6.4.4 The chemistry of small boranes and their anions ($B_1 - B_4$)

Diborane occupies a special place because all the other boranes can be prepared from it (directly or indirectly); it is also one of the most studied and synthetically useful reagents in the whole of chemistry.[1,23] B_2H_6 gas can most conveniently be prepared in small quantities by the reaction of I_2 on $NaBH_4$ in diglyme [$(MeOCH_2CH_2)_2O$], or by the reaction of a solid tetrahydroborate with an anhydrous acid:

$$2NaBH_4 + I_2 \xrightarrow[\text{(98\% yield)}]{\text{diglyme}} B_2H_6 + 2NaI + H_2$$

$$2NaBH_4(c) + 2H_3PO_4(l) \xrightarrow{\text{(70\% yield)}}$$
$$B_2H_6(g) + 2NaH_2PO_4(c) + 2H_2(g)$$

When B_2H_6 is to be used as a reaction intermediate without the need for isolation or purification, the best procedure is to add Et_2OBF_3 to $NaBH_4$ in a polyether such as diglyme:

$$3NaBH_4 + 4Et_2OBF_3 \xrightarrow[25°]{\text{diglyme}}$$
$$2B_2H_6(g) + 3NaBF_4 + 4Et_2O$$

On an industrial scale gaseous BF_3 can be reduced directly with NaH at 180° and the product trapped out as it is formed to prevent subsequent pyrolysis:

$$2BF_3(g) + 6NaH(c) \xrightarrow{180°} B_2H_6(g) + 6NaF(c)$$

Some 200 tonnes per annum of B_2H_6 is produced commercially, worldwide. Care should be taken in all these reactions because B_2H_6 is spontaneously flammable; its heat of combustion $(-\Delta H°)$ is higher per unit weight of fuel than for any other substance except

H_2, BeH_2 and $Be(BH_4)_2$: $[-\Delta H°(B_2H_6) = 2165 \text{ kJ mol}^{-1} = 78.2 \text{ kJ g}^{-1}]$.

The pyrolysis of gaseous B_2H_6 in sealed vessels at temperatures above 100° is exceedingly complex and has only recently been fully elucidated.[24−27] The initiating step is the unimolecular equilibrium dissociation of B_2H_6 to give $2\{BH_3\}$, and the $\{BH_3\}$ then reacts with further B_2H_6 to give $\{B_3H_7\}$ plus H_2 in a concerted rate-controlling reaction via a $\{B_3H_9\}$ transition state. This explains the observed 1.5-order of the kinetics and also successfully interprets all other aspects of the initial reaction:

$$B_2H_6 \rightleftharpoons 2\{BH_3\}$$

$$\{BH_3\} + B_2H_6 \longrightarrow \{B_3H_7\} + H_2$$

In these and subsequent reactions, unstable intermediates that have but transitory existence are placed in curly brackets, {}.

The first stable intermediate, B_4H_{10}, is then formed followed by B_5H_{11}:

$$\{BH_3\} + \{B_3H_7\} \rightleftharpoons B_4H_{10}$$

$$B_2H_6 + \{B_3H_7\} \longrightarrow \{BH_3\} + B_4H_{10}$$
$$\rightleftharpoons B_5H_{11} + H_2$$

A complex series of further steps gives B_5H_9, B_6H_{10}, B_6H_{12}, and higher boranes, culminating in $B_{10}H_{14}$ as the most stable end product, together with polymeric materials BH_x and a trace of *conjuncto*-icosaboranes $B_{20}H_{26}$.

Careful control of temperature, pressure and reaction time enables the yield of the various intermediate boranes to be optimized. For example, B_4H_{10} is best prepared by storing B_2H_6 under pressure at 25° for 10 days; this gives a 15% yield and quantitative conversion according to the

[23] L. H. LONG, Chap. 22 in *Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. 5, Supplement 2, Part 2, pp. 52–162, Longmans, London, 1981.

[24] J. F. STANTON, W. N. LIPSCOMB and R. J. BARTLETT, *J. Am. Chem. Soc.* **111**, 5165–73 (1989).

[25] R. GREATREX, N. N. GREENWOOD and S. M. LUCAS, *J. Am. Chem. Soc.* **111**, 8721–2 (1989).

[26] N. N. GREENWOOD and R. GREATREX, *Pure Appl. Chem.* **59**, 857–68 (1987).

[27] N. N. GREENWOOD, *Chem. Soc. Revs.* **21**, 49–57 (1992).

overall reaction:

$$2B_2H_6 \longrightarrow B_4H_{10} + H_2$$

B_5H_{11} can be prepared in 70% yield by the reaction of B_2H_6 and B_4H_{10} in a carefully dimensioned hot/cold reactor at $+120°/-30°$:

$$2B_4H_{10} + B_2H_6 \rightleftharpoons 2B_5H_{11} + 2H_2$$

Alternative high-yield syntheses of these various boranes via hydride-ion abstraction from borane anions by BBr_3 and other Lewis acids have recently been devised[19] (see p. 162).

From the foregoing it is clear that {BH_3} is a fugitive reaction species: it exists only at exceedingly low concentrations but can be isolated and studied using matrix isolation techniques. Thus it can be generated by thermal dissociation of loosely bound 1:1 adducts with Lewis bases, such as $PF_3.BH_3$, and its reactions studied.[28] The relative stability of the adducts $L.BH_3$ has been determined from thermochemical and spectroscopic data and leads to the following unusual sequence:

$$PF_3 < CO < Et_2O < Me_2O < C_4H_8O < C_4H_8S$$

$$< Et_2S < Me_2S < py < Me_3N < H^-$$

Note that both PF_3 and CO form isolable although weak adducts, and that organic sulfide adducts are more stable than those of ethers, thereby showing that BH_3 has some class b acceptor ("soft acid") characteristics despite the absence of low-lying d orbitals on boron (see p. 909). The ligand H^- is a special case since it gives the symmetrical tetrahedral ion BH_4^-, isoelectronic with CH_4 and NH_4^+. Many other complexes of BH_3 with N, P, As, O, S etc. donor atoms are also known and they are readily formed by symmetrical homolytic (cleavage of the bridge bonds in B_2H_6. Occasionally, however, unsymmetrical (heterolytic) cleavage products result, perhaps partly as a result of steric effects,[29] e.g. NH_3, $MeNH_2$ and Me_2NH give unsymmetrical cleavage products whereas Me_3N gives the symmetrical cleavage product, $Me_3N.BH_3$ (see scheme below).

In addition to pyrolysis and cleavage reactions, B_2H_6 undergoes a wide variety of substitution, redistribution, and solvolytic reactions of which the following are representative. Gaseous HCl yields $B_2H_5Cl_t$ whereas Cl_2 (and F_2) give BX_3 directly even at low temperatures and high dilution. Methylation with $PbMe_4$ yields B_2H_5Me, but comproportionation with BMe_3 affords $Me_nB_2H_{6-n}$ ($n = 1$–4), the two BHB bridge bonds remaining intact. Hydrolysis gives the stoichiometric amount of $B(OH)_3$. The related alcoholysis reaction was much used in earlier times as a convenient means of total analysis

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[28] T. P. FEHLNER, Chap. 4 in ref. 9, pp. 175–96.

[29] S. G. SHORE, Chap. 3 in ref. 9, pp. 79–174.

Symmetrical
(homolytic)

Unsymmetrical
(heterolytic)

since the volatile $B(OMe)_3$ could readily be distilled off and determined while the number of moles of H_2 evolved equalled the number of H atoms in the borane molecule:

$$B_2H_6 + 6MeOH \longrightarrow 2B(OMe)_3 + 6H_2$$

This works well for all *nido-* and *arachno-*boranes but not for the *closo-*dianions, which are much less reactive. Reactions of B_2H_6 with NH_3 are complex and, depending on the conditions, yield aminodiborane, $H_2B(\mu\text{-}H)(\mu\text{-}NH_2)BH_2$, or the diammoniate of diborane, $[BH_2(NH_3)_2]$-$[BH_4]$ (p. 165); at higher temperatures the benzene analogue borazine, $(HNBH)_3$, results (see p. 210).

The remarkably facile addition of B_2H_6 to alkenes and alkynes in ether solvents at room temperatures was discovered by H. C. Brown and B. C. Subba Rao in 1956:

$$3RCH{=}CH_2 + \tfrac{1}{2}B_2H_6 \longrightarrow B(CH_2CH_2R)_3$$

This reaction, now termed hydroboration, has opened up the quantitative preparation of organoboranes and these, in turn, have proved to be of outstanding synthetic utility.[30,31] It was for his development of this field that H. C. Brown (Purdue) was awarded the 1979 Nobel Prize in Chemistry. Hydroboration is regiospecific, the boron showing preferential attachment to the least substituted C atom (anti-Markovnikov). This finds ready interpretation in terms of electronic factors and relative bond polarities (p. 144); steric factors also work in the same direction. The addition is stereospecific *cis (syn)*. Recent extensions of the methodology have encompassed the significant development of generalized chiral syntheses.[32]

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[30] H. C. BROWN, *Organic Syntheses via Boranes*, Wiley, New York, 1975, 283 pp., *Boranes in Organic Chemistry*, Cornell University Press, Ithaca, New York, 1972, 462 pp.

[31] D. J. PASTO, Solution reactions of borane and substituted boranes, Chap. 5 in ref. 7, pp. 197–222.

[32] H. C. BROWN and B. SINGARAM, *Pure Appl. Chem.* **59**, 879–94 (1987); H. C. BROWN and P. V. RAMACHANDRAN, *Pure Appl. Chem.* **63**, 307–16 (1991) and references cited therein.

Diborane reacts slowly over a period of days with metals such as Na, K, Ca or their amalgams and more rapidly in the presence of ether:

$$2B_2H_6 + 2Na \longrightarrow NaBH_4 + NaB_3H_8$$

$B_3H_8^-$ prepared in this way was the first polyborane anion (1955); it is now more conveniently made by the reaction

$$B_2H_6 + NaBH_4 \xrightarrow[100°]{\text{diglyme}} NaB_3H_8 + H_2$$

Alternatively, $BH_3.thf$ can be reduced by alkali metal amalgams (M = K, Rb, Cs) to give good yields of solvent-free products:[33]

$$2M/Hg + 4BH_3.thf \xrightarrow{thf} MBH_4 + MB_3H_8$$

Tetrahydroborates, $M(BH_4)_x$, were first identified in 1940 (M = Li, Be, Al) and since then have been widely exploited as versatile nucleophilic reducing agents which attack centres of low electron density (cf. electrophiles such as B_2H_6 and LBH_3 which attack electron-rich centres). The most stable are the alkali derivatives MBH_4: $LiBH_4$ decomposes above ~380° but the others (Na–Cs) are stable up to ~600°. MBH_4 are readily soluble in water and many other coordinating solvents such as liquid ammonia, amines, ethers ($LiBH_4$) and polyethers ($NaBH_4$). They can be prepared by direct reaction of MH with either B_2H_6 or BX_3 at room temperature though the choice of solvent is often crucial, e.g.:

$$2LiH + B_2H_6 \xrightarrow{Et_2O} 2LiBH_4$$

$$2NaH + B_2H_6 \xrightarrow{\text{diglyme}} 2NaBH_4$$

$$4LiH + Et_2OBF_3 \longrightarrow LiBH_4 + 3LiF + Et_2O$$

$$4NaH + BCl_3 \xrightarrow{Al_2Et_6} NaBH_4 + 3NaCl$$

These laboratory-scale syntheses are clearly unsuitable for large-scale industrial production;

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[33] T. G. HILL,   R. A. GODFROID,   J. P. WHITE   and S. G. SHORE, *Inorg. Chem.* **30**, 2952–4 (1991).

here the preferred route, introduced in the early 1960s is the Bayer process which uses borax (or ulexite), quartz, Na and H_2 under moderate pressure at 450–500°:[34]

$$(Na_2B_4O_7 + 7SiO_2) + 16Na + 8H_2$$

$$\longrightarrow 4NaBH_4 + 7Na_2SiO_3$$

The resulting mixture is extracted under pressure with liquid NH_3 and the product obtained as a 98% pure powder (or pellets) by evaporation. An alternative route is:

$$B(OMe)_3 + 4NaH \xrightarrow{250-270°} NaBH_4 + 3NaOMe$$

The resulting mixture is hydrolysed with water and the aqueous phase extracted with Pr^iNH_2.

Worldwide production of $NaBH_4$ is now about 3000 tonnes per annum (1990) and the price for powdered $NaBH_4$ in 1991 was \$48.39/kg.

Reaction of MBH_4 with electronegative elements is also often crucially dependent on the solvent and on the temperature and stoichiometry of reagents. Thus $LiBH_4$ reacts with S at $-50°$ in the presence of Et_2O to give $Li[BH_3SH]$, whereas at room temperature the main products are Li_2S, $Li[B_3S_2H_6]$, and H_2; at $200°$ in the absence of solvent $LiBH_4$ reacts with S to give $LiBS_2$ and either H_2 or H_2S depending on whether S is in excess. Similarly, MBH_4 react with I_2 in cyclohexane at room temperature to give BI_3, HI and MI, whereas in diglyme B_2H_6 is formed quantitatively (p. 164).

The product of reaction of BH_4^- with element halides depends on the electropositivity of the element. Halides of the electropositive elements tend to form the corresponding $M(BH_4)_x$, e.g. M = Be, Mg, Ca, Sr, Ba; Zn, Cd; Al, Ga, Tl^I; lanthanides; Ti, Zr, Hf and U^{IV}. Halides of the less electropositive elements tend to give the hydride or a hydrido-complex since the BH_4 derivative is either unstable or non-existent: thus $SiCl_4$ gives SiH_4;

PCl_3 and PCl_5 give PH_3; Ph_2AsCl gives Ph_2AsH; $[Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl]$ gives $[Fe(\eta^5\text{-}C_5H_5)(CO)_2H]$, etc.

A particularly interesting reaction (and one of considerable commercial value in the BOROL process for the *in situ* bleaching of wood pulp) is the production of dithionite, $S_2O_4^{2-}$, from SO_2:

$$NaBH_4 + 8NaOH + 8SO_2 \xrightarrow{90\% \text{ yield}}$$

$$4Na_2S_2O_4 + NaBO_2 + 6H_2O$$

In reactions with organic compounds, $LiBH_4$ is a stronger (less selective) reducing agent than $NaBH_4$ and can be used, for example, to reduce esters to alcohols. $NaBH_4$ reduces ketones, acid chlorides and aldehydes under mild conditions but leaves other functions (such as $-CN$, $-NO_2$, esters) untouched; it can be used as a solution in alcohols, ethers, dimethylsulfoxide, or even aqueous alkali (pH > 10). Perhaps the classic example of its selectivity is shown below where an aldehyde group is hydrogenated in high yield without any attack on the nitro group, the bromine atom, the olefinic bond, or the thiophene ring:

Industrial interest in $LiBH_4$, and particularly $NaBH_4$, stems not only from their use as versatile reducing agents for organic functional groups and their use in the bleaching of wood pulp, but also for their application in the electroless (chemical) plating of metals. Traditionally, either sodium hypophosphite, NaH_2PO_2, or formaldehyde have been used (as in the silvering of glass), but $NaBH_4$ was introduced on an industrial scale in the early 1960s, notably for the deposition of Ni on metal or non-metallic substrates; this gives corrosion-resistant, hard, protective coatings, and is also useful for metallizing plastics prior to

^{34} R. WADE, in R. THOMPSON (ed.), *Speciality Inorganic Chemistry*, Royal Soc. Chem., London, 1981, pp. 25–58; see also *Kirk–Othmer Encyclopedia of Chemical Technology*, 4th edn., John Wiley, New York, 1992, Vol. 4, pp. 490–501.

further electroplating or for depositing contacts in electronics. Chemical plating also achieves a uniform thickness of deposit independent of the geometric shape, however complicated.

The BH_4^- ion is essentially non-coordinating in its alkali metal salts. However, despite the fact that it is isoelectronic with methane, BH_4^- has been found to act as a versatile ligand, forming many coordination compounds by means of 3-centre B–H→M bonds to somewhat less electropositive metals.[35-37] Indeed, BH_4^-

affords a rare example of a ligand that can act in at least 6 coordination modes: η^1, η^2, η^3, $\mu(\eta^2,\eta^2)$, $\mu(\eta^3)$ and $\mu(\eta^4)$. Such complexes are usually readily prepared by reacting the corresponding (or closely related) halides with BH_4^- in what are essentially ligand replacement reactions. Some examples follow:

η^1: $[Cu(\eta^1\text{-}BH_4)(PMePh_2)_3]$ (see   Fig. 6.14a); $[Cu(\eta^1\text{-}BH_4)\{MeC(CH_2PPh_2)_3\}]$; $[FeH(\eta^1\text{-}BH_4)\text{-}$

[35] B. D. JAMES and M. G. H. WALLBRIDGE, *Prog. Inorg. Chem.* **11**, 99–231 (1970).

[36] P. A. WEGNER, Chap. 12 in ref. 9, pp. 431–80.
[37] T. J. MARKS and J. R. KOLB, *Chem. Rev.* **77**, 263–93 (1977).

(a) $[Cu^I(\eta^1\text{-}BH_4)(PMePh_2)_3]$

(b) $[Cu^I(\eta^2\text{-}BH_4)(PPh_3)_2]$

(c) $[Zr^{IV}(\eta^3\text{-}BH_4)_4]$

(d) $[\{RuH(tripod)\}_2\,(\mu{:}\eta^2,\eta^2\text{-}BH_4)]^+$

Figure 6.14   Examples of the various coordination modes of BH_4^- (continued on facing page).

(e) $[Co(\mu:\eta^3\text{-}BH_4)_2\{(\mu\text{-}Ph_2P(CH_2)_5PPh_2\}]_2$

(f) $[Ce(\mu:\eta^4\text{-}BH_4)(\eta^5\text{-}C_5H_3Bu^t_2)]_2$

Figure 6.14   continued

(dmpe)] (dmpe = $Me_2PCH_2CH_2PMe_2$); [*trans*-$V(\eta^1\text{-}BH_4)_2$ (dmpe)$_2$]; (also $B_2H_7^-$, i.e. [$BH_3(\eta^1$-$BH_4)]^-$)

η^2: [$Al(\eta^2\text{-}BH_4)_3$] (see p. 230); [$Cu(\eta^2\text{-}BH_4)$-$(PPh_3)_2$] (Fig. 6.14b); [$Ti^{III}(\eta^2\text{-}BH_4)_3$(dme)] (dme = 1,2-dimethoxyethane); [$Sc(\eta^2\text{-}BH_4)(\eta^5$-$Cp^{II})_2$] ($Cp^{II}$ = {$C_5H_3(SiMe_3)_2$}); [$Y(\eta^2\text{-}BH_4)$-$(\eta^5\text{-}Cp^{II})_2$(thf)]

η^3: [$M(\eta^3\text{-}BH_4)_4$] (M = Zr, Hf, Np, Pu; see Fig. 6.14c); [$Ln(\eta^3\text{-}BH_4)(\eta^5\text{-}Cp^{II})_2$(thf)] (Ln = La, Pr, Nd, Sm); [$U^{IV}(\eta^3\text{-}BH_4)_3(\eta^5\text{-}C_5H_5)$]

$\mu(\eta^2,\eta^2)$: [{RuH(tripod)}$_2(\mu:\eta^2,\eta^2\text{-}BH_4)]^+$ (Fig. 6.14d)

$\mu(\eta^3)$: [$Co(\mu:\eta^3\text{-}BH_4)\{\mu\text{-}Ph_2P(CH_2)_5PPh_2\}]_2$ (Fig. 6.14e); [(tmeda)Li-$\mu(\eta^3\text{-}BH_4)]_2$ (tmeda = tetramethylethylenediamine)

$\mu(\eta^4)$: [$Ce(\mu:\eta^4\text{-}BH_4)(\eta^5\text{-}C_5H_3Bu^t_2)]_2$ (Fig. 6.14f)

Many complexes have more than one coordination mode of BH_4^- featured in their structure, e.g. [$U^{III}(\eta^2\text{-}BH_4)(\eta^3\text{-}BH_4)_2$(dmpe)$_2$]. Likewise, whereas [$M(BH_4)_4$] are monomeric 12-coordinate complexes for M = Zr, Hf, Np, Pu, they are polymeric for M = Th, Pa, U: the coordination number rises to 14 and each metal centre is coordinated by two η^3-BH_4^- and four bridging η^2-BH_4^- groups. It is clear that among the factors which determine the mode adopted are the size of the metal atom and the steric requirements of the co-ligands. Many of the complexes

are fluxional on an nmr timescale in solution; indeed, this property of fluxionality, which has been increasingly recognized to occur in many inorganic and organometallic systems, was first observed (1955) on the tris-bidentate complex [$Al(\eta^2\text{-}BH_4)_3$].[38]

The $B_3H_8^-$ ion (p. 166) is a triangular cluster of C_s (rather than C_{2v}) symmetry (see Fig. 6.15a);[39] the bridging H_μ atoms are essentially in the B_3 plane with H_t above and below. While it has been conventional to represent the cluster bonding in terms of two BHB and one B–B bond (Fig. 6.15b), recent high-level computations[40] suggest the presence of a 3-centre BBB bond, as depicted approximately in Fig. 6.15c.

The *arachno*-anion $B_3H_8^-$ is the only binary triboron species that is stable at room temperature and above. It can be viewed as a ligand-stabilized {B_3H_7} group, i.e. (L.B_3H_7], in which the ligand is H^- (cf. BH_4^-). However, the ion is completely fluxional in solution, all three boron atoms (and all eight protons) being equivalent on an nmr timescale. The $B_3H_8^-$ anion has an

[38] R. A. OGG and J. D. RAY, *Disc. Faraday Soc.* **19**, 239–46 (1955).

[39] H. J. DEISEROTH, O. SOMMER, H. BINDER, K. WOLFER and B. FREI, *Z. anorg. allg. Chem.* **571**, 21–8 (1989).

[40] M. SIRONI, M. RAIMONDI, D. L. COOPER and J. GERRATT, *J. Phys. Chem.* **95**, 10617–23 (1991).

B_3H_8 (2013)   (2103)

(a)   (b)   (c)

Figure 6.15 (a) Structure of $B_3H_8^-$ showing C_s symmetry; (b) dimensions and representation of the bonding using a direct B–B bond (2013) for the longer (unbridged) B–B distance; (c) most recent (2103) description of the bonding in terms of a 3-centre BBB bond. (See p. 158 for *styx* formalism.)

extensive reaction chemistry both as a reducing agent and as a source of *arachno*-B_4H_{10} (p. 162). Conversely, unsymmetrical (heterolytic) cleavage of B_4H_{10} with ligands, L, such as NH_3 yield $[L_2BH_2]^+[B_3H_8]^-$.

The $B_3H_8^-$ ion is also a versatile ligand and forms bidentate and even tridentate complexes with many metal centres.[41] The octahedrally coordinated 18-electron manganese(I) complex $[Mn(\eta^2\text{-}B_3H_8)(CO)_4]$ is a particularly instructive example. As can be seen from Fig. 6.16a it has a cluster structure that is clearly related to that of B_4H_{10} (13). When heated to 180°C or irradiated with ultraviolet light the complex loses one of the four CO ligands and this enables a further B–H group to coordinate to give the trihapto complex *fac*-$[Mn(\eta^3\text{-}B_3H_8)(CO)_3]$ (Fig. 6.16b). Treatment of this product with an excess of CO under moderate pressure regenerates the original dihapto species by a simple ligand replacement reaction.[42]

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[41] D. F. GAINES and S. J. HILDEBRANDT, Chap. 3 in R. N. GRIMES (ed.), *Metal Interactions with Boron Clusters*, Plenum Press, New York, 1982, pp. 119–43.

[42] S. J. HILDEBRANDT, D. F. GAINES and J. C. CALABRESE, *Inorg. Chem.* **17**, 790–4 (1978).

6.4.5 Intermediate-sized Boranes and their Anions (B_5–B_9)

Pentaborane(9), *nido*-B_5H_9, is by far the most studied borane in this group. It can be prepared by passing a 1:5 mixture of B_2H_6 and H_2 at subatmospheric pressure through a furnace at 250°C with a residence time of 3 s (or at 225° with a 15 s residence time); there is a 70% yield and 30% conversion. Alternatively B_2H_6 can be pyrolysed for 2.5 days in a static hot/cold reactor at 180°/−80°. B_5H_9 is a colourless, volatile liquid, bp 60.0°; it is thermally stable but chemically very reactive and spontaneously flammable in air. Its structure is essentially a square-based pyramid of B atoms each of which carries a terminal H atom and there are 4 bridging H atoms around the base (structure 9, p. 154). The slant edge of the pyramid, B(1)–B(2), is 168 pm and the basal interboron distances, B(2)–B(3) etc, are 178 pm; other key dimensions are B–H_t 122 pm, B–H_μ 135 pm and B–H_μ–B 83°. Calculations suggest that B(1) has a slightly higher electron density than the basal borons and that H_μ is slightly more positive than H_t. Apex-substituted derivatives 1-XB_5H_8 can

Figure 6.16 Ligand replacement reaction of $[Mn(\eta^2\text{-}B_3H_8)(CO)_4]$ (see text).

readily be prepared by electrophilic substitution (e.g. halogenation or Friedel-Crafts alkylation with RX or alkenes), whereas base-substituted derivatives $2\text{-}XB_5H_8$ result when nucleophilic reaction is induced by amines or ethers, or when $1\text{-}XB_5H_8$ is isomerized in the presence of a Lewis base such as hexamethylenetetramine or an ether:

$$B_5H_9 \xrightarrow{I_2/AlX_3} 1\text{-}IB_5H_8 \xrightarrow[\;(CH_2)_6N_4\;]{\text{base}} 2\text{-}IB_5H_8$$

$$\xrightarrow{SbF_3} 2\text{-}FB_5H_8$$

Further derivatives can be obtained by metathesis, e.g.

$$2\text{-}ClB_5H_8 + NaMn(CO)_5 \longrightarrow$$

$$2\text{-}\{(CO)_5Mn\}B_5H_8 \text{ (also Re)}$$

B_5H_9 reacts with Lewis bases (electron-pair donors) to form adducts, some of which have now been recognized as belonging to the new series of *hypho*-borane derivatives B_nH_{n+8} (p. 152). Thus PMe_3 gives the adduct $[B_5H_9(PMe_3)_2]$ which is formally analogous to $[B_5H_{11}]^{2-}$ and the (unknown) borane B_5H_{13}. $[B_5H_9(PMe_3)_2]$ has a very open structure in the form of a shallow pyramid with the ligands attached at positions 1 and 2 and with major rearrangement of the H atoms (Fig. 6.17a). Chelating phosphine ligands such as $(Ph_2P)_2CH_2$

and $(Ph_2PCH_2)_2$ have similar structures but $[B_5H_9(Me_2NCH_2CH_2NMe_2)]$ undergoes a much more severe distortion in which the ligand chelates a single boron atom, $B(2)$, which is joined to the rest of the molecule by a single bond to the apex $B(1)$ (Fig. 6.17b).[43] With NH_3 as ligand (at $-78°$) complete excision of one B atom occurs by "unsymmetrical cleavage" to give $[(NH_3)_2BH_2]^+[B_4H_7]^-$

B_5H_9 also acts as a weak Brønsted acid and, from proton competition reactions with other boranes and borane anions, it has been established that acidity increases with increasing size of the borane cluster and that *arachno*-boranes are more acidic than *nido*-boranes:

nido : $B_5H_9 < B_6H_{10} < B_{10}H_{14} < B_{16}H_{20} < B_{18}H_{22}$

arachno : $B_4H_{10} < B_5H_{11} < B_6H_{12}$ and

$$B_4H_{10} > B_6H_{10}$$

Accordingly, B_5H_9 can be deprotonated at low temperatures by loss of H_μ to give $B_5H_8^-$ providing a sufficiently strong base such as a lithium alkyl or alkali metal hydride is used. Bridge-substituted derivatives of B_5H_9 can then be obtained by reacting MB_5H_8 with chloro compounds such as R_2PCl, Me_3SiCl, Me_3GeCl,

⁴³ N. W. ALCOCK, H. M. COLQUHOUN, G. HARAN, J. F. SAWYER and M. G. H. WALLBRIDGE, *J. Chem. Soc., Chem. Commun.*, 368–70 (1977); *J. Chem. Soc., Dalton Trans.*, 2243–55 (1982).

(a) $[B_5H_9(PMe_3)_2]$ (b) $[B_5H_9(Me_2NCH_2CH_2NMe_2)]$

Figure 6.17 Structure of *hypho*-borane derivatives: (a) $[B_5H_9(PMe_3)_2]$ — the distances B(1)-B(2) and B(2)-B(3) are as in B_5H_9 (p. 170) but $B(3)\cdots B(4)$ is 295 pm (cf. $B\cdots B$ 297 pm in B_5H_{11}, structure 14, p. 154), and (b) $[B_5H_9(Me_2NCH_2CH_2NMe_2)]$ — the distances $B(2)\cdots B(3)$ and $B(2)\cdots B(5)$ are 273 and 272 pm respectively.

or even Me_2BCl to give compounds in which the 3-centre $B-H_\mu-B$ bond has been replaced by a 3-centre bond between the 2 B atoms and P, Si, Ge or B respectively. Many metal-halide coordination complexes react similarly, and the products can be considered as adducts in which the $B_5H_8^-$ anion is acting formally as a 2-electron ligand via a 3-centre $B-M-B$ bond.[44,45] Thus $[Cu^I(B_5H_8)(PPh_3)_2]$ (Fig. 6.18a) is readily formed by the low-temperature reaction of KB_5H_8 with $[CuCl(PPh_3)_3]$ and analogous 16-electron complexes have been prepared for many of the later transition elements, e.g. $[Cd(B_5H_8)Cl(PPh_3)]$, $[Ag(B_5H_8)(PPh_3)_2]$ and $[M^{II}(B_5H_8)XL_2]$, where M^{II} = Ni, Pd, Pt; X = Cl, Br, I; L_2 = a diphosphine or related ligand. By contrast, $[Ir^I(CO)Cl(PPh_3)_2]$ reacts by oxidative insertion of Ir and consequent cluster expansion to give $[(IrB_5H_8)(CO)(PPh_3)_2]$ which, though superficially of similar formula, has the structure of an irida-*nido*-hexaborane

(Fig. 6.18b).[46] In this, the $\{Ir(CO)(PPh_3)_2\}$ moiety replaces a basal BH_tH_μ unit in B_6H_{10} (structure 10, p. 154).

Cluster-expansion and cluster-degradation reactions are a feature of many polyhedral borane species. Examples of cluster-expansion are:[11,47]

$$LiB_5H_8 + \tfrac{1}{2}B_2H_6 \xrightarrow[\text{(fast)}]{Et_2O/-78°} LiB_6H_{11}$$

$$\xrightarrow{HCl} B_6H_{12}$$

$$LiB_5H_8 + B_2H_6 \xrightarrow[\text{(slow)}]{Me_2O/-78°} \{LiB_7H_{14}\}$$

$$\longrightarrow B_6H_{10} + LiBH_4$$

$$1.8B_5H_9 + MH \xrightarrow[\text{15 h}]{\text{thf/r.t.}} MB_9H_{14} + H_2 \text{ plus}$$

minor products (M=Na, K)

[44] N. N. GREENWOOD and I. M. WARD, *Chem. Soc. Revs.* **3**, 231-71 (1974).

[45] N. N. GREENWOOD, *Pure Appl. Chem.* **49**, 791-802 (1977).

[46] N. N. GREENWOOD, J. D. KENNEDY, W. S. MCDONALD, D. REED and J. STAVES, *J. Chem. Soc., Dalton Trans.*, 117-23 (1979).

[47] N. S. HOSMANE, J. R. WERMER, ZHU HONG, T. D. GETMAN and S. G. SHORE, *Inorg. Chem.* **26**, 3638-9 (1987), and references cited therein.

Figure 6.18   (a) Structure of $[Cu(B_5H_8)(PPh_3)_2]$, showing η^2-bonding of $B_5H_8^-$ (phenyl groups omitted for clarity); (b) Structure of $[(IrB_5H_8)(CO)(PPh_3)_2]$ showing the structure about the iridium atom and the relationship of the metallaborane cluster to that of $nido$-B_6H_{10}.

$$KB_9H_{14} + 0.4B_5H_9 \xrightarrow[20\,h]{glyme/85°} KB_{11}H_{14} + 1.8H_2$$

Cluster degradation has already been mentioned in connection with the unsymmetrical cleavage reaction (p. 165) and other examples are:

$$[NMe_4]B_5H_8 + 6Pr^iOH \longrightarrow [NMe_4]B_3H_8$$
$$+ 2B(OPr^i)_3 + 3H_2$$

$$\text{and } B_5H_9 \xrightarrow{tmed} B_5H_9(tmed) \xrightarrow{MeOH} B_4H_8(tmed)$$
$$+ B(OMe)_3 + 2H_2$$

(where Pr^i is Me_2CH- and tmed is $Me_2NCH_2-CH_2NMe_2$).

Replacement of a {BH} unit in B_5H_9 by an "isoelectronic" organometallic group such as {Fe(CO)₃} or {Co(η^5-C₅H₅)} can also occur, and this illustrates the close interrelation between metalloboranes, metal–metal cluster compounds, and organometallic complexes in general (see Panel).

The structures of several other $nido$- and $arachno$- B_5–B_9 boranes are given on page 154 but a detailed discussion of their chemistry is beyond the scope of this treatment. Further information is in refs. 9, 11, 27, 51 and 52.

6.4.6 Chemistry of nido-decaborane, B₁₀H₁₄

Decaborane is the most studied of all the polyhedral boranes and at one time (mid-1950s) was manufactured on a multitonne scale in the USA as a potential high-energy fuel. It is now obtainable in research quantities by the pyrolysis of B_2H_6 at 100–200°C in the presence of catalytic amounts of Lewis bases such as Me_2O. $B_{10}H_{14}$ is a colourless, volatile, crystalline solid (see Table 6.2, p. 163) which

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Copyrolysis of B_5H_9 and $[Fe(CO)_5]$ in a hot/cold reactor at 220°/20° for 3 days gives an orange liquid (mp 5°C) of formula $[1-\{Fe(CO)_3\}B_4H_8]$ having the structure shown in (a).[48] The isoelectronic complex $[1-\{Co(\eta^5-C_5H_5)\}B_4H_8]$ (structure b) can be obtained as yellow crystals by pyrolysis at 200° of the corresponding basal derivative $[2-\{Co(\eta^5-C_5H_5)\}B_4H_8]$ (structure (c)) which is obtained as red crystals from the reaction of NaB_5H_8 and $CoCl_2$ with NaC_5H_5 in thf at $-20°$.[49] The course of these reactions is obscure and other products are also obtained.

(a) $[1-\{Fe(CO)_3\}B_4H_8]$

(b) $[1-\{Co(\eta^5-C_5H_5)\}B_4H_8]$

(c) $[2-\{Co(\eta^5-C_5H_5)\}B_4H_8]$

(d) Geometric structure of $[Fe(CO)_3(\eta^4-C_4H_4)]$

(e) Conventional bonding diagram

(f) Bonding scheme analogous to that in B_5H_9

(g) $[1-\{Fe(CO)_3\}B_4H_8]$ stressing relation to B_5H_9 (4120)

(h) Bonding in $[1-\{Fe(CO)_3\}B_4H_8]$ cf. $Fe(CO)_5$ and $[Fe(CO)_3(\eta^4-C_4H_4)]$

As $\{BH_2\}$ is isoelectronic with $\{CH\}$, these metalloborane clusters are isoelectronic with the cyclobutadiene adduct $[Fe(\eta^4-C_4H_4)(CO)_3]$, see (d), (e) and (f). Likewise $\{Fe(CO)_3\}$ or $\{Co(\eta^5-C_5H_5)\}$ can replace a $\{BH\}$ group in B_5H_9 and two descriptions of the bonding are given in (g) and (h): the Fe atom supplies 2 electrons and 3 atomic orbitals to the cluster (as does BH), thereby enabling it to form 2 Fe–B σ bonds and to accept a pair of electrons from adjacent B atoms to form a 3-centre BMB bond. In this description the Fe atom is formally octahedral Fe^{II} (d^6). Alternatively, diagram (h) emphasizes the relation between $[1-\{Fe(CO)_3\}B_4H_8]$ and $[Fe(CO)_3(\eta^4-C_4H_4)]$ or $[Fe(CO)_5]$: the Fe atom accepts 2 pairs of electrons to form two 3-centre BMB bonds and is formally Fe^0 with a trigonal bipyramidal arrangement of bonds.

It is possible to replace more than one $\{BH\}$ group in B_5H_9 by a metal centre, e.g in the dimetalla species $[1,2-\{Fe(CO)_3\}_2B_3H_7]$;[50] it is also notable that the iron carbonyl cluster compound $[Fe_5(CO)_{15}C]$ (p. 1108) features the same square-pyramidal cluster in which 5 $\{Fe(CO)_3\}$ groups have replaced the five $\{BH\}$ groups in B_5H_9, and the C atom (in the centre of the base) replaces the 4 bridging H atoms by supplying the 4 electrons required to complete the bonding.

Many other equivalent groups can be envisaged and the formalism permits a unified approach to possible synthetic routes and to probable structures of a wide variety of compounds.[17,51-53]

[48] N. N. GREENWOOD, C. G. SAVORY, R. N. GRIMES, L. G. SNEDDON, A. DAVISON and S. S. WREFORD, *J. Chem. Soc., Chem. Commun.*, 718 (1974).

[49] V. R. MILLER and R. N. GRIMES, *J. Am. Chem. Soc.* **95**, 5078-80 (1973).

[50] K. J. HALLER, E. L. ANDERSEN and T. P. FEHLNER, *Inorg. Chem.* **20**, 309-13 (1981).

[51] N. N. GREENWOOD and J. D. KENNEDY, Chap. 2 in R. N. GRIMES (ed.), *Metal Interactions with Boron Clusters*, Plenum, New York, 1982, pp. 43-118.

[52] J. D. KENNEDY, *Prog. Inorg. Chem.* **32**, 519-679 (1984); **34**, 211-434 (1986).

[53] T. P. FEHLNER (ed.), *Inorganometallic Chemistry*, Plenum, New York, 1992, 401 pp.

is insoluble in H_2O but readily soluble in a wide range of organic solvents. Its structure (36) can be regarded as derived from the 11 B atom cluster $B_{11}H_{11}^{2-}$ (p. 153) by replacing the unique BH group with 2 electrons and appropriate addition of $4H_\mu$. MO-calculations give the sequence of electron charge densities at the various B atoms as 2, 4 > 1, 3 > 5, 7, 8, 10 > 6, 9 though the total range of deviation from charge neutrality is less than ±0.1 electron per B atom. The chemistry of $B_{10}H_{14}$ can be conveniently discussed under the headings (a) proton abstraction, (b) electron addition, (c) adduct formation, (d) cluster rearrangements, cluster expansions, and cluster degradation reactions, and (e) metalloborane and other heteroborane compounds.

$B_{10}H_{14}$ can be titrated in aqueous/alcoholic media as a monobasic acid, pK_a 2.70:

$$B_{10}H_{14} + OH^- \rightleftharpoons B_{10}H_{13}^- + H_2O$$

Proton abstraction can also be effected by other strong bases such as H^-, OMe^-, NH_2^-, etc. The $B_{10}H_{13}^-$ ion is formed by loss of a bridge proton, as expected, and this results

in a considerable shortening of the B(5)–B(6) distance from 179 pm in $B_{10}H_{14}$ to 165 pm in $B_{10}H_{13}^-$ (structures 36, 37). Under more forcing conditions with NaH a second H_μ can be removed to give $Na_2B_{10}H_{12}$; the probable structure of $B_{10}H_{12}^{2-}$ is (38) and the anion acts as a formal bidentate (tetrahapto) ligand to many metals (p. 177).

Electron addition to $B_{10}H_{14}$ can be achieved by direct reaction with alkali metals in ethers, benzene or liquid NH_3:

$$B_{10}H_{14} + 2Na \longrightarrow Na_2B_{10}H_{14}$$

A more convenient preparation of the $B_{10}H_{14}^{2-}$ anion uses the reaction of aqueous BH_4^- in alkaline solution:

$$B_{10}H_{14} \xrightarrow{+BH_4^- - \{BH_3\}} B_{10}H_{15}^- \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} B_{10}H_{14}^{2-}$$

Structure (39) conforms to the predicted (2632) topology (p. 158) and shows that the 2 added electrons have relieved the electron deficiency to the extent that the 2 $B–H_\mu–B$ groups have been

(36) $B_{10}H_{14}$ (37) $B_{10}H_{13}^-$ (38) $B_{10}H_{12}^{2-}$

(39) $B_{10}H_{14}^{2-}$ (40) $B_{10}H_{12}(MeCN)_2$

converted to B–H$_t$ with the consequent appearance of 2BH$_2$ groups in the structure. Calculations show that this conversion of a *nido-* to an *arachno*-cluster reverses the sequence of electron charge density at the 2, 4 and 6, 9 positions so that for B$_{10}$H$_{14}^{2-}$ the sequence is 6, 9 > 1, 3 > 5, 7, 8, 10 > 2, 4; this is paralleled by changes in the chemistry. B$_{10}$H$_{14}^{2-}$ can formally be regarded as B$_{10}$H$_{12}$L$_2$ for the special case of L = H$^-$. Compounds of intermediate stoichiometry B$_{10}$H$_{13}$L$^-$ are formed when B$_{10}$H$_{14}$ is deprotonated in the presence of the ligand L:

$$B_{10}H_{14} \xrightarrow{\text{Et}_2\text{O/NaH}} B_{10}H_{13}^- \xrightarrow{\text{Et}_2\text{O/L}} [B_{10}H_{13}L]^-$$
$$\xrightarrow{\text{NMe}_4^+} [NMe_4][B_{10}H_{13}L]$$

The adducts B$_{10}$H$_{12}$L$_2$ (structure 40) can be prepared by direct reaction of B$_{10}$H$_{14}$ with L or by ligand replacement reactions:

$$B_{10}H_{14} + 2MeCN \longrightarrow B_{10}H_{12}(MeCN)_2 + H_2$$
$$B_{10}H_{12}L_2 + 2L' \longrightarrow B_{10}H_{12}L'_2 + 2L$$

Ligands L, L' can be drawn from virtually the full range of inorganic and organic neutral and anionic ligands and, indeed, the reaction severely limits the range of donor solvents in which B$_{10}$H$_{14}$ can be dissolved. The approximate sequence of stability is:

$$SR_2 < RCN < AsR_3 < RCONMe_2 < P(OR)_3$$
$$< py \approx NEt_3 \approx PPh_3$$

The stability of the phosphine adducts is notable as is the fact that thioethers readily form such adducts whereas ethers do not. Bis-ligand adducts of moderate stability play an important role in activating decaborane for several types of reaction to be considered in more detail in subsequent paragraphs, e.g.:

Substitution: $B_{10}H_{12}(SR_2)_2 + HX \xrightarrow{\text{C}_6\text{H}_6/20°}$
$$6\text{-}(5\text{-})XB_{10}H_{13} \ (X = F, Cl, Br, I)$$
Cluster rearrangement: *arachno*-B$_{10}$H$_{12}$(NEt$_3$)$_2$
$$\longrightarrow [NEt_3H]^+{}_2[\textit{closo}\text{-}B_{10}H_{10}]^{2-}$$
Cluster addition: *arachno*-B$_{10}$H$_{12}$(SR$_2$)$_2$ +
$$2RC{\equiv}CR \longrightarrow \textit{closo}\text{-}B_{10}H_{10}(CR)_2$$
$$+ 2SR_2 + H_2$$

Cluster degradation: B$_{10}$H$_{12}$L$_2$ + 3ROH $\longrightarrow$
$$B_9H_{13}L + B(OR)_3 + L + H_2$$

In this last reaction it is the coordinated B atom at position 9 that is solvolytically cleaved from the cluster.

Electrophilic substitution of B$_{10}$H$_{14}$ follows the sequence of electron densities in the ground-state molecule. Thus halogenation in the presence of AlCl$_3$ leads to 1- and 2-monosubstituted derivatives and to 2,4-disubstitution. Similarly, Friedel–Crafts alkylations with RX/AlCl$_3$ (or FeCl$_3$) yield mixtures such as 2-MeB$_{10}$H$_{13}$, 2,4- and 1,2-Me$_2$B$_{10}$H$_{12}$, 1,2,3- and 1,2,4-Me$_3$B$_{10}$H$_{11}$, and 1,2,3,4-Me$_4$B$_{10}$H$_{10}$. By contrast, nucleophilic substitution (like the adduct formation with Lewis bases) occurs preferentially at the 6 (9) position; e.g., LiMe produces 6-MeB$_{10}$H$_{13}$ as the main product with smaller amounts of 5-MeB$_{10}$H$_{13}$, 6,5(8)-Me$_2$B$_{10}$H$_{12}$ and 6,9-Me$_2$B$_{10}$H$_{12}$.

B$_{10}$H$_{14}$ undergoes numerous cluster-addition reactions in which B or other atoms become incorporated in an expanded cluster. Thus in a reaction which differs from that on p. 175 BH$_4^-$ adds to B$_{10}$H$_{14}$ with elimination of H$_2$ to form initially the *nido*-B$_{11}$H$_{14}^-$ anion (structure 41, p. 178) and then the *closo*-B$_{12}$H$_{12}^{2-}$:

$$B_{10}H_{14} + LiBH_4 \xrightarrow{\text{monoglyme/90°}} LiB_{11}H_{14} + 2H_2$$
$$B_{10}H_{14} + 2LiBH_4 \longrightarrow Li_2B_{12}H_{12} + 5H_2$$

A more convenient high-yield synthesis of B$_{12}$H$_{12}^{2-}$ is by the direct reaction of amine-boranes with B$_{10}$H$_{14}$ in the absence of solvents:

$$B_{10}H_{14} + 2Et_3NBH_3 \xrightarrow{90-100°}$$
$$[NEt_3H]_2{}^+[B_{12}H_{12}]^{2-} + 3H_2$$

Heteroatom cluster addition reactions are exemplified by the following:

$$B_{10}H_{14} + Me_3NAlH_3 \xrightarrow{\text{Et}_2\text{O}}$$
$$[NMe_3H]^+[AlB_{10}H_{14}]^- + H_2$$
$$B_{10}H_{14} + 2TlMe_3 \xrightarrow{\text{Et}_2\text{O}}$$
$$[TlMe_2]^+[B_{10}H_{12}TlMe_2]^-$$

The Concept of Boranes as Ligands

Boranes are usually regarded as being electron-deficient, in the sense that they have an insufficient number of electrons to form classical 2-centre 2-electron bonds between each contiguous pair of atoms. However, in the mid-1960s several groups began to realize that, far from being deficient in electrons, many boranes and their anions could act as very effective polyhapto ligands: that is, they could form donor–acceptor complexes (coordination compounds, Chap. 19) in which the borane cluster itself was acting as the electron donor or ligand. The application of this astonishing idea has extended enormously the range of boron hydride compounds which can be made.[54] Many aspects have already been alluded to in the preceding pages and these are briefly summarized in this Panel.

Boranes can act as ligands either by forming 3-centre, 2-electron B–H–M bonds (analogous to BHB bonds) or by forming direct B_nM bonds ($n = 1$–6, analogous to B–B, BBB etc bonds). All hapticities from η^1–η^6 and occasionally beyond are known. The various coordination modes of BH_4^- and $B_3H_8^-$ were discussed on pp. 168–71; these involve the conversion of B–H_t bonds to B–H→M bonds. Likewise, the use of $B_5H_8^-$ as an η^2-ligand was described on pp. 172–3; this involves the notional donation to a metal centre of the electron pair in a B–B bond, thus forming a BMB 3-centre bond. $B_5H_8^-$ can also act as a notional η^1-donor by replacement of a terminal H atom in B_5H_9 with a metal centre: e.g. direct reaction of B_5H_8Cl or B_5H_8Br with $NaM(CO)_5$ to give $[M(\eta^1$-2-$B_5H_8)(CO)_5]$ (M = Mn, Re).

It is clear that some boranes are amphoteric Lewis acid/bases — that is they can act either as electron-pair donors as above or as electron-pair acceptors (e.g. in $L.BH_3$ and $L.B_3H_7$). It follows that a borane donor could conceivably ligate to a borane acceptor to form a borane–borane complex, i.e. a larger borane, e.g. $BH_4^- + \{BH_3\} \longrightarrow B_2H_7^-$ (p. 154). In this sense B_2H_6 itself could be regarded either as a coordination complex of BH_4^- with the notional cation $\{BH_2^+\}$, or as the mutual coordination of two monodentate $\{BH_3\}$ units. Replacement of these donors with stronger ligands such as NH_3 or NMe_3 would then result in either unsymmetrical or symmetrical cleavage of B_2H_6 as discussed on p. 165. Likewise, B_4H_{10} could be regarded either as a complex between η^2-$B_3H_8^-$ and $\{BH_2^+\}$ or as a mutual coordination between $\{B_3H_7\}$ and $\{BH_3\}$; reaction with stronger ligands, L, would then yield either $[L_2BH_2]^+[B_3H_8]^-$ or $L.B_3H_7$ and $L.BH_3$ by ligand displacement reactions (pp. 169–70).

The neutral *nido*-borane B_6H_{10} (structure 10) has a basal B–B bond (see p. 159) and this enables it to act as a ligand by displacing ethene from Zeise's salt (p. 930).

$$K[Pt(\eta^2\text{-}C_2H_4)Cl_3] + 2B_6H_{10} \longrightarrow trans\text{-}[Pt(\eta^2\text{-}B_6H_{10})_2Cl_2] + C_2H_4 + KCl$$

Similarly, reaction of B_6H_{10} with $Fe_2(CO)_9$ (p. 1104) at room temperature results in the smooth elimination of $Fe(CO)_5$ to form $[Fe(\eta^2\text{-}B_6H_{10})(CO)_4]$ as a stable, volatile yellow solid. Use of these electron-donor properties of B_6H_{10} towards reactive (vacant orbital) borane radicals resulted in the preparation of several new *conjuncto*-boranes, e.g. $B_{13}H_{19}$, $B_{14}H_{22}$ and $B_{15}H_{23}$ (p. 162).

Another important concept is the notion of stabilization by means of coordination. A classic example is the stabilization of the fugitive species cyclobutadiene, $\{C_4H_4\}$ by coordination to $\{Fe(CO)_3\}$ (p. 936). As the C atom is isoelectronic with $\{BH\}$, so $\{C_4H_4\}$ is isoelectronic with the borane fragment $\{B_4H_8\}$ which is similarly stabilized by coordination to $\{Fe(CO)_3\}$ or the isoelectronic $\{Co(\eta^5\text{-}C_5H_5)\}$ (see Panel on p. 174). Indeed it is a general feature of metallaborane chemistry that such clusters are often much more stable than are the parent boranes themselves.

As a result of the systematic application of coordination-chemistry principles, dozens of previously unsuspected structure types have been synthesized in which polyhedral boranes or their anions can be considered to act as ligands which donate electron density to metal centres, thereby forming novel metallaborane clusters.[36,44,45,51–54] Some 40 metals have been found to act as acceptors in this way (see also p. 178). The ideas have been particularly helpful in emphasizing the close interconnection between several previously separated branches of chemistry, notably boron hydride cluster chemistry, metallaborane and metallacarbaborane chemistry (pp. 189–95), organometallic chemistry and metal–metal cluster chemistry. All are now seen to be parts of a coherent whole.

It is also noteworthy that Alfred Stock, who is universally acclaimed as the discoverer of the boron hydrides (1912),[10] was also the first to propose the use of the term "ligand" (in a lecture in Berlin on 27 November 1916).[55] Both events essentially predate the formulation by G. N. Lewis of the electronic theory of valency (1916). It is therefore felicitous that, albeit some 20 years after Stock's death in 1946, two such apparently disparate aspects of his work should be connected in the emerging concept of "boranes as ligands".

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[54] N. N. GREENWOOD, Chap 28 in G. B. KAUFFMAN (ed.), *Coordination Chemistry: A Century of Progress* A.C.S. Symposium Series No. 565 (1994) pp. 333–45.

[55] A. STOCK, *Berichte* **50**, 170 (1917).

(41) *nido*-$B_{11}H_{14}^{-}$

(The open face comprises a fluxional system involving the two H_μ atoms and the *endo*-H_t atom of the BH_2 group)

(42) *nido*-$[B_{10}H_{12}TlMe_2]^{-}$

(43) $[Zn(B_{10}H_{12})_2]^{2-}$

$$B_{10}H_{14} + 2ZnR_2 \xrightarrow{Et_2O} [B_{10}H_{12}Zn(Et_2O)_2]$$

$$\xrightarrow{H_2O/Me_4NCl} [NMe_4]^+{}_2[Zn(B_{10}H_{12})_2]^{2-}$$

The structure of the highly reactive anion $[AlB_{10}H_{14}]^{-}$ is thought to be similar to *nido*-$B_{11}H_{14}^{-}$ with one facial B atom replaced by Al. The metal alkyls react somewhat differently to give extremely stable metallo-borane anions which can be thought of as complexes of the bidentate ligand $B_{10}H_{12}^{2-}$ (structures 42, 43).[44,51,52] Many other complexes $[M(B_{10}H_{12})_2]^{2-}$ and $[L_2M(B_{10}H_{12})]$ are known with similar structures except that, where M = Ni, Pd, Pt, the coordination about the metal is essentially square-planar rather than pseudo-tetrahedral as for Zn, Cd and Hg. Such compounds were among the first examples to be recognized of the novel and extremely fruitful perception that "electron-deficient" boranes and their anions can, in fact, act as powerful stabilizing electron-donor ligands (see Panel on p. 177).

6.4.7 Chemistry of closo-$B_nH_n^{2-(1,56,57)}$

The structures of these anions have been indicated on p. 153. Preparative reactions are often mechanistically obscure but thermolysis under controlled conditions is the dominant

procedure (pp. 162–3). Many of the product *closo*-boranes are not degraded even when heated to 600°C. Salts of $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ are particularly stable and their reaction chemistry has been extensively studied. As expected from their charge, they are extremely stable towards nucleophiles but moderately susceptible to electrophilic attack. For $B_{10}H_{10}^{2-}$ the apex positions 1,10 are substituted preferentially to the equatorial positions; reference to structure (5) shows that there are 2 geometrical isomers for monosubstituted derivatives $B_{10}H_9X_2^{-}$, 7 isomers for $B_{10}H_8X_2^{2-}$ and 16 for $B_{10}H_7X_3^{2-}$. Many of these isomers exist, additionally, as enantiomeric pairs. Because of its higher symmetry $B_{12}H_{12}^{2-}$ has only 1 isomer for monosubstituted species $B_{12}H_{11}X^{2-}$, 3 for $B_{12}H_{10}X_2^{2-}$ (sometimes referred to as *ortho-*, *meta-* and *para-*) and 5 for $B_{12}H_9X_3^{2-}$. A particularly important derivative of $B_{12}H_{12}^{2-}$ is the thiol $[B_{12}H_{11}(SH)]^{2-}$ which has found use in the treatment of brain tumours by neutron capture therapy (see Panel on next page).

Oxidation of *closo*-$B_{10}H_{10}^{2-}$ with aqueous solutions of Fe^{III} or Ce^{IV} (or electrochemically) yields *conjuncto*-$B_{20}H_{18}^{2-}$ (44) which can be photoisomerized to *neo*-$B_{20}H_{18}^{2-}$ (45). If the oxidation is carried out at 0° with Ce^{IV},

[56] E. L. MEUTTERTIES and W. H. KNOTH, *Polyhedral Boranes*, Marcel Dekker, New York, 1968, 197 pp.

[57] R. L. MIDDAUGH, Chap. 8 in ref. 9, pp. 273–300.

Boron-10 Neutron Capture Therapy[58,59]

Every year more than 600 000 people throughout the world contract brain tumours and about 1700 die from this cause every day. Treatment by surgical excision is usually impossible because of the site of the malignant growth and the lack of a distinct boundary (gliomas). Likewise, conventional radiotherapy (X-rays, γ-rays etc.) from outside the skull is rarely effective. An ingenious approach to this problem which has given encouraging results so far is impregnation of the tumour with a suitable boron compound, followed by irradiation with thermal neutrons which readily pass harmlessly through normal tissue but are strongly absorbed by the isotope ^{10}B. As can be seen from Table 6.1 (p. 144) ^{10}B is 767 000 times more effective than ^{11}B and, in fact, has one of the highest neutron absorption cross-sections for any nuclide. The strategy is thus to synthesize cluster compounds enriched in ^{10}B, thereby enhancing the neutron absorption cross-section of the boron nearly five-fold, and then to attach these clusters to the cells comprising the brain tumour. A single injection of, say, Na$_2$[^{10}B$_{12}$H$_{11}$SH] usually suffices. Treatment with thermal neutrons from a nuclear reactor then releases huge amounts of energy right within the tumour tissue (and nowhere else) as a result of the nuclear reaction:

$$^{10}_{5}\text{B} + ^{1}_{0}\text{n} \longrightarrow \{^{11}_{5}\text{B}^*\} \longrightarrow ^{4}_{2}\text{He} + ^{7}_{3}\text{Li} + \gamma$$

The recoiling α-particle ($^{4}_{2}$He) and lithium nucleus ($^{7}_{3}$Li) between them carry 2.4 MeV of energy and this is shed within just a few μm, the α-particle travelling about 9 μm and the Li nucleus about 5.5 μm in the opposite direction. The radiation damage is thus confined within the cancerous tissue alone.

This is a very active area of research which involves collaboration between synthetic inorganic chemists, biochemists, neurosurgeons, nuclear physicists and reactor engineers, and there is considerable scope for advance in all of these areas.[58,60,61]

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or in a two-phase system with Fe^{III} using very concentrated solutions of B$_{10}$H$_{10}$$^{2-}$, the intermediate H-bridged species B$_{20}$H$_{19}$$^{3-}$ (46) can be isolated. Reduction of *conjuncto*-B$_{20}$H$_{18}$$^{2-}$ with Na/NH$_3$ yields the equatorial–equatorial (ee) isomer of *conjuncto*-B$_{20}$H$_{18}$$^{4-}$ (47), and this can be successively converted by acid catalyst to the ae isomer (49) and, finally, to the aa isomer (48). Careful protonation of this aa isomer yields the elusive anion [aa-B$_{20}$H$_{19}$]$^{3-}$ in which the *conjuncto* B–B bond in structure (48) is replaced by an unsupported B–H$_\mu$–B bond (angle 91(3)°, B–H$_\mu$ 136(5) pm, B$_a$···B$_a$ 193.6 pm), though the two *closo* clusters still share a common axis through their B(1)-B(10) vertices.[61a] An extensive derivative chemistry of these various

species has been developed. Another important (though mechanistically obscure) reaction of *conjuncto*-B$_{20}$H$_{18}$$^{2-}$ is its degradation in high yield to *n*-B$_{18}$H$_{22}$ by passage of an enthanolic solution through an acidic ion exchange resin; *i*-B$_{18}$H$_{22}$ is also formed as a minor product. The relation of these 2 edge-fused decaborane clusters to the B$_{20}$ species is illustrated in structures (31) and (32) (p. 156).

When salts of *closo*-B$_{10}$H$_{10}$$^{2-}$ and *closo*-B$_{12}$H$_{12}$$^{2-}$ are passed through an acid ion exchange resin, hydrates of the strong acids H$_2$B$_n$H$_n$ are obtained. For example, [NEt$_4$]$^+$$_2$-[B$_{10}H_{10}$]$^{2-}$ gives H$_2$B$_{10}$H$_{10}$.4H$_2$O which, on careful dehydration, yields the dihydrate, [H$_3$O]$^+$$_2$[B$_{10}H_{10}$]$^{2-}$. Repeated low-pressure evaporation of benzene solutions of this acid at room temperature results in reductive cluster opening to give the *nido*-decaborane derivative [6,6'-(B$_{10}$H$_{13}$)$_2$O] in good yield, probably via *nido*-6-B$_{10}$H$_{13}$(OH).[62] The structure of the readily sublimable bis(*nido*-decaboranyl) oxide,

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[59] H. HATANAKA, *Boron Neutron Capture Therapy for Tumours*, Nishimura, Niigata, Japan, 1986. R. G. FAIRCHILD, V. P. BOND and A. D. WOODHEAD (eds.), *Clinical Aspects of Neutron Capture Therapy*, Plenum, New York, 1989, 370 pp.

[60] M. F. HAWTHORNE, *Pure Appl. Chem.* **63**, 327–34 (1991).

[61] B. J. ALLEN, D. E. MOORE and B. V. HARRINGTON (eds.), *Progress in Neutron Capture Therapy for Cancer* (Proc. 4th Internat. Conf.), Plenum, New York, 1992, 668 pp.

[61a] R. A. WATSON-CLARK, C. B. KNOBLER and M. F. HAW-THORNE, *Inorg. Chem.* **35**, 2963–6 (1996).

[62] B. BONNETOT, A. TANGI, M. COLOMBIER and H. MONGEOT, *Inorg. Chem. Acta* **105**, L15–L16 (1985).

(44) *Conjuncto*-$B_{20}H_{18}^{2-}$

(45) *neo*-$B_{20}H_{18}^{2-}$

(46) Most stable isomer
(ac) of $B_{20}H_{19}^{3-}$

(47)

(48)

(49)

Structures of the 3 isomers of *conjuncto*-$B_{20}H_{18}^{4-}$

$(B_{10}H_{13})_2O$, prepared by other routes, had previously been established by X-ray diffraction analysis[63] and by nmr spectroscopy.[64] Another interesting derivative is [*closo*-1,10-$B_{10}H_8(N_2)_2$] in which the apical H atoms in $B_{10}H_{10}^{2-}$ have been replaced by end-on dinitrogen ligands (see pp. 414–6): the B–N distance is 149.9 pm and the N–N distance is 109.1 pm[65] (cf 109.8 pm in gaseous N_2). The isoelectronic ligand CO fulfils the same function in [*closo*-1,10-$B_{10}H_8(CO)_2$].[66,67] The closely related stable, volatile, icosahedral molecule [*closo*-1,12-$B_{12}H_{10}(CO)_2$] can be prepared by the reaction of $H_2B_{12}H_{12}.4H_2O$ with CO at 130°C and 800–1000 atm. pressure in the presence of dicobaltoctacarbonyl as catalyst.[67] In the absence of this catalyst, approximately equal amounts of the 1,7- and 1,12-isomers are formed.

[63] N. N. GREENWOOD, W. S. McDONALD and T. R. SPAL-DING. *J. Chem. Soc., Chem. Commun.*, 1251–2 (1980).

[64] J. D. KENNEDY and N. N. GREENWOOD, *Inorg. Chem. Acta* **38**, 93–6 (1980).

[65] T. WHELAN, P. BRINT, T. R. SPALDING, W. S. McDONALD and D. R. LLOYD, *J. Chem. Soc., Dalton Trans.*, 2469–73 (1982).

[66] W. H. KNOTH, J. C. SAUER, H. C. MILLER and E. L. MUE-TTERTIES, *J. Amer. Chem. Soc.* **86**, 115–6 (1964).

[67] W. H. KNOTH, J. C. SAUER, J. H. BALTHIS, H. C. MILLER and E. L. MUETTERTIES, *J. Amer. Chem. Soc.* **89**, 4842–50 (1967). See also P. BRINT, B. SANGCHAKR, M. McGRATH, T. R. SPALDING and R. J. SUFFOLK, *Inorg. Chem.* **29**, 47–52 (1990) for references to more recent work.