Coordination Chemistry Reviews, 30 (1979) 137—233

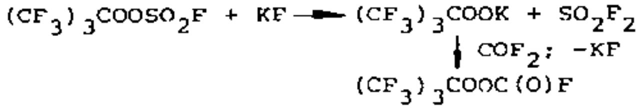
Chapter 4

ELEMENTS OF GROUP 4

P.G. Harrison

4.1 CARBON

The chemistry of perfluoromethyl compounds has aroused interest during 1978. Several new perfluorinated peroxides have been synthesised. The fluoroformyl peroxide, $(CF_3)_3COOC(O)F$, is obtained by nucleophilic substitution of $(CF_3)_3COOSO_2F$ affording the potassium peroxide, $(CF_3)_3COOK$, followed by reaction with carbonyl fluoride:



$$\begin{array}{l} (CF_3)_3COOSO_2F + KF \longrightarrow (CF_3)_3COOK + SO_2F_2 \\ \qquad\qquad\qquad\qquad\qquad\quad \downarrow COF_2;\ -KF \\ \qquad\qquad\qquad\qquad\qquad (CF_3)_3COOC(O)F \end{array}$$

The peroxide $(CF_3)_3COOC(O)OCF_3$ is also obtained via a side-reaction. Other peroxides may be synthesised from $(CF_3)_3COOC(O)F$. Thus, reaction with caesium fluoride at -78°C yields $(CF_3)_3COOCF_2OF$, caesium fluoride and chlorine fluoride at -78°C give the unstable chloro-analogue, $(CF_3)_3COOCF_2OC\ell$, which decomposes at -65°C to $(CF_3)_3COOC\ell$ and COF_2, and hydrolysis at 0°C affords the parent peracid, $(CF_3)_3COOH$.[1] The preparation of the corresponding peroxyl fluoride, $(CF_3)_3COOF$, is achieved by the reaction of fluorine with the $(CF_3)_3COO^-$ anion, generated as before, at low temperatures, and reacts with $KOC(CF_3)_3$ to form the unstable trioxide, $(CF_3)_3COOOC(CF_3)_3$. Addition of $(CF_3)_3COOF$ to the alkene $CF_2CFC\ell$ proceeds by a free-radical mechanism to afford both possible isomeric products:[2]

$$\begin{array}{l} (CF_3)_3COOF + CF_2CFC\ell \longrightarrow (CF_3)_3COOCF_2CF_2C\ell \\ \qquad\qquad\qquad\qquad\qquad\qquad + (CF_3)_3COOCFC\ell CF_3 \end{array}$$

Bis(trifluoromethyl)phosphoryl-μ-oxo-bis(trifluoromethyl)phosphine, $(CF_3)_2P(O)OP(CF_3)_2$, the mixed anhydride of a phosphinous and a phosphinic acid, has been prepared in quantitative yield by the reaction:

$$(CF_3)_2P\ _2O + (CF_3)_2P(O)C\ell \longrightarrow (CF_3)_2P(O)OP(CF_3)_2 + (CF_3)_2PC\ell$$

which probably proceeds via the formation of $(CF_3)_2P(O)O(O)P(CF_3)_2$, and is subsequently reduced by $[(CF_3)_2P]_2O$. The same mixed anhydride is also produced by the reaction of $P_2(CF_3)_4$ with nitric oxide in the gas phase at 50°C. The yield by this method is also high (84%) since further oxidation by nitric oxide is difficult. However, in the liquid phase only $(CF_3)_2P(O)O(O)P(CF_3)_2$ (90%) and no $(CF_3)_2P(O)OP(CF_3)_2$ is formed. Cleavage of the mixed anhydride by $HC\ell$ at 20°C takes place at the phosphinyl-oxygen bond yielding $(CF_3)_2PC\ell$ and $(CF_3)_2POOH$. The reaction with KC proceeds similarly. With $Ni(CO)_4$ at 25°, CO is lost, but the exact nature of the nickel product was not fully determined.[3]

The thermal decomposition of CF_3CN diluted to 0.2 and 0.5 mol % in argon behind incident shock waves over the temperature range 2450-3610K gives C_2F_6, C_2N_2, C_2F_4 and a trace of FCN. The course of the primary process of decomposition:

$$CF_3CN + Ar \longrightarrow CF_3 + Ar + CN$$

was followed by monitoring the CN(0-1) violet absorption centred at 421.5nm, and the rate constants so obtained were interpreted by classical collision theory, afforded a value of the dissociation energy $D_0(CF_3\text{-}CN)$ of 102.7 kcal mol^{-1}. The formation of C_2F_4 and FCN as minor products are strongly suggestive of subsequent decomposition of CF_3 to CF_2 and F.[4] The photolysis of $(CF_3)_2CO\text{-}CH_4$ mixtures at 313nm at temperatures in the range 298-443K yields CF_3H and C_2F_6, as well as the four oxygen-containing products, CH_3COCF_3, $(CF_3)_3COH$, $(CF_3)_2(CH_3)COH$ and $(CF_3)_2(CH_3)COCF_3$, produced according to the radical mechanism:[5]

$$(CF_3)_2CO \xrightarrow{h\nu} 2CF_3 + CO$$
$$2CF_3 \longrightarrow C_2F_6$$
$$CF_3 + CH_4 \longrightarrow CF_3H + CH_3$$
$$CF_3 + (CF_3)_2CO \longrightarrow (CF_3)_3CO$$
$$(CF_3)_3CO + CH_4 \longrightarrow (CF_3)_3COH + CH_3$$
$$CH_3 + (CF_3)_2CO \longrightarrow (CF_3)_2(CH_3)CO$$
$$(CF_3)_2(CH_3)CO \longrightarrow CF_3COCH_3 + CF_3$$
$$(CF_3)_2(CH_3)CO + CH_4 \longrightarrow (CF_3)_2(CH_3)COH + CH_3$$
$$(CF_3)_2(CH_3)CO + CF_3 \longrightarrow (CF_3)_2(CH_3)COCF_3$$

Attempts have been made to study the kinetics of the reaction of atomic hydrogen with $(CF_3)_2CO$ vapour. Atomic hydrogen was generated from dihydrogen by Hg-photosensitization in the presence of C_2H_4 and $(CF_3)_2CO$, but the system was complicated by the loss of C_2H_5 radicals by addition to $(CF_3)_2CO$ making the kinetic results intractable.

When the atomic hydrogen was generated from C_3H_8, the kinetics were again obscured by some unidentified reactions which became more important at higher $[(CF_3)_2CO]/[C_3H_8]$ ratios. An estimate of the rate constant for the addition of H to $(CF_3)_2CO$ was possible at low $[(CF_3)_2CO]/[C_3H_8]$ ratios, and the value $8.5 \times 10^5\ \ell mol^{-1} s^{-1}$ was deduced. Among the reaction products, only CF_3CHO could be identified with any reliability; many of the heavier products remained unidentified.[6]

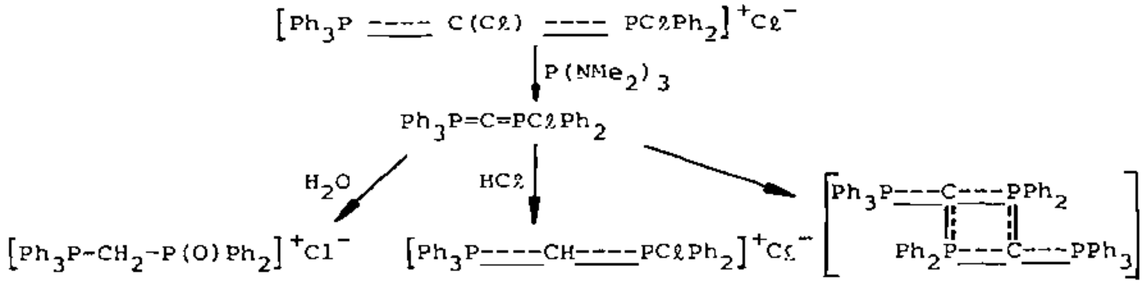
Carbon tetrachloride reacts with tertiary phosphines to give chloromethine-bridged phosphonium salts:[7]

$$3R_2R'P + CC\ell_4 \longrightarrow [R_2R' \underline{----} C(C\ell) \underline{----} PR'R_2]^+C\ell^- + R_2R'PC\ell_2$$

R = R' = Et, Bu

R = Et, R' = Ph

Dechlorination of the analogous chlorophosphonium salt, $[Ph_3P \underline{----} C(C\ell) \underline{----} PC\ell\,Ph_2]^+C\ell^-$, by tris(dimethylamino)phosphine yields the thermally unstable, but isolable double ylid, $Ph_3P{=}C{=}PC\ell Ph_2$, which gives other phosphonium salts by dimerisation and reaction with water and $HC\ell$:[8]



The structures of cis-1,2-difluoroethene,[9] ethyl methyl ether,[10] and ethyl methyl thioether[11] have been examined in the gas phase by electron diffraction. The relative abundances of the trans and gauche conformers in the gas phase at 20°C for the two latter compounds, given by $n_t/(n_t + n_g)$, are 0.80(8) for EtOMe, but only 0.25(15) for EtSMe. The barrier heights to internal rotation in CH_3SeCN and CD_3SeCN have been deduced to be 1241 ± 50 and 1228 ± 50 cal mol^{-1}, respectively, from an examination of their microwave rotational spectra.[12] The vibrational data for $F_3C{-}C{\equiv}C{-}C{\equiv}C{-}CF_3$ fit D_{3d} selection rules establishing that the molecule possesses a linear carbon skeleton. The CF_3 groups rotate freely in the vapour phase, but conformers exist in the liquid and solution phases.[13] Microwave data for three isotopomers of carbonyl chloride have also been reported, yielding structural parameters [C–Cℓ=1.7401(8)Å, C–O=1.1794(17)Å, Cℓ–C–Cℓ=111.93(8)°] which are rather different from the previously reported values.[14]

The crystal structures of three more oxalate anions, methyl oxalate,[15] S-methyl monothiooxalate,[15] and S,S'-dimethyl trithiooxalate,[16] have been determined. All three are approximately planar, and the ester groups, which are in mutually trans positions in the latter, have the normal Z conformation.

Albano and his coworkers have reported the structures of two complex metal carbide species, neutral [$Ru_{12}C_2(CO)_{25}$] (formed from the rather unstable [$Rh_6C(CO)_{15}$]$^{2-}$ anion)[17] and anionic [$Co_8C(CO)_{18}$]$^{2-}$ with $Co_4(CO)_{12}$ in isopropanol at 60°.[18] [$Rh_6C(CO)_{15}$]$^{2-}$ comprises a central asymmetric metal atom cluster, which can be described in terms of layer-packing of atoms (see Figure 1), in which the carbide carbon atoms lie as a [C_2] unit (C–C, 1.48(2)Å). Of the fourteen rhodium-carbon contacts, nine are short (mean 2.22Å) and five long (mean 2.58Å). The [$Co_8C(CO)_{18}$]$^{2-}$ anion consists of a deformed tetragonal antiprism of metal atoms (idealized D_2 symmetry), with the carbon atom occupying the centre of the cluster (see Figure 2). As in the rhodium complex, there are short cobalt-carbon distances (mean 1.99Å) and also longer, weaker contacts (mean 2.15Å).[18]

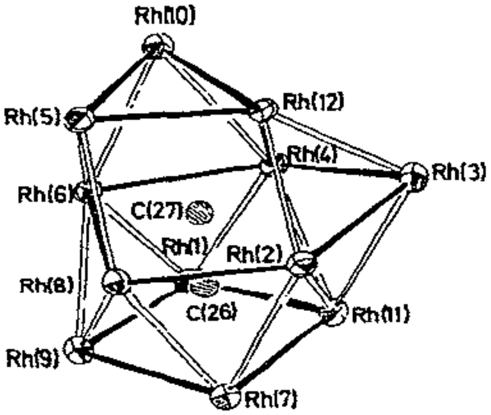


Figure 1. View of the $Rh_{12}C_2$ cluster showing its rationalisation in terms of the layers of metal atoms (reproduced by permission of the Chemical Society).

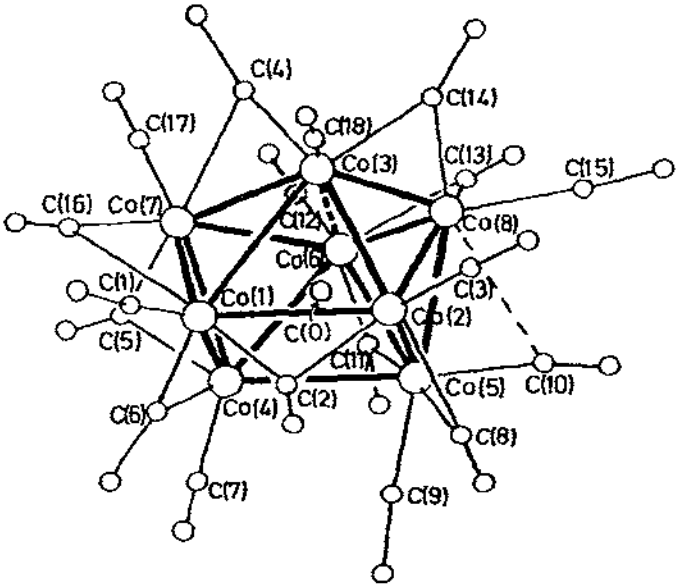


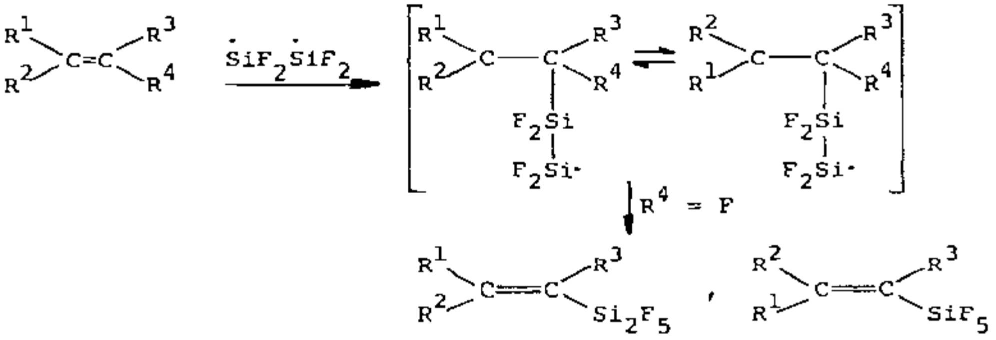
Figure 2. View of the $[Co_8C(CO)_{18}]^{2-}$ anion (reproduced by permission of the Chemical Society).

4.2 SILICON, GERMANIUM, TIN AND LEAD

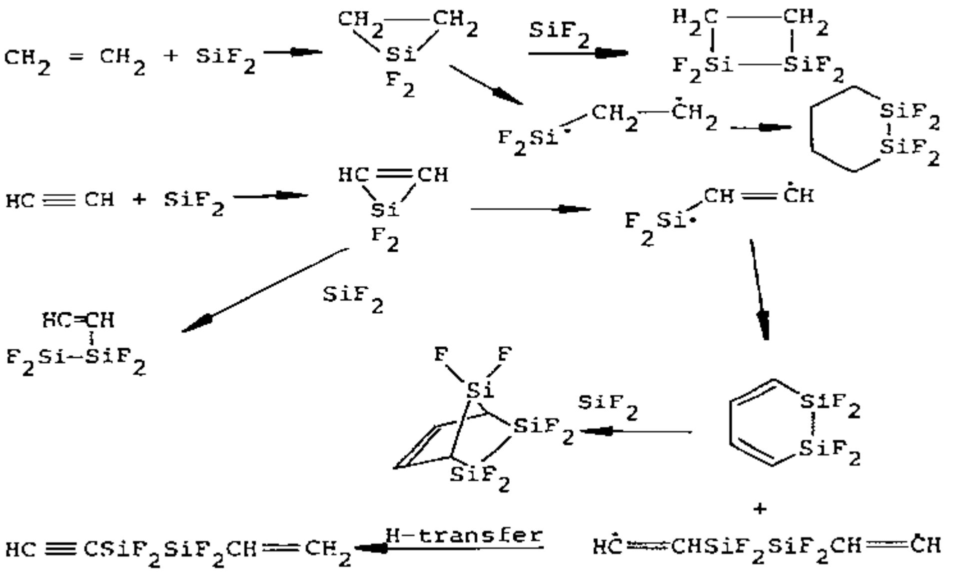
4.2.1 Reactions Involving Unstable Silicon, Germanium and Tin Intermediates

The reaction of silicon atoms from the $^{31}P(n,p)^{31}Si$ nuclear transformation in phosphine-butadiene mixtures yield $[^{31}Si]$-1-silacyclopent-3-ene, which is also obtained in 46% yield from the reaction of thermally generated SiH_2 with butadiene together with a product believed to be $[^{31}Si]$-1-silacyclopenta-2,4-diene. However, the variation of the product yields with composition of the PH_3-SiH_4-C_4H_6 recoil reaction mixtures casts doubt on the participation of ground state singlet $^{31}SiH_2$ as a reaction intermediate, as does the failure to detect any of the thermal adduct of SiH_2 to cyclopentadiene, 1-silacyclohexa-2,4-diene, from the reactions of ^{31}Si in PH_3-SiH_4-C_5H_6 mixtures.[19] The kinetics of the reactions of ground state $Sn(5^3P_0)$ tin atoms with several small molecules have been studied. The bimolecular reactions with O_2, $C\ell_2$ and NO_2 are exothermic, whilst that with NO is endothermic.[20] Absolute rate data have also been reported for the bimolecular reactions of Sn(5^3P_o) atoms with O_2, D_2, CH_4, CF_4, SF_6, $SnMe_4$, CO_2 and N_2O, and for the termolecular reactions with C_2H_4, C_2H_2 and NO.[21]

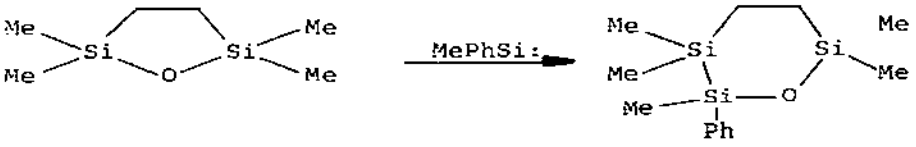
An infrared and e.p.r. study of the reaction of SiF_4 with lithium in an argon matrix has demonstrated that difluorosilylene, SiF_2, and either SiF_2^- or a diradical SiF_2 species are produced.[22] Monomeric $^{31}SiF_2$, formed in a nuclear recoil system reacts with 1,3-butadiene, cis- and trans-pentadiene, and 2-methyl-1,3-butadiene to give equivalent amounts of difluorosilacyclopent-3-ene-^{31}Si and its methyl derivatives. The singlet:triplet $^{31}SiF_2$ ratios evaluated from these systems are all ca. 1:3, and a similar equivalence in product yields is also observed for the reaction of $^{31}SiH_2$ with the same diene systems. The reactivity of the silylenes is increased by addition of trace amounts of O_2 and NO, due to the formation of $^{31}SiF_2$-donor complexes. Minor steric hindrance is responsible for the lower reactivities of the pentadienes, however, the large steric effect between the trans- and cis-pentadienes towards a triplet $^{31}SiF_2$-donor complex was attributed to a direct [1,4]-addition process.[23] The origin of disilanyl products in reactions involving SiF_2 has attracted interest. Liu and Hwang[24] have proposed that such products arise from the participation of oligomeric $(SiF_2)_n$ diradicals. These workers observed that, in the reaction of SiF_2 with cis- and trans-difluoroethene, 1:3, 1:2 and small quantities of 1:1 adducts were formed. In addition, the reactions were non-stereospecific, which indicated a pathway involving initial attack of oligomeric diradical at the C=C bond followed by rearrangement, thus leading to the production of both isomers:



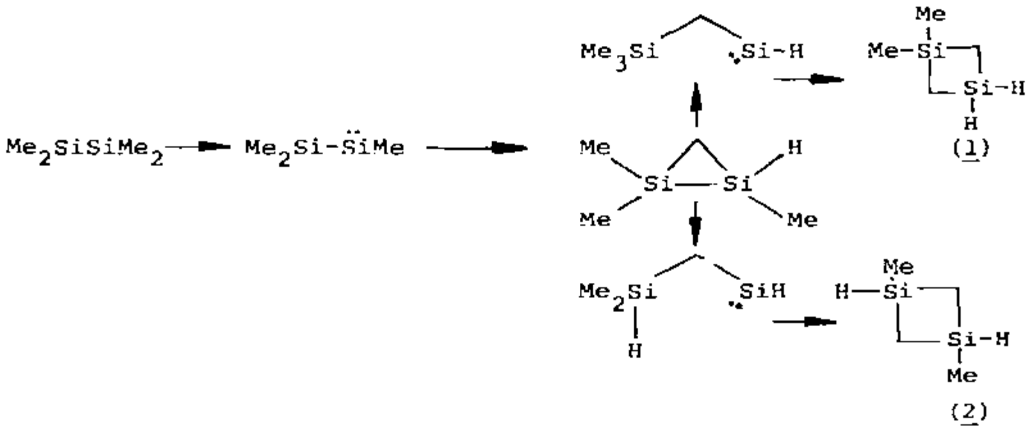
However, Seyferth and Duncan[25] have put forward alternative mechanisms based on the intermediate formation of highly reactive difluorosilirane and -silirene species (*vide infra*) viz:



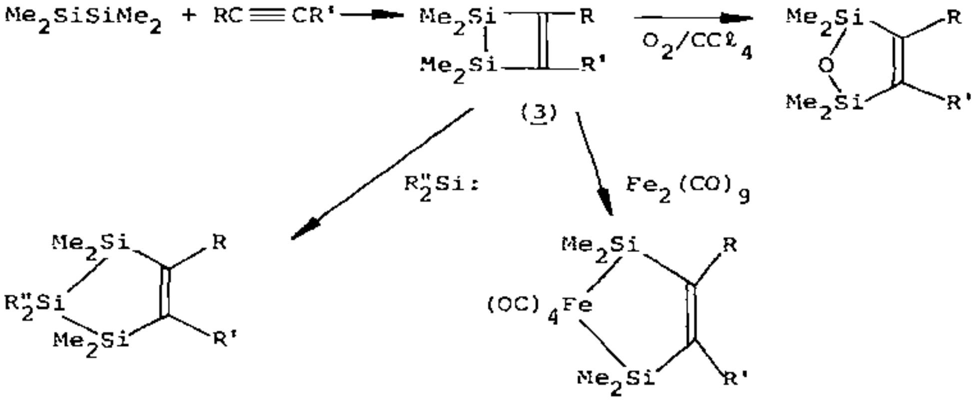
Methylphenylsilylene, produced by the photolysis of 2,3-diphenyltetrasilanes, is less reactive towards insertion into Si-O single bonds than dimethylsilylene. Thus, no reaction could be detected with cyclo-$(Me_2SiO)_3$, but insertion into 1,1,3,3-tetramethyl-2-oxo-1,3-disilacyclopentane did occur:[26]



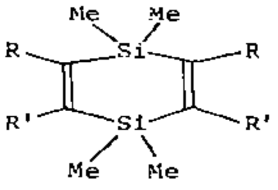
Trimethylsilyl(methyl)silylene, $Me_3Si\text{-}\ddot{S}iMe$, and trimethylsilylmethylsilylene, $Me_3SiCH_2\ddot{S}iMe$, are formed during the low-pressure gas-phase pyrolysis of $Me_3Si.SiC\ell Me_3$ and $Me_3SiCH_2SiC\ell Me.SiMe_3$, respectively, at 600-700°C. $Me_3Si\text{—}\ddot{S}iMe$ results from a rearrangement of the disilene, $Me_2SiSiMe_2$, and undergoes intramolecular C-H insertion to form disilacyclopropene, which subsequently undergoes Si-Si bond fission accompanied by either H- or CH_3-migration to form (silylmethyl)silylenes, which yield the final products, 1,3-disilacyclobutanes, (1) and (2):[27]



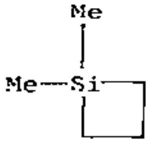
Reaction of tetramethyldisilene with alkynes leads to the formation 1,2-disilacyclobutenes (3). These compounds are extremely air-senstive, and undergo ring-expansion reactions:



Further reaction of (3) with alkyne is very slow even at $350^{\circ}C$, but proceeds smoothly at temperatures of 25-$80^{\circ}C$ in the presence of a palladium complex catalyst to yield 1,4-disilahexadienes (4):[28]

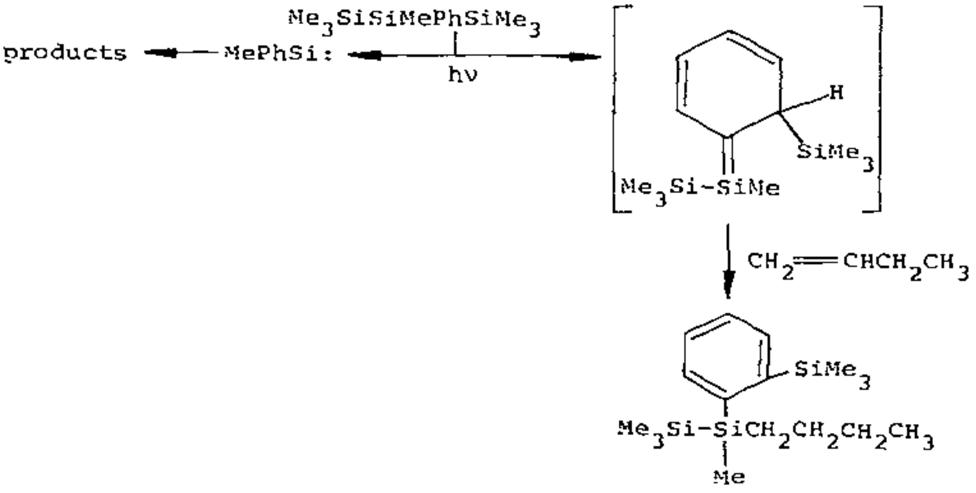


(4)



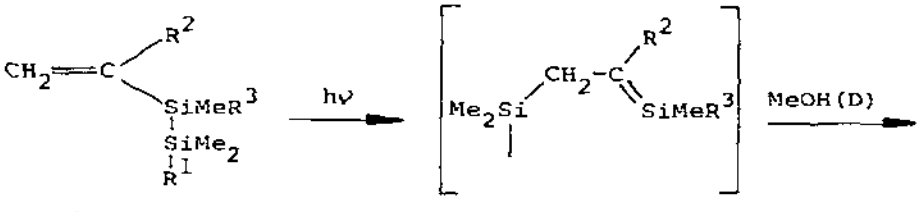
(5)

Gas-phase photolysis of 1,1-dimethylsilacyclobutane (5) using 147nm light gives as the major product C_2H_4, inferring the coproduction of 1,1-dimethylsilaethene, $Me_2Si{=}CH_2$, with small quantities of methane, ethane, propane, propene and cyclopropene. The formation of the two latter compounds suggests elimination of Me_2Si: as a second mode of photodecomposition.[29] Silicon-carbon double-bonded species have also been postulated as intermediates in order to rationalise the formation of some products. Thus, whilst most of the products formed in the photolysis of $Me_3SiSiMePhSiMe_3$ may be rationalised by the elimination of MePhSi:, the formation of (6) may only be rationalised by a silyl-migration to the aromatic ring:



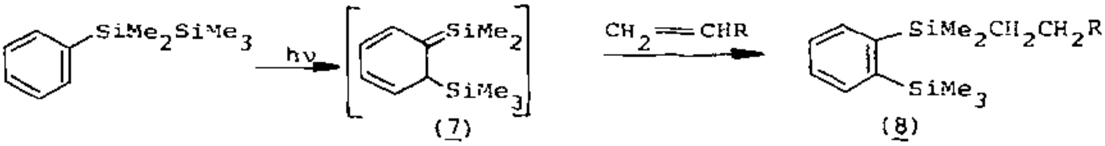
(6)

The photolysis of 1-phenyl- or 1-alkenyldisilanes generally leads to the formation of silaethene intermediates. Such intermediates formed from 1-alkenyldisilanes react with MeOH(D) to give the corresponding methoxysilanes in high yield:[31]

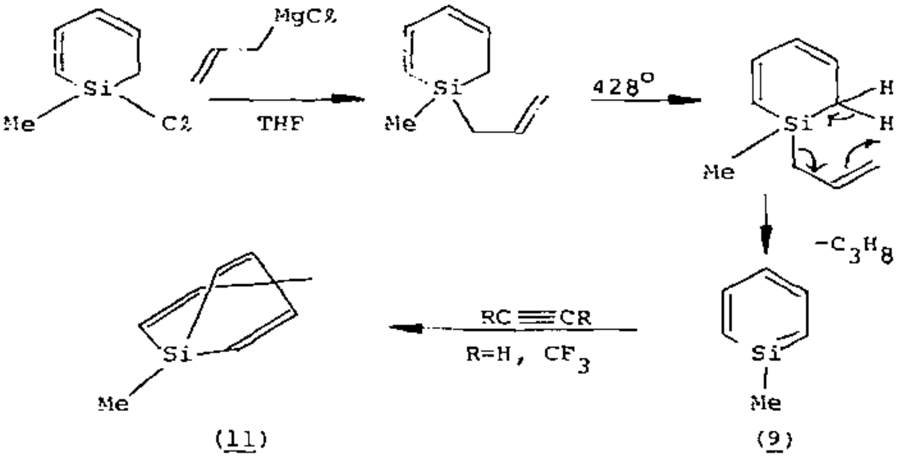


$R^1Me_2SiCH_2CR^2(D){-}SiMeR^3(OMe)$

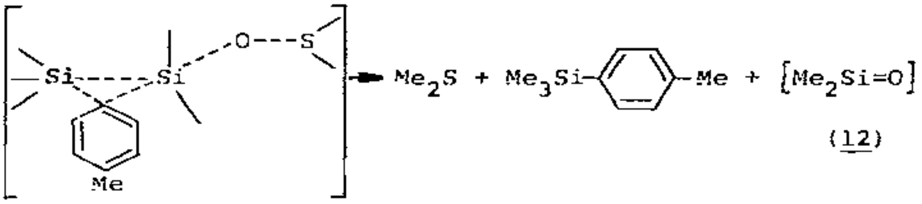
whilst with 1-phenyldisilanes, silyl-migration occurs as proposed for $Me_3SiSiMePhSiMe_3$ (vide supra) yielding intermediates (7) which react with alkenes to afford 1,2-disilyl-substituted aromatic compounds (8), e.g.:



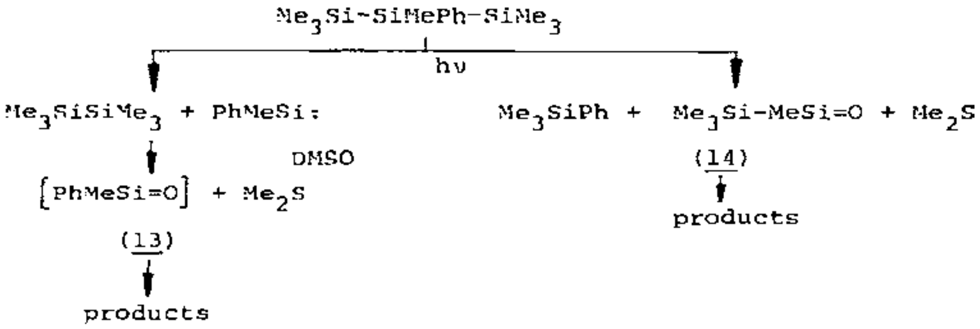
Addition of the intermediates to cis alkenes always afforded better yields of adducts than the corresponding trans isomers due to steric crowding.[31] The unambiguous generation and trapping of a silabenzene (9) has been reported by Barton and Burns.[32] Generation of (9) involved the thermolysis of the 1-alkenyl-1-sila-cyclohexa-2,4-diene (10) in a quartz tube packed with quartz chips at 428°C. When an alkyne was used as the carrier gas, (9) could be trapped as the 1-silabicyclo[2,2,2]octatrienyl derivatives (11):



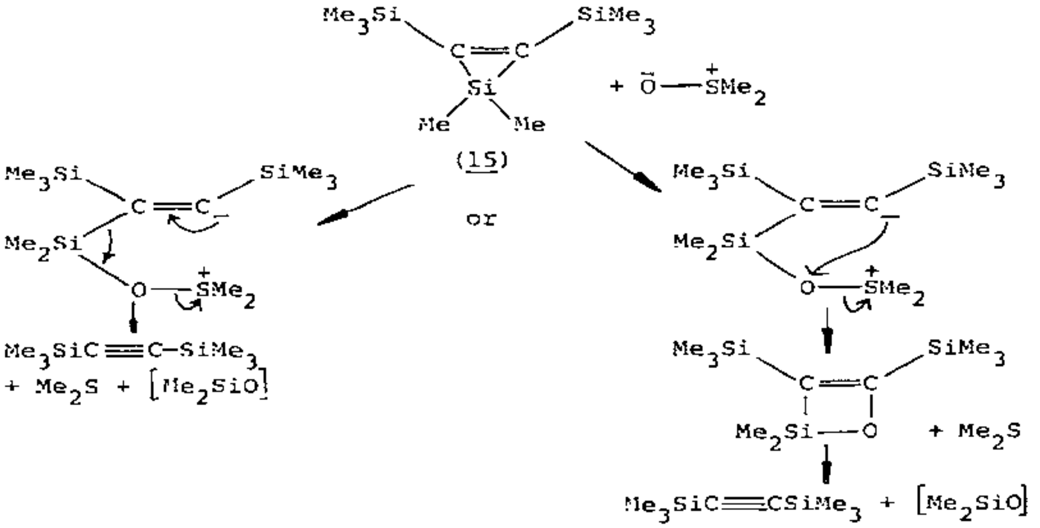
Photolysis of aryl-substituted disilanes in the presence of DMSO, yields the silicon-oxygen double-bonded intermediate, dimethylsilanone $Me_2Si{=}O$, (12), which is produced by a mechanism involving nucleophilic attack of the DMSO oxygen on the photoexcited disilane at the silyl centre bearing the aryl group, followed by the migration of the aryl group to the other silicon atom:[33]

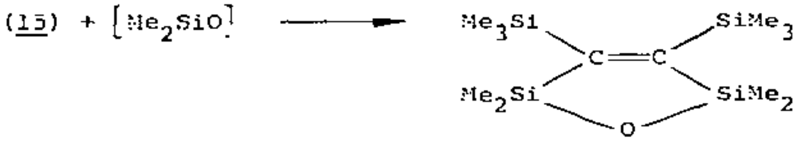


The photolysis of $Me_3SiSiMePhSiMe_3$ and $Me_3SiSiMePhSiMePhSiMe_3$ in the presence of DMSO occurs by two major pathways. The first involves the loss of [MePhSi:], which subsequently reacts with DMSO to yield methylphenylsilanone (13) and Me_2S. The second pathway involves the direct generation of methyl(trimethylsilyl)-silanone (14) by nucleophilic attack of DMSO at silicon as above. Both (13) and (14)may be trapped by $(Me_2SiO)_3$ or 2-oxa-1,3-disilacyclopentane, e.g.:[34]



Dimethylsilanone is also produced by the reaction of the silirene (15) with DMSO, or an amine oxide such as C_5H_5NO or Me_3NO. The reaction of (15) with DMSO at 0°C in dry benzene produces Me_2S, $Me_3SiC{\equiv}CSiMe_3$, and the heterocycle (16) via either a stepwise or concerted process:

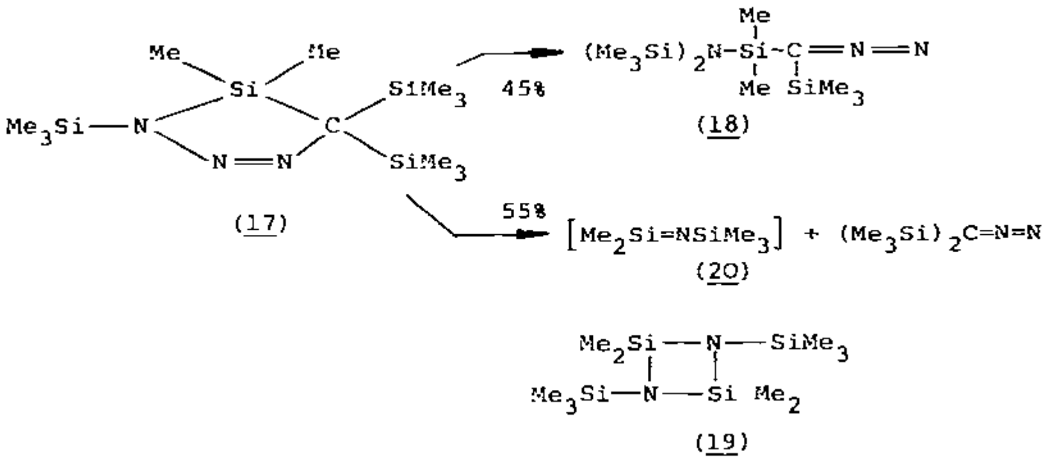




(16)

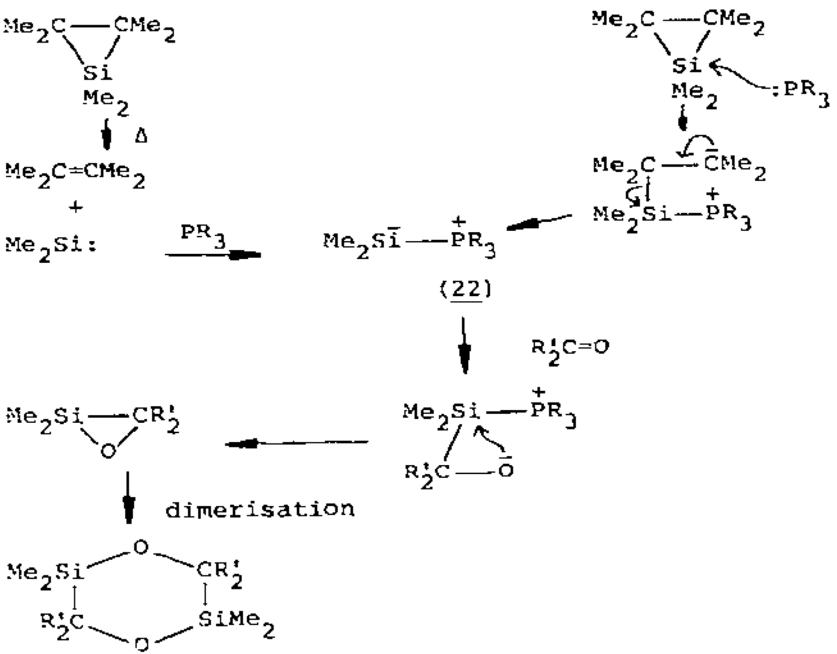
Dimethylsilanone produced in this way can also be trapped by other trapping reagents such as $(Me_3SiO)_3$ or $Me_2Si(OMe)_2$. Hexamethylsilirane reacts similarly with DMSO to give the same products, but is less reactive.[35]

Besides the now well-established Si=O and Si=C intermediates, several other silicon and germanium multiply-bonded species have been proposed. The thermolysis of the heterocycle (17) affords the acyclic isomer (18) as well as $(Me_3Si)_2C{=}N{=}N$ and the four-membered heterocycle (19), derived by dimerisation of the iminosilene (20):

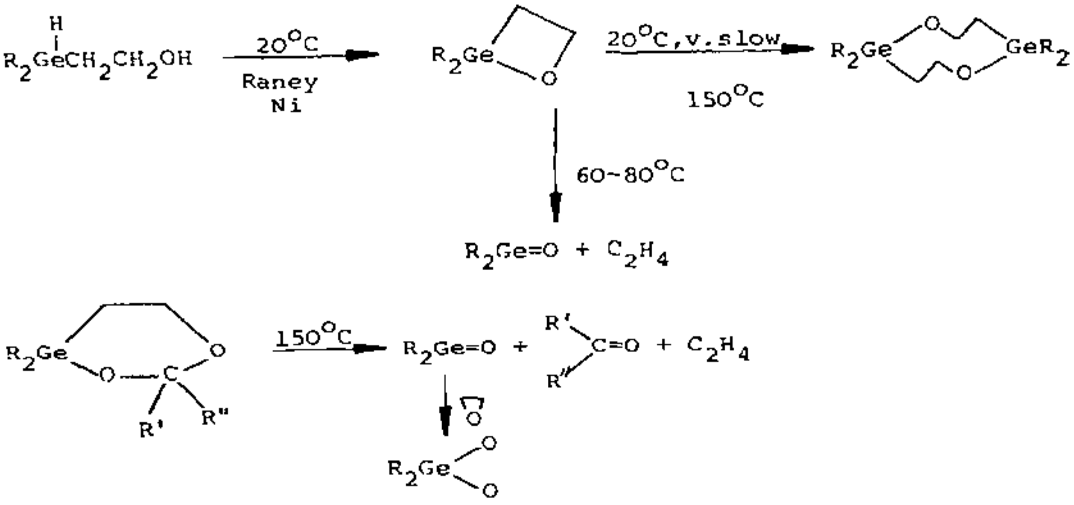


Compound (20) shows a tendency, albeit considerably lower than the silaethene analogue, $Me_2Si{=\!=}C(SiMe_3)_2$ (21) to undergo [2+2] cycloaddition reactions with itself or benzophenone, but its reactivity towards insertion into Si-X single bonds appears to be greater than for the carbon analoge (21). The efficacy of trimethylsilyl compounds as trapping agents for (20) are in the order $(Me_2SiO)_3 << Me_3SiNMe_2 < Me_3SiOMe < Me_3SiCl < Me_3SiN_3$.[36] A silylphosphorane (22) has been proposed as an intermediate in the reaction of hexamethylsilirane with carbonyl compounds in the presence of tertiary phosphines. Thus, when a solution containing PPh_3, hexamethylsilirane and cyclohexanone were heated at 75°C for 14 hours, 1,4-dioxa-2,5-disilacyclohexane (26%) was produced. A nearly quantitative yield (92%) was obtained when the more nucleophilic Me_2PhP was employed, consistent with the mechanism.[37] (See Scheme 1).

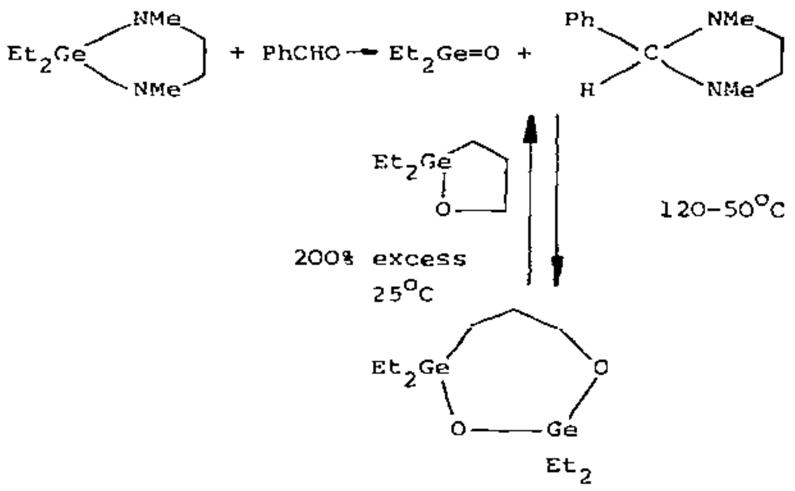
The thermolysis of germanium oxetanes and adducts of germanium dioxolanes, oxazalidines and diazolidines with carbonyl compounds leads to transient dialkylgermanones, $R_2Ge{=}O$, which may be characterised by addition of alkoxygermanes and oxagermacyclopentanes to the Ge=O bond, and by insertion and ring-expansion reactions with ethylene oxide.[38] (See Scheme 2).



Scheme 1

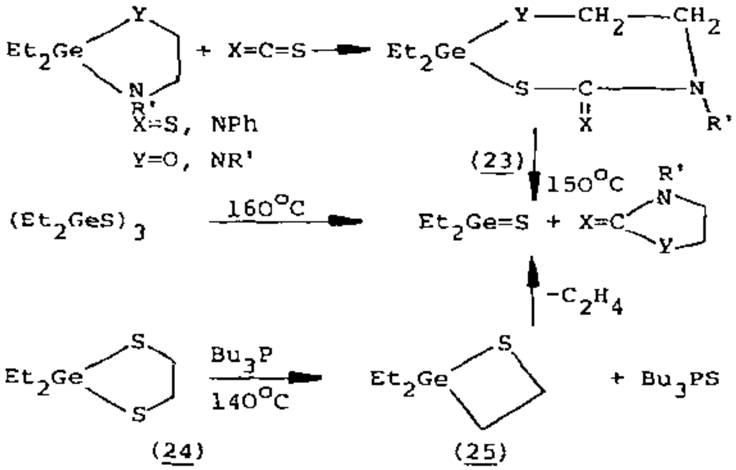


Scheme 2

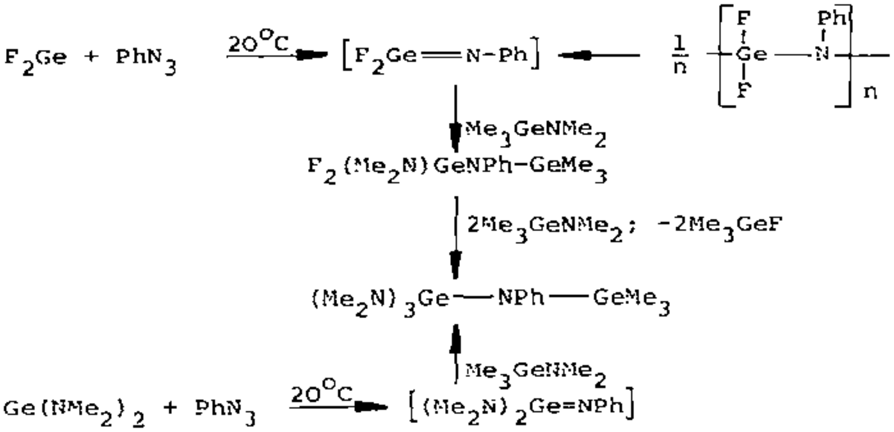


Scheme 2 (cont.)

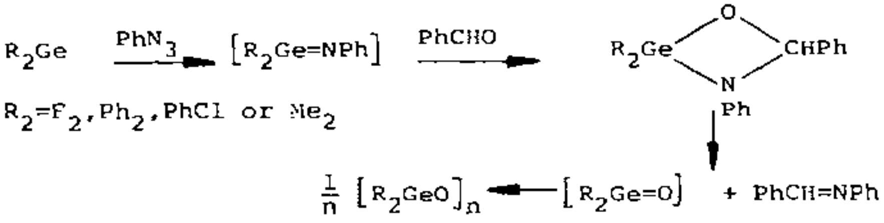
Treatment of some germaoxazolidines and germadiazolidines with CS_2 or PhNCS results in the formation of analogous transient dialkylgermathiones, $R_2Ge=S$, by a similar β-elimination reaction of the resulting adduct (23). The same transient species may also be derived by the thermolysis of trimeric $(R_2GeS)_3$, and by the desulphuration of the germadithiolane (24) by Bu_3P, a reaction which probably proceeds via transient germathiacyclobutane (25). Characterisation of the germathiones was achieved by addition of Et_3GeSMe, and ring expansion reactions with ethylene oxide and sulphide:[39]



The reaction of germylenes with phenyl azide leads to the formation of transient germaimines, $R_2Ge{=}NR'$, which undergo polycondensation to the corresponding cyclic or linear germazanes and insertion into the Ge-N bond, e.g.:



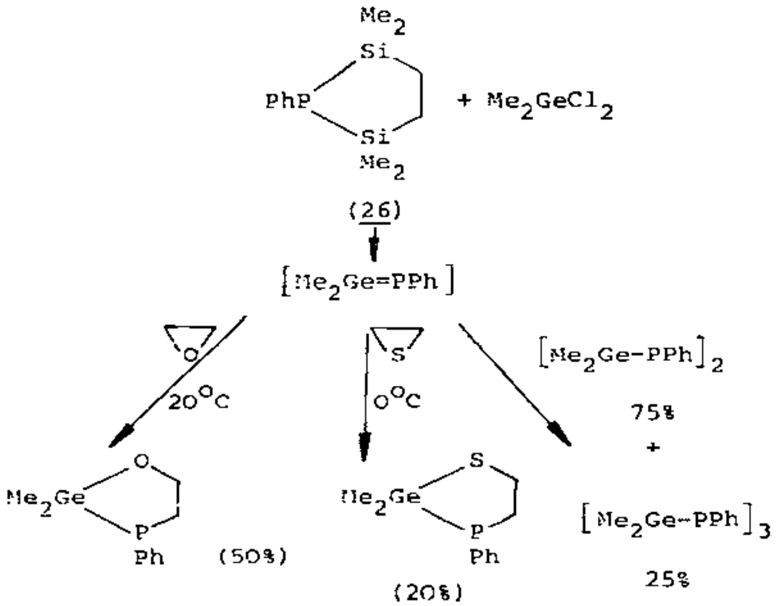
The germaimines also participate in a pseudo-Wittig reaction with benzaldehyde, producing the corresponding germoxanes via new germanone intermediates:



The analogous germaphosphinimines, $R_2Ge{=}PR'$, are obtained by the exchange reaction between Me_2GeCl_2 and the 2,5-disilaphospholane (26) in THF at 20°C, and undergo the same types of characterisation reactions.[41] (See Scheme 3).

4.2.2 Bivalent Germanium, Tin and Lead Compounds

Continuing the trend of the last few years, the chemistry of the +2 oxidation state of the Group 4 metals is an area of substantial activity. Perhaps the most significant report to appear during 1978 concerns the 'in vitro' biomethylation of Sn(II).[42] Methylcobalamin has been found to methylate Sn(II) in the presence of an equimolecular amount of aquocobalamin under nitrogen at pH 1.0 in 1.0M NaCl to give methyltin (IV) species. No reaction was observed



Scheme 3

between Sn(II) and methylcobalamin in the absence of oxidizing agents such as aquocobalamin or Fe(III), and catalytic amounts of aquocobalamin produced no significant cleavage. Significantly, no cleavage occurred with Sn(IV).

The phase diagram of the $SnCl_2$–$SnBr_2$ system shows the presence of two regions of solid solution (from 0–35% and 45–100% $SnCl_2$), with a small intermediate miscibility gap in spite of the isomorphism of the two compounds. No terniary compounds exist in the $SnCl_2$–$SnBr_2$–SnI_2 system, but a ternary solid solution based on $SnBr_2$ can form.[43] Two lead(II) iodide bromides have been characterised in the PbI_2–$PbBr_2$–H_2O system. One, Pb_5-I_4Br_6, may also be obtained by high temperature synthesis, the other, $Pb_5I_2Br_8$, is only stable below 220°C at which temperature it undergoes an irreversible solid-state transformation.[44] The ternary tin(II) sulphide iodide, Sn_4SI_6, has been prepared by annealing stoichiometric amounts of SnI_2 and SnS at 280°C, and has a structure based on that of SnI_2. All four tin atoms are crystallographically independent; one is approximately octahedrally coordinated by six iodine atoms as in SnI_2, the others are irregularly six- or seven-coordinated by sulphur and iodine atoms.[45] The structures of several other halogenometal(II) compounds have been determined by X-ray crystallography and follow previously established patterns. Thus, both $RbGeCl_3$[46] and NH_4SnF_3[47] consist of M^+ cations and MX_3^- anions, which have typical pyramidal coordination with three additional longer M-X contacts. Tin(II) enjoys the same type of pyramidal coordination in Sn_3BrF_5, which has a structure built up from layers of interconnected $(Sn_{12}F_{20})_n^{4n+}$ macrocations and isolated bromide anions.[48] However, in both Sn(NCS)F[49] and Sn_2IF_3[50] the tin atoms are four-coordinated. The latter compound, obtained by adding HI to a warm aqueous solution of SnF_2 and allowing to cool, also has a layer structure composed of $(Sn_2F_3)_n$ layers and isolated iodide anions. Tin(II) isothiocyanate fluoride was obtained by mixing and concentrating aqueous solutions of the two symmetrical compounds has a chain structure very similar to that of SnClF, in which the fluorine atoms bridge adjacent tin atoms (see Figure 3). Perhaps not surprisingly, the structure of

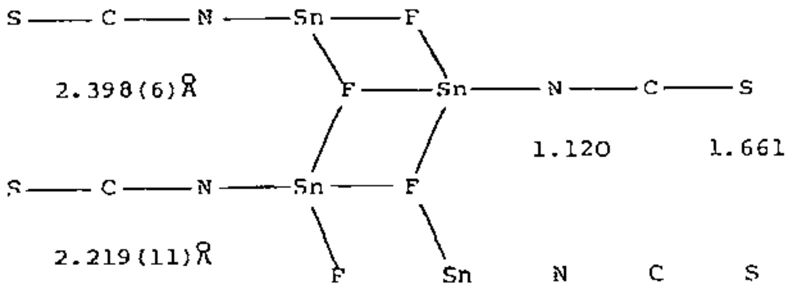


Figure 3 Schematic representation of the chain structure of Sn(NCS)F.

$Sn(NCS)_2$ shown in Figure 4 is very similar to that of the orthorhombic tin(II) halides (the $PbCl_2$-structure), in which the tin atom is primarily coordinated by two nitrogen and one sulphur atoms, with contacts to a further six atoms.[51]

The methylammonium salts, $MeNH_3SnBr_xI_{3-x}(x=0-3)$[52] and $MeNH_3PbX_3$ (X=Cl,Br,I)[53] have the cubic perovskite structure and are intensely coloured. The tin compounds possess conducting properties, though the lead compounds show none under normal

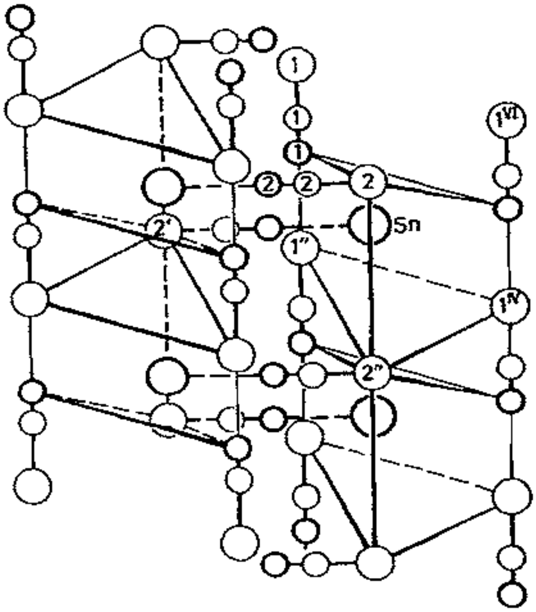
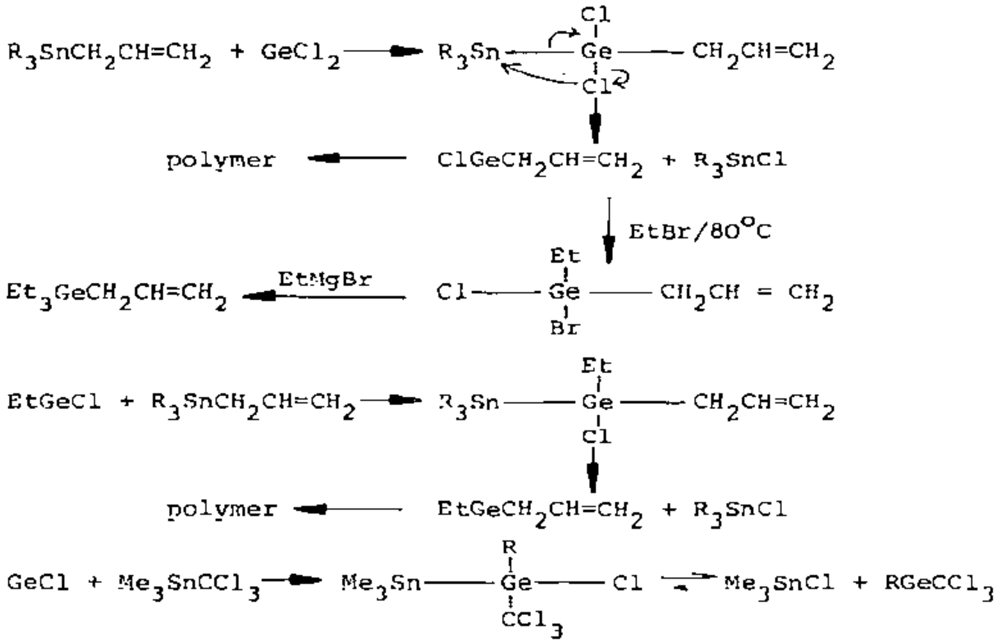


Figure 4 The structure of $Sn(NCS)_2$ (reproduced by permission of the Chemical Society).

conditions. Although only exhibited by tin(II) when coordinated by heavy ligands such as iodine and tellurium, cubic coordination of bivalent lead is much more common. Crystals of the complex $[Co(en)_3]_2\ Pb_2Cl_9\ Cl.3H_2O$ are composed of cations and infinite $[Pb_2Cl_9]_n^{4n-}$ anion chains formed from $[PbCl_6]$ octahedra by alternate sharing of vertices and edges.[54,55] Examination of the structure of molten $PbCl_2$ by X-ray diffraction shows that each lead atom is surrounded by ca. eight chlorine atoms at a distance of 2.92Å, which is close to the sum of the ionic radii of Pb^{2+} and Cl^-. As an increasing amount of lithium chloride is incorporated into the melt, however, the coordination at lead is lowered to six.[56]

Tricker and Donaldson[57] have rationalised the ^{119}Sn Mössbauer parameters of alkali metal trihalogenostannate(II) salts, $MSnX_3$ (M=K,Na,Rb,Cs; X=F,Cl,Br,I), using the concept of orbital matching. The heats of solution of the tin(II) halides in the donor solvents DMSO and DMF are exothermic in the order $SnI_2 > SnBr_2 > SnCl_2 > SnF_2$; the heats of solution in DMF being substantially greater than in DMSO for each halide.[58] The electrical conductivity of $SnCl_2.2H_2O$ single crystals, measured both with injecting and with metallic electrodes, shows two contributions: a critical, frequency-dependent, behaviour around the phase-transition temperature, and a temperature-activated process, both in the disordered and the ordered phase. This second process causes a very large conductivity along the crystallographic $\underline{c}$ axis at room temperature of the order of $10^{-6}\Omega^{-1}$ cm^{-1}. The conduction shows ohmic behaviour at low fields, but is non-ohmic at higher fields, and is probably protonic in nature.[59]

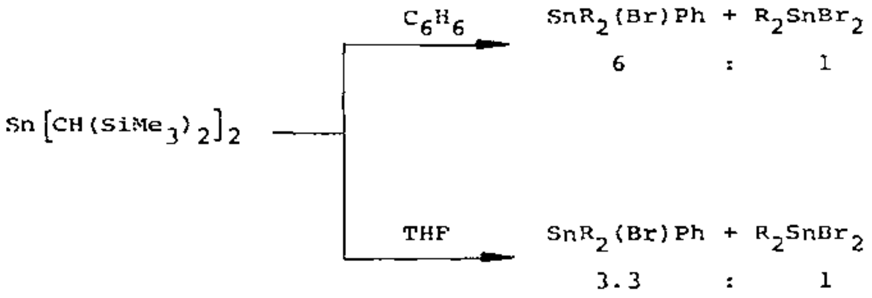
Halogenometal(II) compounds are carbene analogues, and as such, not surprisingly, take part in insertion reactions. The germylenes $GeCl_2$ and EtGeCl react with allyl- and trichloromethyl-trialkylstannanes with insertion into the Sn–C bond. The resulting germylstannanes undergo subsequent α-elimination reactions yielding bivalent germanium species carrying an allyl or trichloromethyl substituent, which rapidly polymerise but can be trapped by reaction with ethyl bromide:

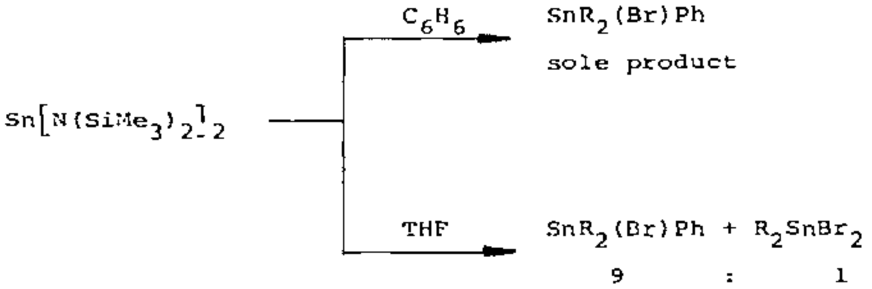


R=Et,Cl

The germylenes $RGeCCl_3$ so produced can be characterised by insertion into ethyl bromide followed by treatment with EtMgBr. Alkyl(dichloromethyl)germylenes may also be generated by an α-elimination reaction from alkyl(dichloromethyl)methoxyhydrogermanes.[60] Insertion of tin(II) and lead(II) halides into alkyl halides has been employed to synthesise alkylmetal(IV) trihalides. The reaction of $SnCl_2$ with MeCl takes place in fused salts such as $NaAlCl_4$ and $NaAlCl_4/KAlCl_4$ mixtures at 365°C.[61] Trimethylantimony catalyses the reaction of PbI_2 with alkyl iodides at 140°C in a closed reactor to afford alkyllead triiodides as yellow orange crystalline solids with low melting points.[62] Insertion of anhydrous $SnCl_2$ into the Ru–Cl bond of $(+)_{578}$- and $(-)_{578}$-$(\eta$-$C_6H_6)RuCl(Me)\ Ph_2PNHCHMePh$ in THF is stereoselective, and $(+)_{578}$- and $(-)_{578}$- $(\eta$-$C_6H_6)Ru(SnCl_3)(Me)[Ph_2PNHCHMePh]$ are produced. The stereoselectivity is dependent on the reaction solvent and may be the result of overall retention or inversion of configuration at the ruthenium atom, but the new complexes are configurationally stable in a wide variety of solvents up to 60°C.[63] Cotton[64,65] has studied the insertion reactions of $GeCl_2$, $SnCl_2$ and $SnBr_2$ with Fe–C σ-bonds. Reaction with $(C_5H_5)(CO)_2FeR$ (R=Me,Et,n-Pr, p-MeC_6H_4, $PhCH_2$ and p-$CF_3C_6H_4$) leads to complexes with germanium or tin bonded to iron via a radical chain process. A small substituent effect is observed in all cases for the benzyl series, the reaction being favoured by increasing electron-donating ability of the para-substituent. The major products of insertion when R=allyl(CH_2CMe=CH_2 or CH_2CH=CH_2) are the complexes $(C_5H_5)(CO)_2FeMX_2$(allyl), but in the presence of excess metal(II) halide, these slowly react to form $(C_5H_5)(CO)_2FeMX_3$ complexes. These insertion reactions are inhibited by small amounts of radical scavenger, and occur initially with an allylic rearrangement. In methanol, the process is more complex, and an unknown species, possibly an iron-alkene dipolar intermediate, and substantial amounts of Fe–MX_3 compounds are formed additionally.

Similar radical insertions of tin(II) alkyls and amides into phenyl bromide and n-butyl chloride have been studied by Lappert.[66] The reactions of SnR_2 with PhBr (R=$CH(SiMe_3)_2$, $N(SiMe_3)_2$) and with n-BuCl (R=$N(SiMe_3)_2$) in benzene are catalysed by a trace of the more reactive halide EtBr. No reaction is observed in hexane in the absence of EtBr, and when THF is employed as the solvent, a larger proportion of the product is the corresponding tin(IV) dihalide rather than the 1:1 insertion product, viz:





The reactions of PhBr with $Sn[CH(SiMe_3)_2]_2$ were found to be first-order for both the catalysed and uncatalysed reactions, but the rate constant for the latter was 2-3 fold higher. The principal pathway for the catalysis was suggested to follow the chain process:

$$SnR_2 + EtBr \rightarrow .SnR_2Br + Et.$$

$$.SnR_2Br + PhBr \rightarrow SnR_2Br_2 + Ph.$$

$$SnR_2 + Ph. \rightarrow .SnR_2Ph$$

Propagation

$$.SnR_2Ph + PhBr \rightarrow SnR_2(Br)Ph + Ph.$$

Or, alternatively, the Ph. radical may be generated by reaction of PhBr with the Et. radical, and subsequently react with the tin-centred $.SnR_2Br$ radical to afford the insertion product.

The effect of $PbCl_2$ and $PbBr_2$ on the efficacy of heterogeneous oxidation catalysts for the control of motor vehicle exhaust emissions has been studied in detail. Introduction of the lead(II) halides on the surface of the catalysts (Ni,Co,Mn,Cu-oxides, both neat and alumina-supported, as well as alumina-supported Pt) caused a reduction in catalytic activity. The decrease in activity is not due to the formation of a new, catalytically-inactive phase, but in the case of Ni-, Mn- and possibly Co-oxides, the poisoning effect could be satisfactorily accounted for by the formation of a monolayer of lead compound on the catalyst surface. The results obtained on the Co-oxide are, however, less satisfactorily explained. At low temperatures, $PbCl_2$ in monolayer amounts caused complete deactivation, but at higher temperatures considerably greater amounts were required to eliminate catalytic activity. Under all conditions a large excess of $PbBr_2$ was required to deactivate the Co-oxide completely. With supported catalysts, the lead halides appeared to be preferentially adsorbed on the alumina support. Again, however, the supported Co-oxide catalyst behaved atypically in that no such preferential adsorption took place, and even sub-monolayer amounts of $PbCl_2$ caused the complete elimination of catalytic activity.[67]

With a lone pair and a vacant orbital in their valence shell, the germanium(II) and tin(II) halides can function both as Lewis bases and Lewis acids. With phosphines such as $t\text{-}Bu_3P$ or $(Me_2N)_3P$, tin(II) chloride and bromide form stable 1:1 adducts, whose spectra were interpreted in terms of an ylidic-type of bonding. In THF solution or with HCl the complexes undergo dissociation:

$$(Me_2N)_3PSnCl_2 + nTHF \rightleftharpoons (Me_2N)_3P + (THF)_n\text{-}SnCl_2$$

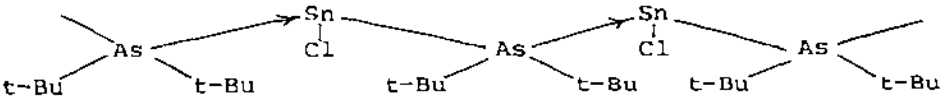
$$t\text{-}Bu_3PSnCl_2 + HCl \longrightarrow tBu_3PH^+SnCl_3^-$$

but reaction with Me_3SiPR_2 produces the tin(II) phosphine, R_2PSnX:[68]

$$t\text{-}Bu_3PSnX_2 + R_2PSiMe_3 \longrightarrow t\text{-}Bu_3P + R_2PSnX + Me_3SiX$$

The same method has also been employed in the synthesis of the tin(II) arsine, $t\text{-}Bu_2AsSnCl$, from $SnCl_2.PEt_3$ and $t\text{-}Bu_2AsSiMe_3$ at low temperatures.

The physical properties of yellow crystalline t-$Bu_2AsSnCl$ indicate a polymeric structure with bridging t-Bu_2As groups but terminal Sn-Cl bonds suggestive of a structure as in (27).[69] A complex in which the $SnCl_2.P^tBu_3$ unit functions as a Lewis acid may be obtained by displacing THF from the complex $(OC)_5WSnCl_2.THF$ with t-Bu_3P at 0°C in toluene. The resulting complex, $(OC)_5WSnCl_2$-PBu_3, is soluble in aromatic hydrocarbons, ether and CH_2Cl_2.[70] Substitution reactions at the Group 4 metal in such complexes can lead to the formation of complexes of metal(II) compounds which cannot (as yet) be obtained directly. Thus, reaction of the complexes $(OC)_5M.GeCl_2.THF$ (M=Cr,W) with silylthioethers produces complexes of germanium(II) thiolates (28):



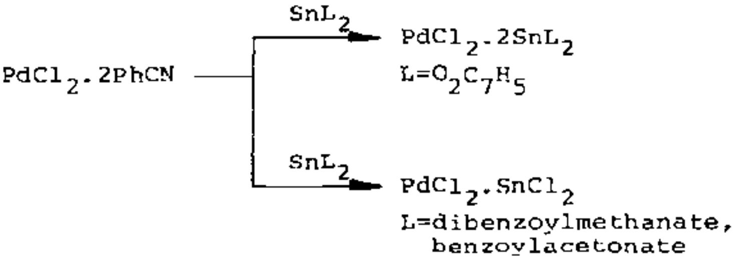
(27)

$$(OC)_5M.GeCl_2.THF + 2Me_3SiSR \longrightarrow \underset{(\underline{28})}{(OC)_5MGe(SR)_2} + \underset{+THF}{2Me_3SiCl}$$

M=Cr,W

The structure of one such complex is illustrated in Figure 5. The complexes (28) can incorporate further base (Me_3N,C_5H_5N,Ph_3P) which coordinates to the germanium atom.[71]

Other monomeric tin(II) compounds also form complexes with transition metals. Tin(II) diketonates displace PhCN from $MCl_2.2PhCN$ (M=Pd,Pt) complexes in benzene to afford palladium(II) and platinum(II) complexes:



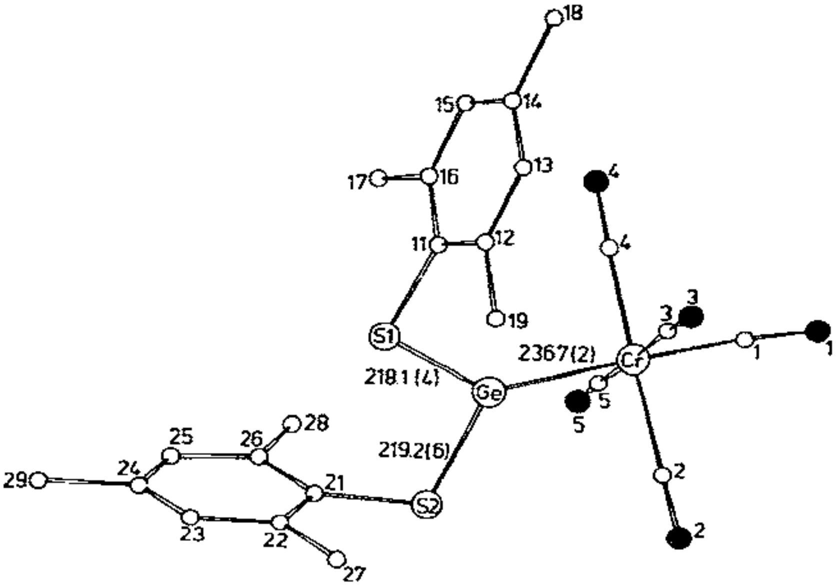
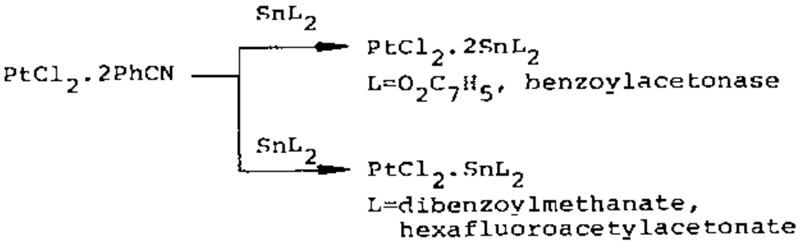


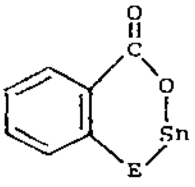
Figure 5. The structure of $(OC)_5Cr.Ge(SC_6H_2Me_3\text{-}2,4,6)_2$ (reproduced by permission from ref. 71).



The stoichiometry adopted appears to be largely controlled by steric factors.[72]

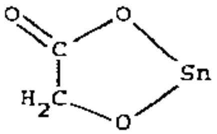
Tin(II) alkoxides have been recognised as useful synthetic intermediates for some time, and further details of the chemistry of these compounds have appeared during 1978. Tin(II) dimethoxide is readily protolysed, and reaction with bifunctional hydroxy- and thiolato-compounds yields tin(II)-oxygen and -sulphur heterocycles such as (29)-(36).[73]

Careful hydrolysis of $Sn(OMe)_2$ leads to the isolation of $Sn_6O_4(OMe)_4$, the first such isolated hydrolysis product, the adamantyl structure of which is shown in Figure 6.[74] Wakeshima and his coworkers have investigated the reactions of tin(II)

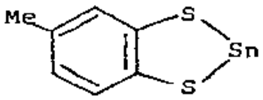


E=O,S

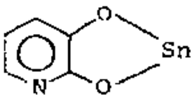
(<u>29</u>)



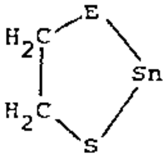
(<u>30</u>)



(<u>31</u>)

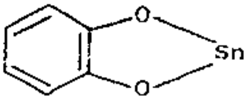


(<u>32</u>)

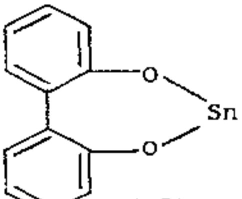


E=O,S

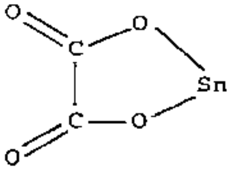
(<u>33</u>)



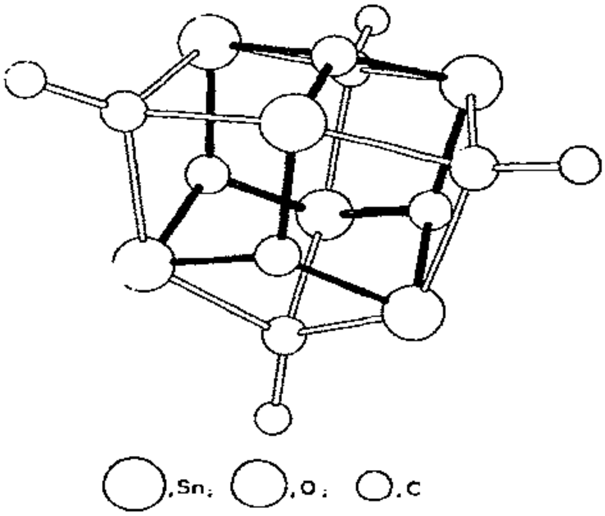
(<u>34</u>)



(<u>35</u>)

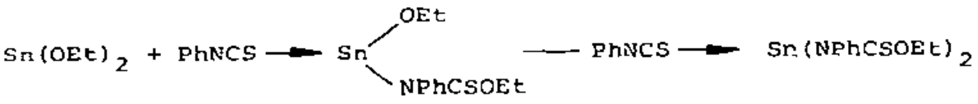


(<u>36</u>)



<u>Figure 6.</u> The structure of $Sn_6O_4(OMe)_4$ (reproduced by permission of the Chemical Society).

alkoxides with heterocumulenes such as PhNCS, CS_2[75] and EtNCO.[76] At room temperatures, $Sn(OEt)_2$ and PhNCS yield both 1:1 and 1:2 adducts:



$$Sn(OEt)_2 + PhNCS \longrightarrow Sn\begin{matrix}OEt\\ NPhCSOEt\end{matrix} \xrightarrow{PhNCS} Sn(NPhCSOEt)_2$$

but when the reaction is carried out at 80°C, a tin sulphide and diethyl-N-phenylcarbonimidate, $PhN{=}C(OEt)_2$ are formed. Reaction of PhNCS with $Sn(OCH_2CH_2NMe_2)_2$ is exothermic and yields only a 1:1 adduct even when excess PhNCS is used. An adduct of stoichiometry $2Sn(OC_6H_4Me)_2.PhNCS$ was obtained from $Sn(OC_6H_4Me)_2$, but $Sn(OPh)_2$ did not react. CS_2 was less reactive, and no reaction was observed with $Sn(OPh)_2$ or $Sn(OC_6H_4Me)_2$, but with $Sn(OEt)_2$ diethylthiocarbonate, diethylcarbonate and tetraethylorthocarbonate were produced.[75]

The reactivity of the tin(II) alkoxides towards EtNCO decreases in the order $Sn(OCH_2CH_2NMe_2)_2$ > bis o-(ethoxycarbonyl)phenolato tin > $Sn(OPh)_2$ > bis(ethoxycarbonylacetonato)tin > bis(3-ethoxycarbonyl-2-pentanoato)tin > bis(1-phenylbutane-1,3-dionato)tin > bis(dibenzoylmethanato)tin. Triethylcyanurate was the main product of the reactions with $Sn(OCH_2CH_2NMe_2)_2$, bis(o-ethoxycarbonylphenolato)tin and $Sn(OPh)_2$ but with the other compounds both the isocyanurate and 6-ethylimino-1,3,5-triethylhexahydro-1,3,5-triazine-2,4-dione were produced.[76] Verville[77] has studied the effect of organic compounds (polypropylene glycol, hydroxyphenylsulphonic acid, methanol, ethanol, formic acid) on the rate of formation of the 1Sn(II)-4Sn(IV) charge transfer complex in acidic $SnSO_4$ solutions and their stability.

It would appear that the four-coordinated pseudo-trigonal bipyramidal geometry with a stereochemically active lone pair is much more common for bivalent tin than thought a few years ago. Tin(II) fluoride, Sn(NCS)F,[49] Sn_2IF_3,[50] and $Sn_6O_4(OMe)_4$[74] (*vide infra*) have already been observed to exhibit this type of geometry, which appears to be preferred when very electronegative ligands are bonded to tin. Other compounds which also exhibit this geometry are tin(II)formate,[78] $Sn\ H_2PO_4{}_2$,[79] and the $[Cl_3SnOClO_3]^{2-}$ anion.[80] The gross structures of the materials, however, vary considerably. Crystals of $Sn_6O_4(OMe)_4$ contain molecular units in which each oxide and methoxy group triply bridge the tin atoms

(Figure 6), but in tin(II) formate, each formate group bridges adjacent tin atoms leading to a two-dimensional sheet structure as shown in Figure 7. Crystals of $Sn[H_2PO_4]_2$ are different still (see Figure 8). Here adjacent tin atoms are bridged by a single oxygen atom from each of four different $[H_2PO_4]$ groups giving infinite $[SnO_4]_\infty$ chains. Crystals containing the $[Cl_3SnOClO_3]^{2-}$

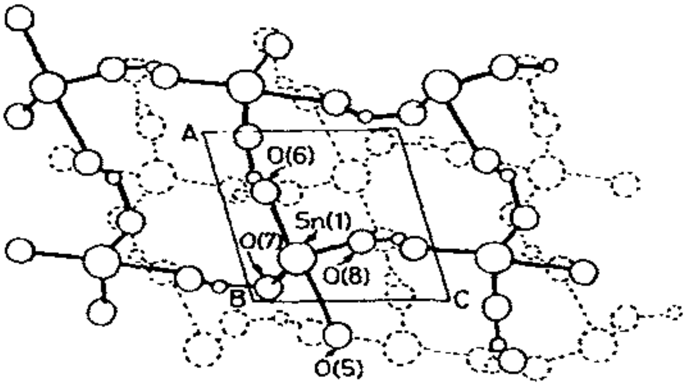


Figure 7. The layer structure of tin(II) formate (reproduced by permission of the Chemical Society).

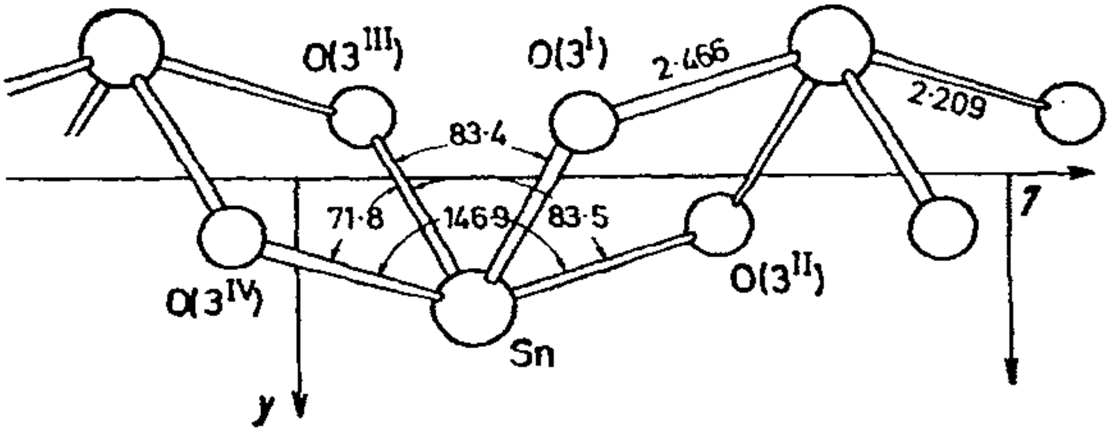


Figure 8. The $[SnO_4]_\infty$ chains in $Sn[H_2PO_4]_2$ (reproduced by permission of the Chemical Society).

anion were prepared from a hydrochloric acid solution of $SnCl_2$ and (benzenesulphinato-S)pentammine-cobalt(III) perchlorate. The structure of the anion is shown in Figure 9. The Sn-O interaction is fairly long (2.91(1)Å), but is presumably the initial step in the transfer of oxygen from perchlorate to tin(II) responsible for the slow oxidative decomposition of the compound over several days at room temperature.[80] In contrast, the metal(II) atoms in

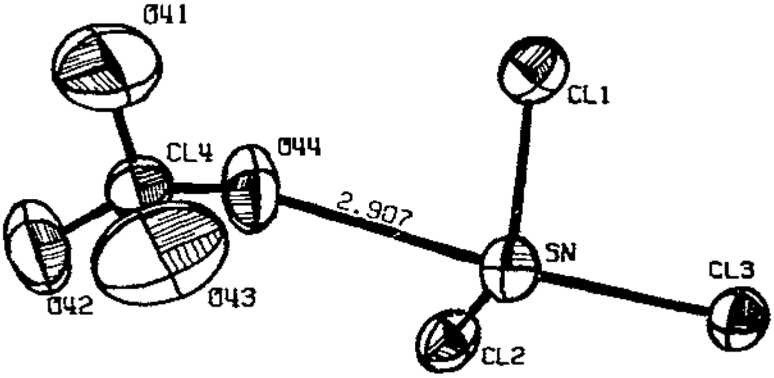


Figure 9. View of the $[Cl_3SnOClO_3]^{2-}$ anion (reproduced by permission from ref. 80).

$K_2Sn_2O_3$[81] and K_4PbO_3[82] experience pyramidal coordination by oxygen. Both compounds were obtained by heating appropriate molar ratios of slightly oxygen defficient K_2O and SnO or PbO at high temperatures (ca. 500°) for 7 days. The lead derivative contains isolated PbO_3 groups possessing approximately C_{3v} symmetry, which are ordered in a very complicated manner and connected by K^+ cations forming a layered structure. $K_2Sn_2O_3$ crystallises with a perovskite lattice in which half of the anions are missing in a regular manner again resulting in a layered structure in which $-Sn-O_3-Sn-$ layers are stacked parallel to the base in a rhombohedral sequence. The material hydrolyses immediately on exposure to air to give black SnO. The ternary lead oxides, M_2PbO_2 (M=K,Rb,Cs) were prepared similarly (450°C, 21 days, evacuated glass ampoule), and a crystallographic study of the potassium compound showed the presence of isolated $[Pb_2O_4]$ groups also arranged in a layered structure with pyramidal coordination of lead.[83]

Several other mixed oxide systems involving lead have been studied. New mixed valency lead oxyiodides of variable composition $Pb(II)_{4-x}Pb(IV)_xO_4I_{2x}$ have been synthesised by different routes. Treatment of the massicot modification of PbO with iodine in water at room temperature yields a brown powder consisting of crystals of almost colloidal dimensions of stoichiometry $1<x<2$ which appear to have body-centred tetragonal symmetry. Better crystallised specimens with similar stoichiometry were obtained by the reaction of PbI_2 and Pb_3O_4 at 500°C. Crystalline samples with a higher iodine content, e.g. $Pb(II)_{2.5}\ Pb(IV)_{1.5}\ O_4I_3$, could be prepared by the reaction of PbO_2 with PbI_2 in the temperature range 430-550°C.[84] The phase relation of products obtained in the reaction between PbO and TiO_2 under hydrothermal conditions up to 500°C and 500 kg cm^{-2} for 5 hours has been investigated. The yield and crystalline properties of purified $PbTiO_3$ depend upon the $PbO:TiO_2$ molar ratio in the raw mixtures as well as the temperature. Both $PbTiO_3$ and $PbTi_3O_7$ may be synthesised at a remarkably low temperature under hydrothermal conditions (cf. the ignition process). Pure and well-crystallised $PbTiO_3$ is obtained by heat-treating above 400°C at Pb:Ti ratios greater than 1.0 and dissolving the excess PbO with acetic acid. $PbTi_3O_7$ coexists occasionally with $PbTiO_3$ to some extent at Pb:Ti ratios less than 1.0, but appears as a single phase in the temperature range 100-450°C at a Pb:Ti ratio of 0.33. The unit cell volume of $PbTiO_3$ prepared at the lower temperature is considerably larger, suggesting a loosely packed structure.[85] The structure of pure perovskite $PbTiO_3$ has been refined at -183, -115, 25 and 55°C by the Rietveld neutron powder profile method; however, no evidence could be obtained to confirm the low-temperature phase transition reported previously.[86] The same method has also been applied to $PbZr_{0.9}Ti_{0.1}O_3$ at various temperatures in the range 25-300°C. Cation displacements and octahedral distortions were observed to decrease smoothly with increasing temperature, as expected for a ferroelectric material.[87] The equilibrium diagram of the $PbO-Mn_2O_3$ system in the temperature range 20-1200°C in air shows the formation of two compounds: $Pb_6Mn_6O_{17}$ which decomposes at 830°C to afford $Pb_3Mn_6O_{13}$ and PbO.[88] The equilibrium diagram for the $PbO-Sb_2O_3$ system in air shows the formation of several phases: $PbSb_2O_6$, $Pb_{3+x}Sb_2O_{8+x}$ (with a homogeneity range of 23-30 mole % Sb_2O_3), $Pb_4Sb_2O_9$ and $Pb_6Sb_2O_4$.[89] The reactions of PbO,

PbO_2, $PbCO_3$ or $Pb(OAc)_2.3H_2O$ with Sb_2O_3 in a 2:1 molar ratio at temperatures up to 700°C yield a cubic pyrochlore together with $PbSb_2O_6$. The pyrochlore contains Pb(IV), and has the approximate composition $Pb(II)_2\ Pb(IV)_{0.5}Sb(V)_{1.5}\ O_{0.75}$. After heating to 900°C, rhombohedral $Pb_2Sb_2O_7$ is formed, but there was no evidence for the formation of a cubic modification with the pyrochlore structure.[90] Crystalline hydrated lead(II) pertechnetate and perrhenate, $Pb(MO_4)_2.2H_2O$ (M=Ti,Re) may be prepared by treating $PbCO_3$ or PbO with the appropriate acid, but are extremely unstable in air losing all of its water of crystallisation even at room temperature.[91] The molybdate, $K_2Pb(MoO_4)_2$, is obtained from the interaction of the two binary molybdates, and has a structure based on that of palmierite, $K_2Pb(SO_4)_2$.[92]

The thermodynamics of the dissociation of solid $PbSO_3$ into PbO (tetragonal) and SO_2 in the temperature range 328-375°C have been investigated. The enthalpy and entropy of reaction were determined to be 33.1(1.0) kcal $mole^{-1}$ and 40.9(1.5) e.u. respectively.[93] The structure of lead selenite, $PbSeO_3$ has been reported. Each lead atom has nine contacts to oxygen, four at short distances (2.53-2.67Å) and a further five at 2.83 - 3.05Å.[94] Lead orthotellurate, Pb_3TeO_6, has been obtained as a yellow crystalline solid by heating a mixture of elemental tellurium with PbO and Na_2CO_3. At temperatures above 400°C, however, slow decomposition to $PbTeO_3$ and PbO occurs.[95] The two lead atoms in $Pb_2Te_3O_8$ are crystallographically non-equivalent. Both have highly irregular coordination; one with eight contacts to neighbouring oxygen atoms and the other nine within the range 2.28(7) - 3.33(3)Å.[96] Crystals of $Pb_2P_4O_{12}.4H_2O$ are transformed into the dihydrate, $Pb_2P_4O_{12}.2H_2O$, by heating at 100°C. Further heating at 150°C results in the formation of crystalline $Pb_2H_3P_3O_{10}$ which occludes amorphous H_3PO_4. The structures of both products have been determined, and each lead atom forms eight contacts to oxygen.[97,98] Static isothermal heating of $2SnHAsO_4.H_2O$ yields first $Sn_2O(H_2AsO_4)_2$ and then $Sn_2As_2O_7$.[99]

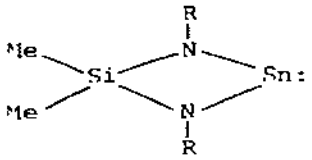
The cyclopentadienyl derivatives of bivalent germanium, tin and lead have been the subject of detailed examination over the past few years. Nevertheless, in 1978 several new types of reaction of these compounds were reported. Photolysis of $(C_5H_5)_2Sn$ yields the $C_5H_5\cdot$ radical (e.s.r.) and a yellow solid separates from solution, presumably the ultimate product resulting from the inferred other product, the Sn(I) $C_5H_5Sn\cdot$ radical.[100] No reactions involving substitution on the cyclopentadienyl ring have as yet been reported. However, refluxing a mixture of $(C_5H_5)_2Sn$ with Me_3SnNEt_2 in benzene for six hours yields $(Me_3SnC_5H_4)_2Sn$ as an extremely oxygen and moisture sensitive, slightly yellowish-green oily liquid. Substantial amounts of $(Me_3Sn)_2C_5H_4$ and $(Me_3Sn)_3C_5H_3$ were also formed in the reaction.[101]

The lack of any substantial ring-substitution chemistry is most probably a consequence of the facile protolysis of the Sn(II)-C_5H_5 bond, and many such reactions, including that with $W(C_5H_5)(CO)_3H$ to give $Sn[W(C_5H_5)(CO)_3]_2$, have been reported previously. Treatment of $(C_5H_5)_2Sn$ with a three mole excess of $Mo(C_5H_5)(CO)_3H$ leads to the formation of $HSn[Mo(C_5H_5)(CO)_3]_2$(37), presumably by an initial protolysis reaction affording $Sn[Mo(C_5H_5)(CO)_3]_2$ as an intermediate which subsequently inserts into the Mo-H bond of a further molecule of $Mo(C_5H_5)(CO)_3H$. Treatment of (37) with chloroalkanes converts it into $ClSn[Mo(C_5H_5)(CO)_3]_3$, whilst reaction with HCl and acetic acid produce $X_2Sn[Mo(C_5H_5)(CO)_3]_2$ (X=Cl,OAc).[102] As had been recognised previously, the ^1H and ^{13}C n.m.r. data for $(MeC_5H_4)_2M$ (M=Ge,Sn,Pb) confirm a skew sandwich structure for all three.[103] The photoelectron spectra of $(C_5H_5)_2M$ (M=Sn,Pb) have been interpreted in light of their structures. The results do not support the separation of covalent centrally-bonded metal cyclopentadienyls into π-bonded and σ-bonded classes. Rather, the evidence suggests that π-bonding of some type is essential for the formation of the centrally-bonded structure, and when this is not possible or effective, the peripherally-bonded structure is adopted.[104]

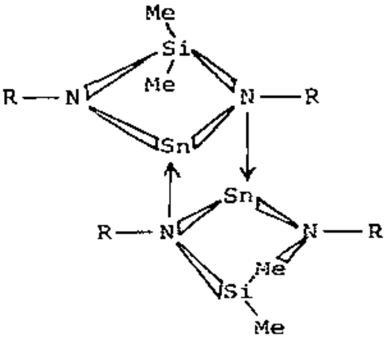
From a comparison of infrared data with other Group 2 metal-$Fe(CO)_4$ derivatives, $PbFe(CO)_4$ is associated in the solid-state.[105]

The structure of GeS, previously determined by Zachariasen in 1932, has been reinvestigated. The germanium atoms are each pyramidally coordinated by three sulphur atoms in a layer structure parallel to the [100] plane.[106] Lanthanum and cerium thiogermanates(II) and thiostannates(II), $M_2M'S_4$ (M=Ln,Ce; M'=Ge,Sn), are obtained as red-brown, isostructural solids on heating a mixture of La_2S_3, C_2S_3 and M'S at temperatures around 600°C.[107] The kinetics of growth of oxide films on the 100 face of a PbS single crystal are initially linear but subsequently follow a parabolic rate law. Lanarkite $PbO.PbSO_4$ and $PbSO_4$ were detected in the product films.[108]

Veith[109-111] has published details of the chemistry of 1,2,3,4λ^2-diazasilastannetidines. Whether these compounds exist as a monomer (38) or as a Lewis acid-Lewis base dimer (39) depends on the

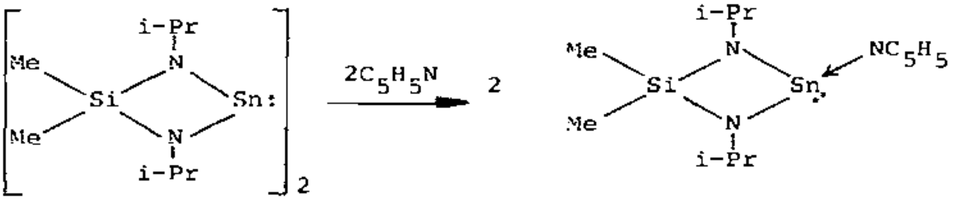


(38)

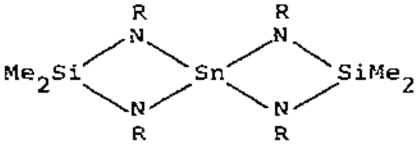


(39)

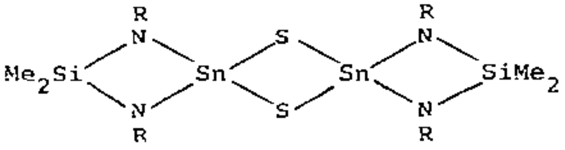
nature of the organic substituent on nitrogen. At room temperature when R=t-Bu the compound exists as a red monomeric liquid, but on cooling below 0°C two crystalline modifications are found. The monoclinic phase contains both monomeric and dimeric units, whilst the other triclinic phase presumably only contains dimers. When R=i-Pr, only dimeric units are present in both solid and liquid phases. The intermolecular association may also be broken down by the addition of pyridine:[109,110]



Oxidation of (38) (R=t-Bu) with oxygen at -78°C in pentane or ether yields the spiro-tetraazastannane (40), but with sulphur in benzene the dispiro[3,3,3]distannadisulphadisilatetrazane (41) is produced. This latter compound may react further with the

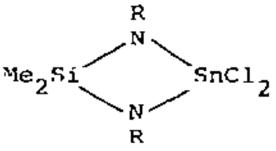


(40)

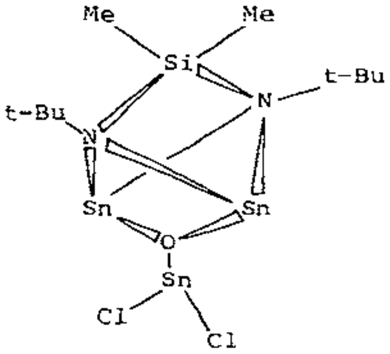


(41)

starting stannylene (38) (36h at 130°C) to yield (40) and SnS, a reaction for which an activation energy of 48.6 kJ mol^{-1} was determined. Compound (38) also reacts with $SnCl_4$ in 2:1 or 1:1 molar ratio in benzene to afford the spiro-tetraazastannane (40) and the diazadichlorostannane (41), respectively. Again, further reaction with (38) may take place giving (40).[111] The reaction



(41)



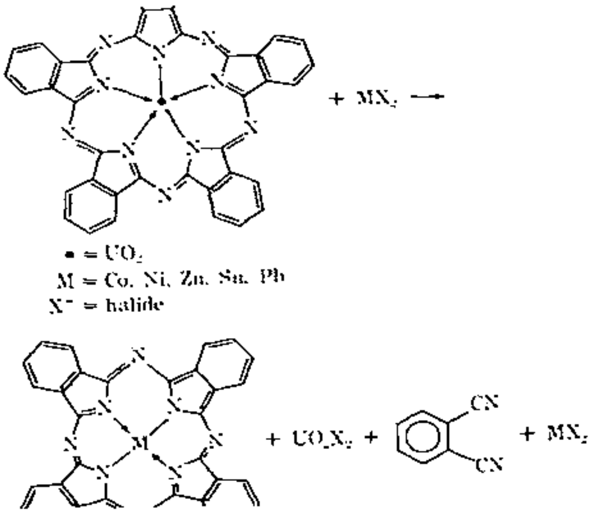
(42)

of (41) and (38) in the presence of moisture yields a product of stoichiometry $Me_3Si(Nt\text{-}Bu)_2Sn.SnO.SnCl_2$. The structure of this compound is dominated by a $[SnCl_2]$ ribbon to which $[Me_2Si(t\text{-}BuN)_2Sn_2O]$ cage units are connected via the oxygen atom acting as an electron donor. The "molecular" unit is shown schematically in (42). The cage may be understood as a regular $[N_2Sn_2]$ tetrahedron (Sn-N, 2.31Å) bridged by a $[Me_2Si]$ group across the N-N edge and by an oxygen atom across the opposite Sn-Sn edge (Sn-O, 2.09Å).[112]

The products of reaction of $SnCl_2$ and $Sn(NCS)_2$ with 18-crown-6 have been formulated in terms of a cationic moiety SnX^+ (X=Cl,NCS) bonded to the crown ether and anionic SnX_3^- on the basis of tin-119 Mössbauer data. In contrast, the product from 18-crown-6 and $Sn(ClO_4)_2.3H_2O$ contains only one type of tin atom.[113] The rates of complexation and decomplexation of 15-crown-5 and 18-crown-6 complexes of Pb^{2+} have been determined from ultrasonic adsorption measurements over the 15-205 MHz frequency range at 25°C. The data obtained could be fitted to a two-step mechanism, in which loss of coordinated water from the ions was proposed as the rate-determining step.[114]

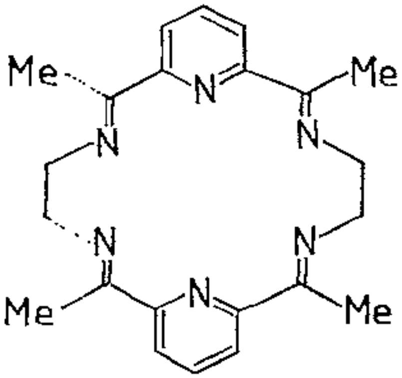
The kinetics of replacement of cyclic polyethers (Y) by the cyclic tetraamine $(CH_2CH_2NH)_4$ (=L) for Pb^{2+} in acetate buffer solutions have been measured. The formation of PbL^{2+} is first-order in $[L]$ $[Pb(OAc)^+]$, and in $[PbY^{2+}]$, and the relative rates of replacement of Y by L are approximately inversely proportional to the relative stabilities of the PbY^{2+} complexes, with 18-crown-6 being replaced most slowly.[115]

The reaction of dioxocyclopentakis(1-iminoisoindolinato)uranium(VI) with $SnCl_2$ and $Pb(OAc)_2$ results in a ring-contraction:[116]



• = UO_2
M = Co, Ni, Zn, Sn, Pb
X^- = halide

Hexagonal bipyramidal lead(II) complexes of the hexaimine macrocyclic ligand (43) (=L^3) are obtained by the reaction of 2,6-



(43)

diacetylpyridine and 1,2-diaminoethane in the presence of $Pb(NCS)_2$ or $Pb(ClO_4)_2$. Metathesis with the perchlorate complex yields $PbL^3(NCS)_2$. Preliminary structural data for $PbL^3(NCS)_2$ shows the lead atom to be 8-coordinated, with the six nitrogen atoms of the macrocycle defining the equatorial girdle and the NCS groups, one nitrogen-bonded the other sulphur-bonded, occupying the two axial sites. The macrocycle is distorted significantly from planarity.[117]

4.2.3 Hydrides

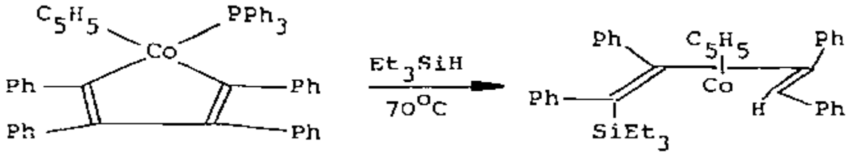
Silane decomposition in a single pulse shock tube at 1200-1300K takes via an initial molecular hydrogen elimination reaction ($SiH_4 \rightarrow SiH_2 + H_2$), rather than via the bond fission process ($SiH_4 \rightarrow .SiH_3 + H.$). The results for SiD_4 pyrolysis in the presence of excess toluene show conclusively that the deuterium atoms generated in SiD_4 decomposition under shock conditions arise from the fast dissociation of SiD_2.[118] The reactions of SiH_4 with regulated amounts of zeolitic water in zeolite Na-Y and in Na-mordenite have been studied. Between 60 and 200°C, the reaction proceeds more readily in the three-dimensional channel system of zeolite Y than in the one-dimensional channels of mordenite. The reaction products are not displaced by outgassing at 360°C, and are probably low molecular weight condensation polymeric molecules.[119] *Ab initio* Hartree-Fock M.O. calculations have been carried out on SiH_4, SiH_3F, SiH_2F_2[120] and Si_2H_6.[121] Adding silicon 3d functions to the basis set does not substantially alter the combined s and p electronic populations for the first three molecules.[120] The barrier to internal rotation in Si_2H_6 has been predicted to be 2.317 kJ mole^{-1}.[121]

The alkynylsilanes and -germanes, $H(D)_3SiC{\equiv}CCl$, $H_3SiC{\equiv}CBr$, $H_3GeC{\equiv}CCl$, and $H_3MC{\equiv}CMH_3$ (M=Si and Ge) are obtained by the reaction of silyl or germyl halides with $LiC{\equiv}CCl$, Li_2C_2 or $NaC{\equiv}CBr$.[122] Small amounts of BCl_3 catalyse the reaction of benzene and Cl_3SiH at 300-350°C to give $PhSiCl_3$ and H_2. The proposed mechanism involves the intermediacy of boron hydride and boron phenyl species.[123] 2-Germa-acetic acid decomposes in dilute acetic acid to yield carbon monoxide, an orange-yellow solid of approximate composition $GeH_{0.6}$, and small amounts of germane. In strongly acidic solution, however, carbon monoxide is evolved quantitatively, and no solid hydride or germane forms;

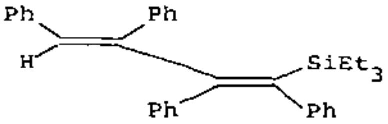
rather the solution contains the GeH_3^+ (or $GeH_3(OH_2)^+$) cation. It would appear, therefore, that the germyl cation is not stable in less acidic solution forming germylene, GeH_2, which disproportionates.[124]

Complexes of several transition metals, principally rhodium, cobalt and nickel, are active hydrosilylation catalysts. Phosphine complexes of nickel, ruthenium rhodium, palladium and platinum ($(Ph_3P)_3RhCl$) is the most effective and convenient) catalyse the hydrosilylation of 1-hexene by Cl_2SiH_2 to give n-hexyldichlorosilane exclusively.[125] $(Ph_3P)_3RhCl$ also catalyses the reactions of hex-1-yne[126] and benzylidene aniline[127] with Et_3SiH. The reaction with hex-1-yne affords cis- and trans-n-$BuCH{=}CHSiEt_3$ as the major products, the former product being favoured by a decrease in catalyst concentration, increase in temperature, or increase in the silane/alkyne ratio. The trans product isomerises on treatment with the catalyst, but only in the presence of silane.[126] The silyl-rhodium complex, $(Ph_3P)_2$-$(Et_3Si)Rh(H)Cl$, is probably the active intermediate in such hydrosilylations.

The hydrosilylation of a multitude of alkenes $R'{-}CH{=}CH_2$ ($R'{=}C_3H_7{-}C_{10}H_{21}$, Ph, $SiMe_3$, $CH_2\ NMe_2$, $CH_2N[Si(OEt)_3]_2$) and cyclopentadiene with a variety of silanes $HSiR''_nX_{3-n}$ (n=1,2; R"=Me,Et; X=Cl; n=0, X=Cl, OEt) in the presence of catalytic amounts of $CO_2(CO)_8$ and $Rh_4(CO)_{12}$ have been described. Alkylchloro(ethoxy)silanes and cyclopentenylchloro(ethoxy)alkylsilanes are obtained in quantitative yields after reaction times varying from 0.5 to several hours depending on the nature of the metal carbonyl, alkene structure, and reaction temperature. Hydrosilytion of vinyl- and isopropenyl-O-carboranes occurs at 20-30°C over 2-3 days to give only 20-35% yields of the corresponding silanes.[128] Hydrosilylation of alkenes by Me_2SiH_2 catalysed by the system $Ni(acac)_2{-}AlR_3{-}PPh_3$ involves only one of the Si-H bonds to afford dimethylorganylsilanes.[129] Cobaltacyclopentadiene complexes react with Et_3SiH to give diene complexes or uncomplexed, highly substituted butadienes, e.g.



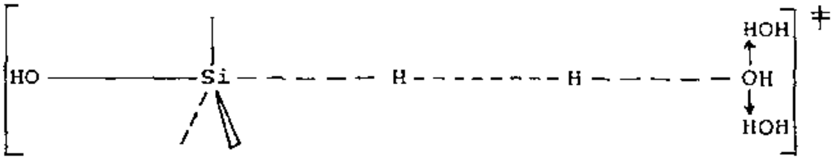
When this reaction is carried out at 120°C, (44) is obtained.[130]



(44)

Chlorinated hydrocarbons such as CCl_4, CCl_3CH_3, and 1,1,1,3-tetrachloroalkanes are selectively reduced by silanes to give $CHCl_3$, 1,1-dichloroethane, and 1,1,3-trichloroalkanes, respectively, in high yields in the presence of catalytic amounts of ruthenium(II) complexes. The catalysis is rationalised on the basis of successive oxidative-addition, reductive-elimination, and hydrogen-halogen exchange on the phosphine-ruthenium complex.[131]

The alcoholysis of the Si-H bond is heterogeneously catalysed by alkali metal salts such as KF, CsF, KNCS, or potassium or caesium carboxylates. The reaction is highly selective, and by choice of conditions it is possible to prepare mono-, di- or tri-alkoxysilanes by changing the salt catalyst or the temperature and/or the [silane]/[alcohol] ratio. The proposed mechanism of the catalysis involves the coordination of the salt anions to the silane, causing delocalisation of the Si-H electron pair, and the reaction then takes place by nucleophilic attack of the alcohol molecule at the silicon atom.[132] The role of the solvent in the alkali catalysed hydrolysis of 3-[(2-methoxy)ethoxy]-propyldimethylsilane has been investigated kinetically in dioxane/water varying the solvent composition. Statistical analysis of the kinetic data indicated that approximately three molecules of water are involved in the rate-determining step in a transition state such as (45).[133]



(45)

Trimethyltin hydride cleaves the M-E bond of $R_nEM(CO)_5$ (M=Mn,Re; E=P,As; R=CF_3,n=2) and $IRe(CO)_5$ to afford the corresponding trimethyltin derivative and $HM(CO)_5$.[134]

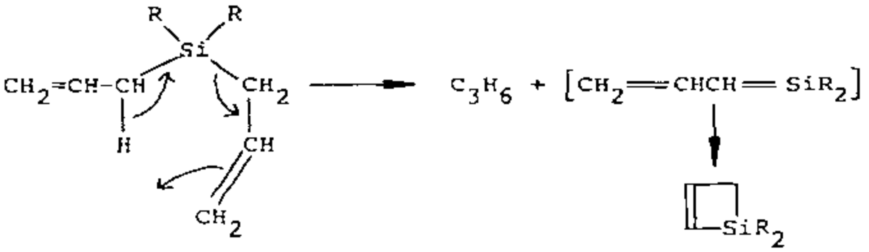
4.2.4 Compounds with Four Metal-Carbon Bonds

Purely organometallic compounds are beyond the scope of the present article. However, certain aspects are worthy of note here. The structure of tetravinyltin in the gas phase has been studied by electron diffraction. The preferred model (of S_4 symmetry) predicts that all four vinyl groups are intermediate between the staggered and eclipsed conformations.[135] The proximity of a bulky iodine atom in Ph_3SnCH_2I has a negligable effect on the stereochemistry at tin, although ^{119}Sn n.m.r. data show that some perturbation of electronic distribution occurs.[136] The crystal structures of C,C'-bis(trimethylstannyl)-B-[β-(trimethylsilyl)-methyl]-m-carborane[137] and 1,1,6,6,-tetraphenyl-1,6-distannacyclodecane[138] have also been reported. The latter has a 'boat-chair-boat' type conformation in the solid, but in solution at room temperature undergoes rapid interconversion between the possible conformers (^{13}C and ^{119}Sn n.m.r.).

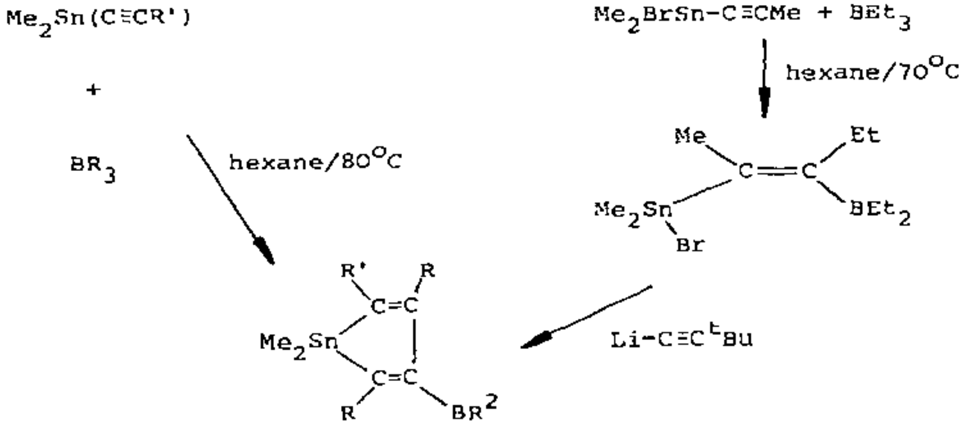
^{1}H and ^{13}C n.m.r. studies have established unequivocally that the metallotropic rearrangements of cyclonona-2,4,6,8-tetraenyltrimethylstannane[139] proceed by successive [1,5] migrations and of cyclohepta-2,4,6-trienyltrimethylstannane[140] by either [1,4] or [1,5] migrations, rather than [1,2] shifts. Similarly, cyclohepta-1,3-dienyltriphenylstannane undergoes [1,5] shifts. It is therefore quite probable that rearrangements in cyclopentandienyl- and indenyltin compounds also proceed by [1,5] shifts, contrary to previous suggestions.[140] The Mössbauer spectrum of $(Me_3Sn)_2CN_2$ exhibits a quadrupole splitting of 1.0mm s^{-1} indicating a strongly deshielded tin atom. N.m.r. data (^{1}H, ^{13}C, ^{15}N and ^{119}Sn) reveal a regular distribution of enhanced electron density along the CNN moiety, and force constant calculations indicate a decrease of bond order in the N-N bonding and an increase in the N-C bonding.[141]

Convenient, high yield syntheses of perfluoromethyl derivatives of the heavier Group 4 metals are still elusive. Although several new routes have been investigated, none is satisfactory. Controlled, low-temperature direct fluorination of Me_4Sn does yield partially fluorinated derivatives, but Sn-C bond cleavage occurs as well.[142] Bis(trifluoromethyl)mercury is a useful CF_3 group source, and undergoes group exchange with a number of germanium, tin and lead compounds. Exchange with $GeBr_4$ and GeI_4 yields all the perfluoromethyl derivatives $(CF_3)_nGeX_{4-n}$ (n=1-4; X=Br,I) but only mono- and bis-tin derivatives can be prepared using $SnBr_4$.[143] Exchange of one CF_3 group for one methyl group occurs for Me_4Sn, Me_3SnCF_3 and Me_4Pb, but product yields are low. Metal-metal bond cleavage with formation of Me_3SnCF_3 occurs with Me_6Sn_2, but no analogous reaction takes place with Me_6Si_2 or the hexaphenyl derivatives Ph_6M_2 (M=Ge,Sn, Pb).[144]

The thermolysis of Me_4Si in a pulsed stirred-flow system takes place by different mechanisms above and below 950K. At higher temperatures, decomposition occurs via a non-chain process with homolytic Si-C bond fission as the rate-determining step ($D(Me_3Si-Me) = 355 \pm 6$ kJ mole^{-1}). In contrast, the kinetic data at lower temperatures indicate a short chain sequence.[145] The pyrolysis of diallyldiorganosilanes at ca. 700°C provides a simple one-step synthesis of silacyclobutenes, possibly via a retroene-type mechanism:[146]



Cyclic and acyclic alkenyl derivatives of tin continue to provoke interest. The type of product obtained from the reaction of diorganodialkynylstannanes and triorganoboranes depends upon the organic subsituents on each. Reaction of $Me_2Sn(C{\equiv}CR')_2$ (R'=t-Bu, $SiMe_3$) with BMe_3 or BEt_3 affords the 1-stannacyclo pentadienes (<u>46</u>), which are also obtained by stepwise synthesis:[147]



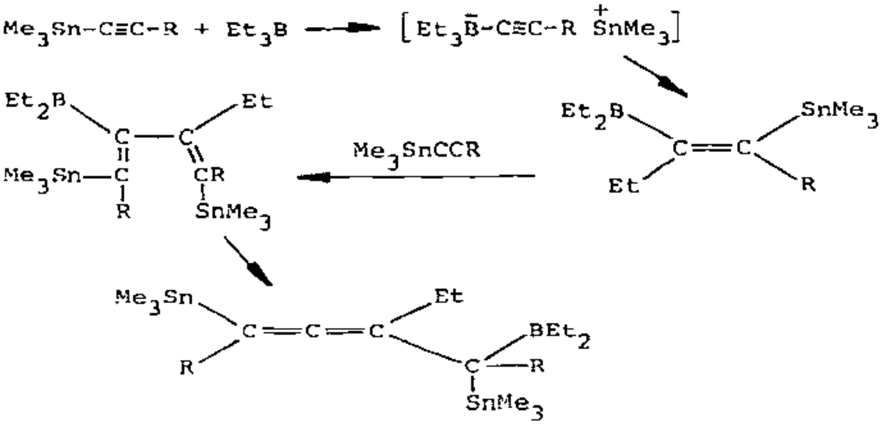
(46)

With less bulky organic substituents on the alkynyl groups, six-membered 1-stanna-4-boracyclohexadienes (47) or 2,5-bis(dialkylboryl)-1-stannacyclopent-3-enes (48) are produced depending upon the ratio of starting compounds, R and R', and the solvent.[148]

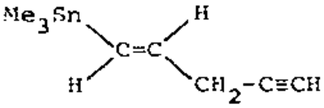
(47)

(48)

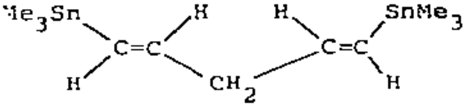
The reaction of Et_3B with $Me_3Sn-C\equiv CR$ compounds produces high yields of substituted allenes:[149]



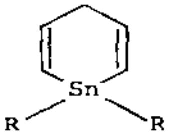
Addition of Me_3SnH to 1,4-pentadiyne yields both mono-(49)and di-(50) addition products, but with R_2SnH_2 (R=Me,Bu) the cyclostannahexadienes (51) are obtained.



(49)

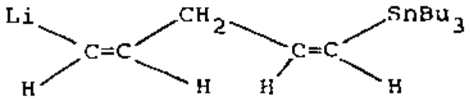


(50)

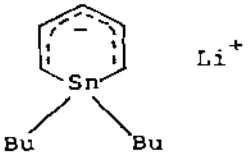


(51)

Alkyllithium reagents cleave the endocyclic Sn-C bonds of (51) yielding lithium reagents of the type (52),[150] but with lithium amides (53) is produced.[151]



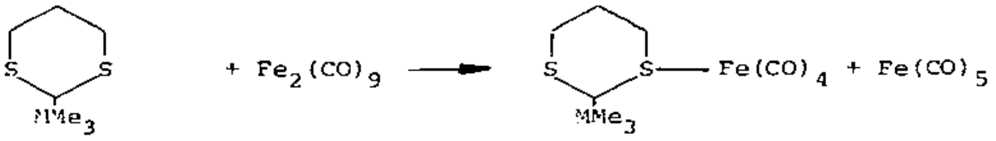
(52)



(53)

The preparation of *trans*-1,2-dilithioethylene by the action of 2 moles of BuLi on *trans*-1,2-(tributylstannyl)ethylene is not possible since only one Bu_3Sn is cleaved. Such reagents can, however, be obtained by a stepwise procedure, e.g. the successive treatment of *trans*-$Bu_3SnCH{=}CHSnBu_3$ with molar equivalents of BuLi, Me_3SiCl, BuLi and acetone produces *trans*-$Me_3SiCH{=}CHCMe_2OH$ in 63% yield.[152]

The rate of acid cleavage of allyltin compounds decreases markedly upon the introduction of vinyl substituents at tin. Simultaneously, the entropy of activation increases, suggesting a progressive decrease in solvation of the transition state.[153] Bulten has continued his studies of the chemistry of small-ring monostannacycloalkanes. Halodemetallation (with Cl_2, Br_2, I_2) and transalkylation (with $Me_{4-n}SnCl_n$, $GeCl_4$, $HgCl_2$) reactions with 1,1-dimethyl-1-stannacyclopentane proceed exclusively by ring cleavage, rather than by demethylation, indicating substantial ring strain, producing unsymmetrical compounds such as $Me_2ClSn(CH_2)_4SnCl_nMe_{3-n}$ (n=1-3), $Me_2ClSn(CH_2)_4M$ (M=$GeCl_3$, HgCl). Reactions of the corresponding six- and seven-membered ring systems with iodine likewise proceed by preferential cleavage of the endo-cyclic Sn-C bond, with an order of reactivity: $(CH_2)_4Sn>(CH_2)_5Sn>(CH_2)_6Sn>SnMe$. With tin and mercury halides, however, the order of reactivity is: $(CH_2)_4Sn>MeSn>(CH_2)_5Sn>(CH_2)_6Sn$.[154] As with the corresponding β-sulphides, the reactions of $Ph_3SnCH_2CH_2NMe_2$ with electrophilic reagents proceed in two distinct ways: (i) Sn-Ph bond cleavage (with $HgCl_2$, Br_2 and I_2), and (ii) formation of Ph_3SnX, $CH_2=CH_2$ and $ENMe_2$ (with $p\text{-}MeC_6H_4SO_2\text{-}Cl$, $o\text{-}NO_2C_6H_4S\text{-}Cl$, MeCOCl and Me-I (E-X)), each electrophile reacting predominantly, if not exclusively, via one of these reactions.[155] Amido-methyl derivatives of silicon, germanium and tin such as $Ph_3MCH_2CONEt_2$ (M=Si,Ge,Sn) and $ClPh_2SnCH_2CONEt_2$ have been obtained using the zinc reagent $BrZnCH_2CONEt_2$.[156] The reaction of the 2-metalla-1,3-dithiones (54) with $Fe_2(CO)_9$ yield the tetracarbonyl-iron complexes (55).[157]



(54) (55)

4.2.5 Compounds with Metal-Halogen Bonds

A method of preparing high purity $SnBr_4$ (levels of Mg,Al,Fe,Cu, Pb and Sb $<10^{-4}\%$) has been described.[158] Group exchange between $SnCl_4$ and Et_2Pr_2Sn at 200°C gives $EtPrSnCl_2$ in high yield (85%).[159] The phase diagram of the binary Sn-Cl system is very similar to the Sn-Br and Sn-I systems, showing the formation of only two compounds,

$SnCl_2$ and $SnCl_4$.[160] The reaction of SiF_4(g) and Si(c) has been studied by effusion mass spectroscopy in the temperature range 1590-1782K, yield values of $\Delta H_f(298)$ of -5.8(5), -140.6(3) and -259.3(5) kcal mol^{-1}, respectively, for SiF(g), SiF_2(g) and SiF_3(g).[161] First-order reaction kinetics have been observed for the reactions of $SiCl_4$, $SiBr_4$ and $GeCl_4$ with a large excess of oxygen.[162]

As in previous years, there have been many studies involving complexes of (organo)metal(IV) halides. $SiCl_4$ and $GeCl_4$, like CCl_4, absorb heat when mixed with acrylonitrile, and the resultant mixtures have vapour pressures in excess of those predicted from Raoult's law. With $SnCl_4$, crystalline $SnCl_4.2CH_2CHCN$ is obtained.[163] The thermal dissociation of the adducts, SiF_4.2Am (Am=aniline, p-toluidine, p-anisidine, p-phenetidine, p-chloro- or p-bromoaniline) into their components are first order with activation energies in the range 17-19 kcals mol^{-1}.[164] $SnCl_4$ and HCl have been found to react with 1,1-diphenylpropene to give a small equilibrium amount of the diphenylethylcarbonium ion (with $SnCl_5^-$ as the gegenion).[165]

^{19}F n.m.r. spectroscopy has been employed to study ligand distribution in the GeF_6^{2-} - $Ge(NCS)_4$ - MeCN system. Mixed anions such as $GeF_5(NCS)^{2-}$ and _cis_- and _trans_-$GeF_4(NCS)_2^{2-}$ are observed, but with a large excess of $Ge(NCS)_4$, neither these species nor GeF_6^{2-} are present, and _cis_- and _trans_-$GeF_3(NCS)_3^{2-}$ and _cis_-$GeF_2(NCS)_4^{2-}$ are formed instead.[166] The anisotropic e.p.r. spectra detected in powdered samples of $BaGeF_6$, K_2SnF_6 and $BaPbF_6$ at 30K under γ-irradiation have been assigned to the hexafluoride MF_6^{3-} anion radicals.[167] Vibrational anisotropy of the tin atom in $NiSnF_6.6H_2O$ has been studied by Mössbauer spectroscopy.[168] The same technique, along with ^1H and ^{19}F n.m.r. second moment data, have demonstrated the occurrence of a phase transition in $[(NH_2)_3C]_2SnF_6$ at _ca_. 165K.[169] K_2SnCl_6 is known to undergo two phase transitions at 261 and 255K. At room temperature (280K) the material has the cubic K_2PtCl_6 structure, but is tetragonal at 265K and monoclinic at 190K. The structural changes involve mainly two successive rotations of the $SnCl_6$ octahedra: (i) an alternating rotation about [100] in layers perpendicular to the _c_ axis, and (ii) an in-phase rotation around $[1\bar{1}0]$.[170] Solid phases such as $Rb_2SnF_6.4HOAc$ and $(NH_4)_2SnF_6.nHOAc$ (n=2,4) have been isolated from solutions of the salts in acetic acid at 25°C.[171]

Stable 1:1 adducts, thought to be of the type $[HMPA \rightarrow SiMe_3]^+ X^-$, have been isolated from the interaction of HMPA with halogenosilanes, Me_3SiX (X=Br,I). Conductometric studies show that the equilibrium for the formation of these adducts in CH_2Cl_2 lies well over to the adduct for X=Br or I, but for X=Cl the equilibrium lies close to the reactants.[172] Organosilicon isocyanates show no evidence of Lewis acidity, but the isothiocyanates, $R_nSi(NCS)_{4-n}$ $(0<n<3)$ react with (4-n) molecules of Lewis bases giving adducts of high stability. Enthalpy data for the formation of adducts of various bases with Me_3SiNCS, $Me_2Si(NCS)_2$ and $Si(NCS)_4$ in MeCN solution suggest that the sulphur atoms behave as the Lewis acid centres. $Si(NCS)_4$ forms an adduct with five molecules of pyridine-N-oxide; the first four molecules probably coordinating to the four sulphur atoms and the fifth to the silicon.[173] Kriegsmann[174] et al have estimated the strength of the intramolecular interactions in Me_3MF (M=C,Si,Ge,Sn) compounds (from vibrational data). Chemical shift and coupling constant data have been reported for Me_3SnBr, Me_2SnBr_2 and Me_2SnI_2 in 29 different organic solvents. Strong donors (based on coupling constant data) were found to be: DMSO∿DMF∿formamide>pyridine∿EtOH∿2-picoline, whilst moderate donors were: acetone∿MeCN>THF∿2,4,6-trimethylpyridine> 1,4-dioxane∿toluidine>$PhNO_2$∿Et_2O.[175] The crystal structures of several organotin complexes have been determined. $Me_3SnCl.HMPA$ is a neutral complex with trigonal bipyramidal coordination, but the corresponding bromide is an ionic compound with $[Me_3Sn(HMPA)_2]^+$ and $[Me_3SnBr_2]^-$ ions of the same geometry.[176] The Sn-Cl bond distances in the $[Ph_3SnCl_2]^-$ anion are the same 2.58(1) and 2.60(1)Å , but are different in the $[Bu_3SnCl_2]^-$ anion 2.573(7) and 2.689(6)Å .[177] Ph_2SnCl_2 forms 1:1 adducts with both benzthiazole and 2.aminobenzthiazole, for which Mössbauer quadrupole splitting data suggest trigonal bipyramidal and distorted octahedral geometries, respectively. The structure of the former compound has been confirmed by an X-ray study. Both phenyl groups occupy equatorial sites, with the remaining equatorial site and one axial site occupied by the two chlorines (see Figure 10).[178] The complexes, $Me_nSnX_{4-n}\cdot 2HMPA$ (n=0-2; X=Cl,Br) are all octahedral and centrosymmetric with trans donor molecules (and methyl groups).[179,180] The structure of $Me_2SnBr_2.2DMSO$ is similar, but in $Me_2SnCl_2\cdot 2DMF$ the DMF molecules are mutually cis.[180,181] In $MeSnCl_3.2DMF$, the donor groups are again cis, and the methyl

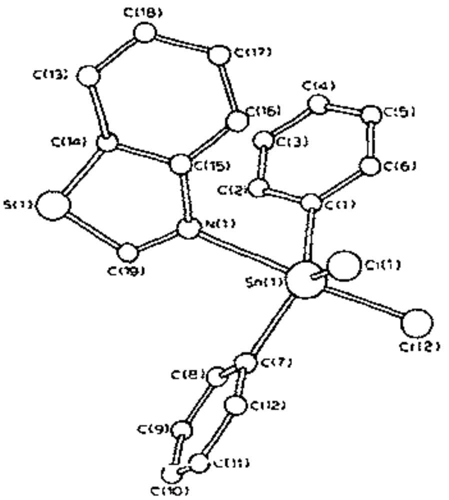
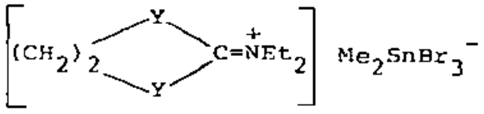


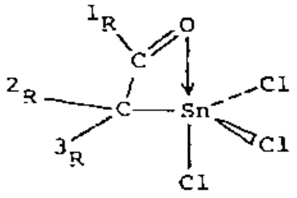
Figure 10. The structure of Ph_2SnCl_2·benzthiazole (reproduced from ref. 178).

group is randomly averaged. $MeSnBr_3\cdot 2DMF$ has a trigonal bipyramidally coordinated tin.[182] The adducts, $RSnCl_3$.pyz (R=Me,Bu, Oct,Ph; pyz=pyrazine), are polymeric compounds in which the ligand acts as a bridging bis-monodentate group to adjacent six-coordinated tin atoms. The three chlorine atoms were deduced to be in meridional positions.[183] The complexes (56) have been synthesised by the reaction of $Me_2Sn(Y_2CNEt_2)_2$ (Y=S,Se) compounds with α,ω-dibromoalkanes. The complexes react with Li^+ $TCNQ^{\bar{\cdot}}$ to afford the corresponding $TCNCl^{\bar{\cdot}}$ salts.[184]

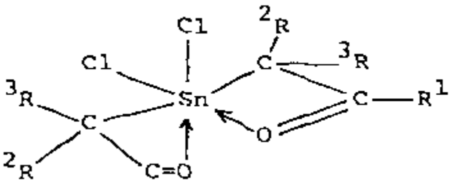


(56)

Organotin(IV) chlorides of coordination number greater than four through intermolecular coordination of a donor function remote in the organic ligand have received considerable attention. β-carbonylethyltin chlorides are obtained in high yields by the reaction of a carbonyl-activated alkene, HCl, and either tin(II) chloride or metallic tin. When $SnCl_2$ is employed, the five-coordinate monoalkyltin trichlorides (57) are produced, but the major products starting from tin metal are the corresponding dialkyltin dichlorides (58).[185]

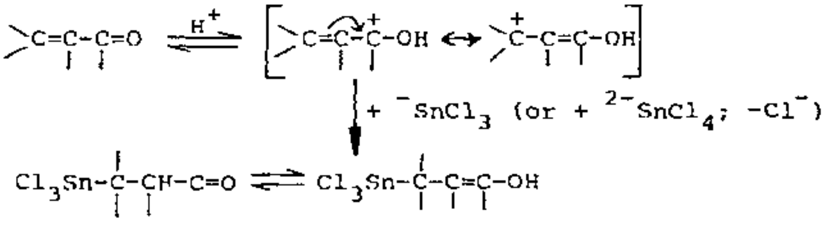


(57)



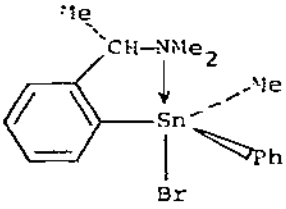
(58)

Although the synthetic procedure is exceedingly simple, the mechanisms by which the products are formed are not totally clear. The initial suggestion that the reactions proceed via the formation of chlorostannane intermediates such as $HSnCl_3$, which has been reported to be formed as an etherate when HCl is passed through a suspension of $SnCl_2$ in ether, and their subsequent addition to the alkene appear to have no foundation. Rather, the composition of the pale yellow oily phase which separates out in the $SnCl_2$-HCl-ether system has since been shown to be principally the tetrachlorostannate(II) species, $H_2SnCl_4.2Et_2O$, with only small amounts of $HSnCl_3.Et_2O$.[186] A similar viscous yellow oily phase of composition $H_2SnBr_4.3Et_2O$ (59) is obtained in the corresponding $SnBr_2$-HBr-Et_2O system. By the addition of pyridine (py) or aniline (an) to (59), other adducts such as $HSnBr_3.2an$, $HSnBr_3.3py$, $H_2SnBr_4.2an$ and $H_2SnBr_4.2py$ may be produced.[187] The protons in these species are highly acidic, and the preferred mechanism for the formation of (57) has been rationalised in terms of a 1,4-addition involving initial protonation of the carbonyl oxygen atom of the carbonyl-stabilised alkene:

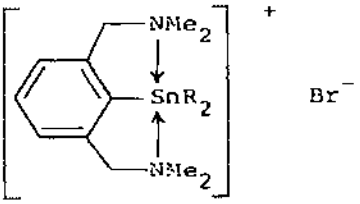


It is also unlikely that the reactions involving tin metal proceed via such species as H_2SnCl_2 or HSnCl. Since the reaction of tin metal and HCl in ether yields the identical $H_2SnCl_4.2Et_2O$ phase as does $SnCl_2$ under the same conditions, and in addition tin metal promotes the disproportionation of monoorganotin trichlorides to the corresponding diorganotin dichlorides, it would appear that the reaction with tin metal follows a similar course to that for $SnCl_2$ alone, with a subsequent disproportionation of the organotin trichloride initially produced.[186]

Triorganotin halides with an intramolecularly coordinated amino-substituted aryl group are obtained by the reaction of diorganotin dihalides with aryl-lithium, aryl-copper, or aryl-gold lithium intermediates. This method has been employed to synthesise the chiral triorganotin bromide (60), whose absolute configuration was determined by X-ray crystallography,[188] and also the ionic bromides (61).[189] The dimethyltin compound (61;R=Me) is completely dissociated in water. N.m.r. data show that the cation has the trigonal bipyramidal geometry in which the nitrogen atoms occupy axial sites. Dynamic n.m.r. spectra of the corresponding methyl-phenyltin compound show that above -90°C rate-determining Sn-N bond dissociation occurs, and that above 5°C a second process involving rate-determining rotation of the substituted aryl group around the $(N_2)C-Sn$ bond begins.[189] New chiral halogen-tin derivatives, methylpropylfluorenyltin and propylphenylfluorenyltin chlorides and iodides, have been synthesised by Lequan *et al.*, and have the lowest rate of intermolecular exchange yet observed for organotin halides.[190]



(60)



(61)

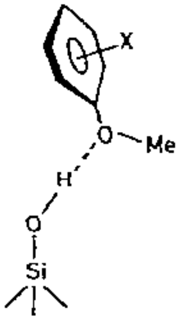
4.2.6 Oxides

The major areas of interest here concern investigations of the neat and modified metal(IV) oxides themselves, principally adsorption and chemisorption studies, and the natural and synthetic silicate and germanate minerals.

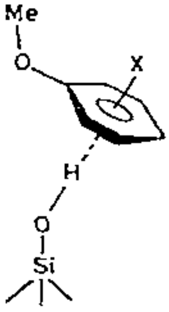
An *ab initio* SCF calculation has predicted a $^1\Sigma_g^+$ electronic ground state and $D_{\infty h}$ symmetry for molecular SiO_2,[191] which may be matrix-isolated by condensing evaporated SiO and atomic oxygen generated by microwave excitation. Force constant data for matrix isolated SiO and SiO_2 are very similar, indicating no further increase in bond order in the two-atom species (*cf*. CO and CO_2).[192] The rutile modification of GeO_2 has been obtained by using the chemical transport method with chlorine as the transporting agent and deposition temperatures lower than 900°. The colour of the columnar crystals varied from yellow to amber.[193]

Chemisorption on to silica from the gas phase has been studied for some time, and present investigations in this area are largely concerned with silica-supported metal catalyst systems, but their large volume precludes coverage here. Of interest, however, is a comparative study of nitrogen (at 78K) and water vapour (at 273-298K) adsorption isotherms with precipitated silica, a flame hydrolysed product (cabosil), and with cabosil the surface of which had been modified by treatment with Me_3SiCl to give a surface covered with hydrophobic $Si\text{-}OSiMe_3$ groups. For relatively mild outgassing conditions (e.g. 373-423K), cabosil and precipitated silica gave water isotherms of BET type II, and isosteric enthalpies of adsorption were consistent with a physisorption mechanism with hydrogen-bonding to surface hydroxyl groups. Following the completion of an isotherm, evacuation at 298K invariably left some residual water on the sample. Most of the hydrogen-bonded hydroxyl groups are removed from silica by evacuation at 773K, whilst most of the free hydroxyl groups are removed from cabosil at 1173K. The water isotherm on a cabosil sample so treated was of BET type III, typical of a hydrophobic surface. The trimethylsilyl-modified cabosil obtained by soaking were of BET type II, but samples modified by refluxing were generally of type IV. The hydrogen-bonded hydroxyl groups of these samples were progressively removed at temperatures in excess of 400K, but the $[Me_3SiO]$ groups are only appreciably affected at 973K. Complete dehydroxylation is achieved at 1073K.[194]

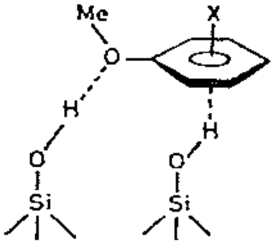
Novel are studies of chemisorption on to silica from solution. Two main types of surface-adsorbate interaction can be identified from heptane solutions of anisoles[195] and phenols[196] involving the formation of hydrogen-bonds between silanol groups and the aromatic π-electron systems and the oxygen atoms in the adsorbate (62-64). Electron-withdrawing substituents weaken both types of interaction. In addition, hydrogen-bonds may also be formed with suitable functional substituents on the aromatic ring, e.g. nitro groups (65). Similarly, hydrogen-bond formation takes place between surface silanol groups and mono- and diketones from CCl_4 solution.[197] Analysis of infrared absorbance data for 2- and 3- component liquid systems of these types can yield the relative proportions of adsorption.[198]



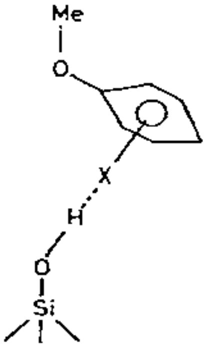
(62)



(63)



(64)



(65)

The catalytic activity of tin(IV) oxide and metal-'doped' tin(IV) oxide has stimulated a large number of investigations into the chemisorption and other properties of these materials. Tin(IV) oxide differs from silica by possessing a high Lewis acidity and a high oxidising capacity, but a low Brönsted acidity. This, however, is increased in mixed oxide systems such as $SnO_2.Sb_2O_3$ and $SnO_2.MoO_3$. Mössbauer studies of tin-antimony oxides of composition $Sn_{1-x}Sb_xO_2$ (x=0.01-0.10) form solid solutions after calcination at 873K in which the Mössbauer parameters steadily depart from those of SnO_2 itself, but provide no evidence for the formation of localised Sn(II) sites. E.s.r. measurements also indicate the presence of a spin-free surface. At compositions above x=0.10, a two phase system is formed.[199] Water isotherms on neat SnO_2 exhibit a discontinuity due to physisorption of water molecules with surface hydroxyl groups, probably on the [100] crystal plane. The discontinuity can be removed by pretreatment *in vacuo* or by hydrogen, but was restored by treatment with oxygen.[200,201] The influence of SO_2 on the chlorination of SnO_2 has been studied. Chemisorption of SO_2 on SnO_2 starts at 400°C and of Cl_2 at 650°C. By 700°C, the surface coverage of SO_2 corresponds to that of a monolayer. No chemisorption of oxygen on to pure SnO_2 was observed, but in the presence of sorbed SO_2, irreversible adsorption of oxygen takes place above 500°C and SO_3 appears in the gas phase. At the same temperature, chlorine adsorption onto the SO_2-treated surface is facilitated, and both $SnCl_4$ and SO_3 are desorbed.[202]

Both SnO_2 and transition metal-'doped' SnO_2 catalyse the CO-O_2 and CO-NO reactions, important in vehicle exhaust emission control, and much effort has been invested in the elucidation of the surface species present and the mechanisms involved. Surface unidentate carbonate and bicarbonate are formed slowly when SnO_2 is exposed to CO-O_2 mixtures, essentially independent of the gas mixture composition in the range 10-70% CO, but pretreatment at 723K affords a bidentate carbonate. Hydration of the surface severely inhibits adsorption, as does ammonia pretreatment, which with CO_2 leads to the formation of a surface carbamate.[203] Adsorption of NO on reduced SnO_2 causes replacement of oxide deficiencies in the surface layer with the formation of N_2 and N_2O, even at room temperature. On oxidised SnO_2, the NO radical is first coordinated to a Sn^{4+} site, and then reacts with further NO to give surface $(NO)_2$ dimer species.[204] SnO_2-catalysis of the CO-NO reaction starts below 200°C, but complete conversion is only achieved at temperatures in excess of 300°C. Very large increases in the rate and amount of adsorbed NO are obtained by adding 1% Cr_2O_3 to SnO_2, and complete conversion in the CO-NO reaction occurs at temperatures of 150-220°C. CO, however, soon poisons oxide surfaces towards the CO-NO reaction but, rather surprisingly, such poisoned surfaces are still highly active for the CO-O_2 reaction catalysed by SnO_2.[205] Catalysis of the CO-NO reaction by SnO_2 ion-exchanged with Cr(III), Mn(II), Fe(III), Co(II) and Cu(II) has been studied by adsorption of CO and NO individually, and CO-NO mixtures. Adsorption of CO takes place via carbon at a surface transition metal cation for all except the Cu(II)-exchanged oxide, to which CO bonds via oxygen. Surface carbonate species also bonded to transition metal sites were also observed, which could be either uni- or bidentate depending on the metal. The nature of the surface species resulting from NO adsorption varies significantly with the transition metal. The presence of a carbonate species and, in most cases, physisorbed CO_2 is consistent with a redox mechanism for the CO-NO catalysis. Interestingly, however, the mechanism for the Co(II)-exchanged oxide appears to be different from the others. This catalyst preferentially adsorbs CO from CO-NO mixtures, and selectively reduces NO to N_2. Others, notably the Co(II), Ni(II) and Fe(III)-exchanged oxides, adsorb NO from the gas mixture, and selectively reduce NO to N_2O.[206] The mechanism of the CO-NO reaction on SnO_2-Cr_2O_3 has been proposed to involve dissociative chemisorption of NO to give surface nitrogen sites. These could then react with further NO to give surface]-N-N-O (desorbs as N_2O) or CO to give surface isocyanate groups]-N-C-O (which react with further NO giving N_2 and CO_2).[205] The mechanism of formation of surface isocyanate on SnO_2.0.55CuO has been intensively studied using ^{13}C, ^{15}N and ^{18}O isotopic substitution. The results of this study, however, show unequivocally that the oxygen atom of the surface isocyanate originates from NO rather than the oxide surface or CO, indicating a mechanism involving initial dissociative chemisorption of CO, formation of an intermediate fulminate,]-C-N-O, which rearranges to give the isocyanate.[207]

Brönsted acidic oxides such as $SnO_2.MoO_3$ and $SnO_2.Sb_2O_5$ are catalysts for alkene oxidation and isomerisation, and alcohol dehydrogenation. Electronically-excited singlet molecular oxygen, which could play an important role in hydrocarbon oxidation reactions, can be thermally generated and desorbed from a Li-Sn-P-O catalyst.[208] Oxidation of propene to acetone over $SnO_2.MoO_3$ proceeds via oxidation of strongly surface-bound propene by lattice oxygen to give surface isopropoxide groups, which then undergo oxidative dehydrogenation.[209,210] The catalytic oxidation of isobutene to methacrolein over mixed Sn-Sb-O catalysts is very similar,[211] whilst methacrylonitrile is formed by passage of a mixture of isobutene-ammonia-air-water vapour over a Sn-Sb-Fe-O catalyst. Acceptable yields (70% at 425°C) of nitrile are observed only with hydrocarbon-poor (3%) and steam-rich(20%) mixtures, and excess of ammonia. Methacrolein is the main product at low conversions.[212] The isomerisation of alkenes over room-temperature-outgassed $SnO_2.Sb_2O_3$ probably proceeds via a carbonium ion-type of mechanism with Brönsted acid sites as the source of protons. The rates of reaction increase with increasing antimony content to a maximum at <u>ca</u>.50 atom % Sb, and decline thereafter. Oxides outgassed at higher temperatures were only active at compositions with less than 50 atom % Sb, and could be poisoned by treatment with bases or sodium acetate.[213,214]

The Mg^{2+} and Fe^{2+} cations in annealed, synthetic samples of olivines, $Mg_{2-x}Fe_xSiO_4$, are not randomly distributed. When $0.1 \leq x \leq 0.6$, the larger Fe^{2+} cations preferentially replace Mg^{2+} cations in octahedral sites, and the lattice dimensions do not change in this range. Quenching tends to yield samples with more randomly distributed cations, and the lattice dimensions now approach those of natural olivines.[215] Several other monosilicates have been studied. Single crystals of $CdNd_4[SiO_4]_3O$ have been obtained from molten alkali metal fluoride melts, and contain columns of $[SiO_4]$ tetrahedra.[216] Sodium titanium silicate, Na_2TiO_5, contains layers of $[SiO_4]$ tetrahedra and $[TiO_5]$ square pyramids joined by sharing corners and separated by layers of sodium ions.[217] Tribarium silicate, Ba_3OSiO_4, is isostructural with $Cs_3ClCoCl_4$, with slightly distorted SiO_4 tetrahedra.[218] The structures of the thorium silicate polymorphs, huttonite and thorite, have been reinvestigated. Huttonite has been confirmed to be isostructural with monazite, consisting of $[SiO_4]$ monomers and a compact arrangement of edge-sharing $[ThO_9]$ polyhedra. Thorite is isostructural with zircon, consisting of $[SiO_4]$ tetrahedra and a relatively open arrangement of edge-sharing $[ThO_8]$ polyhedra.[219] An electron microprobe analysis of crystals of Malayaite, $CaSnOSiO_4$, a rare tin silicate found in skarns and high-temperature hydrothermal veins gave the composition as $Ca_{0.98}Sn_{0.94}Ti_{0.05}O\ Si_{1.02}O_4$. The structure consisted of chains of vertex-sharing tin octahedra cross-linked by isolated silicate tetrahedra. Calcium occupies a large irregular polyhedron.[220] The composition of sklodowskite, generally given as $MgO\text{-}2UO_3\text{-}2SiO_2\text{-}6H_2O$, actually contains seven molecules of water thus making it isostructural with cuprosklodowskite.[221] The fundamental structural units in both sklodowskite and kasolite, $Pb(UO_2)(SiO_4).H_2O$ are $[(UO_2)_2(SiO_4)_2]^{4-}$ sheets.[221,222] The halogen apatites, $M_4La_6(XO_4)_6Z_2$, and oxyapatites, $M_4La_8(XO_4)_6O_2$ (M=Sr,Pb,Ba; X=Si, Ge; Z=F,Cl) have been prepared from $M_3La_6(XO_4)_6$. The products "$M_3La_6(XO_4)_6$" and "$M_4La_6(XO_4)_6O$" are actually mixtures of various phases. Their respective apatite phase is a solid solution between $M_2La_8(XO_4)_6O_2$ and the defect apatite $M_4La_6(XO_4)_6O$, whose compositions mostly approximate to $M_2La_8(XO_4)_6O_2$.[223]

The high temperature reactions between samarium metal and the Group 4 metal(VV) oxides, MO_2 (M=Si,Ge,Sn), have been investigated by T.G.A., X.R.D. and infrared. With SiO_2, initial oxidation of samarium to β-Sm_2O_3 takes place at *ca*. 500°C, with $Sm_4(SiO_4)_3$ being formed at temperatures 800°C. Reaction with SnO_2 at *ca*. 500°C yields $Sm_2Sn_2O_7$, which has the pyrochlore structure, and β-tin. Germanium metal and Sm_2O_3 are the chief products of reaction with GeO_2.[224] Coprecipitation from chromium silicate solutions with sodium sulphide or thiosulphate yields an amorphous silicate which is stable up to 300°C, but which above this temperature decomposes to Cr_2O_3, SiO_2 and Na_2CrO_4. Further heating at and above 800°C results in the formation of $NaCrSi_2O_6$, stable up to 1050°C.[225] The synthetic orthopyroxenes, $(Mg_{0.776}Co_{0.224})SiO_3$ and $(Mg_{0.925}Mn_{0.075})SiO_3$, show partial cation ordering over the two non-equivalent octahedral sites in the structure. The preference for the M(2) site follows the order Mn Co Mg.[226] Crystals of synthetic $Li_2Cu_5(Si_2O_7)_2$ contain pyrosilicate $[Si_2O_7]$ groups, three kinds of Cu^{2+} coordination polyhedra, and trigonal bipyramidally-coordinated Li^+ ions.[227]

Modifying influences on the general structure of the feldspars, $SrGa_2Si_2O_8$, $BaGa_2Si_2O_8$ and $BaGa_2Ge_2O_8$, arise from the size of the metal cations, the mean Si-O and Ge-O bond lengths and the tetrahedral cation combination.[228] Sodium metagermanate, Na_2GeO_3, is isostructural with Na_2SiO_3. The bridging Ge-O bond distance of the $[Ge_2O_6]^{4-}$ anion is 0.088Å larger than the terminal Ge-O distance.[229] The crystalline hydrated basic strontium digermanate $Sr_3(OH)_2\ Ge_2O_4(OH)_4\ .2H_2O$ has been synthesised by cooling solutions containing SrO, GeO_2 and 1-2N NaOH. X.R.D. and infrared studies of the thermal decomposition show the loss of two molecules of water at 250°C. At 312°C the inner-sphere hydroxyl groups of the digermanate decomposes with the formation of α-$SrGeO_3$.[230] The structures of the scandium garnets, $Ca_3Sc_2Si_3O_{12}$, $Ca_3Sc_2Ge_3O_{12}$ and $Cd_3Sc_2Ge_3O_{12}$, have been refined.[231] That of $K_2Ba[Ge_4O_9]_2$ is closely related to $K_2Ge_4O_9$ and $BaGe_4O_9$, and consists of rings built up from $[GeO_4]$ tetrahedra, which are linked by $[GeO_6]$ octahedra forming a three-dimensional network. Powder X.R.D. shows that the corresponding sodium and rubidium compounds, and $M_2Sr[Ge_4O_9]$ (M=Na,K), are isostructural.[232] A new series of sodium ion conductors of the type $Na_5MSi_4O_{12}$ (M=Fe,In,Sc, Y, and the rare earths Lu-Sm) have been prepared by hydrothermal solid-state reactions. The sodium ion conductivities are proportional to the size of the M^{3+} cation, and range from $2x10^{-3}$ $(cm)^{-1}$ for M=Sc to $3x10^{-1}$$(cm)^{-1}$ for M=Sm at 300°C. The behaviour is consistent with a structure consisting of $[Si_{12}O_{36}]$ rings stacked to form columns held apart by $[MO_6]$ octahedra. Immobile sodium ions are situated within the rings and mobile sodium ions between the columns. The size of the channels is dictated by the size of the $[MO_6]$ octahedra.[233]

An analysis of experimentally determined Si-O-Si geometries of a number of silicates has demonstrated that the determining factors are very often the almost constant Si-O(bonded) and Si...Si (non-bonded) distances.[234] Samples of the layered orthosilicate, chloritoid (idealised formula $(Mg,Fe)_2Al(Al_3Si_2O_{10})(OH)_4$) from three distinct geological sources, in both naturally-occurring and heat-treated forms, have been examined by Mössbauer spectroscopy. Only one type of site of O_h symmetry is occupied by Fe^{2+} ions. The Fe^{3+} ions are present to such a small extent as to preclude an evaluation of their preferred siting. The Rhode Island sample displayed an anomalous Fe^{2+} doublet arising from minute intergrowths of ilmenite ($FeTiO_3$).[235] Zeolites, including variants of retite, zeolite A, zeolite L, Zeolite M, faujasite and gismondiril, have been obtained from the Na_2O-BaO-Al_2O_3-SiO_2-H_2O system.[236]

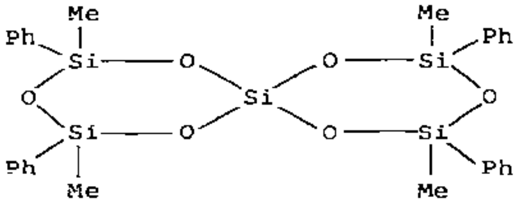
The trimethylsilylation technique has been employed to follow changes in the constitution of hemimorphite, $Zn_4(OH)_2(Si_2O_7).H_2O$, on heating at various temperatures up to 1300°C. The changes were also followed by T.G.A., D.T.A. and X.R.D. An abrupt change in the chromatographic pattern occurs at 600-630°C corresponding to the disappearance of the $[Si_2O_7]$ and emergence of the $[SiO_4]$ derivatives as the main product of the trimethylsilylation, coinciding with the loss of hydroxyl groups and formation of β-Zn_2SiO_4. The initial stage of the reaction at 627°C shows first-order kinetics. At 835°C, the transformation of β-Zn_2SiO_4 into α-Zn_2SiO_4 commences.[237] The application of the same method to dioptase, $Cu_6Si_6O_{18}.6H_2O$, yields $Si_6O_{18}(SiMe_3)_{12}$ and $Si_6O_{17}(SiMe_3)_{10}$ as the main products. Three isomers of each product are observed. When HCl is added to the reaction mixture, the predominant product is $Si_6O_{17}(SiMe_3)_{10}$, indicating that the $[Si_6O_{18}]^{12-}$ ion is converted mainly into the $[Si_6O_{17}]^{10-}$ ion in an acidic aqueous medium.[238] Silicate minerals also react similarly with Me_3GeCl in the presence of water to afford analogous trimethylgermyl derivatives.[239] The reaction of the $[SiW_{12}O_{40}]^{4-}$ anion with an excess of hydroxyl ion at an ionic strength of 1.0 m dm^{-3} to form the $[SiO_4]^{4-}$ and $[WO_4]^{2-}$ anions has been studied. The reaction proceeds in three distinct stages, with the $[SiW_{11}O_{39}]^{8-}$ and $[SiW_9O_{34}]^{10-}$ anions being formed as intermediates. The first stage proceeds via a base-dependent path, the second-order rate constant decreasing in the order $K^+ > Na^+ > Li^+$. The second stage, the hydrolysis of the $[SiW_{11}O_{39}]^{8-}$ anion, proceeds via both base-dependent and -independent pathways to give silicate and tungstate anions directly in this medium. The third stage, the hydrolysis of the $[SiW_9O_{34}]^{10-}$ anion, shows a very large dependence on the choice of cation, and studies in mixed-cation media suggest the formation of larger ion aggregates.[240] _Meso_-tetraphenylporphyrin reacts with selected cations in the interlamellar surfaces of montmorillonite, a swelling layer lattice silicate related to mica. Strongly acidic hydrated Fe^{3+} and VO^{2+} cations react quantitatively with the free-base porphyrin to give the protonated porphyrin dication in the form of intercalated monolayers. Monolayers of the porphyrin dication are also formed by reaction of the hydronium ions on the silicate surfaces, but weakly acidic hydrated Na^+ and Mg^{2+} ions on surface-exchanged sites afford only traces of the dication. Co^{2+}, Cu^{2+} and Zn^{2+} cations react to give mainly the metalloporphyrin in solution and a hydronium-exchanged form of the silicate.[241]

4.2.7 Molecular Compounds with Metal-Oxygen Bonds

Valence shell orbital energy level data for Me_3SnOMe, $R_3Snacac$ (R=Me,Et), R_2SnCl_2 (R=Me,Bu), R_2=Sn(acac)$_2$ (R=Me,Bu) and $Me_2Sn(tfac)_2$ have been evaluated from He(I) photoelectron spectra.[242]

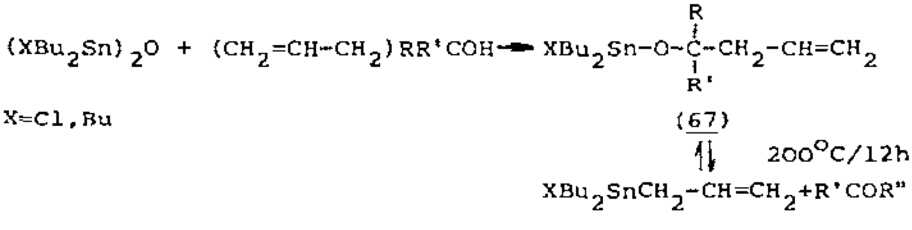
The silicon atom in $Ph_2Si(OH)_2$ is four-coordinated, but each oxygen maintains two hydrogen-bonds forming an infinite network about and along the _c_ axis.[243] The ionic hydroxy-silicon species, $[Si(OH)_2(bipy)_2]I_2.2H_2O$, is formed by the partial hydrolysis of $SiI_4(bipy)_2$. The yellow crystalline material, which decomposes at 120°C, contains _cis_-octahedral $[Si(OH_2)(bipy)_2]^{2+}$ cations with C_2 symmetry and exceptionally short Si-O bonds (1.643(4)Å). Each water molecule hydrates exclusively one of the two hydroxyl ligands by hydrogen-bonds.[244] Ph_3SnOH and Ph_3PbOH are isomorphous and isostructural, comprising zig-zag chains parallel to the _c_ axis in which planar Ph_3M fragments are joined by hydroxyl groups. In each compound the metal-oxygen distances are unequal.[245]

The crystal structures of $(Ph_3Si)_2O$[246] and $(Ph_3Sn)_2O$[247] have been determined. Both contain isolated molecules, however the former compound is exactly (crystallographic symmetry) linear at oxygen, whereas the tin analogue is bent (SnOSn 137.0(1)°). Microwave data for CH_3OSiF_3 and CD_3OSiF_3 are consistent with a very short (only 1.56(1)Å) Si-O bond distance and an angle of 132(1.5)° at oxygen.[248] The antisymmetric Si-O-Si stretching mode of $(Cl_3Si)_2O$ in argon,krypton and nitrogen matrices is split into a doublet, the highest separation (1117 and 1147 cm^{-1}) being observed in solid nitrogen. These data have been interpreted in terms of a quasi-linear structure for the compound, but with a sufficiently high barrier to linearity that the molecule obeys C_{2v} symmetry selection rules for the fluid phases.[249] Some nineteen products have been identified from the photolysis of $(Me_3Si)_2O$ at 15°C with a low-pressure mercury arc (eff.λ =185nm). The main event in the photolysis is the rupture of a Si-C bond. No Si-O bond fission is observed at all. The major products are $(Me_3SiOSiMe_2)_2$, CH_4 and C_2H_6.[250] The reaction of (HO)PhMeSi $_2$O with $SiCl_4$ produces racemic <u>trans,</u> <u>trans</u>-2,4,8,10-tetramethyl-2,4, 8,10-tetraphenylspiro 5.5 pentasiloxane(<u>66</u>), whose structure has been studied by X-ray diffraction. The two trisiloxane rings are almost mutually perpendicular (dihedral angle 80.7°), and the average SiOSi bond angle is 132.7°.[251] The thermal decomposition of CuOSiMe_3 $_4$ at 70-80°C and 10^{-3} torr proceeds by loss of



(<u>66</u>)

$(Me_3Si)_2O$ to afford $Cu_{18}O_2[OSiMe_3]_{14}$. This compound possesses a structure comprising large spherical molecules with an inner core consisting of the copper and oxygen atoms and the Me_3SiO groups distributed over its surface.[252] The reaction of $SnCl_4$ and $K[Al(Oi\text{-}Pr)_4]$ yields $Sn[Al(Oi\text{-}Pr)_4]_4$, proposed to contain eight-coordinated tin.[253] Germanium and tin butenoxides such as $Ge(OCMe_2CH=CH_2)_4$ and $Bu_nSn(OCMe_2CH=CH_2)_{4-n}$ (n=1-3),[254] and organotin amidoximes, $R_3SnON=C(NH_2)R'$ (R=Me,Bu,Ph; R'=Me,Et,Pr,Ph),[255] have been prepared by standard methods. Allyl-alkoxytin derivatives eliminate ketones on thermolysis:[256]



$$(XBu_2Sn)_2O + (CH_2=CH-CH_2)RR'COH \longrightarrow XBu_2Sn-O-\overset{R}{\underset{R'}{C}}-CH_2-CH=CH_2$$

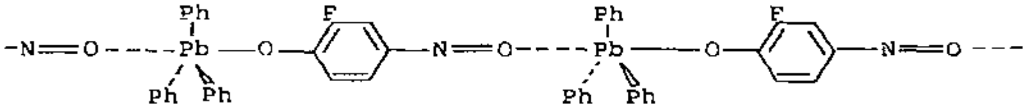
X=Cl,Bu

(67)

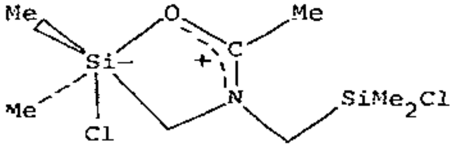
$$\xrightleftharpoons{200^{\circ}C/12hr.}$$

$$XBu_2SnCH_2-CH=CH_2+R'COR"$$

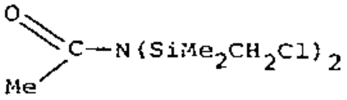
The last reaction is often reversible, and tributylallyltin chloride adds to ketones and alkehydes to give organotin alkoxides of the same type as (67).[257] The structure of $Ph_3PbOC_6H_3(F-2)NO-4$ consists of infinite chains in which adjacent Ph_3Pb groups are bridged by the organic residue:[258]



The product from the transilylation of bis(trimethylsily)-acetamide with $(ClCH_2)Me_2SiCl$ has been shown to actually be (68) rather than (69).[259]

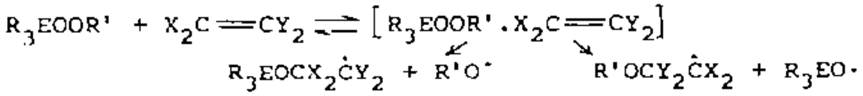


(68)



(69)

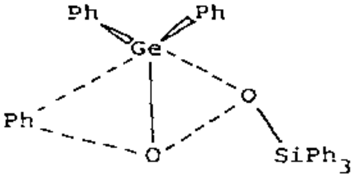
The kinetics of the decomposition of the peroxy-derivatives, R_3EOOR' (E=Si,Ge,Sn; R=Me,Et;R'=t-Bu,CMe_2Ph) in alkenes,[260] and of the KCN-catalysed rearrangement of $Ph_3GeOOSiPh_3$[261] have been investigated. The peroxides, R_3EOOR', and alkenes initially form 1:1 complexes, which facilitate the peroxide decomposition via a homolytic mechanism:



$$R_3EOOR' + X_2C{=}CY_2 \rightleftharpoons [R_3EOOR'.X_2C{=}CY_2]$$

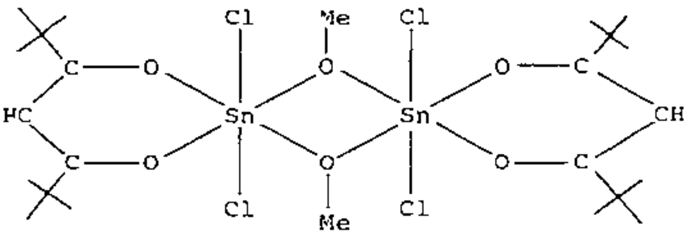
$$R_3EOCX_2\dot{C}Y_2 + R'O^{\cdot} \qquad R'OCY_2\dot{C}X_2 + R_3EO\cdot$$

The base-assisted rearrangement of $Ph_3GeOOSiPh_3$ proceeds with the formation of $Ph_2(PhO)GeOSiPh_3$ in a first-order reaction with an activation energy of 13.5(8) kcal mol^{-1} in a benzene PrOH mixture (cf. 27.7 kcal mol^{-1} for the thermal rearrangement in anisole). Of the various sites available to the nucleophile, the germanium atom is less sterically hindered than silicon, and interaction of the nucleophile leads to a distribution of electron density and contributes to the migration of the organic group from germanium to oxygen via a transition state such as (70).[261]



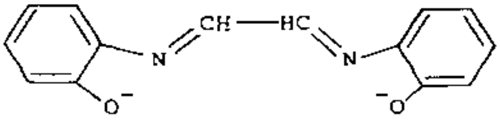
(70)

Ligand isotope exchange between $Ge(acac)_3\ ClO_4$ and Hacac ^{14}C has been studied in C_2Cl_4, $MeNO_2$ and MeCN at 100-120°C. The data indicate that the rate-controlling step of the exchange is governed by the ease of proton-transfer between incoming and leaving acac groups in an intermediate.[262] N.m.r. data for methoxy(β-diketonato)tin dihalides indicate an octahedral conformation with D_{2h} skeletal symmetry (71). Such dimers are very stable in the solid, but undergo facile disproportionation in solution.[263] The organotin derivative of monothio-β-diketones, $R_nSn(R'CSCHCOR'')_{4-n}$, have been obtained by standard procedures.[264]



(71)

A series of bis(substituted oxinato)tin dichlorides has been prepared by the cleavage of phenyl groups from Ph_2SnCl_2 at 180°C.[265] Mössbauer data for several organotin oxinates have been reported.[266] ^1H n.m.r. and infrared data show that the water molecule in the complex $Me_2Pb(qbha).H_2O$ (qbha = (<u>72</u>)) is coordinated to the metal



(<u>72</u>)

thus making it seven-coordinated. Deprotonation-ionisation of the complex takes place in DMSO and HMPA.[267]

Mehrotra *et al.*[268] have synthesised tin(IV) tetracarboxylates (<u>73</u>) by the reaction of tin(IV) tetrathiolates with acid anhydrides:

$$Sn(SR)_4 + 4(R'CO)_2O \longrightarrow Sn(O_2CR')_4 + HR'COSR$$

R=Et,Bu; R'=Me,Et (<u>73</u>)

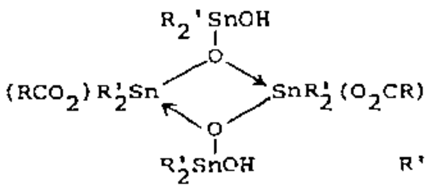
The mixed compounds, $Sn(SR)_n(O_2CR')_{4-n}$, could not be obtained by any of the various methods tried, but mixed chloride acetates, $SnCl_n(OAc)_{4-n}$ (n=1,2) were prepared by mixing the symmetrical compounds in the correct proportions. Higher homologues and mixed carboxylates were obtained by transacylation, e.g.:

$$Sn(OAc)_4 + nRCO_2H \longrightarrow Sn(OAc)_{4-n}(O_2CR)_n + nHOAc$$

n=1-4; R=$ClCH_2$, Cl_2CH, Pr,Ph

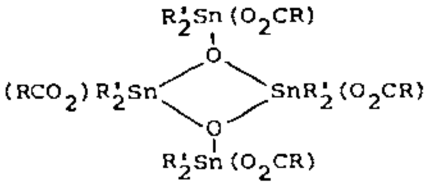
The reaction of $Sn(O_2CR)_4$ (R=Me,Et) with β-diketones in refluxing toluene or chloroform yields tin(IV)mono-β-diketonate tricarboxylates and di-β-diketonate dicarboxylates as stable monomeric compounds. The latter derivatives are the final products even when the β-diketone is in excess, but the carboxylate ligands are easily replaced by thiobenzoate and thioacetate groups.[269] Several types of product are obtained from the reaction of divinyldiallyltin and carboxylic acids, RCO_2H(R=H,Me,CH_2Cl,$CHCl_2$, CCl_3,CF_3), in water-acetone medium at room temperature depending on the nature of R. Trivinyltin carboxylate is the sole product when R=H or Me, but when R=CH_2Cl the two distannoxanes (<u>74</u>) and

(75) are produced as well. Both distannoxanes (74) and (75) are obtained when R = $CHCl_2$ and CCl_3, but when R=CF_3 only (75) is found.



(74)

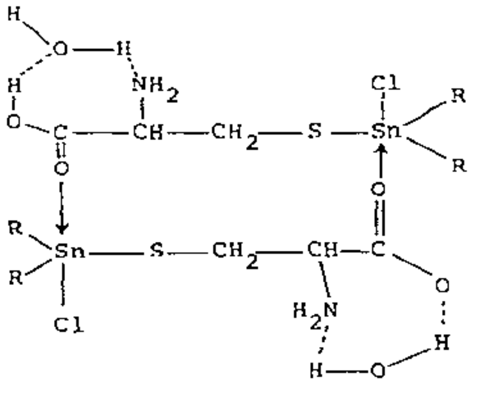
R'=vinyl



(75)

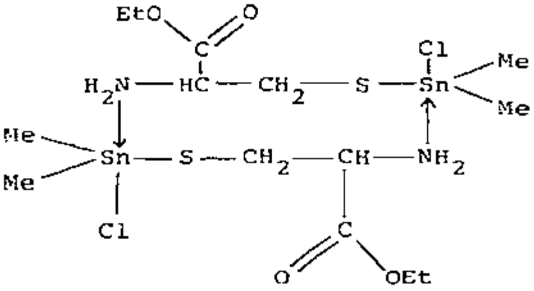
The trivinyltin carboxylates appear to result from the disproportionation of the appropriate distannoxanes, a process which was established experimentally for R=CH_2Cl, and is favoured by protic media such as water-acetone and methanol in comparison with aprotic solvents such as MeCN and $CHCl_3$.[270] The structure of another example of a distannoxane of type (75), $\{[Me_2Sn(O_2CCF_3)]_2O\}_2$, has been reported, and is very similar to that determined previously for $\{[Bu_2Sn(O_2CCCl_3)]_2O\}_2$. The dimeric unit lies on a mirror plane, with both carboxylate groups functioning as bridging ligands but in different ways. Both tin atoms have basic trigonal bipyramidal coordination with one or two further neighbours.[271] The structures of bis(trimethyltin)malonate[272] and $[Me_2Sn(O_2CCH_2Cl)]_2$[273] have also been reported. Again the coordination at tin in each is trigonal bipyramidal. In bis(trimethyltin)malonate, planar trimethyltin moieties are bridged by each oxygen atom of the malonate residue forming a three-dimensional network, whilst discrete dimeric units are present in $[Me_2Sn(O_2CCH_2Cl)]_2$. In these, the two methyl groups and the Sn-Sn bond occupy equatorial positions, with the carboxylate group bridging slightly asymmetrically the two tin atoms via the axial sites. Mössbauer spectroscopy has also been employed in the structural analysis of organotin carboxylates. Data for several tributyltin carboxylates taken at 80K indicate pentacoordinated polymeric structures at this temperature, but room temperature infrared data supported the presence of tetracoordinated monomeric species.[274] The Mössbauer spectrum of an aged sample of $Ph_3SnO_2CCl_3$ exhibited peaks due to two species, the original monomeric complex and a second with a quadrupole splitting ($\sim$3.8 mm s^{-1}) suggestive of a polymeric form. Whether monomeric or polymeric forms of such triphenyltin carboxylates are obtained by reaction of Ph_3SnOH with the acid depend on both the solvent and the reaction conditions. Procedures involving non-polar solvents, e.g. CCl_4 or benzene, and those involving heating tend to cause Ph-Sn bond fission (to give for example $PhSn(O)O_2CCl_3$), but such bond rupture may be inhibited by the use of a polar solvent at room temperature. Thus Ph_3SnOH and Cl_3CCO_2H in anhydrous methanol at room temperature yield the solvate, $Ph_3SnO_2CCl_3 \cdot MeOH$, which on recrystallisation from CCl_4 affords monomeric $Ph_3SnO_2CCl_3$. However, if the reaction is carried out in absolute ethanol, a product is obtained which is dried only with difficulty, and after 4 days at *ca.* 10^{-2} torr white, powdery polymeric $Ph_3SnO_2CCl_3$ is obtained.[275] Analysis of the Zeeman hyperfine spectrum for diphenyltin glycylglycinate shows that the quadrupole splitting is of negative sign (-2.235 mm s^{-1}) with an asymmetry parameter η of 0.805 (*cf.* values from a point charge calculation Q.S. -2.70, $\eta = 0.84$). The electronic charge is thus inferred to be concentrated in the equatorial ($NSnPh_2$) plane.[276] Mössbauer data for several polynuclear dithiooxalato-copper(I)-tin(IV) complexes have been reported.[277]

Organotin derivatives of L-cysteine, L-cysteine ethyl ester, and DL-penicillamine have been synthesised by the reaction of the diorganotin oxide, HCl and the amino acid in alcohol-water. The tin-sulphur bonded structures (76),(77) and (78) were proposed for the products.[278] Roy and Ghosh[279] have investigated the demetallation of triorganotin carboxylates by mercury(II) salts. Products resulting from sequential demetallation and/or hydrolysis are observed.

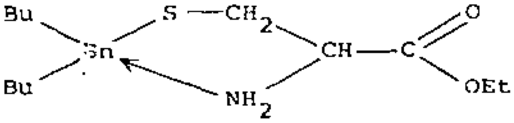


R = Me,Bu

(76)



(77)



(78)

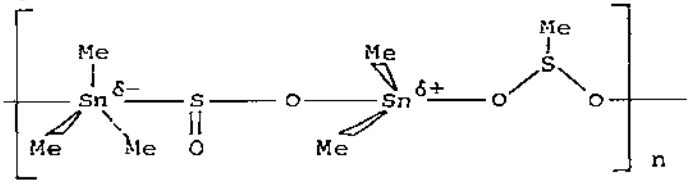
Tin(IV) nitrate reacts with triphenylphosphine and -arsine to give the polymeric products (79) with bridging phosphonate/arsonate groups and uridentate nitrate as white amorphous solids:

$$Sn(NO_3)_4 + EPh_3 \longrightarrow (Ph_2EO_2)_2Sn(NO_3)_2$$

E = P,As (79)

Polymeric $\{OSn(NO_3)_2\}$ is obtained from the reaction of $Sn(NO_3)_4$ and nitric oxide both in CCl_4 solution and in the gas phase. Solvolysis occurs on dissolution of $Sn(NO_3)_4$ in carboxylic acids and anhydrides. With acetic acid or anhydride, $Sn(OAc)_4$ is formed, but the nitronium salt $2NO_2^+\{Sn(O_2CCF_3)_6\}^{2-}$ and its solvate $2NO_2^+\{Sn(O_2CCF_3)_6\}^{2-}\cdot CF_3CO_2H$ result from dissolution in $(CF_3CO)_2O$ and CF_3CO_2H, respectively.[280] The structures of the two complexes, $Ph_2Sn(NO_3)_2(Ph_3PO)$[281] and $Ph_2Sn(NO_3)_2(Ph_3AsO)$[282] are similar. Both contain seven-coordinated tin, with bidentate nitrate groups and the Ph_3EO ligand occupying equatorial sites and the two phenyl groups in axial positions. However, the arsenic compound differs from the analogous phosphine oxide complex in several ways: (i) the nitrate ligands are essentially symmetrical in the arsine, (ii) the CSnC group is nearly linear (178°) in the phosphine but bent (156°) in the arsine, and (iii) the Sn-O(ligand) distance is substantially longer (2.15Å) in the phosphine compared to the arsine (2.03Å).

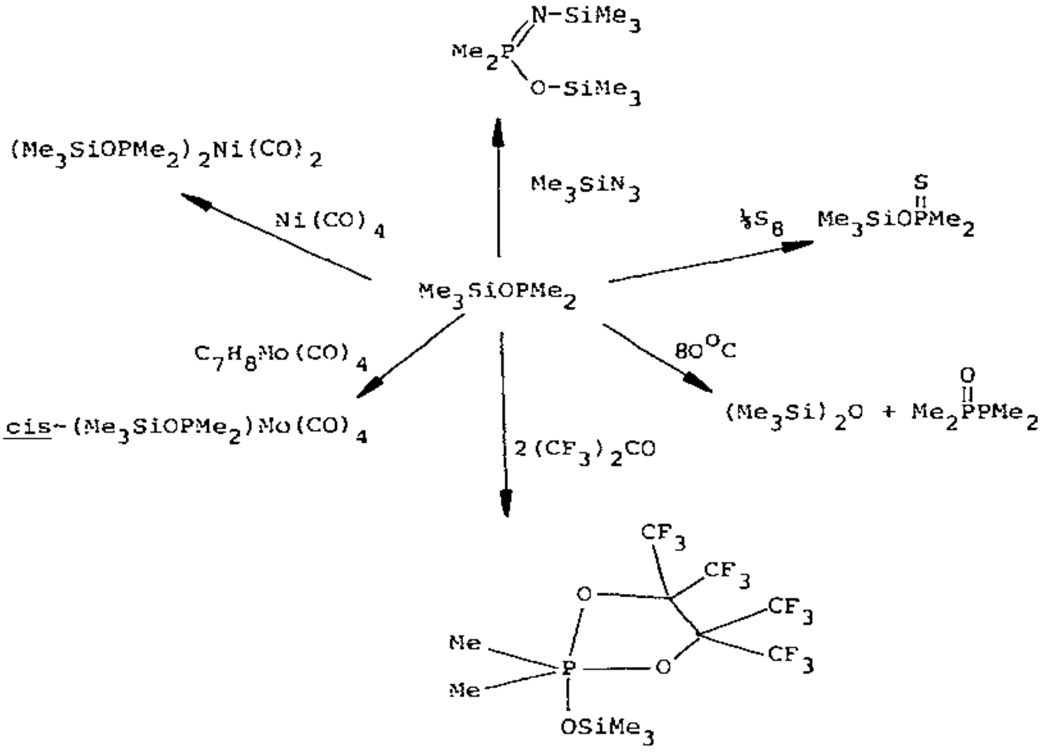
Extremely hydrolytically sensitive di- and trisulphinic esters of silicon, $R_nSi(OSR')_{4-n}$ (n=1,2; R=R'=Me,Ph; R=Ph,R'=p-tolyl), have been synthesised from $RnSnCl_{4-n}$ and AgO_2SR'.[283] The reactions of tin compounds with SO_2 have been investigated in detail over the past years. However, contrary to a previous report, simultaneous cleavage of the Sn-C and Sn-Sn bonds occurs when Me_6Sn_2 reacts with liquid or dissolved SO_2. The structure of the product, $Me_6Sn_2.2SO_2$, was proposed to be (80) from spectroscopic data. Decomposition to Me_2SnSO_4 and Me_3SnO_2SMe occurred at 125-130°C.[284] Tin metal reacts with the mixed solvent DMSO-SO_2 to yield $Sn(DMSO)_6(S_2O_7)_2$, whereas lead metal reacts to yield the metal sulphate.[285]



(80)

Several types of Group 4 metal selenites have been prepared. The derivatives, R_3EO_2SeR' (E = Si,Ge,Sn,Pb; R=Me,Ph; R'=Me,Et,Ph), are obtained by the reaction of R_3ECl or R_3EBr with the sodium or silver salts of the selenic acid. The silicon and germanium derivatives have an ester-type structure, in which the metal is linked to only one oxygen atom. The tin and lead compounds, on the other hand, have polymeric structures in which the $[O_2SeR']$ ligand bridges triorganometal moieties, - a structure which was confirmed crystallographically for Me_3SnO_2SeMe.[286] The polymeric diorganotin and -lead selenites, $R_2E(O_2SeR')_2$ (R=Me,Et,Bu,Ph; R'=Me,Et,Ph) were obtained similarly,[287] but the monomeric selenites, $(R_3SnO)_2SeO$ (R=Me,Bu,Ph) were synthesised by insertion of SeO_2 into the Sn-O bonds of $(R_3Sn)_2O$. The reaction of Me_3SnOH with SeO_2 yields $(Me_3SnO)_2SeO$ or $Me_3SnOSe(O)OH$ depending on the ratio of reactants.[288] The formation constants of trimethyllead complexes of SO_3^{2-}, SeO_3^{2-}, $S_2O_3^{2-}$, SCN^-, HPO_4^{2-}, CO_3^{2-}, Cl^-, Br^- and I^- have been determined in aqueous solution. The values are generally fairly small and the extent to which the complex is formed is strongly dependent on the pH.[289]

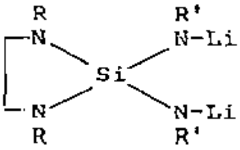
Trimethylsilylphosphinite, $Me_3SiOPMe_2$, has been synthesised from Me_3SiNMe_2 and $Me_2P(O)H$, and its chemical reactions investigated (Scheme 4).[290] Difluorophosphonic acid reacts with $SnCl_4$ to afford the phosphate-bridged, polymeric compound, $SnCl_2(O_2PF_2)_2$.[291]

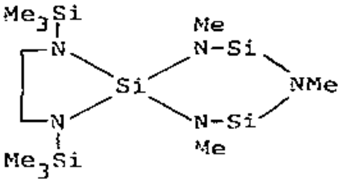


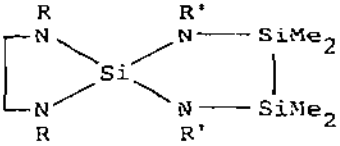
Scheme 4

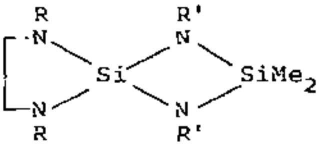
4.2.8 Compounds with Bonds to Group V Elements

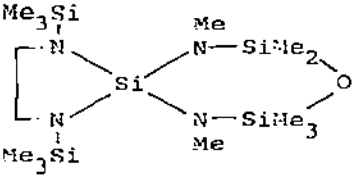
Several new heterocyclic compounds containing Si-N bonds have been synthesised using established procedures, principally by Wannagat and his coworkers, and the major new structural frameworks are portrayed in structures (81)-(86)[292], (87)-(89)[293], (90), (91)[294], (92)-(94)[295], (95)-(100)[296], (101)[297], (102),(103)[298] and (104)[299].

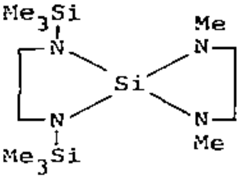

(81)

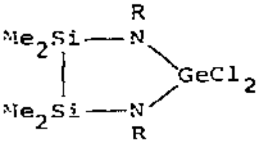

(82)

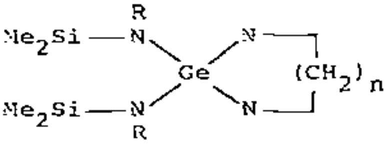

(83)


(84)

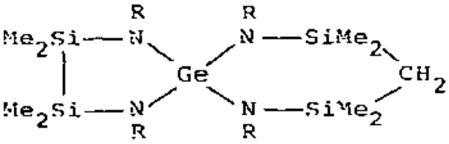

(85)

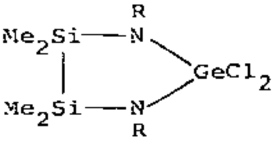

(86)

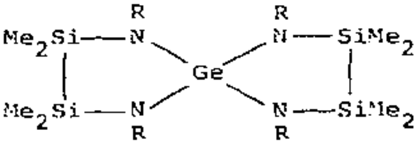

(87)

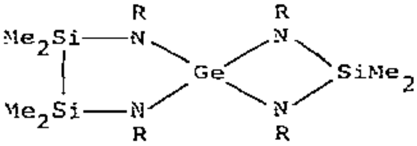

n=2,3

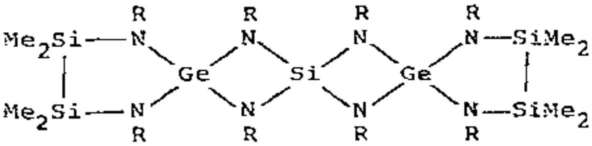
(88)

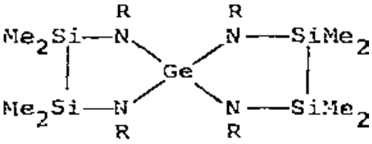

(89)

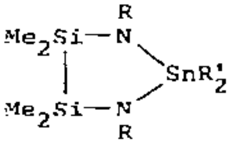

(90)


(91)

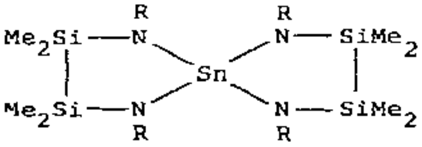

(92)


(93)

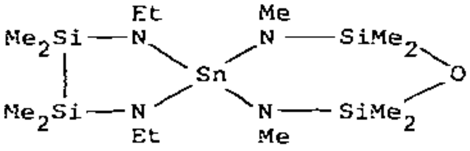

(94)



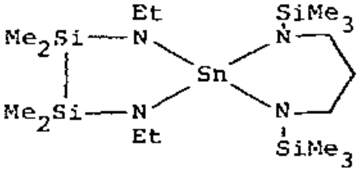
(95)



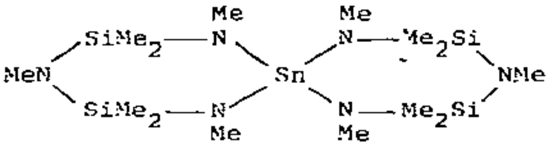
(96)



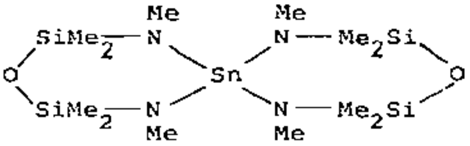
(97)



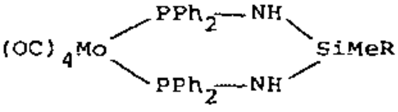
(98)



(99)

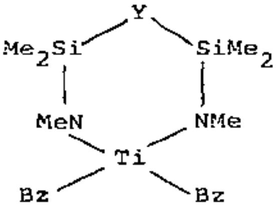


(100)



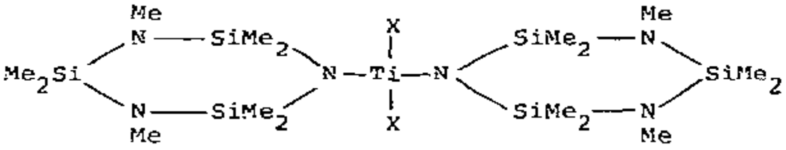
R=Me,Ph

(101)



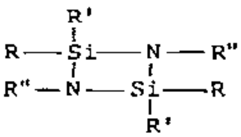
(Y= —,
NMe, CH_2)

(102)

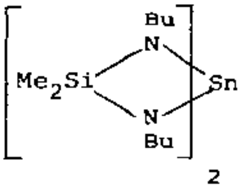


(X=Cl,Br,$PhCH_2$)

(103)



(104)



(105)

The tetraazastannane (105) crystallises at room temperature in the monoclinic space group C2/c with four molecules per unit cell, in which two of the cell edge distances are remarkably similar (*a*=*c*=18.604(10)Å, *b*=8.993(5)°, β=116.1(1)°). The molecules in this modification occupy a 2(C_2) site, but their inherent symmetry does not deviate much from $\bar{4}2m$ (D_{2d}). When the temperature is raised above 365K, this pseudo-orthorhombic cell is transformed into a truly orthorhombic cell, passing through an intermediate phase between 341 and 365K (X-ray powder). The high temperature phase belongs to the space group F_{ddd} with eight molecules per cell and *a*=20.47(2), *b*=9.657(7) and *c*=31.06(5), the molecules attaining 222 (D_2) site symmetry. The phase change between the two modifications only entails a change in the *y*-axis parameters, and hence the molecules thus suffer a loss of symmetry by packing ($\bar{4}2m \rightarrow 2$), but which is partially recovered when heated in the solid ($2 \rightarrow 222$).[300]

The structures of two more tris[bis(trimethylsilyl)-amido]-metal derivatives, the thallium[301] and neodymium[302] compounds, have been determined. The former is isomorphous with the aluminium and iron derivatives with a planar skeleton. In contrast, the neodymium derivative is non-planar. Trimeric $[LiN(SiMe_3)_2]_3$ has a planar Li_3N_3 central ring.[303] The X-ray patterns for the trimethyl-metal (Si,Ge and Sn) derivatives of hydrazine can all be indexed as face-centred cubic. However, on cooling these "plastic" phases, which are stable over a wide temperature range (*ca*.250°C), undergo a transformation, via another mesophase, to a low-temperature form with a regular van der Waals packing of the molecules. The intermediate mesophase is primitive cubic.[304] A normal coordinate analysis of Me_3MNMe_2(M=Si,Ge,Sn) has been performed.[305]

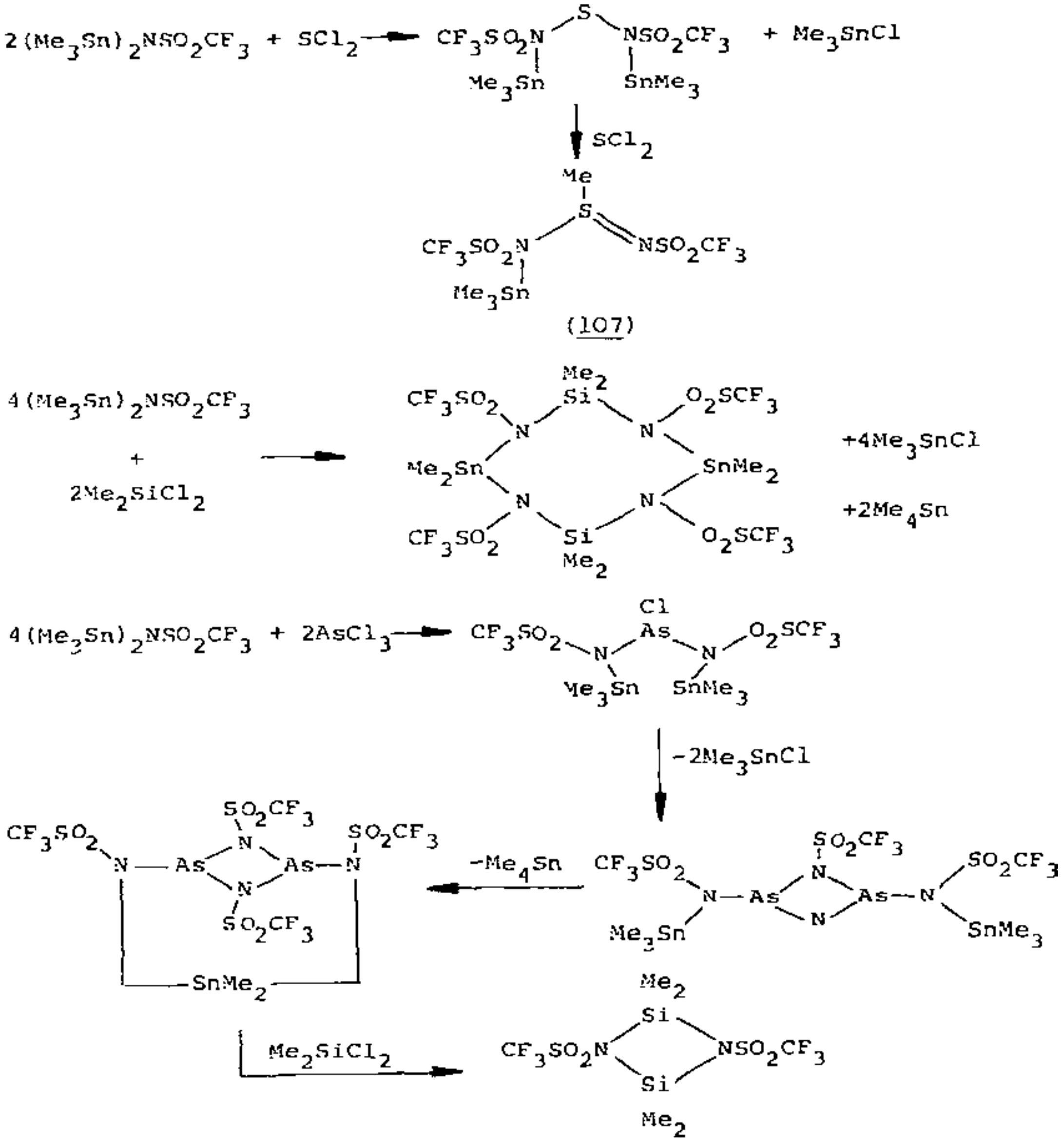
The first primary lead amine, t-Bu_3PbNH_2, has been prepared by the reaction of t-Bu_3PbI with KNH_2 in liquid ammonia at -30°.[306] Bis(trimethylsilyl- and stannyl)amines react with $CF_3SO_2N{=}S{=}O$ to form (106):

$$CF_3SO_2N{=\!=}S{=\!=}O + (Me_3M)NR' \longrightarrow CF_3SO_2N(MMe_3)_2$$

(106)

M = Si; R' = Me, $SiMe_3$
M = Sn; R' = $SnMe_3$

The stannyl derivative (106) is very reactive, and reacts with a variety of halogen compounds:



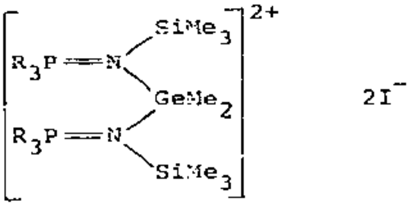
(107)

The structure of (107) was determined by X-ray crystallography and contains trigonal bipyramidally coordinated tin.[307,308]

The reactions of $Me_3Si-N=N-SiMe_3$ with $(C_5H_5)_2TiCl_2$ and $(C_5H_5)_2M$ (M=V,Cr,Mn) afford $(C_5H_5)_2TiNN(SiMe_3)_2$, $(C_5H_5)_2VNN(SiMe_3)_2$, $[(C_5H_5)CrNN(SiMe_3)_2]_2$ and $[(C_5H_5)MnNN(SiMe_3)_2]_2$, respectively. In the case of the titanium and possibly the vanadium compounds, the bis(trimethylsilyl)isodiazene ligand is terminally bound to the metal, in the manganese (X-ray analysis) and possibly the chromium compound, the ligand bridges two metal atoms.[309] N-Silylphosphinimines, $Me_3SiN=PX_2OSiMe_3$, rather than the isomeric phosphine oxides, $(Me_3Si)_2NP(O)X_2$, result from the reaction of $LiN(SiMe_3)_2$ with the phosphoryl chlorides, $ClP(O)X_2$ (X=F,Cl,Ph).[310] The silyl-, germyl- and stannyl-phosphinimines, $R_3P=N-MMe_3$ (M=Si,Ge;Sn), exchange with halogenogermanes:

$$R_3P{=\!=}N-MMe_3 + R'_{4-n}GeX_n \longrightarrow R_3P=N-GeR'_{3-n}X_n + Me_3MX$$

but $R_3P=N-SiMe_3$ and Me_2GeI_2 form an adduct (<u>108</u>).[311] X-ray analysis of the germyl-phosphinime, $Me_3P=NGeCl_3$, shows the presence of a centrosymmetric dimer as well as two symmetry-related monomers in the unit cell. The dimer contains a planar four-membered Ge_2N_2 ring with trigonal bipyramidal geometry at germanium.[312]

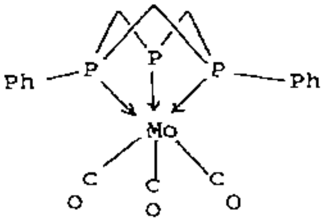


(<u>108</u>)

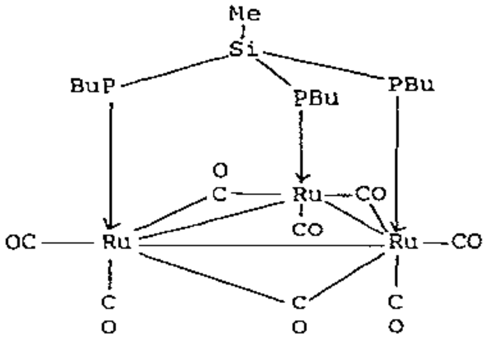
Pommier[313] has investigated the mechanism of the primary steps of the reactions between Grignard reagents and dichlorogermyl- and dichlorostannyl-porphyrin. The results show that when alkylation does not occur at the metal, the primary attack is at the macrocycle, which is reduced through the intermediate formation of a free-radical species.[313]

Rings and cages appear to have been the most important aspect of silylphosphine chemistry during 1978. Metathesis between the α,ω-dichlorooligosilanes, $Cl(SiMe_2)_nCl$ (n=1-6) and Li_2PPh yields heterocyclic phosphasilanes. When n=4-6, the corresponding

5-,6- and 7-membered ring compounds are formed, but when n=3, a polymeric material of probable formula $[PhP(SiMe_2)_3]_2$ is formed. A six-membered ring, $[PhP(SiMe_2)_2]_2$, is obtained when $Cl(SiMe_2)_2Cl$ is employed. The product obtained from the reaction with Me_2SiCl_2 depends upon the temperature. At -40° the dimer, $(PhPSiMe_2)_2$, is formed which is stable at room temperature, but is converted at $150^{\circ}C$ to the trimer, $(PhPSiMe_2)_3$ (109), the product obtained when the reaction is carried out at $40^{\circ}C$. Compound (109) displaces cycloheptatriene from $(CO)_3MoC_7H_8$ forming (110).[314] A similar cage complex (111) results from the reaction of $MeSi(PBu_2)_3$ with

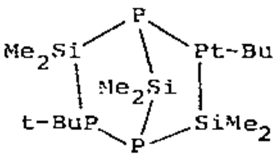


(110)

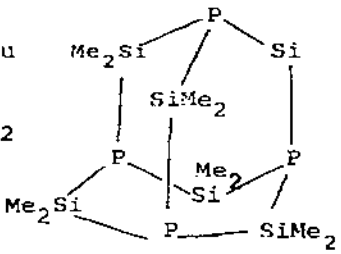


(111)

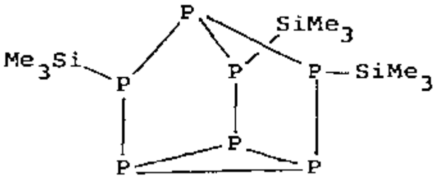
$Ru_3(CO)_{12}$ in refluxing benzene.[315] Fritz and Uhlmann[316] have employed the monolithium salt of the methylphosphine to prepare $(Me_2SiPMe)_3$, $(MeHSiPMe)_3$ and $(t\text{-}BuSiPMe)_2$. The reactions proceed via the initial formation of $R_2Si(PHMe)_2$, which subsequently decompose, - a reaction sequence confirmed in the reaction of LiPHt-Bu with Me_2SiCl_2, from which $Me_2Si(PHt\text{-}Bu)_2$, $(Me_2SiPt\text{-}Bu)_2$, and $(Me_2Si)_3P_4(t\text{-}Bu)_2$ (112) were isolated. On heating to $190^{\circ}C$, $Me_2Si(PHt\text{-}Bu)_2$ decomposed to afford the two latter compounds. The cage compound with the adamantane skeleton (113) has been



(112)



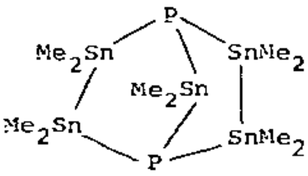
(113)



(114)

prepared by the thermolysis of a variety of compounds including $(Me_3Si)_2P-SiMe_2-P(SiMe_3)_2$, $(Me_3Si)_2P-SiMe_2Cl$, $Me_2Si(PH_2)_2$, and (114),[317] which was itself obtained by the reaction of white phosphorus with Na/K alloy and subsequent treatment with Me_2SiCl_2.[318] The structures of (112)[319], (113)[320] and (114)[321] have been confirmed by X-ray analysis.

The reaction of white phosphorus with dimethylstannane in ether in the presence of DMF yields $(Me_2Sn)_5P_2$, which has the structure (115). In the absence of organic bases such as DMF or pyridine, $(Me_2Sn)_6P_4$ is produced.[322] Tris(trimethylstannyl)phosphine is cleaved by methyl lithium in ether solvents (ether, DME) to afford $(Me_3Sn)_2PLi(ether)$, which reacts with Me_3SnCl to regenerate $(Me_3Sn)_3P$.[323] Silyl- and germyl-phosphines, $Me_3E-Pt-Bu_2$ (E=Si,Ge) are cleaved by silver chloride in toluene to give Me_3ECl and $t-Bu_2PAg$, but silver bromide and iodide form 1:1 complexes, $t-Bu_2(Me_3E)PAgX$ (X=Br,I). The reaction of $Me_3SnPt-Bu_2$ with silver bromide affords a fairly soluble material which exhibits two broad signals in the ^{31}P n.m.r. spectrum, but which eliminates Me_3SnBr in significant quantities even at -15°C after 48h.[324] The reactions of $Hg(CF_3)_2$ and Me_3SnCF_3 with germyl phosphines and phospholanes lead to insertion of CF_2 into the Ge-P bond.[325] $t-Bu_2(Me_3Sn)Sb$ and $(Me_3Sn)_4Sb_2$ are formed in the reaction of $(Me_3Sn)_3Sb$ and t-BuI.[326]



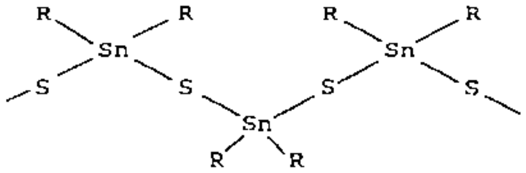
(115)

4.2.9 Compounds with Bonds to Sulphur, Selenium and Tellurium

Compounds in this section fall into two categories, molecular compounds and metal chalcogenide derivatives.

The glass formation tendency of GeS_2 is influenced by chemical disorder in the melt, and the high rate of cooling (17^oS^{-1}) necessary for glass formation results from the presence of structural units richer in germanium.[327] The glasses, Ge_2S_3 and Ge_2Se_3, are soluble in solutions of Na_2E (E=S,Se) in methanol yielding $Na_6Ge_2E_3.4MeOH$, which lose methanol on heating. Vibrational data show the presence of $[Ge_2E_6]^{6-}$ anions.[328] A second compound, Ag_2GeS_3, which has an orthorhombic variant of the Wurtzite structure, has been synthesised from Ag_2S-GeS_2 mixtures. Treatment in a AgI/AgCl eutectic yields the quaternary compound Ag_7GeS_5I.[329] Crystals of $Eu_3Ge_3S_9$ contain the cyclic $[Ge_3S_9]^{6-}$ anions, which have the chair conformation.[330] Heating a mixture of the two binary sulphides in a quartz ampoule at 400-540°C under argon yields Au_2BaSnS_4, which is structurally similar to the Cu_2BaSnS_4 and Ag_2BaSnS_4 analogues. Each of the three crystallographically independent tin atoms is tetrahedrally coordinated by sulphur atoms.[331] All the lead atoms in $Pb_3I_{6.67}S_{13}$ and $Pb_4In_9S_{17}$ are in irregular eight-fold coordination.[332] Crystals of $K_6\ Si_2Te_6$ are obtained by heating a stoichiometric mixture of the elements in an evacuated quartz vessel at 630°C. The structure contains discrete $[Si_6Te_6]$ anions in the staggered conformation.[333] Ag_8GeTe_6 has a pseudo-cubic rhombohedral structure with $[GeTe_4]$ tetrahedra.[334]

The atom-atom potential method has been used to calculate the equilibrium geometry and barriers to internal rotation in organotin sulphides and thiolates.[335] Dimethyltin telluride (from Me_2SnH_2 and elemental tellurium) is trimeric,[336] and presumably has the same twist-boat conformation as has been determined for the selenium analogue.[337] The corresponding sulphide is also trimeric, but the reaction of $i\text{-}Pr_2SnCl_2$ with sodium sulphide yields crystals of $(i\text{-}Pr_2SnS)_n$, with the linear structure (116), if the initially-formed low molecular weight product is allowed to stand under DMF.[338] Bis(2-pyridylthiolato)tin dichloride has a distorted octahedral structure with the 2-pyridylthiolato ligands chelating the metal.[339] U.V. photoelectron and variable temperature ^1H n.m.r. spectra of $\overline{\mathrm{Sn{-}S{-}C{-}C{-}S}}$ heterocyclic compounds demonstrate the non-planarity of the ring and the flexibility of



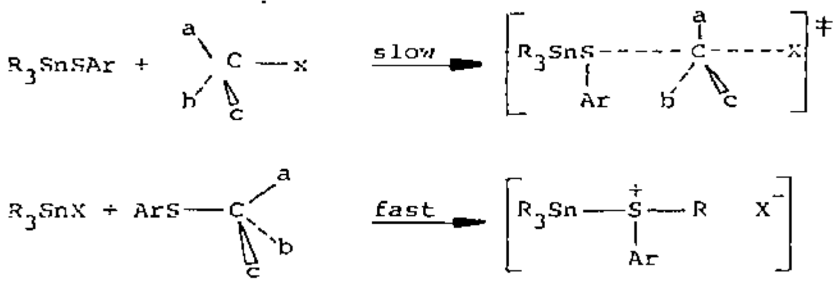
(<u>116</u>)

the S-Sn-S intracyclic angle.[340]

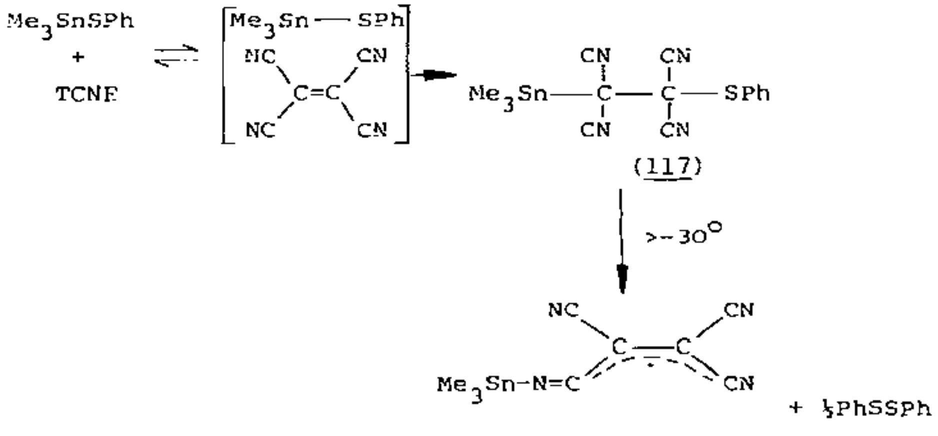
The germyl chalcogenides, $(Me_nH_{3-n}Ge)_2E$ (E=O,S,Se,Te; n=0-3) are effectively synthesised by the reaction:

$$2Me_nH_{3-n}GeI + Li_2E \longrightarrow (Me_nH_{3-n}Ge)_2E + 2LiI$$

whilst germanethiols and -selenols, $Me_nH_{3-n}GeEH$ (n=0-3) are isolated as intermediates in the reaction of the digermoxanes with H_2E and from equilibrium mixtures of $(Me_nH_{3-n}Ge)_2E$ and excess H_2E.[341] The reaction of haloalkenes and Me_3SnSAr follows second-order kinetics and with inversion of configuration with optically-active (+)-1-methylheptyl bromide indicating a mechanism involving bimolecular nucleophilic attack on the haloalkene:[342]



With Me_3SnSMe and MeI, Me_3SnI and the sulphonium salt $Me_3S^+I^-$ were produced.[343] A stable orange solution of a charge-transfer complex results from the interaction of TCNE with $Sn(SPh)_4$ in benzene, from which the components can be isolated even after 72h. However, the charge-transfer complex initially formed with Me_3SnSPh undergoes conversion to the extremely unstable insertion product (<u>117</u>) which decomposes on heating to above -30°C:[344]



Several more diorganotin bis(dithiocarbamates) have been prepared by standard routes.[345]

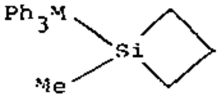
4.2.10 Compounds with Bonds to Main Group Metals

The cathodic reduction of triorganohalosilanes using DME as solvent and BU_4NClO_4 as supporting electrolyte yields the corresponding disilanes in nearly quantitative current efficiency. In contrast, $ClMe_2SiSiMe_3$ and $ClMe_2SiSiMe_2Cl$ do not react. Ph_2SiCl_2 affords cyclo-$(SiPh_2)_4$ as well as polymeric products, whilst $MeSiCl_3$ and $SiCl_4$ yield only yellow polymers.[346] Cyclo-$(Me_2Si)_6$ may be obtained quantitatively in high purity by the reaction:[347]

$$6Me_2SiCl_2 + 12Li \xrightarrow[0^\circ C/6h]{THF} 12LiCl + (Me_2Si)_6$$

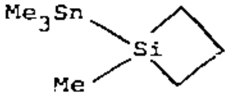
Cyclo-$(Ph_2Si)_4$ contains an essentially square, quasi-planar four-membered Si_4 ring,[348] but cyclo-$(Ph_2Si)_5$ has a puckered five-membered Si_5 ring.[349]

1-Chloro-1-methylsilacyclobutane reacts with organometal(IV) lithium compounds to give (118) and (119) as monomers.[350] Procedures to cleave Si-Si bonds in industrial chlorosilane residues have been devised. One procedure employs a pressure of hydrogen (25 bars) in the presence of HMPT/$(C_5H_5)_2Ni$ mixture or nickel (resulting from the reduction of dry $NiCl_2$ by Et_3SiH) leading to the formation of $MeSiCl_2H$, $MeSiCl_3$ and Me_2SiClH.[351]



M=Si,Ge

(118)



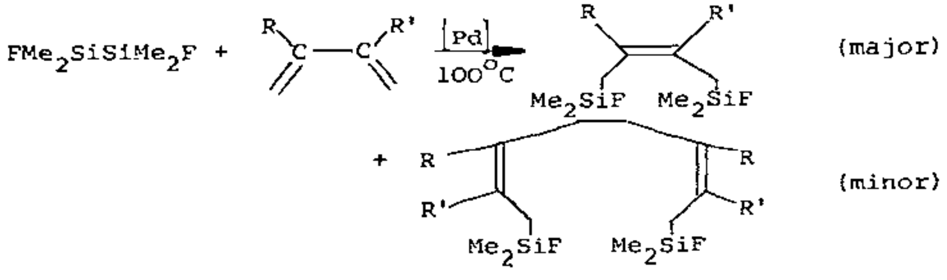
(119)

The methylchlorodisilanes, $Cl_2MeSiSiMeCl_2$, $ClMe_2SiSiMeCl_2$ and $ClMe_2SiSiMe_2Cl$, are cleaved by HCl in the presence of $Pd(PPh_3)_4$ to give methylchlorohydrosilanes in good yields, e.g.[352]

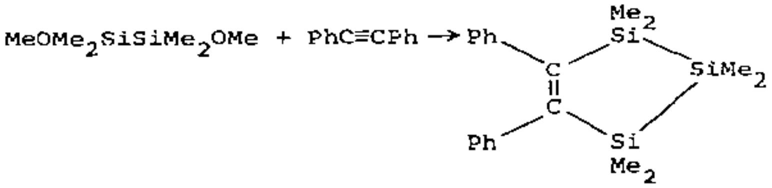
$$Cl_2MeSiSiMeCl_2 + HCl \xrightarrow[140^\circ C]{Pd^0} MeSiHCl_2 + MeSiCl_3$$

(50:50; 90% combined yield).

Palladium complexes ($Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$) also catalyse the addition of fluorinated disilanes to 1,3-dienes, methyl vinyl ketone and p-benzoquinone to afford mainly 1,4-addition products, e.g.[353]

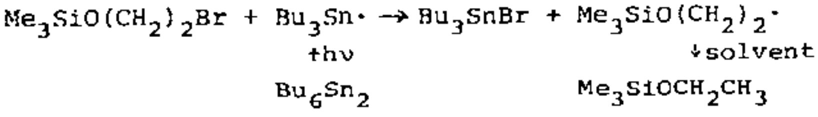


The reaction of $MeOMe_2SiSiMe_2OMe$ with the PhC CPh in THF at room temperature with sodium methoxide as catalyst yields (<u>120</u>), which is fairly stable in air:[354]



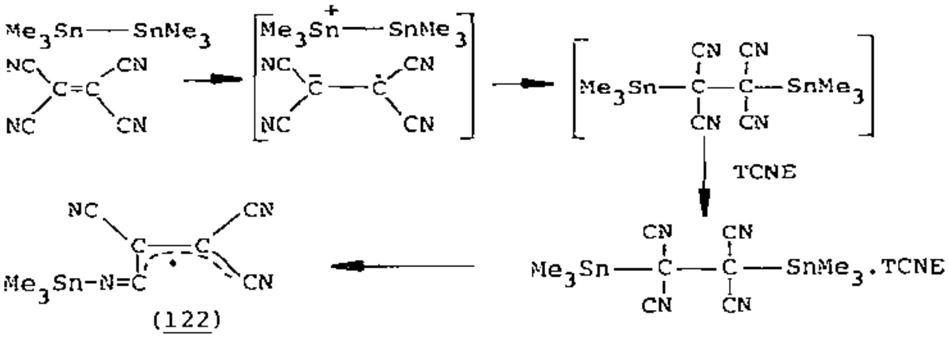
(<u>120</u>)

Gielen and Tondeur[355] have synthesised the first example of an optically-active hexaorganodistannane, $[Ph(PhCMe_2CH_2)MeSn]_2$, by the stereoselective decomposition of the corresponding organotin hydride in the presence of palladium. The reactions of $t\text{-}Bu(PhCMe_2CH_2)PhSn^{*}H$ with Me_2Hg and of $Me(PhCMe_2CH_2)i\text{-}Pr(trityl)Sn$ with $LiAlH_4$ afforded racemic distannanes. Very sterically crowded hexaorganodistannanes, R_6Sn_2 ($R=2,4,6\text{-}Me_3C_6H_2$, $.2,4,6\text{-}Et_3C_6H_2$) reversibly dissociate on heating. Bond dissociation energies (derived from e.s.r. intensity measurements) were 198(8) kJ mol^{-1} and only 125(5) kJ mol^{-1}, respectively, for the methyl and ethyl derivatives (cf. 210-240 kJ mol^{-1} for Me_6Sn_2).[356] Tributylstannyl radicals generated by photolysis of Bu_6Sn_2 abstract bromine from $Me_3SiO(CH_2)_2Br$:[357]



$$Me_3SiO(CH_2)_2Br + \underset{\underset{Bu_6Sn_2}{\uparrow h\nu}}{Bu_3Sn\cdot} \rightarrow Bu_3SnBr + \underset{\underset{Me_3SiOCH_2CH_3}{\downarrow solvent}}{Me_3SiO(CH_2)_2\cdot}$$

However, no reaction occurred between Me_6Sn_2 and 2,4,6-$Me_3C_6H_2$-CH=NPh in the presence of t-Bu_2O_2.[358] The reaction of Me_6Sn_2 with TCNE takes place by the initial formation of a 1:1 complex:[359]



(122)

(121)

Complex (121) may be isolated in 30% yield when the reaction is carried out in CH_2CCl_2. It is almost insoluble, colourless, and extremely susceptible to homolysis and atmospheric oxidation when it isomerises to black (122) reported previously. The kinetics of HCl cleavage of Ph_6Pb_2 have been examined in anhydrous dioxane, $CHCl_3$ and 20%MeOH-80%C_6H_6, and are consistent with a four-centre mechanism involving preferential cleavage of the Pb-C bond by undissociated HCl. A $[Ar_5Pb_2Cl]$ species was proposed as an intermediate, which could either rapidly disproportionate or suffer further Pb-C bond cleavage.[360]

The dissolution of sodium/tin alloys of compositions near $NaSn_{2.25}$ in ethylenediamine yield orange-red solutions containing the Sn_9^{4-} anion. The ^{119}Sn n.m.r. spectra of such solutions exhibit a single resonance with ^{117}Sn-^{119}Sn coupling demonstrating that the individual environment of the static monocapped square antiprism structure are averaged intramolecularly in some manner. Na-Sn-Pb alloys afford solutions containing all possible mixed $(Pb_nSn_{9-n})^{4-}$ (n=0-9) anions.[361]

The reduction of aryldigermanes and -disilanes by $LiAlH_4$ leads to the corresponding hydrogermanes and -silanes in high yields. The reactions proceed via intermediate lithium germyl or silyl aluminates which are stable under inert atmospheres, e.g.[362]

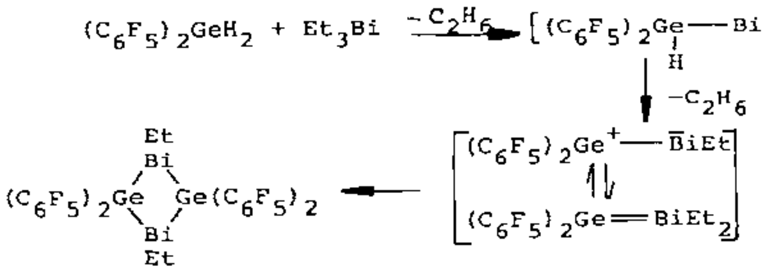
$$\begin{tikzcd}[column sep=small]
Ph_3GeGeBu_3 + LiAlH_4 \arrow[r, "THF"] & Bu_3GeH + Li^+[(Ph_3Ge)H_3Al]^-.THF \arrow[d, "THF;\ -LiH"] \\
 & Ph_3GeLi + LiAlH_4
\end{tikzcd}$$

A neutral Ge-Al bonded compound has been synthesised by mercury displacement:

$$3Hg(GeMe_3)_2 + 2Al \xrightarrow[pentane]{THF} 2Al(GeMe_3)_3.THF + 3Hg$$

Attempts to prepare the corresponding tin compound failed; instant decolourisation of $(Me_3Sn)_2Hg$ occurs in contact with aluminium, but the desired product decomposes below room temperature.[363] Triethylbismuth undergoes Bi-C bond cleavage with $(C_6F_5)_3GeH$ and $(C_6F_5)_2GeH_2$:[364]

$$\begin{tikzcd}[column sep=small]
 & Et_3Bi + (C_6F_5)_3GeH \arrow[dl, "90-100^{\circ}C"'] \arrow[dr, "170^{\circ}C"] & \\
(C_6F_5)_3GeBiEt_2 & & [(C_6F_5)_3Ge]_2BiEt_2
\end{tikzcd}$$



Tin carboranes may be prepared by the reaction of $SnCl_2$ with bis{O- or m-carboranyl-(9)}mercury:[365]

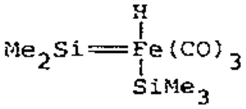
$$(C_2H_2B_{10}H_9)_2Hg + SnCl_2 \longrightarrow (C_2H_2B_{10}H_9)_2SnCl_2 + Hg$$

$Me_2SnB_{10}H_{12}$ is cleaved by bromine and iodine to give Me_2SnX_2 (X=Br,I) and $B_{10}H_{12}X_2$ as products. With a deficiency of bromine, $Me_2BrSnB_{10}H_{12}Br$ is produced.[366] The treatment of a solution of

Me_3SnLi in THF with one equivalent of PhSCu affords $PhS(Me_3Sn)CuLi$, a new reagent for the transformation of β-iodo-enones into β-trimethylstannyl-α,β-unsaturated ketones.[367]

4.2.11 Compounds with Bonds to Transition Metals

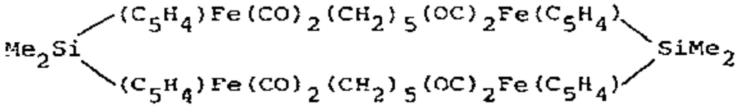
The reaction of $HMe_2SiSiMe_3$ with $Fe_2(CO)_9$ in benzene at room temperature yields the extremely air-sensitive silanediyl-iron complex (123). The silanyl and silanediyl ligands are displaced by



$$Me_2Si{=}\overset{H}{\underset{SiMe_3}{Fe}}(CO)_3$$

(123)

PPh_3, $(PhCH{=}CH)_2$ and PhC≡CPh.[368] Insertion of cyclohexyl isocyanide (RNC) into the Si-Fe bond of $(C_5H_5)Fe(Cu)_2SiMe_3$ does not take place even under photolysis. Rather, sequential replacement of both carbonyl groups by RNC occurs leading to racemic $(C_5H_5)Fe(CO)(RNC)SiMe_3$ and $(C_5H_5)Fe(RNC)_2SiMe_3$.[369] 1,3-Dienes react with $HFe(CO)_4SiCl_3$ by addition of the Fe-H function to the multiple-bond system. Isoprene appears to add predominantly by [1,4] addition, but [1,2] addition occurs with 2,3-dimethyl-1,3-butadiene. Both types occur with butadiene. Stable (π-allyl)$Fe(CO)_3SiCl_3$ complexes are formed with both isoprene and butadiene.[370] $Me_2Si\ (\eta^5 - C_5H_4)Fe(CO)_2C_5H_{11}\ _2$ thermally decomposes principally by a β-hydrogen elimination process, whilst (124) eliminates 1-pentene:[371]

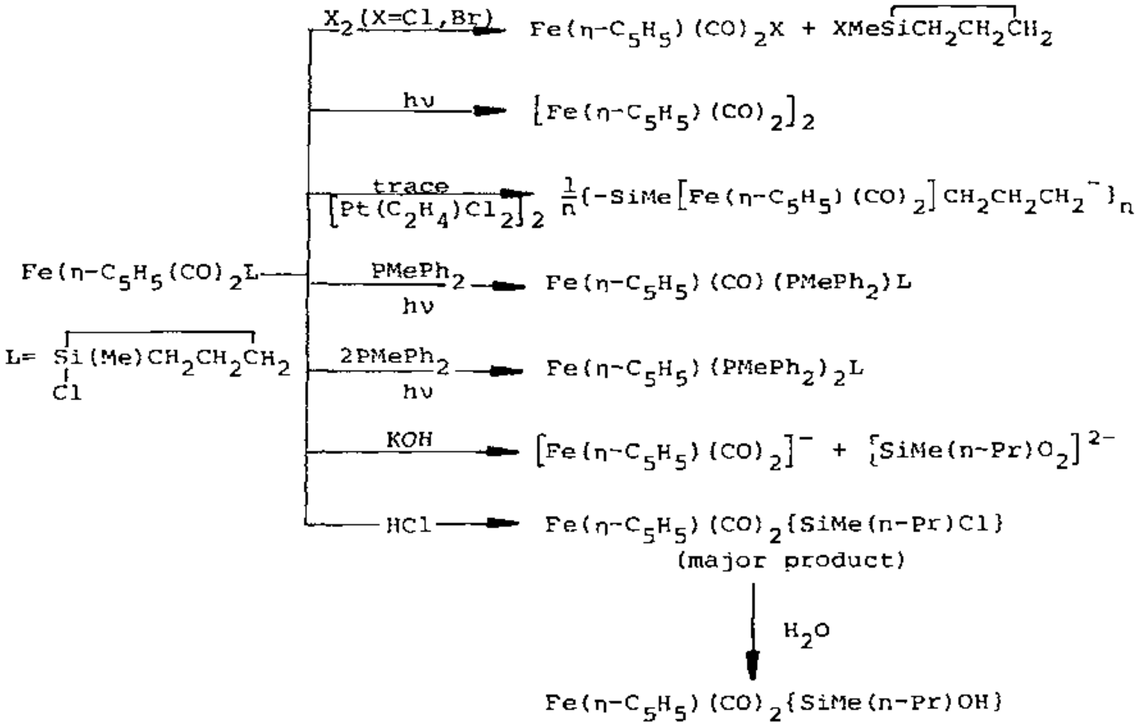


(124)

$$\downarrow\Delta$$

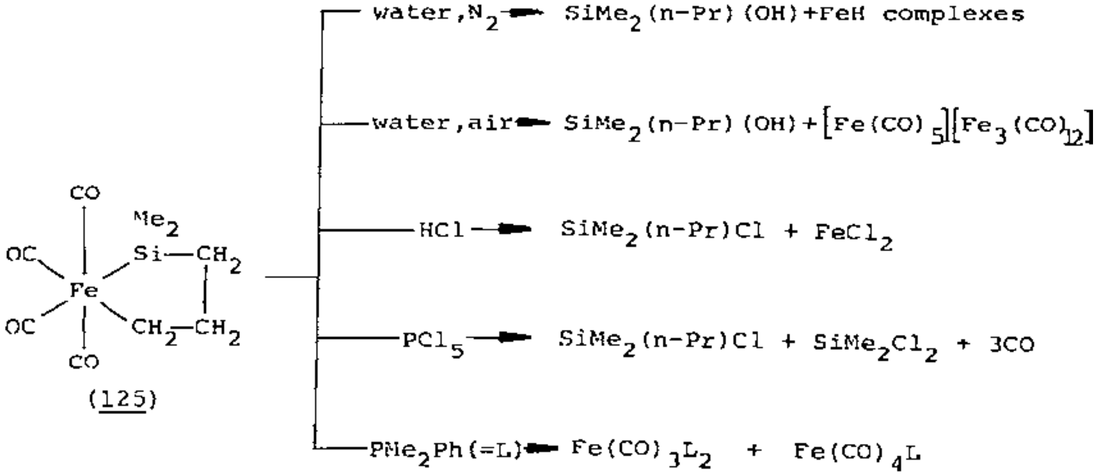
$$2C_3H_7CH{=}CH_2 + 2Me_2Si\ (\eta^5 - C_5H_4)Fe(CO)_2\ _2$$

The complexes $M(Si(Me)CH_2CH_2CH_2)$ ($M{=}Fe(C_5H_5)CO_2$, $Mn(CO)_5$) have been prepared by substitution of 1-chloro-1-methylsilacyclobutadiene. Reactions of the iron product are summarised in Scheme 5.[372]



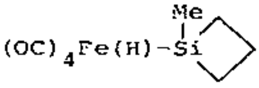
Scheme 5

The silaferracyclopentane (125) is obtained by the reaction of dimethylsilacyclobutane with $Fe_2(CO)_9$ (preferred route) or, with u.v. irradiation $Fe(CO)_5$ or $Fe_3(CO)_{12}$. The compound may also be prepared by the reaction of $ClMe_2Si(CH_2)_3Cl$ with $Na_2[Fe(CO)_4]$. Reactions of (125) are described in Scheme 6.[373] Ring-expansion as a route to silaferracyclopentanes seems to be independent of the exocyclic groups attached to silicon, which may be MeO and Cl in addition to Me. 1-Methyl-1-hydrosilacyclobutane and $Fe_2(CO)_9$ give both substitution and insertion products, (126) and (127), whilst reaction with $(Ph_3P)_2(C_2H_4)Pt$ affords (128).[374]

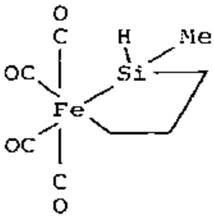


(125)

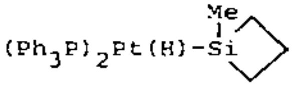
Scheme 6



(126)



(127)



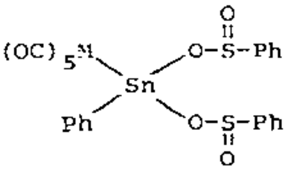
(128)

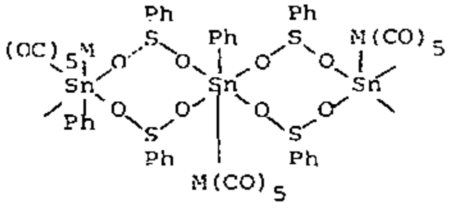
cis-$(Me_3Ge)Fe(CO)_4$[375] and *cis*-$(MeH_2Ge)Fe(CO)_4$[376] have been prepared by reaction of the halogermane with $Na_2[Fe(CO)_4]$. The trimethylgermyl derivative rearranges *in vacuo* yielding $(Me_3Ge)_2O$, $Fe(CO)_5$ and $Fe_3(CO)_{12}$, whilst the hydromethylgermyl compounds, *cis*-$(Me_nH_{3-n}Ge)Fe(CO)_4$ (n=1,2) eliminate the corresponding methylgermane.[377] Reacting patterns of $(MeH_2Ge)_2Fe(CO)_4$ with halogen compounds have been investigated in detail. Halogenation by milder reagents e.g. $SiCl_4$ is stepwise and alternately at each germanium atom. More reactive hydrogen halides also cause substitution, and subsequently cleave the Fe-Ge bonds.[378] Digermanyl chloride reacts with $Na[Co(CO)_4]$ in ether to afford $Co(CO)_4(Ge_2H_5)$, the Ge-Co bond of which is cleaved by $HgCl_2$. Reaction with $[Mn(CO)_5]^-$ gives $Mn(CO)_5(Ge_2H_5)$.[379]

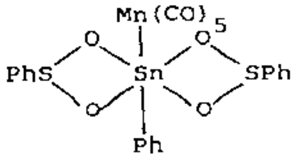
Three distinct reaction pathways may occur in the reactions of Me_nSiCl_{4-n} (n=0-3) and $Na[Co(CO)_4]$ depending on the acidity of the chlorosilane and the basicity of the solvent: (i) attack at the silicon via the cobalt atom of $[Co(CO)_4]^-$ forming Si-Co bonds, (ii) reaction involving a carbonyl ligand leading to the formation of clusters such as $R_3SiOCCo_3(CO)_9$, and (iii) chlorosilane-induced attack of $[Co(CO)_4]^-$ on the solvent yielding products derived from THF, eg $HO(CH_2)_4CCo_3(CO)_9$.[380] The miscellaneous complexes, $Ph_3Sn(Ph_3P)Co(CO)_3$[381] and $(C_5H_5)Fe(CO)(L)SnPh_3$ (L=CS,CNMe, $C(N_2C_2H_6)$)[382] have also been synthesised.

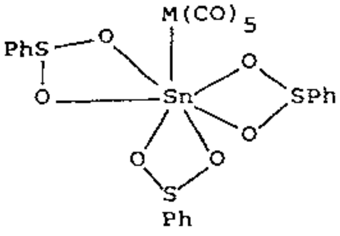
Ionisation and appearance potential data for several compounds containing Mn, Fe, and Co bonds to silicon and tin have been measured.[383] Detailed analyses of the vibrational spectra of $(C_5H_5)Fe(CO)_2MPh_3$,[384] $[(C_5H_5)Fe(CO)_2]_2MCl_2$ and $(C_5H_5)Fe(W)_2MX_2$ (M=Sn,Ge; X=Cl,Br)[385] have been presented.

Optically-active germyl-lithium compounds displace carbonyl ligands from transition metal carbonyls to afford complexes with optically-active germanium bonded to the transition metal e.g. $MePhNpGeM^-Li^+$ (M=$W(CO)_5$, $Mo(CO)_5$, $Fe(CO)_4$).[386] Several organotin-manganese complexes of the type R_3Sn- and ClR_2Sn-$Mn(CO)_3L_2$ (L=$P(OPh)_3$; PPh_3) have been prepared by the substitution method.[387] Only the Sn-C bonds of $Ph_3SnM(CO)_5$ (M=Mn,Re) are cleaved in liquid SO_2. The primary bis(O-sulphinato) complexes (<u>129</u>) formed at 20°C rearrange easily to the more stable polymeric O,O'-sulphinates (<u>130</u>) and monomeric (<u>131</u>). In the range 20-60°C, monomeric tris(O,O'-sulphinato) complexes (<u>132</u>) are formed.[388]

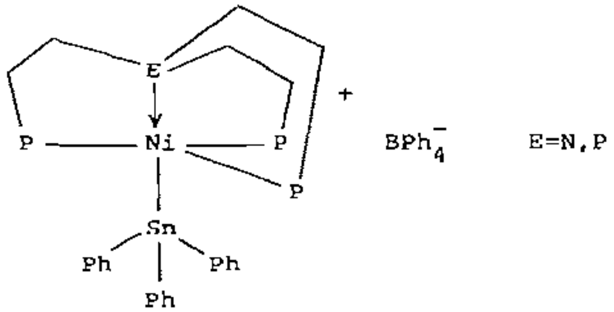

(<u>129</u>)


(<u>130</u>) M = Mn, Re


(<u>131</u>)


(<u>132</u>)

Several cationic Sn-Ni(II) complexes have been reported. Complexes of the general formula $MNi(PPh_3)_3(EPh_3)(THF)_x$ (M=Li, Na; E=Ge,Sn,Pb) and $Me_3Ni(PPh_3)(EPh_3)_3(THF)_x$ (E=Ge,Sn) are formed by substitution of $(Ph_3P)_2Ni(C_2H_4)$ by $MEPh_3$. The analogous silicon complexes could not be obtained because of the formation of $SiPh_4$ from $LiSiPh_3$ and coordinated PPh_3.[389] Similar cationic complexes (<u>133</u>) result from the reaction of $LiSnPh_3$ with $NiCl(L)\ BPh_4$ in THF at -70°C:[390,391]

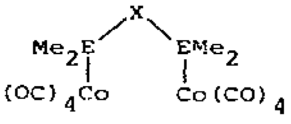


(<u>133</u>)

Cyclooctatetraenes (C_8H_7R, R=H,Me,Ph,$SiMe_3$) react with $Ru(SiMe_3)_2(CO)_4$ in refluxing hexane to give trimethylsilyl-migration products $Ru(SiMe_3)(CO)_2\{C_8H_7R(SiMe_3)\}$ together with ring-closed tetrahydropentalenyl complexes $Ru(SiMe_3)(CO)_2(C_8H_8R)$. The structure of the former product (R=H) was established by X-ray analysis. Heating the cyclooctatetraenes with $Ru(SiMe_3)_2(CO)_4$ or the complexes $Ru(SiMe_3)(CO)_2\{C_8H_7R(SiMe_3)\}$directly in heptane effects ring-closure with the elimination of the C-bonded Me_3Si group giving diruthenium pentalene complexes $Ru_2(SiMe_3)_2(CO)_4(C_8H_5R)$ in moderate yield, again confirmed by an X-ray determination.[392,393] The silylruthenium complexes $RuH_3(SiR_3)(PPh_3)_2$ and $RuH(SiR_3)(PPh_3)_2$ are effective catalysts for the addition of CCl_4 to 1-octene.[394] The lemon-yellow crystalline product from the reaction of $SnCl_2$, PPh_3 and the red ruthenium solution obtained by treating $RuCl_3xH_2O$ in EtOH with CO is actually $[RuCl(SnCl_3)(CO)(PPh_3)_2](OCMe_2)$ Me_2Co (X-ray), and not $\{Ru_2Cl_3(SnCl_3)(CO)_2(PPh_3)_3\}(OCMe_2)_2$ as previously thought.[395] The structure of $(Me_2PhP)_2AuSnCl_3$ has been determined. Gold is coordinated by the two phosphines and an $[SnCl_3]$ ligand in a trigonal geometry, but with considerable distortion towards a linear PAUP group and an uncoordinated $SnCl_3^-$ anion.[396] The rare earth complexes $(C_5H_5)_2MSnPh_3$ (M=Er,Yb) and

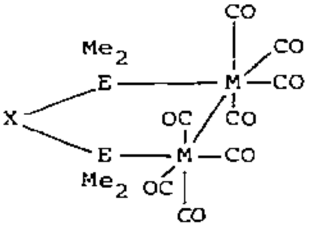
$(C_5H_5)_2ErGePh_3$ result from the reaction of Ph_3MLi with the corresponding rare earth chlorides.[397]

$Co_2(CO)_8$ reacts readily with $Me_4Si_2H_2O$, $Me_4Ge_2H_2O$ and $(Me_2HSi)_2CH_2$ to yield the complexes (134), which decompose slowly at -78°C under nitrogen to $Co_4(CO)_{12}$ and polysiloxanes and -germoxanes. With $Fe(CO)_5$ or $Ru_3(CO)_{12}$ under u.v. photolysis, the five-membered heterocycles (135) are obtained.[398] Similar four-membered



(134)

X=O;E=Si,Ge
X=CH$_2$; E=Si
M=Fe, Ru



(135)

metallocycles, $L_2Pd(Si_2Me_2O)$, $L_2(CO)HIr(Si_2Me_4O)$, $L_2(CO)HIr(Si_2Me_4CH_2)$, $L_2Pt(Si_2Me_4CH_2)$ and $L_2Pd(Si_2Me_4CH_2)$ ($L=PPh_3$) have also been prepared and act as catalysts for the disproportionation of tetramethyldisiloxane into dimethylsiloxane and linear polysiloxanes in neutral medium at room temperature.[399]

Eaborn has continued his studies of the reactions of organotin compounds with Pt(II) complexes. Aryl-for-chlorine group exchange occurs between $ArSnMe_3$ and $[Pt(Cod)Cl_2]$,[400] $[Pt(Cod)Cl(PMe_2Ph)]BF_4$,[401] or cis-$[Pt(C_2H_4)Cl_2(PPh_3)]$.[402] In the former case, one or both chlorines can be replaced. The use of one mole of $ArSnMe_3$ usually affords the monoaryl derivative in high yield, whilst the diaryl complex is obtained when two or more moles of reagent are employed. With cis-$[Pt(C_2H_4)Cl_2(PPh_3)]$, the chloride-bridged complexes $[Pt_2Ar_2Cl_2(LPPh_3)_2]$ are obtained with one mole of $ArSnMe_3$, but excess causes decomposition to $[PtArCl(PPh_3)_2]$ complexes. The reactions of $[Pt(C_2H_4)(PPh_3)_2]$ with organotin halides R_nSnX_{4-n} (n=0-4) proceed by insertion of platinum into the Sn-R(Ar) or Sn-X bonds depending on the nature of the tin substrate, affording complexes of the types cis-$[PtR(PPh_3)_2(SnR_2X)]$, cis-$[PtPh(PPh_3)_2(SnPhX_2)]$, and cis- and trans-$[Pt(PPh_3)_2(SnR_2X)X]$.[403] The reaction between trans-$[PtH_3\{P(hexyl)_3\}$- and MXH_3 (M=Si; X=H,Cl,SiH_3: M=Ge, X=H) compounds yield trans-$PtH(Y)\{P(hexyl)_3\}]$ (Y=MXH_2) complexes, probably via intermediate

$[PtH_3(Y)\{P(hexyl)_3\}]$. Unusually, the silyl group is *trans* to the hydride in $[PtH(SiH_3\{P(hexyl)_3\}]$.[404] Similar insertion reactions of $[Pt(Me_2)_2(N\text{-}N)]$ (N-N=bipyridyl, substituted phenanthroline) complexes into Ge-X (X=Cl,Br) bonds of organo-germanium halides have been demonstrated by Kuyper.[405]

Bimetallic Pt-Sn complexes containing up to six tin atoms are formed between amine-Pt(II) complexes and chlorotin compounds. In solution, competing equilibria are established.[406] The Pt-Sn-Cl system has been shown to be an effective homogeneous catalyst for the water gas shift reaction. A typical catalyst system consisted of K_2PtCl_4 (0.25mmole) and $SnCl_4.5H_2O$ (7.1mmole) in 40ml glacial acetic acid with 10ml concentrated HCl and 10ml water, giving a rate of catalysis at 88°C of *ca*. 25 turnovers/day/platinum ion, with no loss of activity upon recharging. $[Pt(Cl(CO)(SnCl_3)_2]^-$ was considered to be most probably responsible for the catalysis of H_2 formation, and $[PtCl_2(CO)(SnCl_3)]^-$ responsible for CO_2 generation.[407] Photoirradiation of a homogeneous solution in propan-2-ol of a Rh-Sn-Cl catalyst markedly enhances the endothermic reaction rate to produce acetone and H_2.[408]

Trans-$[PdL_2(SnCl_3)_2]$ and *cis*-$[PdL_2(SnCl_3)Cl]$ (L=phosphine) complexes have been prepared by the reaction of phosphines with Pd-$SnCl_3$ complexes in HCl-EtOH.[409] Thermal analysis studies show that the *cis*-$[PtL_2(SnCl_3)Cl]$ (L=phosphine) complexes are converted into the more stable *trans* isomers when heated in the solid state. Heats of isomerisation were in the range 5-11 kcal mol^{-1}.[410] The reactivity of $[Pt(SnMe_3)_2(PPh_2CH_2)_2]$ towards air, base, acids, thiols and organic and metal halides has been examined. Many reagents cleave both Pt-Sn bonds in a stepwise fashion.[411]

REFERENCES

1 S.L. Yu and D.D. DesMarteau, Inorg. Chem., 17, (1978) 304.
2 S.L. Yu and D.D. DesMarteau, Inorg. Chem., 17, (1978) 2484.
3 A.B. Burg, Inorg. Chem., 17, (1978) 2322.
4 K. Odaka, O. Kajimoto and T. Fueno, Bull.Chem.Soc.Jpn., 51 (1978)443.
5 E.C.Wu, R.R. Clark and Y.N. Tang, Can.J.Chem., 56(1978)1989.
6 D.W. Grattan and K.O. Kutsche, Can.J.Chem., 56(1978)2638.
7 R. Appel and H.F. Schöler, Chem.Ber., 111(1978)2056.
8 R. Appel and H.D. Wihler, Chem.Ber., 111(1978)2054.
9 A. Spelbos, P.A.G. Huisman, F.C. Mijlhoff and G.H. Renes, J.Mol.Struct., 44(1978)159.
10 K.Oyanagi and K.Kuchitsu, Bull.Chem.Soc.Jpn., 51(1978)2237.
11 K.Oyanagi and K.Kuchitsu, Bull.Chem.Soc.Jpn., 51(1978)2243.
12 T.Sakaizumi, Y.Kohri, O.Ohashi and I.Yamaguchi, Bull.Chem.Soc. Jpn., 51(1978)3411.
13 D.H. Lemmon, J.Mol.Struct., 44(1978)71.
14 J.H. Carpenter and D.F. Rimmer, J.Chem.Soc.Faraday Trans.II, 74(1978)466.
15 U.Niemer and R. Mattes, Chem.Ber., 111(1978)2118.
16 U.Niemer, K.Hennemann and R. Mattes, Chem.Ber., 111(1978)2113.
17 V.G.Albano, P.Chini, S. Martinengo, M. Sansoni and D. Strumolo, J.Chem.Soc.Dalton Trans., (1978) 459.
18 V.G. Albano, P.Chini, S. Martinengo and M. Sansoni, J.Chem.Soc., Dalton Trans., (1978) 463.
19 R.J.Hwang and P.P.Gaspar, J.Amer.Chem.Soc., 100(1978)6626.
20 J.R. Weisenfeld and M.J.Yuen, J.Phys.Chem., 82(1978)1225.
21 M.A. Chowdhury and D. Husain, J.Chem.Soc.Faraday Trans.II, 74 (1978)1065.
22 D.L. Perry, P.F. Meier, R.H. Hauge and J.L. Margrave, Inorg.Chem., 17(1978)1365.
23 E.E. Siefert, R.A. Ferrieri, O.F. Zeck and Y.N. Tang, Inorg.Chem.,17 (1978)2802.
24 C.S. Liu and T.L. Hwang, J.Am.Chem.Soc., 100(1978)2577.
25 D. Seyferth and D.P. Duncan, J.Am.Chem.Soc., 100(1978)7734.
26 H.Okinoshima and W.P. Weber, J.Organomet.Chem., 150(1978)C25.
27 W.D. Wulff, W.F. Goure and T.J. Barton, J.Am.Chem.Soc., 100(1978) 6236.
28 H. Sakurai, T. Kobayashi and Y. Nakadaira, J.Organomet.Chem., 162(1978)C43.
29 S.Tokach, P.Boudjouk and R.D. Koob, J.Phys.Chem., 82(1978)1203.
30 M.Ishikawa, K.I. Nakagawa, M. Ishiguro, F. Ohi and M. Kumada, J.Organomet.Chem., 152(1978)155.
31 M.Ishikawa, T. Fuchikama and M. Kumada, J.Organomet.Chem., 149 (1978)37; 162(1978)223.
32 T.J. Barton and G.J. Burns, J.Am.Chem.Soc., 100(1978)5246.
33 H.Okinoshima and W.P. Weber, J.Organomet.Chem., 149(1978)279.
34 H.Okinoshima and W.P. Weber, J.Organomet.Chem., 155(1978)165.
35 D. Seyferth, T.F.O. Lim and D.P. Duncan, J.Am.Chem.Soc., 100 (1978)1626.
36 N. Wiberg and G. Preiner, Angew.Chem., Int.Ed.Engl., 17(1978)362.
37 D. Seyferth and T.F.O. Lim, J.Am.Chem.Soc., 100(1978)7074.
38 H. Lavayssiere, J. Barrau, G. Dousse, J.Satge and M. Bouchaut, J.Organomet.Chem., 154(1978)C9.
39 H.Lavayssiere, G. Dousse, J. Barrau, J. Satge and M. Bouchaut, J.Organomet.Chem., 161(1978)C59.
40 P.Riviere, A. Caze, A. Castel, M. Riviere-Baudet and J. Satge, J.Organomet.Chem., 155(1978)C58.
41 C. Couret, J.Satge, J.D. Andriamizaka and J. Escudie, J.Organomet.Chem., 157(1978)C35.

42 L.J. Dizikes, W.P. Ridley and J.M. Wood, J.Am.Chem.Soc., 100 (1978)1010.

43 F.Thevet, C. Dagron and J. Flahaut, Bull.Soc.Chim.Fr.,I, (1978) 455.

44 H. Hirsch, J.Inorg.Nucl.Chem., 40(1978)1623.

45 J.Fenner, Z.Naturforsch., 33b(1978)479.

46 D.Messer, Z.Naturforsch., 33b (1978)366.

47 G.Bergerhoff and H.Namgung, Acta Crystallogr., B34(1978)699.

48 S. Vilminot, W. Granier and L. Cot, Acta Crystallogr., B34(1978) 35.

49 S. Vilminot, W. Granier, Z.Al.Oraibi and L.Cot, Acta Crystallogr., B34(1978)3306.

50 S. Vilminot, W. Granier, Z.Al.Oraibi and L. Cot, Acta Crystallogr., B34(1978)3308.

51 A.G. Filby, R.A. Howie and W. Moser, J.Chem.Soc.Dalton Trans., (1978)1797.

52 D. Weber, Z.Naturforsch., 33b(1978)862.

53 D. Weber, Z.Naturforsch., 33b(1978)1443.

54 H.J.Haupt and F.Huber, Z.Anorg.Allg.Chem., 442(1978)31.

55 A. Aquilino, M. Cannas, A. Christini and G. Marongiu, J.Chem.Soc. Chem.Commun., (1978)347.

56 H.Ohno, M. Yoroki, K. Furukawa, Y. Takagi and T. Nakamura, J.Chem.Soc.Faraday Trans.I, 74(1978)1861.

57 M.J. Tricker and J.D. Donaldson, Inorg.Chim.Acta, 31(1978)L445.

58 R.A.Geanangel, J.Inorg.Nucl.Chem., 40(1978)603.

59 E.R. Mognaschi, A. Chierico and G. Parravicini, J.Chem.Soc. Faraday Trans.I, 74(1978)2333.

60 J. Barrau and J. Satge, J.Organomet.Chem., 148(1978)C9.

61 W. Lutz, W. Sundermeyer and W. Towae, Z.Anorg.Allg.Chem., 444 (1978)21.

62 G. Chobert and M. Devaud, J.Organomet.Chem., 153(1978)C23.

63 H. Brunner and R.G. Gastinger, J.Organomet.Chem., 145(1978)365.

64 J.D. Cotton and G.A. Morris, J.Organomet.Chem., 145(1978)245.

65 J.D. Cotton, J.Organomet.Chem., 159(1978)465.

66 M.J.S. Gynane, M.F. Lappert, S.J. Miles and P.P. Power, J.Chem. Soc.Chem.Commun., (1978)192.

67 J.G. Bucknell, C.F. Cullis and D.J. Hucknall, J.Chem.Soc. Faraday Trans.I, 74(1978)1922.

68 W.W. Du Mont and B. Neudert, Z.Anorg.Allg.Chem., 441(1978)86.

69 W.W. Du Mont, Inorg.Chim.Acta, 29(1978)L195.

70 W.W. Du Mont, J. Organomet.Chem., 153(1978)C11.

71 P. Jutzi, W. Steiner, E. König, G. Huttner, A. Frank and U. Schubert, Chem.Ber., 111 (1978)606.

72 P.F.R. Ewings and P.G. Harrison, Inorg.Chim.Acta, 28(1978)L167.

73 W.D. Honnick and J.J. Zuckerman, Inorg.Chem., 17(1978)501.

74 P.G. Harrison, B.J. Haylett and T.J. King, J.Chem.Soc.Chem. Commun., (1978)112.

75 I.Wakeshima, Y.Saitoh and I.Kijima, Bull.Chem.Soc.Jpn., 51(1978) 3549.

76 I. Wakeshima and I. Kijima, Bull.Chem.Soc.Jpn., 51(1978)815.

77 G. Verville, Canad.J.Chem., 56(1978)2624.

78 P.G. Harrison and E.W. Thornton, J.Chem.Soc.Dalton Trans. (1978) 1274.

79 R. Herak, B.Prelesnik, M. Curic and P. Vasic, J.Chem.Soc.Dalton Trans., 566(1978).

80 R.C. Elder, M.J. Heeg and E. Deutsch, Inorg.Chem., 17(1978)427.

81 R.M. Braun and R. Hoppe, Angew.Chem., Int.Engl., 17(1978)449.

82 K.P. Martens and R. Hoppe, Z.Anorg.Allg.Chem., 438(1978)105.

83 K.P. Martens and R. Hoppe, Z.Anorg.Allg.Chem., 440(1978)81.

84 M.A. Bredig, C.E. Bamberger and D.M. Richardson, J.Inorg.Nucl. Chem., 40(1978)1497.

85 S. Kaneko and F. Imoto, Bull.Chem.Soc.Jpn., 51(1978)1739.
86 A.M. Glazer and S.A. Mabud, Acta Crystallogr., B34(1978)1065.
87 A.M. Glazer, S.A. Mabud and R. Clarke, Acta Crystallogr., B34 (1978)1060.
88 A.A. Bush, A.V. Titor, B.I.Al'shin and Yu.N.Venevtsev, Russ.J. Inorg.Chem., 22(1977)1211.
89 A.A. Bush and Yu.N.Venevtsev, Russ.J.Inorg.Chem., 23(1978)1207.
90 G. Burchard and W. Rüdorf, Z.Anorg.Allg.Chem., 447(1978)149.
91 L.L. Zaitseva, M.I. Konarev, A.V. Velichko and N.M. Morgunora, Russ.J.Inorg.Chem., 22(1977)803.
92 V.E. Efremov and V.K. Trunov, Dokl.Chem., 235(1978)438.
93 A.V. Vishnyakov, V.I. Dubrovin and P.V. Kovtunenko, Russ.J.Inorg. Chem., 23(1978)1235.
94 M. Koskenlinna and J. Valkonen, Cryst.Struct.Commun., 6(1977)813.
95 R.N. Knyazeva, T.A. Larionova and I.A. Shevchenko, Russ.J.Inorg. Chem., 22(1977)1117.
96 J.C. Dewan, A.J. Edwards, G.R. Jones and I.M. Young, J.Chem.Soc. Dalton Trans., (1978)1528.
97 H. Worzala, Z.Anorg.Allg.Chem., 445(1978)27.
98 H. Worzala and K.H. Jost, Z.Anorg.Allg.Chem., 445(1978)36.
99 M.A. Nabar and A.P. Dalvi, Z.Anorg.Allg.Chem., 440(1978)265.
100 A.G. Davies and M.W. Tse, J.Chem.Soc.Chem.Commun., (1978)353.
101 E.J. Bulten and H.A. Budding, J.Organomet.Chem., 157(1978)C3.
102 C.D. Hoff and J.W. Connolly, J.Organomet.Chem., 148(1978)127.
103 A.Bonny, A.D. McMaster and S.R. Stobart, Inorg.Chem., 17(1978) 735.
104 S. Cradock and W. Duncan, J.Chem.Soc.Faraday Trans.II, 74(1978) 194.
105 R.D. Ernst and T.J. Marks, Inorg.Chem., 17(1978)1477.
106 G. Bissert and K.F. Hesse, Acta Crystallogr., B34(1978)1322.
107 V.V. Serebrenniko and V.P. Gus'kova, Russ.J.Inorg.Chem., 23(1978) 1242.
108 Yu.V.Zaikin, A.N. Olonovskii, V.P. Ziumanov and Yu.A.Zarif'yants, Russ.J.Inorg.Chem., 22(1978)1123.
109 M.Veith, Z.Naturforsch., 33b(1978)1.
110 M.Veith, Z.Naturforsch., 33b(1978)7.
111 M.Veith, O.Recktenwald and E. Humpfer, Z.Naturforsch., 33b(1978) 14.
112 M.Veith, Chem.Ber., 111(1978)2536.
113 R.H. Herber and A.E. Smelkinson, Inorg.Chem., 17(1978)1023.
114 L.J. Rodriguez, G.W. Liesegang, M.M. Farrow, N. Purdie and E.M. Eyring, J.Phys.Chem., 82(1978)647.
115 M. Kodama and E. Kimura, Inorg.Chem., 17(1978)2446.
116 T.J. Marks and D.R. Stojakovic, J.Amer.Chem.Soc., 100(1978)1695.
117 J.de O. Cabral, M.F. Cabral, W.J. Cummins, M.G.B. Drew, A. Rodgers and S.M. Nelson, Inorg.Chim.Acta, 30(1978)L313.
118 C.G. Newnan, M.A. Ring and H.E. O'Neal, J.Am.Chem.Soc., 100(1978) 5945.
119 R.M. Barrer and J.C. Trombe, J.Chem.Soc.Dalton Trans., (1978) 1746.
120 F.F. Roelandt, D.F. Van de Vondel and G.P. Van der Kelen, J.Mol.Struct., 50(1978)147.
121 A. Hinchliffe, J.Mol.Struct., 48(1978)279.
122 S. Cradock, E.A.V. Ebsworth and A.R. Green, J.Chem.Soc. Dalton Trans. (1978)759.
123 A. Wright, J.Organomet.Chem., 145(1978)307.
124 D.J. Yong and W.L. Jolly, Inorg.Chem., 17(1978)621.
125 N. Watanabe, M. Aoki, N.Sakurai, K.I.Watanabe and Y. Nagai, J.Organomet.Chem., 160(1978)C1.

126 H.M. Dickens, R.N. Haszeldine, A.P. Mather and R.V. Parish, J.Organomet.Chem., 161(1978)91.
127 K.A. Andrianov, M.I. Filimonova and V.I. Sidorov, J.Organomet. Chem., 144(1978)27.
128 G.K.I. Magomedov, K.A. Andrianov, O.V. Shkolnik and V.N.Kalinin, J.Organomet.Chem., 149(1978)29.
129 I.M. Salimgareeva, V.V. Kaverin and V.P. Jurjev, J.Organomet. Chem., 148(1978)23.
130 Y. Wakatsuki and H. Yamazaki, J.Organomet.Chem., 149(1978)385.
131 H. Kono, H. Matsumoto and Y. Nagai, J.Organomet.Chem., 148 (1978)267.
132 J. Boyer, R.J.P. Corriu, R. Perz and C. Reye, J.Organomet.Chem., 157(1978)153.
133 O.W. Steward, A.G. Lutkis and J.B. Greenshields, J.Organomet. Chem., 144(1978)147.
134 J. Grobe and R. Rau, J.Organomet.Chem., 157(1978)281.
135 L.S. Khaikin, V.P. Novikov and L.V. Vilkov, J.Mol.Struct., 44 (1978)43.
136 P.G. Harrison and K.C. Molloy, J.Organomet.Chem.,152(1978)53.
137 S.N. Gurkova, N.V. Alekseev, A.I. Gusev, S. Ya.Pechurina and V.I. Grigos, J.Struct.Chem., 18(1977)308.
138 A.G. Davies, M.W. Tse, J.D. Kennedy, W. McFarlane, G.S. Pyne, M.F.C. Ladd and D.C. Povey, J.Chem.Soc.Chem.Commun., (1978)791.
139 A. Bonny and S.R. Stobart, Inorg.Chim.Acta, 31(1978)L437.
140 B.E. Mann, B.F. Taylor, N.A. Taylor and R. Wood, J.Organomet. Chem., 162(1978)137.
141 A. Fadini, E. Glozbach, P. Krommes and J. Lorberth, J.Organomet. Chem., 149(1978)297.
142 E.K.S. Liu and R.J. Lagow, Inorg.Chem., 17(1978)618.
143 R.J. Lagow, R. Eujen, L.L. Gerchman and J.A. Morrison, J.Am. Chem.Soc., 100(1979)1722.
144 R. Eujen and R.J. Lagow, J.Chem.Soc.Dalton Trans.(1978)541.
145 A.C. Baldwin, I.M.T. Davidson and M.D. Reed, J.Chem.Soc. Faraday Trans.I, 74(1978)2171.
146 E. Block and L.K. Revelle, J.Am.Chem.Soc., 100(1978)1630.
147 L. Killian and B. Wrackmeyer, J.Organomet.Chem., 148(1978)137.
148 L. Killian and B. Wrackmeyer, J.Organomet.Chem., 153(1978)153.
149 B. Wrackmeyer and R. Zentgraf, J.Chem.Soc.Chem.Commun., (1978) 402.
150 P. Jutzi and J. Baumgärtner, J.Organomet.Chem., 148(1978)257.
151 P. Jutzi and J. Baumgärtner, J.Organomet.Chem., 148(1978)247.
152 D. Seyferth and S.C. Vick, J.Organomet.Chem., 144(1978)1.
153 G. Plazzogna, V. Peruzzo and G. Rossetto, Inorg.Chim.Acta, 31, (1978)L395.
154 E.J. Bulten and H.A. Budding, J.Organomet.Chem., 153(1978)305.
155 J.L. Wardell, Inorg.Chim.Acta, 26(1978)L18.
156 R.C. Poller and D. Silver, J.Organomet.Chem., 157(1978)247.
157 D.J. Cane, W.A.G. Graham and L. Vancea, Canad.J.Chem., 56(1978) 1538.
158 G.G. Gospodinov and D.B. Gospodinova, Russ.J.Inorg.Chem., 22 (1977)1559.
159 K.L. Jaura, K.K. Dhingra, R.K. Mahajan and K. Lal, Z.Anorg. Allg.Chem., 445(1978)242.
160 A.P. Popov, T.I. Kurdina and K.T. Panina, Russ.J.Inorg.Chem., 23(1976)463.
161 M. Farber and R.D. Srivastava, J.Chem.Soc.Faraday Trans.I, 74 (1978)1089.
162 W.G. French, L.J. Pace and V.A. Foertmeyer, J.Phys.Chem., 82 (1978)2191.

163 J.A. Daniels, J.R. Jennings, P.G. Huggett and K. Wade, Inorg. Nucl.Chem.Letters, 14(1978)445.

164 A.A. Ennan and V.I. Nikitin, Russ.J.Inorg.Chem., 22(1977)1281.

165 S. Bywater and D.J. Worsfold, Canad.J.Chem., 56(1973)2093.

166 Yu.A. Buslaev, V.O. Gel'mbol'dt and S.P.Petrosyants, Dokl. Chem., 236(1977)572.

167 A.R. Boate, J.R. Morton and K.F. Preston, J.Phys.Chem., 82 (1978)718.

168 V.A. Varnek and L.N. Mazalov, J.Struct.Chem., 19(1978)219.

169 V.A. Varnek, S.P. Gabuda and B.I. Obmoin, J.Struct.Chem., 18 (1977)212.

170 H. Boysen and A.W. Hewat, Acta Crystallogr., B34(1978)1414.

171 A.A. Opalovskii, T.F. Gudimovich, L.D. Ishkova, M.K. Akhmadeev and T.Z. Tevletskaya, Russ.J.Inorg.Chem., 22(1977)1393.

172 J. Chojnowski, M. Cypryk and J. Michalski, J.Organomet.Chem., 161(1978)C31.

173 D.P. Graddon and B.A. Rana, J.Organomet.Chem., 148(1978)17.

174 P. Koehler, K. Licht and H. Kriegsmann, Z.Anorg.Allg.Chem., 447(1978)75.

175 K.L. Richie and G. Eng, Inorg.Chim.Acta, 31(1978)L417.

176 L.A. Aslanov, V.M. Attiya, V.M. Ionov, A.B. Permin and V.S. Petrosyan, J.Struct.Chem., 18(1977)884.

177 P.G. Harrison, K.C. Molloy, R.C. Phillips, A.J. Crowe and P.J. Smith, J.Organomet.Chem., 160(1978)421.

178 P.G. Harrison and K.C. Molloy, J.Organomet.Chem., 152(1978)63.

179 L.A. Aslanov, V.M. Ionov, V.M. Attiya, A.B. Permin and V.S. Petrosyan, J.Struct.Chem., 18(1977)876.

180 L.A. Aslanov, V.M. Ionov, V.M. Attiya, A.B. Permin and V.S. Petrosyan, J.Organomet.Chem., 144(1978)39.

181 L.A. Aslanov, V.M. Ionov, V.M. Attiya, A.B. Permin and V.S. Petrosyan, J.Struct.Chem., 19(1978)91.

182 L.A. Aslanov, V.M. Ionov, V.M. Attiya, A.B. Permin and V.S. Petrosyan, J.Struct.Chem., 19(1978)269.

183 F. Riverola, A. Silvestri and R. Barbieri, Inorg.Chim.Acta, 28(1978)223.

184 S. Araki, H. Ishida and T. Tanaka, Bull.Chem.Soc.Jpn., 51, (1978)407.

185 R.E. Hutton, J.W. Burley and V. Oakes, J.Organomet.Chem., 156 (1978)369.

186 E.J. Butten and J.W.G. van den Hurk, J.Organomet.Chem., 162 (1978)161.

187 A.G. Galinos, J.M. Tsangaris and A.A. Kouroumalis, Inorg.Nucl. Chem.Letters, 14(1978)87.

188 G.van Koten, J.T.B.H. Jastrzebski, J.G. Noltes, W.M.G.F.Pontenagel, J. Kroon and A.L. Spek, J.Am.Chem.Soc., 100(1978)5021.

189 G.van Koten, J.T.B.H. Jastrzebski, J.G. Noltes, A.L. Spek and J.C. Schoone, J.Organomet.Chem., 148(1978)233.

190 M. Lequan, Y. Besace and J.P. Ballaguet, J.Organomet.Chem., 144(1978)C39.

191 J.Pacansky and K. Hermann, J.Chem.Phys., 69(1978)963.

192 H. Schnöckel, Angew.Chem., Int.Ed.Engl. 17(1978)616.

193 W. Redlich and R. Gruehn, Z.Anorg.Allg.Chem., 438(1978)25.

194 P.B. Barraclough and P.G. Hall, J.Chem.Soc. Faraday Trans.I, 74(1978)1360.

195 C.H. Rochester and D.A. Trebilco, J.Chem.Soc.Faraday Trans.I, 74(1978)1125.

196 C.H. Rochester and D.A. Trebilco, J.Chem.Soc.Faraday Trans.I, 74(1978)1137.

197 S.N.W. Cross and C.H. Rochester, J.Chem.Soc.Faraday Trans.I, 74 (1978)2130.

198 A.D. Buckland, C.H. Rochester, D.A. Trebilco and K. Wigfield, J.Chem.Soc.Faraday Trans.I, 74(1978)2393.
199 F.J. Berry and A.G. Maddock, Inorg.Chim.Acta, 31(1978)181.
200 S. Kittaka, S. Kanemoto and T. Morimoto, J.Chem.Soc.Faraday Trans.I, 74(1978)676.
201 T. Morimoto, Y. Yokota and S. Kittaka, J.Phys.Chem., 82(1978) 1996.
202 L.E. Derlyukova and V.I. Evdokimov, Russ.J.Inorg.Chem., 23 (1978)962.
203 P.G. Harrison and E.W. Thornton, J.Chem.Soc.Faraday Trans.I, 74(1978)2597.
204 M. Niwa, T. Minami, H. Kodama, T. Hattori and Y. Murakami, J.Catalysis, 53(1978)198.
205 F. Solymosi and J. Kiss, J.Catalysis, 54(1978)42.
206 P.G. Harrison and E.W. Thornton, J.Chem.Soc.Faraday Trans.I, 74(1978)2703.
207 P.G. Harrison and E.W. Thornton, J.Chem.Soc.Faraday Trans.I, 74(1978)2604.
208 J.P. Guillory and C.M. Shiblom, J.Catalysis, 54(1978)24.
209 Y. Takita, Y.Moro-Oka and A. Ozaki, J.Catalysis, 52(1978)95.
210 T. Ono and Y. Kubokawa, J.Catalysis, 52(1978)412.
211 A. Perrard and J.E. Germain, Bull.Chim.Soc.Fr.II, (1978)55.
212 A. Perrard and J.E. Germain, Bull.Chim.Soc.Fr.II, (1978)59.
213 E.A. Irving and D. Taylor, J.Chem.Soc.Faraday Trans.I, 74(1978) 206.
214 E.A. Irving and D. Taylor, J.Chem.Soc.Faraday Trans.I, 74(1978) 1590.
215 C. Riekel and A. Weiss, Z.Naturforsch., 33b (1978)731.
216 P.M. Sidorov, E.L. Belokoneva, N.F. Fedorov, T.A. Tunik, M.A. Simonov and N.V. Belov, J.Struct.Chem., 18(1977)319.
217 H. Nyman, M.O'Keefe and J.O. Bovin, Acta Crystallogr., B34 (1978)905.
218 E. Tillmanns and H.P. Grosse, Acta Crystallogr., B34(1978)649.
219 M. Taylor and R.C. Ewing, Acta Crystallogr., B34(1978)1074.
220 J.B. Higgins and F.K. Ross, Cryst.Struct.Commun., 6(1977)179.
221 R.R. Ryan and A. Rosenzweig, Cryst.Struct.Commun., 6(1977)611.
222 A. Rosenzweig and R.R. Ryan, Cryst.Struct.Commun., 6(1977)617.
223 G. Engel, H.Jäckle and L.Häbe-Rapf, Z.Anorg.Allg.Chem., 438 (1978)142.
224 S.S. Batsanov, V.A. Egorov, V.P. Bokarev, L.I. Kopaneva and G.V. Dorogova, Russ.J.Inorg.Chem., 22(1977)1752.
225 N.A. Berg, T.A.Ust'yantseva, B.P. Seveda, A.A. Soloshenko and G.A. Kravchenko, Russ.J.Inorg.Chem., 22(1977)1125.
226 F.C. Hawthorne and J. Ho, Acta Crystallogr., B34(1978)891.
227 K. Kawamura, A. Kawahara and J.T. Iiyama, Acta Crystallogr., B34(1978)3181.
228 H. Kroll, M.W. Phillios and H. Pentinghaus, Acta Crystallogr., B34(1978)359.
229 D.W.J. Cruikshank, A. Kalman and J.S. Stephens, Acta Crystallogr., B34(1978)1333.
230 E.A. Knyazev, Russ.J.Inorg.Chem., 23(1978)777.
231 B.V. Mill, E.L. Belokoneva, M.A. Simonov and N.V. Belov, J.Struct.Chem., 18(1977)321.
232 O. Baumgartner and H. Völlenkle, Monatsh.Chem., 109(1978)1145.
233 R.D. Shannon, B.E. Taylor, T.E. Gier, H,Y-Chen and T. Berzins, Inorg.Chem., 17(1978)958.
234 M. O'Keefe and B.G. Hyde, Acta Crystallogr., B34(1978)27.
235 M.J. Tricker, D.A. Jefferson, J.M. Thomas, P.G. Manning and C.J. Elliott, J.Chem.Soc.Faraday Trans.II, 74(1978)174.
236 R.M. Barrer and W. Sieber, J.Chem.Soc.Dalton Trans.(1978)598.

237 J. Götz and C.R. Masson, J.Chem.Soc.Dalton Trans., (1978)1134.
238 H.P. Calhoun and C.R. Masson, J.Chem.Soc.Dalton Trans. (1978) 1342.
239 H.P. Calhoun and C.R. Masson, J.Chem.Soc.Dalton Trans., (1978) 560.
240 D.L. Kepert and J.H. Kyle, J.Chem.Soc.Dalton Trans. (1978)137.
241 S.S. Cady and T.J. Pinnavaia, Inorg.Chem., 17(1978)1501.
242 C. Cauletti, C. Furlani and M.N. Pianeastelli, J.Organomet.Chem., 149(1978)289.
243 L. Parkanyi and G. Bocelli, Cryst. Struct. Commun., 7(1978)335.
244 G. Sawitzki, H.G. von Schnering, D.Kummer and T. Seshadri, Chem.Ber., 111(1978)3705.
245 C. Glidewell and D.C. Liles, Acta Crystallogr., 834(1978)129.
246 C. Glidewell and D.C. Liles, Acta Crystallogr., B34(1978)125.
247 C. Glidewell and D.C. Liles, Acta Crystallogr., B34(1978)1693.
248 J.D. Odom, E.J. Stampf, Y.S. Li and J.R. Durig, J.Mol.Struct., 49(1978)1.
249 J.R. Durig, E.L. Varetti, W.J. Natter and A. Müller, J.Mol. Struct., 49(1978)43.
250 H.P.Schuchmann,A. Ritter and C. Von Sonntag, J.Organomet.Chem., 148(1978)213.
251 V.E. Shklover, Yu.T.Struchkov, A.B. Zachetnyuk and K.A. Andrianov, J.Struct.Chem., 19(1978)98.
252 T. Greiser, O.Jarchow, K.H. Klaska and E. Weiss, Chem.Ber., 111(1978)3360.
253 R.C. Mehrotra, A.K. Rai and N.C. Jain, J.Inorg.Nucl.Chem., 40 (1978)349.
254 S.C. Goel, V.K. Singh and R.C. Mehrotra, Z.Anorg.Allg.Chem., 447(1978)253.
255 A.B. Goel and V.D. Gupta, J.Organomet.Chem., 144(1978)49.
256 G. Tagliavini, V. Peruzzo and D. Marton, Inorg.Chim.Acta, 26 (1978)L41.
257 V. Peruzzo and G. Tagliavini, J.Organomet.Chem., 162(1978)37.
258 N.G. Bokii, A.I. Udel'nov, Yu.T.Struchkov, D.N. Kravtsov and V.M. Pachevskaya, J.Struct.Chem., 18(1977)814.
259 K.D. Onan, A.T. McPhail, C.H. Yoder and R.W. Hillyard, J.Chem. Soc.Chem.Commun., (1978)209.
260 Yu.A. Alexandrov, V.V. Gorbatov, N.V. Yablokova and V.G. Tsvetkov, J.Organomet.Chem., 157(1978)267.
261 V.A. Yablokov, G.S. Kalinina, N.V. Yablokova, T.A. Basalgina, N.S. Vyazankin and G.A. Razuvaev, J.Organomet.Chem., 153(1978) 25.
262 A. Nagasawa and K. Saito, Bull.Chem.Soc.Jpn., 51(1978)2015.
263 P. Finocchiaro, J.Organomet.Chem., 146(1978)229.
264 S.K. Saini, V.D. Gupta and R.C. Mehrotra, Inorg.Nucl.Chem. Letters, 14(1978)109.
265 D.F. Martin and B.S. Jurmack, J.Inorg.Nucl.Chem., 40(1978)1493.
266 S.N. Bhide, P. Umapathy, M.P. Gupta and D.N. Sen, J.Inorg.Nucl. Chem., 40(1978)1003.
267 T. Majima and Y. Kawasaki, Bull.Chem.Soc.Jpn. 51(1978)1893.
268 E.N. Vasanta, G. Srivastava and R.C. Mehrotra, Inorg.Chim.Acta, 26(1978)47.
269 E.N. Vasanta, G. Srivastava and R.C. Mehrotra, Inorg.Chim.Acta, 30(1978)23.
270 V. Peruzzo, G. Plazzogna and D. Marton, Inorg.Chim.Acta, 30(1978) 145.
271 R. Faggiani, J.P. Johnson, I.D. Brown and T. Birchall, Acta Crystallogr., B34(1978)3743.
272 V. Schubert, J.Organomet.Chem., 155(1978)285.

273 R. Faggiani, J.P. Johnson, I.D. Brown and T. Birchall, Acta Crystallogr., B34(1978)3742.
274 D.W. Allen, J.S. Brookes, R. Formstone, A.J. Crowe and P.J. Smith, J.Organomet.Chem., 156(1978)359.
275 B.F.E. Ford and J.R. Sams, Inorg.Chim.Acta, 28(1978)L173.
276 R. Barbieri, L. Pellerito and F. Huber, Inorg.Chim.Acta, 30 (1978)L321.
277 D. Petriodis, Inorg.Chem., 17(1978)3719.
278 G. Domazetis, R.J. Magee and B.D. James, J.Organomet.Chem., 162 (1978)239.
279 A. Roy and A.K. Ghosh, Inorg.Chim.Acta, 29(1978)L275.
280 P.G. Harrison, M.I.Khalil and N. Logan, Inorg.Chim.Acta, 30 (1978)165.
281 M. Nardelli, C. Pelizzi and G. Pelizzi, J.Chem.Soc.Dalton Trans. (1978)131.
282 M. Nardelli, C. Pelizzi, G. Pelizzi and P. Tarasconi, Inorg. Chim.Acta, 30(1978)179.
283 E. Lindner and U. Ansorge, J.Organomet.Chem., 153(1978)209.
284 U. Kunze and L. Steinmann, J.Organomet.Chem., 150(1978)39.
285 W.D. Harrison, J.B. Gill and D.C. Goodall, J.Chem.Soc.Dalton Trans., (1978)1431.
286 U. Ansorge, E. Lindner and J. Strähle, Chem.Ber., 111(1978) 3048.
287 E. Lindner and U. Ansorge, Z.Anorg.Allg.Chem., 442(1978)189.
288 E. Lindner and U. Ansorge, Chem.Ber., 111(1978)2455.
289 R.K. Millar, C.A. Evans and D.L. Rubenstein, Can.J.Chem., 56 (1978)3104.
290 M. Volkholz, O. Stelzer and R. Schmutzler, Chem.Ber., 111(1978) 890.
291 N. Krüger, K. Dehnicke and A.F. Shihada, Z.Anorg.Allg.Chem., 438(1978)169.
292 U. Wannagat and G. Eisele, Z.Naturforsch., 33b(1978)471.
293 U. Wannagat and R. Seifert, Monatsh.Chem., 109(1978)209.
294 U. Wannagat, R. Seifert and M. Schlingmann, Z.Anorg.Allg.Chem., 439(1978)83.
295 R. Seifert and U. Wannagat, Z.Anorg.Allg.Chem., 439(1978)90.
296 U. Wannagat, M.Schlingmann and R. Seifert, Z.Anorg.Allg.Chem., 440(1978)105.
297 G.M. Gray and C.S. Kraihanzel, J.Organomet.Chem., 146(1978)23.
298 D.J. Brauer, H. Bürger and K. Wiegel, J.Organomet.Chem., 150 (1978)215.
299 U. Klingebiel, J.Organomet.Chem., 152(1978)33.
300 M. Veith, Z.Anorg.Allg.Chem., 46(1978)227.
301 R. Allmann, W. Henke, P. Krommes and J. Lorberth, J.Organomet. Chem., 162(1978)283.
302 R.A. Anderson, D.H. Templeton and A. Zalkin, Inorg.Chem., 17 (1978)2317.
303 R.D. Rogers, J.L. Atwood and R. Grüning, J.Organomet.Chem., 157(1978)229.
304 M. Veith, Z.Anorg.Allg.Chem., 446(1978)237.
305 A. Marchand, M.T. Forel, M. Riviere-Baudet and M.H. Soulard, J.Organomet.Chem., 156(1978)341.
306 H.J. Götze and W. Garbe, Chem.Ber., 111(1978)2051.
307 H.W. Roesky, M. Diehl, H. Fuess and J.W. Bats, Angew.Chem., Int.Ed.Engl., 17 (1978)58.
308 H.W. Roesky, M. Diehl and M. Banek, Chem.Ber., 111(1978)1503.
309 N. Wiberg, H.W. Häring, G. Huttner and P. Friedrich, Chem.Ber., 111(1978)2708.

310 R.H. Neilson, R.D. Jacobs, R.W. Scheirman and J.C. Wilburn, Inorg.Chem., 17(1978)1880.

311 W. Wolfsberger and H.H. Pickel, J.Organomet.Chem., 145(1978)29.

312 W.S. Sheldrick, D. Schomburg and W. Wolfsberger, Z.Naturforsch. 33b(1978)493.

313 C. Cloutour, D. Lafargue and J.C. Pommier, J.Organomet.Chem., 161(1978)327.

314 R.T. Oakley, D.A. Stanislawski and R. West, J.Organomet.Chem., 157(1978)389.

315 J.J. de Boer, J.A. van Doorn and C. Masters, J.Chem.Soc.Chem. Commun., (1978)1005.

316 G. Fritz and R. Uhlmann, Z.Anorg.Allg.Chem., 442(1978)95.

317 G. Fritz, R. Uhlmann and W. Hölderich, Z.Anorg.Allg.Chem., 442 (1978)86.

318 G. Fritz and R. Uhlmann, Z.Anorg.Allg.Chem., 440(1978)168.

319 W. Hönle and H.G. von Schnering, Z.Anorg.Allg.Chem., 442(1978) 107.

320 W. Hönle and H.G. von Schnering, Z.Anorg.Allg.Chem., 442(1978) 91.

321 W. Hönle and H.G. von Schnering, Z.Anorg.Allg.Chem., 440(1978) 171.

322 B. Mathiasch and M. Dräger, Angew.Chem.Int.Ed.Engl., 17(1978) 767.

323 H. Schumann, L. Rösche and W. Schmidt-Fritsche, Z.Naturforsch., 33b(1978)1186.

324 W.W. du Mont, Inorg.Chim.Acta, 26(1978)L25.

325 J. Escudie, C. Couret and J. Satge, Bull.Soc.Chim.Fr.II, (1978) 361.

326 H.J. Breunig, Z.Naturforsch., 33b(1978)990.

327 B. Voigt, Z.Anorg.Allg.Chem., 447(1978)153.

328 A. Feltz and G. Pfaff, Z.Anorg.Allg.Chem., 442(1978)41.

329 A. Nagel and K.J. Range, Z.Naturforsch., 33b(1978)1461.

330 G. Bugli, D. Carre and S. Barnier, Acta Crystallogr., B34(1978) 3186.

331 C.L. Teske, Z.Anorg.Allg.Chem., 445(1978)193.

332 D. Ginderow, Acta Crystallogr., B34(1978)1804.

333 G. Dittmar, Acta Crystallogr., B34(1978)2390.

334 J. Unterrichter and K.J. Range, Z. Naturforsch., 33b(1978)866.

335 T.V. Timofeeva, D.N. Krautsov, N.G. Bokii and Yu.T. Struchkov, J.Struct.Chem., 18(1977)701.

336 A. Blecher and B. Mathiasch, Z.Naturforsch., 33b(1978)246.

337 M. Dräger, A. Blecher, H.J. Jacobson and B. Krebs, J.Organomet. Chem., 161(1978)319.

338 H. Puff, A. Bongartz, R. Sievers and R. Zimmer, Angew.Chem. Int.Ed.Engl., 17(1978)939.

339 M. Masaki, S. Matsunami and H. Ueda, Bull.Chem.Soc.Jpn., 51 (1978)3298.

340 M.A. Delmas and J.C. Maire, J.Organomet.Chem., 161(1978)13.

341 J.E. Drake, B.M. Glavincevski, H.E. Henderson and R.T. Hemmings Can.J.Chem., 56(1978)465.

342 S. Kozuka and S. Ohya, Bull.Chem.Soc.Jpn., 51(1978)2651.

343 S. Kozuka and S. Ohya, J.Organomet.Chem., 149(1978)161.

344 O.A. Reutov, V.I. Rozenberg, G.V. Gavrilova and V.A. Nikanorov, Dokl.Chem., 237(1977)665.

345 T.N. Srivastava, V. Kumar and R.B. Rastogi, J.Inorg.Nucl.Chem. 40(1978)399.

346 E. Hengge and G. Litscher, Monatsh.Chem., 109(1978)1217.

347 M. Laguerre, J. Dunogues and M. Calas,J.Chem.Soc.Chem.Commun., (1978)272.

348 L. Parkanyi, K. Sasvari and I. Barta, Acta Crystallogr., B34 (1978)883.
349 L. Parkanyi, K. Sasvari, J.P. Declercq and G. Germain, Acta Crystallogr., B34(1978)3678.
350 C.S. Cundy, M.F. Lappert and C.K. Yuen, Inorg.Chem., 17(1978) 1092.
351 R. Calas, G. Deleris, J. Dunogues, M. Lefort and C. Simmonet, J.Organomet.Chem., 148(1978)119.
352 H. Matsumoto, T. Motegi, M. Hasegawa and Y. Nagai, Bull.Chem. Soc.Jpn., 51(1978)1913.
353 K. Tamao, S. Okazaki and M. Kumada, J.Organomet.Chem., 146 (1978)87.
354 H. Watanabe, K. Higuchi, M. Kobayashi and Y. Nagai, J.Chem.Soc. Chem.Commun., (1978)1029.
355 M. Gielen and Y. Tondeur, J.Chem.Soc.Chem.Commun., (1978)81.
356 H.U. Buschhaus and W.P. Neumann, Angew.Chem., Int.Ed.Engl., 17(1978)59.
357 P. Fostein and J.C. Pommier, J.Organomet.Chem., 150(1978)187.
358 W.P. Neumann and F. Werner, Chem.Ber., 111(1978)3904.
359 O.A. Reutov, V.I. Rozenberg, V.A. Nikanorov and G.V. Gavrilova, Dokl.Chem., 237(1977)690.
360 V.G. KumarDas, N.S. Weng and L.H. Gan, J.Organomet.Chem., 157 (1978)219.
361 R.W. Rudolph, W.L. Wilson, F. Parker, R.C. Taylor and D.C.Young, J.An.Chem.Soc., 100(1978)4629.
362 N. Duffaut, J. Dunogues, R. Calas, J.Gerval, P. Riviere, J. Satge and A. Cazes, J.Organomet.Chem., 149(1978)57.
363 L. Rösch and W. Erb, Angew.Chem.Int.Ed.Engl., 17(1978)604.
364 M.N. Bochkarev, N.I. Gur'ev and G.A. Razuvaev, J.Organomet. Chem., 162(1978)289.
365 V.I. Bregadze, V.T. Kampel and N.N. Godovikov, J.Organomet. Chem., 157(1978)C1.
366 T.J. Dupont, R.E. Loffredo, R.C. Haltiwanger, C.A. Turner and A.D. Norman, Inorg.Chem., 17(1978)2062.
367 E. Piers and H.E. Morton, J.Chem.Soc.Chem.Commun., (1978)1033.
368 H. Sakurai, Y.Kamiyama and Y. Nakadaira, Angew.Chem.Int.Ed. Engl., 17(1978) 674.
369 T.M. Chan, J.W. Connolly, C.D. Hoff and F. Millich, J.Organomet. Chem., 152(1978)287.
370 J.W. Connolly and C.D. Hoff, J.Organomet.Chem., 160(1978)467.
371 P.A. Wegner and G.P. Sterling, J.Organomet.Chem., 162(1978)C31.
372 C.S. Cundy, M.F. Lappert and C.K. Yuen, J.Chem.Soc.Dalton Trans., (1978) 427.
373 C.S. Cundy and M.F. Lappert, J.Chem.Soc.Dalton Trans., (1978) 665.
374 C.S. Cundy and M.F. Lappert, J.Organomet.Chem., 144(1978)317.
375 A. Bonny and K.M. Mackay, J.Organomet.Chem., 144(1978)389.
376 A. Bonny and K.M. Mackay, J.Chem.Soc.Dalton Trans., (1978)506.
377 A. Bonny and K.M. Mackay, J.Chem.Soc.Dalton Trans., (1978)722.
378 A. Bonny and K.M. Mackay, J.Chem.Soc.Dalton Trans., (1978)1569.
379 F.S. Wong and K.M. Mackay, J.Chem.Soc.Dalton Trans., (1978)1752.
380 B.K. Nicholson and J. Simpson, J.Organomet.Chem., 155(1978)237.
381 K. Inkrott, R. Goetze and S.G. Shore, J.Organomet.Chem.,154 (1978)337.
382 M.H. Quick and R.J. Angelici, J.Organomet.Chem., 160(1978)231.
383 T.R. Spalding, J.Organomet.Chem., 149(1978)371.
384 S.L. Barker, L. Harland, S.F.A. Kettle and F.F. Stephens, Inorg.Chim.Acta, 31(1978)223.

385 S.L. Barker, L. Harland and S.F.A. Kettle, Inorg.Chim.Acta, 31 (1978)217.
386 R. Colomer and R.J.P. Corriu, J.Chem.Soc.Chem.Commun., (1978) 435.
387 S. Onaka, Y.Yoshikawa and H. Yamateva, J.Organomet.Chem., 157 (1978)187.
388 U.Kunze and S.B. Sastrawan, J.Organomet.Chem., 154(1978)223.
389 E. Uhlig, B. Hipler and P. Müller, Z.Anorg.Allg.Chem., 447 (1978)18.
390 S. Midollini, A. Orlandini and L.Sacconi, J.Organomet.Chem., 162(1978)109.
391 S. Midollini, A. Orlandini and L. Sacconi, Cryst.Struct. Commun., 6(1977)733.
392 P.J. Harris, J.A.K. Howard, S.A.R. Knox, R.J. McKinney, R.P. Phillips, F.G.A. Stone and P. Woodward, J.Chem.Soc. Dalton Trans., (1978)403.
393 J.A.K. Howard and P. Woodward, J.Chem.Soc.Dalton Trans., (1978)410.
394 H. Matsumoto, T. Nakano, Y. Nagai and H. Kono, Bull.Chem.Soc. Jpn., 51(1978)2445.
395 R.O. Gould, W.J. Sime and T.A. Stephenson, J.Chem.Soc.Dalton Trans., (1978)76.
396 W. Clegg, Acta Crystallogr., B34(1978)278.
397 H. Schumann and M. Cygon, J.Organomet.Chem., 144(1978)C43.
398 J. Greene and M.D. Curtis, Inorg.Chem., 17(1978)2324.
399 M.D. Curtis and J. Greene, J.Am.Chem.Soc., 100(1978)6363.
400 C. Eaborn, K.J. Odell and A. Pidcock, J.Chem.Soc.Dalton Trans., (1978)357.
401 C. Eaborn, K.J. Odell and A. Pidcock, J.Organomet.Chem., 146 (1978)17.
402 C. Eaborn, K.J. Odell and A. Pidcock, J.Chem.Soc.Dalton Trans., (1978)1288.
403 G. Butler, C. Eaborn and A. Pidcock, J.Organomet.Chem., 144 (1978)C23.
404 E.A.V. Ebsworth, V.M. Marganian, F.J.S. Reed and R.O. Gould, J.Chem.Soc.Dalton Trans., (1978)1167.
405 J.Kuyper, Inorg.Chem., 17(1978)77.
406 E.F. Strizhev, D.S. Masloboev and Yu.N. Kukushkin, Russ.J.Inorg. Chem., 23(1978)1178.
407 C.H. Cheng and R. Eisenberg, J.Am.Chem.Soc., 100(1978)5968.
408 S. Shinoda, H. Moriyama, Y. Kise and Y. Saito, J.Chem.Soc. Chem.Commun., (1978)348.
409 Yu.N.Kukushkin, P.G. Antonov, L.N. Mitronina, G.N. Sedova and B.I. Ionin, Russ.J.Inorg.Chem., 23(1978)568.
410 Yu.N. Kukushkin, G.N. Sedov, P.G. Antonov and L.N. Mitronina, Russ.J.Inorg.Chem., 22(1977)1512.
411 F. Glockling and P.J.M.L. Ssebuwufu, Inorg.Chim.Acta, 31(1978) 105.