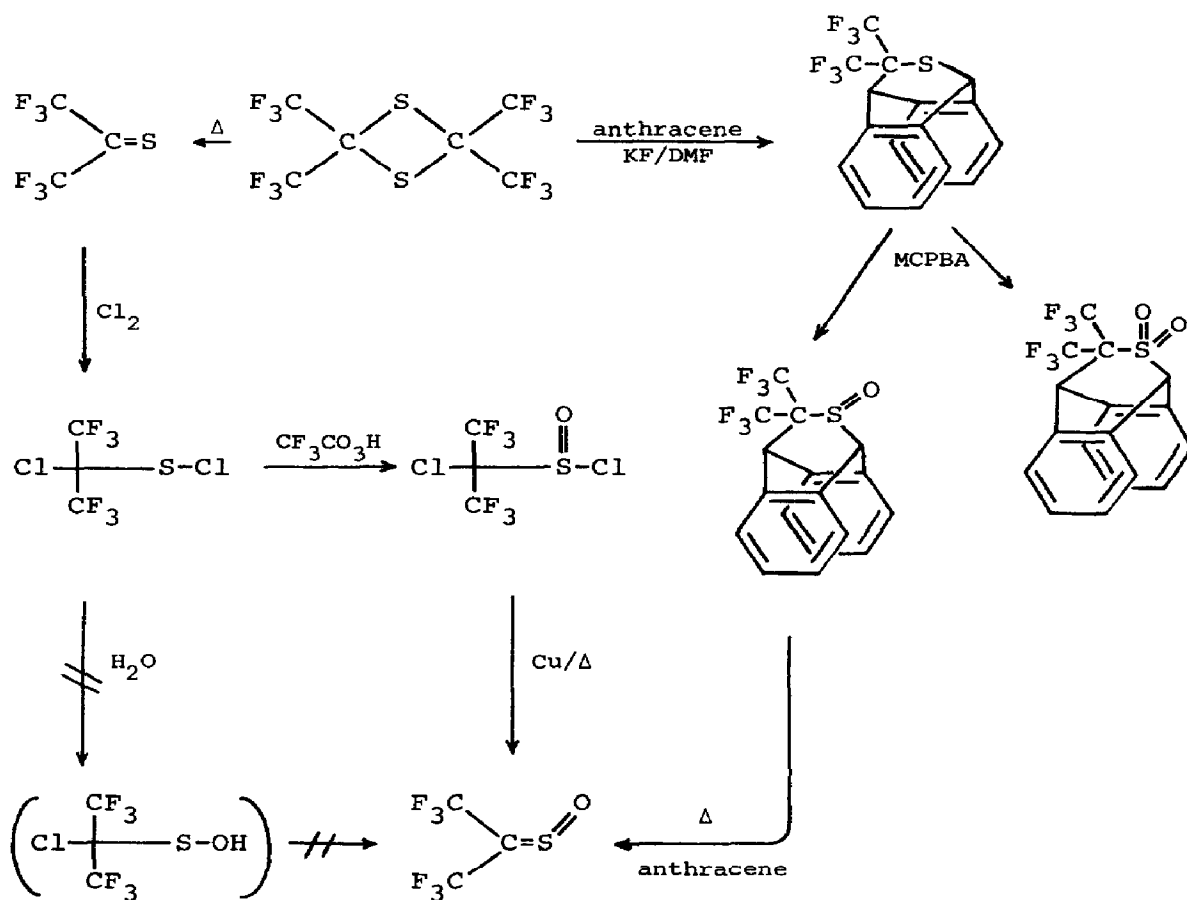
The photolysis and thermal decomposition of both pyruvic acid, $\text{CH}_3\text{C}(=\text{O})\text{CO}_2\text{H}$,¹⁴ and glyoxylic acid, $\text{H}\text{C}(=\text{O})\text{CO}_2\text{H}$,¹⁵ have been investigated. The major products from the photolysis of glyoxylic acid (1-6 Torr and 355K) were CO_2 and formaldehyde, with minor amounts of CO and H_2 . Primary processes involve H-atom transfer followed by dissociation. The same major products were also formed during thermal decomposition at 740-710K, although the formation of formaldehyde was always less than stoichiometric and the CO/CO_2 ratio was observed to increase with increasing temperature. CO_2 and acetaldehyde were formed in the photolysis

of pyruvic acid. Again the primary process was an internal H-atom transfer, followed by dissociation into CO_2 and $\text{CH}_3\text{-C-OH}$, with this species rearranging to give acetaldehyde and other products.

The thermal decomposition of the potentially explosive azide, F_2HCN_3 , has been studied in a controlled way by using a flow system under reduced pressure and PE spectroscopic gas analysis. Decomposition leads to the formation of N_2 , FCN and HF , presumably via the intermediate nitrene, F_2HCN .¹⁶ Treatment of a suspension of NaCN in acetonitrile with an excess of C_2F_4 resulted in the formation of a red solution. Evaporation of this solution to dryness yielded a red amorphous solid, which, after redissolution in water and addition of a solution of Ph_4AsCl , afforded two salts, yellow $[\text{Ph}_4\text{As}^+][\text{CF}_3\text{C(O)C(CN)}_2^-]$ and red $[\text{Ph}_4\text{As}^+][(\text{NC})_2\text{CC(CN)C(F)NC(CN)}_2]$.¹⁷ Hydrogen halide addition to trifluoromethyl isocyanide results in the formation of both isomers of the compounds, $\text{CF}_3\text{N=CHF}$, $\text{CF}_3\text{N=CHCl}$, and CF_3CHBr . Electron diffraction studies indicate that the E isomers of the fluoro and chloro compounds predominate, with isomeric ratios (from n.m.r. data) of 15.4:1 (fluoro compound), 6.7:1 (chloro compound), 3.8:1 (bromo compound). All three methanimines dimerize slowly, forming the corresponding aminomethanimines, $\text{CF}_3\text{N=C(H)N(CF}_3\text{)(CX}_2\text{H)}$ ($\text{X} = \text{F, Cl, Br}$). The addition of SF_5Br to $\text{CF}_3\text{N}\equiv\text{C}$ yields the pentafluorothio-substituted methanimine, $\text{CF}_3\text{N=C(Br)SF}_5$.¹⁸ Both exo conformers, eq-exo and ax-exo, fit the experimental electron diffraction data for perfluoronitrosocyclobutane, $\text{C}_3\text{F}_5\text{NO}$, almost equally well and therefore not permitting any estimation of the ratio of isomers.¹⁹ The perfluorophosphaalkene, $\text{F}_3\text{CP=CF}_2$, reacts as a dienophile at temperatures between -20 and $+15^\circ\text{C}$ with cyclopentadiene, 1,3-cyclohexadiene, butadiene and 2,3-dimethylbutadiene to give the Diels-Alder adducts (7)-(10) in high yields.²⁰ The same adducts may also be obtained in a one-pot procedure by reaction of F_3CPI_2 with tin(II) chloride in the presence of the corresponding 1,3-dienes.²¹



Several new methods for the synthesis of bis(trifluoromethyl)-sulphine, $(\text{CF}_3)_2\text{C}=\text{S}=\text{O}$, have been reported, and are summarised in Scheme 2. Reactions are summarised in Scheme 3.²²

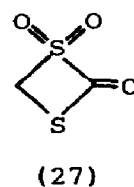
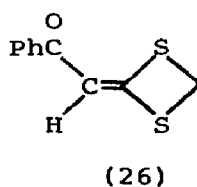
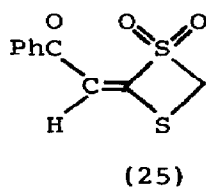
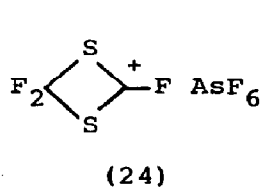


MCPBA = m-chloroperoxybenzoic acid

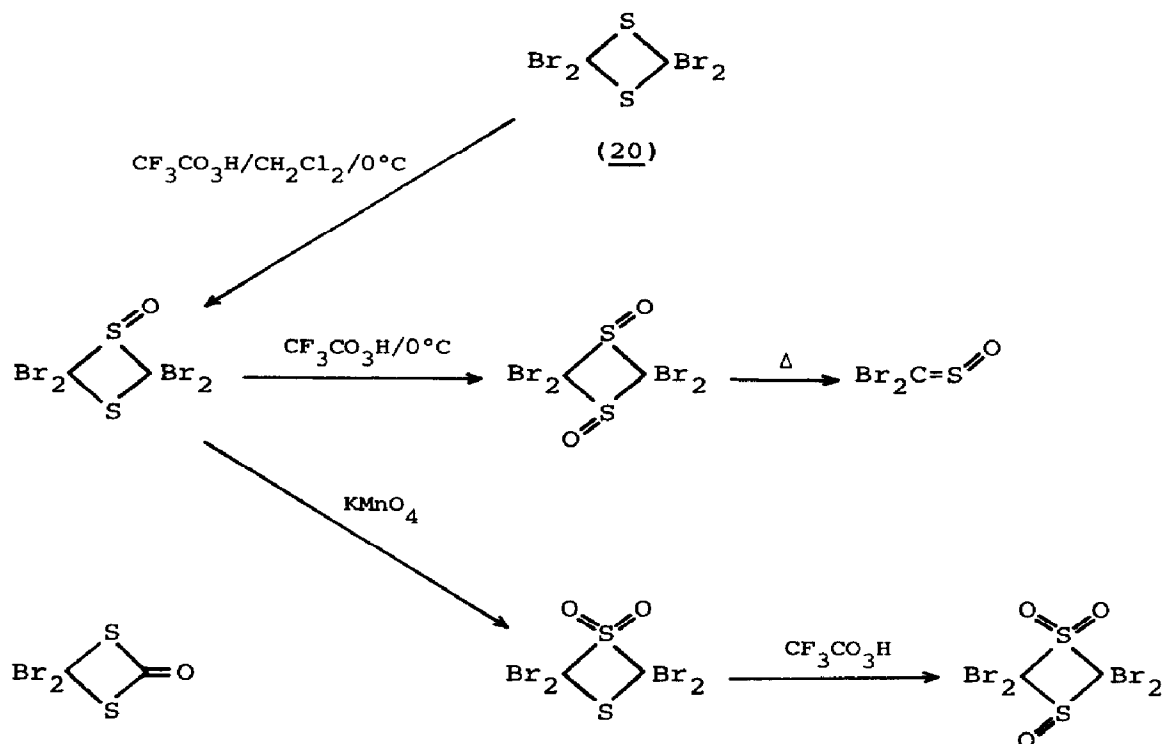
Scheme 2

All five corresponding S-oxides (11)-(15) have been obtained by the oxidation of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (16). Thermal decomposition of these S-oxides yields $(\text{F}_3\text{C})_2\text{C}=\text{S}=\text{O}$, the thiirane (17), $(\text{F}_3\text{C})(\text{F}_2\text{C}=\text{C})\text{CSO}_2\text{F}$, and $\text{F}_3\text{C}-\text{C}=\text{C}(\text{CF}_3)_2$, depending on the oxide. Oxidation of the thiirane (17) affords only the episulphoxide (18), but not the episulphone (19) (Scheme 4).²³

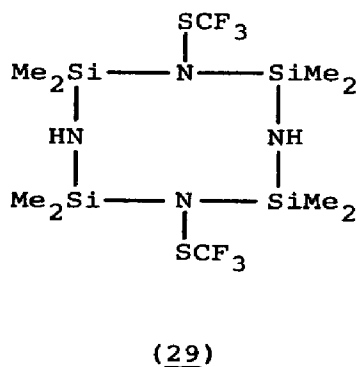
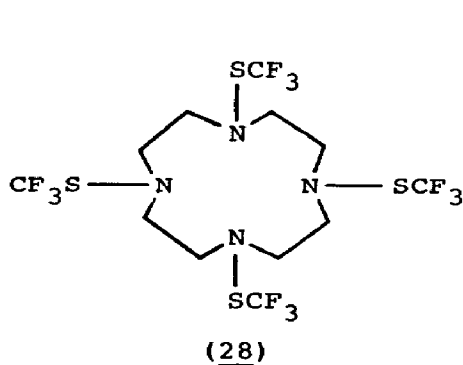
The behaviour of 1,1,3,3-tetrachloro- and 1,1,3,3-tetrabromo-1,3-dithietanes ((20) and (21), respectively) is generally quite similar (Schemes 5 and 6). Thermolysis of the tetrachloro-1,3-dithietane 1,1-dioxide (22) provides a convenient synthesis of the tetrachlorothiirane (23).²⁴ Reaction of 2,2,4,4-tetrafluoro-1,3-dithietane with the Lewis acids MF_5 ($\text{M} = \text{As}, \text{Sb}$) affords the stable 2,4,4-trifluoro-1,3-dithietan-2-ylum salts (24).²⁵ The crystal structure of the arsenic derivative has been determined. The C-F and C-S bonds to the cationic carbon are significantly shorter than those to the saturated carbon.²⁶ Ozonolysis of 2-(benzoylmethylene)-1,3-dithietane 1,1-dioxide (25), prepared via the oxidation of 2-(benzoylmethylene)-1,3-dithietane (26) affords 1,3-dithietane (27), the first dithietane containing an α -oxosulphone structure.²⁷

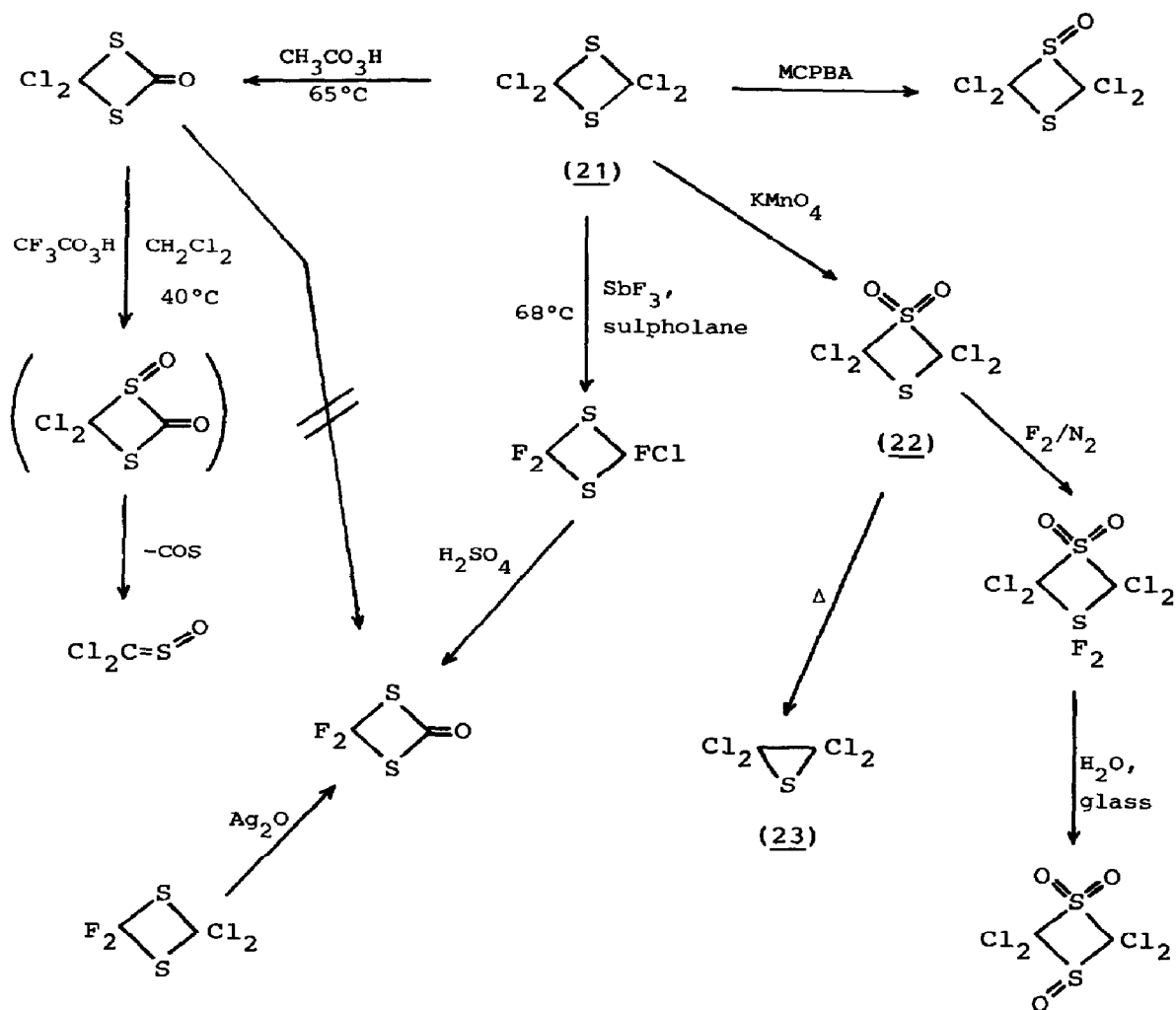


Trifluoroethyldynesulphur trifluoride, $\text{CF}_3\text{C}\equiv\text{SF}_3$, the first compound with a carbon-sulphur triple bond, has been prepared by the dehydrofluorination of $\text{CF}_3\text{CH}=\text{SF}_4$ or $\text{CF}_3\text{CH}_2\text{SF}_5$ and is a colourless gas, mp. -122.8°C and an estimated bp. of -15°C . The C-C \equiv S linkage is almost linear (angle 171.5°) with a C \equiv S bond distance of 1.394\AA (determined by low-temperature (-130°C) crystallography). Dimerization of the molecule occurs on warming up to -30°C , which is probably formed on internal cleavage into the carbene, $\text{CF}_3\text{C}-\text{SF}_3$. The dimer is a substituted butene, $\text{CF}_3(\text{SF}_3)\text{C}=\text{C}(\text{CF}_3)\text{SF}_3$, with a trans (E) configuration.²⁸ The alkenes, $\text{CF}_3\text{SF}_4\text{CF}=\text{CF}_2$ and $\text{CF}_3\text{SF}_4\text{CH}=\text{CF}_2$, are formed on dehydrochlorination of $\text{CF}_3\text{SF}_4\text{CHFCF}_2\text{Cl}$ and $\text{CF}_3\text{SF}_4\text{CH}_2\text{CF}_2\text{Cl}$, respectively. Addition across the C=C double bond of $\text{CF}_3\text{SF}_4\text{CF}=\text{CF}_2$ occurs on reaction with SO_2F_2 , SF_4 (or SOF_2), $\text{S}_2\text{O}_6\text{F}_2$ and ClF to afford the compounds, $(\text{CF}_3\text{SF}_4\text{CFCF}_3)_2\text{SO}_2$, $\text{CF}_3\text{SF}_4\text{CF}[\text{S}(\text{O})\text{F}]\text{CF}_3$, $\text{CF}_3\text{SF}_4\text{CF}(\text{SO}_3\text{F})\text{CF}_2(\text{SO}_3\text{F})$, and $\text{CF}_3\text{SF}_4\text{CFCF}_3$, respectively. $\text{CF}_3\text{SF}_4\text{Cl}$ behaves as a chlorofluorinating agent towards highly hindered alkenes such as $\text{FSO}_2\text{C}(\text{CF}_3)\text{FCF}_2\text{OCF}_2\text{CF}=\text{CF}_2$ and $\text{CF}_3\text{SF}_4\text{CF}=\text{CF}_2$, although with $\text{CF}_3\text{C}\equiv\text{CH}$ equimolecular amounts of $\text{CF}_3\text{SF}_4\text{C}(\text{CF}_3)=\text{CHCl}$ and $\text{CF}_3\text{C}(\text{Cl})=\text{C}(\text{SF}_4\text{CF}_3)\text{H}$ are obtained.²⁹

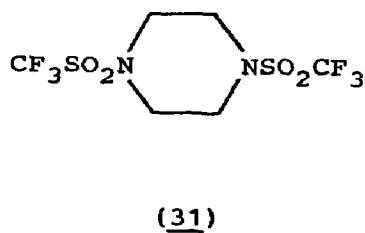
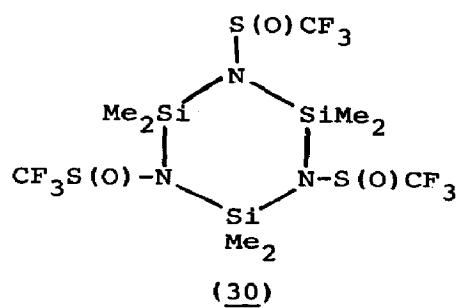
Scheme 5

(Trifluoromethyl)sulphenyl chloride, (trifluoromethyl)sulphinyl chloride, and (trifluoromethyl)sulphonyl chloride react with cyclic amines to afford the corresponding N-substituted derivatives such as **(28)**–**(31)**.³⁰

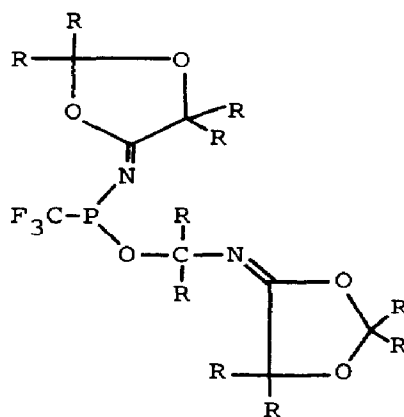




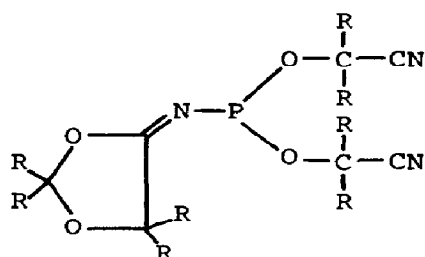
Scheme 6



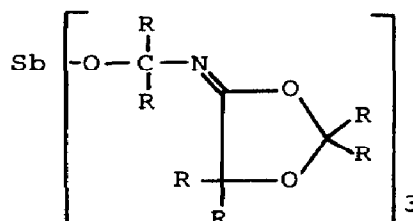
Hexafluoroacetone reacts with the Group V nitriles, $\text{CF}_3\text{P}(\text{CN})_2$, $\text{P}(\text{CN})_3$, and $\text{Sb}(\text{CN})_3$, via E-CN bond cleavage to yield the compounds (32)-(34), respectively.³¹



(32)

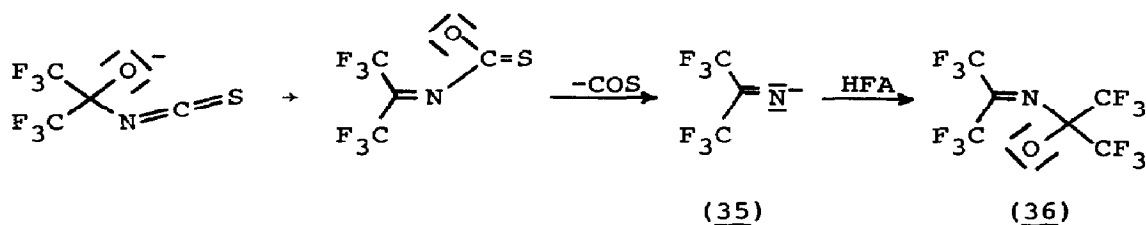


(33)



(34)

Sodium thiocyanate reacts with hexafluoroacetone in a 1:2 molar ratio to give the anion (36), possibly via the anion (35):



(35)

(36)

Hydrolysis of (36) in aqueous $\text{Ph}_4\text{P}^+\text{Cl}^-$ affords the crystalline hydrate, $[(\text{CF}_3\text{C}(\text{OH})_2 \cdot (\text{CF}_3)_2\text{C}(\text{O})\text{OH})]^- [\text{Ph}_4\text{P}]^+$. Dimeric dianions are observed in the solid-state, which are connected via four unsymmetrical and two symmetrical $\text{O} \cdots \text{H} \cdots \text{O}$ bonds.³²

The nitriles, R-CN ($\text{R} = \text{Cl}, \text{CF}_3, \text{CCl}_3, \text{CH}_3$) react with chlorine and bromine in the presence of HgF_2 to form the N,N -dihalogeno-1,1-difluoroamines, $\text{R-CF}_2\text{-NX}_2$ ($\text{X} = \text{Cl}, \text{Br}$) in high yields. The analogous bromochloroamines, RCF_2NBrCl , could not be isolated in a pure state. The diazines, $(\text{R-CF}_2\text{-N=})_2$, were obtained by either photolysis or thermolysis of the amines.³³ A new general method for the synthesis of perfluoropolyethers from hydrocarbon polyesters has been described, which involves three steps: (1) perfluorination of the hydrocarbon polyester, (2) reaction of SF_4 with the ester carbonyl to produce a CF_2 unit, and (3) high temperature cleavage to volatile perfluoropolyethers and oligomers.³⁴ A review of the chemistry of hexafluoropropane oxide has been published.³⁵

Formamide reacts with carbon disulphide in the presence of sodium hydride to yield crude sodium N -formyl dithiocarbamate, $\text{Na}[\text{S}_2\text{C-CH-CO-H}]$. Acidolysis with HCl produces the free N -formyl dithiocarbamic acid, which can be converted into other M^{I} salts by treatment with the metal alkoxide.³⁶ Crystals of the potassium salt comprise a hydrogen-bonded sixteen-membered ring system formed by four $[\text{S}_2\text{X-NH-CO-H}]^-$ anions.³⁷ Alkyl esters, $\text{H-CO-NH-CS}_2\text{R}$, have also been characterised.³⁸ Analogous N -thioformyl-dithiocarbamate salts can be prepared by using thioformamide.³⁹ The crystal structure of the tetra- n -butylammonium N -thioformyl dithiocarbamate salt is built up of dimeric aggregates consisting of two alkylammonium cations and two $[\text{S}_2\text{C-NH-CS-H}]^-$ anions, which are linked together by $-\text{CS} \cdots \text{H-N}$ bridges.⁴⁰ The alkyl esters, H-CS-NH-CS-SR , are obtained from the reaction of this salt with an alkyl iodide. Oxidation of N -thioformyl dithiocarbamates with iodine yields 1,2,4-dithiazole-3-thione, H-C=N-CS-S-S .⁴¹ The reaction of a solution of potassium N -methyl N -formyl dithiocarbamate, $\text{K}[\text{S}_2\text{C-NMe-CO-H}]$ (obtained as before from N -methyl formamide,⁴² in acetone- d_6 with gaseous HCl at -78°C affords unstable N -methyl N -formyl dithiocarbamic acid, H-CO-NMe-CS-SH , characterised by n.m.r.,⁴³ whilst reaction with alkyl iodides produce the N -methyl N -formyl dithiocarbamate esters.⁴⁴ N -methyl thioformamide has been obtained by the treatment of N -methylform-

amide with P_4S_{10} , and reacts with carbon disulphide in the presence of metal hydroxides to yield the corresponding N-methyl N-thioformyl dithiocarbamate salts, $M[S_2C-NMe-CS-H]$. Attempts to prepare the free acid were unsuccessful.⁴⁵ The S-methyl ester of N-methyl N-thioformyl dithiocarbamic acid, $H-CS-NMe-CS-SMe$, has been obtained from the reaction of potassium N-methyl N-thioformyl dithiocarbamate with methyl iodide.⁴⁶ Reaction of metal 1,2-ethanedithiolates with carbon disulphide gives the corresponding 1,2-ethane-bis(trithiocarbonates), $M_2[S_2C-SCH_2CH_2S-CS_2]$.⁴⁷ With hydrochloric acid at $0^\circ C$, the potassium salt gives the unstable deep yellow 1,2-ethane-bis(trithiocarbonic) acid, whilst alkyl iodides afford the corresponding esters.⁴⁸ Crystals of the dimethyl ester, $MeS-CS-SCH_2CH_2S-CS-SMe$, comprise isolated molecules.⁴⁹ The mixed dithiocarbamate-dithiocarbimate, $Na_2[S_2C-NH-N=CS_2] \cdot 7H_2O$, and the 1,2-hydrazine-bis(dithioformates), $M_2[S_2C-NH-NH-CS_2]$, have been prepared by the reaction of hydrazine hydrate, carbon disulphide and NaOH in aqueous solution.^{50,51} $[S_2C-NH-NH-CS_2]^{2-}$ anions are linked by N-H...S hydrogen bonds in crystals of the potassium salt.⁵² The S-methyl ester of dithiocarbazic acid reacts with carbon disulphide in the presence of sodium or potassium hydride at $-15^\circ C$ to yield the salts of the S-methyl ester of N-dithiomethylene-dithiocarbazic acid, $M_2[S_2C=N-NH-CS-SMe]$.⁵³

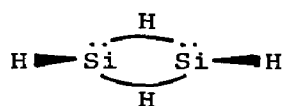
Ultrasonic irradiation of water under an atmosphere of argon containing small amounts of CO_2 affords oxygen as the major product together with a small amount of formic acid. The main products from the decomposition of methane under similar conditions were hydrogen, ethane, ethene, C_3 and C_4 hydrocarbons, and carbon monoxide.⁵⁴

4.2 SILICON, GERMANIUM, TIN AND LEAD

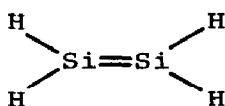
4.2.1 Theoretical Studies

The structures and energies of SiH_n^{2+} dications ($n = 1-5$) have been calculated. SiH^{2+} is predicted to be a strongly bound species and SiH_2^{2+} a kinetically stable species. The higher homologues, SiH_3^{2+} , SiH_4^{2+} , and SiH_5^{2+} , in contrast, are weakly bound complexes of SiH_2^{2+} with atomic and/or molecular hydrogen.⁵⁵ Studies of the two-dimensional potential energy surface for the insertion of singlet silylene into the H_2 molecule have shown this reaction proceeds in a similar fashion to the insertion of singlet

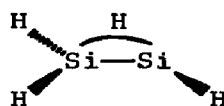
methylene, with an activation energy of $6.3 \text{ kcal mol}^{-1}$ at 600K. The data also yielded an activation energy for the thermal decomposition of silane of $60.2 \text{ kcal mol}^{-1}$ at 600K.⁵⁶ Least-motion versus non-least-motion pathways for the dimerization of methylene and silylene in both singlet and triplet states has been investigated. Ground-state triplet methylenes combine in the non-least-motion path to give ground-state ethylene without barrier. Ground-state singlet silylenes give a ground-state disilene with barrier in the least-motion path and without barrier in the non-least-motion path. A ground-state methylene and an excited-state silylene give a ground-state silaethylene without barrier in the least-motion path, and an excited-state methylene and a ground-state silylene also give ground-state silaethylene without barrier in the non-least-motion path.⁵⁷ Ab initio MO calculations for Si_2H_2 have been reviewed.⁵⁸ New MNDO calculations confirm that the dibridged structure (37) is superior to the classical structures (38)-(40).⁵⁸ Ab initio



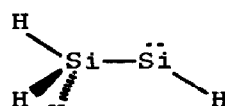
(37)



(38)



(39)



(40)

calculations on Sn_2H_4 with better than double ζ basis indicate that the non-planar trans-folded conformation is more stable than a planar structure by 26 kJ mol^{-1} and also that the optimal angle between the Sn-Sn vector on the SnH_2 planes is 46° .⁵⁹ The photoelectron spectrum of dichlorosilylene exhibits three single and two double bands, and has been employed to optimise synthetic routes thereto.⁶⁰ Ab initio MO calculations with basis sets of split valence plus polarization function quality have been carried out on the fully substituted silylenes, SiX_2 , disilenes, X_2SiSiX_2 , and silylsilenes, XSiSiX_3 , ($\text{X} = \text{Me}, \text{Li}, \text{F}$). All three silylenes are strongly bent in both their singlet ground-states and triplet excited-states, except for SiLi_2 has a triplet ground-state with a linear geometry and a bent singlet excited-state. The Si_2Me_4 isomers resemble the analogous Si_2H_4 species. Thus, the singlet disilenes and silylsilylenes are almost isoenergetic, the disilene dissociation energies toward two simple silylenes are comparable, and both disilenes feature very

flat potential energy surfaces for bending of the geminal groups in a mutual trans fashion or twisting around the Si-Si bond. In contrast, no closed shell minimum could be located for F_2SiSiF_2 corresponding to a disilene. A minimum was obtained for the diradical-like triplet, $\cdot F_2SiSiF_2$, but this was considerably less stable than the singlet silylsilylene, $:FSiSiF_3$. No minima could be located either for a conventional disilene or a silylsilylene for the model Si_2Li_4 species. The global minimum for singlet Si_2Li_4 was a distorted, planar structure with two bridging lithium atoms with C_{2h} symmetry.⁶¹ The photolytic fragmentation of trisilane to disilane and silylene has been studied by means of a pseudopotential method.⁶²

Two ab initio MO studies of bonding between silicon and phosphorus have been published.^{63,64} Nominally normal single (pyramidal), double (planar) and triple (linear) Si-P bonds were predicted to be stable with positive harmonic force fields. Both studies included data for phosphasilene, $HP=SiH_2$, which were in close agreement. The barrier of insertion of silylene into the P-H bond of phosphine is predicted to be just 2 kcal mol^{-1} (consistent with experimental evidence), while the barrier to insertion of phosphinosilylene into H_2 is ca. 17 kcal mol^{-1} . The 40 kcal mol^{-1} barrier for the singlet 1,2-hydrogen shift from phosphinesilene to the corresponding silylene is similar to the barrier found for other 1,2-shifts. The potential energy surface of the dimerization of silanone has been predicted to proceed with no barrier to yield the cyclic product $(H_2SiO)_2$ by forming stepwise two new bonds. The dimer, like $(H_2SiS)_2$, has a planar four-membered ring with D_{2h} symmetry.⁶⁵

The SiC π bond strength has been calculated to be 37 kcal mol^{-1} , intermediate between the values for the CC (65 kcal mol^{-1}) and SiSi (22 kcal mol^{-1}) π bond strengths.⁶⁶ The reaction of silene with formaldehyde to give silanone and ethylene via a 1,2-sila-oxetane intermediate has been studied at the SCF level. Whilst the reaction is exothermic by ca. 30 kcal mol^{-1} , the proposed intermediate is more stable than both the reactants and products by at least 50 kcal mol^{-1} , although if the product is the silanone dimer the reaction is more exothermic with the products lying 25 kcal mol^{-1} below the silaoxetane.⁶⁷ Ab initio calculations for monosilabenzene, 1,4-disilabenzene, hexasila-benzene, and their valence isomers illustrate the reduced aromat-

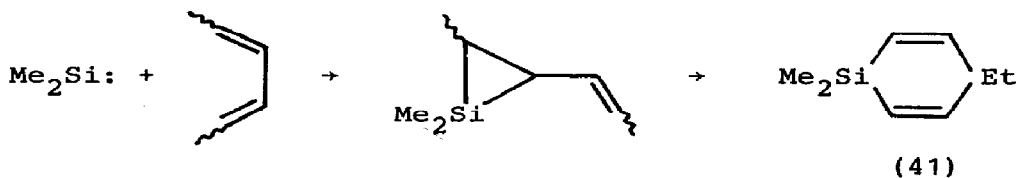
icity of the silabenzenes and the relative weakness of Si-C π bonds compared to C-C π bonds and Si-Si σ bonds.^{68,69}

Multipeaked cyclic voltammograms for silicon phthalocyanine monomer-oligomer sets can be predicted from initial-state MO energy levels if field shifts are used to allow for the charges of the anions and cations. For the dimers, a 45° staggered conformation is predicted to be slightly more stable than the eclipsed conformation.⁷⁰

The MNDO approximation has been applied in several areas including pentacoordination in silicon chemistry,⁷¹ dicyclopentadienylsilenes,⁷² stannylenes,⁷³ organotin radical cations,^{74,75} 2,4,6-trithia-1,3,5-tristannaadamantane,⁷⁶ and a large number of lead compounds.⁷⁷ When tetrahedral silicon is involved in the formation of an additional donor-acceptor Si+Y bond, it acquires a higher positive charge compared with the tetracoordinated state, and electron density is transferred to the equatorial and axial ligands, affecting predominantly the charge on the other axial atom.⁷¹ The most stable form of $(C_5H_5)_2Si$ has been calculated to be the bis-monohapto isomer with a CSiS angle of 105.4°. The bis-pentahapto isomer is of comparable energy, with a minimum energy (but not a genuine minimum) for a structure of D_{5d} symmetry. In the silene derivatives $(\eta^1-C_5H_5)_2SiCY_2$, the unique SiC interaction is a genuine Si=C double bond and the molecular $[C_2SiCY_2]$ skeleton is planar. However, in the isomeric pentahapto species $(\eta^5-C_5H_5)_2SiCY_2$, which do not represent genuine energy minima, the unique Si-C interaction is a long, highly polar bonded in a twisted $[X_2SiCY_2]$ skeleton in which the X_2SiC and $SiCY_2$ planes are perpendicular.⁷² Dimethylstannylene is predicted to have a singlet ground-state and a CSnC bond angle of 99.1°. Insertion reactions of dimethylstannylene into the Sn-Cl bonds of Me_2SnCl_2 and Me_3SnCl and also into the C-I bond of methyl iodide have also been studied.⁷⁴ The results of a combined gas-phase UV photoelectron spectroscopic study and pseudopotential ab initio calculations on the nature and mechanism of interactions between $\pi_{C=C}$ and σ_{Sn-C} orbitals in organotin acetylides clearly indicate that the σ/π conjugation is quite extensive along the whole series and that the mechanism is critically controlled by the substituents at both the tin atom and the alkynyl moiety.⁷⁸

4.2.2 Transient Intermediates and Their Stable Analogues

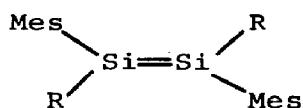
The high-temperature cation radicals $^{28}\text{SiO}^+$ and $^{29}\text{SiO}^+$ have been generated by both electron bombardment and photoionization methods and trapped in neon matrices at ca. 4K. The SiO(g) sample was prepared by vapourization of SiO(s) and $\text{SiO}_2\text{(s)}$ at $\approx 2000\text{K}$.⁷⁹ Dehalogenation of organochlorosilanes (a wide variety - some 21 examples) with K/Na alloy vapours at 0.1-1 torr and $300\text{-}320^\circ\text{C}$ yields products derived from the reactions of short-lived intermediates such as silyl and silylmethyl radicals, silylenes, and sila-alkenes. Small ring silacycles of low stability are formed as the intermediates in some reactions. Combination and hydrogen-atom abstraction are the main reactions of silyl and silylmethyl radicals, but these radicals are not prone to decomposition reactions when C-H, C-C, or Si-C bonds are at the β -position to the radical centre. The pentamethyldisilanylmethyl radical decomposes at the $\beta(\text{Si-Si})$ bond with the formation of $\text{Me}_2\text{Si-CH}_2$ and the trimethylsilyl radical. The generation of alkylmethylsilylenes is accompanied by their decomposition with the formation of 1-alkene and methylsilane.⁸⁰ Dimethyldiazido-silane, $\text{Me}_2\text{Si(N}_3)_2$, and the trisilane, $\text{PhMe}_2\text{Si-SiMe}_2\text{-SiPhMe}_2$, have also been employed as precursors for the photochemical generation of dimethylsilylene, the assignment of the UV-visible spectrum of which has been confirmed.⁸¹ Dimethylsilylene abstracts chlorine atoms from carbon tetrachloride. The resulting CCl_3 radicals dimerise to hexachloroethane.⁸² Extrusion of dimethylsilylene from 1,1-dimethyl-1-silacyclopent-3-enes occurs on vacuum flow pyrolysis at 700°C , and can be trapped by addition to 1,3-dienes.⁸³ The formation of cis-3,3-dimethyl-3-silahepta-1,4-diene (41) as the major product from addition of dimethylsilylene to cis,cis-hexa-2,4-diene is probably a result of a concerted 1,5-sigmatropic hydrogen shift in the rearrangement of the vinylsilacyclopropane intermediate formed by a concerted 1,2-cis-addition of the silylene (Scheme 7):⁸⁴



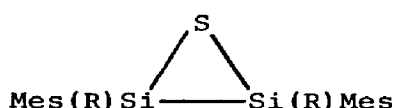
Scheme 7

Free dimethylgermylene undergoes cycloadditions with two molecules of α -substituted styrenes via a regiospecific but not stereospecific mechanism, forming equal amounts of syn/anti 3,4-diphenylgermacyclopentanes. The 4,4,5,5-tetraphenyl derivative has an extraordinarily strained five-membered ring with a very long C₃-C₄ bond (1.626Å).⁸⁵ In dilute solution 1,8-diazabicyclo[5.4.0]undec-7-ene dehydrochlorinates organochlorohydrogermanes such as PhCl₂GeH and R₂ClGeH leading to the corresponding germylene via an anionic germanate species.⁸⁶

The photochemically induced or palladium salt catalysed cleavage of hexa-*t*-butylcyclotrisilane leads to di-*t*-butylsilylene, Bu^t₂Si:, and tetra-*t*-butyldisilene, Bu^t₂Si=SiBu^t₂, both of which can be trapped by a wide variety of multiply-bonded reagents such as phenylacetylene and ketones (Scheme 8).⁸⁷ The stable disilenes (42) react with elemental sulphur in benzene at 25° to give the disilathiiranes (43), the crystal structure of one of which (R = mesityl) has been determined.⁸⁸ Similar sterically

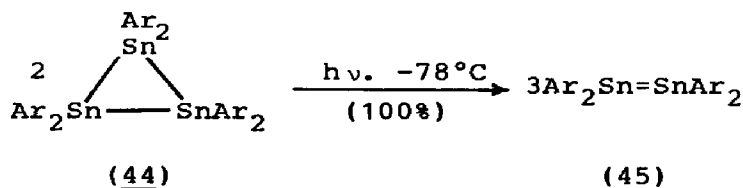


(42)



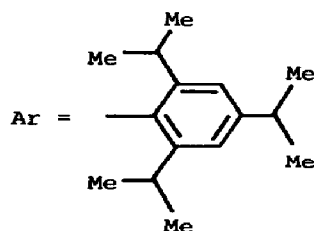
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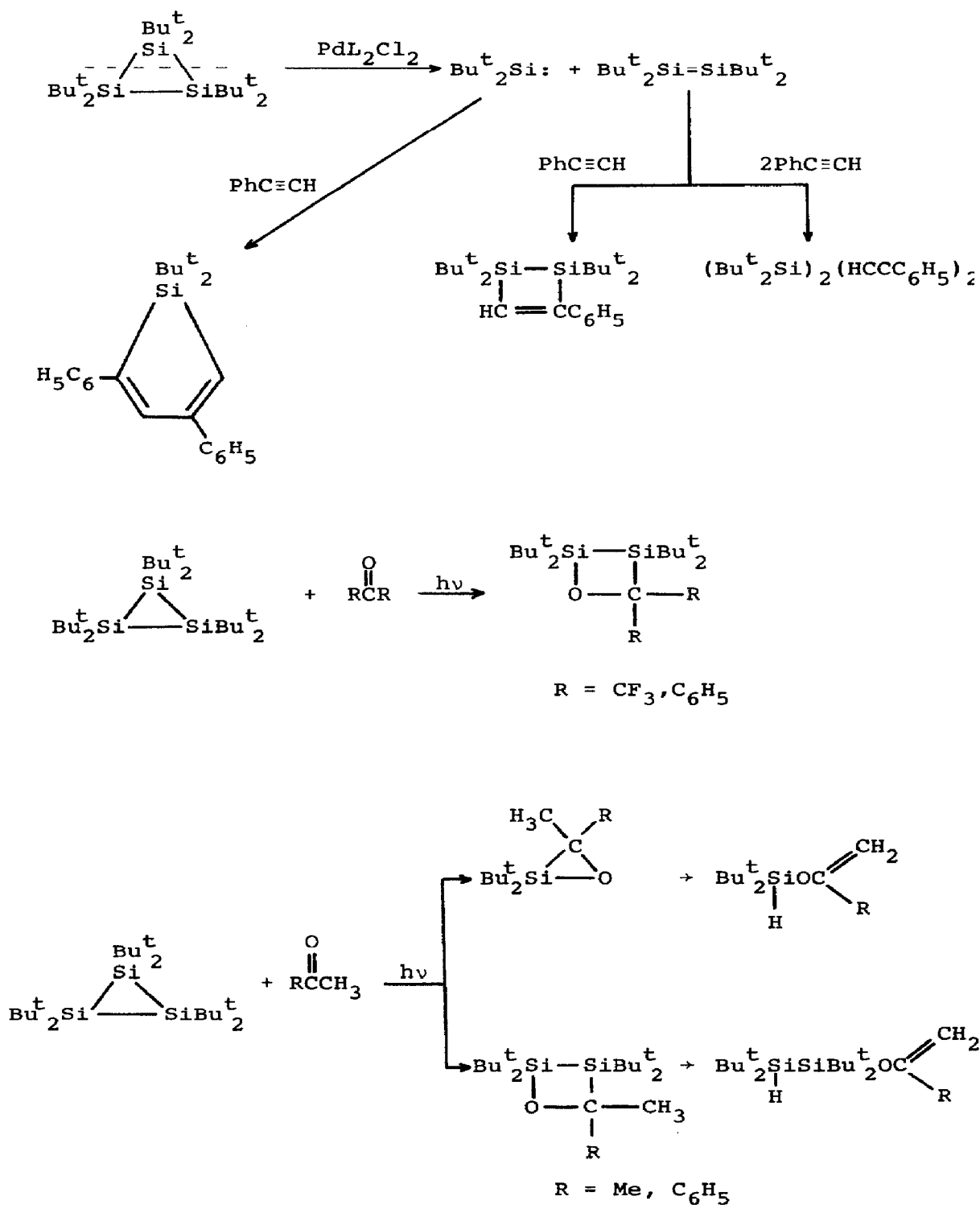
congested disilenes interact with alkali metals to produce tetraorganodisilenyl radical anions, [R₂Si=SiR₂]⁻.⁸⁹ Hexakis-(2,4,6-triisopropylphenyl)cyclotristannane (44) may be transformed photochemically into tetrakis(2,4,6-triisopropylphenyl)-distannene (45) with which it is in rapid equilibrium at room temperature or above.⁹⁰



(44)

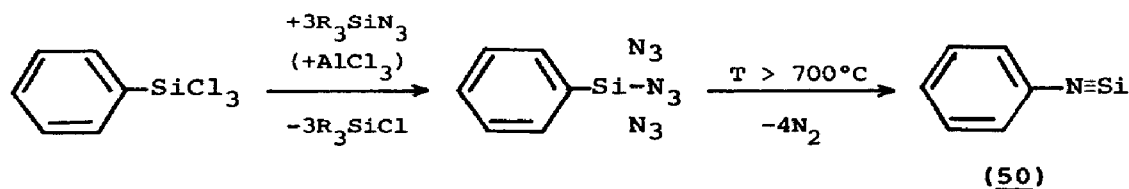
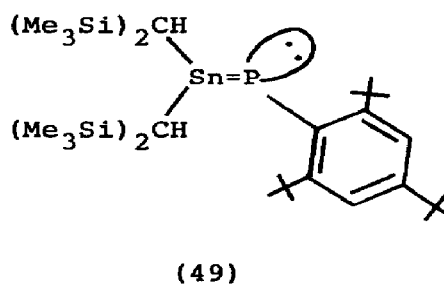
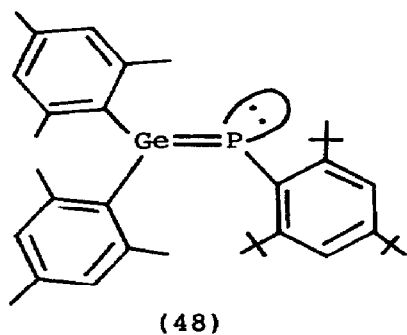
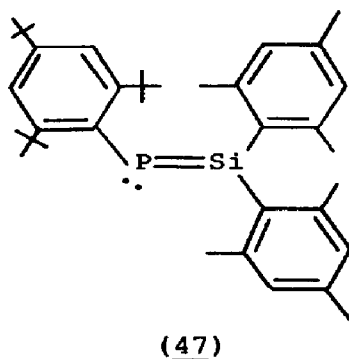
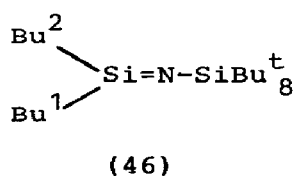
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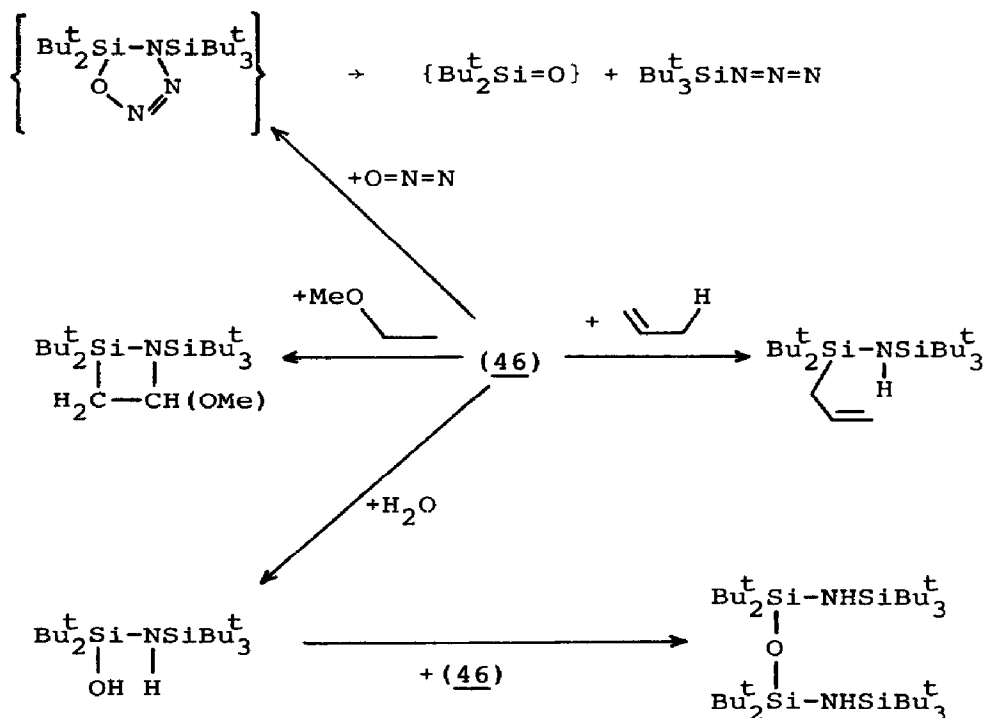


Scheme 8

Significant advances have been made in the chemistry of compounds containing Group IV - Group V multiple bonds. The first stable silaketimine (46),⁹¹ silaphosphene (47),⁹² germaphosphene (48),⁹³ and stannaphosphene (49)⁹⁴ have been reported, whilst phenyl silaisocyanide (50), the first example of a species containing a Si≡N triple bond has been generated according to Scheme 9.⁹⁵ Some reactions of (46) are illustrated in Scheme 10.



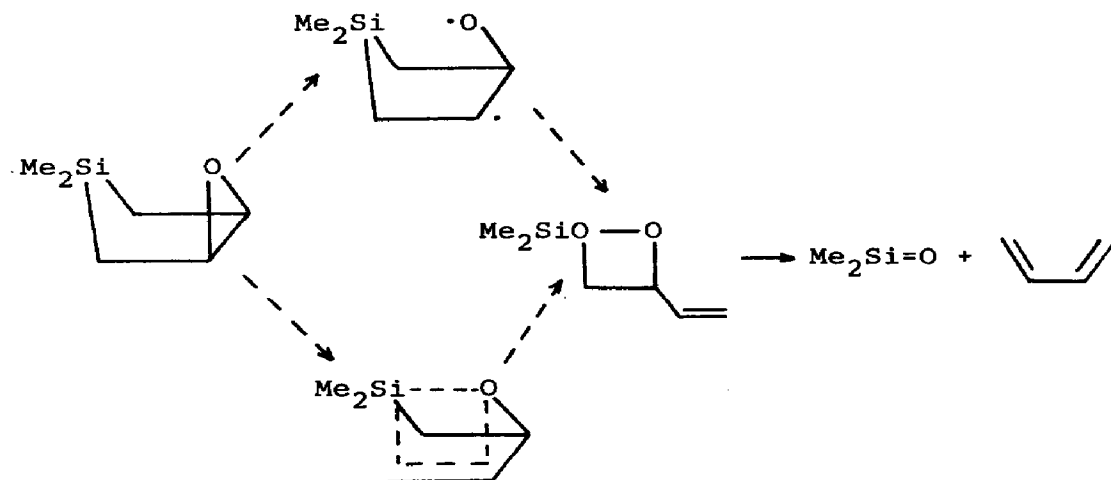
Scheme 9



Scheme 10

Pyrolysis of 6-oxa-3,3-dimethyl-3-silabicyclo[3.1.0]hexane is a convenient method for the generation of dimethylsilanone. The decomposition most probably involves the intermediacy of a silaoxetane which could be formed by either a concerted or a biradical mechanism (Scheme 11).^{96,97} The dominant feature in the visible portion of the chemiluminescence spectrum obtained from the reaction of ozone with silane at low pressure in a beam-gas apparatus was thought to correspond to emission from silanone, H_2SiO .⁹⁸

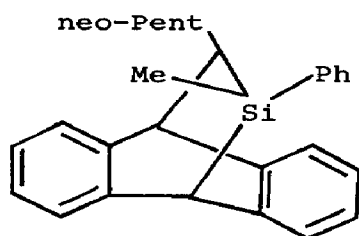
Pyrolysis of 1,3,5,7-tetramethyl-1,3,5,7-tetrakis(trimethylsilyl)cyclotetrasiloxane in the presence of 1,3-butadiene affords the silacyclopentene product from trapping of the siloxysilylene, $\text{Me}_3\text{SiOSiMe}$. Although this observation is consistent with isomerization of the silanone, $\text{Me}_3\text{Si}(\text{Me})\text{Si}=\text{O}$, to the silylene by a 1,2-silyl shift, an alternative route to the silylene cannot be excluded. No evidence for the reverse isomerization of $\text{Me}_3\text{SiOSiMe}$ to the silanone could be found, although the silylene



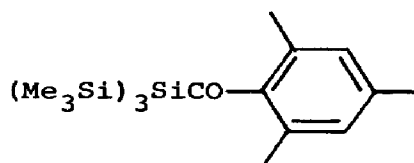
Scheme 11

apparently decomposes to silanones.⁹⁹ The Si=O stretching frequency in silanone $\text{H}_2\text{Si}=\text{O}$ has been assigned as 1202 cm^{-1} , close to that in dimethylsilanone (1204 cm^{-1}).¹⁰⁰

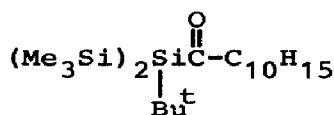
Silenes have been obtained in a number of ways: thermolysis of the strained molecule (51) at 330° ,¹⁰¹ photolysis of acylsilanes such as (52) and (53),^{102,103} or by the elimination of LiF from (54).¹⁰⁴ The structures of two stable silenes, (55) (formed from



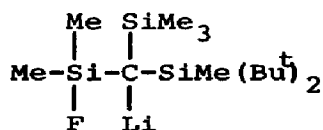
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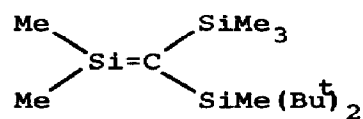
(52)



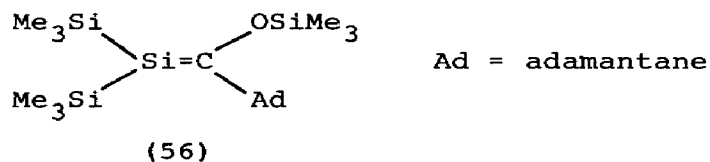
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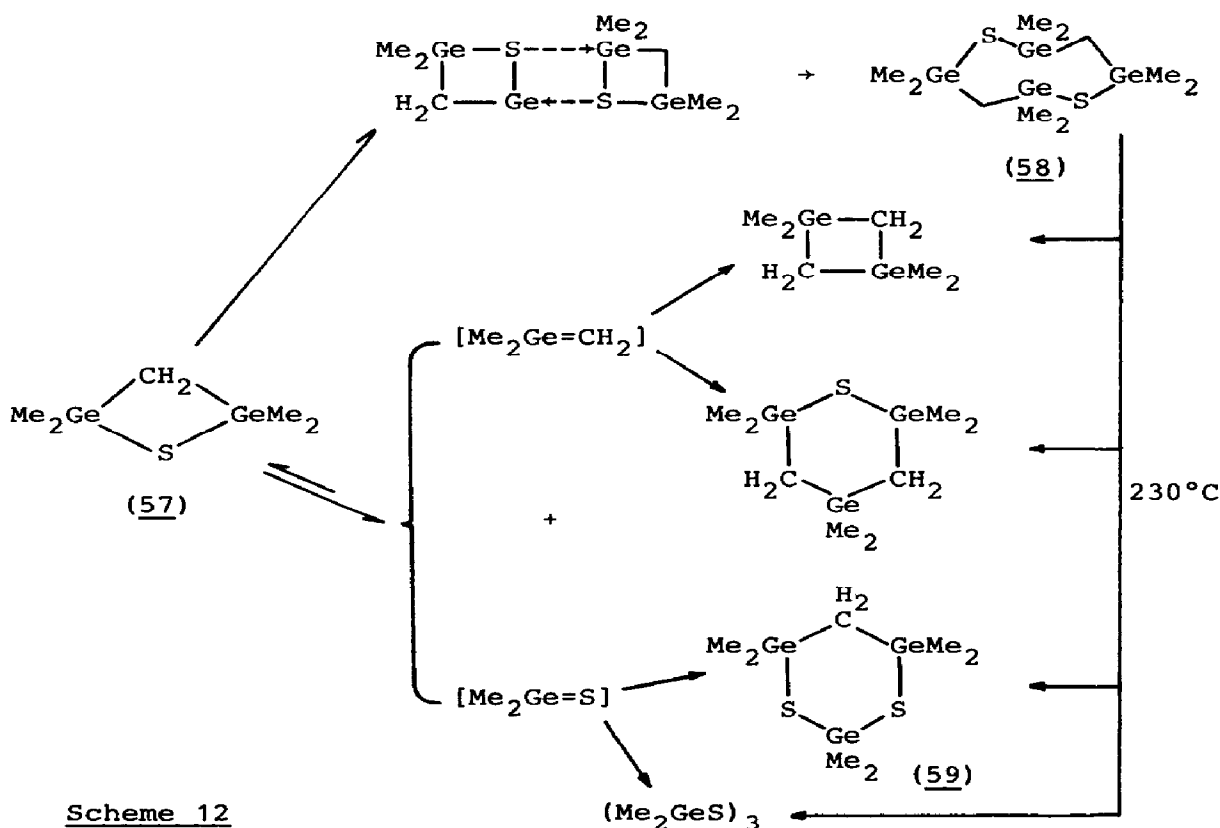
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(55)



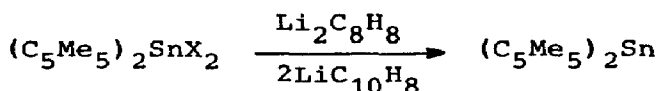
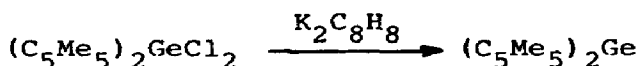
(54)) and (56) (formed from (53)) have been determined.^{104,105} The Si=C bond distances, however, vary substantially. That for (55) (1.702(5)Å) fits very nicely into the range (1.69–1.71Å) predicted by ab initio calculations, whilst that of (56) is considerably longer at 1.764(3)Å. Nevertheless, both are considerably shorter than Si-C single bond distances (1.87–1.94Å). 2,2,4,4-tetramethyl-2,4-digermanthietane, (57), although relatively stable in solution at room temperature, but simultaneously dimerizes and easily dissociates on heating. The decomposition reaction proceeds with formation of germathione and germaethylene and leads to (58) and (59) (Scheme 12). Pyrolysis of digermathietane dimer at 230°C leads to the same heterocycles.¹⁰⁶



Scheme 12

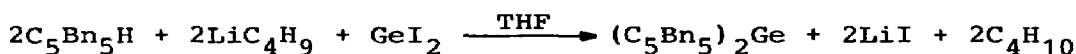
4.2.3 Low-valent compounds

Bis(pentamethylcyclopentadienyl)germanium and -tin are readily obtained from the corresponding diorganometal(IV) dichlorides by reduction using alkali metal cyclooctatetraenides or naphthalenides:¹⁰⁷



X = Cl, Br.

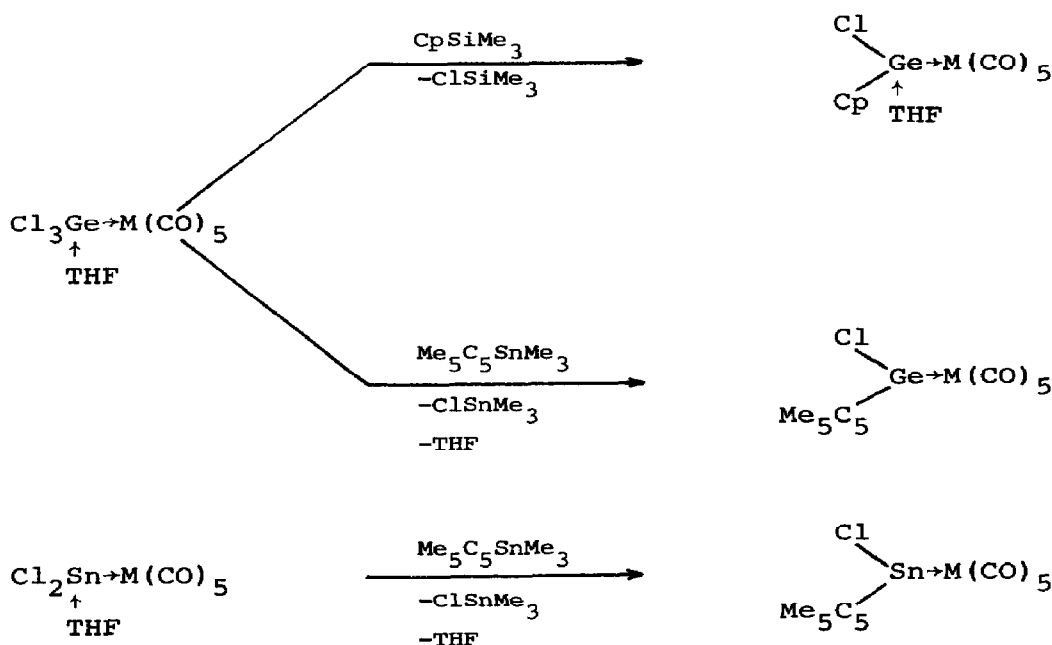
Decabenzylgermanocene, prepared by addition of GeI_2 to a freshly prepared solution of pentabenzylcyclopentadienyllithium:



$\text{Bn} = \text{C}_6\text{H}_5\text{CH}_2$

is monomeric and air-stable with an angle of 31° between the planes of the two C_5 rings. One of the phenyl groups appears to form an additional interaction with the lone pair of the metal atom.¹⁰⁸ Despite also having bent structures, both pentamethylgermanocene and -stannocene, exhibit photoelectron spectral patterns similar to those expected for higher (D_{5d}) symmetry. There is no unambiguous evidence for the involvement of metal p subshells in the metal-ring bonding, and the high ionization energies associated with the ns^2 electrons are indicative of a pronounced "inertness" of the metal lone pair, and therefore of almost ionic metal-ligand bonding.¹⁰⁹ $\text{Ge}[\text{CH}(\text{SiMe}_3)_2]_2$ is a V-shaped monomer in the gas-phase at ca. 430K, with a CGeC angle of 107° .⁵⁹ Bis(dichloromethyl)stannylene has been obtained as a tetrahydrofuran solvate, $(\text{CHCl}_2)_2\text{Sn} \cdot x\text{THF}$, from the low-temperature reaction of LiCHCl_2 with tin(II) chloride. The stannylene associates via Sn-Sn bond formation upon removal of the solvent.¹¹⁰ η^5 -acetyl- and alkoxycarbonyl-cyclopentadienyltin(II) compounds, $\eta^5\text{-RC(=O)C}_5\text{H}_4\text{SnC}_5\text{H}_5\text{-}\eta^5$ (R = Me, OMe, OEt) have been obtained from the reaction of the substituted cyclopentadienylsodium salts and η^5 -cyclopentadienyltin(II) chloride.¹¹¹ The structure of Main

Group Lewis acid complexes is not as simple as first thought. The material originally formulated as the donor-acceptor complex, $(C_5H_5)_2Sn: \rightarrow BF_3$ is actually a three-dimensional lattice comprising the four types of unit, $\{[BF_4]^{-}\}$, $\{(\eta^5-C_5H_5)_2Sn\}$, $\{[\eta^5-C_5H_5Sn]^{+}\}$, and THF. The lone pair of electrons play no role in bonding.¹¹² The reaction of 1,1'-di-*t*-butylstannocene with BF_3 in dichloromethane affords $[\eta^5-Bu^tC_5H_4Sn]^{+}[BF_4]^{-}$, whose structure comprises anions and cations.¹¹³ Pentacarbonylchromium and -tungsten complexes of chloro(cyclopentadienyl)germylenes and stannylenes have been prepared by the alkylation of the dichlorometal complexes, $Cl_2(THF)M^{IV} \rightarrow M(CO)_5$ ($M^{IV} = Ge, Sn$; $M = Cr, W$) (Scheme 13).

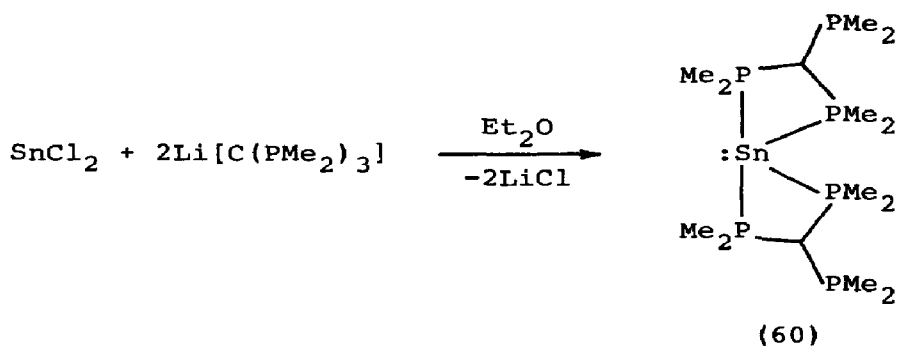


$M = Cr, W.$

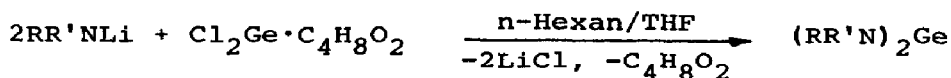
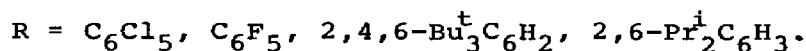
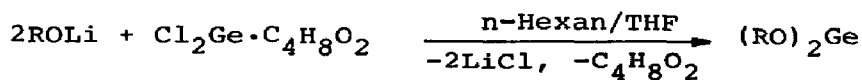
Scheme 13

An X-ray analysis of the germylene complex, $Me_5C_5(Cl)Ge \rightarrow W(CO)_5$, confirms the general structure, and shows further that the bonding of the C_5 ring changes on complexation from η^5 to η^2 in nature.¹¹⁴ A novel boron-nitrogen ring-substituted stannocene, bis(1-*tert*-butyl-2,3-dimethyldihydro-1,2-azaborolyl)tin, has been synthesised by the reaction of tin(II) chloride with 1-*tert*-butyl-2,3-dimethyldihydro-1,2-azaborolyl lithium in THF at $-45^\circ C$. The

compound is unstable and decomposes with the formation of metallic tin above -20°C . Structurally the compound resembles other stannocenes, with η^5 rings forming an angle of 46.5° with each other.¹¹⁵ The analogous reaction with $\text{Li}[\text{C}(\text{PMe}_2)_3]$ in ether does not afford a tin(II)-carbon bonded species. Rather the tetraphosphanetin(II) complex (60) with a pseudo trigonal bipyramidal geometry is formed.¹¹⁶



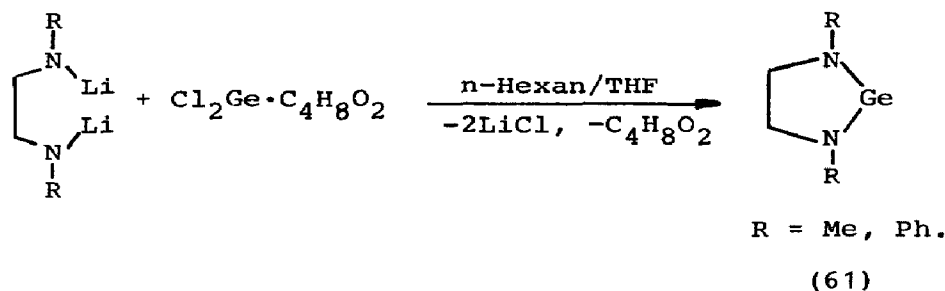
Bis(aryloxy)germylenes and diaminogermaylenes are formed in the reaction of $\text{GeCl}_2 \cdot \text{dioxane}$ and lithiated ortho-substituted phenols and sterically-hindered amines, respectively:



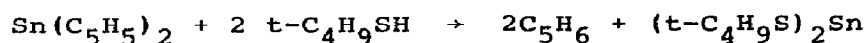
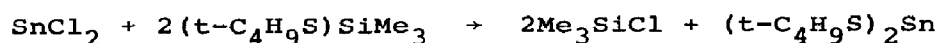
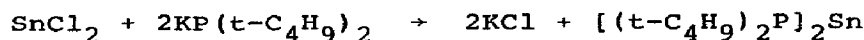
$\text{R}, \text{R}' = 2,2,6,6\text{-tetramethylpiperidino}$

$\text{R} = 2\text{-MeC}_6\text{H}_4, 2\text{-FC}_6\text{H}_4, 2,6\text{-Me}_2\text{C}_6\text{H}_3, 2,4,6\text{-Me}_3\text{C}_6\text{H}_2, 2,6\text{-Pr}_2^i\text{C}_6\text{H}_3$

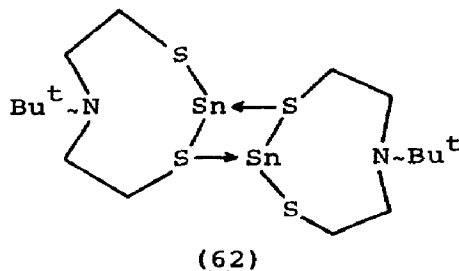
$\text{R}' = \text{SiMe}_3$



Mixed compounds of the type $\text{R}(\text{Me}_3\text{Si})\text{N}-\text{Ge}-\text{O}^t\text{Bu}$ are obtained on lithiation of the amines with tert-butyllithium in n-hexane/THF. The use of dilithiated amines leads to the formation of the diazagermacyclopentanes (61).¹¹⁷ Gaseous tin(II) tert-butoxide has a trans-dimeric structure with the remarkably small endocyclic OSnO angle of 76° . Both germanium(II) and tin(II) bis(tri-tert-butyl)methoxides exhibit 'V'-shaped monomeric structures in the solid state.¹¹⁸ Bis(di-tert-butylphosphino)tin(II), $[(\text{Bu}^t)_2\text{P}]_2\text{Sn}$, has been obtained by metathesis using the potassium salt of the phosphide, whilst bis(tert-butylthio)tin(II), $(\text{Bu}^t\text{S})_2\text{Sn}$, results from either the reaction of tin(II) chloride and (tert-butylthio)-trimethylsilane or by the pyrolysis of stannocene:

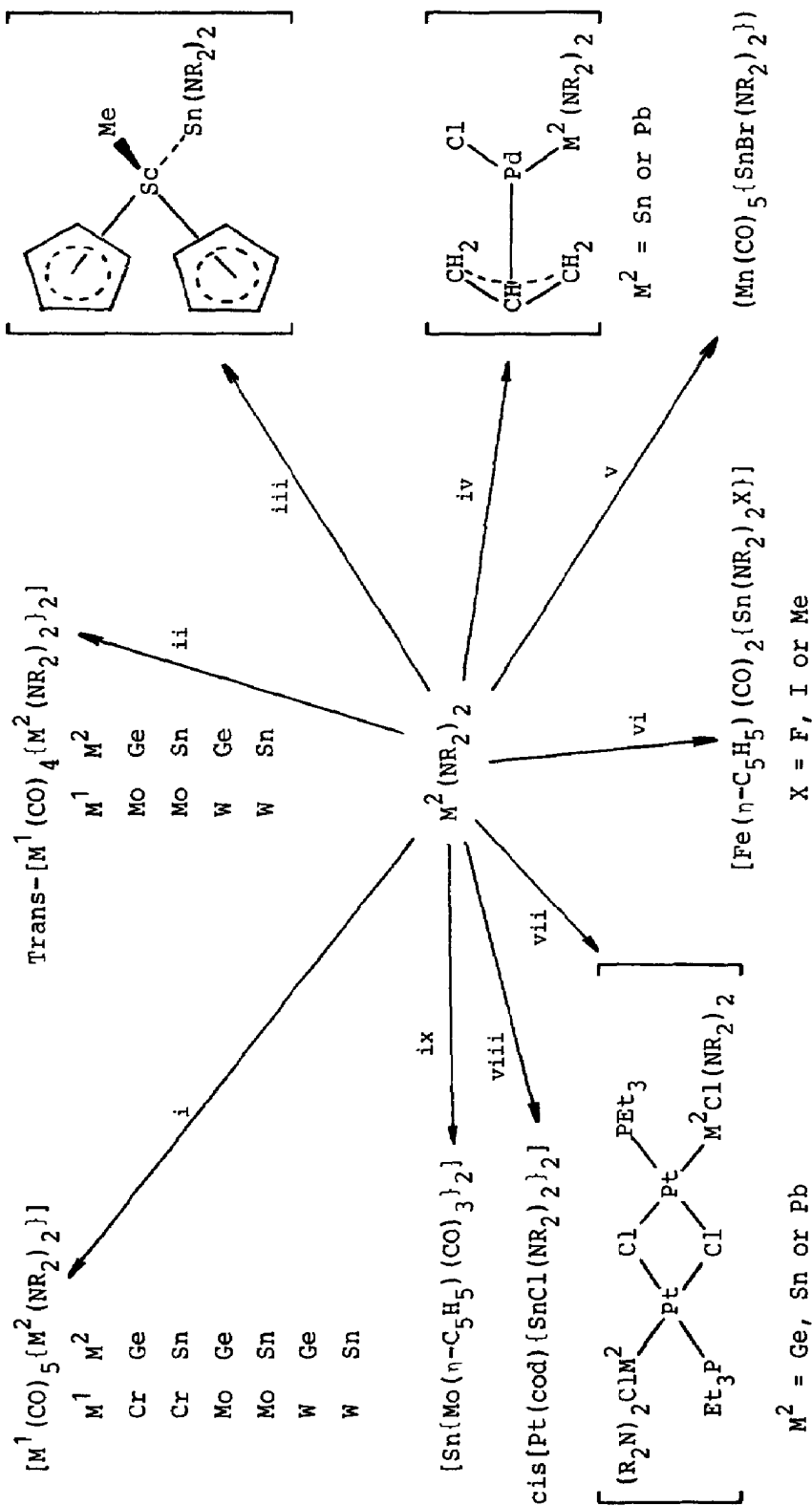


In solution both compounds are dimers with bridging electro-negative groups.¹¹⁹ 5-tert-Butyl-5-aza-2,8-dithia-1-stanna(II)-bicyclo[3.3.0^{1,5}]octane, $[\text{Sn}(\text{SC}_2\text{H}_4)_2\text{NBu}^t]_2$, is also dimeric with a central four-membered $[\text{Sn}_2\text{S}_2]$ ring (62).¹²⁰



The crystal structure of lead(II) ethane-1,2-thiolate comprises polymeric sheets of lead and sulphur atoms. Each dithiolate ligand chelates one lead atom, which interacts further with four additional sulphur atoms to give distorted six-coordination for lead. The valence angles at the metal suggest some stereochemical activity for the lone pair.¹²¹ The thiolato- and selenatostannate(II) anions, $[\text{Sn}(\text{EPH})_3]^+$, are obtained on addition of tin(II) chloride to solutions containing ≥ 3 moles of the appropriate sodium salts. Both have the expected pyramidal geometry.¹²² 1,3-Di-tert-butyl-2,2-dimethyl-1,2,3,4- λ^2 -diazasilastannetene forms 1:1 crystalline adducts with triphenylphosphine oxide and triorganophosphorus ylides. No stable adducts could be isolated with triorganophosphines or with triphenylphosphine sulphide. Protolysis occurs with triphenylphosphineimine and $\text{Sn}(\text{NPPH}_3)_4$ is obtained. The structures of both the latter compound, which contains tetrahedrally coordinated tin, and the adduct with Ph_3BCH_2 have been determined.¹²³ The cubane-like cage compounds, $(\text{MNBu}^t)_4$ ($\text{M} = \text{Ge}, \text{Sn}$), form 1:2 adducts with two moles of aluminium trichloride, which unlike other adducts do contain Ge-Al and Sn-Al bonds.¹²⁴

Several modes of behaviour of silylamidometal(II) compounds with transition metal complexes have been distinguished: function as a neutral two-electron donor, insertion into transition metal-halogen bonds, and cleavage of the amido group from the Group IV metal to give other metal(II) derivatives.¹²⁵⁻¹³⁰ Typical chemistry is illustrated in Scheme 14. Irradiation of $\text{M}(\text{CO})_6$ ($\text{M} = \text{Mo}, \text{W}$) with $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ in hexane with UV light results in the formation of mono- and both cis and trans-disubstituted complexes, $\text{M}(\text{CO})_5\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ and $\text{M}(\text{CO})_4\{\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2\}_2$.¹²⁵ Homoleptic d^{10} complexes of Pd and Pt, $\text{M}(\text{M}^1\text{NR}_2)_3$ ($\text{M} = \text{Pd}$ or Pt ; $\text{M}^1 = \text{Ge}$ or Sn ; $\text{R} = \text{SiMe}_3$), have been obtained by reaction of excess of the bivalent donor and $\text{Pd}(\text{cod})\text{Cl}_2$ or $\text{Pt}(\text{cod})_2$ (cod = cycloocta-1,5-diene). With CO, these complexes are converted into the heterobimetallic trinuclear clusters, $(\text{M}(\mu\text{-M}^1\text{NR}_2)_2\text{CO})_3$. The complex $\text{Pd}(\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2)_3$ has a trigonal planar environment at each of Pd, Sn and N.¹²⁷ The tin(II) amide displaces cyclooctene from $\{\text{Rh}(\eta\text{-C}_8\text{H}_{14})_2\text{Cl}\}_2$ affording the complex $[\text{Rh}(\mu\text{-Cl})\{\text{Sn}(\text{NR}_2)_2\}_2]_2$, which can be transformed into the arene complex $\text{Rh}(\eta\text{-PhMe})(\eta\text{-C}_8\text{H}_4)\{\text{SnCl}(\text{NR}_2)_2\}$. Arene complexes are more generally obtained by treating $\{\text{Rh}(\text{alkene})_2(\mu\text{-Cl})\}_2$ with



Reagents: i, $[M(CO)_6]$, $n-C_6H_{14}$, irradiation, 30–40h, 25°C; ii, $[M(CO)_4(nbd)]$, $n-C_6H_{14}$, reflux, 12–24h; iii, $[Sc(\eta-C_5H_5)_2(\mu-Me)_2AlMe_2]$, $n-C_6H_{14}$, 25°C, 24h; iv, $[CPr(\mu-C_3H_5)(\mu-Cl)_2]$, $n-C_6H_{14}$ -PhMe, 0°C; v, $[MnBr(CO)_5]$, $n-C_6H_{14}$, 20°C, 1h; vi, $[Fe(\eta-C_5H_5)(CO)_2X]$, $n-C_6H_{14}$, 25°C; viii, $cis-[PtCl_2(cod)]$, $n-C_5H_{12}$, 0°C, 2h; ix, $[Mo(\eta-C_5H_5)(CO)_3H]$, $n-C_6H_{14}$, 25°C.

Scheme 14

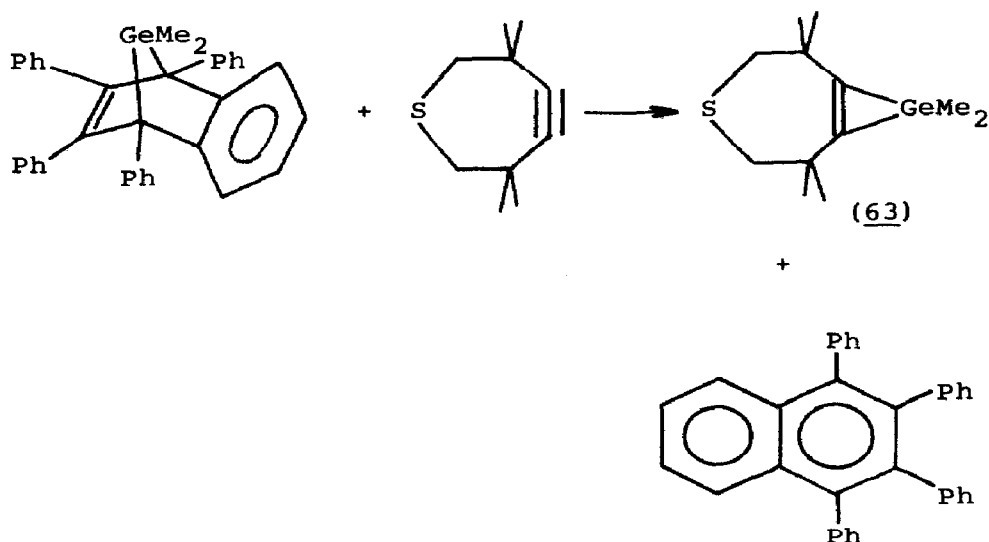
tin(II) amide and excess of arene.¹²⁸ The platinum and palladium complexes $(M(\mu_2-M^1(NR_2)_2)(CO)_3$ ($M = Pd$ or Pt ; $M^1 = Ge$ or Sn ; $R = SiMe_3$) undergo reversible one-electron reduction to afford e.s.r.-characterised reduction products, which contain a Pd_nSn_2 or Pt_3Sn_3 core in the case of the tin complexes. The tin complexes have a planar $[MSn(CO)]_3$ framework.¹³¹

The previously reported ^{119}Sn Mössbauer parameters for the β , γ and liquid phases of tin(II) fluoride are erroneous and due to a SnF_2 hydrolysis product. Revised data show that the β and γ phases have parameters which are indistinguishable within experimental error from those of $\alpha-SnF_2$.¹³² Enthalpies of mixing of the liquid mixtures of $PbO + PbF_2$ have been measured at 1170K. Values are negative and show a well-defined minimum of ca. $-320 J.mol^{-1}$ near $N_{PbO} = 0.7$.¹³³ Amines, amides, and dmsO can be intercalated in the layered structure of tin(IV) hydrogen phosphate hydrate. Pyridine, 4,4'-bipyridine and dmsO form a monolayer, while piperidine, aniline, m-toluidine, and 3,5-dimethylaniline form a bilayer. Many molecules, such as urea, thiourea and formamide, do not intercalate. However, N,N-dimethylformamide does. The thermal decomposition of the resulting intercalates takes place in three stages: dehydration, removal of the organic molecule, and condensation of the hydrogen phosphate to pyrophosphate.¹³⁴ The lead(II) complex of phenoxyacetic acid is a two-dimensional polymer with a repeating dimer sub-unit. One lead atom has an irregular $[MO_8]$ coordination, whilst the second has an irregular $[MO_7]$ coordination.¹³⁵ Complex formation between lead(II) and different non-cyclic ligands, crown ethers, aza crown ethers, and cryptands have been studied in methanol.^{136,137} Lead(II) ions interact with DNA in two different ways: (i) via the phosphate chain leading to stabilization of a double-helical structure, and (ii) via base donors destabilizing a double-stranded structure.¹³⁸

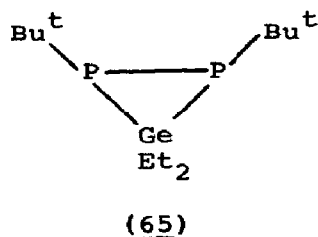
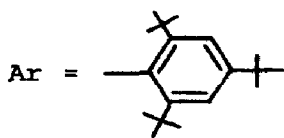
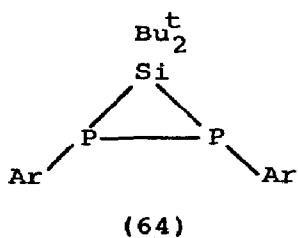
4.2.4 Molecular Tetravalent Compounds

Bis(triphenylphosphine)palladium dichloride catalyses two reactions of 1,1-dimethyl-2,3-bis(trimethyl)silirene: formal dimethylsilylene extrusion followed by trapping by unsaturated species and insertion of unsaturated substrates into the silirene ring.¹³⁹ Nickel-catalyzed reactions of silacyclopropenes and (phenylethynyl)polysilanes with phenyl(trimethylsilyl)acetylene

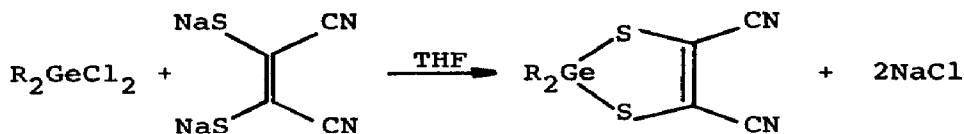
have also been studied.¹⁴⁰ The structures of three three-membered heterocycles have been determined. That of (63), the first representative germirene and prepared according to the reaction:



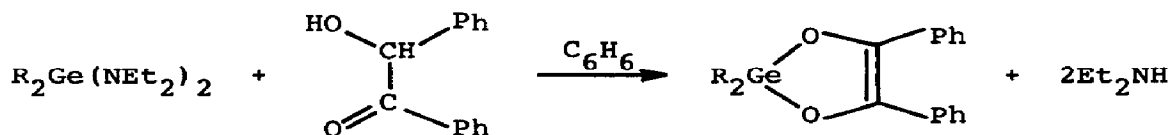
exhibits intramolecular Ge-C bond distances which are distinctly shorter than usually observed for Ge-C(sp²) bonds.¹⁴¹ Reaction of di-*t*-butyldiidosilane with excess lithium naphthalenide followed by treatment with dichloro(2,4,5-tri-*t*-butylphenyl)-phosphane leads to inter alia the 1,2,3-diphosphasilirane (64).¹⁴² The P-P distance in both this and the similar diphosphagermirane (65)¹⁴³ are somewhat elongated.



Several new methods for the synthesis of dioxygermoles and dithiagermoles have been described:

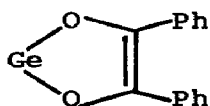


(R = Me, Et, Ph)



(R = Me, Ph, Prⁱ)

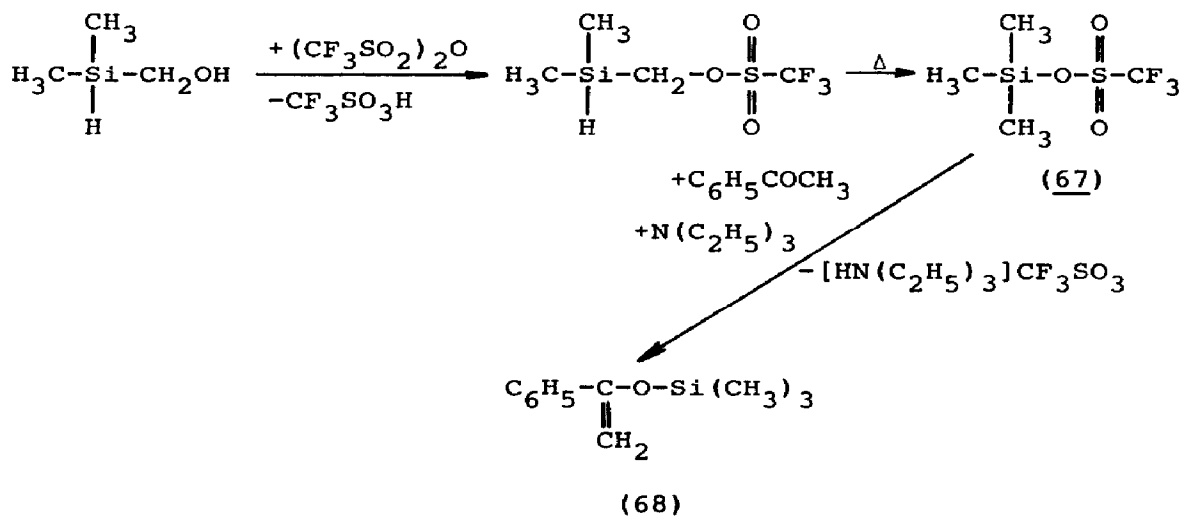
Exchange reactions between dioxygermoles or dithiagermoles and thiophosgene afford a dioxoethione and a dithioethione, respectively. With $\text{GeCl}_2 \cdot \text{dioxane}$, the new stable germylene (66) is formed.¹⁴⁴



(66)

Silicon and germanium hydrides are obtained in high yield by the reduction of the corresponding halo and alkoxy derivatives with LiAlH_4 in the presence of phase-transfer catalysts.¹⁴⁵ Tributyltin hydride reduces halopentaboranes(9) to the parent pentaborane(9) as well as other haloboranes and halometalloboranes. The use of tributyltin deuteride gives deuterio-substituted products.¹⁴⁶ Catalytic amounts of aluminium chloride

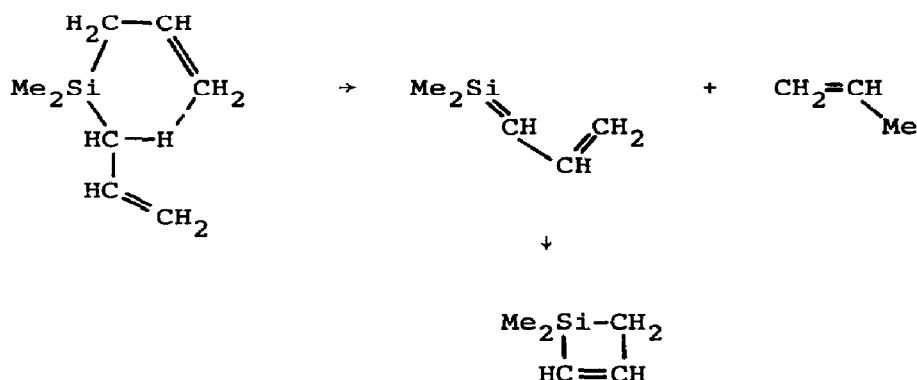
or bromide effect the selective mono-, di-, tri-, or tetramethylation of GeCl_4 by tetramethylsilene. The proposed mechanism involves the initial formation of Me_4Ge (regardless of the proportions of starting reagents) followed by disproportionation reactions.¹⁴⁷ Trimethylsilyl trifluoromethanesulphonate (67) is generated by the thermally-induced rearrangement of (dimethylsilyl)methyl trifluoromethanesulphonate:



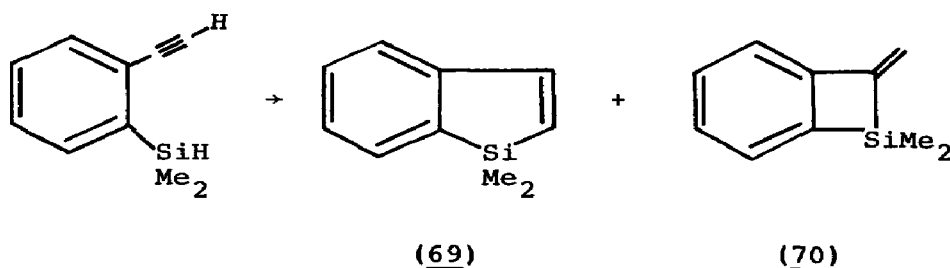
Transformation to the enolate (68) occurs with acetophenone in the presence of triethylamine.¹⁴⁸ Trimethylsilylmethanesulphinic acid and derivatives of the type $\text{Me}_3\text{SiCH}_2\text{S}(\text{O})-\text{Y}$ ($\text{Y} = \text{OH}, \text{OM}, \text{OR}, \text{NR}_2$) are formed by the insertion of SO_2 and RNSO into $\text{Me}_3\text{SiCH}_2\text{MgCl}$.¹⁴⁹ Addition of organotin anions to CS_2 affords stannanedithiocarboxylates, $\text{R}_3\text{SnCS}_2^-$, which can be allylated to give the dithioesters, $\text{R}_3\text{SnCS}_2\text{R}'$. The synthesis of transition metal complexes such as $\text{R}_3\text{SnCS}_2\text{M}(\text{CO})_4$ ($\text{M} = \text{Mn}, \text{Re}$) requires the initial isolation of the dioxane adducts, $\text{R}_3\text{SnCS}_2\text{M}' \cdot n\text{C}_4\text{H}_8\text{O}_2$ ($\text{M}' = \text{Li}, \text{Na}, \text{K}$).¹⁵⁰

Striking similarities in the spectra of TCNE complexes of the Group IV element tetraphenyl derivatives indicate that there is no appreciable $p\pi \rightarrow d\pi$ bonding between the phenyl groups and the central atoms and that the energies of the phenyl π orbitals are unaffected by the size or electronegativities of the central atoms.¹⁵¹ The main reaction in the gas-phase pyrolysis of diallyldimethylsilane is the retroene elimination of propene with

the formation of a silacyclobutene (Scheme 15). Extensive secondary reactions also occur.¹⁵² Flash vacuum pyrolysis of [o-(dimethylsilyl)phenyl]acetylene at 800°C produces 1,1-dimethyl-1-silaindene (69) in 84% yield via largely an insertion of an intermediate vinylidene into the Si-H bond (Scheme 16). At 650°C, however, the isomeric 1,1-dimethyl-2-methylenebenzo-1-silacyclobutene (70), arising from an initial 1,5-hydrogen shift from silicon, is also obtained.¹⁵³



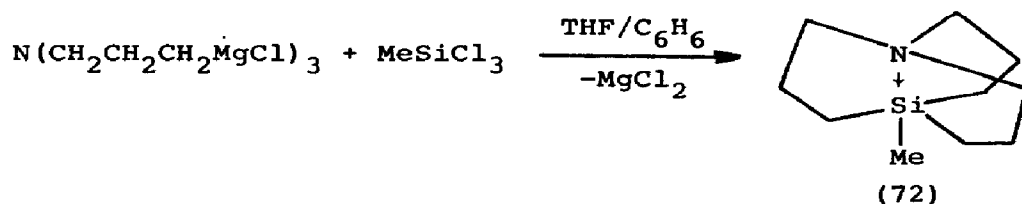
Scheme 15



Scheme 16

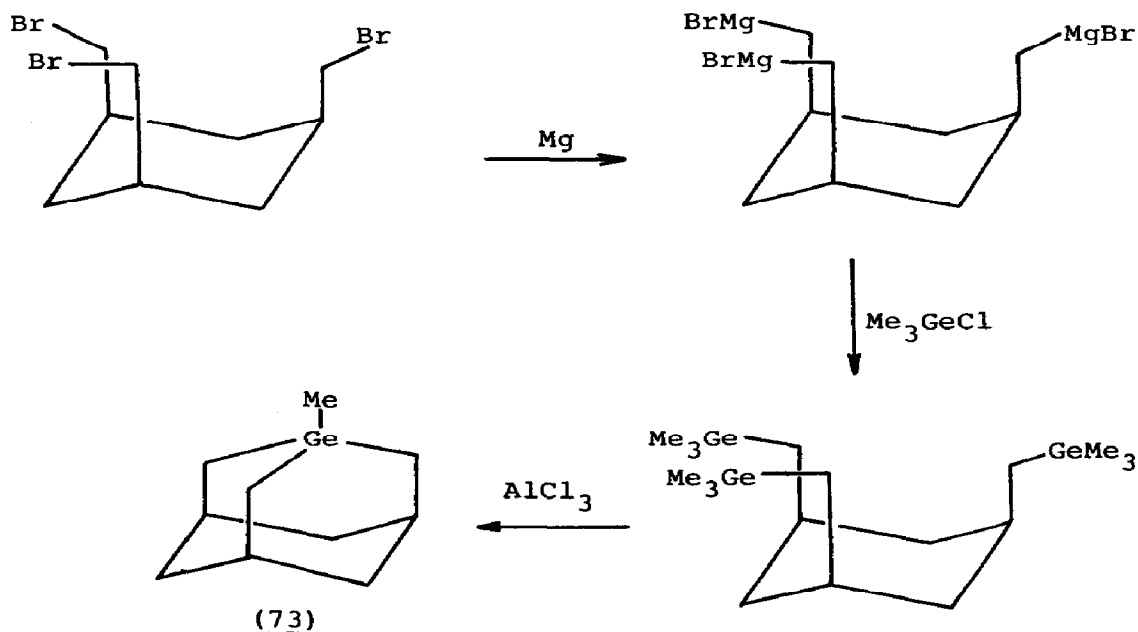
The first stage intercalation compound of potassium in graphite, C_8K , reacts with tin(II) chloride to afford tin-graphite, which with allyl bromide gives diallyltin dibromide via a double oxidative-addition reaction.¹⁵⁴ Treatment of $\text{CH}_2(\text{MgBr})_2$ with THF

The carbasilatrane derivatives (71) and (72) have been prepared by the Grignard method:¹⁵⁹



The Si+N coordinate bond distance (2.291Å) in 1-phenylcarbasilatrane is some 0.13Å longer than in other phenylsilatranes.¹⁶⁰

1-Methyl-1-germaadamantane (73) has been synthesised according to Scheme 17. The methyl group can be replaced by chlorine using

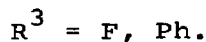
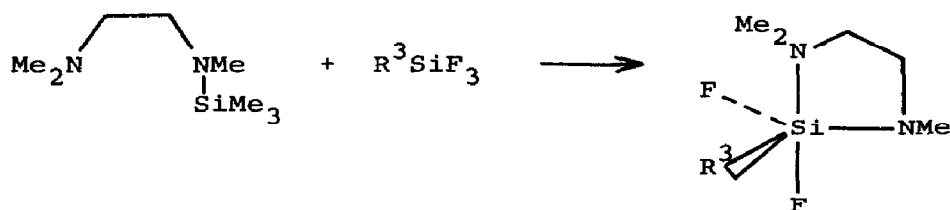
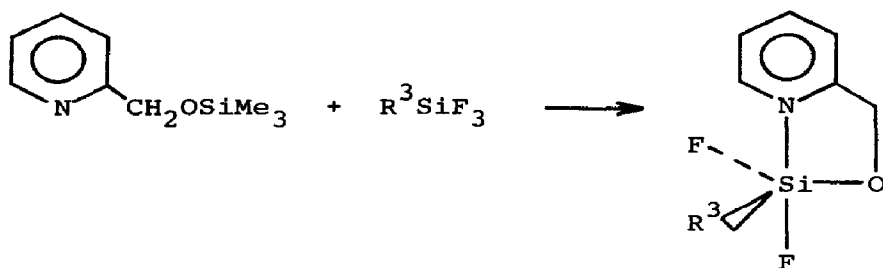
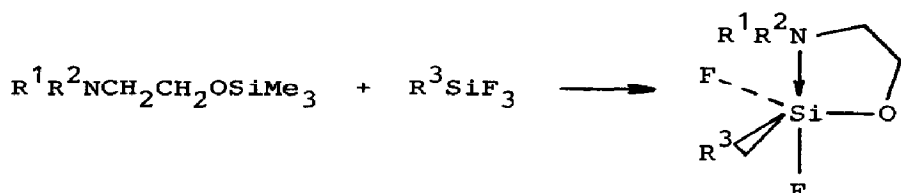


Scheme 17

excess trichlorosilane with a catalytic amount of chloroplatinic acid.¹⁶¹ Molecules of ClSn(CH₂CH₂CH₂)₃N contain trigonal bipyramidally coordinated tin, with the tin, nitrogen, and chlorine atoms lying on the crystallographic three-fold axis.¹⁶² The relative rates of reaction of several silatranes and mercury(II) chloride in acetone-d₆ to yield the corresponding organomercury compounds are of the order of ca. 5 × 10⁻¹ l.mol⁻¹ s⁻¹, rates which are unexpectedly high compared to the essentially inert parent organotrialkoxysilanes. Thus the apical Si-C bond of silatranes is extraordinarily susceptible to direct electrophilic attack by mercury(II).¹⁶³

Stannane and the methylstannanes react in fluorosulphuric acid at -90°C to produce SnMe_{3-n}H_n⁺ (n = 0-3) cations. At higher temperatures decomposition to Sn²⁺ and/or SnMe₂²⁺ cations occurs.¹⁶⁴ Crystals of silylfluoride at 96K comprise chains of molecules with intermolecular F---Si interactions. The Si-F

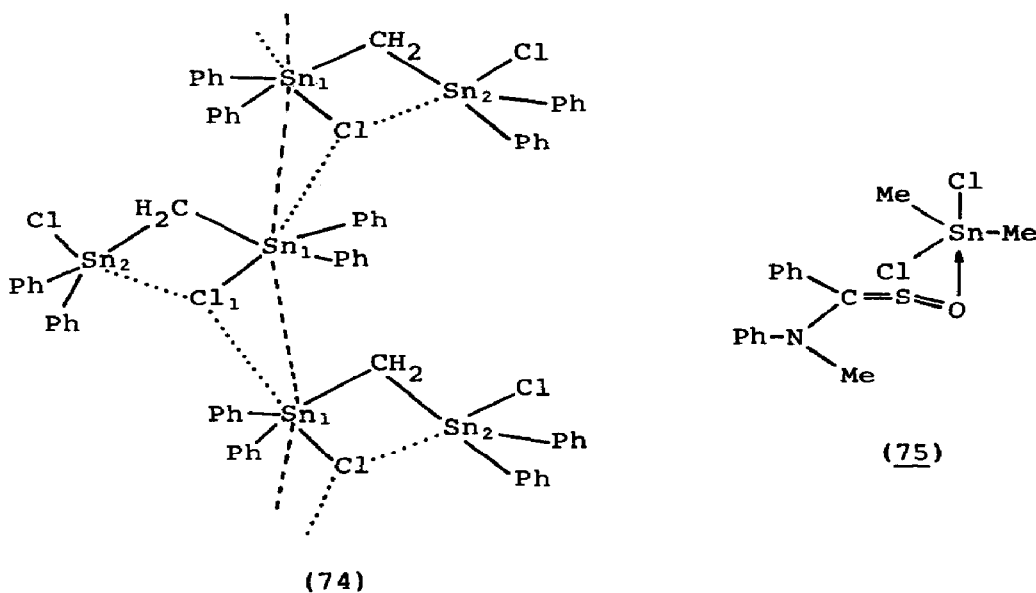
bond distance is lengthened from the gas-phase value.¹⁶⁵ Silicon tetrafluoride and PhSiF_3 react with O -trimethylsilyl derivatives of N,N -disubstituted aminoethanols and with the N -trimethylsilyl derivative of N,N,N' -trimethylethylenediamine to yield monofluoro-silyl compounds which possess strong $\text{N} \rightarrow \text{Si}$ intramolecular bonds:¹⁶⁶



The thermal decomposition of $\text{K}_2[\text{SiF}_6]$ is influenced by the presence of traces of oxygen and water introduced during preparative procedures.¹⁶⁷ The reaction of silicon tetrachloride with NEt_4SH in liquid hydrogen sulphide followed by recrystallisation of the product from $\text{CH}_2\text{Cl}_2/\text{CCl}_4$ mixture afforded crystals of $\text{NEt}_4[\text{SiSCl}_3] \cdot 0.5\text{CCl}_4$. Crystals comprise discrete ions with disorder of sulphur and chlorine atoms. The germanium

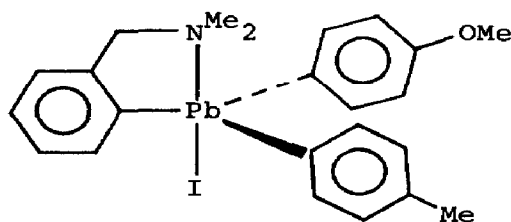
analogue prepared similarly is isomorphous.¹⁶⁸

The Lewis acidities of trimethylchlorosilane, -germane, and -stannane have been determined calorimetrically and follow the order $\text{Sn} > \text{Ge} > \text{Si}$. The chlorosilane exhibits Lewis behaviour similar to that of the germane, and the previously reported acidity of the chlorosilane is attributed to hydrolysis.¹⁶⁹ The structure of three organotin halides are worthy of note. That of bis(chlorodiphenylstannyl)methane is illustrated schematically in (74) showing both the inter- and intramolecular chlorine bridging.¹⁷⁰ Dicyclohexyltin dichloride is also associated by chlorine bridging giving a severely distorted trans-octahedral geometry at tin,¹⁷¹ but crystals of bis(biphenyl-2-yl)tin dichloride comprise discrete monomeric units with very distorted tetrahedral coordination at tin.¹⁷²



Aminosulphines form 1:1 adducts with Me_2SnCl_2 via 2'-O coordination as in (75).¹⁷³ The structures of several other dimethyltin dichloride adducts have been determined. The tin atoms in the adduct with 2-(p-methoxyphenyliminomethyl)phenol¹⁷⁴ and the diaquadichlorodimethyltin-purine(1/4) complex¹⁷⁵ have the all-trans octahedral geometry. The $[\text{SnMe}_2\text{Cl}_4]^{2-}$ anion in the tetrathiafulvalene complex $[\text{ttf}][\text{SnMe}_2\text{Cl}_4]$ are disordered with respect to the Sn-Me and Sn-Cl bonds. In the analogous complex $[\text{ttf}][\text{SnMe}_2\text{Cl}_3]$, the anions exist as dimers.¹⁷⁶ Both cis and

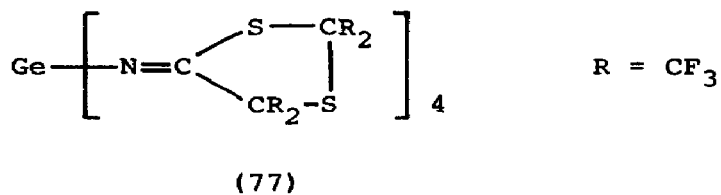
trans isomers of the complex of dichlorobis(4-chlorophenyl)tin with 4,4'-dimethyl-2,2'-bipyridine can be obtained.¹⁷⁷ Four different phases have been isolated from the $\text{PCl}_5\text{-SnCl}_4$ system depending on the conditions such as solvent, relative concentrations and temperature: $[\text{PCl}_4]_2[\text{SnCl}_6]$, $[\text{PCl}_4]_3[\text{SnCl}_6]\text{-}[\text{PCl}_6]$, $[\text{PCl}_4][\text{Sn}_2\text{Cl}_{10}]$, and $[\text{PCl}_4][\text{SnCl}_5]$.¹⁷⁸ Other tin halide structures which have been determined included $\text{SnCl}_4\cdot 2\text{DMSO}$,¹⁷⁹ and $\text{SnI}_4\cdot 2\text{DPSO}$ ¹⁸⁰ (which both have a cis-octahedral geometry), (DMSO = dimethylsulphoxide; DPSO = diphenylsulphoxide), $\text{EtSiI}_3\cdot 2\text{DPSO}$ (cis DPSO ligands; ethyl groups trans to one DPSO);¹⁸⁰ and $(\text{NMe}_4)_2\text{EtSnCl}_5$, $(\text{NMe}_4)_2\text{BuSnBr}_5$ and $(\text{NMe}_4)_2\text{SnBr}_6$.¹⁸¹ Air-stable chloroform solutions of Schiff base complexes of Co^{II} undergo rapid cobalt oxidation on addition of n-butyltin trichloride affording complexes such as $\text{Bu}^n\text{Sn}(\text{OME})\text{Cl}_2\cdot \text{CoCl}(\text{salen})$. In this complex the methoxy group bridges the two metals.¹⁸² Dimethylethylene urea and dimethylpropylene urea form adducts of the types $\text{Ph}_3\text{SnX}\cdot \text{L}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), $\text{Ph}_3\text{PbX}\cdot \text{L}$ ($\text{X} = \text{Br}, \text{I}$), $3\text{Ph}_3\text{PbCl}\cdot 2\text{DMEU}$, and $2\text{Ph}_3\text{PbCl}\cdot \text{DMPU}$, with triphenyltin and -lead halides. N.m.r. studies indicate rapid ligand exchange occurs in solution.¹⁸³ The structure of (76), the first chiral lead compound, has been determined.¹⁸⁴



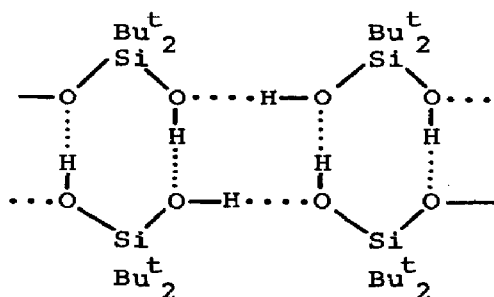
(76)

Germanium(IV) cyanide reacts with $[(\text{CF}_3)_2\text{CS}]_2$ to afford (77) which contains tetrahedrally coordinated germanium.¹⁸⁵ The 18-crown-6 adduct of dimethyltin dithiocyanate (as a dihydrate) comprises alternating $[\text{Me}_2\text{Sn}(\text{NCS})_2(\text{OH}_2)_2]$ and 18-crown-6 moieties linked by hydrogen bonds to form a linear polymer. The crown ether is quite distorted from the regular geometry.¹⁸⁶ Triphenyltin pseudohalides, Ph_3SnX ($\text{X} = \text{NCO}, \text{NCS}, \text{N}_3$), undergo facile halogenodephenylation with iodine monochloride and/or bromide to yield mixed diphenyltin halide pseudohalides. With DMSO,

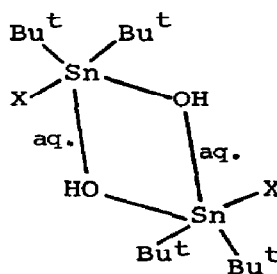
$\text{Ph}_2\text{Sn}(\text{NCS})\text{Br}$ forms the adduct $\text{Ph}_2\text{Sn}(\text{NCS})\text{Br} \cdot 2\text{DMSO}$.¹⁸⁷



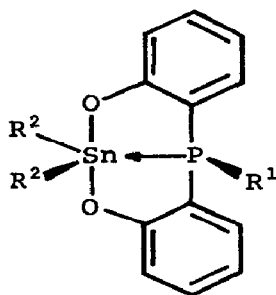
Several papers report studies on sterically-hindered silane and stannane compounds. The crystal structures of five silanols have been described. $\text{Bu}_2^t\text{Si}(\text{OH})\text{F}$ crystallizes as a O-H...O hydrogen-bonded tetramer. The fluorine atoms do not participate in the association.¹⁸⁸ $\text{Bu}_2^t\text{Si}(\text{OH})_2$ forms hydrogen-bonded dimers which are linked by additional hydrogen bonds into a ladder structure (78).¹⁸⁹ The structures of $[(\text{Me}_3\text{Si})_3\text{Cl}(\text{Ph})\text{Si}(\text{OH})_2]$ and $[(\text{Me}_3\text{Si})_3\text{Cl}(\text{Ph})\text{Si}(\text{OMe})\text{OH}]$ also comprise hydrogen-bonded dimers, but in the latter compound the two components are held together by a single hydrogen-bond.¹⁹⁰ The triol, $[(\text{Me}_3\text{SiO})_3\text{CSi}(\text{OH})_3]$, has an hexameric cage structure which is extremely stable.^{191,192}



(78)



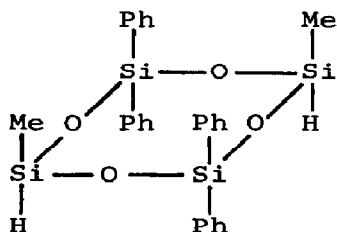
(79)



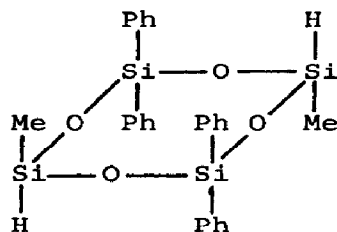
(80)

Tin-119 n.m.r. and Mössbauer data for tetrakis(adamantyl)stannane indicate some charge separation of the type $\text{Ad}_3\text{Sn}^{\Delta-} \dots \text{Ad}^{\Delta+}$. Other sterically-hindered compounds exhibit similar, but less dramatic effects.¹⁹³ Tin-119 n.m.r. has been employed to examine the stability and self-association of $(\text{neophyl}_3\text{Sn})_2\text{O}$, $\text{neophyl}_3\text{SnOH}$, and $(\text{neophyl}_3\text{Sn})_2\text{CO}_3$ in solution. Facile dehydration of the hydroxide occurs even at room temperature, thus preventing its isolation from solution, in sharp contrast to previous reports that the bulky alkyl groups render the hydroxide stable with respect to dehydration. Both the hydroxide and carbonate, unlike their n-alkyl homologues are unassociated in solution.¹⁹⁴ Di-tert-butyltin hydroxide halides, $\text{Bu}^t_2\text{Sn}(\text{OH})\text{X}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$), have been obtained either by hydrolysis of the corresponding dihalides or by reaction of the oxide with hydrogen halide. All three compounds are dimeric, with two five-coordinated tin atoms linked by oxygen atoms in a central four-membered $[\text{Sn}_2\text{O}_2]$ ring (79). These dimeric molecules are further held together in the crystal by $\text{O-H} \dots \text{X}$ hydrogen bonding.¹⁹⁵ t-Butyltris(diethylamino)stannane, $\text{Bu}^t\text{Sn}(\text{NEt}_2)_3$, has been synthesised by alkylation of tetrakis(diethylamino)stannane using t-butyllithium. Alcoholysis with t-butanol affords $\text{Bu}^t(\text{OBu}^t)_3$, whilst reaction with trimethylchlorosilane gives Bu^tSnCl_3 , which decomposes rapidly at room temperature to tin(II) chloride and t-butyl chloride.¹⁹⁶ Di-n-butyltin dimethoxide reacts with organo-bis-o-hydroxyphenylphosphines to afford the five-coordinated benzoxaphosphastannolins (80).¹⁹⁷

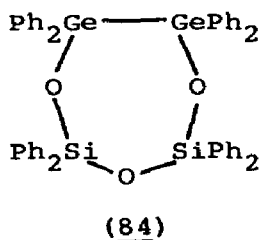
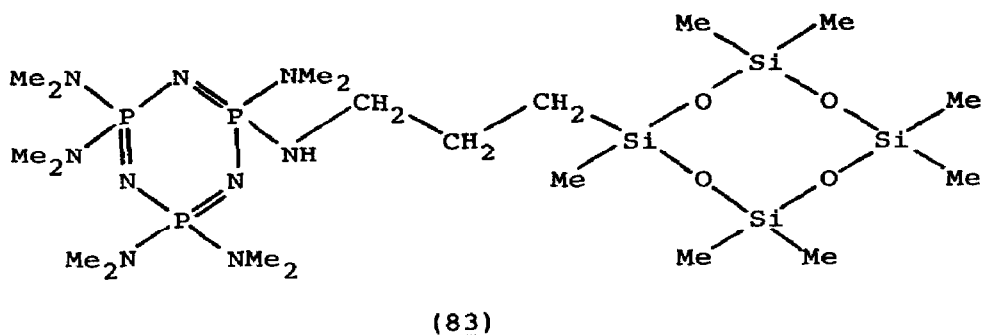
1,5-Dihydro-1,5-dimethyl-3,3,7,7-tetraphenylcyclotetrasiloxane exists in two isomers, cis (81) and trans (82) in the crystal.¹⁹⁸ In (83), the $[\text{PN}]_3$ and $[\text{SiO}_4]$ rings form a dihedral angle of 100.1° .¹⁹⁹ Octaphenyldigermadisilatrioxane (84) has been



(81)



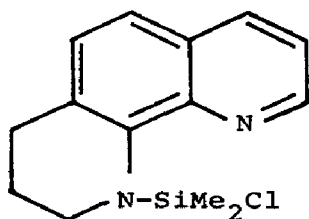
(82)



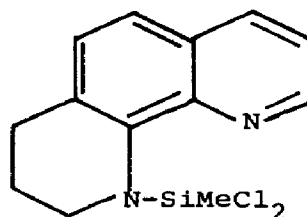
synthesized by the reaction of $\text{ClPh}_2\text{GeGePh}_2\text{Cl}$ with $\text{Ph}_2\text{Si}(\text{OH})_2$, and has only a slightly puckered ring with C_2 symmetry.²⁰⁰ The cobalt complex $\text{CoH}(\text{N}_2)(\text{PPh}_3)_3$ selectively promotes C-O bond cleavage in allylic and vinylic trimethylsilyl ethers at room temperature to give $\text{Co}(\text{OSiMe}_3)(\text{PPh}_3)_3$ and releasing the corresponding olefins. In contrast the rhodium complex $\text{RhH}(\text{PPh}_3)_4$ is active principally for Si-O bond cleavage at 80°C , whilst the ruthenium complex $\text{RuH}_2(\text{PPh}_3)_4$ promotes the cleavage of both bonds at 80°C . Mechanism of C-O bond cleavage is thought to proceed via insertion of the olefinic double bond into the M-H bond followed by β -elimination of the $[\text{Me}_3\text{SiO}]$ group from the transition metal complex. The Si-O bond cleavage is compatible with nucleophilic attack of the metal hydrides in the silyl ethers.²⁰¹ The formation of iminodioxolane derivatives has been observed in the reaction of tributyltin ω -halo-alkoxides, $\text{Bu}_3\text{SnO}(\text{CH}_2)_n\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), with isocyanates. Yields are affected substantially by various factors including solvent, temperature, the halogen, and the substituent on the isocyanate.²⁰²

The expansion of the coordination sphere of silicon from four to five has been mapped using known structural data. The

correlation diagrams are interpreted in terms of geometrical transformations along the S_N2 inversion pathway, and provide a possible model for the molecular motions of dynamic rearrangements involving an intermediate coordination number ($5 \rightarrow 4 \rightarrow 5$) at silicon in chelated complexes of five-coordinated silicon.²⁰³ Rapid positional exchange of the fluorine atoms occurs for 1-(trifluorosilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline at room temperature (^{19}F n.m.r.), which occurs as an intramolecular reaction by an irregular mechanism involving the instability of the coordinative bonding. Intermolecular fluorine exchange does occur but is relatively slow.²⁰⁴ The structure of two analogues, (85) and (86), have been determined, both of which exhibit trigonal bipyramidal five-coordination at silicon. Whereas the silicon is achiral in (85), that in (86) is chiral and both enantiomers are found in the crystal.²⁰⁵ The structures of no less than eleven



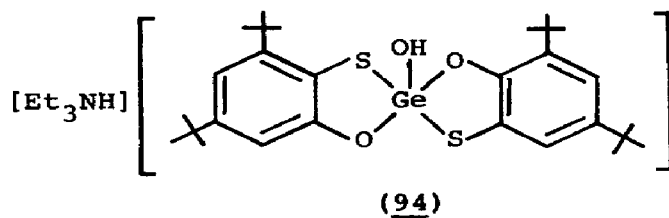
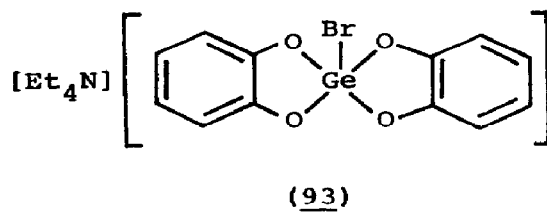
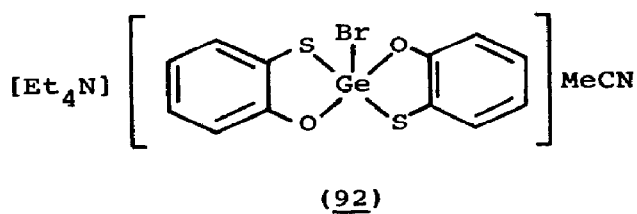
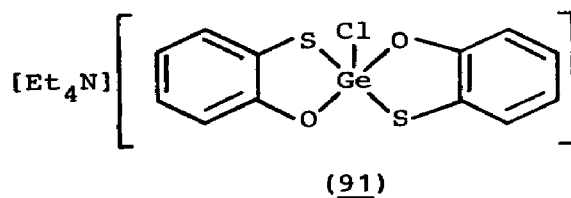
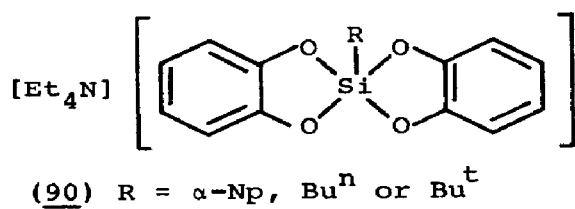
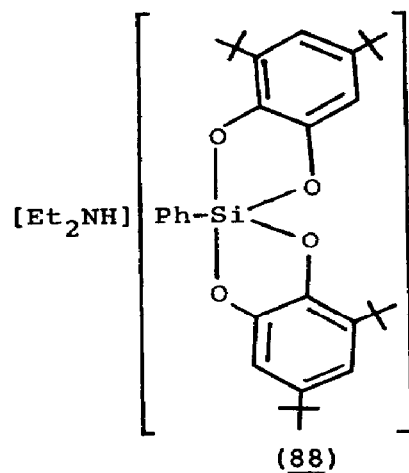
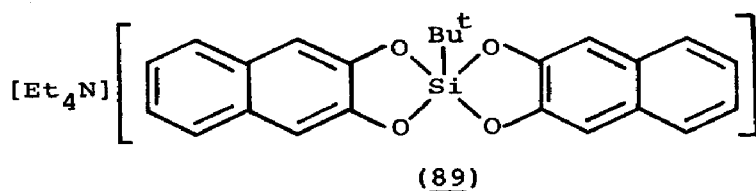
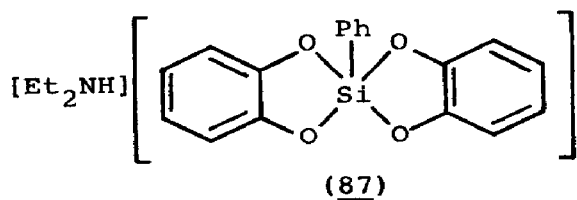
(85)

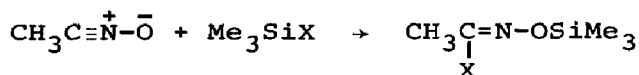


(86)

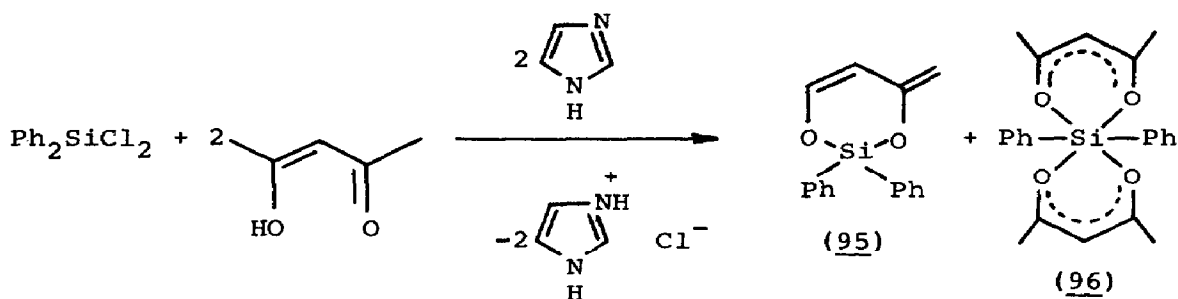
spirocyclic five-coordinated silicates and germanates (87)-(94) have been determined.²⁰⁶⁻²⁰⁸ Hydrogen bonding between the cation and the oxygen atoms of the spirocyclic framework, e.g. in (87), causes displacement of the geometry towards a rectangular pyramid. When this is precluded by bulky substituents, e.g. in (88), the trigonal bipyramidal geometry is found. Increase in the electron donor ability of the organic substituent on the silicon also causes a displacement of the geometry towards a rectangular pyramid. The same general rules for the observation of a trigonal bipyramid versus a rectangular bipyramidal geometry also apply for five-coordinated germanium species.

The reaction of trimethylsilyl derivatives Me_3SiX ($\text{X} = \text{Cl}, \text{I}, \text{NCS}, \text{CN}, \text{N}_3, \text{NEt}_2, \text{SMe}, \text{H}, \text{F}, \text{OMe}, \text{NCO}, \text{O}_2\text{CMe}$) with acetonitrile oxide leads to the formation of O-trimethylsilylacetoxyamoyl adducts:²⁰⁹

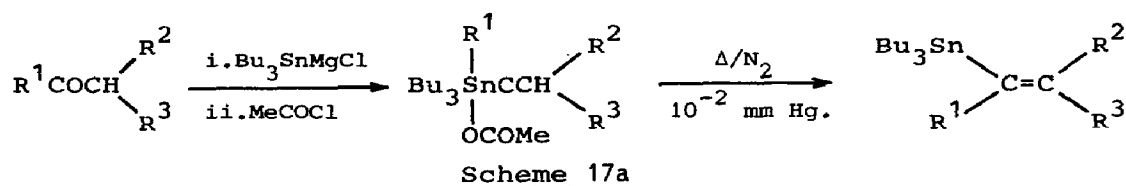


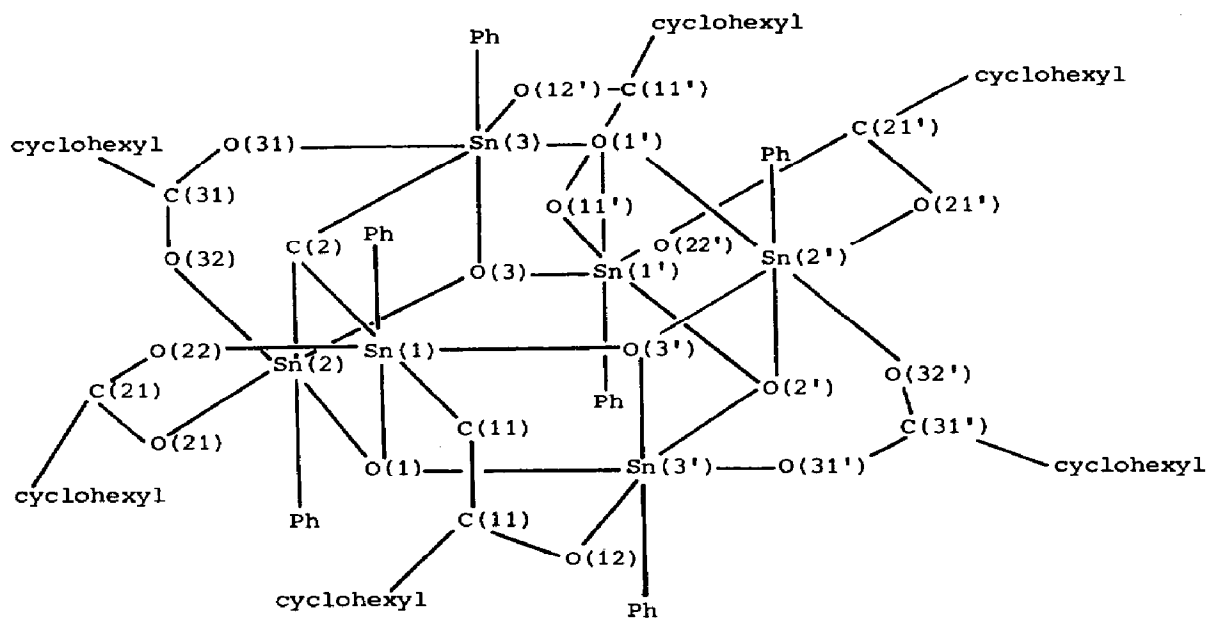


Diphenyldichlorosilane reacts with acetonitrile in the presence of imidazole yields the known dienolate (95) in addition to the new stable hexacoordinate complex (96):²¹⁰

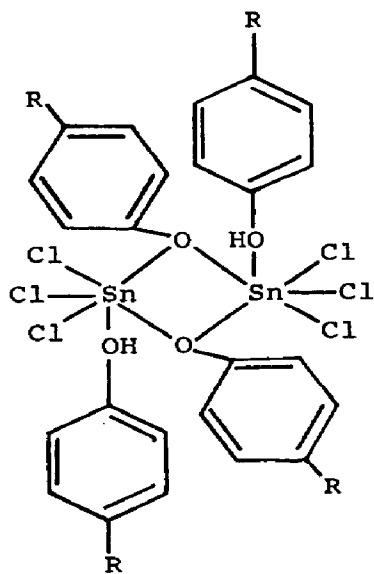


Germyl acetate adopts a cis-planar conformation in the gas-phase with the Ge-O bond eclipsing the C=O bond.²¹⁰ Trimethylsilyl trichloroacetate in refluxing solvent (toluene, chloroform, or dichloromethane) in the presence of a phase transfer catalyst and solid dry potassium fluoride is a useful dichlorocarbene source.²¹¹ Flash pyrolysis of alkyltributyltin acetates at temperatures of 600–850°C under a moderate vacuum leads to the formation of vinyltin compounds (Scheme 17a).²¹² Phenyltin oxycyclohexanecarboxylate has an extremely unusual hexameric structure (97) in which the tin has an octahedral coordination.²¹³ Other crystal structures worthy of note include the diphenyltin dinitrate complexes of cis and trans 1,2-bis(diphenylphosphoryl)ethylene, which both contain tin in a pentagonal bipyramidal environment,²¹⁴ the silver-tin complexes, $[\text{Ag}(\text{AsPh}_3)_4][\text{SnPh}_2(\text{NO}_3)_3]$ and $[\text{AgPh}_3)_4][\text{SnPh}_2(\text{NO}_3)_2\text{Cl}]$,²¹⁵ the dimeric trichlorotin phenoxide (98)²¹⁶ and chlorotriphenyl(quinolinium-2-carboxylato)tin(IV) monohydrate.²¹⁷ The structures of tin compounds containing a four-membered $[\text{Sn}_2\text{O}_2]$ ring have been critically analysed.²¹⁸





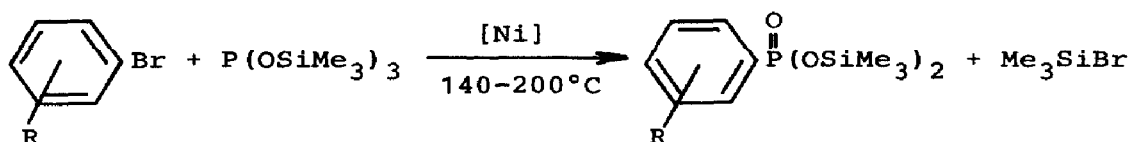
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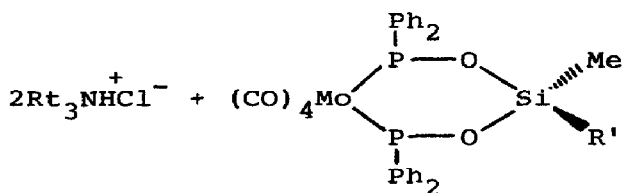
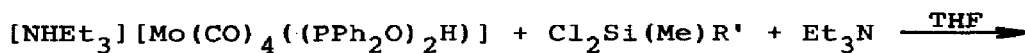
(98)

Tetrathiafulvalene (TTF) and tetraselenafulvalene (TSF) salts with $[\text{cis-R}_2\text{Sn}(\text{C}_2\text{O}_4)_2]^{2-}$, $[\text{TTF or TSF}]_{2.0-4.0}[\text{cis-R}_2\text{Sn}(\text{C}_2\text{O}_4)_2]$ ($\text{R} = \text{Me, Et}$) have been prepared by the reaction of $[\text{TTF or TSF}]_3^- [\text{BF}_4]_2$ with $[\text{cis-R}_2\text{Sn}(\text{C}_2\text{O}_4)_2]^{2-}$ in acetonitrile, and by the electrolysis of TTF or TSF in acetonitrile solutions containing $[\text{NBu}_4]^n_2[\text{cis-R}_2\text{Sn}(\text{C}_2\text{O}_4)_2]$ as electrolytes.²¹⁹

Esters of carbonic acid, $\text{Me}_3\text{EOCOOMe}$, ($\text{E} = \text{C, Si, Ge, Sn, Pb}$) have been obtained by several methods.²²⁰ Various aryl-bis-(trimethylsilyl)phosphonic acid esters have been prepared from $\text{P}(\text{OSiMe}_3)_3$ or a mixture of $\text{HP}(\text{O})(\text{OSiMe}_3)_2/\text{P}(\text{OSiMe}_3)_3/(\text{Me}_3\text{Si})_2\text{NH}$ in the presence of nickel compounds, e.g.:²²¹

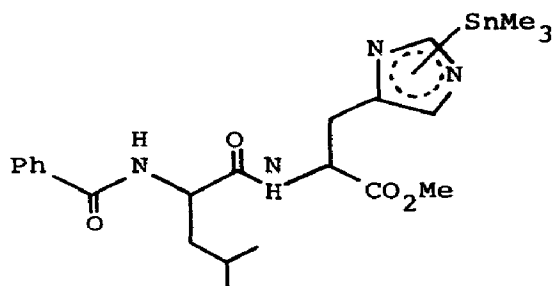


Bis(trimethylsilyl)hypophosphite undergo oxidation with chalcogenides giving $(\text{Me}_3\text{SiO})_2\text{P}(\text{X})\text{H}$ ($\text{X} = \text{O, S, Se, Te}$).²²² The complexes (99) containing a heterocyclic $[\text{MoP}_2\text{O}_2\text{Si}]$ ring have been obtained by the route:²²³

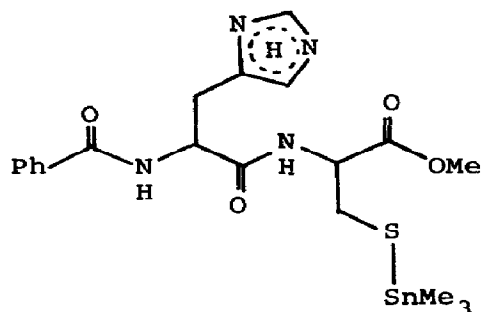


(99)

Several reports of organotin derivatives of biologically-active molecules have appeared including complexes of thiopicolinamides,²²⁴ 6-thiopurine,²²⁵ adenine, adenosine and 9-methyladenine,²²⁶ and derivatives of bipyridylum cations.²²⁷ The trimethyltin complexes of two terminally-protected dipeptides, (100) and (101), have been synthesised as models for



(100)



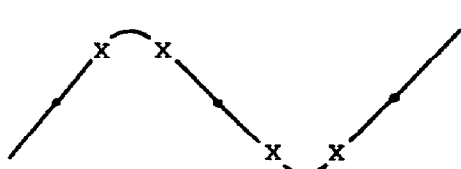
(101)

the interaction of trimethyltin with proteins.²²⁸ In the solid, intermolecular association occurs for both compounds (variable temperature Mössbauer), but is broken down in solution where isomers due to the restricted rotation about the peptide and amide bond are observed (^{13}C n.m.r.).

Mössbauer spectroscopy and n.m.r. have been employed extensively in the characterisation of tin compounds. Variable temperature Mössbauer data for a large number of phenyl- and cyclohexyltin compounds has extended further the use of these data for the classification of solid lattices. Lattices based upon non-interacting units, or polymers which are helical (102) or 'S-shaped' (103), show the highest temperature coefficients. The value of this parameter is generally reduced for zig-zag polymers (104), while the most rigid lattices are based upon a rod-like architecture (105).²²⁹



(102)



(103)



(104)



(105)

Variable-temperature Mössbauer data have indicated polymeric structures for the compounds $\text{SnCl}_3\text{CN}(\text{Me}_3\text{SiCN})$ (from SnCl_4 with Me_3SiCN in CCl_4 solution) and $\text{SnCl}_2\text{BrCN}(\text{THF})$, and an oligomeric structure for $\text{SnCl}_2\text{ICN}(\text{THF})$ (both from the reaction of XCN ($\text{X} = \text{Br}, \text{I}$) and SnCl_2 in THF).²³⁰ Mössbauer isomer shifts of a wide variety of triorganotin compounds correlate with partial atomic charges on tin.²³¹ Other Mössbauer studies include studies of tin(IV) chloride trapped in the pores of a Corning Vycor 'thirsty glass',²³² cis and trans isomers of SnCl_4L_2 ($\text{L} = \text{dma}, \text{dmf}, \text{dmsO}$, and tetrahydrothiophen) and $\text{SnBr}_4(\text{dmf})_2$,²³³ and ditin compounds of the types $(\text{R}_n\text{X}_{3-n}\text{Sn})_2\text{Y}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{OAc}, \text{OH}, \text{SPh}; n = 0-3$; $\text{Y} = \text{CH}_2, \text{CH}_2\text{CH}_2\text{CH}_2, \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ or $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$).²³⁴

Molecular interaction of dimethyltin dichloride with Lewis bases has been investigated by measuring the concentration and temperature dependence of the two-band coupling constant $^2J(^{119}\text{Sn}-^1\text{H})$. Both 1:1 and 1:2 complexes are formed concurrently in solution, and thermodynamic data were derived.²³⁵ Proton n.m.r. data confirm that Cl/mercaptoester exchange reactions in butyl- and β -carbomethoxyethyltin compounds occur readily in deuteriochloroform at 35°C . The positions of equilibria are determined by intramolecular carbonyl-to-tin coordination from the mercaptoester groups in the butyltin cases, but in the analogous β -carbomethoxyethyl systems carbonyl-to-tin coordination from the β -carbomethoxyethyl groups also competes.²³⁶ ^{13}C data has been obtained for the first time on solid methyltin compounds employing the proton-decoupled, cross-polarization magic angle spinning technique.²³⁷⁻²³⁹ The methyltin ^{13}C chemical shift is insensitive to slight variations in bond angles and bond distances. However, as in solution the one-bond coupling constant, $^1J(^{119}\text{Sn}-^{13}\text{C})$ varies monotonically with the MeSnMe bond angle. Multiple methyltin resonances were observed for trimethyltin acetate and trimethyltin hydroxide indicating hindered rotation of the trigonal planar $[\text{Me}_3\text{Sn}]$ group in these one-dimensional polymers. The single ^{17}O chemical shift observed in the spectra of tri-n-butyl and di-n-butyltin carboxylates has been interpreted in terms of a fast exchange of the oxygen atoms of the carboxylato group bonded to the tin atom.²⁴⁰ Triorganotin(IV) oxinates have been shown by a combination of ^{13}C , ^{15}N , and ^{119}Sn n.m.r. to contain five-coordinated tin in both non-coordinating solvents. In the former

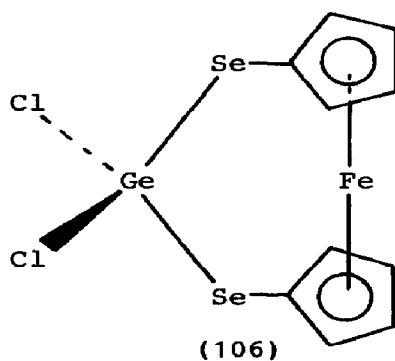
type and in the neat liquids the geometry is cis-trigonal bipyramidal, whilst in donor solvents a trans-trigonal bipyramidal arrangement is found with the oxinate group unidentate.²⁴¹ The ^{119}Sn chemical shift is indicative of coordination number in tricyclohexyltin derivatives, with the chemical shift moving to lower frequency on increase in coordination number. Thus the oxide, chloride, bromide, iodide, hydroxide, acetate and benzoate are all monomeric and four-coordinate in solution, whereas the tropolonate is five-coordinated.²⁴² Values of the C-Sn-C bond angles in octahedral complexes of the types R_2SnCh_2 (Ch = bidentate ligand) have been estimated from the n.m.r. $^1\text{J}(^{119}\text{Sn}-^{13}\text{C})$ and $^2\text{J}(^{119}\text{Sn}-\text{C}-\text{H}^1)$ coupling constants. Complexes with β -ketoenolato ligands have trans alkyl structure with angles between 174° and 180° . 8-Hydroxyquinolato complexes have very nearly cis geometries with angles in the range $109-126^\circ$, whereas the sterically-crowded 2-methyl-8-hydroxyquinolato complexes have intermediate skew-cis structures. Trapezoidal bipyramidal frameworks were observed for the tropolonates and 1-picolinates.²⁴³ The isomers of the 1:1 adduct, $\text{Ph}_2\text{SnClBr.O=PBU}_3$, undergo rapid Berry pseudorotation with a calculated barrier of 35 kJ mol^{-1} above approximately -75°C in dichloromethane solution.²⁴⁴ Two-dimensional ^{119}Sn NOESY n.m.r. spectra have demonstrated unambiguously that the ditin compound, $\text{CH}_2[\text{PhSn}(\text{SCH}_2\text{CH}_2)_2\text{NMe}]_2$, isomerizes at the tin centre in an uncorrelated way.²⁴⁵ The magnitude of the $^2\text{J}(^{119}\text{Sn}-^{117}\text{Sn})$ coupling constant in hexaorganodistannoxanes is strongly dependent upon the nature of the organic group. The effect is attributed to changes in the Sn-O-Sn bond angle which should strongly influence the magnitude of the Fermi contact term.²⁴⁶ Tin-tin coupling has also been detected for the first time in tetraorganodistannoxanes, with a marked difference observed between halogen- and oxygen-bridged distannoxanes. In the former type one kind of coupling was interpreted in terms of an anionic chloride bridge, whilst a covalently bonded oxygen bridge was suggested on the basis of the appearance of additional coupling in the latter compounds.²⁴⁷ The mixed species, $\text{Sn}(\text{SPh})_x(\text{TePh})_{4-x-y}$ have been characterised by ^{77}Se , ^{119}Sn and ^{125}Te , n.m.r.²⁴⁸ ^{13}C n.m.r. spectra of dihydroxo-5,10,15,20-tetraphenylporphyrinatotin(IV) exhibit unusual $^{13}\text{C}-^1\text{H}$ residual couplings which are rationalised by 'through space' interactions

between the centrally coordinated hydroxy hydrogen and porphyrin carbon nuclei.²⁴⁹

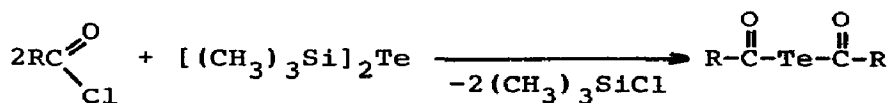
One-bond $^1J(^{15}\text{N}-^{29}\text{Si})$ coupling constants are readily measured from the ^{15}N satellites in ^{29}Si n.m.r. spectra. Values are strongly dependent on the nitrogen hybridisation and the nature of the Si-N bond.²⁵⁰ Positive ion fast atom bombardment mass spectra of phenyl-substituted germanium, tin, and lead compounds are generally similar to the corresponding electron impact spectra.²⁵¹ The applications of both UV/PES and X-ray/PES in organometallic chemistry has been reviewed.²⁵² Asymmetry parameters for the electric field gradient at the ^{35}Cl nuclei of polycrystalline $\text{Cl}(\text{CH}_2)_3\text{SnCl}_3$ at 77K are consistent with a trigonal-bipyramidal structure.²⁵³ Bromine-n.q.r. measurements have shown that the anion in $[\text{NHMe}_3]_2[\text{SnBr}_6]$ has a regular octahedral structure in the temperature range 77-300K. $[\text{SMe}_3]_2^-[\text{SnBr}_6]$ may well have a similar structure at room temperature, whereas $[\text{NMe}_4]_2[\text{SnBr}_6]$ undergoes a phase transition to a less regular structure between 178 and 77K.²⁵⁴

The structures of several compounds containing bonds to sulphur have been reported. Condensation of Ph_3SiSH gives $\text{Ph}_3\text{SiSSiPh}_3$, which is remarkably resistant to hydrolysis, and is bent at sulphur ($\text{SiSSi} = 112.0^\circ$).²⁵⁵ Reaction between sodium methylene dimercaptide and SiCl_4 affords spiro-bis(ethylenedithia)silane, in which the Si-S bond distances are quite short (mean Si-S = 2.116Å).²⁵⁶ Whereas mercury(II) bis-tr-tert-butoxysilanethiolate, $\text{Hg}[\text{SSi}(\text{O}^t\text{Bu})_3]_2$, is monomeric with a linear S-Hg-S unit,²⁵⁷ the corresponding silver(I) salt is tetrameric with a central eight-membered $[\text{Ag}_4\text{S}_4]$ ring.²⁵⁸ Coordination around tin in $\text{ClPhSn}[(\text{SCH}_2\text{CH}_2)_2\text{S}]$ is trigonal bipyramidal with two Sn-S bonds and the phenyl group occupying equatorial sites, and the chlorine and a transannular Sn---S interaction the axial sites.²⁵⁹ The structures of both orthorhombic and triclinic modifications of $\text{Ph}_2\text{Pb}[(\text{SCH}_2\text{CH}_2)_2\text{O}]$ have been determined at -160°C . Both contain transannular Pb---O interactions, but the triclinic modification has an additional intermolecular S---Pb contact.²⁶⁰ Crystals of Ph_3PbSPh comprise discrete tetrahedral monomeric molecules.²⁶¹ Other structures which have been reported include the dithiophosphato compounds, $\text{Ph}_3\text{GeS}_2\text{P}(\text{OMe})_2$, $\text{Ph}_2\text{Ge}[\text{S}_2\text{P}(\text{OMe})_2]_2$ (both with unidentate dithiophosphate groups),²⁶² $\text{Ph}_3\text{PbS}_2\text{P}(\text{OEt})_2$ (unidentate) and $\text{Ph}_2\text{Pb}[\text{S}_2\text{P}(\text{OCH}_2\text{Ph})_2]_2$ (anisobidentate groups),²⁶¹

$\text{Ph}_2\text{SnCl}(\text{SCOPr}^i)$ (^{119}Sn n.m.r. data reported as well),²⁶³
 $\text{BuPhSnCl}[\text{S}_2\text{CNEt}_2]$,²⁶⁴ $\text{BuPh}_2\text{SnS}_2\text{CNMe}_2$,²⁶⁵ $\text{Ph}_3\text{SnS}_2\text{CN}(\text{CH}_2)_4$ and
 $\text{Ph}_3\text{PbS}_2\text{CN}(\text{CH}_2)_4$.²⁶⁶ That of 1,3-diselena-2,2-dichlorogermyl-
 [3]ferrocenophane (106) has also been determined at 163K.²⁶⁷ The
 two cyclopentadienyl rings are eclipsed and inclined to one
 another by 6.1° .

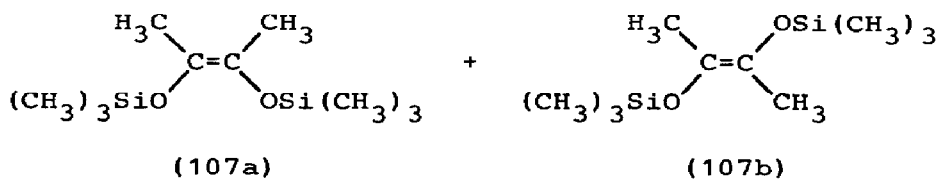
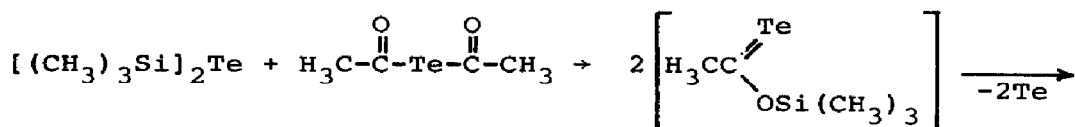


The structures of alkyltin isooctyl thioglycollates
 $\text{R}_2\text{SnCl}_n(\text{IOTG})_{2-n}$ ($n = 0,1$) and $\text{RSnCl}_n[\text{IOTG}]_{3-n}$ ($n = 0-2$) have been
 investigated by infrared and ^1H and ^{119}Sn n.m.r. Redistribution
 of Cl and IOTG ligands proceeds to maximise the degree of ligand
 mixing and of chelation stabilisation by $\text{BuOCOCH}_2\text{CH}_2$ and IOTG
 groups.²⁶⁸ The syntheses and spectroscopic properties of a
 large number of organotin and organoleaddithiolates have been
 reported.²⁶⁹ Reactions of 4,5-dimethyl-1,2,3-selenadiazole with
 hexaalkylditins or trialkyltin anion followed by quenching with
 trialkyltin chloride affords only dimethylacetylene and
 $(\text{Me}_3\text{Sn})_2\text{Se}$.²⁷⁰ Bis(trimethylsilyl) telluride, $(\text{Me}_3\text{Si})_2\text{Te}$, does
 not react with simple ketenes, but does undergo spontaneous
 reaction with acyl halides:



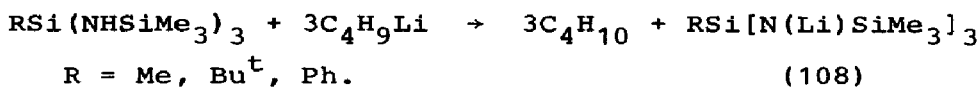
Mixing $(\text{Me}_3\text{Si})_2\text{Te}$ and MeCOTeCOMe at -20°C without solvent results
 in the separation of elemental tellurium and an intense blue
 colouration, the final products of the reaction being the (Z) and

(E) isomers, (107a) and (107b) (Scheme 18):²⁷¹



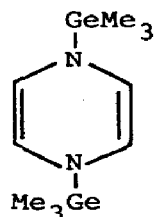
Scheme 18

The molecular structures of the silylamines, $\text{NMe}(\text{SiH}_2\text{Me})_2$,²⁷² $\text{NMe}(\text{SiHMe}_2)_2$ ²⁷² and hexamethylcyclodisilazene, $[\text{Me}_2\text{SiNMe}]_2$,²⁷³ have been determined by electron diffraction. In the latter, the four-membered ring and the nitrogen bond configuration are planar or nearly so. The structures of several other amine derivatives have been determined by X-ray crystallography. The three trillithio derivatives (108), prepared by the reaction:

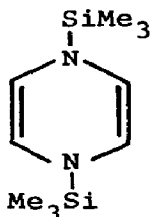


form dimers in the solid state. The dimers have a central, electron-deficient $[\text{Li}_6\text{N}_6]$ core, in which the six lithium atoms are arranged in a trigonal antiprism and to which two $[\text{RSi}(\text{NSiMe}_3)_3]$ fragments are attached.²⁷⁴ Both 1,4-bis(trimethyl-germyl)- and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (109) and (110) exhibit virtually planar six-membered ring conformations and very little pyramidalisation at the nitrogen atoms. In contrast, the more sterically crowded 2,3,5,6-tetramethyl-1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (111) has a pronounced boat conformation with a dihedral angle of ca. 140° between the ring halves.²⁷⁵

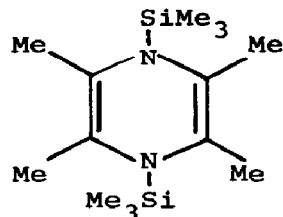
The structure of (112) is unusual, and consists of two four-



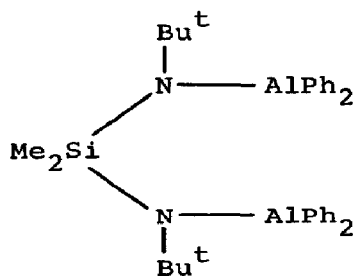
(109)



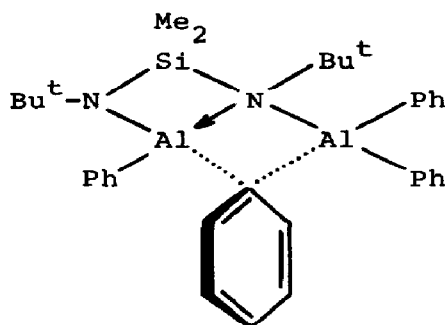
(110)



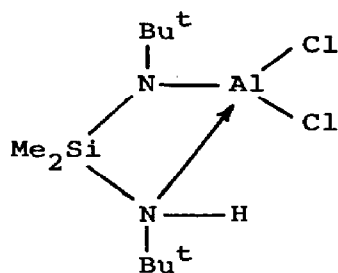
(111)



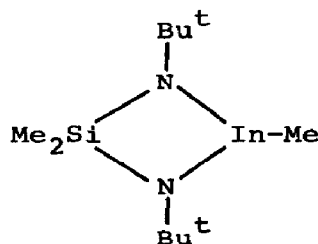
(112)



(113)



(114)

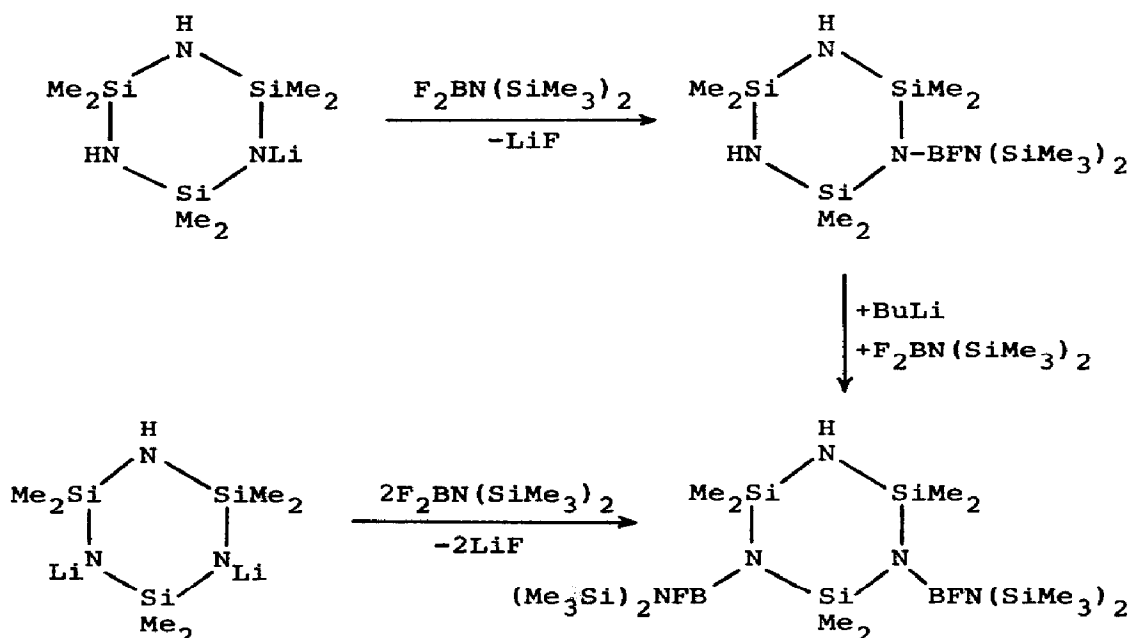


(115)

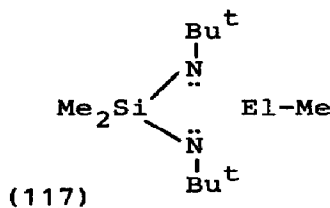
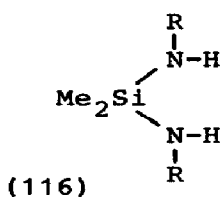
membered rings which share a common Al-N edge. One of the rings consists of a tetravalent silicon, a three-valent nitrogen, and an aluminium and nitrogen atom with four-fold coordination. The second ring unites the two latter atoms together with a tetrahedral aluminium and carbon atom of a phenyl group. The structure is therefore better represented by (113). In non-polar solvents, the compound is fluxional at low temperatures. In (114), an intramolecular N-Al bond is responsible for the formation of a four-membered [SiN₂Al] ring. The indium compound

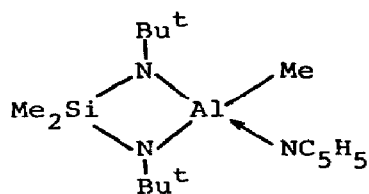
(115) may be described as a polycyclic unit built up of three four-membered rings standing orthogonally against each other and sharing common edges.²⁷⁶

Fluorosilylamines, $R_2SiF(NH_2)$, ($R = Pr^i, NMeSiMe_3$), are obtained by the reaction of the corresponding difluorosilanes with $LiNH_2$ and react with butyllithium to form the lithium salts, $R_2SiF(NHLi)$. Elimination of LiF from $Pr^i_2SiF(NHLi)$ leads to the formation of cyclodi-, -tri and -tetrasilazanes, but with $(Me_3SiNMe)_2SiF(NHLi)$ only a cyclotrisilazane is obtained.²⁷⁷ Hexamethylcyclotrisilazanes and their lithium salts react with $F_2BN(SiMe_3)_2$ to afford mono-, bis-, and tris(fluoroboryl)cyclotrisilazanes, eg.²⁷⁸

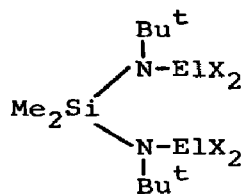


The hydrogen atoms in (116) can be substituted by Main Group III elements to which organic groups or chlorine atoms are attached. Several families of compounds have been characterised including (117) - (121).²⁷⁹

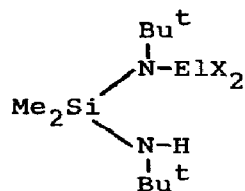




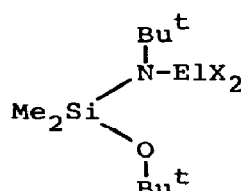
(118)



(119) El = Al, Ga, In
X = Me, Cl

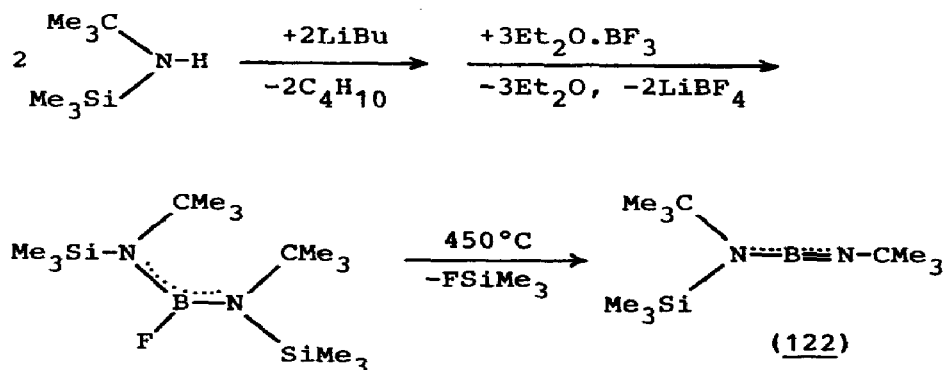


(120) El = B, Al, Ga, In, Tl
X = Me, Cl



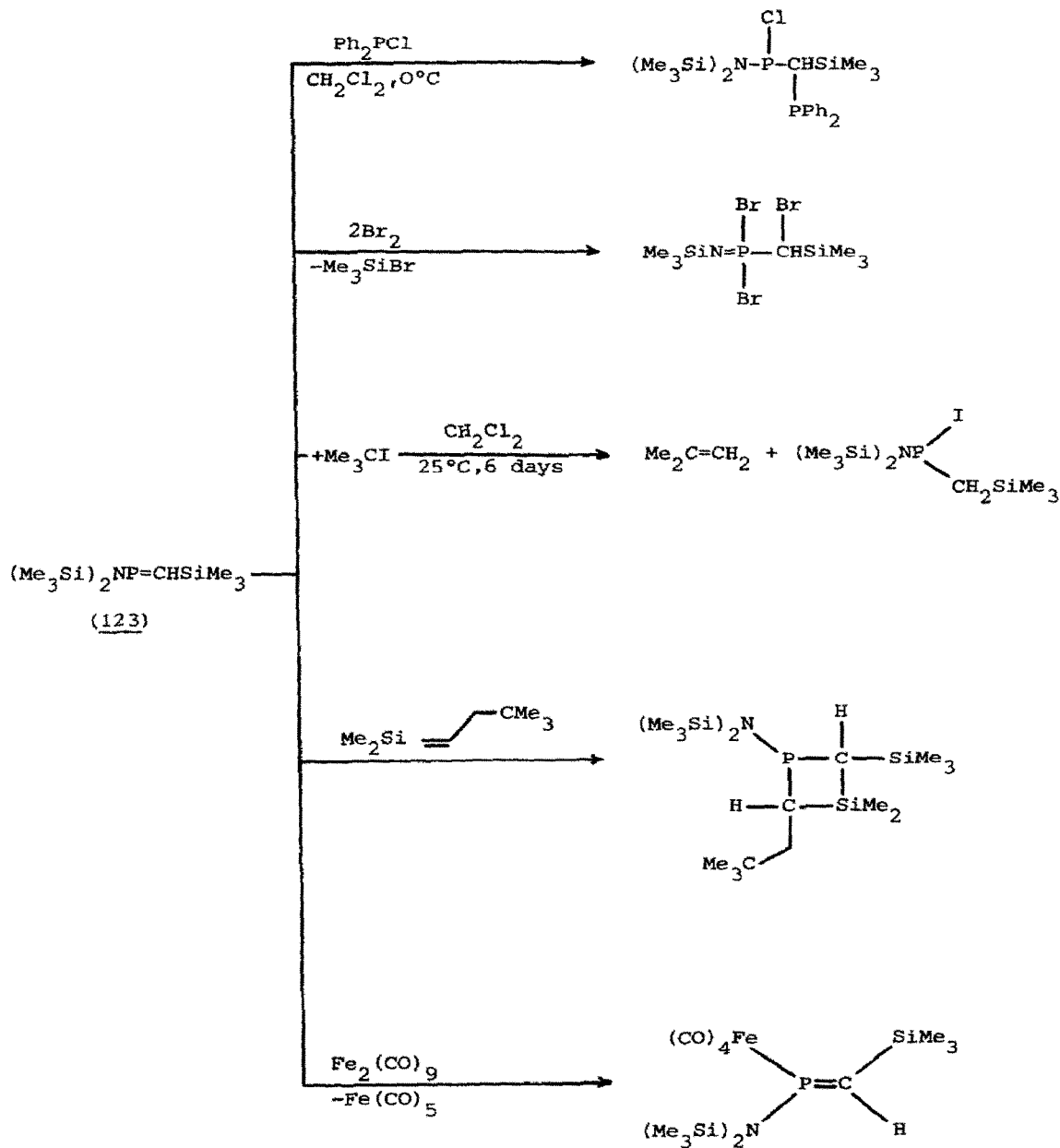
(121) El = Al, Ga
X = Me, Cl

The reaction of $\text{LiN}(\text{SiMe}_3)\text{R}'$ ($\text{R}' = \text{CMe}_3, \text{SiMe}_3$) with NSF yields linear (eg. $(\text{Me}_3\text{C}-\text{N}=\text{S}=\text{N})_2\text{S}$, $\text{Me}_3\text{C}-\text{N}=\text{S}=\text{N}-\text{CMe}_3$, $\text{Me}_3\text{Si}-\text{N}=\text{S}=\text{N}-\text{SiMe}_3$, and $(\text{Me}_3\text{Si})_2\text{N}-\text{S}=\text{N}=\text{S}=\text{N}-\text{SiMe}_3$) as well as cyclic thiazenes.²⁸⁰ Trimethylsilyl azide, Me_3SiN_3 , reacts with the chromium and tungsten carbene complexes $(\text{CO})_5\text{M}[\text{CPh}_2]$ ($\text{M} = \text{Cr}, \text{W}$) to afford the complexes, $(\text{CO})_5\text{M}[\text{N}(\text{H})=\text{CPh}_2]$.²⁸¹ The aminoimino borane, $\text{Bu}^t(\text{Me}_3\text{Si})\text{N}-\text{B}=\text{NBu}^t$ (122) has been obtained by the LiF-elimination route and dimerises at room temperature, although it may be stored at -30°C (Scheme 19). Typical reactions of (122) involve additions to the more unsaturated BN band.²⁸²



Scheme 19

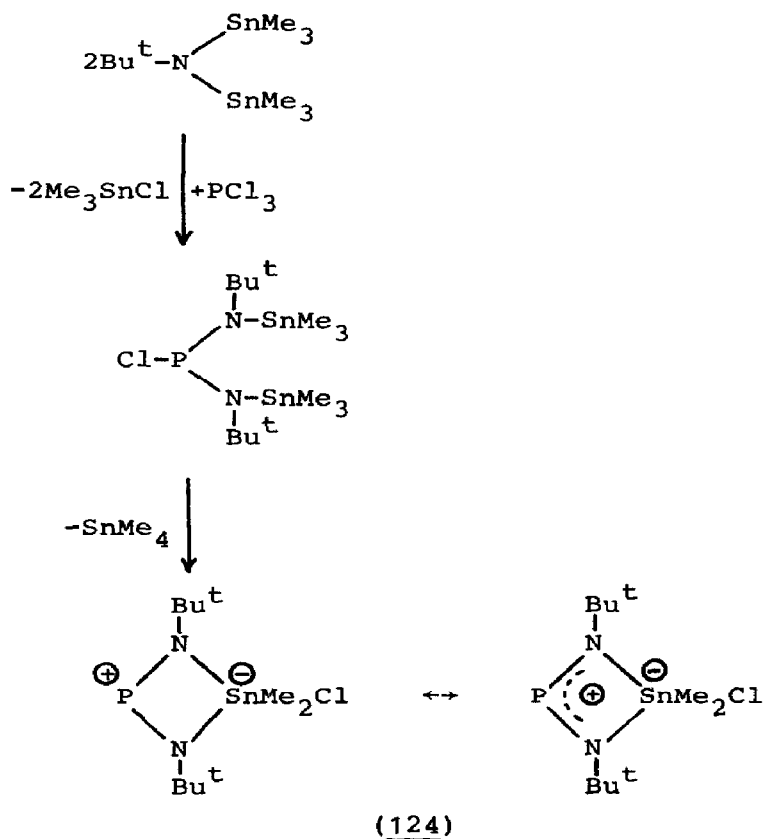
Several new reactions, including a variety of 1,2-additions and complexation to $\text{Fe}(\text{CO})_4$ of the trisilylated aminomethylene-phosphine, (123), have been reported, and are shown in Scheme 20.²⁸³



Scheme 20

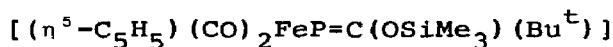
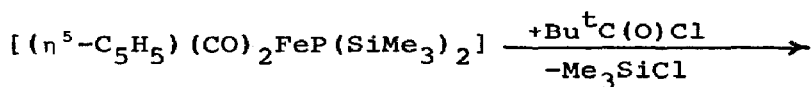
Trimethylsilyldiethylamine and MoOCl_4 undergo a free radical readox reaction in CH_2Cl_2 or Et_2O to form $\text{MoCl}_3\text{O}(\text{HNEt}_2)$.²⁸⁴ $\text{Me}_3\text{Sn-N}\equiv\text{VCl}_3$ is obtained from the reaction of VCl_4 and Me_3SiN_3 and forms volatile orange-red crystals which are extremely moisture sensitive and comprise monomeric molecules with an almost linear $[\text{SiNV}]$ axis. With 2,2'-bipyridine and $\text{PPh}_4[\text{Me}_3\text{SiNVCl}_4]$ are formed.²⁸⁵ Antimony(III) chloride and $\text{Na}[\text{N}(\text{SiMe}_3)_2]$ give monomeric $\text{MeSb}[\text{N}(\text{SiMe}_3)_2]_2$, which is converted to $\text{MeSbCl}_2[\text{N}(\text{SiMe}_3)_2]_2$ by SO_2Cl_2 .²⁸⁶ Zirconium(IV) and hafnium(IV) halides react with one equivalent of $\text{LiN}(\text{SiMe}_2\text{CH}_2\text{PR}_2)_2$ ($\text{R} = \text{Me}$, Pr^i , Bu^t) to give the complexes $\text{MCl}_3[\text{N}(\text{SiMe}_2\text{CH}_2\text{PR}_2)_2]$ ($\text{M} = \text{Zr}, \text{Hf}$). The stereochemistries of $\text{HfCl}_3[\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2]$ and $\text{ZrCl}_3[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}_2)_2]$ exhibit stark differences. The latter, in both monoclinic and orthorhombic modifications has the facial geometry, whilst in the zirconium complex the tridentate ligand is bound in a meridional fashion.²⁸⁷ The lanthanide thiolate complexes $[\text{LnL}_2(\mu\text{-SBu}^t)]_2$ ($\text{L} = \text{N}(\text{SiMe}_3)_2$; $\text{Ln} = \text{Eu}, \text{Gd}, \text{Y}$) have been prepared by metathesis between $[\text{LnL}_2\text{Xl}(\text{THF})]_2$ ($\text{Ln} = \text{Eu}, \text{Gd}$) or $\text{YL}_2\text{Cl}(\text{THF})_2$ with LiSBu^t . The structure of the gadolinium complex has been determined.²⁸⁸ The metal-carbon bond of the four-membered metallacycles $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{MCH}_2\text{SiMe}_2\text{NSiMe}_3$ ($\text{M} = \text{U}, \text{Th}$) reacts under mild conditions with acidic hydrogens of alcohols, phenols and alkynes with pyridine to give the orthometallated products from sp^2 C-H activation.²⁸⁹ PCl_3 reacts with $\text{Bu}^t(\text{Me}_3\text{Si})_2\text{N}$ in a 1:2 molar ratio to give $\text{ClP}[\text{NBu}^t(\text{SnMe}_3)]_2$ which has only been detected spectroscopically, and eliminates Me_4Sn to give the zwitterion (124), whose structure has been determined (Scheme 21).²⁹⁰

Trimethyliodosilane and Me_3GeBr react with allylphosphine in CH_2Cl_2 in the presence of Et_3N to afford the unsymmetrically substituted (silyl)- and (germyl)-allylphosphines, which are unstable and undergo redistribution to allylphosphine and the corresponding symmetrical phosphine, $(\text{Me}_3\text{M})_2\text{PCH}_2\text{CHCH}_2$ ($\text{M} = \text{Si}, \text{Ge}$).²⁹¹ Reaction of $\text{KP}(\text{Bu}^t\text{P})_2$ with Me_3SiCl or Me_3SnCl leads to the cyclotriphosphanes $(\text{Bu}^t\text{P})_2\text{SiMe}_3$ and $(\text{Bu}^t\text{P})_2\text{PSnMe}_3$, although a better route to the latter compound is by the cyclocondensation of $\text{Cl}(\text{Bu}^t\text{P})\text{-P}(\text{Bu}^t\text{P})\text{Cl}$ with $\text{P}(\text{SnMe}_3)_3$.²⁹² Tris(trimethylsilyl)-heptaphosphanonortricyclene, $\text{P}_7(\text{SiMe}_3)_3$, undergoes cleavage in the presence of triphos-nickel and -cobalt species to give compounds containing the cyclic triphosphirene unit.²⁹³ The disilyl-



Scheme 21

phosphidoiron complex, $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeP}(\text{SiMe}_3)_2]$, reacts with pivaloyl chloride to give the phosphaaalkenyl complex (125):²⁹⁴



(125)

Bis(trimethylsilyl)phosphines, $\text{RP}(\text{SiMe}_3)_2$ ($\text{R} = \text{Me}, \text{Ph}, \text{Bu}^t, \text{C}_6\text{H}_{11}$) and phenyl isothiocyanate give the insertion products (126):^{295,11)}



confirmed by X-ray crystallography.²⁹⁶

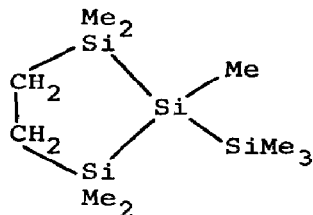
4.2.5 Compounds with Metal-Metal Bonds

²⁹Si ENDOR signals have also been observed for the radical anions, (Bu^tMeSi)₄⁻ and (Et₂Si)₅⁻. The data show only a small hyperfine anisotropy for ²⁹Si, consistent with Si-Si σ* or 3d spin population but not with π-type delocalisation.³⁰¹ The perhalogenated cyclopentasilanes, Si₅Br₁₀ and Si₅I₁₀ are isomorphous and

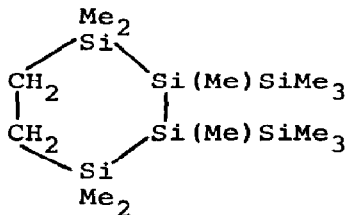


exhibit Si_5 ring conformations which are intermediate between envelope and twist.³⁰² Aliphatically substituted polydiorganosilylenes display reversible thermochromic behaviour in solution with a bathochromic shift occurring with decreasing temperature. The temperature dependence of the UV absorption maxima is thought to be due to conformational changes occurring along the polymer backbone with temperature.^{303,304} Photolysis of the high polymer $(n\text{-C}_6\text{H}_{13}\text{MeSi})_n$ in carbon tetrachloride leads to the formation of C_2Cl_6 , indicating that the photodegradation pathway of these polymers includes the formation of silyl radicals. Mechanisms involving both the extrusion of silylene units and the formation of silyl radical terminated polymer fragments were proposed to explain the observed silane products.³⁰⁵ The first stage of the reaction of *n*-decamethyltetrasilane with peroxybenzoic acid involves the oxidation of one of the two terminal Si-Si bonds, rather than the oxidation of the central Si-Si bond.³⁰⁶

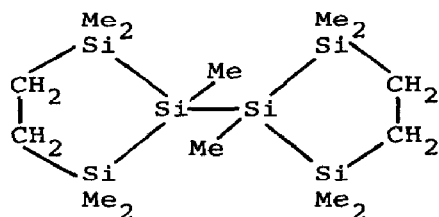
The four silyl-substituted polysilacycloalkanes (129)-(132) have been prepared by co-condensation of 1,2-bis(chlorodimethylsilyl)-



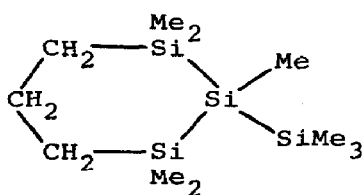
(129)



(130)

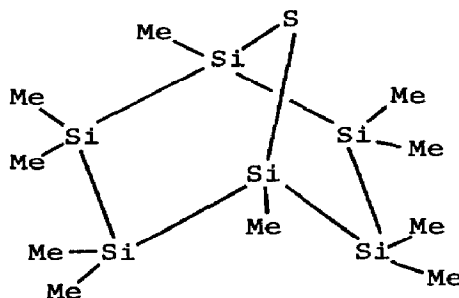


(131)



(132)

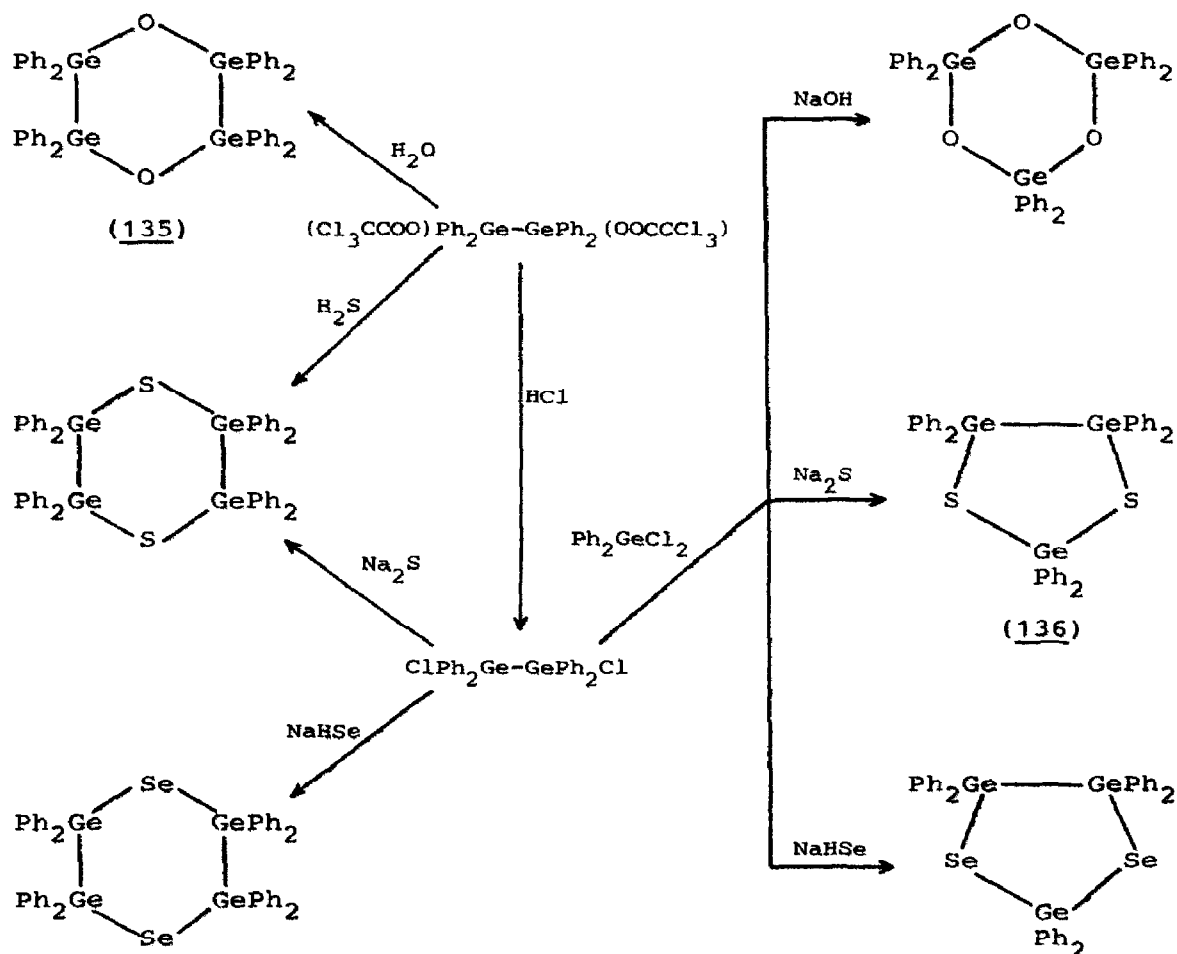
alkanes and 1,1-dichlorotetramethyldisilane with a lithium dispersion in the presence of a catalytic amount of Ph_3SiLi in thf. Photolysis of (129)-(132) involves elimination of silylenes.³⁰⁷ 1,2,2,3,3,4,5,5,6,6-Decamethyl-7-thia-1,2,3,4,5,6-hexasilanorbornane (133) is formed in a surprisingly simple reaction from 1,4-dichlorodecamethylcyclohexasilane and H_2S with the elimination of HCl .³⁰⁸



(133)

Potassium silyl reacts preferentially as a powerful reducing agent rather than as a nucleophilic substitution agent. PCl_3 and Me_2PCl give polymers with P-H bonds. Me_3SiCl undergoes transmetalation with complicated consequences. CO_2 is reduced to CO and potassium formate, and nitrous oxide is reduced to nitrogen. Silane and polymeric silicon hydrides are produced in all reactions.³⁰⁹ Potassium disilanyl, 2-potassium trisilanyl, and 2-potassium isotetrasilanyl are formed by the reaction of KSiH_3 with di-, tri-, n-tetra-, iso-tetra, and pentasilanes, respectively. Product purity varies between 95-99%, and the stability increases with increasing number of silicon atoms.^{310,311} Lithium tris(trimethylsilyl)silanide (134) (as a 1.5DME adduct), synthesised from $(\text{Me}_3\text{Si})_4\text{Si}$ and methylolithium in DME, has a structure built up from two $[\text{LiSi}(\text{SiMe}_3)_3]$ units which are connected via a bridging DME molecule.³¹² (134) reacts with halogenosilanes to give thermally stable compounds of the type $(\text{Me}_3\text{Si})_3\text{Si-Si(X)}<$ ($\text{X} = \text{halogen}$),³¹³ and with cp_2WCl_2 to afford the tungstenocene derivative $[(\text{Me}_3\text{Si})_3\text{SiC}_5\text{H}_4]_2\text{WH}_2$.³¹⁴

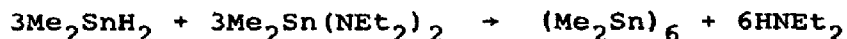
Several substitution reactions of the digermanes $[\text{XPh}_2\text{GeGePh}_2\text{X}]_2$ ($\text{X} = \text{Cl}, \text{Cl}_3\text{CCO}_2$) are shown in Scheme 22. The structures of both (135) and (136) have been determined. The six-membered $[\text{Ge}_4\text{O}_2]$ ring of (135) has the chair conformation (molecular symmetry C_{2h}).



Scheme 22

The five-membered $[\text{Ge}_3\text{Se}_2]$ ring in (136) has the half-chair conformation.³¹⁵ Symmetrical ketones (Ar_2CO) or α -diketones ($(\text{ArCO})_2$) are obtained from the reaction of aryl chlorides (ArCOCl) with hexaethylditin.³¹⁶ 1,2-Dichlorotetraalkyldistannanes, $\text{ClR}_2\text{SnSnR}_2\text{Cl}$ ($\text{R} = \text{Me}, \text{Et}, \text{Bu}$), have been prepared by the electrolysis of acetonitrile solutions of the appropriate dialkyltin dichloride on a mercury cathode.³¹⁷ The tin-tin bond in $(\text{SnClR}_2)_2$ ($\text{R} = \text{CH}(\text{SiMe}_3)_2$) is relatively $(2.844(1)\text{\AA})$.¹²⁹ The reaction of triorganotin oxides with formic acid provides a good route to hexaorganodistannanes. In addition, this route affords small quantities of several new linear polystannanes.³¹⁸ Pure dodecamethylcyclohexastannane and its perdeuterio analogue have

been prepared in high yield according to the route:

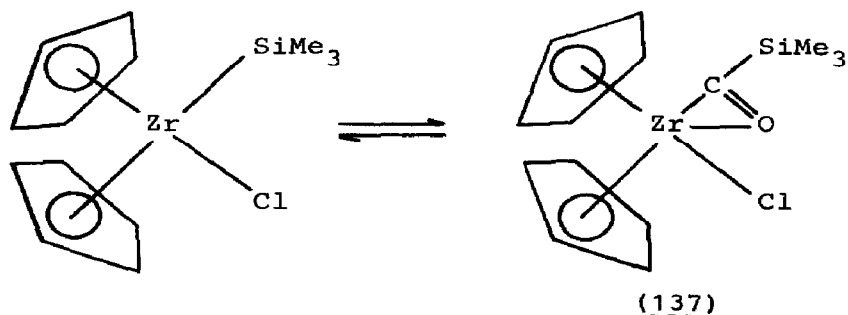


In solution, the cyclohexastannane equilibrates even at 20°C but more extensively at 80°C with three other cyclostannanes, $(\text{Me}_2\text{Sn})_n$ ($n = 5, 7$, and 8).³¹⁹ Controlled cleavage of $(\text{Bu}_2^t\text{Sn})_4$ with iodine in toluene solution affords the linear 1,4-diodotetrestannane, $\text{I}(\text{Bu}_2^t\text{Sn})_4\text{I}$, which has an all-trans structure in the crystal.³²⁰ Unsymmetrical diplumbanes have been synthesised from R_3PbLi and $\text{R}'_3\text{PbCl}$ at -60°C in tetrahydrofuran, although products exhibit migrations of R and R' in the transition state. Thus, the crystal structure of $\text{Pb}_2\text{Ph}_3(\text{p-tol})_3$ shows it to comprise two independent molecules of composition, $\text{Ph}(\text{p-tol})_2\text{PbPbPh}_2(\text{p-tol})$.³²¹ (Tricyclohexylstannayl)tricyclohexyllead has been synthesised from $(\text{C}_6\text{H}_{11})_3\text{PbLi}$ and $(\text{C}_6\text{H}_{11})_3\text{SnCl}$ in thf at -50°C, but decomposes at room temperature.³²² The reaction of trimethylstannylalkalies $(\text{Me}_3\text{SnM}, \text{M} = \text{Li}, \text{Na}, \text{K})$ with alkyl halides has been studied by two groups in several solvents. The reactions occur by electron-transfer processes involving radical intermediates.^{323,324} $(2,2,2\text{-crypt-K}^+)_3(\text{KSn}_9)^{3-}$ is the major product of the reaction of the ternary alloy KHgSn with 2,2,2-crypt in ethylenediamine. In addition to the cations, crystals contain infinite chains of composition $\text{K}-(\text{Sn}_9)-\text{K}-(\text{Sn}_9)-\dots$. The Sn_9 cluster has a mono-capped square antiprismatic structure.³²⁵ Mössbauer data have been recorded for $[\text{Sn}_5]^{2-}$, $[\text{Sn}_9]^{4-}$, $[\text{TlSn}_8]^{5-}$, $[\text{Sn}_2\text{Si}_2]^{2-}$, $[\text{SnSe}_4]^{4-}$, $[\text{SnTe}_4]^{4-}$ and $[\text{SnSe}_{3-x}\text{Te}_x]_z^{2z-}$ ($x = 0-3, z = 1, 2$) and the data interpreted in terms of known crystallographic information.³²⁶

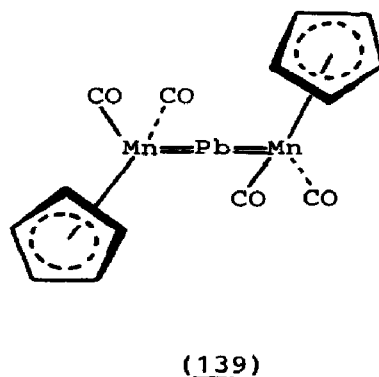
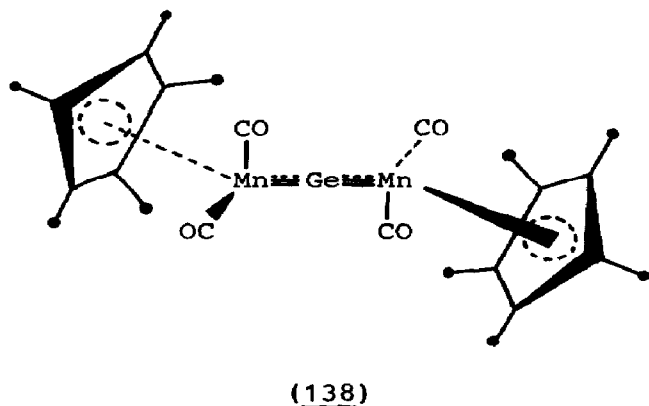
Product and kinetic studies on the reactions of $\text{Me}_3\text{SnMMe}_3$ ($\text{M} = \text{Si}, \text{Ge}, \text{Sn}$) with HCl in methanol show that both Sn-M and Sn-Me cleavage occur at similar rates and are followed by other reactions giving a complex mixture of products. Similar behaviour is observed for trifluoroacetolysis in CCl_4 solution, whereas that of $\text{Me}_3\text{SnC}(\text{CH}_3)_3$ results in exclusive Sn-Me cleavage.³²⁷ Reactions of $\text{Me}_3\text{SnMMe}_3$ ($\text{M} = \text{Si}, \text{Ge}$) with Me_3SnCl or Me_2SnCl_2 in methanol involve Sn-Me cleavage.³²⁸

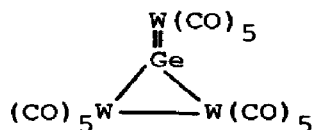
A large number of papers report chemistry of compounds with bonds to transition metals. Notable is the report of the reversible insertion of carbon monoxide into a silicon-zirconium

bond yielding the silaacyl complex (137):

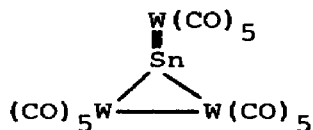


in which the silaacyl group is bonded to the zirconium atom in a bidentate fashion.³²⁹ Structures with 'naked' germanium and lead atoms have been described. The germanium complex (138) has been obtained by the hydride route from GeH_4 and $(\text{C}_5\text{Me}_5)\text{Mn}(\text{CO})_2(\text{THF})$ in the presence of sulphuric acid. In the crystal two conformers are present in a 1:1 ratio. The conformers are related by a 180° rotation of the $[(\text{C}_5\text{Me}_5)\text{Mn}(\text{CO})_2]$ fragment around the $[\text{Mn-Ge-Mn}]$ vector.³³⁰ The same synthetic strategy is unsuccessful in the case of lead. However, the lead analogue (139) was obtained using lead(II) chloride. The Mn-Pb-Mn unit is almost linear ($177.2(1)^\circ$).³³¹ Reaction of $\text{Na}_2\text{W}_2(\text{CO})_{10}$ with germanium(IV) or tin(IV) chlorides afford the complexes (140) and (141), respectively, which contain trigonally planar coordinated germanium and tin.³³² (141) reacts with THF to form (142) and with H_2Te to give (143).³³³

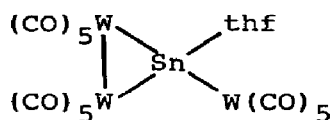




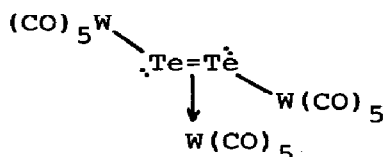
(140)



(141)



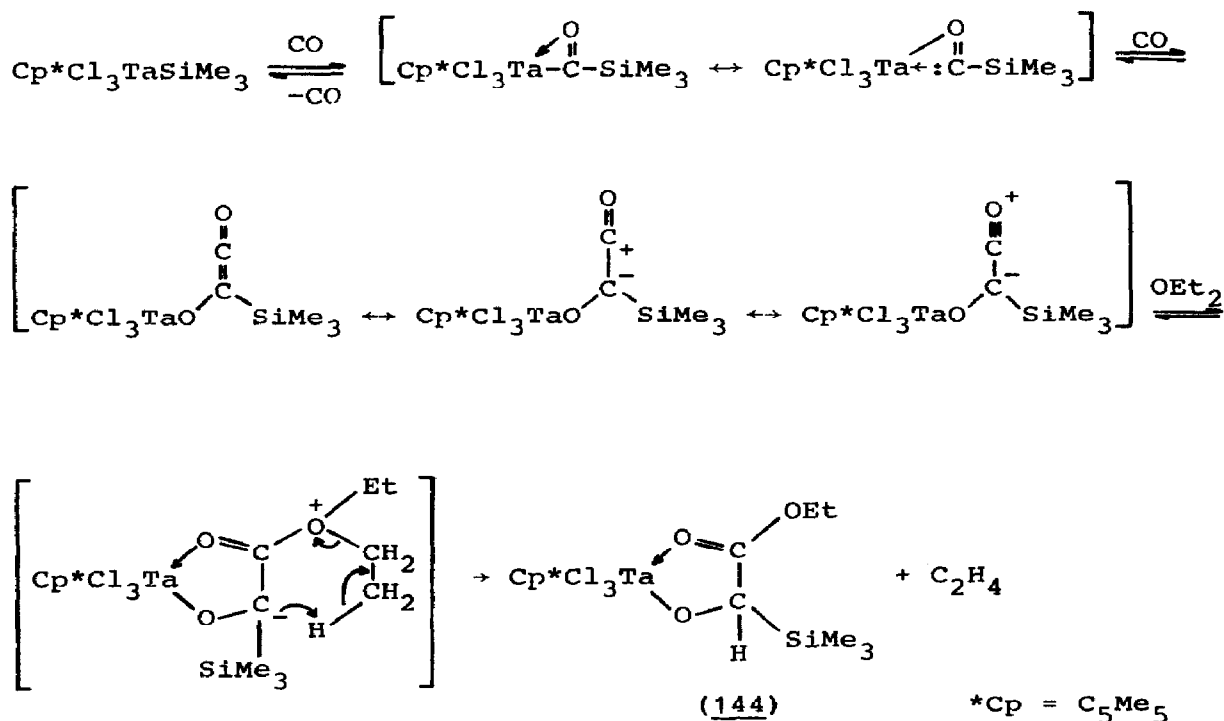
(142)



(143)

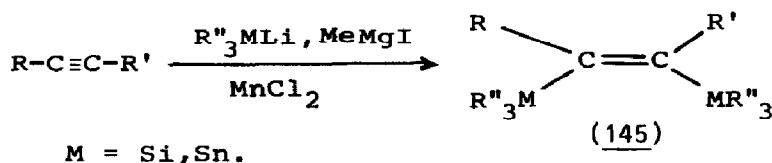
A wide variety of chemistry involving bonds between Main Group and Transition metals has been reported, and many complexes have been characterised by X-ray crystallography. The zirconium and hafnium complexes, $(\text{Cp})_2\text{M}(\text{SiMe}_3)\text{Cl}$ ($\text{M} = \text{Zr}, \text{Hf}$) have been obtained from the dichlorides $(\text{Cp})_2\text{MCl}_2$ and $\text{Al}(\text{SiMe}_3)_3 \cdot \text{OEt}_2$. The zirconium derivative reacts with oxygen to give the siloxide, $(\text{Cp})_2\text{Zr}(\text{OSiMe}_3)\text{Cl}$, whereas water cleaves the metal-metal bond. The chloride ligands are readily substituted to afford the complexes $(\text{Cp})_2\text{M}(\text{SiMe}_3)\text{X}$ ($\text{X} = \text{S}_2\text{CNET}_2, \text{BH}_4, \text{OCMe}_3$). In the structure of $(\text{Cp})_2\text{Zr}(\text{SiMe}_3)(\text{S}_2\text{CNET}_2)$, the silicon and two sulphur atoms are bonded to the zirconium in a plane which nearly bisects the two cyclopentadienyl rings.³³⁴ Photolysis of the manganese complexes $(\text{MeCp})(\text{CO})_2(\text{PR}_3)\text{Mn}$ with diphenylsilane or diethylsilane gives hydrido silyl complexes of the type $(\text{MeCp})(\text{CO})(\text{PR}_3)\text{Mn}(\text{H})\text{Si}(\text{H})\text{R}'_2$ containing Mn-H-Si three-centre bonds.³³⁵ Treatment of the thf complex, $(\text{C}_5\text{Me}_5)\text{Mn}(\text{CO})_2\text{thf}$, with monosilane similarly affords the dinuclear complex $(\mu\text{-SiH}_2)[(\text{C}_5\text{Me}_5)\text{Mn}(\text{CO})_2\text{H}]_2$, which has a bent Mn-Si-Mn framework. Thermolysis yields elemental hydrogen, but the other expected (unknown) complex $(\mu\text{-Si})[(\text{C}_5\text{Me}_5)\text{Mn}(\text{CO})_2]_2$ is not observed.³³⁶ Reaction of the tetraphenylporphyrinatotin complexes $(\text{TPP})\text{SnCl}_2$ with $\text{Hg}[\text{Mn}(\text{CO})_5]_2$ and $\text{Hg}[\text{Co}(\text{CO})_4]_2$ gives the complexes, $(\text{TPP})\text{Sn-Mn}(\text{CO})_4\text{-Hg-Mn}(\text{CO})_5$ and $(\text{TPP})\text{Sn-Co}(\text{CO})_3\text{-Hg-Co}(\text{CO})_4$. The structure of the former complex has been determined, and contains a bent four metal atom unit with one of the shortest Sn-Mn bonds

yet observed (2.554(7)Å). The tin lies about 0.85Å above the plane defined by the four nitrogen atoms of the porphyrin ring.³³⁷ Niobocene and tantalocene hydrides, Cp_2MH_3 ($\text{M} = \text{Nb}, \text{Ta}$) react with PhMe_2SiH to give $\text{Cp}_2\text{M}(\text{H}_2)\text{SiPhMe}_2$ complexes. The structure of the tantalum derivative was confirmed by X-ray crystallography. No Nb-Si complex was isolated using Et_3SiH , but Cp_2NbH_3 and $\text{Me}_3\text{SiOSiMe}_2\text{H}$ give low yields of $\text{Cp}_2\text{Nb}(\text{H})_2\text{SiMe}_2\text{OSiMe}_3$. Cp_2NbH_3 catalyses H/D exchange between Et_3SiH and C_6D_6 , and produces deuterated $[\text{Cp}(\mu-\eta^1, \eta^5-\text{C}_5\text{H}_4)\text{HNb}]_2$ as the major organometallic product.³³⁸ CO inserts in the Ta-Si bond of $(\text{C}_5\text{Me}_5)\text{Ta}(\text{SiMe}_3)\text{Cl}_3$ to give (144). A possible mechanism is shown in Scheme 23.³³⁹



Scheme 23

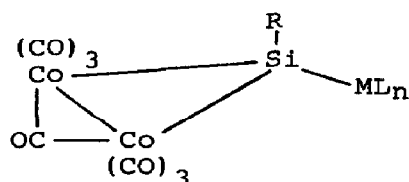
Acetylenes may be disilylated or distannylated using Si-Mn or Sn-Mn reagents:³⁴⁰



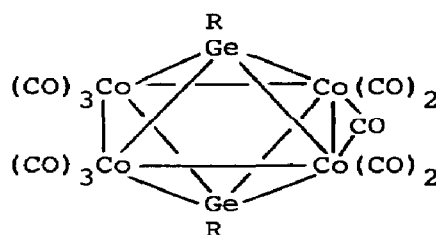
The method can be successfully applied to the synthesis of the highly strained tetrakis(trimethylsilyl)ethene (which is not readily available by other known routes) from $\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{SiMe}_3$. Reaction of the molybdenum complexes, $(\text{bipy})(\text{P})\text{Mo}(\text{CO})_3$ ($\text{bipy} = 2,2'$ -bipyridine; $\text{P} = \text{P}(\text{C}_6\text{H}_4\text{X}-4)_3$, $\text{X} = \text{Cl}, \text{F}, \text{Me}, \text{MeO}$), with SnCl_4 yield the novel seven-coordinate complexes, $(\text{bipy})(\text{P})(\text{CO})_2\text{Mo}(\text{Cl})(\text{SnCl}_3)$. Methyl- and phenyltin trichlorides behave similarly affording the dicarbonyl complexes, $(\text{bipy})(\text{P})(\text{CO})_2\text{Mo}(\text{Cl})(\text{SnRCl}_2)$, and $(\text{bipy})(\text{CO})_3\text{Mo}(\text{Cl})(\text{SnRCl}_2)$ ($\text{R} = \text{Me}, \text{Ph}$).³⁴¹ Crystals of the complex $(\text{C}_5\text{H}_5)_2\text{Mo}[\text{Me}_2\text{SnCl}]_2$, comprise two independent, isolated molecules containing Mo-Sn bonds of different lengths. The inequivalence of the distances within the molecules appears to be accounted for by the formation of a secondary intramolecular SnCl---Sn bond (Sn---Sn, 3.616Å; Cl---Sn, 2.89Å).³⁴²

The extent of reaction of the cobalt complexes $\text{Co}(\text{C}_5\text{H}_5)(\text{CO})(\text{X})\text{SnX}_3$ with CO in chloroform at 20°C and 1 atmosphere is markedly dependent on X. When $\text{X} = \text{Cl}$, the reductive elimination of SnCl_4 is complete within 30 minutes, and $\text{Co}(\text{C}_5\text{H}_5)(\text{CO})_2$ is formed almost quantitatively, but also reversibly. No detectable reaction occurs when $\text{X} = \text{I}$, but when $\text{X} = \text{Br}$ an intermediate solution is observed with both starting material and product present in the reaction mixture. In contrast, substitution reactions take place with both $(\text{PhO})_3\text{P}$ and $\text{Ph}_3\text{P}(\text{L})$ giving $\text{Co}(\text{C}_5\text{H}_5)(\text{L})(\text{X})(\text{SnX}_3)$. The course of the reactions of the complexes $\text{Co}(\text{C}_5\text{H}_5)(\text{L})(\text{X})(\text{SnX}_3)$ with CO depends upon the ligand L. When $\text{L} = \text{P}(\text{OPh})_3$ and $\text{X} = \text{Br}$, the sole product is $\text{Co}(\text{C}_5\text{H}_5)(\text{CO})_2$, but when $\text{L} = \text{Ph}_3\text{P}$ and $\text{X} = \text{Br}$ $\text{Co}(\text{C}_5\text{H}_5)(\text{CO})(\text{Br})(\text{SnBr}_3)$ and then some $\text{Co}(\text{C}_5\text{H}_5)(\text{CO})_2$ are formed. $\text{Co}(\text{C}_5\text{H}_5)(\text{PPh}_3)(\text{Cl})(\text{SnCl}_3)$ does not appear to react with CO.³⁴³ Reaction of the hydridosilyl-metal carbonyls, $\text{RSiH}_2\text{-ML}_n$ ($\text{ML}_n = \text{CrCp}(\text{CO})_3, \text{MoCp}(\text{CO})_3, \text{WCp}(\text{CO})_3, \text{FeCp}(\text{CO})_2, \text{Co}(\text{CO})_4$) (obtained from RSiH_2Br ($\text{R} = \text{Me}, \text{Ph}$) and carbonyl metalates) with $\text{Co}_2(\text{CO})_8$ produced the open trinuclear complexes $\text{R}(\text{ML}_n)\text{SiCo}_2(\text{CO})_7$ (146), but only for $\text{ML}_n = \text{MoCp}(\text{CO})_3, \text{WCp}(\text{CO})_3$ and $\text{FeCp}(\text{CO})_2$. Subsequent thermolysis of the molybdenum and tungsten complexes gave the mixed metal clusters, $\text{RSiCo}_2\text{MCp}(\text{CO})_8$.³⁴⁴ The trinuclear complexes $\text{RGeCo}_3(\text{CO})_9$ ($\text{R} = \text{Me}, \text{Ph}, \text{Bu}^t$) as well as the new tetranuclear clusters $(\text{RGe})_2\text{Co}_4(\text{CO})_{11}$ ($\text{R} = \text{Ph}, \text{Bu}^t$) (147) are formed in the reaction of organogermanium trihalides with

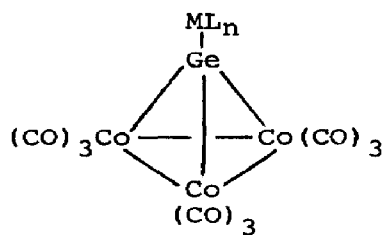
KCo(CO)_4 . The dinuclear complexes $\text{L}_n'\text{M-GeI}_2\text{-ML}_n$ ($\text{ML}_n = \text{FeCp(CO)}_2, \text{Co(CO)}_4, \text{NiCpCO}$) (from the insertion of GeI_2 into the metal-metal bonded precursor) also react with KCo(CO)_4 to form the clusters (148). Crystal structures were determined for both $\text{Cp(CO)}_2\text{Fe-GeCo}_3(\text{CO})_9$ and $(\text{Bu}^t\text{Ge})_2\text{Co}_3(\text{CO})_8\text{NiCp}$ confirming their structures.³⁴⁵ The germylidine clusters (149) ($\text{R} = \text{Me}, \text{Ph}, \text{Bu}^t$) open to form the complexes (150) on heating with CO under pressure. With PPh_3 , either addition to form (151) or substitution to give (152) occurs. Organometal dimethylarsenides $\text{Cp(CO)}_3\text{M-AsMe}_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) react similarly for $\text{R} = \text{Me}$ or Ph to yield the addition products (153) or for $\text{R} = \text{Bu}^t$ to give (154). Thermolysis of these complexes affords complexes such as (155)-(157).³⁴⁶ The clusters (158) and (159) are formed by reaction of $\text{RGeCo}_3(\text{CO})_9$ and $[\text{CpM(CO)}_3]_2$ ($\text{M} = \text{Mo}, \text{W}$).³⁴⁷



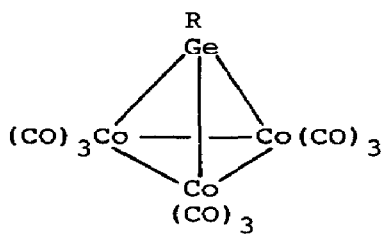
(146)



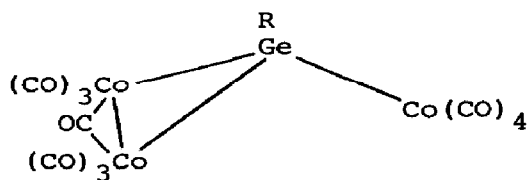
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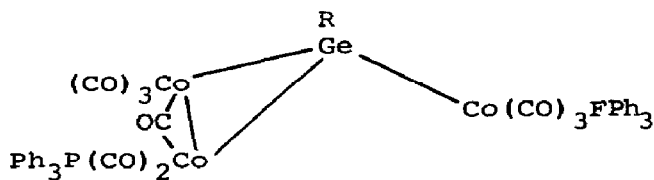
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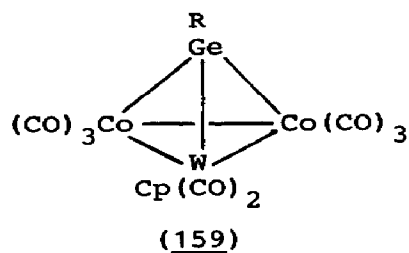
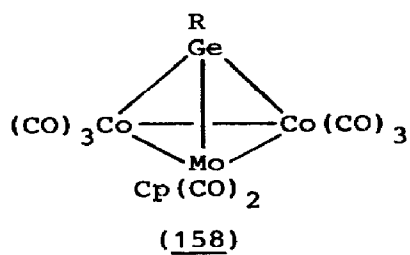
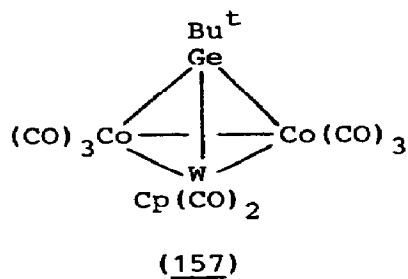
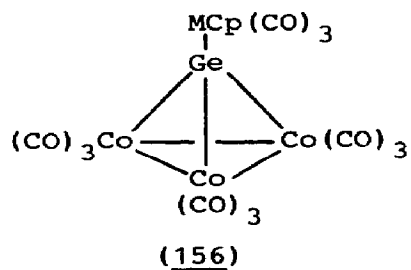
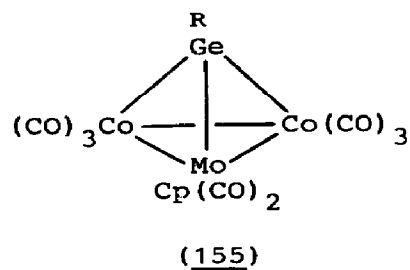
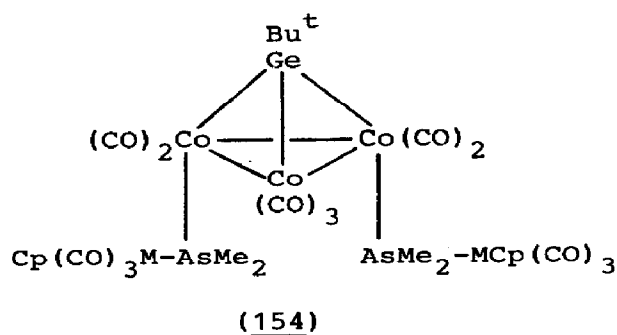
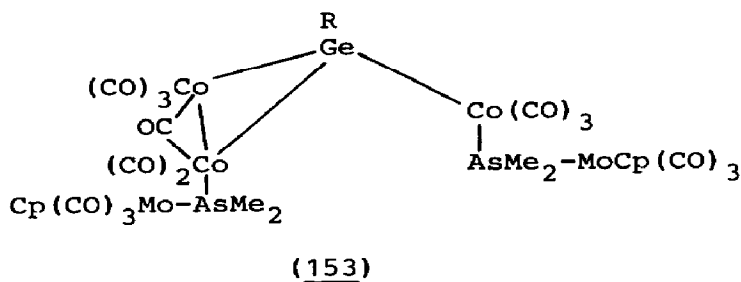
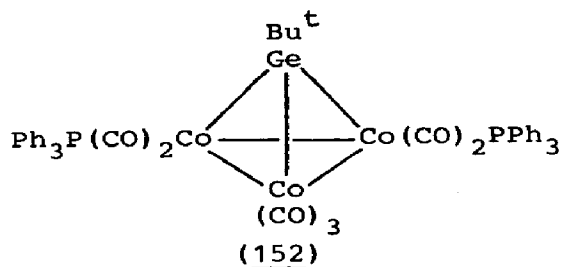
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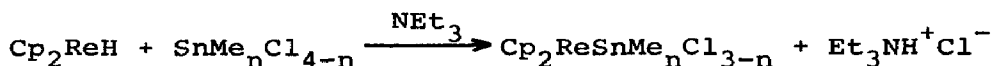
(150)



(151)



The electrochemical behaviour of the silyl- and stannyl clusters, $\text{PhMCo}_3(\text{CO})_n$ ($M = \text{Si}$, $n = 11$; $M = \text{Sn}$, $n = 12$), have been examined by cyclic voltametry in dichloromethane solution. In both cases the radical anions $\text{PhMCo}_3(\text{CO})_n^-$ are unstable and rearrange to the $\text{Co}(\text{CO})_4^-$ anion amongst other products. With the silyl cluster, however, the radical anion is sufficiently stable to allow detection of anion reoxidation at medium scan speeds. The half-life of $\text{PhSiCo}_3(\text{CO})_{11}^-$ was determined to be 2.3 s at 25°C.³⁴⁸ All Ge-Ge and Ge-H bonds are cleaved in the reaction of polygermanes or silylgermanes with $\text{Co}_2(\text{CO})_8$. Digermane gives the known complex $(\mu_4\text{-Ge})[\text{Co}_2(\text{CO})_7]$ together with the new compound, $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$, which is also formed from $\text{Me}_2\text{Si}(\text{GeH}_3)_2$. $\text{Me}_3\text{GeGeH}_3$ and $\text{Me}_3\text{SiGeH}_3$ form mainly $(\mu_4\text{-Ge})[\text{Co}_2(\text{CO})_7]$ and $\text{Me}_3\text{MCo}(\text{CO})_4$ ($M = \text{Si}$, Ge). $\text{Ge}_2\text{Co}_6(\text{CO})_{20}$ loses CO quantitatively at 50–60°C to give $\text{Ge}_2\text{Co}_6(\text{CO})_{10}$, whose structure comprises a quadrilateral of cobalt atoms bicapped by $\{\mu_4\text{-GeCo}(\text{CO})_4\}$ groups, and having one $\text{Co}(\text{CO})_2\text{-Co}(\text{CO})_2$ edge symmetrically bridged, the opposite $\text{Co}(\text{CO})_3\text{-Co}(\text{CO})_3$ edge unbridged, and the other two edges semibridged by CO.³⁴⁹ The Re-Sn bonded complexes $\text{Cp}_2\text{ReSnCl}_3$, $\text{Cp}_2\text{ReSnMeCl}_2$ and $\text{CpReSnMe}_2\text{Cl}$ have been synthesised according to the route:

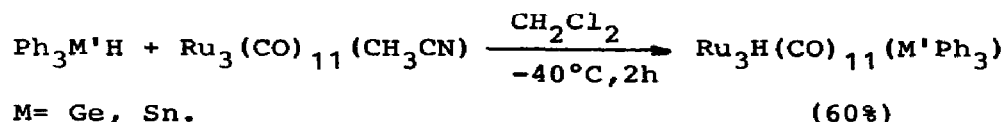
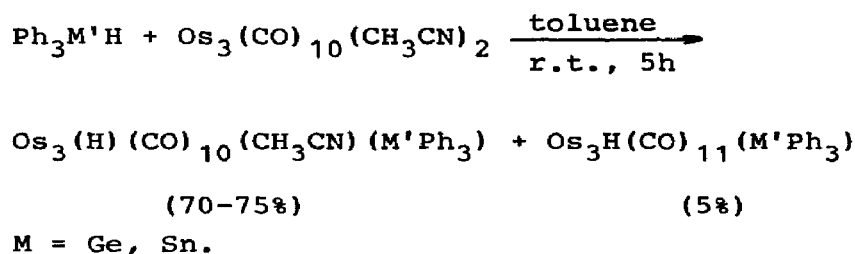
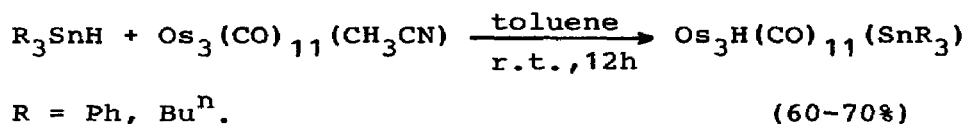
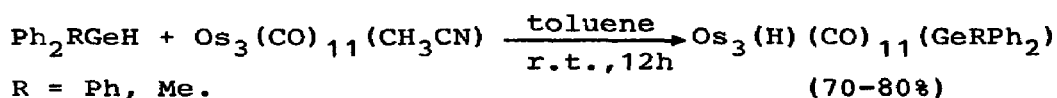


All three complexes exhibit a marked shortening of the metal-metal bond compared to the sum of the covalent radii and a sharp deviation of the $\{\text{SnMe}_n\text{Cl}_{3-n}\}$ fragment from tetrahedral geometry.³⁵⁰

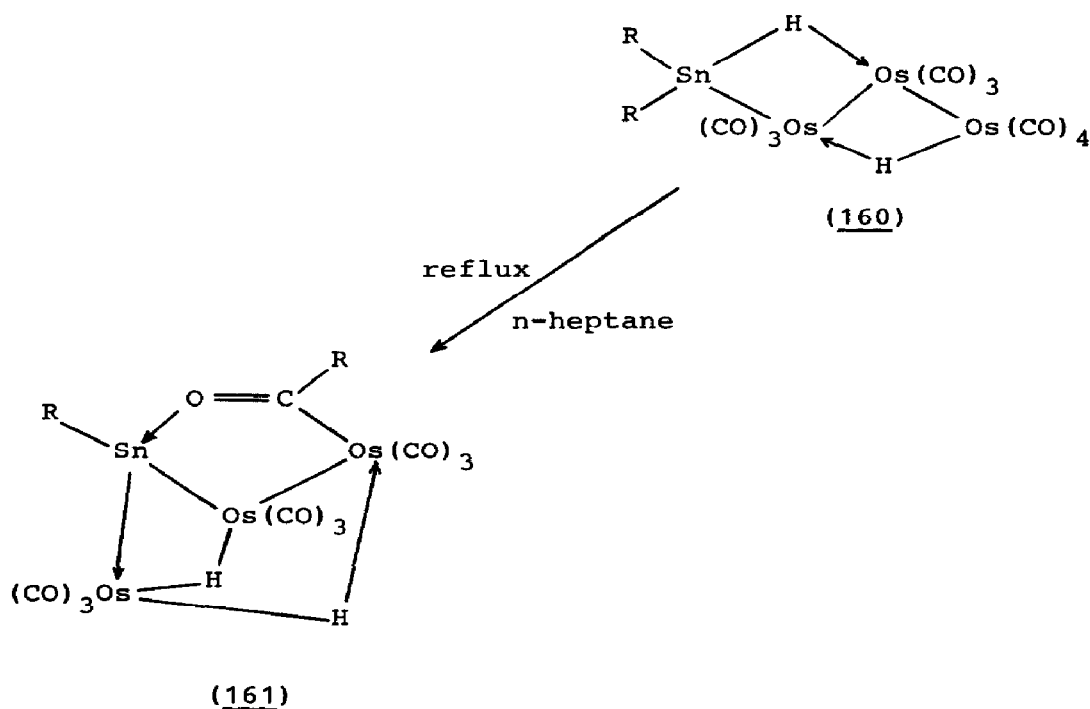
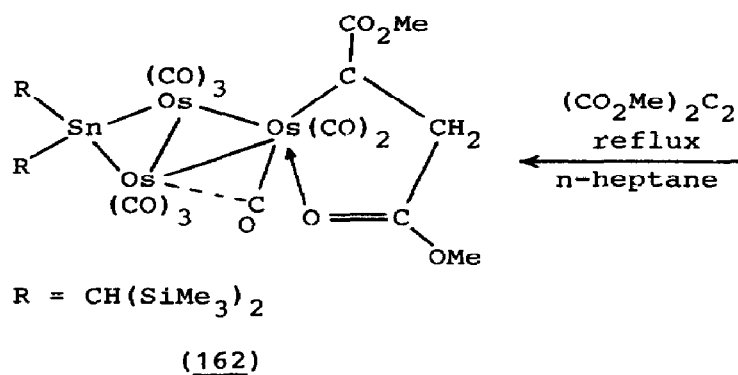
²⁹Si n.m.r. spectra of a large number of silyl derivatives of the iron-Group metals have been recorded, and several empirical relationships found:

- (i) for series of $\text{M}(\text{SiMe}_{3-n}\text{Cl}_n)$ ($n = 0-3$) compounds, MeSiMeCl_2 derivatives usually gave the ²⁹Si resonance to lowest field,
- (ii) for $\text{M}(\text{SiMe}_{3-n}\text{Cl}_n)$ complexes the ²⁹Si resonance shifts upfield on going to the transition metal (M) lower in the Periodic Table,
- (iii) for $\text{M}(\text{CO})_4(\text{SiMe}_{3-n}\text{Cl}_n)$ the resonance of the trans isomer came to lower field than that of the cis isomer, and
- (iv) for (arene) $\text{Ru}(\text{CO})(\text{SiCl}_3)_2$ there is a linear correlation

between the ^{29}Si chemical shift and the CO stretching frequency.³⁵¹ In the solid state, the three ruthenium atoms of the cluster anion, $[\text{HRu}_3(\text{CO})_{10}(\text{SiEt}_3)_2]^-$, form a triangle, the longest edge of which is bridged by the μ_2 -hydride. The triethylsilyl groups occupy equatorial positions at the two bridgehead ruthenium atoms. In solution, only the four carbonyl groups of the unbridged ruthenium atoms are fluxional, and the hydride bridge presumably undergoes a rocking movement perpendicular to the $[\text{Ru}_3]$ plane. At a platinum electrode, the anion is oxidized to give a neutral species.³⁵² Displacement of the (CH_3CN) ligand from the compounds $\text{M}_3(\text{CO})_{12-n}(\text{MeCN})$ ($n = 1$ or 2 ; $\text{M} = \text{Ru}, \text{Os}$) by organogermanes and -stannanes provides a general method for the preparation of triosmium- and triruthenium clusters of the type $\text{M}_3(\text{H})(\text{CO})_{11}(\text{M}^1\text{R}_3)$ and $\text{Os}_3(\text{H})(\text{CO})_{10}(\text{CH}_3\text{CN})-(\text{M}^1\text{R}_3)$ ($\text{M} = \text{Ru}, \text{Os}$; $\text{M}^1 = \text{Ge}, \text{Sn}$):³⁵³



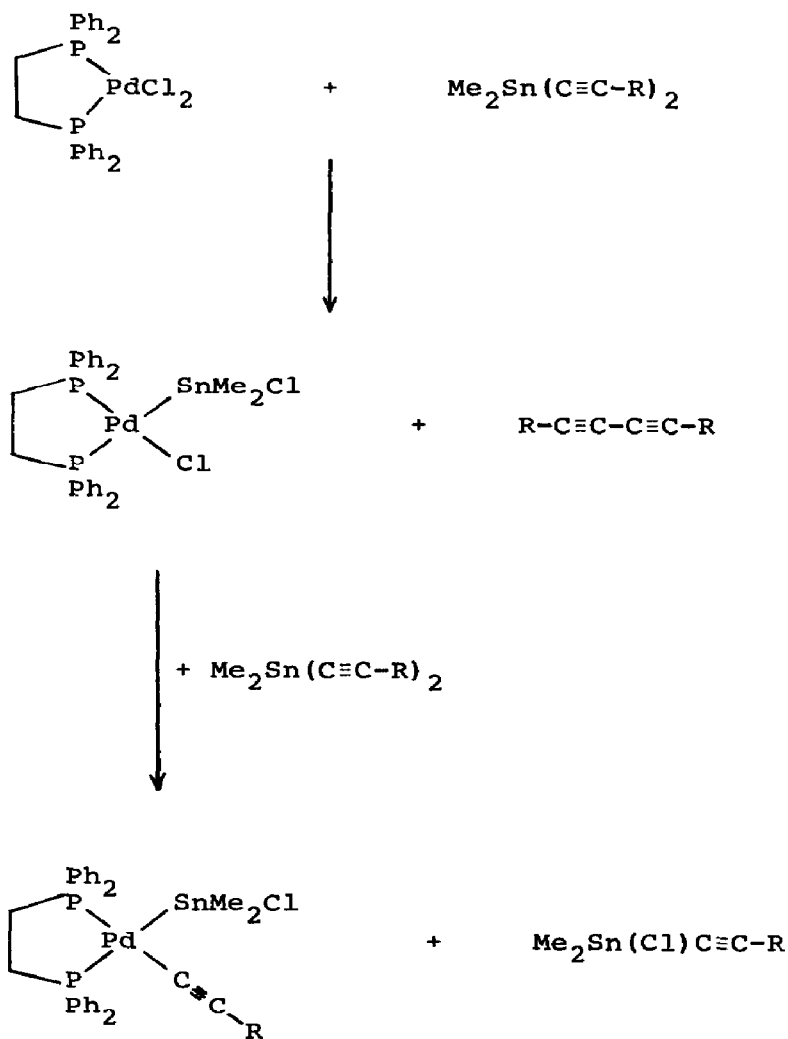
Two reactions of the osmium-tin cluster (160) have been reported:



(161) is obtained essentially quantitatively on heating (160) in heptane, whilst (162) is formed only in low yield.³⁵⁴

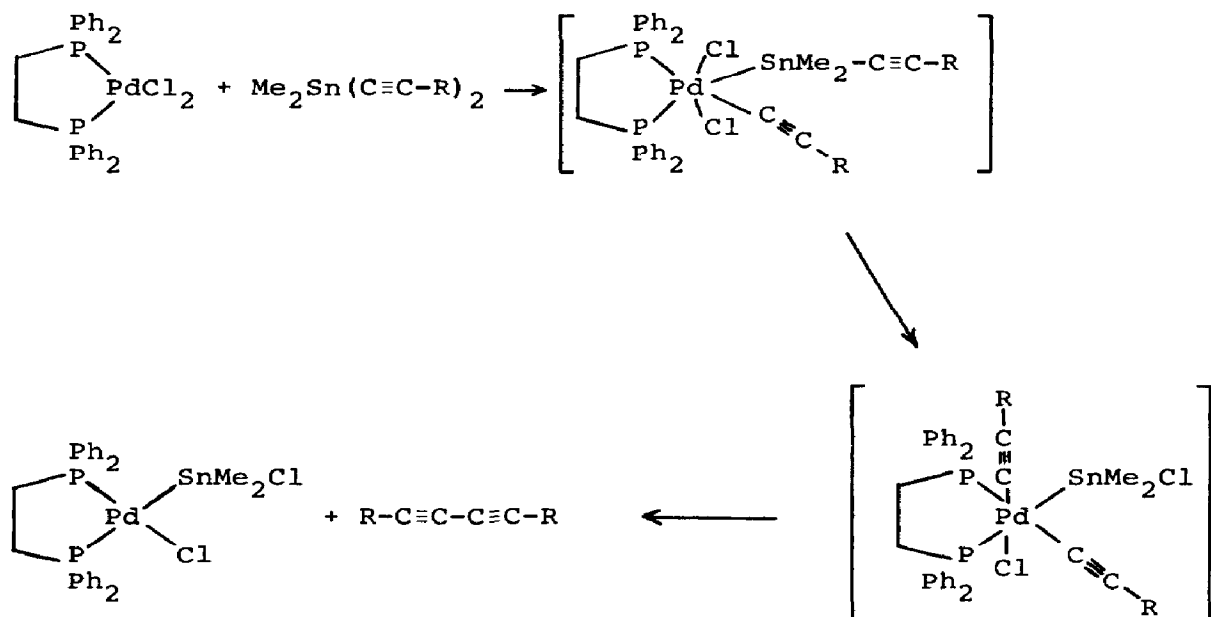
The reaction of $(\text{dppe})\text{PdCl}_2$ (dppe = bis(diphenylphosphino)-ethane) with bis(dialkynyl)stannanes yields diynes and the stable palladium(II)-stannyl complexes $(\text{dppe})\text{Pd}(\text{Cl})\text{SnMe}_2\text{Cl}$ and

$(dppe)Pd(C\equiv CR)SnMe_2Cl$ ($R = H, Me, Bu^t$) (Schemes 24 and 25).³⁵⁵



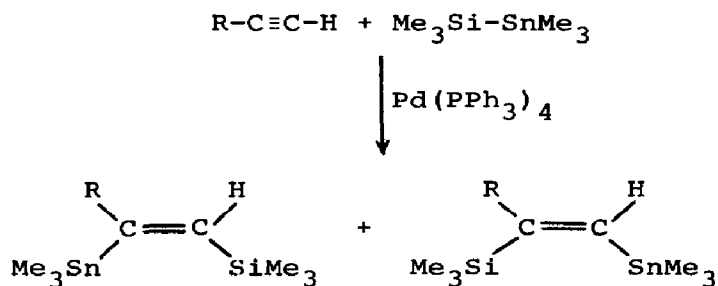
($R = H, Me, Bu^t$)

Scheme 24



Scheme 25

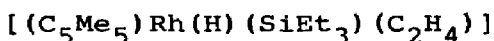
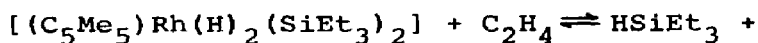
(Trimethylsilyl)trimethylstannane adds to alk-1-ynes in the presence of $\text{Pd}(\text{PPh}_3)_4$ both regio- and stereospecifically:



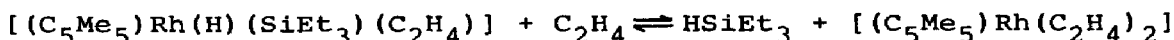
$\text{R} = \text{Bu}^n, \text{Ph}, \text{PhCH}_2, \text{Me}_2\text{NCH}_2, \text{MeOCH}_2, \text{HOCH}_2, \text{HOCHMe}, \text{HOCMe}_2,$
and HOCH_2CH_2 .

Regiospecific addition to 1,1-dimethylallene was also observed.³⁵⁶ The $[\text{RhH}(\text{SnCl}_3)_4\text{Cl}]^{3-}$ appears to be the predominant species initially present in the organic phase when rhodium(III) chlorides are extracted into 4-methylpentan-2-one from dilute hydrochloric

acid containing tin(II) chloride.³⁵⁷ The equilibria

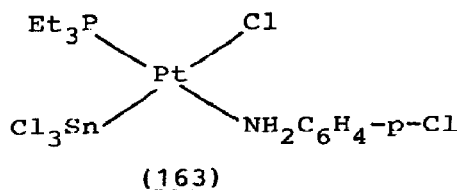


and

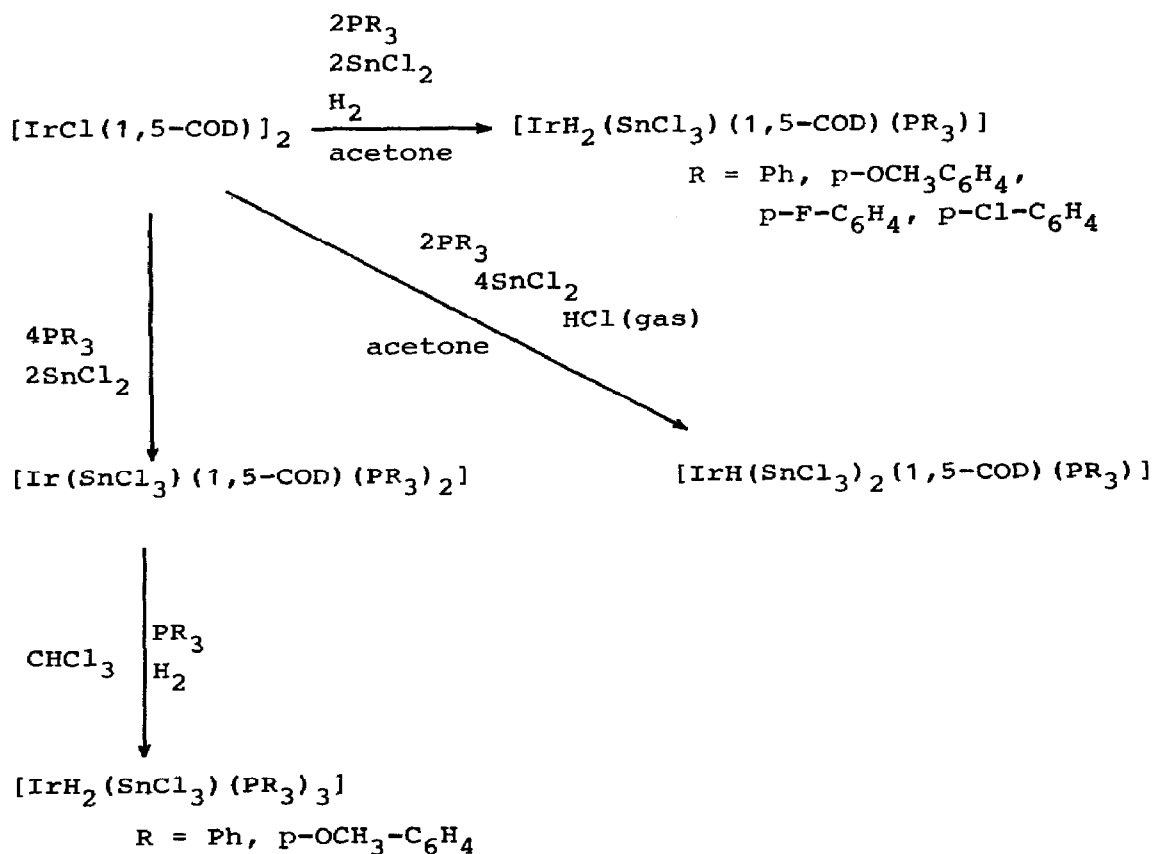


can be induced either thermally or photochemically starting from either side.³⁵⁸ The macrocycle $Rh_2(CO)_2Cl_2[\mu-(Ph_2P)_2py]_2$ reacts with tin(II) chloride to form the complex $Rh_2Sn_2(CO)_2Cl_6[\mu-(Ph_2P)_2py]_2$, the molecular core of which consists of the bent chain, $Rh-Sn-Rh-SnCl_3$. The central tin atom resides within the cavity of the macrocycle, and is coordinated to two nitrogens, two rhodium atoms, and one chloride.³⁵⁹ The role of alkyl derivatives of rhodium and platinum in homogeneous olefin hydrogenation and isomerisation has been discussed.³⁶⁰ The asymmetric hydroformylation of the three isomeric straight butenes catalysed by $[(R,R)\text{-Diop}]Pt(SnCl_3)Cl$ (Diop = 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane) has been reinvestigated. Depending on the conditions, hydroformylation can be accompanied by extensive isomerisation and hydrogenation of the substrate.³⁶¹ The trans- $[PtCl(CO\text{-}n\text{-hexyl})(PPh_3)_2]/SnCl_2$ has been investigated by ^{31}P n.m.r. In CD_2Cl_2 or acetone- d_6 two species are observed at low temperature in equilibrium with the starting complex. One is assigned as the complex trans- $[Pt(SnCl_3)(CO\text{-}n\text{-hexyl})(PPh_3)_2]$; the other shows no P-Sn coupling and is tentatively ascribed as a complex having chloride bridging platinum and tin centres. Formation of the former complex is prevented by adding ethanol to the solvent mixture.³⁶² ^{31}P , ^{119}Sn , and ^{195}Pt n.m.r. data for the similar complexes, trans- $[Pt(SnCl_3)(\text{carbon ligand})(PEt_3)_2]$ have been reported. Values of the one-bond coupling constant $^1J(^{119}Sn\text{-}^{195}Pt)$ vary from 2376Hz to 11895Hz, with the $COPh$ ligand having the smallest value, and the C_6Cl_5 ligand the largest. Trans- $[Pt(SnCl_3)(COPh)(PEt_3)_2]$ has a slightly distorted square planar geometry, and the longest Pt-Sn bond yet observed for square-planar Pt-SnCl₃ complexes. The Pt-Sn bond correlates well with the $^1J(^{119}Sn\text{-}$

^{195}Pt) values.³⁶³ $[\text{PtCl}(\text{SnCl}_3)(p\text{-chloroaniline})(\text{PEt}_3)]$ also has a slightly distorted square planar geometry, with the ligand disposed as in (163).³⁶⁴



The iridium(III) complexes, $[\text{Ir}(\text{H})(\text{SnCl}_3)_2(1,5\text{-COD})\text{L}]$, $[\text{Ir}(\text{H})_2(\text{SnCl}_3)(1,5\text{-COD})\text{L}]$, and $[\text{Ir}(\text{H})_2(\text{SnCl}_3)\text{L}_3]$ (L = tertiary arylphosphine) have been obtained according to Scheme 26, and characterised by n.m.r.



Scheme 26

The complexes $[\text{Ir}(\text{H})_2(\text{SnCl}_3)(1,5\text{-COD})\text{L}]$ exist as *cis,cis*- and *cis,trans*-(L *trans* to SnCl_3^-) isomers in solution. The three phosphine ligands in $[\text{Ir}(\text{H})_2(\text{SnCl}_3)(\text{PPh}_3)_3]$ are in a pseudo-meridional arrangement and the two hydrides mutually *cis*.³⁶⁵ The first direct observation of resolved ^7Li - ^1H coupling has been seen in the complexes, $(\text{C}_5\text{Me}_5)\text{Ir}(\text{H})_2(\text{SiMe}_3)\text{Li}(\text{pmdeta})$ and $(\text{C}_5\text{Me}_5)\text{Ir}(\text{H})_3\text{Li}(\text{pmdeta})$.³⁶⁶ A silyl-iridium(I) complex, $[\text{Ir}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiMe}_2)(\text{PPh}_3)(\text{CO})_2]$, has been isolated and characterised by X-ray crystallography. The silicon atom occupies an axial site in the five-coordinate geometry.³⁶⁷ A one-bond ^{51}V - $^{117,119}\text{Sn}$ coupling of 900Hz has been observed in the $[\text{CpV}(\text{SnCl}_3)(\text{CO})_3]^-$ anion.³⁶⁸

Bis(cyclopentadienyl)samarium and -lutetium chlorides react with Me_3SiLi in dme to give the complexes $[\text{Li}(\text{dme})_3][\text{Cp}_2\text{Ln}(\text{SiMe}_3)_2]$ (Ln = Sm, Lu). The structure of the samarium compound was determined.³⁶⁹

4.2.6 Binary and Ternary Chalcogenides and Pnictides

MAS ^{29}Si n.m.r. continues to be of immense value in the study of silicates. The large difference in the spin-lattice relaxation times allows the distinction of microcrystalline and non-crystalline regions in lithium silicate glass.³⁷⁰ The technique can also be used to demonstrate the uniqueness of zeolites of very similar structures, eg. ZSM-5 and ZSM-11,³⁷¹ and indicate phase transitions such as that occurring in ZSM-5 in the temperature range 295-363K.³⁷² Studies on (Di,Poly) calcium hydrogen silicate prove it to contain end and middle $[\text{SiO}_4]$ tetrahedra (di- and polysilicate) only.³⁷³ The two phases (α and δ) phases of phyllosilicic acids $(\text{H}_2\text{Si}_2\text{O}_5)_x$ can be distinguished by the different isotropic values of the chemical shift. The α -phase has a regular layer structure, while the δ -phase is characterised as a phyllosilicic acid with partial highly-condensed areas. Compared with the α -phase, the Si-OH groups in the δ -phase form weaker hydrogen bonds.^{374,375} Two intermediate phases have been identified in the dehydration of afwillite, $\text{Ca}_3(\text{SiO}_3\text{OH})_2 \cdot 2\text{H}_2\text{O}$. A non-crystalline phase with a structure similar to the mineral killalaite, $\text{Ca}_3\text{OH}(\text{Si}_2\text{O}_6\text{OH})$ is formed at 250-300°C. Between 300 and 500°C, this compound is converted to a non-crystalline kilchoanito-like phase $\gamma\text{-Ca}_2\text{SiO}_4 \cdot \text{Ca}_4\text{Si}_3\text{O}_{10}$, consisting of ordered $\gamma\text{-Ca}_2\text{SiO}_4$ and

disordered trisilicate layers.³⁷⁶ The new silicic acid trimethylsilylester, $(\text{Me}_3\text{Si})_{14}\text{Si}_7\text{O}_{21}$, has been obtained by the trimethylsilylation of barium chloride silicate, $2\text{BaO} \cdot 3\text{BaCl}_2 \cdot 2\text{SiO}_2$.³⁷⁷ Polysilicate equilibria have been studied in a 0.6 mol dm^{-3} NaCl medium at 25°C . Besides a dimer, $\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$, a cyclic $\text{Si}_3\text{O}_6(\text{OH})_3^{3-}$ and linear $\text{Si}_3\text{O}_5(\text{OH})_5^{3-}$ trimer are formed, but the prevailing polysilicate is tetrameric.³⁷⁸ Species with higher nuclearities are formed in minor amounts. Upto 16 different oligomeric silicate anions have been detected and quantitatively estimated in 0.1M – 3M tetrapropylammonium and tetraethylammonium silicate solutions.³⁷⁹ The organosilicomolybdate complex anions, $\text{R}_3\text{SiOMoO}_3^-$ ($\text{R} = \text{Ph}, \text{Bu}^t$) have been proposed as models for silica-supported MoO_3 catalysts,³⁸⁰ whilst the polysilicic acid ester, $[\text{Si}_8\text{O}_{12}](\text{OMe})_8$, has been synthesised as a molecular building block for the synthesis of ceramic materials.³⁸¹ The structures of both compounds have been determined. Light-blue manganese-doped monocrystals of Ca_2SiO_4 have been grown from a CaCl_2 flux using raw mixes ($2\text{CaCO}_3 + 1\text{SiO}_2$) with different contents of MnCO_3 .³⁸² Annealing of such crystals at temperatures in excess of 1450°C causes decolourization.³⁸³ Crystals of $\text{Na}_2\text{CaSi}_2\text{O}_6$ contain puckered six-membered $[\text{Si}_6\text{O}_{18}]^{12-}$ rings of silicate tetrahedra.³⁸⁴ Both $\text{Rb}_2\text{Li}_2\text{SiO}_4$ and $\text{Rb}_2\text{Li}_2\text{GeO}_4$ have been prepared from the respective binary oxides at 800°C and 850°C , respectively.³⁸⁵ Single crystals of K_2GeO_3 have been prepared by heating K_2O and GeO_2 ($\text{K}:\text{Ge} = 3.0:1.0$) in a silver cylinder at 700 – 800°C for 10 days.³⁸⁶ The structures of two phases of BaGe_2O_5 have been determined. The low pressure, high temperature phase ($\text{BaGe}_2\text{O}_5(\text{II})$) has three kinds of parallel chains of germanate polyhedra, whilst the high pressure, low temperature phase ($\text{BaGe}_2\text{O}_5(\text{III})$) has a sheet structure.³⁸⁷ Opaque blue crystals of a new mixed-valence cerium germanate containing $[\text{GeO}_4]^{4-}$, $[\text{Ge}_2\text{O}_7]^{6-}$ and $[\text{Ge}_3\text{O}_{10}]^{8-}$ anions, have been prepared at 1555K .³⁸⁸ New modifications of the phases PbGeO_3 and $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ have been obtained by the simultaneous hydrolysis of lead and germanium aloxides, followed by washing and drying. These modifications are transformed to the known monoclinic and hexagonal modifications, respectively, at temperatures of 575 – 610°C and 410 – 450°C .³⁸⁹

The disproportionation of tin(II) oxide has been investigated in the temperature range 200 – 750°C and over various time periods.

Reaction starts at about 250°C producing metallic tin and an intermediate oxide of formula Sn_3O_4 . This intermediate slowly decomposes in the temperature range 425–550°C to tin metal and SnO_2 . At temperatures in excess of 550°C the disproportionation products are the thermodynamically stable phases Sn and SnO_2 .³⁹⁰ The effects of heat treatments in air or water at high pressure on an hydrous tin(IV) oxide ion exchanger have been studied. The exchanger in the H^+ form is stable in both air and water up to ca. 80°C, but above this the exchange capacity progressively decreases with temperature, being only about one quarter of the initial value at 300°C. Crystallisation begins at 300°C, forming cassiterite crystals by 500°C. In contrast, the Na^+ form of the exchanger is more stable, and retains 40% of the initial capacity at 400°C.³⁹¹ Metal hexahydroxystannates, $\text{MSn}(\text{OH})_6$ ($\text{M} = \text{Mg}, \text{Co}, \text{Zn}, \text{Mn}, \text{Cd}, \text{Ca}, \text{Sr}, \text{Ba}$), and their solid solutions have been prepared by coprecipitation from aqueous solutions of $\text{Na}_2\text{Sn}(\text{OH})_6$ and MCl_2 . Decompositions of these salts afforded MSnO_3 materials. The structure of $\text{MSn}(\text{OH})_6$ depends strongly on the radius of the M^{2+} ions, being cubic with a NaCl-type structure below 1.26Å and hexagonal above 1.26Å. Crystalline MSnO_3 were obtained by calcination above 500–600°C, and their structure is also related to the cation radius, having an ilmenite-type structure below 1.09Å and a perovskite-type above 1.14Å.³⁹² Both the high-temperature and low-temperature polymorphs of LiFeSnO_4 with ramsdellite-related structures undergo lithium insertion reactions with $n\text{-BuLi}$ at ambient temperatures to stoichiometries $\text{Li}_2\text{FeSnO}_4(\text{HT})$ and $\text{Li}_{1.8}\text{FeSnO}_4(\text{LT})$.³⁹³ The formation of tin-molybdenum oxides by the calcination of precipitates involves the initial dehydration of amorphous gels to give, at low temperatures, highly disordered rutile-type solids capable of accommodating high concentrations of molybdenum. Excess molybdenum segregates, under the influence of moderate thermal treatment, from the crystallising rutile-type phase to form macroscopically distinguishable MoO_3 which volatilises at higher temperatures. Prolonged calcination at high temperatures gives materials which may be described as solid solutions containing low concentrations of Mo(V) in the SnO_2 rutile-type lattice.³⁹⁴ Alkylamines intercalate into the $\text{Sn}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ layer structure. n -Alkylamines intercalate as a bimolecular film of extended molecules with the carbon chain backbone roughly inclined at 66°C

to the plane of the sheet. Infrared spectra and thermal data suggest that the alkylamines exist as alkylammonium ions within the layers. The intercalate $[\text{Sn}(\text{nBuNH}_2)_2](\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ readily exchanges transition metal ions.³⁹⁵ Tin(IV) selenophosphate has been synthesised by mixing aqueous solutions of tin(IV) chloride, sodium selenite, and sodium dihydrogenphosphate in a 1:1:2 ratio at pH = 0.³⁹⁶

The structure of $\text{Pb}_3\text{O}_2(\text{OH})_2$ has been determined by Rietveld analysis of neutron powder diffraction data. The solid comprises discrete dodecahedral clusters with composition $\text{Pb}_6\text{O}_4(\text{OH})_4$ and $\bar{4}$ symmetry, and connected by hydrogen bonds.³⁹⁷ The structures of two modifications of PbV_2O_6 , monoclinic and (metastable) orthorhombic, have been determined. The former comprises columns of edge-sharing $[\text{VO}_5]$ square pyramids in between which are dispersed the lead atoms. The latter has a structure with zig-zag chains of corner sharing $[\text{VO}_4]$ tetrahedra with the lead atoms in parallel planes.^{398,399} Single crystals of PbRe_2O_6 , obtained from a stoichiometric mixture of PbO and ReO_3 at 500°C , are isotypic with the trigonal modification of PbNb_2O_6 , and contain the $[\text{Re}_2\text{O}_{10}]$ unit.⁴⁰⁰ The cubic pyrochlore $\text{Pb}_2^{\text{II}}[\text{Li}_{0.5}\text{Sb}_{1.5}]\text{O}_{6.5}$ has been characterised.⁴⁰¹ The complex phosphate $\text{Pb}_2\text{Cs}_3(\text{P}_4\text{O}_{12})(\text{PO}_3)_2$ contains a tetrameric cyclic $(\text{P}_4\text{O}_{12})^{4-}$ ion and a linear infinite $(\text{PO}_3)_\infty$ chain.⁴⁰²

Some 45 new polytypes of SnS_2 ,^{403,404} as well as 6 large period polytypes of SnSe_2 ,⁴⁰⁵ have been characterised. The oxysulphide of lanthanum and tin, $(\text{LaO})_4\text{Sn}_2\text{S}_6$, comprises alternating independent layers of $(\text{LaO})_n$ and $(\text{SnS})_{3n}$ parallel to the (001) plane. The tin has a distorted octahedral environment.⁴⁰⁶ $\text{Ba}_3\text{CdSn}_2\text{S}_6$ and $\text{Ba}_6\text{CdAg}_2\text{Sn}_4\text{S}_{16}$ are isotypic.⁴⁰⁷ Both Ba_2SiSe_4 and Ba_2SiTe_4 are isotypic with Sr_2GeS_4 . The latter is the first telluridosilicate with discrete $[\text{SiTe}_4]^{4-}$ anions.⁴⁰⁸ In $\text{Na}_6\text{Si}_2\text{Se}_8$, two $[\text{SiSe}_4]$ tetrahedra are connected by a Se-Se covalent bond, forming a discrete $[\text{Si}_2\text{Se}_8]^{6-}$ anion.⁴⁰⁹ $\text{Na}_4\text{Si}_4\text{Se}_{10}$ contains adamantane-like $[\text{Si}_4\text{Se}_{10}]^{4-}$ anions.⁴¹⁰ Na_4GeSe_4 (from Na_2Se , Ge and Se at 750°C) contains discrete, almost regular tetrahedral, $[\text{GeSe}_4]^{4-}$ anions.⁴¹¹ Na_2GeSe_3 is isotypic with Na_2GeSe_3 , and contains infinite chains of corner-sharing $[\text{GeSe}_4]$ tetrahedra. The structure of $\text{Na}_8\text{Ge}_4\text{Se}_{10}$ is analogous to that of $\text{Na}_8\text{Ge}_4\text{Te}_{10}$ (modification I), with two octahedral $[\text{Ge}_2\text{Se}_6]$ units connected by a common edge to form a

$[\text{Ge}_4\text{Se}_{10}]^{8-}$ anion (of the silicon analogue above).⁴¹⁰ The zintl anions, SnX_3^{2-} and SnX_4^{4-} ($\text{X} = \text{Se}, \text{Te}$) have been obtained by extraction of the appropriate Zintl $\text{KM}(\text{Te/Se})$ or $\text{NaM}(\text{Te/Se})$ phase with ethylenediamine or liquid ammonia in the presence of 2,2,2-crypt. SnX_3^{2-} are trigonal-planar and SnX_4^{4-} tetrahedral.⁴¹² The ternary phosphides $\text{Na}_{10}\text{M}_2\text{P}_6$ ($\text{M} = \text{Si}, \text{Ge}$) contain $[\text{MP}_4]$ tetrahedra connected by a common edge giving $[\text{M}_2\text{P}_6]^{10-}$ anions.⁴¹³ In contrast the $[\text{Sn}_2\text{As}_6]$ anions in $\text{Ca}_5\text{Sn}_2\text{As}_6$ are made up of corner-sharing $[\text{SnAs}_4]$ tetrahedra.⁴¹⁴

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