Previous Page

in the coordination sphere, possibly indicating a stereochemically active lone pair.(50) Again, $[Pb(phen)_4(OClO_3)]ClO_4$ features 9-fold, capped square antiprismatic coordination about Pb,(51) whereas in $[Pb[tpy)_3][ClO_4]_2$ (tpy = 2, 2′:6′,2″-terpyridine) there is an unusual D_3 9-coordinate environment around the Pb^{II} centre.(52)

10.3.5 Other inorganic compounds

Few of the many other inorganic compounds of Ge, Sn and Pb call for special comment. Many pseudo-halogen derivatives of Sn^{IV}, Pb^{IV} and Pb^{II} have been reported, e.g. cyanides, azides, isocyanates, isothiocyanates, isoselenocyanates and alkoxides.(39,53)

All 9 chalcogenides MX are known (X = S, Se, Te). GeS and SnS are interesting in having layer structures similar to that of the isoelectronic black-P (p. 482). The former is prepared by reducing a fresh precipitate of GeS_2 with excess H_3PO_2 and purifying the resulting amorphous red-brown powder by vacuum sublimation. SnS is usually made by sulfide precipitation from Sn^{II} salts. PbS occurs widely as the black opaque mineral galena, which is the principal ore of Pb (p. 368). In common with PbSe, PbTe and SnTe, it has the cubic NaCl-type structure. Pure PbS can be made by direct reaction of the elements or by reaction of $Pb(OAc)_2$ with thiourea; the pure compound is an intrinsic semiconductor which, in the presence of impurities or stoichiometric imbalance, can develop either n-type or p-type semiconducting properties (p. 332). It is also a photoconductor (like PbSe and PbTe) and is one of the most sensitive detectors of infrared radiation; the photovoltaic effect in these compounds is also widely used in photoelectric cells, e.g. PbS in photographic exposure meters. The three compounds are also unusual in that their colour diminishes with increasing molecular weight: PbS is black, PbSe grey, and PbTe white.

Of the selenides, GeSe (mp 667°) forms as a dark-brown precipitate when H_2Se is passed into an aqueous solution of $GeCl_2$. SnSe (mp 861°) is a grey-blue solid made by direct reaction of the elements above 350°. PbSe (mp 1075°) can be obtained by volatilizing $PbCl_2$ with H_2Se, by reacting $PbEt_4$ with H_2Se in organic solvents, or by reducing $PbSeO_4$ with H_2 or C in an electric furnace; thin films for semiconductor devices are generally made by the reaction of $Pb(OAc)_2$ with selenourea, $(NH_2)_2CSe$. The tellurides are best made by heating Ge, Sn or Pb with the stoichiometric amount of Te.

Other chalcogenides that have been described include GeS_2, $GeSe_2$, Sn_2S_3 and $SnSe_2$, but these introduce no novel chemistry or structural principles. Of more interest, perhaps, is the polymeric anion $[Sn_5S_{12}{}^{4-}]_\infty$ (1) which occurs in $Cs_4Sn_5S_{12}.2H_2O$ and which contains both trigonal bipyramidal and octahedral Sn^{IV}.(54) The compound was prepared by hydrothermal reaction of Cs_2CO_3 with SnS_2 at 150°C. A similar reaction between Rb_2CO_3 and SnS_2 in saturated aqueous H_2S solution at 190°C afforded $Rb_2Sn_3S_7.2H_2O$ in which the polymeric $[Sn_3S_7{}^{2-}]_\infty$ anion (2) features both SnS_4 tetrahedra and SnS_6 octahedra.(55) Another new structural form, in which a *commo*-Sn atom joins a double cube, is found in the discrete $\{Sn_7S_6O_2\}$ cluster core (3) of $[\{Bu^tSn(S)L\}_3]_2Sn$; the diphosphinate ligand L = μ-η^2-O_2PPh_2 bridges the three non-*commo* Sn atoms in each of the cubes.(56) Examples of

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(50) L. M. Engelhardt, J. M. Patrick and A. H. White, *Aust. J. Chem.* **42**, 335–8 (1989). See also L. M. Engelhardt, B. M. Furphy, J. McB. Harrowfield, J. M. Patrick, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 595–9 (1989).

(51) L. M. Engelhardt, D. L. Kepert, J. M. Patrick and A. H. White, *Aust. J. Chem.* **42**, 329–34 (1989).

(52) D. L. Kepert, J. M. Patrick, B. W. Skelton and A. H. White, *Aust. J. Chem.* **41**, 157–8 (1988).

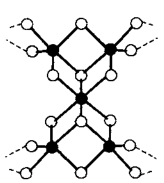
(53) E. W. Abel, Tin, Chap. 17 in *Comprehensive Inorganic Chemistry*, Vol. 2, pp. 43–104, Pergamon Press, Oxford, 1973.

(54) W. S. Sheldrick *Z. anorg. allg. Chem.* **562**, 23–30 (1988).

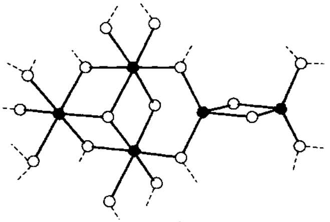
(55) W. S. Sheldrick and B. Schaaf, *Z. anorg. allg. Chem.* **620**, 1041–5 (1994).

(56) K. C. K. Swamy, R. O. Day and R. R. Holmes, *J. Am. Chem. Soc.* **110**, 7543–4 (1988).

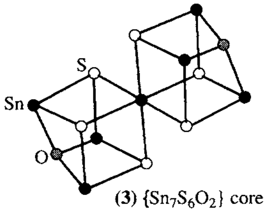
square-pyramidal 5-coordinate Sn$^{\text{IV}}$ (57,58) and pentagonal bipyramidal 7-coordinate Sn$^{\text{IV}}$ (59) have also been recently established in various thio-organotin complexes.



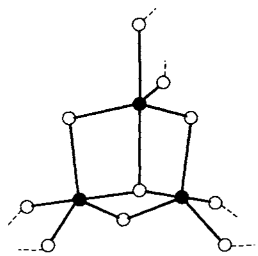
(1) $[Sn_5S_{12}{}^{4-}]_\infty$



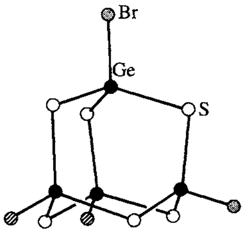
(2) $[Sn_3S_7{}^{2-}]_\infty$



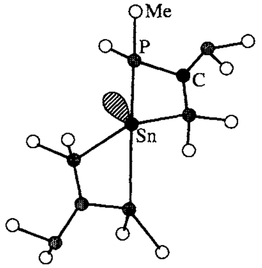
(3) $\{Sn_7S_6O_2\}$ core



(4) $[Sn_3Se_7{}^{2-}]_\infty$



(5) $Ge_4S_6Br_4$



(6) $[Sn\{C(PMe_2)_3\}_2]$

The discrete anions $[Sn_2Se_6]^{4-}$ and $[Sn_2Te_6]^{4-}$ have the B_2H_6-type structure (p. 154) and are known in $Rb_4(Sn_2Se_6]$,(55) $[enH_2]_2[Sn_2Se_6]$(60) and $[NMe_4]_4[Sn_2Te_6]$.(61) By contrast, $[enH_2]$-$[Sn_3Se_7].\frac{1}{2}$en features a sheet polymeric anion $[Sn_3Se_7{}^{2-}]_\infty$ (4) in which the basic elements are $SnSe_5$ trigonal bipyramids.(60) The adamantane-like anion $[Ge_4Te_{10}]^{4-}$ was identified by X-ray diffraction analysis of the black crystalline salt $[NEt_4]_4[Ge_4Te_{10}]$, prepared in 72% yield by extraction of the alloy of composition $K_4Ge_4Te_{10}$ with ethylene diamine in the presence of Et_4NBr(61a)

The first sulfide halide of Ge was made by the apparently straightforward reaction:

$$4GeBr_4 + 6H_2S \xrightarrow{CS_2/Al_2Br_6} Ge_4S_6Br_4 + 12HBr$$

The unexpectedly complex product was isolated as an almost colourless air-stable powder, and a single-crystal X-ray analysis showed that it had the molecular adamantane-like structure (5).(62) This is very similar to the structure of the "isoelectronic" compound P_4O_{10} (p. 504).

There has been growing interest in the detailed structure and reaction chemistry of monomeric forms of two-coordinate derivatives of Ge$^{\text{II}}$, Sn$^{\text{II}}$ and Pb$^{\text{II}}$ since the first examples were unequivocally established in 1980.(63,64) Thus, treatment of the corresponding chlorides MCl_2 with lithium di-*tert*-butyl phenoxide derivatives in thf affords a series of yellow (Ge$^{\text{II}}$, Sn$^{\text{II}}$) and red (Pb$^{\text{II}}$) compounds $M(OAr)_2$ in high yield.(63) The O–M–O bond angle in $M(OC_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6)_2$ was 92° for Ge and 89° for Sn. Similar reactions

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[57] A. C. SAU, R. O. DAY and R. R. HOLMES, *J. Am. Chem. Soc.* **103**, 1264–5 (1981) and *Inorg. Chem.* **20**, 3076–81 (1981).

[58] S. W. NG, C. WEI, V. G. K. DAS and T. C. W. MAK, *J. Organometallic Chem.* **334**, 283–93 (1987).

[59] S. W. NG, C. WEI, V. G. K. DAS, G. B. JAMESON and R. J. BUTCHER, *J. Organometallic Chem.* **365**, 75–82 (1989).

[60] W. S. SHELDRICK and H. G. BRAUNBECK, *Z. anorg. allg. Chem.* **619**, 1300–6 (1993).

[61] J. C. HUFFMAN, J. P. HAUSHALTER, A. M. UMARJI, G. K. SHENOY and R. C. HAUSHALTER, *Inorg. Chem.* **23**, 2312–15 (1984).

[61a] S. S. DHINGRA and R. C. HAUSHALTER, *Polyhedron* **13**, 2775–9 (1994).

[62] S. POHL, *Angew. Chem. Int. Edn. Engl.* **15**, 162 (1976).

[63] B. CETINKAYA, I. GÜMRÜKÇÜ, M. F. LAPPERT, J. L. ATWOOD, R. D. ROGERS and M. J. ZAWOROTKO, *J. Am. Chem. Soc.* **102**, 2088–9 (1980). See also T. FJELDBERG, P. B. HITCHCOCK, M. F. LAPPERT, S. J. SMITH and A. J. THORNE, *J. Chem. Soc., Chem. Commun.*, 939–41 (1985).

[64] M. F. LAPPERT, M. J. SLADE, J. L. ATWOOD and M. J. ZAWOROTKO, *J. Chem. Soc., Chem. Commun.*, 621–2 (1980).

of $\mathrm{MCl_2}$ with $\mathrm{LiNBu^t_2}$ yielded the (less stable) monomeric di-*tert*-butylamide, $\mathrm{Ge(NBu^t_2)_2}$ (orange), and $\mathrm{Sn(NBu^t_2)_2}$ (maroon);$^{(64)}$ the more stable related bis(tetramethylpiperidino) compound $\mathrm{[Ge\{NCMe_2(CH_2)_3CMe_2\}_2]}$ was found to have a somewhat larger bond angle at Ge (N–Ge–N = 111°) and a rather long Ge–N bond (189 pm). More recent examples are $\mathrm{[Ge\{N(SiMe_3)_2\}_2]}^{(65)}$ and $\mathrm{[GeN(Bu^t)CH{=}CHN(Bu^t)]}$.$^{(66)}$ The first monomeric prochiral $\mathrm{Sn^{II}}$ complexes, $\mathrm{[Sn\{N(SiMe_3)_2\}X]}$, have also been reported, where X is a bulky substituted phenoxy group or a tetramethylpiperidino moiety.$^{(67)}$ These are but illustrative examples of a large and burgeoning field.$^{(68)}$

Turning finally to compounds with bonds from the heavier Group 14 elements to heavier Group 15 elements we may note compounds such as $\mathrm{[Sn\{C(PMe_2)_3\}_2]}$ which has the pseudo trigonal bipyramidal structure (6). This complex, which has Sn bonded exclusively to four P atoms, is formed as yellow crystals by the reaction of $\mathrm{SnCl_2}$ with $\mathrm{2Li\{C(PMe_2)_3\}}$ in $\mathrm{Et_2O}$ at −78°C.$^{(69)}$ A notable feature of the structure is the substantial difference between the equatorial and axial Sn–P distances (260 pm *vs* 279 and 284 pm, respectively) and the small chelate bite angle of 62.9° at the Sn atom. The compound is fluxional in solution even at −90°C due to pseudorotation (p. 499) which equilibrates the axial and equatorial positions. Several similar compounds are known.$^{(69)}$ Germanium analogues of (6) such as the stable crystalline complexes $\mathrm{[Ge\{C(PMe_2)_3\}_2]}$ and $\mathrm{[Ge\{C(PMe_2)_2(SiMe_3)\}_2]}$ can be made by similar procedures, starting from $\mathrm{GeCl_2.dioxane}$:$^{(70)}$ see also next section.

A range of shiny metallic compounds featuring trigonal planar anions $\mathrm{SnX_3}^{5-}$ (X = As, Sb, Bi) have been characterized with composition $\mathrm{M_6(SnX_3)O_{0.5}}$ (M = Rb, Cs); the Sn and X atoms in $\mathrm{SnX_3}^{5-}$ (isostructural with $\mathrm{CO_3}^{2-}$) are coordinated by trigonal prisms of $\mathrm{6M^+}$, and the $\mathrm{O^{2-}}$ ions occupy octahedral sites in the $\mathrm{M^+}$ lattice.$^{(70a)}$

Rather different is the X-ray structural characterization of the 'bare' $\mathrm{Sn^{2+}}$ ion in $\mathrm{[Sn^{2+}][SbF_6{}^-]_2.2AsF_3}$ (prepared by treating the product of the direct reaction between $\mathrm{SnF_2}$ and $\mathrm{SbF_5}$ with $\mathrm{AsF_3}$).$^{(71)}$ The crystal packing is such that each $\mathrm{Sn^{2+}}$ is surrounded by nine F atoms (tricapped trigonal prism) and the average Sn–F distance is 257 pm (cf. the sum of the ionic radii, 251 pm). The Mössbauer spectrum (p. 371) shows zero quadrupole splitting and the highest known chemical shift for any tin(II) species, consistent with the 'bare ion' formulation.

10.3.6 Metal–metal bonds and clusters

The catenation of Group 14 elements has been discussed on pp. 337–42 and 374–5,

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[65] S. M. Hawkins, P. B. Hitchcock, M. F. Lappert and A. K. Rai, *J. Chem. Soc., Chem. Commun.*, 1689–90 (1986) and references cited therein; C. Glidewell, D. Lloyd, K. W. Lumbard and J. S. McKechnie, *J. Chem. Soc., Dalton Trans.*, 2981–7 (1987).

[66] W. A. Herrmann, M. Denk, J. Behm, W. Scherer, F. R. Klingan, H. Bock, B. Solouki and M. Wagner, *Angew. Chem. Int. Edn. Engl.* **31**, 1485–8 (1992).

[67] H. Braunschweig, R. W. Chorley, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1311–13 (1992).

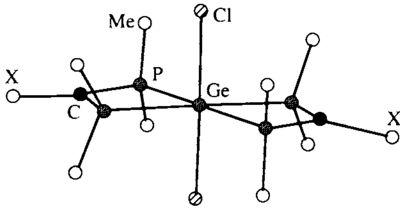
[68] M. Veith and W. Frank, *Angew. Chem. Int. Edn. Engl.* **24**, 223–4 (1985), C. Glidewell, D. Lloyd and K. W. Lumbard, *J. Chem. Soc., Dalton Trans.*, 501–8 (1987), J. Kocher, M. Lehnig and W. P. Neumann, *Organometallics* **7**, 1201–7 (1988), M. Veith, L. Stahl and V. Huch, *J. Chem. Soc., Chem. Commun.*, 359–61 (1990), P. B. Hitchcock, M. F. Lappert and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1587–9 (1990), A. Meller, G. Ossig, W. Maringgele, D. Stalke, R. Herbst-Irmer, S. Freitag and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 1123–4 (1991), R. W. Chorley, P. B. Hitchcock, B. S. Jolly, M. F. Lappert and G. A. Lawless, *J. Chem. Soc., Chem. Commun.*, 1302–3 (1991), R. W. Chorley, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 525–6 (1992), M. Veith, M. Notzel, L. Stahl and V. Huch, *Z. anorg. allg. Chem.* **620**, 1264–70 (1994). See also Polyhedra Symposia-in-Print No. 12, M. J. Hampden-Smith (ed.), *Polyhedron* **10**, 1147–309 (1991).

[69] H. H. Karsch, A. Appelt and G. Müller, *Organometallics* **5**, 1664–70 (1986) and references cited therein.

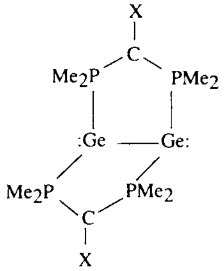
[70] H. H. Karsch, B. Deubelly, J. Reide and G. Müller, *Angew. Chem. Int. Edn. Engl.* **26**, 673–4 (1987).

[70a] M. Asbrand and B. Eisenmann, *Z. anorg. allg. Chem.* **620**, 1837–43 (1994).

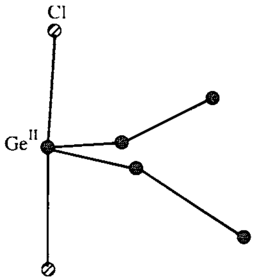
[71] A. J. Edwards and K. L. Khallow, *J. Chem. Soc., Chem. Commun.*, 50–1 (1984).



(7) [Ge^{IV}$\{$C(PMe$_2$)$_2$X$\}_2$Cl$_2$]



(8) [Ge$^I_2$$\{$C(PMe$_2$)$_2X\}_2$]



(9) [Ge$^I_2$$\{\mu$-(PMe$_2$)$_2CX\}_2$]$_2$Ge^{II}Cl$_2$(core)

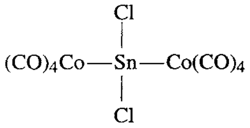
and further examples are in Section 10.3.7. In addition, when the reaction of GeCl$_2$.dioxane with 2Li[C$\{$(PMe$_2$)$_2$X$\}_2$] (mentioned above$^{(70)}$) is varied by using a higher proportion of GeCl$_2$, concurrent redox disproportionation occurs to yield a mixture of [Ge^{IV}$\{$C(PMe$_2$)$_2$X$\}_2$Cl$_2$] (7) and [Ge$^I_2$$\{$C(PMe$_2$)$_2X\}_2$] (8) according to the optimized stoichiometry:$^{(72)}$

$$3\mathrm{GeCl_2.diox} + 4\mathrm{Li[\{C(PMe_2)_2X\}_2]} = (7) + (8) + 4\mathrm{LiCl} + 3\mathrm{C_4H_8O_2}$$

where X + SiMe$_3$ (or PMe$_2$). The Ge–Ge distance in (8) is 254 pm, i.e. about 10 pm longer than in polygermanes. The stereochemically active lone pairs of electrons on Ge^I in (8) can be used as electron-pair donors to a further GeCl$_2$ moiety to form the homonuclear (germanediyl donor)–(germanediyl acceptor) complex [Ge$_2$$\{\mu$-(PMe$_2$)$_2CX\}_2$]$_2$GeCl$_2$ which features a mixed-valent Ge$_5$ chain as shown schematically in (9). The Ge–Ge distances along the Ge^I–Ge^I–Ge^{II}–Ge^I–Ge^I chain are 249.2, 255.4, 256.2 and 248.5 pm, respectively.

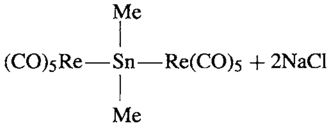
Heteroatomic metal-metal bonds can be formed by a variety of synthetic routes as illustrated below for tin:

Insertion: $\mathrm{SnCl_2 + Co_2(CO)_8 \longrightarrow}$



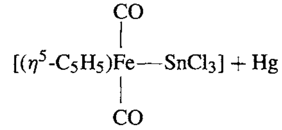
$$\mathrm{(CO)_4Co{-}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{Sn}}{-}Co(CO)_4}$$

Metathesis: $\mathrm{Me_2SnCl_2 + 2NaRe(CO)_5 \longrightarrow}$



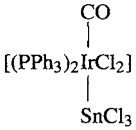
$$\mathrm{(CO)_5Re{-}\overset{\displaystyle Me}{\underset{\displaystyle Me}{Sn}}{-}Re(CO)_5 + 2NaCl}$$

Elimination: $\mathrm{SnCl_2 + [Fe(\eta^5\text{-}C_5H_5)(CO)_2HgCl] \longrightarrow}$



$$\mathrm{[(\eta^5\text{-}C_5H_5)\overset{\displaystyle CO}{\underset{\displaystyle CO}{Fe}}{-}SnCl_3] + Hg}$$

Oxidative addition: $\mathrm{SnCl_4 + [Ir(CO)Cl(PPh_3)_2] \longrightarrow}$



$$\mathrm{\overset{\displaystyle CO}{\underset{\displaystyle SnCl_3}{[(PPh_3)_2IrCl_2]}}}$$

Some representative examples, all featuring tetrahedral Sn, are in Fig. 10.9.$^{(53)}$ Several reactions are known in which the Sn–M bond remains intact, e.g.:

$$\mathrm{Ph_3SnMn(CO)_5 + 3Cl_2 \longrightarrow Cl_3SnMn(CO)_5 + 3PhCl}$$

$$\mathrm{Cl_2Sn\{Co(CO)_4\}_2 + 2RMgX \longrightarrow R_2Sn\{Co(CO)_4\}_2 + 2MgClX}$$

Others result in cleavage, e.g.:

$$\mathrm{Me_3SnCo(CO)_4 + I_2 \longrightarrow Me_3SnI + Co(CO)_4I}$$

$$\mathrm{Me_3SnMn(CO)_5 + Ph_2PCl \longrightarrow Me_3SnCl + \tfrac{1}{2}[Ph_2PMn(CO)_4]_2 + CO}$$

$$\mathrm{Me_3SnMn(CO)_5 + C_2F_4 \longrightarrow Me_3SnCF_2CF_2Mn(CO)_4}$$

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[72] H. H. Karsch, B. Deubelly, J. Reide and G. Müller, *Angew. Chem. Int. Edn. Engl.* **26**, 674–6 (1987).

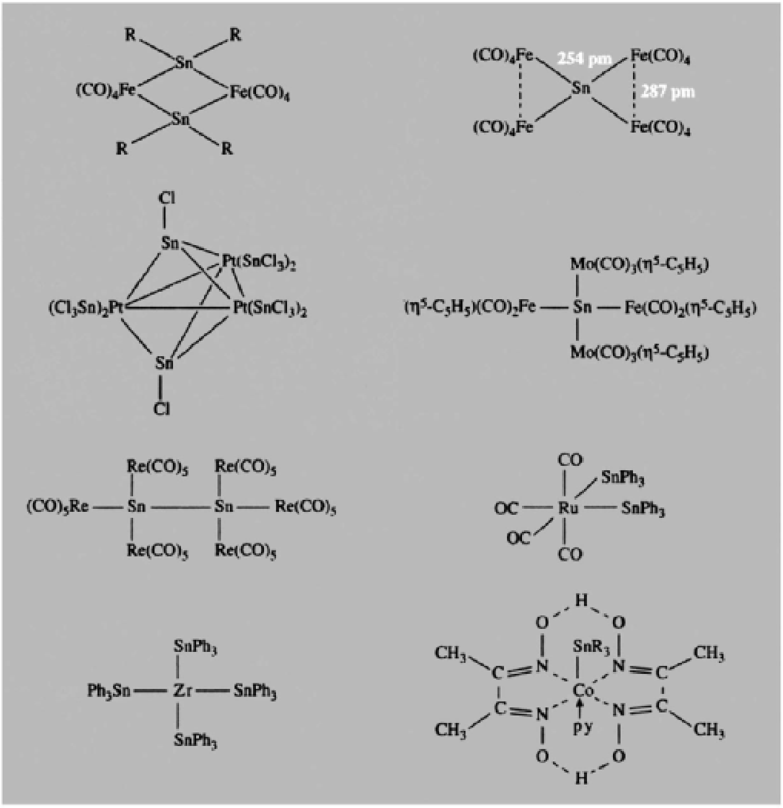

Figure 10.9 Some examples of metal sequences and metal clusters containing tin-transitional metal bonds.

A similar though less extensive range of Pb–M compounds has been established;(39) e.g. $[Ph_2Pb\{Mn(CO)_5\}_2]$, $[Ph_3PbRe(CO)_5]$, $[Ph_2Pb\{Co(CO)_4\}_2]$, $[(PPh_3)_2Pt(PbPh_3)_2]$, $[(CO)_3Fe(PbEt_3)_2]$, and the cyclic dimer $[(CO)_4Fe{-}PbEt_2]_2$. Reaction of these compounds with halogens results in fission of the Pb–M bonds. In the unique case of $[Pb\{Mn(\eta^5\text{-}C_5H_5)(CO)_2\}_2]$ the linear central MnPbMn core (177.2°) and short Mn–Pb distance (246.3 pm) suggest that this is the first example of multiple bonding between Pb and a transition metal, Mn=Pb=Mn.(73) The compound is obtained in 20% yield as air-stable reddish-brown crystals by the reaction of $PbCl_2$ with the substitutionally labile complex $[Mn(\eta^5\text{-}C_5H_5)(CO)_2(thf)]$.

It has been known since the early 1930s that reduction of Ge, Sn and Pb by Na in liquid ammonia gives polyatomic Group 14 metal anions, and crystalline compounds can be isolated using ethylenediamine, e.g. $[Na_4(en)_5Ge_9]$ and $[Na_4(en)_7Sn_9]$. A dramatic advance was achieved(74) in the 1970s by means of the polydentate cryptand ligand $[N\{(C_2H_4)O(C_2H_4)O(C_2H_4)\}_3N]$ (p. 98). Thus, reaction of cryptand in ethylenediamine with the alloys $NaSn_{1-1.7}$ and $NaPb_{1.7-2}$ gave red crystalline salts $[Na(crypt)]_2^+[Sn_5]^{2-}$ and $[Na(crypt)]_2^+[Pb_5]^{2-}$ containing the D_{3h} cluster anions illustrated in Fig. 10.10. If each Sn or Pb atom is thought to have 1 nonbonding pair of electrons then the

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(73) W. A. Herrmann, H.-J. Kneuper and E. Herdtweck, *Angew. Chem. Int. Edn. Engl.* **24**, 1062–3 (1985).

(74) P. A. Edwards and J. D. Corbett, *Inorg. Chem.* **16**, 903–7 (1977). J. D. Corbett and P. A. Edwards, *J. Am. Chem. Soc.* **99**, 3313–7 (1977).

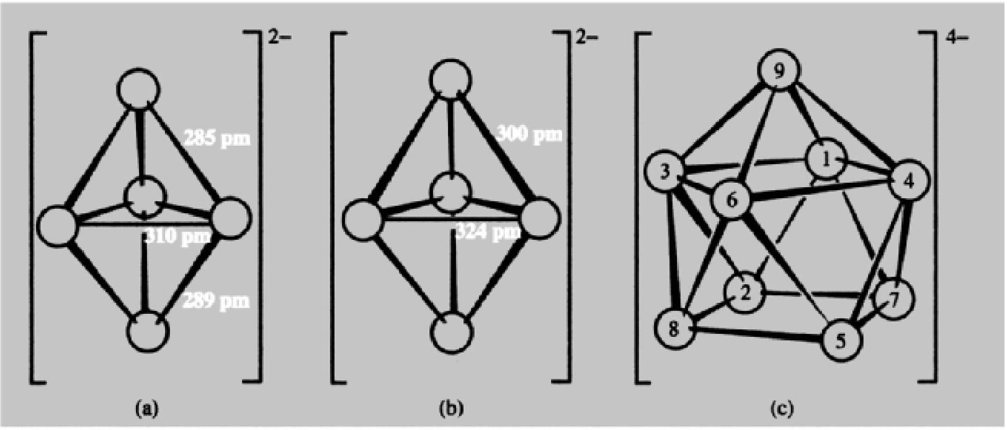

Figure 10.10 The structure of polystannide and polyplumbide anions: (a) the slightly distorted D_{3h} structure of $[Sn_5]^{2-}$, (b) the D_{3h} structure of $[Pb_5]^{2-}$, and (c) the unique C_{4v} structure of $[Sn_9]^{4-}$: all Sn–Sn distances are in the range 295–302 pm except those in the slightly longer upper square (1,3,6,4) which are in the range 319–331 pm; the angles within the two parallel squares are all 90° (±0.8°).

$M_5{}^{2-}$ clusters have 12 framework bonding electrons as has $[B_5H_5]^{2-}$ (p. 161); the anions are also isoelectronic with the well-known cation $[Bi_5]^{3+}$. Similarly, the alloy $NaSn_{\sim 2.25}$ reacts with cryptand in ethylenediamine to give dark-red crystals of $[Na(crypt)]_4^+[Sn_9]^{4-}$; the anion is the first example of a C_{4v} unicapped Archimedian antiprism (Fig. 10.10c) and differs from the D_{3h} structure of the isoelectronic cation $[Bi_9]^{5+}$ which, in the salt $Bi^+[Bi_9]^{5+}[HfCl_6]_3^{2-}$ (p. 591), features a tricapped trigonal prism, as in $[B_9H_9]^{2-}$ (p. 153). The emerald green species $[Pb_9]^{4-}$, which is stable in liquid NH_3 solution, has not so far proved amenable to isolation via cryptand-complexed cations.

The influence of electron-count on cluster geometry has been very elegantly shown by a crystallographic study of the deep-red compound $[K(crypt)]_6^+[Ge_9]^{2-}[Ge_9]^{4-}.2.5en$, prepared by the reaction of KGe with cryptand in ethylenediamine. $[Ge_9]^{4-}$ has the C_{4v} unicapped square-antiprismatic structure (10.10c) whereas $[Ge_9]^{2-}$, with 2 less electrons, adopts a distorted D_{3h} structure which clearly derives from the tricapped trigonal prism (p. 153).(75) The field is one of great interest and activity, as evidenced by papers describing the synthesis of and structural studies on tetrahedral $Ge_4{}^{2-}$ and $Sn_4{}^{2-}$,(76) tricapped trigonal-prismatic $TlSn_8{}^{3-}$,(77) bicapped square-antiprismatic $TlSn_9{}^{3-}$,(77) and the two *nido*-series $Sn_{9-x}Ge_x{}^{4-}$ ($x = 0$–9) and $Sn_{9-x}Pb_x{}^{4-}$ ($x = 0$–9).(78) Other theoretical studies on many of these polymetallic-cluster anions have also been published.(79) Recent synthetic and structural work includes the characterization of the octahedral *closo*-$[Ge_2Co_4]$ grouping in $[1,6\text{-}\{(CO)_4COGe\}_2Co_4(CO)_{11}]$,(80)

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(75) C. H. E. Belin, J. D. Corbett and A. Cisar, *J. Am. Chem. Soc.* **99**, 7163–9 (1977).

(76) S. C. Critchlow and J. D. Corbett, *J. Chem. Soc., Chem. Commun.*, 236–7 (1981). M. J. Rothman, L. S. Bartell and L. L. Lohr, *J. Am. Chem. Soc.* **103**, 2482–3 (1981).

(77) R. C. Burns and J. D. Corbett, *J. Am. Chem. Soc.* **104**, 2804–10 (1982). See also *Inorg. Chem.* **24**, 1489–92 (1985) for $[KSn_9{}^{3-}]$.

(78) R. W. Rudolph, W. L. Wilson and R. C. Taylor *J. Am. Chem. Soc.* **103**, 2480–1 (1981), and references therein. See also W. L. Wilson, R. W. Rudolph, L. L. Lohr, R. C. Taylor and P. Pyykkö, *Inorg. Chem.* **25**, 1535–41 (1985).

(79) L. L. Lohr, *Inorg. Chem.* **20**, 4229–35 (1981); R. C. Burns, R. J. Gillespie, J. A. Barnes and M. J. McGlinchey, *Inorg. Chem.* **31**, 799–807 (1982). G. Kliche, H. G. von Schnering and M. Schwarz, *Z. anorg. allg. Chem.* **608**, 131–4 (1992).

(80) S. P. Foster, K. M. Mackay and B. K. Nicholson, *Inorg. Chem.* **24**, 909–13 (1985).

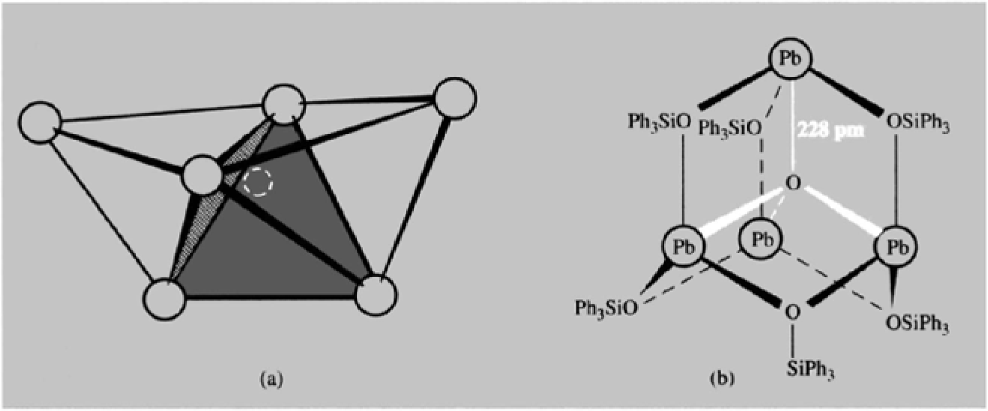

Figure 10.11 (a) The three face-sharing tetrahedra of Pb atoms in the $Pb_6O(OH)_6{}^{4+}$ cluster; only the unique 4-coordinate O atom at the centre of the central tetrahedron is shown (in white). (b) The adamantane-like structure of $[Pb_4O(OSiPh_3)_6]$ showing the fourfold coordination about the central O atom.

the *closo*-10 vertex cluster $[Sn_9Cr(CO)_3]^{4-}$(81) and encapsulated Ge and Sn atoms (E) in species such as $[Ni_{12}(\mu_{12}\text{-E})(CO)_{22}]^{2-}$ and $[Ni(\mu_{10}\text{-Ge})(CO)_{20}]^{2-}$.(82)

The polymeric cluster compound $[Sn_6O_4(OH)_4]$ formed by hydrolysis of Sn^{II} compounds has been mentioned on p. 384. Hydrolysis of Pb^{II} compounds also leads to polymerized species; e.g. dissolution of PbO in aqueous $HClO_4$ followed by careful addition of base leads to $[Pb_6O(OH)_6]^{4+}[ClO_4]_4^-H_2O$. The cluster cation (Fig. 10.11a) consists of 3 tetrahedra of Pb sharing faces; the central tetrahedron encompasses the unique O atom and the 6 OH groups lie on the faces of the 2 end tetrahedra.(83) The extent of direct Pb–Pb interaction within the overall cluster has not been established but it is noted that the distance between "adjacent" Pb atoms falls in the range 344–409 pm (average 381 pm) which is appreciably larger than in the $Pb_5{}^{2-}$ anion. The distance from the central O to the 4 surrounding Pb atoms is 222–235 pm and the other Pb–O(H) distances are in the range 218–267 pm. The structure should be compared with the $[Sn_6O_4(OH)_4]$ cluster (p. 384), which also has larger Sn–Sn distances than in the polystannide anions in Fig. 10.10.

Another polycyclic structure in which a unique O atom is surrounded tetrahedrally by 4 Pb^{II} atoms is the colourless adamantane-like complex $[Pb_4O(OSiPh_3)_6]$, obtained as a 1:1 benzene solvate by reaction of Ph_3SiOH with $[Pb(C_5H_5)_2]$ (p. 404). The local geometry about Pb^{II} is also noteworthy: it comprises pseudo-trigonal bipyramidal coordination in which the bridging $OSiPh_3$ groups occupy the equatorial sites whilst the apical sites are occupied by the unique O atom and axially directed lone pairs of electrons.(84) The first heterometallic oxoalkoxide, $[Pb_6Nb_4O_4(OEt)_{24}]$, has also been prepared, by reacting $[Pb_4O(OEt)_6]$ and $[Nb_2(OEt)_{10}$ in ethanol at room temperature.(85) X-ray structural analysis shows an octahedral Pb_6 framework, four of whose faces are capped by a μ_4-oxo ligand connected to 3Pb atoms and an $\{Nb(OEt)_5\}$ moiety; the remaining

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[81] B. W. Eichhorn, R. C. Haushalter and W. T. Pennington, *J. Am. Chem. Soc.* **110**, 8704–6 (1988). B. W. Eichhorn and R. C. Haushalter, *J. Chem. Soc., Chem. Commun.*, 937–8 (1990).

[82] A. Ceriotti, F. Demartin, B. T. Heaton, P. Ingallina, G. Longoni, M. Manassero, M. Marchionna and N. Masciocchi, *J. Chem. Soc., Chem. Commun.*, 786–7 (1989).

[83] T. G. Spiro, D. H. Templeton and A. Zalkin, *Inorg. Chem.* **8**, 856–61 (1969).

[84] C. Gaffney, P. G. Harrison, and T. J. King, *J. Chem. Soc., Chem. Commun.*, 1251–2 (1980).

[85] R. Papiernik, L. G. Hubert-Pfalzgraf, J.-C. Daran and Y. Jeannin, *J. Chem. Soc., Chem. Commun.*, 695–7 (1990).

four faces of the Pb_6 octahedron are capped by (μ_3-OEt) groups. This leads, to the overall detailed formulation of the compound as $[Pb_6(\mu_4\text{-}O)_4\{Nb(OEt)_2\}_4(\mu_3\text{-}OEt)_4(\mu_2\text{-}OEt)_{12}]$. Alternatively the complex can be described as a tetradentate oxo ligand donating to $4\{Nb(OEt)_2(\mu_2\text{-}OEt)_3\}$ groups i.e. $[Pb_6O_4(OEt)_4\text{-}\{Nb(OEt)_5\}_4]$.

10.3.7 Organometallic compounds[86]

Germanium[87]

Organogermanium chemistry closely resembles that of Si though the Ge compounds tend to be somewhat less thermally stable. They are also often rather more chemically reactive than their Si counterparts, e.g. in ligand scrambling reactions, Ge–C bond cleavage and hydrogermylation. However, GeR_4 compounds themselves are rather inert chemically and R_nGeX_{4-n} tend to be less prone to hydrolysis and condensation reactions than their Si analogues. Again, following expected group trends, germylenes (R_2Ge:) are more stable than silylenes. The table of comparative bond energies on p. 374 indicates that the Ge–C and Ge–H bonds are weaker than the corresponding bonds involving Si but are nevertheless quite strong; Ge–Ge is noticeably weaker. The electronegativity of both Si and Ge are similar to that of H, though the reactivity pattern towards organolithium reagents suggests a slight hydridic character ($H^{\delta-}$) for Ph_3SiH and some protic character ($H^{\delta+}$) for Ph_3GeH:

$$Ph_3Si{-}H + LiR \longrightarrow Ph_3Si{-}R + LiH$$

(metathesis)

$$Ph_3Ge{-}H + LiR \longrightarrow Ph_3Ge{-}Li + RH$$

(metallation)

In fact, the polarity of the Ge–H bond can readily be reversed (umpolung) by an appropriate choice of constituents, e.g.:

$$Et_3Ge^{\delta+}{-}H^{\delta-} + {>}C{=}O \longrightarrow H{-}\overset{|}{\underset{|}{C}}{-}OGeEt_3$$

(germoxane)

$$Cl_3Ge^{\delta-}{-}H^{\delta+} + {>}C{=}O \longrightarrow Cl_3Ge{-}\overset{|}{\underset{|}{C}}{-}OH$$

(germylcarbinol)

Preparative routes to organogermanium compounds parallel those for organosilicon compounds (p. 363) and most of the several thousand known organogermanes can be considered as derivatives of R_nGeX_{4-n} or Ar_nGeX_{4-n} where X = hydrogen, halogen, pseudohalogen, OR, etc. The compounds are colourless, volatile liquids, or solids. Attempts to prepare $(-R_2GeO-)_x$ analogues of the silicones (p. 364) show that the system is different: hydrolysis of Me_2GeCl_2 is reversible and incomplete, but extraction of aqueous solutions of Me_2GeCl_2 with petrol leads to the cyclic tetramer $[Me_2GeO]_4$, mp 92°; the compound is monomeric in water. Organodigermanes and -polygermanes have also been made by standard routes, e.g.:

$$2Me_3GeBr + 2K \xrightarrow{\text{reflux}} 2KBr + Ge_2Me_6$$

(mp −40°, bp 140°)

$$Et_3GeBr + NaGePh_3 \xrightarrow{\text{liq } NH_3} NaBr + Et_3GeGePh_3 \text{(mp 90°)}$$

$$2Ph_3GeBr + 2Na \xrightarrow[\text{xylene}]{\text{boiling}} 2NaBr + Ge_2Ph_6$$

(mp 340°)

$$Ph_2GeCl_2 + 2NaGePh_3 \longrightarrow 2NaCl + Ge_3Ph_8$$

(mp 248°)

In general, the Ge–Ge bond is readily cleaved by Br_2 either at ambient or elevated temperatures but the compounds are stable to thermal cleavage at moderate temperatures. Ge_2R_6 compounds can even be distilled unchanged in air (like Si_2R_6 but unlike the more reactive Sn_2R_6) and are stable towards hydrolysis and ammonolysis.

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[86] C. ELSCHENBROICH and A. SALZER, *Organometallics*, VCH, Weinheim, 1989, pp. 115–46.

[87] P. RIVIÈRE, M. RIVIÈRE-BAUDET and J. SATGÈ, Chap. 10 in G. WILKINSON, F. G. A. STONE and E. W. ABEL (eds.) *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, Vol. 2, pp. 399–518 (1982) (716 refs.).

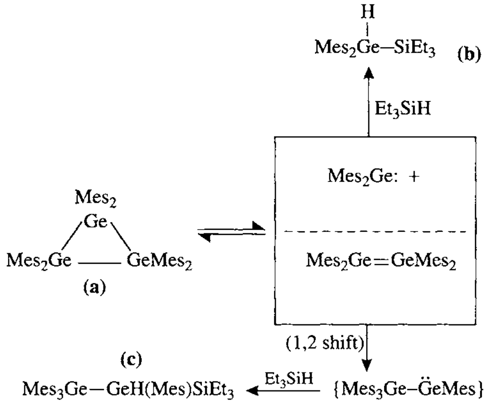
Considerable recent attention has focused on the preparation, structure and stability of germenes (>Ge=C<), germylenes (R_2Ge:), cyclo and polyhedral oligopolygermanes, and Ge^{II} species with coordination numbers greater than 4 (especially 5 and 10). Thus, evidence for fugitive germene species has been known for some 20 years(88) but stable germenes, $R_2Ge{=}CR'_2$, were first reported only in 1987,(89,90) the stabilization being achieved by use of bulky groups both on Ge [e.g. R = mesityl or $-N(SiMe_3)_2$] and on C [e.g. R'_2 = $-B(Bu^t)C(SiMe_3)_2B(Bu^t)-$ or CR'_2 = fluorenylidene]. Numerous other stable germenes have since been characterized.(90)

The first germylene, R_2Ge: [R = $(SiMe_3)_2CH-$], was reported in 1976. It can now be conveniently prepared from $GeCl_2$.diox and Grignard-type derivatives of the bulky bis(trimethylsilyl)methyl R group in Et_2O (e.g. ether complexes of RMgCl or MgR_2); gas-phase electron diffraction at 155°C shows it to be a V-shaped monomer with the angle CGeC 107°.(91) In the solid phase the compound forms bright yellow crystals (mp 182°C) of the centrosymmetric dimer Ge_2R_4 which has a *trans*-folded framework (see structure on p. 403) with a fold angle θ of 32° and a Ge–Ge distance of 235 pm.(92) By contrast, reductive coupling reactions of R_2GeX_2 with a mixture of Mg/$MgBr_2$ in thf affords colourless crystals of cyclotrigermanes or cyclotetragermanes in moderate or good yield:(93)

$$R_2GeCl_2 \xrightarrow{MgBr_2} R_2Ge(Cl)Br \xrightarrow{Mg}$$

$$R_2Ge(Cl)MgBr \xrightarrow{\text{dil HCl}} (GeR_2)_n \quad n = 3, 4$$

Bulky R groups such as mesityl, xylyl or 2,6-diethylphenyl lead to Ge_3 rings whereas sterically less demanding groups such as Pr, Ph or Me_3SiCH_2 yield Ge_4 rings. Note that the compounds $(GeR_2)_n$ feature Ge with the coordination number 2, 3 or 4 depending on whether $n = 1$, 2, or ≥ 3, respectively. Mixed derivatives can also be made: e.g., reductive coupling of Mes(Bu)$GeCl_2$ at room temperature affords [{Ge(Mes)Bu}$_3$], mp 201°. Thermolysis of [{Ge(Mes)$_2$}$_3$], (a) in the presence of Et_3SiH at 105° yields a mixture of dimesityl(triethylsilyl)germane (b) and tetramesityl(triethylsilyl)digermane (c) according to the subjoined scheme:(94)



Polyhedral oligogermanes of varying complexity can be made by careful choice of the organo R group and the metal reductive coupling agent.(95) Thus, treatment of {$(Me_3Si)_2CH$}$GeCl_3$ with Li metal in thf gave thermochroic yellow-orange crystals of the hexamer [Ge_6{$CH(SiMe_3)_2$}$_6$] which were unexpectedly stable to atmospheric

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(88) T. J. Barton, E. A. Kline and P. M. Garvey, *J. Am. Chem. Soc.* **95**, 3078 (1973). J. Barrau, J. Escudie and J. Satgé, *Chem. Rev.* **90**, 283–319 (1990) and references cited therein.

(89) C. Couret, J. Escudie, J. Satgé and M. Lazraq, *J. Am. Chem. Soc.* **109**, 4411–12 (1987).

(90) M. Lazraq, C. Couret, J. Escudie, J. Satgé and M. Soufiaoui, *Polyhedron* **10**, 1153–61 (1991) and references cited therein.

(91) T. Fjeldberg, A. Haaland, B. E. R. Schilling, M. F. Lappert and A. J. Thorne, *J. Chem. Soc., Dalton Trans.*, 1551–6 (1986).

(92) D. E. Goldberg, P. B. Hitchcock, M. F. Lappert, K. M. Thomas and A. J. Thorne, *J. Chem. Soc., Dalton Trans.*, 2387–94 (1986).

(93) W. Ando and T. Tsumuraya, *J. Chem. Soc., Chem. Commun.*, 1514–5 (1987).

(94) K. M. Baines, J. A. Cooke and J. J. Vittal, *J. Chem. Soc., Chem. Commun.*, 1484–5 (1992).

(95) A. Sekiguchi and H. Sakurai, Chap. 7 in R. Steudel (ed.), *The Chemistry of Inorganic Ring Systems*, Elsevier, Amsterdam, pp. 101–24 (1992).

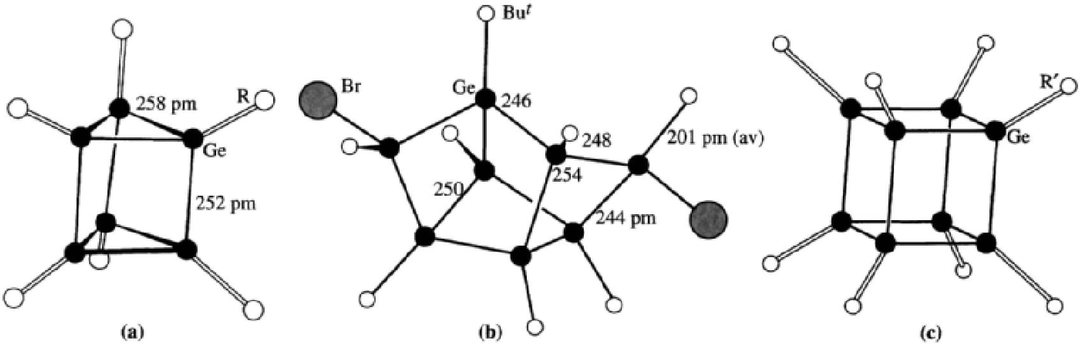

Figure 10.12 (a) Prismane structure of [$Ge_6\{CH(SiMe_3)_2\}_6$] (for clarity only the *ipso* C atoms of the R groups are shown). (b) The tetracyclo structure of [$Ge_8Bu^t_8Br_2$] with only the *ipso* C atoms of the Bu^t groups shown. (c) The cubane structure of [$Ge_8(CMeEt_2)_8$] again with only the *ipso* C atoms of the *t*-hexyl groups shown.

O_2 and moisture.(96) X-ray analysis revealed a prismane structure (Fig. 10.12a) rather than a monocyclic benzenoid structure. The Ge–Ge distances within the two triangular faces (258 pm) are, perhaps surprisingly, longer than those in the prism quadrilateral edges (252 pm) and all the Ge–Ge distances are significantly longer than in other polygermanes (237–247 pm). Again, treatment of $GeBr_4$ with $LiBu^t$ yields a mixture of $Bu^t_2GeBr_2$ and $Bu^tBr_2Ge{-}GeBr_2Bu^t$, and treatment of this latter with an excess of Li/naphthalene afforded the polycyclic octagermane. $Ge_8Bu^t_8Br_2$, in 50% yield.(97) As shown in Fig 10.12b, the molecule is chiral with C_2 skeletal symmetry. The octagermacubane [$Ge_8(CHMeEt_2)_8$] (Fig. 10.12c) was obtained as yellow crystals (mp > 215°) by a simple coupling reaction of R_3GeCl with $Mg/MgBr_2$, and numerous other cyclic, ladder and cluster polygermanes have been described.(95)

The coordination number of Ge in organogermanes is not limited to 2, 3 or 4, and higher coordination numbers are well documented. Examples are 5-coordinate Ge^{II} in the cation of $[Ge(\eta^5\text{-}C_5Me_5)]^+[BF_4]^-$ (10),(98) 6-coordinate Ge^{II} in the corresponding chloride $[(\eta^5\text{-}C_5Me_5)GeCl]$ (11)(98) and 10-coordinate Ge^{II} in $[Ge(\eta^5\text{-}C_5H_5)_2]$ (12)(99) and its ($\eta^5\text{-}C_5R_5$) analogues.(98) These species can now readily be prepared by standard reactions, and structural details are in the leading references cited. Thus, reaction of NaC_5H_5 with $GeCl_2$.diox in thf gives a 60% yield of (12) as colourless crystals, mp 78°C. The angle of aperture between the two C_5H_5 planes in (12) is 50.4° compared with 45.9° or 48.4° for stannocene.(99) By contrast, 5-coordinate Ge^{IV} adopts a structure midway between trigonal bipyramidal and rectangular pyramidal in phenyl-substituted anionic germanates such as $[PhGe(\eta^2\text{-}C_6H_4O_2)_2]^-$ (13), the precise geometry being dictated by the co-cation, e.g. $[NEt_4]^+$, $[N(Et)_3H]^+$ or $[AsPh_4]^+$.(100)

Finally, brief mention should be made of the growing range of heterocyclic organogermanium compounds. Compounds with 3–13(+) atoms in the ring have recently been reviewed.(101) Cyclic organogermapolysilanes are also known, e.g.

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[96] A. Sekiguchi, C. Kabuto and H. Sakurai, *Angew. Chem. Int. Edn. Engl.* **28**, 55–6 (1989).

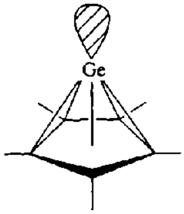
[97] M. Weidenbruch, F.-T. Grimm, S. Pohl and W. Saak, *Angew. Chem. Int. Edn. Engl.* **28**, 198–9 (1989).

[98] P. Jutzi, B. Hampel, M. B. Hursthouse and A. J. Howes, *Organometallics* **5**, 1944–8 (1986).

[99] M. Grenz, E. Hahn, W.-W. du Mont and J. Pickardt, *Angew. Chem. Int. Edn. Engl.* **23**, 61–3 (1984).

[100] R. R. Holmes, R. O. Day, A. C. Sau, C. A. Poutasse and J. M. Holmes, *Inorg. Chem.* **25**, 607–11 (1986) and references cited therein.

[101] P. Mazerolles, pp. 139–93 in H. W. Roesky (ed.), *Rings, Clusters and Polymers of Main Group and Transition Elements*, Elsevier, Amsterdam (1989).



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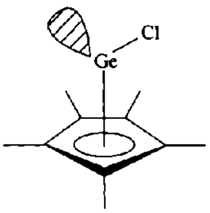

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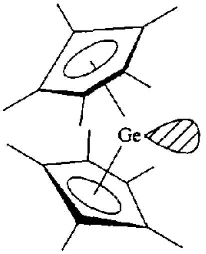

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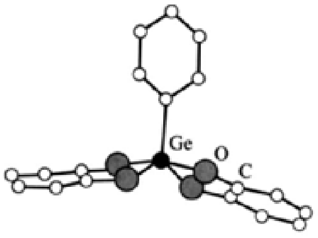

(13)

peralkyl-1-germa-2,3,4-trisilacyclobutanes.(102) Other variants include the novel telluradigermiranes, $\mathrm{Ar_2}\overline{\mathrm{Ge{-}Te{-}Ge}}\mathrm{Ar_2}$,(103) a yellow phosphagermirene $\mathrm{Bu^t}\overline{\mathrm{C{=}P{-}Ge}}\mathrm{R_2}$ [mp. 89° for $\mathrm{R} = \mathrm{(Me_3Si)_2CH{-}}$],(104) and a germaphosphetene featuring a $\overline{\mathrm{GeCCP}}$ ring system.(105) The possibilities are clearly limitless.

Tin(106,107)

Organotin compounds have been much more extensively investigated than those of Ge and, as described in the Panel, many have important industrial applications.(108) Syntheses are by standard techniques (pp. 134, 259, 363) of which the following are typical:

Grignard: $\mathrm{SnCl_4 + 4RMgCl \longrightarrow SnR_4 + 4MgCl_2}$ (also with ArMgCl)

Organo Al: $\mathrm{3SnCl_4 + 4AlR_3 \longrightarrow 3SnR_4 + 4AlCl_3}$ (alkyl only)

Direct (Rochow)† $\mathrm{Sn + 2RX \longrightarrow R_2SnX_2}$ (and $\mathrm{R_nSnX_{4-n}}$) (alkyl only).

All three routes are used on an industrial scale and the Grignard route (or the equivalent organo-Li reagent) is convenient for laboratory scale. Rather less used is the modified Wurtz-type reaction ($\mathrm{SnCl_4 + 4RCl \xrightarrow{8\ Na} SnR_4 + 8NaCl}$). Conversion of $\mathrm{SnR_4}$ to the partially halogenated species is readily achieved by scrambling reactions with $\mathrm{SnCl_4}$. Reduction of $\mathrm{R_nSnX_{4-n}}$ with $\mathrm{LiAlH_4}$ affords the corresponding hydrides and hydrostannation (addition of Sn–H) to C–C double and triple bonds is an attractive route to unsymmetrical or heterocyclic organotin compounds.

Most organotin compounds can be regarded as derivatives of $\mathrm{R_nSn^{IV}X_{4-n}}$ ($n = 1$–4) and even compounds such as $\mathrm{SnR_2}$ or $\mathrm{SnAr_2}$ are in fact cyclic oligomers $\mathrm{(Sn^{IV}R_2)_x}$ (p. 402). The physical properties of tetraorganostannanes closely resemble those of the corresponding hydrocarbons or tetraorganosilanes but with higher densities, refractive indices, etc. They are colourless, monomeric, volatile liquids or solids. Chemically they resist hydrolysis or oxidation under normal conditions though when

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(102) H. Suzuki, K. Okabe, N. Sato, Y. Fukuda and H. Watanabe, *J. Chem. Soc., Chem. Commun.*, 1298–300 (1991).

(103) T. T. Sumuraya, Y. Kabe and W. Ando, *J. Chem. Soc., Chem. Commun.*, 1159–60 (1990).

(104) A. H. Cowley, S. W. Hall, C. M. Nunn and J. M. Power, *J. Chem. Soc., Chem. Commun.*, 753–4 (1988).

(105) M. Andrianarison, C. Couret, J.-P. Declercq, A. Dubourg, J. Escudie and J. Satgé, *J. Chem. Soc., Chem. Commun.*, 921–3 (1987).

(106) A. G. Davies and P. J. Smith, Chap. 11 in G. Wilkinson, F. G. A. Stone and E. W. Abel (eds.) *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, Vol. **2**, pp 519–627 (1982), (722 refs.).

(107) I. Omae, *Organotin Chemistry*, Elsevier, Amsterdam, 1989, 355 pp.

(108) C. J. Evans and S. Karpel, *Organotin Compounds in Modern Technology*, Journal of Organometallic Chemistry Library, **16** Elsevier, Amsterdam, 1985, 280 pp. S. J. Blunden, P. A. Cusack and R. Hill, *The Industrial Uses of Tin Chemicals*, Royal Society of Chemistry, London, 1985, 346 pp. K. Das, S. W. Ng and M. Gielen, *Chemistry and Technology of Silicon and Tin*, Oxford University Press, Oxford, 1992, 608 pp.

† For example, with MeCl at 175° in the presence of catalytic amounts of $\mathrm{CH_3I}$ and $\mathrm{NEt_3}$, the yields were $\mathrm{Me_2SnCl_2}$ (39%), $\mathrm{MeSnCl_3}$ (6.6%), $\mathrm{Me_3SnCl}$ (4.6%).

Uses of Organotin Compounds

Tin is unsurpassed by any other metal in the multiplicity of applications of its organometallic compounds. The first organotin compound was made in 1849 but large-scale applications have developed only recently; indeed, world production figures for organotin compounds increased more than 700-fold between 1950 and 1980:

Year	1950	1960	1965	1970	1975	1980
Tonnes pa	<50	2000	5000	15 000	25 000	35 000

The largest application for organotin compounds (75% by weight) is as stabilizers for PVC plastics; in their absence halogenated polymers are rapidly degraded by heat, light or oxygen to give discoloured, brittle products. The most effective stabilizers are R_2SnX_2, where R is an alkyl residue (typically *n*-octyl) and X is laurate, maleate, etc. For food packaging the *cis*-butenedioate polymer, $[Oct^i_2Sn{-}OC(O)CH{=}CHC(O)O]_n$, and the *S,S′*-bis-(*iso*-octyl mercaptoethanoate), $Oct^i_2Sn\{SCH_2C(O)OOct^i\}_2$ have been approved and are used when colourless non-toxic materials with high transparency are required. The compounds are thought to be such effective stabilizers because (i) they inhibit the onset of dehydrochlorination by exchanging their anionic groups X with reactive Cl sites in the polymer, (ii) they react with and hence scavenge the HCl which is produced and which would otherwise catalyse further elimination, and (iii) they act as antioxidants and thereby prevent breakdown of the polymer initiated by atmospheric O_2.

Another major use of organotin compounds is as curing agents for the room temperature "vulcanization" of silicones; the 3 most commonly used compounds are Bu_2SnX_2, where X is acetate, 2-ethylhexanoate or laurate. The same compounds are also used to catalyse the addition of alcohols to isocyanates to produce polyurethanes.

The next major use of organotin compounds (15–20%) is as agricultural biocides and here triorganotins are the most active materials; the importance of this application can readily be appreciated since, at present, over one-third of the world's food crops are lost annually to pests such as fungi, bacteria, insects or weeds. The great advantage of organotin compounds in these applications is that their toxic action is selective and there is little danger to higher (mammalian) life; furthermore, their inorganic degradation products are completely non-toxic. Bu^n_3SnOH and Ph_3SnOAc control fungal growths such as potato blight and related infections of sugar-beet, peanuts, and rice. They also eradicate red spider mite from apples and pears. Other R_3SnX are effective in controlling insects, either by acting as chemosterilants or by killing the larvae. Again, $O(SnBu^n_3)_2$ is an excellent wood preserver, and derivatives of Ph_3Sn- and $(cyclohexyl)_3Sn$- are also used for this. Related applications are as marine antifouling agents for timber-hulled boats; paints containing Bu^n_3Sn- or Ph_3Sn- derivatives slowly release these groups and provide long-term protection against attachment of barnacles or attack by Teredo woodworm borers. Cellulose and woollen fabrics are likewise protected against fungal attack or destruction by moths. R_3SnX are also used as bacteriostats to control slime in paper and wood-pulp manufacture.

Me_2SnCl_2 is now used as an alternative to $SnCl_4$ for coating glass with a thin film of SnO_2 since it is a non-corrosive solid which is easier to handle. The glass (or ceramic) surface is treated with Me_2SnCl_2 vapour at temperatures above 450° and, depending on the thickness of the oxide film produced, the glass is toughened and the surface can be rendered scratch-resistant, lustrous, or electroconductive (p. 385).

Organotin reagents and intermediates are finding increasing use in organic syntheses.(109)

ignited they burn to SnO_2, CO_2 and H_2O. Ease of Sn–C cleavage by halogens or other reagents varies considerably with the nature of the organic group and generally increases in the sequence Bu (most stable) < Pr < Et < Me < vinyl < Ph < Bz < allyl < CH_2CN < CH_2CO_2R (least stable). The lability of Sn–C bonds and the ease of redistribution in mixed organostannane systems frustrated early attempts to prepare optically active tin compounds and the first synthesis of a 4-coordinate Sn compound in which the metal is the sole chiral centre was only achieved in 1971 with the isolation and resolution of $[MeSn(4\text{-anisyl})(1\text{-naphthyl})\{CH_2CH_2C(OH)Me_2\}]$.(110)

The association of SnR_4 via bridging alkyl groups (which is such a notable feature of many organometallic compounds of Groups 1, 2 and 13) is not observed at all. However, many compounds of general formula R_3SnX or R_2SnX_2 are strongly associated via bridging X-groups

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[109] M. Pereye, J.-P. Quintard and A. Rahm, *Tin in Organic Synthesis*, Butterworths, London, 1987, 342 pp. J. K. Stille, *Angew. Chem. Int. Edn. Engl.* **25**, 508–24 (1986).

[110] M. Gielen, *Acc. Chem. Res.* **6**, 198–202 (1973).

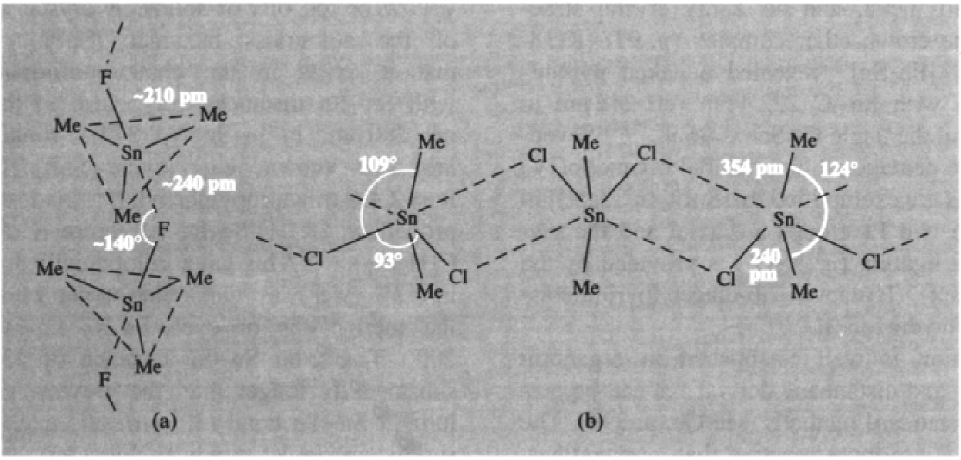

Figure 10.13 Crystal structure of (a) Me_3SnF, and (b) Me_2SnCl_2, showing tendency to polymerize via Sn—X···Sn bonds.

which thereby raise the coordination number of Sn to 5, 6 or even 7. As expected, F is more effective in this role than the other halogens (why?). For example, Ph_3SnF is a strictly linear polymer with 5-coordinate trigonal bipyramidal geometry about Sn; the angles Sn–F–Sn and F–Sn–F are both 180° and the Sn–F distances in the chain are identical (214.6 pm).$^{(111)}$ By contrast, Me_3SnF has a zig-zag chain structure (Fig. 10.13a) with unequal Sn–F distances and a pronounced bend at F (~140°). The volatile chlorine analogue (Me_3SnCl: mp 39.5°, bp 154°) also has a zig-zag chain structure with angle Sn–Cl–Sn 151° and essentially linear Cl–Sn–Cl (177°); The two Sn–Cl distances in the chain are 243 and 326 pm but even this longer distance is substantially shorter than the sum of the van der Waals radii (385 pm).$^{(112)}$ On the other hand crystalline Ph_3SnCl and Ph_3SnBr feature monomeric molecules with 4-coordinate Sn atoms.

Me_2SnF_2 has a layer structure with octahedral Sn and *trans*-Me groups above and below the F-bridged layers as in SnF_4 (p. 381). The weaker Cl bridging in Me_2SnCl_2 leads to the more distorted structure shown in Fig. 10.13b. The O atom is an even more effective ligand than F and, amongst the numerous compounds R_3SnOR' and $R_2Sn(OR')_2$ that have been studied by X-ray crystallography, the only ones with 4-coordinate tin (presumably because of the bulky ligands) are $1,4\text{-}(Et_3SnO)_2C_6Cl_4$ and $[Mn(CO)_3\{\eta^5\text{-}C_5Ph_4(OSnPh_3)\}]$.

The converse of polymerization is heterolytic bond scission leading either to R_3Sn^+ or R_3Sn^- species. Tricoordinate organotin(IV) cations can readily be synthesized at room temperature by hydride or halide abstraction reactions in benzene or other solvents.$^{(113)}$ For example, with R = Me, Bu or Ph:

$$R_3SnH + Ph_3CClO_4 \longrightarrow [R_3Sn]^+[ClO_4]^- + Ph_3CH$$

$$R_3SnCl + AgClO_4 \longrightarrow [R_3Sn]^+[ClO_4]^- + AgCl$$

$$R_3SnH + B(C_6F_5)_3 \longrightarrow [R_3Sn]^+[B(C_6F_5)_3H]^-$$

The highly ionic nature of these (presumably planar) species is revealed by cryoscopy, electrical conductance and the diagnostically large downfield ^{119}Sn nmr chemical shift. Salts of the corresponding anionic species Ph_3Sn^- are easily generated by heating either Ph_3SnH or Sn_2Ph_6

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[111] D. Tudela, E. Gutiérrez-Puebla and A. Monge, *J. Chem. Soc., Dalton Trans.*, 1069–71 (1992).

[112] M. B. Hossain, J. L. Lefferts, K. C. Molloy, D. van der Helm and J. J. Zuckerman, *Inorg. Chim. Acta* **36**, L409–L410 (1979).

[113] J. B. Lambert and B. Kuhlmann, *J. Chem. Soc., Chem. Commun.*, 931–2 (1992).

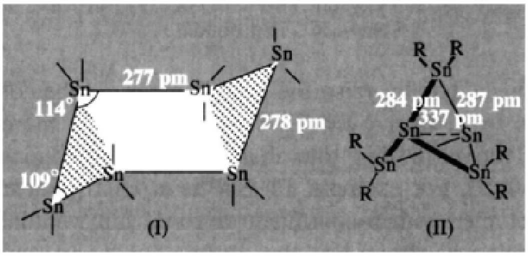
with alkali metal, and an X-ray crystal structure of the crown ether complex (p. 97) $[K(18\text{-crown-}6)]^+[Ph_3Sn]^-$ revealed a naked pyramidal anion with Sn–C 222.4 pm (cf. 212 pm in $SnPh_4$) and the angle C–Sn–C 96.9°.[114] Seven-coordinate pentagonal bipyramidal organotin(IV) complexes are exemplified by $[SnEt_2(\eta^5\text{-dapt})]$ in which the two Et groups are axial and the planar 5-fold ligation (η^5-N_3O_2) is provided by the ligand (dapt), (H_2dapt = 2,6-diacetylpyridinebis-(2-thenoylhydrazone)].[115]

Catenation is well established in organotin chemistry and distannane derivatives can be prepared by standard methods (see Ge, p. 396). The compounds are more reactive than organodigermanes; e.g. Sn_2Me_6 (mp 23°) inflames in air at its bp (182°) and absorbs oxygen slowly at room temperature to give $(Me_2Sn)_2O$. Typical routes to higher polystannanes are:

$$2Me_3SnBr + NaMe_2SnSnMe_2Na \xrightarrow{\text{liq } NH_3} Me_3Sn(SnMe_2)_2SnMe_3 \text{ (oil)}$$

$$3Ph_3SnLi + SnCl_2 \longrightarrow [(Ph_3Sn)_3SnLi] \xrightarrow{Ph_3SnCl} Sn(SnPh_3)_4 (\text{mp} \sim 320°)$$

Unbranched chains up to at least Sn_6 are known, e.g. $Ph_3Sn(Bu^t_2Sn)_nSnPh_3$ ($n = 0$–4).[116] Cyclodialkyl stannanes(IV) can also be readily prepared, e.g. reaction of Me_2SnCl_2 with Na/liq NH_3 yields cyclo-$(SnMe_2)_6$ together with acyclic $X(SnMe_2)_nX$ ($n = 12$–20). Yellow crystalline cyclo-$(SnEt_2)_9$ is obtained almost quantitatively when Et_2SnH_2, dissolved in toluene/pyridine, is catalytically dehydrogenated at 100° in the presence of a small amount of Et_2SnCl_2. Similarly, under differing conditions, the following have been prepared:(34) $(SnEt_2)_6$, $(SnEt_2)_7$, $(SnBu^t_2)_4$, $(SnBu^i_2)_4$, $(SnBu^i_2)_6$, and $(SnPh_2)_5$. The compounds are highly reactive yellow or red oils or solids. A crystal structure of the colourless hexamer $(SnPh_2)_6$ shows that it exists in the chair conformation (I) with Sn–Sn distances very close to the value of 280 pm in α-Sn (p. 372). Small rings are also known, e.g. [cyclo-$(SnR_2)_3$] where R = 2,4,6-triisopropylphenyl,[117] and even the propellane [1.1.1]-Sn_5R_6 (structure II, R = 2,6-$C_6H_3Et_2$).[118] This latter compound was formed in 13% yield as dark blue-violet crystals by the thermolysis of cyclo-Sn_3R_6 in xylene at 200°. The axial Sn–Sn distance of 337 pm is substantially longer than the previously known longest Sn–Sn bond (305 pm) and may indicate significant singlet diradical character).



True monomeric organotin(II) compounds have proved rather elusive. The cyclopentadienyl compound $[Sn(\eta^5\text{-}C_5H_5)_2]$ (which is obtained as white crystals mp 105° from the reaction of NaC_5H_5 and $SnCl_2$ in thf) has a structure similar to that of germanocene (12 pp. 398–9) with the angle subtended at Sn by the midpoints of the C_5 rings 143.7° and 148.0° in the two independent molecules.[119] Interestingly, the mean value of 146° is 1° larger than the value for $[Sn(\eta^5\text{-}C_5Me_5)_2]$, suggesting that the angle is governed predominantly by electronic rather than steric factors. However, with the much more demanding η^5-C_5Ph_5 ligand, the two planar C_5 rings are exactly parallel and staggered, the opposed canting of the phenyl rings with respect to the C_5 rings giving overall

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[114] T. Birchall and J. A. Vetrone, *J. Chem. Soc., Chem. Commun.*, 877–9 (1988).

[115] C. Carini, G. Pelizzi, P. Tarasconi, C. Pelizzi, K. C. Molloy and P. C. Waterfield, *J. Chem. Soc., Dalton Trans.*, 289–93 (1989).

[116] S. Adams and M. Dräger *Angew. Chem. Int. Edn. Engl.* **26**, 1255–6 (1987).

[117] S. Masamune and L. R. Sita, *J. Am. Chem. Soc.* **107** 6390–1 (1985).

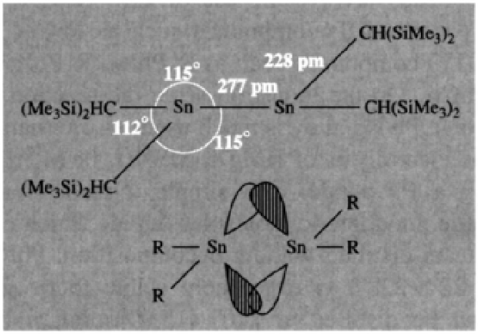
[118] L. R. Sita and R. D. Bickerstaff, *J. Am. Chem. Soc.* **111** 6454–6 (1989).

[119] J. L. Atwood and W. E. Hunter, *J. Chem. Soc., Chem. Commun.*, 925–7 (1981).

S_{10} symmetry.(120) Heterostannocenes such as the pyrrole analogue, $[Sn(\eta^5\text{-}C_4Bu^t_2H_2N)_2]$, (in which a CH group has been replaced by the isoelectronic N atom) have also been reported, the angle subtended by the ring centres at Sn being 142.5° in this case.(121) The related "half-sandwich" cation, *nido*-$[(\eta^5\text{-}C_5Me_5)Sn:]^+$, which is isostructural with *nido*-B_6H_{10} (p. 154), can be made in moderate yield by treating $[Sn(\eta^5\text{-}C_5Me_5)_2]$ with an ethereal solution of HBF_4. The product, $[(\eta^5\text{-}C_5Me_5)Sn]BF_4$, forms colourless crystals which are somewhat sensitive to air and moisture.(122) As its trifluoromethanesulfonate salt ($X^- = CF_3SO_3^-$), the cation undergoes a remarkable reaction with BI_3 which results in replacement of the apical Sn atom with the {BI} group to give a pentacarba analogue of *nido*-B_6H_{10}:(123)

$$nido\text{-}[(\eta^5\text{-}C_5Me_5)Sn]^+X^- + BI_3 \longrightarrow nido\text{-}[(\eta^5\text{-}C_5Me_5)BI]^+X^- + SnI_2$$

The stabilization of σ-bonded dialkyltin(II) compounds, R_2Sn:, (and also those of Ge and Pb) can be achieved by the use of bulky R groups. The first such compound, $[Sn\{CH(SiMe_3)_2\}_2]$, was prepared by direct reaction of $LiCH(SiMe_3)_2$ with $SnCl_2$ or $[Sn\{N(SiMe_3)_2\}_2]$ in ether, and was obtained as air-sensitive red crystals (mp 136°).(124,125) It is monomeric in the gas phase and in benzene solution, and behaves chemically as a "stannylene", displacing CO from $M(CO)_6$ to give orange $[Cr(CO)_5(SnR_2)]$ and yellow $[Mo(CO)_5(SnR_2)]$.(124,126) However, a crystal structure determination showed that the compound dimerizes in the solid state, perhaps by donation of the lone-pair of electrons on each Sn centre into the "vacant" orbital of its neighbour, to give a weak bent double bond as indicated schematically below;(125,127) this would interpret the orientation of the four $\{-CH(SiMe_3)_2\}$ groups.



A synthetic strategy which ensures retention of the monomeric form of SnR_2 even in the crystalline state is to use functionalized R groups which contain a chelating substituent, e.g. by replacing the H atom in $\{-CH(SiMe_3)_2\}$ with a 2-pyridyl group.(128)

Stable stannaethenes, >C=Sn<,(129) and stannaphosphenes, >Sn=P<,(130) have been reported and these, again, exploit the use of bulky groups to prevent oligomerization.

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[120] M. J. Heeg, C. Janiak and J. J. Zuckerman, *J. Am. Chem. Soc.* **106**, 4259-61 (1984).

[121] N. Kuhn, G. Henkel and S. Stubenrauch, *J. Chem. Soc., Chem. Commun.*, 760-1 (1992).

[122] P. Jutzi, F. Kohl and C. Krüger, *Angew. Chem. Int. Edn. Engl.* **18**, 59-61 (1979).

[123] F. Kohl and P. Jutzi, *Angew. Chem. Int. Edn. Engl.* **22**, 56 (1983).

[124] P. J. Davidson and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 317 (1973).

[125] D. E. Goldberg, D. H. Harris, M. F. Lappert and K. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 261-2 (1976).

[126] J. D. Cotton, P. J. Davidson, D. E. Goldberg, M. F. Lappert and K. M. Thomas, *J. Chem. Soc., Chem. Commun.*, 893-5 (1974).

[127] P. J. Davidson, D. H. Harris and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 2268-74 (1976). D. E. Goldberg, P. B. Hitchcock, M. F. Lappert, K. M. Thomas, A. J. Thorne, T.Fjeldberg, A. Haaland and B. E. R. Schilling, *J. Chem. Soc., Dalton Trans.*, 2387-94 (1986). See also U. Lay, H. Pritzkow and H. Grützmann, *J. Chem. Soc., Chem. Commun.*, 260-2 (1992) for isomeric structures of crystalline $[Sn\{C_6H_2(CF_3)_3\text{-}2,4,6\}_2]$, *viz.* a yellow monomeric form (mp 76°) and a bright red form (mp 66°) which features a weakly associated dimer with a very long Sn-Sn interaction (364 pm).

[128] L. M. Engelhardt, B. S. Jolly, M. F. Lappert, C. L. Raston and A. H. White, *J. Chem. Soc., Chem. Commun.*, 336-8 (1988).

[129] H. Meyer, G. Baum, W. Massa, S. Berger and A. Berndt, *Angew Chem. Int. Edn. Engl.* **26**, 546-8 (1987).

[130] H. Ranaivonjatovo, J. Escudie, C. Couret and J. Satgé, *J. Chem. Soc., Chem. Commun.*, 1047-8 (1992).

Lead(131)

The organic chemistry of Pb is much less extensive than that of Sn, though over 2000 organolead compounds are known and $PbEt_4$ has been produced on a larger tonnage than any other single organometallic compound (p. 371). The most useful laboratory-scale routes to organoleads involve the use of LiR, RMgX, or AlR_3 on lead(II) compounds such as $PbCl_2$, or lead(IV) compounds such as R'_2PbX_2, R'_3PbX, or K_2PbCl_6. On the industrial scale the reaction of RX on a Pb/Na alloy is much used; an alternative is the electrolysis of RMgX, M^IBR_4, or M^IAlR_4 using a Pb anode. The simple tetraalkyls are volatile, monomeric molecular liquids which can be steam-distilled without decomposition; $PbPh_4$ (mp 227–228°) is even more stable thermally: it can be distilled at 240° (15–20 mmHg) but decomposes above 270°. Diplumbanes Pb_2R_6 are much less stable and higher polyplumbanes are unknown except for the thermally unstable, reactive red solid, $Pb(PbPh_3)_4$.

The decreasing thermal stability of Group 14 organometallics with increasing atomic number of M reflects the decreasing M–C and M–M bond energies. This in turn is related to the increasing size of M and the consequent increasing interatomic distance (see table).

M	C	Si	Ge	Sn	Pb
M-C distance in MR_4/pm	154	194	199	217	227

Parallel with these trends and related to them is the increase in chemical reactivity which is further enhanced by the increasing bond polarity and the increasing availability of low-lying vacant orbitals for energetically favourable reaction pathways.

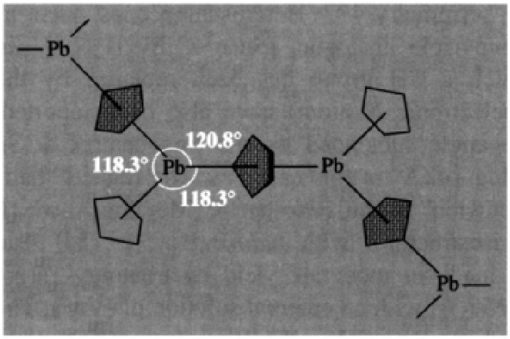

Figure 10.14 Schematic diagram of the chain structure of orthorhombic $Pb(\eta^5\text{-}C_5H_5)_2$. For the doubly coordinated C_5H_5 ring (shaded) Pb–C_{av} is 306 pm, and for the "terminal" C_5H_5 ring Pb–C_{av} is 276 pm; the Pb ··· Pb distance within the chain is 564 pm.

It is notable that the preparation of alkyl and aryl derivatives from Pb^{II} starting materials always results in Pb^{IV} organometallic compounds. The only well-defined examples of Pb^{II} organometallics are purple compound $Pb[CH(SiMe_3)_2]_2$ (see refs on p. 403) and the cyclopentadienyl compound $Pb(\eta^5\text{-}C_5H_5)_2$ and its ring-methyl derivative. Like the Sn analogue (p. 402) $Pb(\eta^5\text{-}C_5H_5)_2$ features non-parallel cyclopentadienyl rings in the gas phase, the angle subtended at Pb being 135 ± 15°. Two crystalline forms are known and the orthorhombic polymorph has the unusual chain-like structure shown in Fig. 10.14:(132) one C_5H_5 is between 2 Pb and perpendicular to the Pb–Pb vector whilst the other C_5H_5 is bonded (more closely) to only 1 Pb. The chain polymer can be thought to arise as a result of the interaction of the lone-pair of electrons on a given Pb atom with a neighbouring (chain) C_5H_5 ring; a 3-centre bond is constructed by overlapping 2 opposite sp^2 hybrids on 2 successive Pb atoms in the chain with the σMO (A_2'') of the C_5H_5 group: this forms one bonding, one nonbonding, and one antibonding MO of which the first 2 are filled and the third empty. By contrast, the deep red crystalline compound $[Pb(\eta^5\text{-}C_5Me_5)_2]$ (mp 100–105°) is monomeric;(119) the angle subtended by the ring centres at Pb is 151° (i.e. even larger than in the Sn analogue) and there is a slight ring slippage

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[131] P. G. Harrison, Chap. 12 in G. Wilkinson, F. G. A. Stone and E. W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, Vol. 2, pp. 629–80 (1982), 419 refs.

[132] C. Panattoni, G. Bombieri, and U. Croato, *Acta Cryst.* **21**, 823–6 (1966).

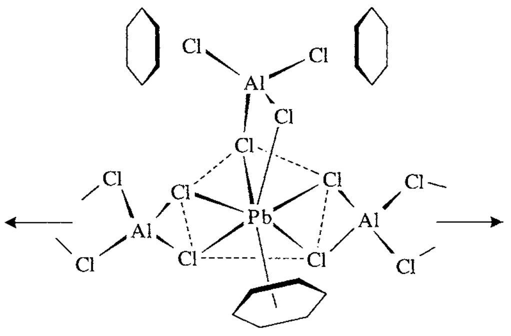

Figure 10.15 Schematic diagram of the chain structure of $[Pb^{II}(AlCl_4)_2(\eta^6\text{-}C_6H_6)].C_6H_6$: Pb–Cl varies from 285–322 pm, Pb–C_{av} (bound) 311 pm, Pb-centre of C_6H_6 (bound) 277 pm.

which leads to a range of Pb–C distances (269–290 pm) to the pentahapto rings.

Another unusual organo-Pb^{II} compound is the η^6-benzene complex $[Pb^{II}(AlCl_4)_2(\eta^6\text{-}C_6H_6)].C_6H_6$ in which Pb^{II} is in a distorted pentagonal bipyramidal site with 1 axial Cl and the other axial site occupied by the centre of the benzene ring (Fig. 10.15). The other C_6H_6 is a molecule of solvation far removed from the metal. One $\{AlCl_4\}$ group chelates the Pb in an axial-equatorial configuration and the other $\{AlCl_4\}$ chelates and bridges neighbouring Pb atoms to form a chain. There is a similar Sn^{II} compound with the same structure. The original paper should be consulted for a discussion of the bonding.(133)

The coordination chemistry of Pb^{II} with conventional ligands from groups 14–16 and with macrocyclic ligands has recently been reviewed.(134)

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[134] J. Parr, Polyhedron **16**, 551–66 (1997).