**Figure 9.16** Symmetry relation between p_π orbital on N and d_π orbitals on the 3 Si atoms in planar {NSi$_3$} compounds such as N(SiH$_3$)$_3$.

MeN(SiH$_3$)$_2$ forms a 1:1 adduct with BH$_3$ at $-80°$ but this decomposes when warmed; Me$_2$N(SiH$_3$) gives a similar adduct which decomposes at room temperature into Me$_2$NBH$_2$ and SiH$_4$ (cf. the stability of Me$_3$NBH$_3$, p. 165). The linear skeleton of H$_3$SiNCO and H$_3$SiNCS has also been interpreted in terms of p_π–d_π N$\equiv$Si bonding.

Compounds containing an Si$=$N double bond are of very recent provenance. The first stable silanimine, Bu$^t_2$Si$=$N–SiBu$^t_3$, was prepared in 1986 as pale yellow crystals, mp 85° (decomp.);[62] it features a short Si$=$N distance (156.8 pm, cf. Si–N 169.5 pm) and almost linear coordination about the N atom (177.8°), suggesting some electronic delocalization as described above. The compound was made by reacting the azidosilane Bu$^t_2$SiCl(N$_3$) with NaSiBu$^t_3$ in Bu$_2$O at $-78°$. The related compound Pr$^i_2$Si$=$NR (R = 2,4,6-Bu$^t_3$C$_6$H$_2^-$) forms stable orange crystals, mp 98°.[63]

Unusual Si/P compounds are also beginning to appear, for example, the tetrasilahexaphospha-adamantane derivative [(Pr^{i}Si)$_4$(PH)$_6$] (1), which is made by reacting Pr^{i}SiCl$_3$ with Li[Al(PH$_2$)$_4$].[64] Again, reaction of white phosphorus, P$_4$, with tetramesityldisilene, Mes$_2$Si$=$SiMes$_2$, in toluene

at 40° gives an 87% yield of the yellow bicyclo (Mes$_2$Si)$_2$P$_2$: this has a "butterfly" structure in which the "hinge" P atoms retain electron donor properties to give adducts such as the bis-W(CO)$_5$ complex (2) (P–P 234.2 pm; Si–P 224.4, 226.7 pm; P–W 256.0 pm; Si $\cdots$ Si 324.4 pm; angle Si–P–Si 91.9°).[65] The now extensive field of phosphorus-rich silaphosphanes has been reviewed.[66] Silaphosphenes, RR'Si$=$PAr are also known.[67]

(1)   (2)
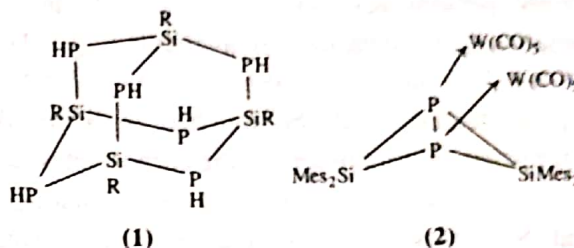
9.3.7 Organosilicon compounds and silicones

Well over 100 000 organosilicon compounds have been synthesized. Of these, during the past few decades, silicone oils, elastomers and resins have become major industrial products. Many organosilicon compounds have considerable thermal stability and chemical inertness; e.g. SiPh$_4$ can be distilled in air at its bp 428°, as can Ph$_3$SiCl (bp 378°) and Ph$_2$SiCl$_2$ (bp 305°). These, and innumerable similar compounds, reflect the considerable strength of the Si–C bond which is, indeed, comparable with that of the C–C bond (p. 338). A further illustration is the compound SiC which closely resembles diamond in its properties (p. 334). Catenation and the formation of multiple bonds are further similarities with carbon chemistry, though these features are less prominent in organosilicon chemistry and much of the work in these areas is of recent

[62] N. WIBERG, K. SCHURZ, G. REBER and G. MÜLLER, *J. Chem. Soc., Chem. Commun.*, 591–2 (1986).

[63] M. HESSE and U. KLINGEBIEL, *Angew. Chem. Int. Edn. Engl.* **25**, 649–50 (1986).

[64] M. BAUDLER, W. OELERT and K.-F. TEBBE, *Z. anorg. allg. Chem.* **598/599**, 9–23 (1991).

[65] M. DRIESS, A. D. FANTA, D. R. POWELL and R. WEST, *Angew. Chem. Int. Edn. Engl.* **28**, 1038–40 (1989).

[66] G. FRITZ *Advances in Inorg. Chem.* **31**, 171–214 (1987).

[67] N. C. NORMAN, *Polyhedron* **12**, 2431–46 (1993) and references cited therein. M. DRIESS, *Adv. Organomet. Chem.* **39**, 193–229 (1996) — also deals with sila-arsenes containing Si$\equiv$As bonds).

origin (e.g. pp. 338 and below). For example, although the word "silicone" was coined by F. S. Kipping in 1901 to indicate the similarity in *formula* of Ph_2SiO with that of the ketone benzophenone, Ph_2CO, he stressed that there was no chemical resemblance between them and that Ph_2SiO was polymeric.[68] It is now recognized that the great thermal and chemical stability of the silicones derives from the strength both of the Si–C bonds and of the Si–O–Si linkages. Many general reviews of the vast subject of organosilicon chemistry are available (e.g. refs 1, 2, 69–74) and only some of the salient or topical features will be touched on here. An interesting subset comprises the carbosilanes, that is compounds with a skeleton of alternating C and Si atoms.[75] These include chains, rings and polycyclic compounds, many of which can be made on a multigram or even larger scale by controlled thermolysis or by standard organometallic syntheses.

Transient reaction species containing Si=C bonds have been known since about 1966 and can be generated thermally, photolytically, or even chemically. A decade later $Me_2Si{=}CHMe$

was isolated in low-temperature matrices[76] but, despite concerted and well-planned attempts over many years, it was not until 1981 that a stable silene was reported.[77] A. G. Brook and his group prepared 2-adamantyl-2-trimethylsiloxy-1,1-bis(trimethylsilyl)-1-silaethene as very pale yellow needles, mp 92°:

$$(Me_3Si)_3SiC(O)(C_{10}H_{15}) \underset{ether/h\nu}{\rightleftharpoons}$$

$$(Me_3Si)_2Si{=}C(OSiMe_3)(adamantyl)$$
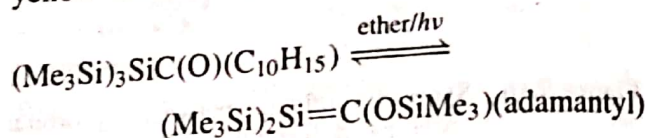
The solid silaethene was stable indefinitely at room temperature in the absence of air or other reagents but in solution it slowly reverted (over several days) to the isomeric acylsilane starting material. An X-ray analysis confirmed the structure and revealed a short >Si=C< bond (176.4 pm, cf. 187–191 pm for single-bonded Si–C) and a planar disposition of *ipso* atoms, the two planes being slightly twisted with respect to each other (14.6°). The use of bulky groups to enhance the stability of the silaethene is also notable, though this is not a necessary feature, at least at the Si centre, since $Me_2Si{=}C(SiMe_3)(SiMeBu^t_2)$ is stable as colourless crystals at room temperature (>Si=C< distance 170.2 pm, Si–C 189.0 pm and a planar $C_2Si{=}CSi_2$ skeleton).[78] The not unrelated planar heterocyclic compounds silabenzene, C_5SiH_6,[15] and silatoluene, C_5H_5SiMe,[16] should also be recalled.

Disilenes, containing the grouping >Si=Si<, can be isolated as thermally stable yellow or orange crystalline compounds provided that the substituents are sufficiently large to prevent

68 F. S. Kipping and L. L. Lloyd, *J. Chem. Soc. (Transactions)* **79**, 449–59 (1901).

69 G. Wilkinson, F. G. A. Stone and E. W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, Vol. 2 (1982): D. A. Armatage, Organosilanes, pp. 1–203; T. J. Barton, Carbocyclic Silanes, pp. 205–303; F. O. Stark, J. R. Falender and A. P. Wright, Silicones, pp. 305–63; R. West, Organopolysilanes, pp. 365–97.

70 S. Pawlenko, *Organosilicon Chemistry*, de Gruyter, Berlin, 1986, 186 pp.

71 J. Y. Corey, E. J. Corey and P. P. Gasper (eds.), *Silicon Chemistry*, Ellis Horwood, Chichester, 1988, 565 pp.

72 M. Zeldin, K. J. Wynne and H. R. Alcock (eds.), *Inorganic and Organometallic Polymers*, ACS Symposium Series **360** (1988) 512 pp.

73 S. Patai and Z. Rappoport (eds.), *The Chemistry of Organic Silicon Compounds* (2 vols.), Wiley, Chichester, 1989, 892 pp. and 1668 pp.

74 N. Auner, W. Ziche and R. West, *Heteroatom Chemistry* **2**, 335–55 (1991). This is a very readable account of current work, and includes an update of ref. 73 with a further 222 references.

75 G. Fritz, *Angew. Chem. Int. Edn. Engl.* **26**, 1111–32 (1987).
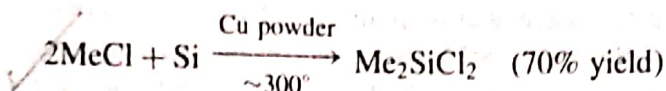
76 O. L. Chapman, C.-C. Chang, J. Kole, M. E. Jung, J. A. Lowe, T. J. Barton and M. L. Tumey, *J. Am. Chem. Soc.* **98**, 7844–6 (1976). M. R. Chedekel, M. Skoglund, R. L. Kreeger and H. Shechter, *ibid.*, 7846–8 (1976).

77 A. G. Brook, F. Abdesaken, B. Guterkunst, G. Guterkunst and R. K. Kallury, *J. Chem. Soc., Chem. Commun.*, 191–2 (1981). A. G. Brook and 8 others, *J. Am. Chem. Soc.*, **104**, 5667–72 (1982). For the most recent review of the chemistry of silenes see A. G. Brook and M. A. Brook, *Adv. Organomet. Chem.*, **39**, 71–158 (1996).

78 N. Wiberg, G. Wagner and G. Müller, *Angew. Chem. Int. Edn. Engl.* **24**, 229–31 (1985). See also N. Wiberg *et al.*, *Organometallics* **6**, 32–5 and 35–41 (1987).

polymerization (e.g. mesityl, *t*-butyl, etc.)[79] The first such compound, Si_2Mes_4, was isolated in 1981 as orange crystals, mp 176°, following photolysis of the trisilane $SiMes_2(SiMe_3)_2$.[80] The Si=Si distance in several such compounds falls in the range 214–216 pm, which is about 10% shorter than the normal single-bonded Si–Si distance. Disilenes are chemically very reactive. Halogens and HX molecules give 1,2-addition products, e.g. $Mes_2Si(Cl)Si(Cl)Mes_2$, whilst aldehydes and ketones undergo [2 + 2] cyclo-addition reactions to give 1,2,3-oxadisilenanes, $\overline{OSi(Mes)_2Si(Mes)_2CHR}$. Controlled oxidation gives predominantly the 1,2-dioxetane $\overline{OSiR_2SiR_2O}$ (80%), plus the 1,3-cyclodisiloxane $\overline{OSiR_2OSiR_2}$ as a minor product. Numerous other novel heterocyles have been prepared by controlled reactions of disilenes with chalcogens, N_2O, P_4 and organic nitro-, nitroso-, azo- and azido-compounds.[81] Transition metal complexes can give η^2-disilene adducts such as $[Pt(PR_3)_2)(\eta^2\text{-}Si_2Mes_4)]$.[79,82]

Another fertile area of current interest is the synthesis of stable homocyclic polysilane derivatives.[83] Typical examples are cyclo-$(SiMe_2)_7$,[84] (cyclo-Si_5Me_9)-$(SiMe_2)_n$-(cyclo-Si_5Me_9), $n = 2$–5,[85] and several new permethylated polycylic silanes such as the colourless crystalline compounds bicyclo[3.2.1]-Si_8Me_{14} (mp 245°), bicyclo[3.3.1]-Si_9Me_{16} (mp $\geq 330°$) and bicyclo[4.4.0]-$Si_{10}Me_{18}$ (mp 165°.[86] Analogues of cubane and tetrahedrane have also been synthesized. Thus, the one-step condensation of $Br_2RSiSiRBr_2$ or even $RSiBr_3$ with Na in toluene at 90° gave yields of up to 72% of the cubane $(SiR)_8$ (R = $SiMe_2Bu^t$) as bright yellow, air-sensitive crystals which are stable up to at least 400°C.[87] The synthesis of a molecular tetrasila-tetrahedrane has also finally been achieved by the following ingenious route (R = $SiBu^t_3$):[88]

$$2SiH_2Cl_2 \xrightarrow{2NaR} 2RSiH_2Cl \xrightarrow{2Na} RSiH_2SiH_2R$$
$$\longrightarrow RSiBr_2SiBr_2R$$

$$2RSiBr_2SiBr_2R + 4NaR \longrightarrow$$
$$Si_4R_4 + 4RBr + 4NaBr$$

The product, $Si_4(SiBu^t_3)_4$, forms intensely orange crystals that are stable to heat, light, water and air, and do not melt below 350°. The Si–Si distances within the *closo*-Si_4 cluster are 232–234 pm and the *exo* Si–Si distances are slightly longer, 235–237 pm (cf. Si–Si 235.17 in crystalline Si). Comparison with the *closo*-anion Si_4^{4-}, which occurs in several metal silicides (p. 337) and is isoelectronic with the P_4 molecule, is also appropriate.

There are three general methods for forming Si–C bonds. The most convenient laboratory method for small-scale preparations is by the reaction of $SiCl_4$ with organolithium, Grignard or organoaluminium reagents. A second attractive route is the hydrosilylation of alkenes, i.e. the catalytic addition of Si–H across C=C double bonds; this is widely applicable except for the crucially important methyl and phenyl silanes. Industrially, organosilanes are made by the direct reaction of RX or ArX with a fluidized bed of Si in the presence of about 10% by weight of metallic Cu as catalyst (cf. the direct preparation of organo compounds of

[79] R. WEST, *Angew. Chem. Int. Edn. Engl.* **26** 1201–11 (1987). R. OKAZAKI and R. WEST, *Adv. Organomet. Chem.* **39**, 232–73 (1996).

[80] R. WEST, M. J. FINK and J. MICHL, *Science* **214**, 1343–4 (1981). See also B. D. SHEPHERD, C. F. CAMPANA and R. WEST, *Heteroatom Chemistry*, **1**, 1–7 (1990).

[81] R. WEST, in R. STEUDEL (ed.), *The Chemistry of Inorganic Ring Systems*, Elsevier, Amsterdam, 1992, pp. 35–50. See also M. WEIDENBRUCH, *ibid.*, pp. 51–74.

[82] C. ZYBILL, *Topics in Current Chemistry* **160**, 1–45 (1992).

[83] E. HENGGE and H. STÜGER, in H. W. ROESKY (ed.), *Rings, Clusters and Polymers of Main Group and Transition Metals*, Elsevier, Amsterdam, 1989, pp. 107–38.

[84] F. SHAFIEE, J. R. DAMEWOOD, K. J. HALLER and R. WEST, *J. Am. Chem. Soc.* **107**, 6950–6 (1985).

[85] E. HENGGE and P. K. JENKNER, *Z. anorg. allg. Chem.* **560**, 27–34 (1988).

[86] E. HENGGE and P. K. JENKNER, *Z. anorg. allg. Chem.* **606**, 97–104 (1991).

[87] H. MATSUMOTO, K. HIGUCHI, Y. HOSHINO, H. KOIKE, Y. NAOI and Y. NAGAI, *J. Chem. Soc., Chem. Commun.*, 1083–4 (1988).

[88] N. WIBERG, C. M. M. FINGER and K. POLBORN, *Angew. Chem. Int. Edn. Engl.* **32**, 1054–6 (1993).
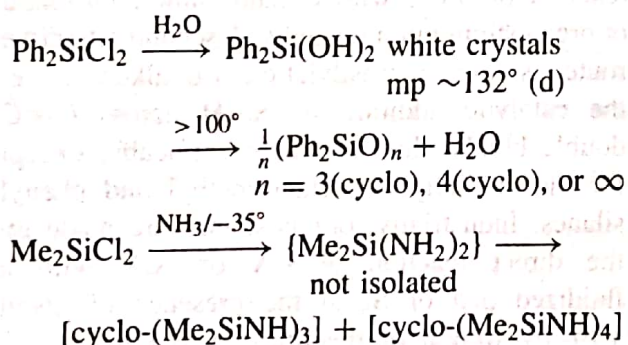
Ge. Sn, and Pb, pp. 396ff). The method was patented by E. G. Rochow in 1945 and ensured the commercial viability of the now extensive silicone industry.[2,69,72]

$$2MeCl + Si \xrightarrow[\sim 300°]{\text{Cu powder}} Me_2SiCl_2 \quad (70\% \text{ yield})$$

By-products are $MeSiCl_3$ (12%) and Me_3SiCl (5%) together with 1–2% each of $SiCl_4$, $SiMe_4$, $MeSiHCl_2$, etc. Relative yields can readily be altered by modifying the reaction conditions or by adding HCl (which increases $MeSiHCl_2$ and drastically reduces Me_2SiCl_2). The overall reaction is exothermic and heat must be removed from the fluidized bed. Because of their very similar bps, careful fractionation is necessary if pure products are required: Me_3SiCl 57.7°, Me_2SiCl_2 69.6°, $MeSiCl_3$ 66.4°. Mixtures of ethylchlorosilanes or phenylchlorosilanes (or their bromo analogues) can be made similarly. All these compounds are mobile, volatile liquids (except Ph_3SiCl, mp 89°, bp 378°).

Innumerable derivatives have been prepared by the standard techniques of organic chemistry.[2,69–75] The organosilanes tend to be much more reactive than their carbon analogues, particularly towards hydrolysis, ammonolysis, and alcoholysis. Further condensation to cyclic oligomers or linear polymers generally ensues, e.g.:

$$Ph_2SiCl_2 \xrightarrow{H_2O} Ph_2Si(OH)_2 \text{ white crystals}$$
$$\text{mp} \sim 132° \text{ (d)}$$
$$\xrightarrow{>100°} \tfrac{1}{n}(Ph_2SiO)_n + H_2O$$
$$n = 3(\text{cyclo}), 4(\text{cyclo}), \text{ or } \infty$$

$$Me_2SiCl_2 \xrightarrow{NH_3/-35°} \{Me_2Si(NH_2)_2\} \longrightarrow$$
$$\text{not isolated}$$
$$[\text{cyclo-}(Me_2SiNH)_3] + [\text{cyclo-}(Me_2SiNH)_4]$$

For both economic and technical reasons, commercial production of such polymers is almost entirely restricted to the methyl derivatives (and to a lesser extent the phenyl derivatives) and hydrolysis of the various methylchlorosilanes has, accordingly, been much studied. Hydrolysis of Me_3SiCl yields trimethylsilanol as a volatile liquid (bp 99°); it is noticeably more acidic than

the corresponding $Bu'OH$ and can be converted to its Na salt by aqueous NaOH (12M). Condensation gives hexamethyldisiloxane which has a very similar bp (100.8°):

$$2Me_3SiCl \xrightarrow[(-2HCl)]{+2H_2O} 2Me_3SiOH \xrightarrow{-H_2O} [O(SiMe_3)_2]$$
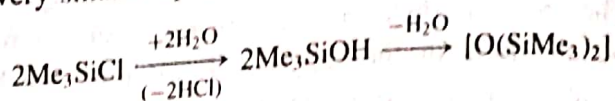
Hydrolysis of Me_2SiCl_2 usually gives high polymers, but under carefully controlled conditions leads to cyclic dimethylsiloxanes $[(Me_2SiO)_n]$ ($n = 3, 4, 5, 6$). Linear siloxanes have also been made by hydrolysing Me_2SiCl_2 in the presence of varying amounts of Me_3SiCl as a "chain-stopping" group, i.e. $[Me_3SiO(Me_2SiO)_xSiMe_3]$ ($x = 0, 1, 2, 3, 4$), etc. Cross-linking is achieved by hydrolysis and condensation in the presence of $MeSiCl_3$ since this generates a third Si–O function in addition to the two required for polymerization:

$$Me_3SiCl \xrightarrow{H_2O} Me_3Si-O- \quad \text{terminal group}$$

$$Me_2SiCl_2 \xrightarrow{H_2O} -O-SiMe_2-O-$$
$$\text{chain-forming group}$$

$$MeSiCl_3 \xrightarrow{H_2O} MeSi(-O-)_3$$
$$\text{branching and bridging group}$$
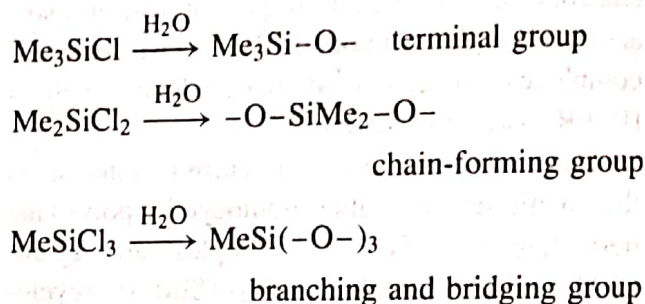
Comparison with the mineral silicates is instructive since there is a 1:1 correspondence between the two sets of compounds, the methyl groups in the silicones being replaced by the formally iso-electronic O^- in the silicates (see p. 366). This reminds us of the essentially covalent nature of the Si–O–Si linkage, but the analogy should not be taken to imply identity of structures in detail, particularly for the more highly condensed polymers. Some aspects of the technology of silicones are summarized in the concluding Panel.

While siloxanes and silicones are generally regarded as being unreactive, it is well to remember that they do indeed react with fluorinating agents and with concentrated hydroxide solutions. In certain cases they can even be employed as mild selective reagents for specific syntheses. For example, $(Me_3Si)_2O$ is a useful reagent for the convenient high-yield

Silicone Polymers[1,2]

Silicones have good thermal and oxidative stability, valuable resistance to high and low temperatures, excellent water repellency, good dielectric properties, desirable antistick and antifoam properties, chemical inertness, prolonged resistance to ultraviolet irradiation and weathering, and complete physiological inertness. They can be made as fluids (oils), greases, emulsions, elastomers (rubbers) and resins.
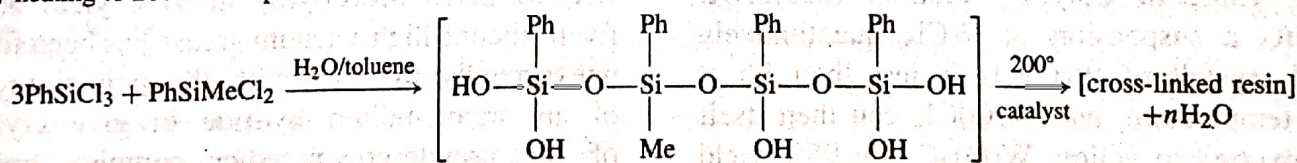
Silicone oils are made by shaking suitable proportions of $[O(SiMe_3)_2]$ and $[cyclo-(Me_2SiO)_4]$ with a small quantity of 100% H_2SO_4; this randomizes the siloxane links by repeatedly cleaving the Si–O bonds to form HSO_4 esters and then reforming new Si–O bonds by hydrolysing the ester group:

$$\equiv Si-O-Si\equiv + H_2SO_4 \longrightarrow \equiv Si-O-SO_3H + \equiv Si-OH$$

$$\equiv Si-OH + HO_3S-O-Si\equiv \longrightarrow \equiv Si-O-Si\equiv + H_2SO_4$$
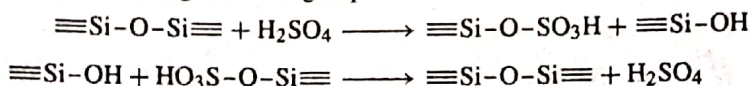
The molecular weight of the resulting polymer depends only on the initial proportion of the chain-ending groups ($Me_3SiO–$ and $Me_3Si–$) and the chain-building groups ($–Me_2SiO–$) from the two components. Viscosity at room temperature is typically in the range 50–300 000 times that of water and it changes only slowly with temperature. These liquids are used as dielectric insulating media, hydraulic oils and compressible fluids for liquid springs. Pure methylsilicone oils are good lubricants at light loads but cannot be used for heavy-duty steel gears and shafts since they contain no polar film-forming groups and so are too readily exuded under high pressure. The introduction of some phenyl groups improves performance, and satisfactory greases can be made by thickening methyl phenyl silicone oil with Li soaps. Other uses are as heat transfer media in heating baths and as components in car polish, sun-tan lotion, lipstick and other cosmetic formulations. Their low surface tension leads to their extensive use as antifoams in textile dyeing, fermentation processes and sewage disposal: about 10^{-2} to $10^{-4}\%$ is sufficient for these applications. Likewise their complete non-toxicity allows them to be used to prevent frothing in cooking oils, the processing of fruit juices and the production of potato crisps.

Silicone elastomers (rubbers) are reinforced linear dimethylpolysiloxanes of exceedingly high molecular weight ($5 \times 10^5 - 10^7$). The reinforcing agent, without which the viscous gum is useless, is usually fumed silica (p. 345). Polymerization can be acid-catalysed but KOH produces a rubber with superior physical properties; in either case scrupulous care must be taken to avoid the presence of precursors of chain-blocking groups [Me_3Si-O-] or cross-linking groups [$MeSi(-O-)_3$]. The reinforced silicone rubber composition can be "vulcanized" by oxidative cross-linking using 1–3% of benzoyl peroxide or similar reagents; the mixture is heated to 150° for 10 min at the time of pressing or moulding and then cured for 1–10 h at 250°. Alternatively, and more elegantly, the process can be achieved at room temperature or slightly above by incorporating a small controlled concentration of Si–H groups which can be catalytically added across pre-introduced $Si-CH\equiv CH_2$ groups in adjacent chains. Again, the cross-linking of 1-component silicone rubbers containing acetoxy groups can be readily effected at room temperature by exposure to moisture: Such rubbers generally have 1 cross-link for every 100–1000 Si atoms and are unmatched by any other synthetic or natural rubbers in retaining their inertness, flexibility, elasticity and strength up to 250° and down to −100°. They find use in cable-insulation sleeving, static and rotary seals, gaskets, belting, rollers, diaphragms, industrial sealants and adhesives, electrical tape insulation, plug-and-socket connectors, oxygen masks, medical tubing, space suits, fabrication of heart-valve implants, etc. They are also much used for making accurate moulds and to give rapid, accurate and flexible impressions for dentures and inlays.

Silicone resins are prepared by hydrolysing phenyl substituted dichloro- and trichloro-silanes in toluene. The Ph groups increase the heat stability, flexibility, and processability of the resins. The hydrolysed mixture is washed with water to remove HCl and then partly polymerized or "bodied" to a carefully controlled stage at which the resin is still soluble. It is in this form that the resins are normally applied, after which the final cross-linking to a 3D siloxane network is effected by heating to 200° in the presence of a heavy metal or quaternary ammonium catalyst to condense the silanol groups, e.g.:

$$3PhSiCl_3 + PhSiMeCl_2 \xrightarrow{H_2O/toluene} \begin{bmatrix} & Ph & Ph & Ph & Ph & \\ & | & | & | & | & \\ HO- & Si-O-Si-O-Si-O-Si & -OH \\ & | & | & | & | & \\ & OH & Me & OH & OH & \end{bmatrix} \xrightarrow[\text{catalyst}]{200°} \text{[cross-linked resin]} + nH_2O$$

a typical intermediate species

Silicone resins are used in the insulation of electrical equipment and machinery, and in electronics as laminates for printed circuit boards; they are also used for the encapsulation of components such as resistors and integrated circuits by means of transfer moulding. Non-electrical uses include high-temperature paints and the resinous release coatings familiar on domestic cooking ware and industrial tyre moulds. When one recalls the very small quantities of silicones needed in many of these individual applications, the global production figures are particularly impressive: they have grown from a few tonnes in the mid-1940s to over 100 000 tonnes in 1969 and an estimated production of 350 000 tonnes in 1982. About half of this is in the USA, distributed so that some 65–70% is as fluid silicones, 25–30% as elastomers, and 5–10% as resins. Over 1000 different silicone products are commercially available.

Orthosilicate $\left[\begin{array}{c} O^- \\ | \\ Si \\ / \ \\ O^- \quad O^- \end{array}\right]$ (with structure)

Tetramethylsilane Me_4Si

Disilicate $\left[O_3Si-O-SiO_3\right]$

Hexamethyl-disiloxane $Me_3Si-O-SiMe_3$

Pyroxenes (chain silicate structure)

Polydimethyl-siloxane (silicone oil)

Cyclic metasilicates

Cyclic dimethylsiloxane

Amphiboles

Methylsil-sesquioxane ladder polymer

Infinite sheet silicates

Siloxenes

Framework silicates

Silicone resins

preparation of oxyhalide derivatives of Mo and W.[89] Thus, in CH_2Cl_2 solution, $(Me_3Si)_2O$ converts a suspension of WCl_6 quantitatively to red crystals of $W(O)Cl_4$ in less than 1 h at room temperature, and $W(O)Cl_4$ can then itself be converted to yellow $W(O)_2Cl_2$ in 95% yield (light petroleum, 100°, overnight). Likewise,

$Mo(O)Cl_4$ when treated with $(Me_3Si)_2O$ in CH_2Cl_2 gives $Mo(O)_2Cl_2$ in 97% yield at r.t. Even silicone high-vacuum grease has been found unexpectedly to react with the potassium salt of an organoindium hydride to give crystals of the pseudo-crown ether complex [cyclo-$(Me_2SiO)_7K^+](K^+)_3[HIn(CH_2CMe_3)_3^-]_4$.[90]

[89] V. C. GIBSON, T. P. KEE and A. SHAW, *Polyhedron* **7**, 579–80 (1988).

[90] M. R. CHURCHILL, C. H. LAKE, S.-H. L. CHAO and O. T. BEACHLEY, *J. Chem. Soc., Chem. Commun.*, 1577–8 (1993).

four faces of the Pb_6 octahedron are capped by (μ_3-OEt) groups. This leads, to the over-all 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. $[Pb_6O_4(OEt)_4\{Nb(OEt)_5\}_4]$.

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:

$$Ph_3Si\text{–}H + LiR \longrightarrow Ph_3Si\text{–}R + LiH$$

(metathesis)

$$Ph_3Ge\text{–}H + LiR \longrightarrow Ph_3Ge\text{–}Li + RH$$

(metallation)

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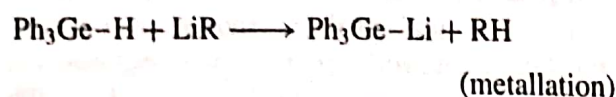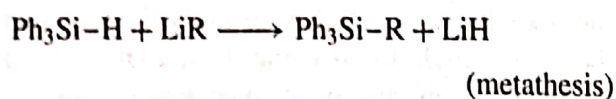
[86] C. ELSCHENBROICH and A. SALZER, *Organometallics*, VCH, Weinheim, 1989, pp. 115–46.

[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.).

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

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

(germoxane)

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

(germylcarbinol)
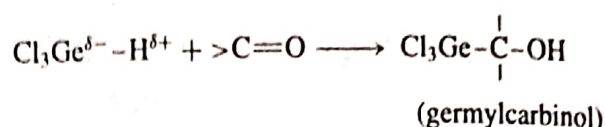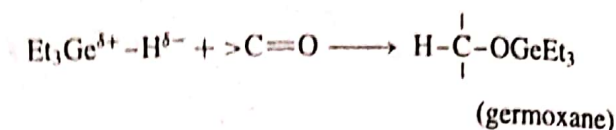
Preparative routes to organogermanium compounds parallel those for organosilicon compounds (p. 363) and most of the several thousand known organogermanes can be considered as derivatives of R_nGeX_{4-n} or Ar_nGeX_{4-n} where X = hydrogen, halogen, pseudohalogen, OR, etc. The compounds are colourless, 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.:

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

$$(\text{mp } -40°, \text{ bp } 140°)$$

$$Et_3GeBr + NaGePh_3 \xrightarrow{\text{liq NH}_3} NaBr$$
$$+ Et_3GeGePh_3 (\text{mp } 90°)$$

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

$$(\text{mp } 340°)$$

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

$$(\text{mp } 248°)$$
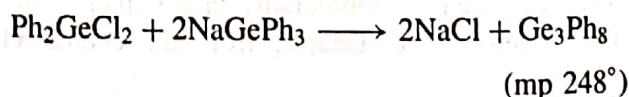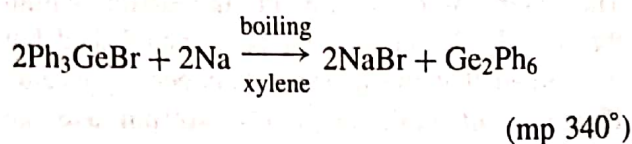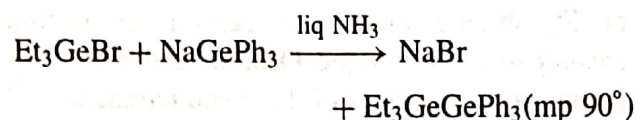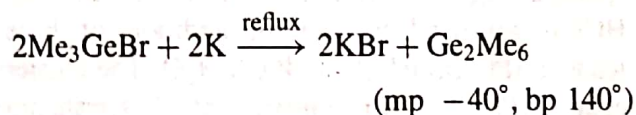
In general, the Ge–Ge bond is readily cleaved by Br_2 either at ambient or elevated temperatures but the compounds are stable to thermal cleavage at moderate temperatures. Ge_2R_6 compounds can even be distilled unchanged in air (like Si_2R_6 but unlike the more reactive Sn_2R_6) and are stable towards hydrolysis and ammonolysis.

Considerable recent attention has focused on the preparation, structure and stability of germenes ($>Ge=C<$), germylenes (R_2Ge:), 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]

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

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

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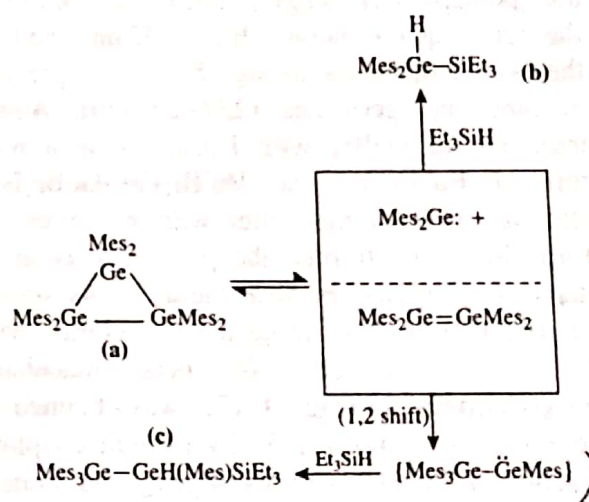
Polyhedral oligogermanes of varying complexity can be made by careful choice of the organo R group and the metal reductive coupling agent.[95] Thus, treatment of $\{(Me_3Si)_2CH\}GeCl_3$ with Li metal in thf gave thermochroic yellow-orange crystals of the hexamer $[Ge_6\{CH(SiMe_3)_2\}_6]$ which were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

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).
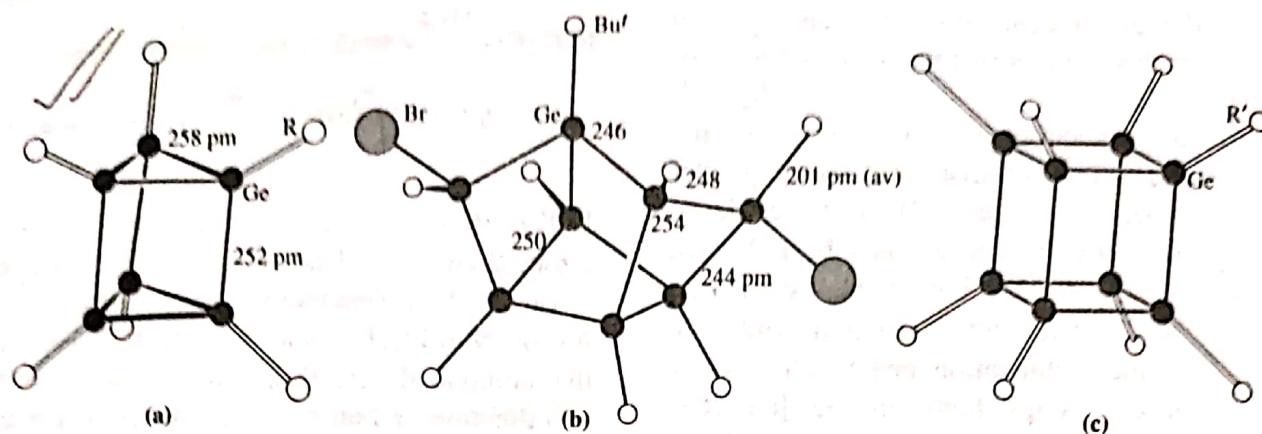
Figure 10.12 (a) Prismane structure of $[Ge_6\{CH(SiMe_3)_2\}_6]$ (for clarity only the *ipso* C atoms of the R groups are shown). (b) The tetracyclo structure of $[Ge_8Bu^t_8Br_2]$ with only the *ipso* C atoms of the Bu^t groups shown. (c) The cubane structure of $[Ge_8(CMeEt_2)_8]$ again with only 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$^t_2$GeBr$_2$ and Bu^{t}Br$_2$Ge–GeBr$_2$Bu^t, and treatment of this latter with an excess of Li/naphthalene afforded the polycyclic octagermane, Ge$_8$Bu$^t_8$Br$_2$, 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$_3$GeCl 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$_5$H$_5$ 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$_5$H$_5$ 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).

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[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).

(10)

(11)

(12)

(13)
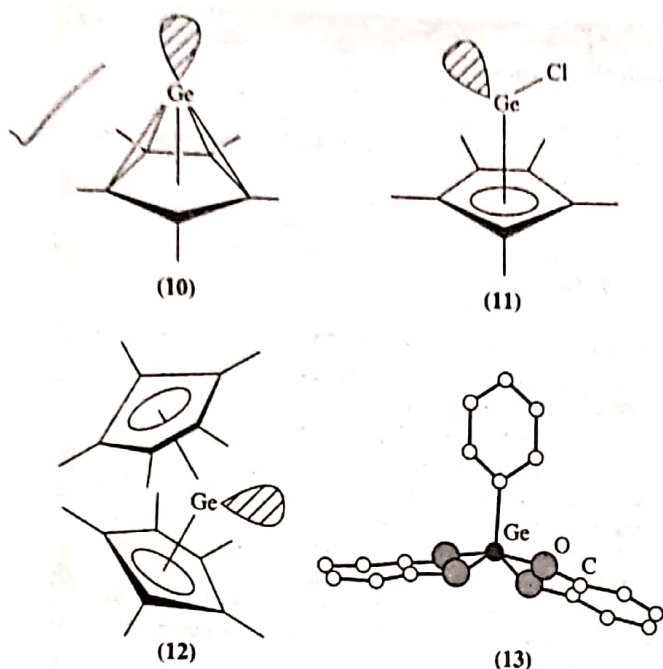
peralkyl-1-germa-2,3,4-trisilacyclobutanes.[102] Other variants include the novel telluradigerm-iranes, $Ar_2Ge-Te-GeAr_2$,[103] a yellow phospha-germirene $Bu^tC{=}P{-}GeR_2$ [mp. 89° for R = $(Me_3Si)_2CH-$],[104] and a germaphosphetene featuring a $GeCCP$ ring system.[105] The possibilities are clearly 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: $SnCl_4 + 4RMgCl \longrightarrow SnR_4$
$$+ 4MgCl_2 \text{ (also with } ArMgCl)$$

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

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

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 ($SnCl_4 + 4RCl \xrightarrow{8\ Na} SnR_4 + 8NaCl$). Conversion of SnR_4 to the partially halogenated species is readily achieved by scrambling reactions with $SnCl_4$. Reduction of R_nSnX_{4-n} with $LiAlH_4$ 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 $R_nSn^{IV}X_{4-n}$ ($n = 1-4$) and even compounds such as SnR_2 or $SnAr_2$ are in fact cyclic oligomers $(Sn^{IV}R_2)_x$ (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

[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 CH_3I and NEt_3, the yields were Me_2SnCl_2 (39%), $MeSnCl_3$ (6.6%), 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 organo-stannane 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 $[MeSn(4-anisyl)(1-naphthyl)-\{CH_2CH_2C(OH)Me_2\}]$.[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

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).
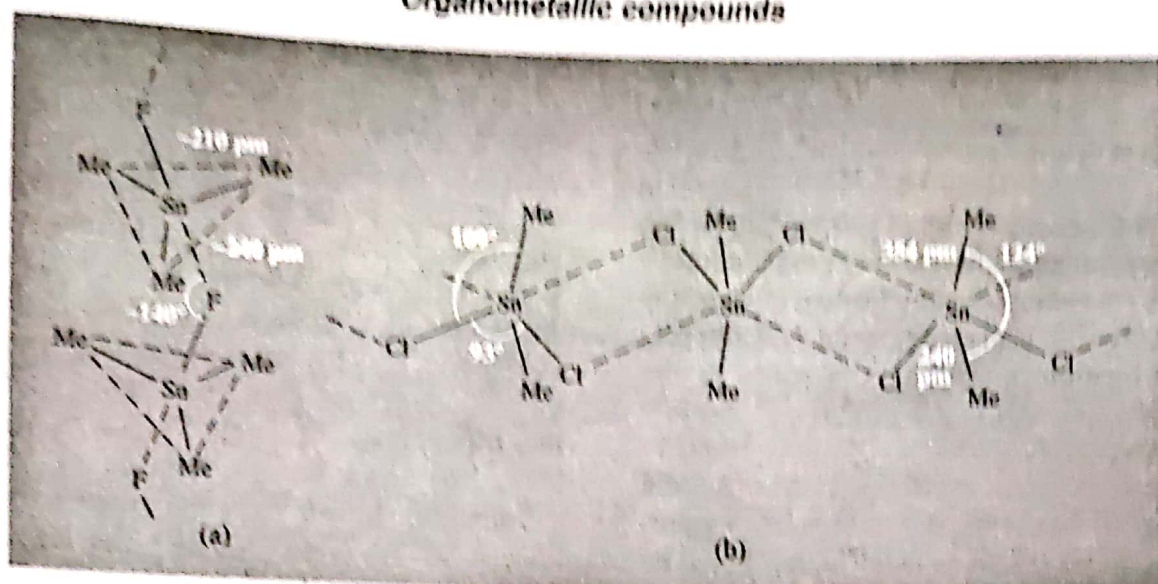
Figure 10.13 Crystal structure of (a) Me₃SnF, and (b) Me₂SnCl₂, showing tendency to polymerize via Sn—X···Sn bonds.

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, Ph₃SnF 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, Me₃SnF 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 (Me₃SnCl: 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 Ph₃SnCl and Ph₃SnBr feature monomeric molecules with 4-coordinate Sn atoms.

Me₂SnF₂ has a layer structure with octahedral Sn and *trans*-Me groups above and below the F-bridged layers as in SnF₄ (p. 381). The

weaker Cl bridging in Me₂SnCl₂ 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 R₃SnOR′ and R₂Sn(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-(Et₃SnO)₂C₆Cl₄ and [Mn(CO)₃{η⁵-C₅Ph₄(OSnPh₃)}].)

The converse of polymerization is heterolytic bond scission leading either to R₃Sn⁺ or R₃Sn⁻ 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:

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

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

$$R_3SnH + B(C_6F_5)_3 \longrightarrow [R_3Sn]^+[B(C_6F_5)_3H]^-$$
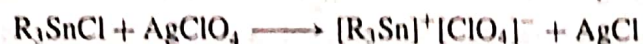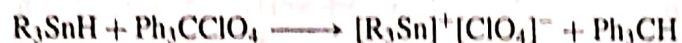
The highly ionic nature of these (presumably planar) species is revealed by cryoscopy, electrical conductance and the diagnostically large downfield ¹¹⁹Sn nmr chemical shift. Salts of the corresponding anionic species Ph₃Sn⁻ are easily generated by heating either Ph₃SnH or Sn₂Ph₆
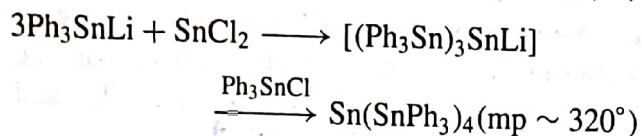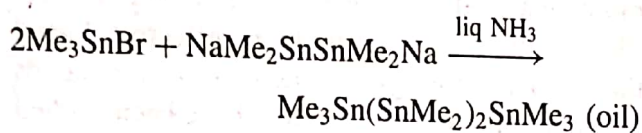
[111] D. TUDELA, E. GUTIÉRREZ-PUEBLA and A. MONGE, *J. Chem. Soc., Dalton Trans.*, 1069–71 (1992).

[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-crown-6)]$^+$[Ph$_3$Sn]$^-$ 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$_2$(η^5-dapt)] in which the two Et groups are axial and the planar 5-fold ligation (η^5-N$_3$O$_2$) is provided by the ligand (dapt), (H$_2$dapt = 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$_2$Me$_6$ (mp 23°) inflames in air at its bp (182°) and absorbs oxygen slowly at room temperature to give (Me$_2$Sn)$_2$O. Typical routes to higher polystannanes are:

$$2Me_3SnBr + NaMe_2SnSnMe_2Na \xrightarrow{\text{liq NH}_3}$$

$$Me_3Sn(SnMe_2)_2SnMe_3 \text{ (oil)}$$

$$3Ph_3SnLi + SnCl_2 \longrightarrow [(Ph_3Sn)_3SnLi]$$

$$\xrightarrow{Ph_3SnCl} Sn(SnPh_3)_4 (mp \sim 320°)$$

Unbranched chains up to at least Sn$_6$ are known, e.g. Ph$_3$Sn(Bu$_2^t$Sn)$_n$SnPh$_3$ ($n = 0$–4).[116] Cyclo-dialkyl stannanes(IV) can also be readily prepared, e.g. reaction of Me$_2$SnCl$_2$ with Na/liq NH$_3$ yields cyclo-(SnMe$_2$)$_6$ together with acyclic X(SnMe$_2$)$_n$X ($n = 12$–20). Yellow crystalline cyclo-(SnEt$_2$)$_9$ is obtained almost quantitatively when Et$_2$SnH$_2$, dissolved in toluene/pyridine, is catalytically dehydrogenated at 100° in the presence of a small amount of Et$_2$SnCl$_2$. Similarly, under differing conditions, the following have been prepared:[34] (SnEt$_2$)$_6$, (SnEt$_2$)$_7$, (SnBu$_2^t$)$_4$, (SnBu$_2^i$)$_4$, (SnBu$_2^i$)$_6$, 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$_5$R$_6$ (structure II, R = 2,6-C$_6$H$_3$Et$_2$).[118] This latter compound was formed in 13% yield as dark blue-violet crystals by the thermolysis of cyclo-Sn$_3$R$_6$ 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).
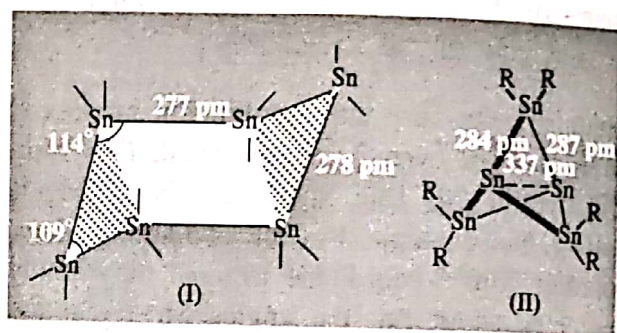

(True monomeric organotin(II) compounds have proved rather elusive. The cyclopentadienyl compound [Sn(η^5-C$_5$H$_5$)$_2$] (which is obtained as white crystals mp 105° from the reaction of NaC$_5$H$_5$ and SnCl$_2$ in thf) has a structure similar to that of germanocene (12 pp. 398-9) with the angle subtended 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(η^5-C$_5$Me$_5$)$_2$], suggesting that the angle is governed predominantly by electronic rather than steric factors. However, with the much more demanding η^5-C$_5$Ph$_5$ 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

[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, $[Sn(\eta^5-C_4Bu^t_2H_2N)_2]$, (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*-$[(\eta^5-C_5Me_5)Sn:]^+$, which is isostructural with *nido*-B_6H_{10} (p. 154), can be made in moderate yield by treating $[Sn(\eta^5-C_5Me_5)_2]$ with an ethereal solution of HBF_4. The product, $[(\eta^5-C_5Me_5)Sn]BF_4$, 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]

$$\textit{nido-}[(\eta^5\text{-}C_5Me_5)Sn]^+X^- + BI_3 \longrightarrow$$
$$\textit{nido-}[(\eta^5\text{-}C_5Me_5)BI]^+X^- + SnI_2$$
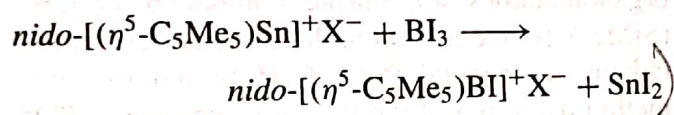
The stabilization of σ-bonded dialkyltin(II) compounds, $R_2Sn:$, (and also those of Ge and Pb) can be achieved by the use of bulky R groups. The first such compound, $[Sn\{CH(SiMe_3)_2\}_2]$, was prepared by direct reaction of $LiCH(SiMe_3)_2$ with $SnCl_2$ or $[Sn\{N(SiMe_3)_2\}_2]$ in ether, and was 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(SiMe₃)₂} groups.
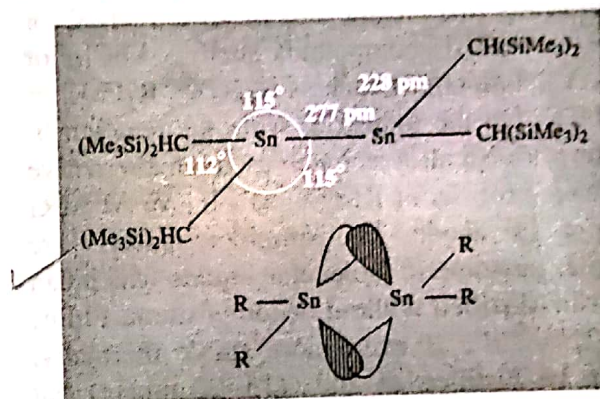
A synthetic strategy which ensures retention of the monomeric form of SnR_2 even in the crystalline state is to use functionalized R groups which contain a chelating substituent, e.g. by replacing the H atom in {−CH(SiMe₃)₂} with a 2-pyridyl group.[128]

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.

[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).
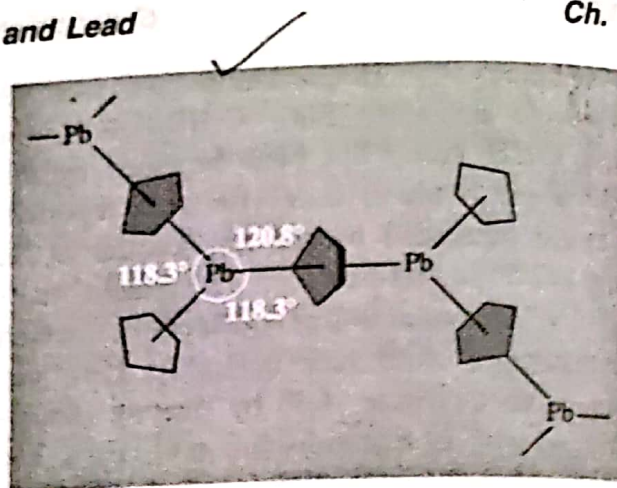
Lead[131]

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$'_2$PbX$_2$, R$'_3$PbX, or K$_2$PbCl$_6$. On the industrial scale the reaction of RX on a Pb/Na alloy is much used; an alternative is the electrolysis of RMgX, M^{I}BR$_4$, or M^{I}AlR$_4$ 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$_2$R$_6$ 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.

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}

[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.
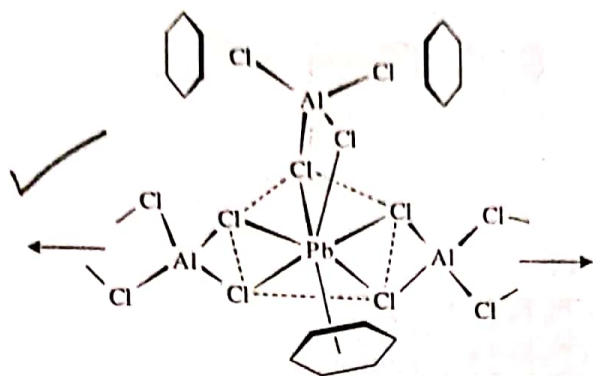

Figure 10.14 Schematic diagram of the chain structure of orthorhombic Pb(η^5-C$_5$H$_5$)$_2$. For the doubly coordinated C$_5$H$_5$ ring (shaded) Pb–C$_{av}$ is 306 pm, and for the "terminal" C$_5$H$_5$ ring Pb–C$_{av}$ is 276 pm; the Pb $\cdots$ Pb distance within the chain is 564 pm.

organometallics are purple compound Pb[CH(SiMe$_3$)$_2$]$_2$ (see refs on p. 403) and the cyclopentadienyl compound Pb(η^5-C$_5$H$_5$)$_2$ and its ring-methyl derivative. Like the Sn analogue (p. 402) Pb(η^5-C$_5$H$_5$)$_2$ 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$_5$H$_5$ is between 2 Pb and perpendicular to the Pb–Pb vector whilst the other C$_5$H$_5$ 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$_5$H$_5$ 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$_5$H$_5$ 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(η^5-C$_5$Me$_5$)$_2$] (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

[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]

[133] A. G. GASH, P. F. RODESILER and E. L. AMMA, *Inorg. Chem.* **13**, 2429-4 (1974). See also J. L. LEFFERTS, M. B. HOSSAIN, K. C. MOLLOY, D. VAN DER HELM and J. J. ZUCKERMAN, *Angew. Chem. Int. Edn. Engl.* **19**, 309-10 (1980).
[134] J. PARR, *Polyhedron* **16**, 551-66 (1997).