

$[\text{Cu}^{\text{II}}(\eta^5\text{-C}_5\text{H}_5)_2]$ is not. Likewise, Fe^{III} and Ni^{IV} carborane derivatives are extremely stable. Conversely, metallocarboranes tend to stabilize lower oxidation states of early transition elements and complexes are well established for Ti^{II} , Zr^{II} , Hf^{II} , V^{II} , Cr^{II} and Mn^{II} : these do not react with H_2 , N_2 , CO or PPh_3 as do cyclopentadienyl derivatives of these elements.

The chemistry of metallocarboranes of all cluster sizes is still rapidly developing and further unusual reactions and novel structures are continually appearing. Furthermore, as Si, Ge, Sn (and Pb) are in the same periodic group as C, heteroboranes containing these elements are to be expected (see p. 394). Likewise, as CC is isoelectronic with BN, the dicarbaboranes such as $\text{C}_2\text{B}_{10}\text{H}_{12}$ can be paralleled by $\text{NB}_{11}\text{H}_{12}$ etc. Numerous azaboranes and their metalladerivatives are known (see p. 211) as indeed are clusters incorporating P, As, Sb (and Bi) (p. 212). The incorporation of the more electronegative element O has proved to be a greater challenge but several examples are now known. Sulfur provides an extensive thia- and polythia-borane chemistry (p. 214) and this is paralleled, although to a lesser extent, by Se and Te derivatives (p. 215). Detailed discussion of these burgeoning areas of borane cluster chemistry fall outside this present treatment but the general references cited on the above mentioned pages provide a

useful introduction into this important new area of chemistry.

6.7 Boron Halides

Boron forms numerous binary halides of which the monomeric trihalides BX_3 are the most stable and most extensively studied. They can be regarded as the first members of a homologous series B_nH_{n+2} . The second members B_2X_4 are also known for all 4 halogens but only F forms more highly catenated species containing BX_2 groups: B_3F_5 , B_4F_6 , B_8F_{12} (p. 201). Chlorine forms a series of neutral *closo*-polyhedral compounds B_nCl_n ($n = 4, 8-12$) and several similar compounds are known for Br ($n = 7-10$) and I (e.g. B_9I_9). There are also numerous involatile subhalides, particularly of Br and I, but these are of uncertain stoichiometry and undetermined structure.

6.7.1 Boron trihalides

The boron trihalides are volatile, highly reactive, monomeric molecular compounds which show no detectable tendency to dimerize (except perhaps in Kr matrix-isolation experiments at 20K). In

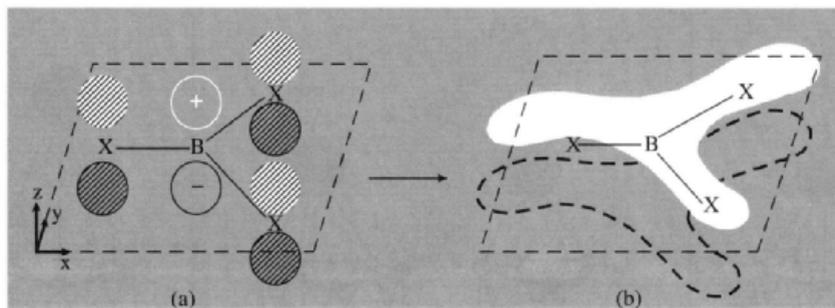


Figure 6.22 Schematic indication of the $p_{\pi}-p_{\pi}$ interaction between the "vacant" p_z orbital on B and the 3 filled p_z orbitals on the 3 X atoms leading to a bonding MO of π symmetry.

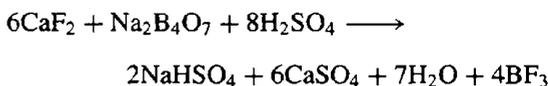
this they resemble organoboranes, BR_3 , but differ sharply from diborane, B_2H_6 , and the aluminium halides and alkyls, Al_2X_6 , Al_2R_6 (p. 259). Some physical properties are listed in Table 6.4; mps and volatilities parallel those of the parent halogens, BF_3 and BCl_3 being gases at room temperature, BBr_3 a volatile liquid, and BI_3 a solid. All four compounds have trigonal planar molecules of D_{3h} symmetry with angle $X-B-X$ 120° (Fig. 6.22a). The interatomic distances $B-X$ are substantially less than those expected for single bonds and this has been interpreted in terms of appreciable $p_{\pi}-p_{\pi}$ interaction (Fig. 6.22b). However, there is disagreement as to whether the extent of this π bonding increases or diminishes with increasing atomic number of the halogen; this probably reflects the differing criteria used (extent of orbital overlap, percentage π -bond character, amount of π -charge transfer from X to B, π -bond energy, or reorganization energy in going from planar BX_3 to tetrahedral LBX_3 , etc.).⁽⁹⁸⁾ For example, it is quite possible for the extent of π -charge transfer from X to B to increase in the sequence $F < Cl < Br < I$ but for the actual magnitude of the π -bond energy to be in

the reverse sequence $BF_3 > BCl_3 > BBr_3 > BI_3$ because of the much greater bond energy of the lighter homologues. Indeed, the mean $B-F$ bond energy in BF_3 is 646 kJ mol^{-1} , which makes it the strongest known "single" bond; if $x\%$ of this were due to π bonding, then even if $2.4x\%$ of the $B-I$ bond energy were due to π bonding, the π -bond energy in BI_3 would be less than that in BF_3 in absolute magnitude. The point is one of some importance since the chemistry of the trihalides is dominated by interactions involving this orbital.

Table 6.4 Some physical properties of boron trihalides

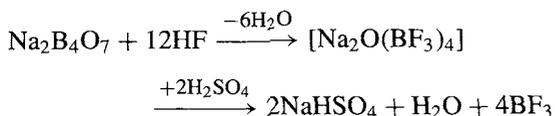
Property	BF_3	BCl_3	BBr_3	BI_3
MP/ $^\circ\text{C}$	-127.1	-107	-46	49.9
BP/ $^\circ\text{C}$	-99.9	12.5	91.3	210
$r(B-X)/\text{pm}$	130	175	187	210
ΔH_f° (298 K)/ kJ mol^{-1} (gas)	-1123	-408	-208	+
$E(B-X)/\text{kJ mol}^{-1}$	646	444	368	267

BF_3 is used extensively as a catalyst in various industrial processes (p. 199) and can be prepared on a large scale by the fluorination of boric oxide or borates with fluorspar and concentrated H_2SO_4 :

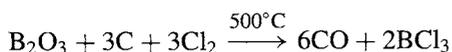


⁹⁸ Some key references will be found in D. R. ARMSTRONG and P. G. PERKINS, *J. Chem. Soc. (A)*, 1967, 1218-22; and in M. F. LAPPERT, M. R. LITZOW, J. B. PEDLEY, P. N. K. RILEY and A. TWEEDALE, *J. Chem. Soc. (A)*, 1968, 3105-10. Y. A. BUSLAEV, E. A. KRAVCHENKO and L. KOLDIZ, *Coord. Chem. Rev.* **82**, 9-231 (1987). V. BRANCHADELL and A. OLIVA, *J. Am. Chem. Soc.* **113**, 4132-6 (1991) and *Theochem.* **236**, 75-84 (1991).

Better yields are obtained in the more modern two-stage process:



On the laboratory scale, pure BF_3 is best made by thermal decomposition of a diazonium tetrafluoroborate (e.g. $\text{PhN}_2\text{BF}_4 \longrightarrow \text{PhF} + \text{N}_2 + \text{BF}_3$). BCl_3 and BBr_3 are prepared on an industrial scale by direct halogenation of the oxide in the presence of C, e.g.:



Laboratory samples of the pure compounds can be made by halogen exchange between BF_3 and Al_2X_6 . BI_3 is made in good yield by treating LiBH_4 (or NaBH_4) with elemental I_2 at 125° (or 200°). Both BBr_3 and BI_3 tend to decompose with liberation of free halogen when exposed to light or heat; they can be purified by treatment with Hg or Zn/Hg.

Simple BX_3 undergo rapid scrambling or redistribution reactions on being mixed and

the mixed halides BX_2Y and BXY_2 have been identified by vibrational spectroscopy, mass spectrometry, or nmr spectroscopy using ^{11}B or ^{19}F . A good example of this last technique is shown in Fig. 6.23, where not only the species $\text{BF}_{3-n}\text{X}_n$ ($n = 0, 1, 2$) were observed but also the trihalogeno species BFCIBr .⁽⁹⁹⁾ The equilibrium concentration of the various species are always approximately random (equilibrium constants between 0.5 and 2.0) but it is not possible to isolate individual mixed halides because the equilibrium is too rapidly attained from either direction (<1 s). The related systems $\text{RBX}_2/\text{R}'\text{BY}_2$ (and $\text{ArBX}_2/\text{Ar}'\text{BY}_2$) also exchange X and Y but not R (or Ar). The scrambling mechanism probably involves a 4-centre transition state. Consistent with this, complexes such as Me_2OBX_3 or Me_3NBX_3 do not scramble at room temperature, or even above, in the absence of free BX_3 ⁽¹⁰⁰⁾ (cf. the stability of CFCl_3 , CF_2Cl_2 , etc.) and species that are

⁹⁹ T. D. COYLE and F. G. A. STONE, *J. Chem. Phys.* **32**, 1892-3 (1960).

¹⁰⁰ J. S. HARTMAN and J. M. MILLER, *Adv. Inorg. Chem. Radiochem.* **21**, 147-77 (1978).

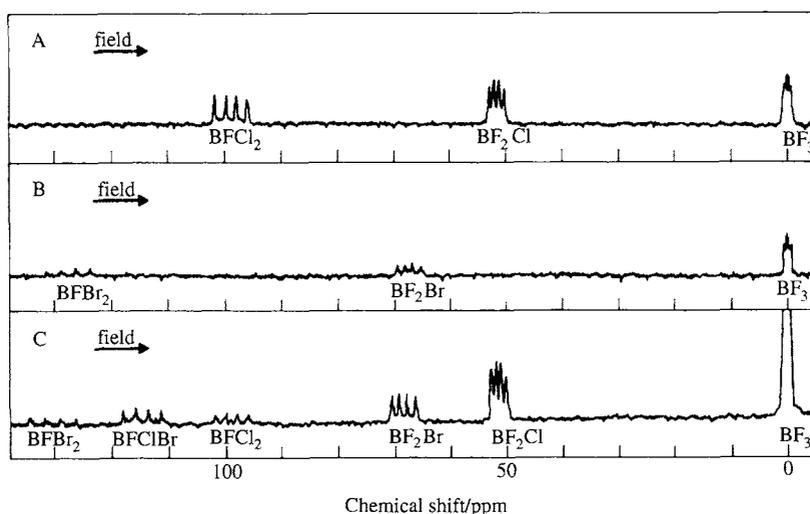


Figure 6.23 Fluorine-19 nmr spectra of mixtures of boron halides showing the presence of mixed fluorohalogenoboranes.

Factors Affecting the Stability of Donor–Acceptor Complexes^(101–103)

For a given ligand, stability of the adduct LBX_3 usually increases in the sequence $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$, probably because the loss of π bonding on reorganization from planar to tetrahedral geometry (p. 196) is not fully compensated for by the expected electronegativity effect. However, if the ligand has an H atom directly bonded to the donor atom, the resulting complex is susceptible to protonolysis of the B–X bond, e.g.:

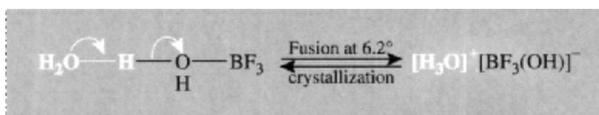


In such cases the great strength of the B–F bond ensures that the BF_3 complex is more stable than the others. For example, BF_3 forms stable complexes with H_2O , MeOH , Me_2NH , etc., whereas BCl_3 reacts rapidly to give $\text{B}(\text{OH})_3$, $\text{B}(\text{OMe})_3$ and $\text{B}(\text{NMe}_2)_3$; with BBr_3 and BI_3 such protolytic reactions are sometimes of explosive violence. Even ethers may be cleaved by BCl_3 to give RCl and ROBCl_2 , etc.

For a given BX_3 , the stability of the complex depends on (a) the chemical nature of the donor atom, (b) the presence of polar substituents on the ligand, (c) steric effects, (d) the stoichiometric ratio of ligand to acceptor, and (e) the state of aggregation. Thus the majority of adducts have as the donor atom N, P, As; O, S; or the halide and hydride ions X^- . BX_3 (but not BH_3) can be classified as type-a acceptors, forming stronger complexes with N, O and F ligands than with P, S and Cl. However, complexes are not limited to these traditional main-group donor atoms, and, following the work of D. F. Shriver (1963), many complexes have been characterized in which the donor atom is a transition metal, e.g. $[(\text{C}_5\text{H}_5)_2\text{H}_2\text{W}^{\text{IV}} \rightarrow \text{BF}_3]$, $[(\text{Ph}_3\text{P})_2(\text{CO})\text{ClRh}^{\text{I}} \rightarrow \text{BBr}_3]$, $[(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{Rh}^{\text{I}} (\text{BCl}_3)_2]^+$, $[(\text{Ph}_3\text{P})_2(\text{CO})\text{ClIr}^{\text{I}} (\text{BF}_3)_2]$, $[(\text{Ph}_3\text{P})_2\text{Pt}^{\text{0}} (\text{BCl}_3)_2]$, etc. Displacement studies on several such complexes indicate that BF_3 is a weaker acceptor than BCl_3 .

The influence of polar substituents on the ligand follows the expected sequence for electronegative groups, e.g. electron donor properties decrease in the order $\text{NMe}_3 > \text{NMe}_2\text{Cl} > \text{NMeCl}_2 \gg \text{NCl}_3$. Steric effects can also limit the electron-donor strength. For example, whereas pyridine, $\text{C}_5\text{H}_5\text{N}$, is a weaker base (proton acceptor) than 2-Me $\text{C}_5\text{H}_4\text{N}$ and 2,6-Me $_2\text{C}_5\text{H}_3\text{N}$, the reverse is true when BF_3 is the acceptor due to steric crowding of the α -Me groups which prevent the close approach of BF_3 to the donor atom. Steric effects also predominate in determining the decreasing stability of BF_3 etherates in the sequence $\text{C}_4\text{H}_8\text{O}(\text{thf}) > \text{Me}_2\text{O} > \text{Et}_2\text{O} > \text{Pr}_2\text{O}$.

The influences of stoichiometry and state of aggregation are more subtle. At first sight it is not obvious why BF_3 , with 1 vacant orbital should form not only $\text{BF}_3 \cdot \text{H}_2\text{O}$ but also the more stable $\text{BF}_3 \cdot 2\text{H}_2\text{O}$; similarly, the 1:2 complexes with ROH and RCOOH are always more stable than the 1:1 complexes. The second mole of ligand is held by hydrogen bonding in the solid, e.g. $\text{BF}_3 \cdot \text{OH}_2 \dots \text{OH}_2$; however, above the mp 6.2°C the compound melts and the act of coordinate-bond formation causes sufficient change in the electron distribution within the ligand that ionization ensues and the compound is virtually completely ionized as a molten salt:⁽¹⁰¹⁾



The greater stability of the 1:2 complex is thus seen to be related to the formation of H_3O^+ , ROH_2^+ , etc., and the lower stability of the 1:1 complexes HBF_3OH , HBF_3OR , is paralleled by the instability of some other anhydrous oxo acids, e.g. H_2CO_3 . The mp of the hydrate is essentially the transition temperature between an H-bonded molecular solid and an ionically dissociated liquid. A transition in the opposite sense occurs when crystalline $[\text{PCl}_4]^+[\text{PCl}_6]^-$ melts to give molecular PCl_5 (p. 498) and several other examples are known. The fact that coordination can substantially modify the type of bonding should occasion no surprise: the classic example (first observed by J. Priestley in 1774) was the reaction $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{c})$.

expected to form stronger π bonds than BX_3 (such as R_2NBX_2) exchange much more slowly (days or weeks).

The boron trihalides form a great many molecular addition compounds with molecules

¹⁰¹N. N. GREENWOOD and R. L. MARTIN *Qt. Revs.* **8**, 1–39 (1954).

¹⁰²V. GUTMANN, *The Donor-Acceptor Approach to Molecular Interactions*, Plenum, New York, 1978, 279 pp.

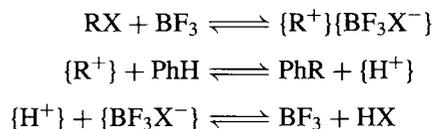
¹⁰³A. HAALAND, *Angew. Chem. Int. Edn. Engl.* **28**, 992–1007 (1989).

(ligands) possessing a lone-pair of electrons (Lewis base). Such adducts have assumed considerable importance since it is possible to investigate in detail the process of making and breaking one bond, and to study the effect this has on the rest of the molecule (see Panel). The tetrahalogeno borates BX_4^- are a special case in which the ligand is X^- ; they are isoelectronic with BH_4^- (p. 165) and with CH_4 and CX_4 . Salts of BF_4^- are readily formed by adding a suitable metal fluoride to BF_3 either in the absence of solvent or in such nonaqueous solvents as HF, BrF_3 , AsF_3 or SO_2 . The alkali metal salts MBF_4 are stable to hydrolysis in aqueous solutions. Some molecular fluorides such as NO_2F and $RCOF$ react similarly. There is a significant lengthening of the B–F bond from 130 pm in BF_3 to 145 pm in BF_4^- . The other tetrahalogenoborates, BX_4^- , are less stable but may be prepared using large counter cations, e.g. Rb, Cs, pyridinium, tetraalkylammonium, tropenium, triphenylcarbonium, etc. The BF_4^- anion is a very weakly coordinating ligand, indeed one of the weakest,⁽¹⁰⁴⁾ however, unstable complexes are known in which it acts as an η^1 -ligand and, in the case of $[Ag(lut)_2(BF_4)]$ it acts as a bis(bidentate) bridging ligand $[\mu_4-\eta^2, \eta^2-BF_4]^-$ to form a polymeric chain of 6-coordinate Ag centres⁽¹⁰⁵⁾ [lut = lutidene, i.e. 2,6-dimethylpyridine].

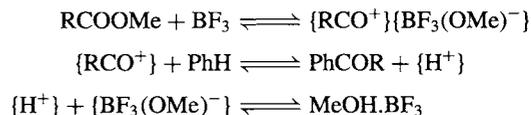
The importance of the trihalides as industrial chemicals stems partly from their use in preparing crystalline boron (p. 141) but mainly from their ability to catalyse a wide variety of organic reactions.⁽¹⁰⁶⁾ BF_3 is the most widely used but BCl_3 is employed in special cases. Thus, BF_3 is manufactured on the multikilotonne scale whereas the production of BCl_3 (USA, 1990) was 250 tonnes and BBr_3 was about 23 tonnes. BF_3 is shipped in steel cylinders containing 2.7 or 28 kg at a pressure of 10–12 atm, or in tube trailers

containing about 5.5 tonnes. Prices for BF_3 are in the range \$4.00–5.00/kg depending on purity and quantity; corresponding prices (USA, 1991) for BCl_3 and BBr_3 were \$8.50–16.75/kg and \$81.50/kg, respectively.

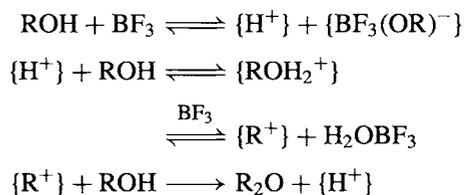
Many of the reactions of BF_3 are of the Friedel–Crafts type though they are perhaps not strictly catalytic since BF_3 is required in essentially equimolar quantities with the reactant. The mechanism is not always fully understood but it is generally agreed that in most cases ionic intermediates are produced by or promoted by the formation of a BX_3 complex; electrophilic attack of the substrate by the cation so produced completes the process. For example, in the Friedel–Crafts-type alkylation of aromatic hydrocarbons:



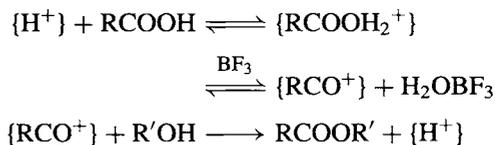
Similarly, ketones are prepared via acyl carbonium ions:



Evidence for many of these ions has been extensively documented.⁽¹⁰¹⁾



A similar mechanism has been proposed for the esterification of carboxylic acids:

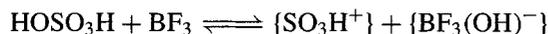
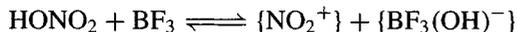


¹⁰⁴ W. BECK and K. SÜNKEL, *Chem. Rev.* **88**, 1405–21 (1988).

¹⁰⁵ E. HORM, M. R. SNOW and E. R. T. TIEKINK, *Aust. J. Chem.* **40**, 761–5 (1987).

¹⁰⁶ G. OLAH (ed.), *Friedel–Crafts and Related Reactions*, Interscience, New York, 1963 (4 vols).

Nitration and sulfonation of aromatic compounds probably occur via the formation of the nityl and sulfonyl cations:

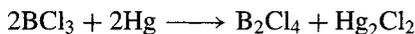


Polymerization of alkenes and the isomerization of alkanes and alkenes occur in the presence of a cocatalyst such as H_2O , whereas the cracking of hydrocarbons is best performed with HF as cocatalyst. These latter reactions are of major commercial importance in the petrochemicals industry.

6.7.2 Lower halides of boron

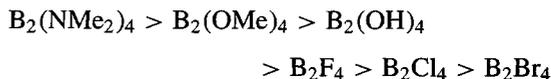
B_2F_4 (mp -56° , bp -34°C) has a planar (D_{2h}) structure with a rather long B–B bond; in this it resembles both the oxalate ion $\text{C}_2\text{O}_4^{2-}$ and N_2O_4 with which it is precisely isoelectronic. Crystalline B_2Cl_4 (mp -92.6°C) has the same structure, but in the gas phase (bp 65.5°) it adopts the staggered D_{2d} configuration (see below) with hindered rotation about the B–B bond (ΔE_r 7.7 kJ mol^{-1}). The structure of gaseous B_2Br_4 is also D_{2d} with B–B 169 pm and ΔE_r 12.8 kJ mol^{-1} . B_2I_4 is presumably similar.

B_2Cl_4 was the first compound in this series to be prepared and is the most studied; it is best made by subjecting BCl_3 vapour to an electrical discharge between mercury or copper electrodes:

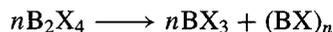


The reaction probably proceeds by formation of a $\{\text{BCl}\}$ intermediate which then inserts into a B–Cl bond of BCl_3 to give the product directly.

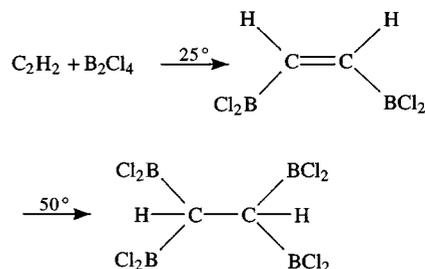
Another route is via the more stable $\text{B}_2(\text{NMe}_2)_4$ (see reaction scheme). Thermal stabilities of these compounds parallel the expected sequence of $p_\pi-p_\pi$ bonding between the substituent and B:



The halides are much less stable than the corresponding BX_3 , the most stable member B_2F_4 decomposing at the rate of about 8% per day at room temperature. B_2Br_4 disproportionates so rapidly at room temperature that it is difficult to purify:

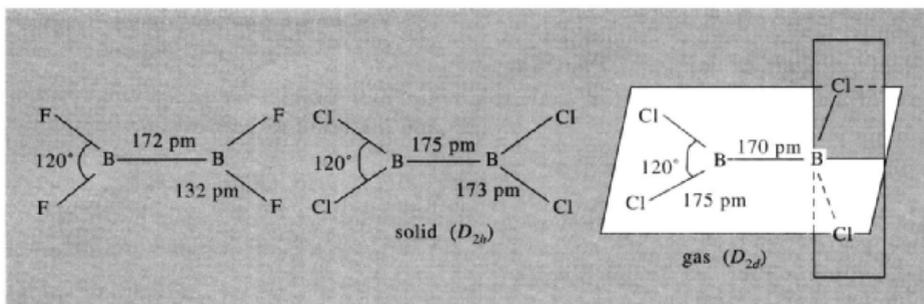


The compounds B_2X_4 are spontaneously flammable in air and react with H_2 to give BHX_2 , B_2H_6 and related hydrohalides; they form adducts with Lewis bases ($\text{B}_2\text{Cl}_4\text{L}_2$ more stable than $\text{B}_2\text{F}_4\text{L}_2$) and add across C–C multiple bonds, e.g.



Other reactions of B_2Cl_4 are shown in the scheme and many of these also occur with B_2F_4 .

When BF_3 is passed over crystalline B at 1850°C and pressures of less than 1 mmHg, the reactive gas BF is obtained in high yield and can



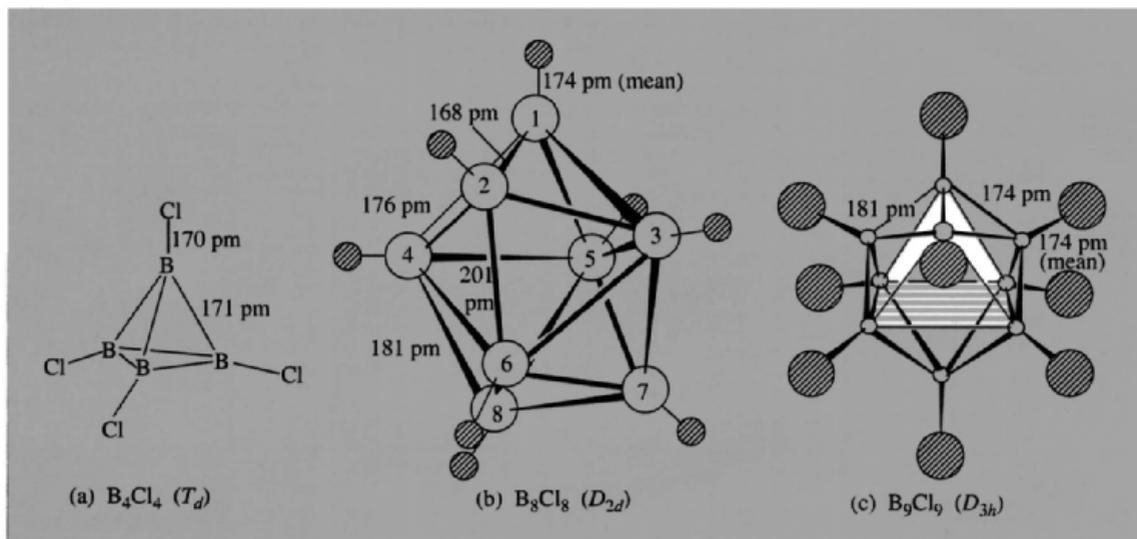


Figure 6.24 Molecular structures of (a) tetrahedral B_4Cl_4 , (b) dodecahedral B_8Cl_8 , and (c) tricapped trigonal pyramidal B_9Cl_9 and B_9Br_9 . In B_8Cl_8 note that the shortest B-B distances are between two 5-coordinate B atoms, e.g. B(1)-B(2) 168 pm; the longest are between two 6-coordinate B atoms, e.g. B(4)-B(6) 201 pm and intermediate distances are between one 5- and one 6-coordinate B atom. A similar trend occurs in B_9Cl_9 .

bonding has been discussed in terms of localized 3-centre bonds above the 4 tetrahedral faces supplemented by p_π interaction with p orbitals of suitable symmetry on the 4 Cl atoms: the 8 electrons available for framework bonding from the 4 {BCl} groups fill 4 bonding MOs of class A_1 and T_2 and there are 2 additional bonding MOs of class E which have correct symmetry to mix with the Cl p_π orbitals. B_8Cl_8 (variously described as dark red, dark purple or green-black crystals) has an irregular dodecahedral (bisphenoid) arrangement of the *closo*- B_8 cluster (Fig. 6.24b) with 14 B-B distances in the range 168–184 pm and 4 substantially longer B-B distances at 193–205 pm. B_9Br_9 is a particularly stable compound; it forms as dark-red crystals together with other subbromides ($n = 7$ –10) when gaseous BBr_3 is subjected to a silent electric discharge in the presence of Cu wool, and can be purified by sublimation under conditions (200°C) which rapidly decompose the other products. B_9Br_9 is isostructural with B_9Cl_9 (yellow-orange) (Fig. 6.24c). The photoelectron

spectra and bonding in B_4Cl_4 , B_8Cl_8 and B_9Cl_9 have been described in detail.⁽¹⁰⁹⁾

Many mixed halides $B_nBr_{n-x}Cl_x$ ($n = 9, 10, 11$) have been identified by mass spectrometry and other techniques, but their separation as pure compounds has so far not been achieved. Chemical reactions of B_nX_n resemble those of B_2X_4 except that alkenes do not cleave the B-B bonds in the *closo*-species. Thus, B_4Cl_4 reacts with LiEt to give the yellow liquids B_4Cl_3Et and $B_4Cl_2Et_2$, whereas $LiBu^t$ afforded $B_4Bu^t_4$ as a glassy solid, mp 45°C.⁽¹¹⁰⁾ By contrast, reaction with Me_3SnH yields *arachno*- B_4H_{10} and $LiBH_4$ yields a mixture of *nido*- B_5H_9 and *nido*- B_6H_{10} , while B_2H_6 gave *nido*- $B_6H_6Cl_4$ and a mixture of *nido*- $B_{10}H_nCl_{14-n}$ ($n = 8$ –12).⁽¹¹¹⁾

¹⁰⁹ P. R. LEBRETON, S. URANO, M. SHAHBAZ, S. L. EMERY and J. A. MORRISON, *J. Am. Chem. Soc.* **108**, 3937–46 (1986).

¹¹⁰ T. DAVAN and J. A. MORRISON, *J. Chem. Soc., Chem. Commun.*, 250–1 (1981).

¹¹¹ S. L. EMERY and J. A. MORRISON, *Inorg. Chem.* **24**, 1612–13 (1985).

6.8 Boron–Oxygen Compounds⁽¹¹²⁾

Boron (like silicon) invariably occurs in nature as oxo compounds and is never found as the element or even directly bonded to any other element than oxygen.[†] The structural chemistry of B–O compounds is characterized by an extraordinary complexity and diversity which rivals those of the borides (p. 145) and boranes (p. 151). In addition, vast numbers of predominantly organic compounds containing B–O are known.

6.8.1 Boron oxides and oxoacids⁽¹¹²⁾

The principal oxide of boron is boric oxide, B₂O₃ (mp 450°, bp (extrap) 2250°C). It is one of the most difficult substances to crystallize and, indeed, was known only in the vitreous state until 1937. It is generally prepared by careful dehydration of boric acid B(OH)₃. The normal crystalline form (*d* 2.56 g cm⁻³) consists of a 3D network of trigonal BO₃ groups joined through their O atoms, but there is also a dense form (*d* 3.11 g cm⁻³) formed under a pressure of 35 kbar at 525°C and built up from irregular interconnected BO₄ tetrahedra. In the vitreous state (*d* ≈ 1.83 g cm⁻³) B₂O₃ probably consists of a network of partially ordered trigonal BO₃ units in which the 6-membered (BO)₃ ring predominates; at higher temperatures the structure becomes increasingly disordered and above 450°C polar —B=O groups are formed. Fused B₂O₃ readily dissolves many metal oxides to give characteristically coloured borate glasses. Its major application is in the glass industry where borosilicate glasses

(e.g. Pyrex) are extensively used because of their small coefficient of thermal expansion and their easy workability. US production of B₂O₃ exceeds 25 000 tonnes pa and the price (1990) was \$2780–2950 per tonne for 99% grade.

Orthoboric acid, B(OH)₃, is the normal end product of hydrolysis of most boron compounds and is usually made (≈160 000 tonnes pa) by acidification of aqueous solutions of borax. Price depends on quality, being \$805 per tonne for technical grade and about twice that for refined material (1990). It forms flaky, white, transparent crystals in which a planar array of BO₃ units is joined by unsymmetrical H bonds as shown in Fig. 6.25. In contrast to the short O—H···O distance of 272 pm within the plane, the distance between consecutive layers in the crystal is 318 pm, thus accounting for the pronounced basal cleavage of the waxy, plate-like crystals, and their low density (1.48 g cm⁻³). B(OH)₃ is a very weak monobasic acid and acts exclusively by hydroxylation acceptance rather than proton donation:

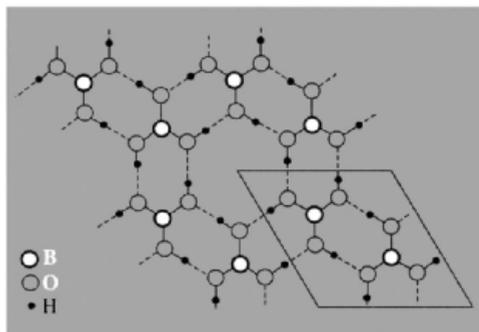
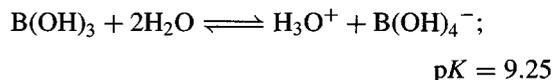


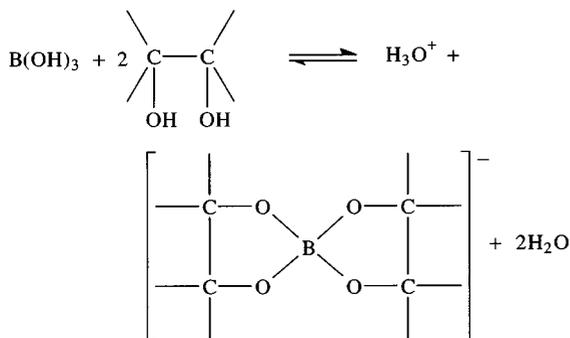
Figure 6.25 Layer structure of B(OH)₃. Interatomic distances are B–O 136 pm, O–H 97 pm, O—H···O 272 pm. Angles at B are 120° and at O 126° and 114°. The H bond is almost linear.

Its acidity is considerably enhanced by chelation with polyhydric alcohols (e.g. glycerol, mannitol) and this forms the basis of its use in analytical chemistry; e.g. with mannitol p*K* drops to 5.15,

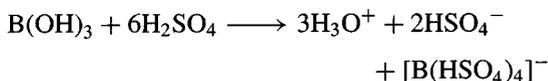
¹¹² Supplement to "Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. V, Boron: Part A, "Boron-Oxygen Compounds", Longman, London, 1980, 825 pp. See also J. R. BOWSER and T. P. FEHLNER, Chap. 1 in H. W. ROESKY (ed.), *Rings, Clusters and Polymers of Main Group and Transition Elements*, Elsevier, Amsterdam, 1989, pp. 1–48.

[†] Trivial exceptions to this sweeping generalization are NaBF₄ (ferrucite) and (K,Cs)BF₄ (avogadrite) which have been reported from Mt. Vesuvius, Italy.

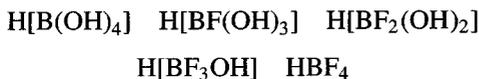
indicating an increase in the acid equilibrium constant by a factor of more than 10^4 .⁽¹¹³⁾



B(OH)_3 also acts as a strong acid in anhydrous H_2SO_4 :



Other reactions include esterification with $\text{ROH}/\text{H}_2\text{SO}_4$ to give B(OR)_3 , and coordination of this with NaH in thf to give the powerful reducing agent $\text{Na[BH(OR)}_3]$. Reaction with H_2O_2 gives peroxoboric acid solutions which probably contain the monoperoxoborate anion $[\text{B(OH)}_3\text{OOH}]^-$. A complete series of fluoroboric acids is also known in aqueous solution and several have been isolated as pure compounds:



The hypohalito analogues $[\text{B(OH)}_3(\text{OX})]^-$ ($\text{X}=\text{Cl}, \text{Br}$) have recently been characterized in aqueous solutions of B(OH)_3 containing NaOX ; the stability constants $\log \beta'$ at 25°C being 2.25(1) and 1.83(4), respectively,⁽¹¹⁴⁾ compared with 5.39(7) for B(OH)_4^- .

¹¹³ J. M. CODDINGTON and M. J. TAYLOR, *J. Coord. Chem.* **20**, 27–38 (1989), and references cited therein, including those which describe its application to conformational analysis of carbohydrates and its use in separation and chromatographic techniques.

¹¹⁴ A. BOUSHER, P. BRIMBLECOMBE and D. MIDGLEY, *J. Chem. Soc., Dalton Trans.*, 943–6 (1987).

Partial dehydration of B(OH)_3 above 100° yields metaboric acid HBO_2 which can exist in several crystalline modifications:

	CN of B	d/g cm ⁻³	mp/°C
Orthorhombic HBO_2	3	1.784	176°
B(OH)_3 $\xrightarrow{140^\circ}$ monoclinic HBO_2	3 and 4	2.045	201°
	4	2.487	236°
B(OH)_3 $\xrightarrow{175^\circ}$ cubic HBO_2	4	2.487	236°

Orthorhombic HBO_2 consists of trimeric units $\text{B}_3\text{O}_3(\text{OH})_3$ which are linked into layers by H bonding (Fig. 6.26); all the B atoms are 3-coordinate. Monoclinic HBO_2 is built of chains of composition $[\text{B}_3\text{O}_4(\text{OH})(\text{H}_2\text{O})]$ in which some of the B atoms are now 4-coordinate, whereas cubic HBO_2 has a framework structure of tetrahedral BO_4 groups some of which are H bonded. The increase in CN of B is paralleled by an increase in density and mp.

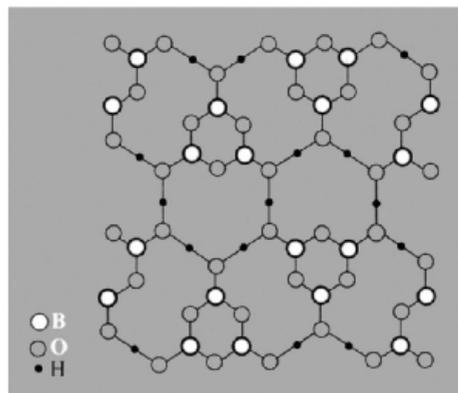


Figure 6.26 Layer structure of orthorhombic metaboric acid $\text{HBO}_2(\text{III})$, comprising units of formula $\text{B}_3\text{O}_3(\text{OH})_3$ linked by $\text{O} \cdots \text{H} \cdots \text{O}$ bonds.

Boron suboxide $(\text{BO})_n$ and subboric acid $\text{B}_2(\text{OH})_4$ were mentioned on p. 201.

6.8.2 Borates^(112,115)

The phase relations, stoichiometry and structural chemistry of the metal borates have been extensively studied because of their geochemical implications and technological importance. Borates are known in which the structural unit is mononuclear (1 B atom), bi-, tri-, tetra- or pentanuclear, or in which there are polydimensional networks including glasses. The main structural principles underlying the bonding in crystalline metal borates are as follows:⁽¹¹⁶⁾

1. Boron can link either three oxygens to form a triangle or four oxygens to form a tetrahedron.
2. Polynuclear anions are formed by corner-sharing only of boron-oxygen triangles and tetrahedra in such a manner that a compact insular group results.
3. In the hydrated borates, protonatable oxygen atoms will be protonated in the following sequence: available protons are first assigned to free O^{2-} ions to convert these to free OH^- ions; additional protons are assigned to tetrahedral oxygens in the borate ion, and then to triangular oxygens in the borate ion; finally any remaining protons are assigned to free OH^- ions to form H_2O molecules.

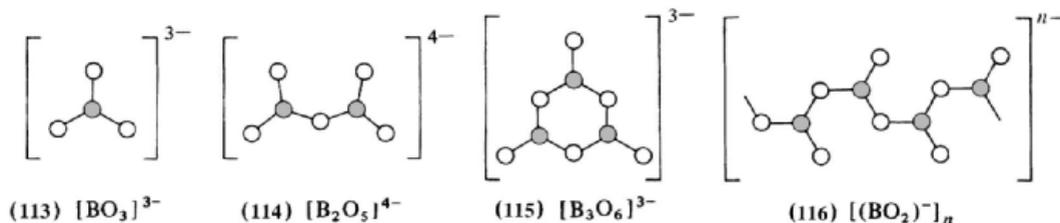
4. The hydrated insular groups may polymerize in various ways by splitting out water; this process may be accompanied by the breaking of boron-oxygen bonds within the polyanion framework.
5. Complex borate polyanions may be modified by attachment of an individual side group, such as (but not limited to) an extra borate tetrahedron, an extra borate triangle, 2 linked triangles, an arsenate tetrahedron, and so on.
6. Isolated $B(OH)_3$ groups, or polymers of these, may exist in the presence of other anions.

Examples of minerals and compounds containing monomeric triangular, BO_3 units (structure 113) are the rare-earth orthoborates $M^{III}BO_3$ and the minerals $CaSn^{IV}(BO_3)_2$ and $Mg_3(BO_3)_2$. Binuclear trigonal planar units (114) are found in the pyroborates $Mg_2B_2O_5$, $Co^{II}_2B_2O_5$ and $Fe^{II}_2B_2O_5$. Trinuclear cyclic units (115) occur in the metaborates $NaBO_2$ and KBO_2 , which should therefore be written as $M_3B_3O_6$ (cf. metaboric acid, p. 204). Polynuclear linkage of BO_3 units into infinite chains of stoichiometry BO_2 (116) occurs in $Ca(BO_2)_2$, and three-dimensional linkage of planar BO_3 units occurs in the borosilicate mineral tourmaline and in glassy B_2O_3 (p. 203).

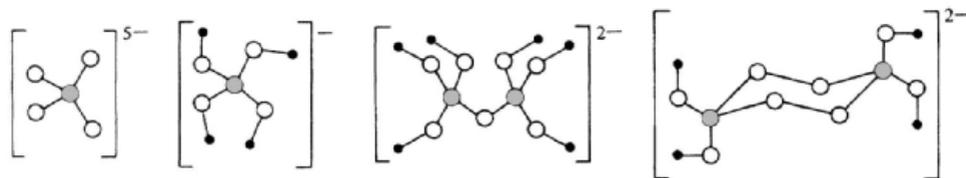
Monomeric tetrahedral BO_4 units (117) are found in the zircon-type compound Ta^VBO_4 and in the minerals $(Ta,Nb)BO_4$ and $Ca_2H_4BAS^VO_8$. The related tetrahedral unit $[B(OH)_4]^-$ (118) occurs in $Na_2[B(OH)_4]Cl$ and $Cu^{II}[B(OH)_4]Cl$. Binuclear tetrahedral units (119) have been found

¹¹⁵ G. HELLER, *Topics in Current Chemistry* No. 131 Springer-Verlag, Berlin, 1986, 39–98 (a survey of structural types with 568 refs.).

¹¹⁶ C. L. CHRIST and J. R. CLARK, *Phys. Chem. Minerals* 2, 59–87 (1977). See also J. B. FARMER, *Adv. Inorg. Chem. Radiochem.* 25, 187–237 (1982).

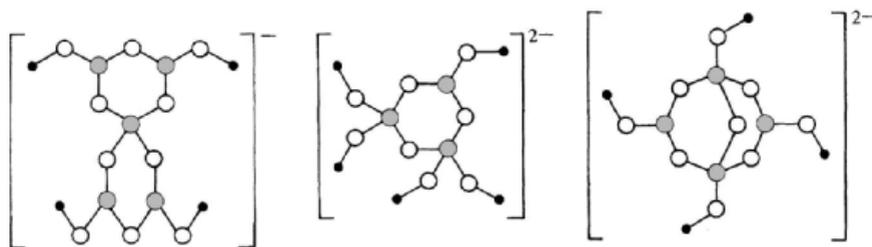


Units containing B in planar BO_3 coordination only



(117) $[\text{BO}_4]^{5-}$ (118) $[\text{B}(\text{OH})_4]^{-}$ (119) $[\text{B}_2\text{O}(\text{OH})_6]^{2-}$ (120) $[\text{B}_2(\text{O}_2)_2(\text{OH})_4]^{2-}$

Units containing B in tetrahedral BO_2 coordination only



(121) $[\text{B}_5\text{O}_6(\text{OH})_4]^{-}$ (122) $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$ (123) $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$

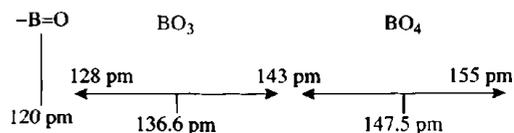
Units containing B in both BO_3 and BO_4 coordination

in $\text{Mg}[\text{B}_2\text{O}(\text{OH})_6]$ and a cyclic binuclear tetrahedral structure (120) characterizes the peroxo-anion $[\text{B}_2(\text{O}_2)_2(\text{OH})_4]^{2-}$ in "sodium perborate" $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$, i.e. $\text{Na}_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4] \cdot 6\text{H}_2\text{O}$. A more complex polynuclear structure comprising sheets of tetrahedrally coordinated $\text{BO}_3(\text{OH})$ units occurs in the borosilicate mineral $\text{CaB}(\text{OH})\text{SiO}_4$ and the fully three-dimensional polynuclear structure is found in BPO_4 (cf. the isoelectronic SiO_2), BaSO_4 and the minerals NaBSi_3O_8 and $\text{Zn}_4\text{B}_6\text{O}_{13}$.

The final degree of structural complexity occurs when the polynuclear assemblages contain both planar BO_3 and tetrahedral BO_4 units joined by sharing common O atoms. The structure of monoclinic HBO_2 affords an example (p. 204). A structure in which the ring has but one BO_4 unit is the spiroanion $[\text{B}_5\text{O}_6(\text{OH})_4]^{-}$ (structure 121) which occurs in hydrated potassium pentaborate $\text{KB}_5\text{O}_8 \cdot 4\text{H}_2\text{O}$, i.e. $\text{K}[\text{B}_5\text{O}_6(\text{OH})_4] \cdot 2\text{H}_2\text{O}$. The anhydrous pentaborate KB_5O_8 has the same structural unit but dehydration of the OH groups link the spiroanions of structure (121) sideways into ribbon-like helical chains. The mineral $\text{CaB}_3\text{O}_3(\text{OH})_5 \cdot \text{H}_2\text{O}$ has 2 BO_4 units in the 6-membered heterocycle (122) and related chain elements $[\text{B}_3\text{O}_4(\text{OH})_3]^{2-}_n$ linked by a common oxygen atom are found in the

important mineral colemanite $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$, i.e. $[\text{CaB}_3\text{O}_4(\text{OH})_3] \cdot \text{H}_2\text{O}$. It is clear from these examples that, without structural data, the stoichiometry of these borate minerals gives little indication of their constitution. A further illustration is afforded by borax which is normally formulated $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, but which contains tetranuclear units $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ formed by fusing 2 B_3O_3 rings which each contain 2 BO_4 (shared) and 1 BO_3 unit (123); borax should therefore be written as $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$.

There is wide variation of B–O distances in these various structures the values increasing, as expected, with increase in coordination:



The extent to which B_3O_3 rings catenate into more complex structures or hydrolyse into smaller units such as $[\text{B}(\text{OH})_4]^{-}$ clearly depends sensitively on the activity (concentration) of water in the system, on the stoichiometric ratio of metal ions to boron and on the temperature ($T\Delta S$).

Many metal borates find important industrial applications (p. 140) and annual world production exceeds 2.9 million tonnes: Turkey 1.2, USA 1.1, Argentina 0.26, the former Soviet Union 0.18, Chile 0.13 Mt. Main uses are in glass-fibre and cellular insulation, the manufacture of borosilicate glasses and enamels, and as fire retardants. Sodium perborate (for detergents) is manufactured on a 550 000 tonne pa scale.

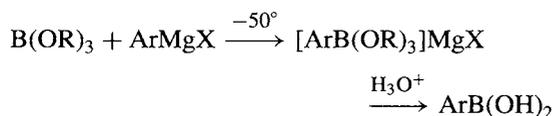
6.8.3 Organic compounds containing boron–oxygen bonds

Only a brief classification of this very large and important class of compounds will be given; most contain trigonal planar B though many 4-coordinate complexes have also been characterized. The orthoborates $B(OR)_3$ can readily be prepared by direct reaction of BCl_3 or $B(OH)_3$ with ROH, while transesterification with $R'OH$ affords a route to unsymmetrical products $B(OR)_2(OR')$, etc. The compounds range from colourless volatile liquids to involatile white solids depending on molecular weight. R can be a primary, secondary, tertiary, substituted or unsaturated alkyl group or an aryl group, and orthoborates of polyhydric alcohols and phenols are also numerous.

Boronic acids $RB(OH)_2$ were first made over a century ago by the unlikely route of slow partial oxidation of the spontaneously flammable trialkyl boranes followed by hydrolysis of the ester so formed (E. Frankland, 1862):



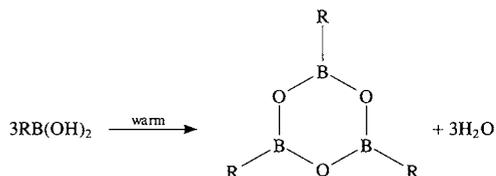
Many other routes are now available but the most used involve the reaction of Grignard reagents or lithium alkyls on orthoborates or boron trihalides:



Phenylboronic acid in particular has proved invaluable, since its complexes with *cis*-diols and -polyols have formed the basis

of chromatographic separations, asymmetric syntheses, enzyme immobilization and the preparation of polymers capable of molecular recognition.⁽¹¹⁷⁾

Boronic acids readily dehydrate at moderate temperatures (or over P_4O_{10} at room temperature) to give trimeric cyclic anhydrides known as trialkyl(aryl)boroxines:



The related trialkoxyboroxines $(ROBO)_3$ can be prepared by esterifying $B(OH)_3$, B_2O_3 or metaboric acid $BO(OH)$ with the appropriate mole ratio of ROH.

Endless variations have been played on these themes and the B atom can be surrounded by innumerable combinations of groups such as acyloxy (RCOO), peroxy (ROO), halogeno (X), hydrido, etc., in either open or cyclic arrays. However, no new chemical principles emerge.

6.9 Boron–Nitrogen Compounds

Two factors have contributed to the special interest that attaches to B–N compounds. First, the B–N unit is isoelectronic with C–C and secondly, the size and electronegativity of the 3 atoms are similar, C being the mean of B and N:

	B	C	N
Number of valence electrons	3	4	5
Covalent single-bond radius/pm	88	77	70
Electronegativity	2.0	2.5	3.0

The repetition of much organic chemistry by replacing pairs of C atoms with the B–N

¹¹⁷ C. D'SILVA and D. GREEN, *J. Chem. Soc., Chem. Commun.*, 227–9 (1991) and leading references cited therein.

grouping has led to many new classes of compound but these need not detain us.⁽¹¹⁸⁾ By contrast, key points emerge from several other areas of B–N chemistry and, accordingly, this section deals briefly with the structure, properties and reaction chemistry of boron nitride, amine-borane adducts, aminoboranes, iminoboranes, cyclic borazines and azaborane clusters.

The synthesis of boron nitride, BN, involves considerable technical difficulty;⁽¹¹⁹⁾ a laboratory preparation yielding relatively pure samples involves the fusion of borax with ammonium chloride, whereas technical-scale production relies on the fusion of urea with $B(OH)_3$ in an atmosphere of NH_3 at 500–950°C. Only a brave (or foolhardy) chemist would attempt to write a balanced equation for either reaction. An alternative synthesis (>99% purity) treats BCl_3 with an excess of NH_3 (see below) and pyrolyses the resulting mixture in an atmosphere of NH_3 at 750°C. The hexagonal modification of BN has a simple layer structure (Fig. 6.27) similar to graphite but with the significant difference that the layers are packed directly on top of each other so that the B atom in one layer is located over an N atom in the next layer at a distance of 333 pm. Cell dimensions and other data for BN and graphite are compared in Table 6.5. Within each layer the B–N distance is only 145 pm; this is similar to the distance of 144 pm in borazine (p. 210) but much less than the sum of single-bond covalent radii (158 pm) and this has been taken to indicate substantial additional π bonding within the layer. However, unlike graphite, BN is colourless and a good insulator; it also resists

attack by most reagents though fluorine converts it quantitatively to BF_3 and N_2 and HF gives NH_4BF_4 quantitatively. Hexagonal BN can be converted into a cubic form (zinc-blende type structure) at 1800°C and 85 000 atm pressure in the presence of an alkali or alkaline-earth metal catalyst. The lattice constant of cubic BN is 361.5 pm (cf. diamond 356.7 pm). A wurtzite-type modification (p. 1210) can be obtained at lower temperatures.

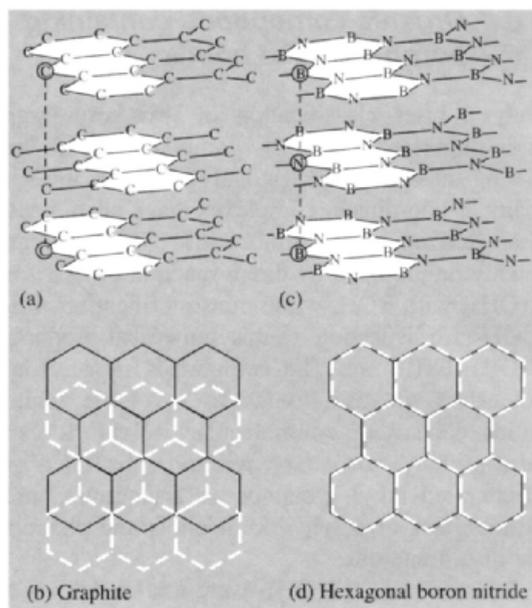


Figure 6.27 Comparison of the hexagonal layer structures of BN and graphite. In BN the atoms of one layer are located directly above the atoms of adjacent layers with B...N contacts; in graphite the C atoms in one layer are located above interstices in the adjacent layer and are directly above atoms in alternate layers only.

Amine-borane adducts have the general formula R_3NBX_3 where R = alkyl, H, etc., and

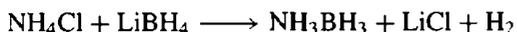
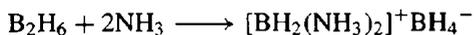
¹¹⁸ I. ANDER, Chap. 1.21 in A. R. KATRITZKY and C. W. REES (eds.), *Comprehensive Heterocyclic Chemistry*, Pergamon, Oxford, 1984, pp. 629–63.

¹¹⁹ R. T. PAINE and C. K. NARULA, *Chem. Rev.* **90**, 73–91 (1990).

Table 6.5 Comparison of hexagonal BN and graphite

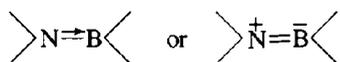
	<i>a</i> /pm	<i>c</i> /pm	<i>c/a</i>	Inter-layer spacing/pm	Intra-layer spacing/pm	<i>d</i> /g cm ⁻³
BN (hexagonal)	250.4	666.1	2.66	333	144.6	2.29
Graphite	245.6	669.6	2.73	335	142	2.255

X = alkyl, H, halogen, etc. They are usually colourless, crystalline compounds with mp in the range 0–100° for X = H and 50–200° for X = halogen. Synthetic routes, and factors affecting the stability of the adducts have already been discussed (p. 165 and p. 198). In cases where diborane undergoes unsymmetrical cleavage (e.g. with NH₃) alternative routes must be devised:

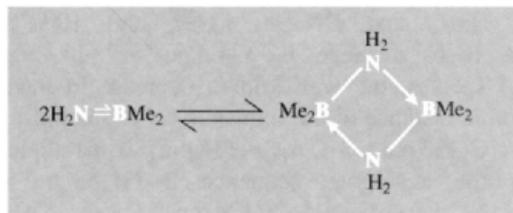


The nature of the bonding in amine-boranes and related adducts has been the subject of considerable theoretical discussion and has also been the source of some confusion. Conventional representations of the donor-acceptor (or coordinate) bond use symbols such as $\text{R}_3\text{N} \rightarrow \text{BX}_3$ or $\text{R}_3\overset{+}{\text{N}} - \overset{-}{\text{B}}\text{X}_3$ to indicate the origin of the bonding electrons and the direction (but not the magnitude) of charge transfer. It is important to realize that these symbols refer to the relative change in electron density with respect to the individual separate donor and acceptor molecules. Thus, $\text{R}_3\overset{+}{\text{N}}$ in the adduct has less electron density on N than has free R_3N , and $\overset{-}{\text{B}}\text{X}_3$ has more electron density on B in the adduct than has free BX_3 ; this does not necessarily mean that N is positive with respect to B in the adduct. Indeed, several MO calculations indicate that the change in electron density on coordination merely reduces but is insufficient to reverse the initial positive charge on the B atom. Consistent with this, experiments show that electrophilic reagents always attack N in amine-borane adducts, and nucleophilic reagents attack B.

A similar situation obtains in the aminoboranes where one or more of the substituents on B is an R_2N group (R = alkyl, aryl, H), e.g. $\text{Me}_2\text{N}-\text{BMe}_2$. Reference to Fig. 6.22 indicates the possibility of some p_π interaction between the lone pair on N and the “vacant” orbital on trigonal B. This is frequently indicated as

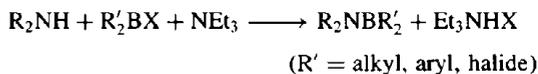
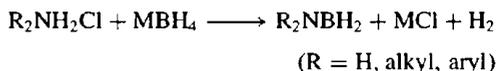


However, as with the amine-borane adducts just considered, this does not normally indicate the actual sign of the net charges on N and B because the greater electronegativity of N causes the σ bond to be polarized in the opposite sense. Thus, N–B bond moments in aminoboranes have been found to be negligible and MO calculations again suggest that the N atom bears a larger net negative charge than does the B atom. The partial double-bond formulation of these compounds, however, is useful in implying an analogy to the isoelectronic alkenes. Coordinative saturation in aminoboranes can be achieved not only through partial double bond formation but also by association (usually dimerization) of the monomeric units to form $(\text{B}-\text{N})_n$ rings. For example, in the gas phase, aminodimethylborane exists as both monomer and dimer in reversible equilibrium:



The presence of bulky groups on either B or N hinders dimer formation and favours monomers, e.g. $(\text{Me}_2\text{NBF}_2)_2$ is dimeric whereas the larger halides form monomers at least in the liquid phase. Association to form trimers (6-membered heterocycles) is less common, presumably because of even greater crowding of substituents, though triborazane $(\text{H}_2\text{NBH}_2)_3$ and its *N*-methyl derivatives, $(\text{MeHNBH}_2)_3$ and $(\text{Me}_2\text{NBH}_2)_3$, are known in which the B_3N_3 ring adopts the cyclohexane chair conformation.

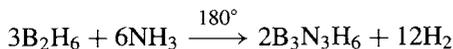
Preparative routes to these compounds are straightforward, e.g.:



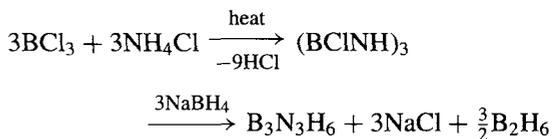
In general monomeric products are readily hydrolysed but associated species (containing 4-coordinate B) are much more stable: e.g. $(\text{Me}_2\text{NBH}_2)_2$ does not react with H_2O at 50° but is rapidly hydrolysed by dilute HCl at 110° because at this temperature there is a significant concentration of monomer present.

Iminoboranes, $\text{R}-\text{N}^{\equiv}\text{B}-\text{R}'$, are isoelectronic with alkynes and contain 2-coordinate boron; their chemistry has recently been reviewed.^(120,121) Likewise for amino iminoboranes, $\text{R}_2\text{N}-\text{B}=\text{NR}'$.⁽¹²²⁾ In both classes of compound inductive and steric effects have an important influence on stability. Another stable 2-coordinate boron species is the linear anion BN_2^{3-} (isoelectronic with CO_2 , CNO^- , NCO^- , N_2O , NO_2^+ , N_3^- and CN_2^{2-}) which occurs in $\text{M}_3^{\text{I}}\text{BN}_2$ and $\text{M}_3^{\text{II}}(\text{BN}_2)_2$. For example, Na_3BN_2 can be prepared as light honey-coloured crystals by heating a 2:1 mixture of NaN_3 and BN at 4 GPa and 1000°C ; the B-N distance is 134.5 pm.⁽¹²³⁾ In neutral species, the well known decrease in interatomic distance in the sequence $\text{C}-\text{C}$ (154 pm) > $\text{C}=\text{C}$ (133 pm), > $\text{C}\equiv\text{C}$ (118 pm) is paralleled by the analogous sequence $\text{B}-\text{N}$ (158 pm) > $\text{B}=\text{N}$ (140 pm) > $\text{B}\equiv\text{N}$ (124 pm).

The cyclic borazine $(-\text{BH}-\text{NH}-)_3$ and its derivatives form one of the largest classes of B-N compounds. The parent compound, also known as "inorganic benzene", was first isolated as a colourless liquid from the mixture of products obtained by reacting B_2H_6 and NH_3 (A. Stock and E. Pohland, 1926):



It is now best prepared by reduction of the B-trichloro derivative:



Borazine has a regular plane hexagonal ring structure and its physical properties closely resemble those of the isoelectronic compound benzene (Table 6.6). Although it is possible to write Kekulé-type structures with $\text{N}\equiv\text{B}$ π bonding superimposed on the σ bonding, the weight of chemical evidence suggests that borazine has but little aromatic character. It reacts readily with H_2O , MeOH and HX to yield 1:3 adducts which eliminate 3H_2 on being heated to 100° , e.g.:

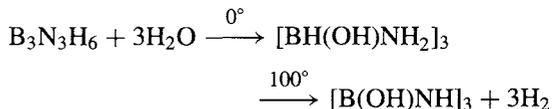


Table 6.6 Comparison of borazine and benzene

Property	$\text{B}_3\text{N}_3\text{H}_6$	C_6H_6
Molecular weight	80.5	78.1
MP/ $^\circ\text{C}$	-57	6
BP/ $^\circ\text{C}$	55	80
Critical temperature	252	288
Density (l at mp)/ g cm^{-3}	0.81	0.81
Density (s)/ g cm^{-3}	1.00	1.01
Surface tension at mp/ dyne cm^{-1} (^a)	31.1	31.0
Interatomic distances/pm	B-N 144 B-H 120 N-H 102	C-C 142 C-H 108

(^a) 1 dyne = 10^{-5} newton.

Numerous other reactions have been documented, most of which are initiated by nucleophilic attack on B. There is no evidence that electrophilic substitution of the borazine ring occurs and conditions required for such reactions in benzenoid systems disrupt the borazine ring by oxidation or solvolysis. However, it is known that the less-reactive hexamethyl derivative $\text{B}_3\text{N}_3\text{Me}_6$ (which can be heated to 460° for 3 h without significant decomposition)

¹²⁰ P. PAETZOLD, *Adv. Inorg. Chem.* **31**, 123-70 (1987).

¹²¹ P. PAETZOLD, *Pure Appl. Chem.* **63**, 345-50 (1991).

¹²² H. NÖTH, *Angew. Chem. Int. Edn. Engl.* **27**, 1603-22 (1988).

¹²³ J. EVERS, M. MÜNSTERKÖTTER, G. OEHLINGER, K. POLBORN and B. SENDLINGER, *J. Less Common Metals* **162**, L17-22 (1990). For the crystal structure of $\text{Sr}_3(\text{BN}_2)_2$, [B-N 135.8(6) pm, angle 180°] see H. WOMELSDORF and H.-J. MEYER, *Z. anorg. allg. Chem.* **620**, 2652-5 (1994).

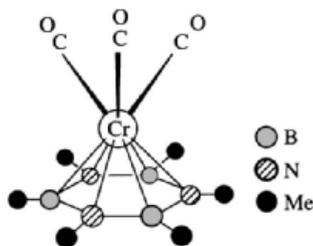
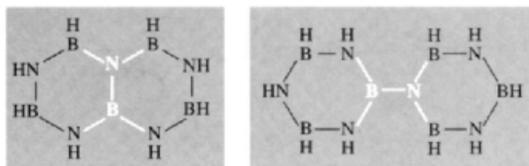


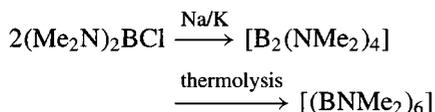
Figure 6.28 Structure of $[\text{Cr}(\eta^6\text{-B}_3\text{N}_3\text{Me}_6)(\text{CO})_3]$.

reacts with $[\text{Cr}(\text{CO})_3(\text{MeCN})_3]$ to give the complex $[\text{Cr}(\eta^6\text{-B}_3\text{N}_3\text{Me}_6)(\text{CO})_3]$ (Fig. 6.28) which closely resembles the corresponding hexamethylbenzene complex $[\text{Cr}(\eta^6\text{-C}_6\text{Me}_6)(\text{CO})_3]$.

N-substituted and *B*-substituted borazines are readily prepared by suitable choice of amine and borane starting materials or by subsequent reaction of other borazines with Grignard reagents, etc. Thermolysis of monocyclic borazines leads to polymeric materials and to polyborazine analogues of naphthalene, biphenyl, etc.:



A quite different structural motif is found in the curious cyclic hexamer $[(\text{BNMe}_2)_6]$ which can be obtained as orange-red crystals by distilling the initial product formed by dehalogenation of $(\text{Me}_2\text{N})_2\text{BCl}$ with Na/K alloy:⁽¹²⁴⁾



The B_6 ring has a chair conformation (dihedral angle 57.6°) with mean B–B distances of 172 pm. All 6 B and all 6 N are trigonal planar and the 6-exocyclic NMe_2 groups are each twisted at an angle of $\sim 65^\circ$ from the adjacent B_3 plane, with

¹²⁴ H. NÖTH and H. POMMERENING, *Angew. Chem. Int. Edn. Engl.* **19**, 482–3 (1980).

B–N 140 pm. Structurally, this cyclohexaborane derivative resembles the radialenes, particularly the isoelectronic $[\text{C}_6(=\text{CHMe})_6]$ in which the C_6 ring likewise adopts the chair conformation.

Finally, the conceptual isoelectronic replacement of C–C by B–N can be applied to carboranes, thus leading (by appropriate synthetic routes) to azaboranes in which one or more of the cluster vertices of the borane is occupied by an N atom. So far, the following species have been characterized,⁽¹²⁵⁾ the relevant cluster geometries and numbering schemes being given by the indicated structures on pp. 153–85: *arachno*-4- NB_8H_{13} (20), *nido*-6- NB_9H_{12} (11), *closo*-1- NB_9H_{10} (5), *arachno*-6,9- $\text{N}_2\text{B}_8\text{H}_{12}$ (21), *nido*-7- $\text{NB}_{10}\text{H}_{13}$ (41), *nido*-7- $\text{NB}_{10}\text{H}_{11}^{2-}$ (80), *closo*-1- $\text{NB}_{11}\text{H}_{12}$ (7, 76) and *anti*-9- $\text{NB}_{17}\text{H}_{20}$ (31).

6.10 Other Compounds of Boron

6.10.1 Compounds with bonds to P, As or Sb

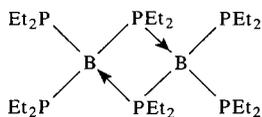
Only minor echoes of the extensive themes of B–N chemistry occur in compounds containing B–P, B–As or B–Sb bonds but there are signs that the field is now beginning to expand rapidly. Few 1:1 phosphine-borane adducts are known, although the recently characterized white crystalline complex $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{PH}_3$, which dissociates reversibly above room temperature, has been suggested as a useful storage material for the safe purification and generation of PH_3 .⁽¹²⁶⁾ The interesting compound $\text{Na}[\text{B}(\text{PH}_2)_4]$ can readily be made by reacting BCl_3 with 4 moles of NaPH_2 ; at moderate temperatures and in the presence of thf it rearranges to the diborate analogue $\text{Na}[(\text{PH}_2)_3\text{B}-\text{PH}_2-\text{B}(\text{PH}_2)_3]$

¹²⁵ T. JELÍNEK, J. D. KENNEDY and B. ŠTÍBR, *J. Chem. Soc., Chem. Commun.*, 677–8 (1994) and references cited therein. L. SCHNEIDER, U. ENGLERT and P. PAETZOLD, *Z. anorg. allg. Chem.* **620**, 1191–3 (1994). H.-P. HANSEN, U. E. ENGLERT and P. PAETZOLD, *Z. anorg. allg. Chem.* **621**, 719–24 (1995).

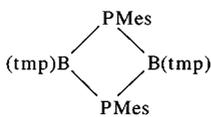
¹²⁶ D. C. BRADLEY, M. B. HURSTHOUSE, M. MOTEVALLI and Z. DAO-HONG, *J. Chem. Soc., Chem. Commun.*, 7–8 (1991).

and with $\text{BH}_3\cdot\text{thf}$ it gives the tetrakis(borane) adduct $\text{Na}[\text{B}(\text{PH}_2\cdot\text{BH}_3)_4]$.⁽¹²⁷⁾

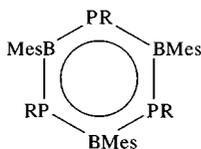
Phosphinoboranes, like their aminoborane analogues (p. 209), tend to oligomerize, although monomeric examples with planar B and pyramidal P atoms have recently been prepared using bulky substituents, e.g. yellow $\text{Mes}_2\text{BPPH}_2$,⁽¹²⁸⁾ orange $(\text{Mes}_2\text{P})_2\text{BBr}$ ⁽¹²⁹⁾ and colourless $(\text{Mes}_2\text{P})_2\text{BOEt}$, mp 163°C ¹³⁰ $(\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{-})$. By contrast, $\text{B}(\text{PEt}_2)_3$ is a dimer with a planar B_2P_2 ring of 4-coordinate B and P atoms (124).⁽¹³⁰⁾ A planar 4-membered ring of 3-coordinate planar B and pyramidal P atoms is featured in the diphosphadiboretane $\{\text{MesPB}(\text{tmp})\}_2$ (125) ($\text{tmp} = 2,2,6,6\text{-tetramethylpiperidino}$);⁽¹³¹⁾ the corresponding diarsadiboretane is also known. A phosphorus analogue of borazine (p. 210) having a planar B_3P_3 ring is the pale yellow crystalline $(\text{MesBPC}_6\text{H}_{11})_3$ (126), synthesized by reacting MesBBR_2 with $\text{C}_6\text{H}_{11}\text{PHLi}$ in hexane at room temperature;⁽¹³²⁾ the B–P distances in



(124)



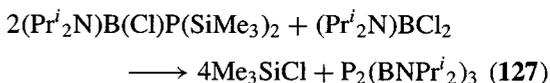
(125)



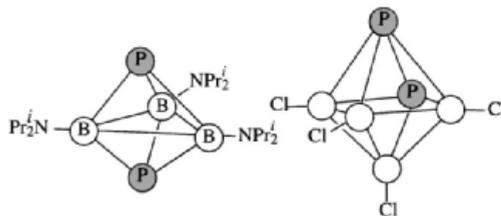
(126)

the boraphosphabenzene are all essentially equal, averaging 184 pm, which is considerably shorter than the known range of single-bond distances (192–196 pm). The cyclohexyl group, C_6H_{11} , can be replaced by Ph, Mes, Bu^t , etc.

Phosphaborane cluster compounds have also been synthesized. For example, thermolysis of a 1:2 mixture of $(\text{Pr}_2\text{N})\text{BCl}$ and $(\text{Pr}_2\text{N})\text{B}(\text{Cl})(\text{SiMe}_3)_2$ at 160°C results in the smooth elimination of Me_3SiCl to give colourless crystals of [*closo*-1,5- $\text{P}_2(\text{BNPr}_2)_3$] (127) in high yield:⁽¹³³⁾



The structural analogy with the dicarbaborane $\text{C}_2\text{B}_3\text{H}_5$ (56) is obvious. Likewise, pyrolysis of a mixture of B_2Cl_4 and PCl_3 yields [*closo*-1,2- $\text{P}_2\text{B}_4\text{Cl}_4$] (128) as hygroscopic colourless crystals.⁽¹³⁴⁾



(127)

(128)

Typical borane clusters incorporating As or Sb atoms are *closo*-1,2- $\text{B}_{10}\text{H}_{10}\text{CHAs}$ and *closo*-1,2- $\text{B}_{10}\text{H}_{10}\text{CHSb}$ in which the group 15 heteroatom replaces a CH vertex in the dicarbaborane (76); they are prepared in 25 and 41% yield, respectively, by direct reaction of $\text{Na}_3\text{B}_{10}\text{H}_{10}\text{CH}$ with AsCl_3 or SbI_3 , and can be isomerized in high yield below 500°C to the 1,7-isomers. Above 500° the 1,12-isomers can be obtained but this is accompanied by substantial decomposition. The diarsa derivative 1,2- $\text{B}_{10}\text{H}_{10}\text{As}_2$ is also known. Likewise, reaction of *nido*- $\text{B}_{10}\text{H}_{14}$ with AsCl_3 and NaH or NaBH_4 affords the 11-vertex anion $7\text{-B}_{10}\text{H}_{12}\text{As}^-$

¹²⁷ M. BAUDLER, C. BLOCK, H. BUDZIKIEWICZ and H. MÜNSTER, *Z. anorg. allg. Chem.* **569**, 7–15 (1989).

¹²⁸ Z. FENG, M. M. OLMSTEAD and P. P. POWER, *Inorg. Chem.* **25**, 4615–6 (1986).

¹²⁹ H. H. KARSCH, G. HANIKA, B. HUBER, K. MEINDL, S. KÖNIG, K. KRÜGER and G. MÜLLER, *J. Chem. Soc., Chem. Commun.*, 373–5 (1989).

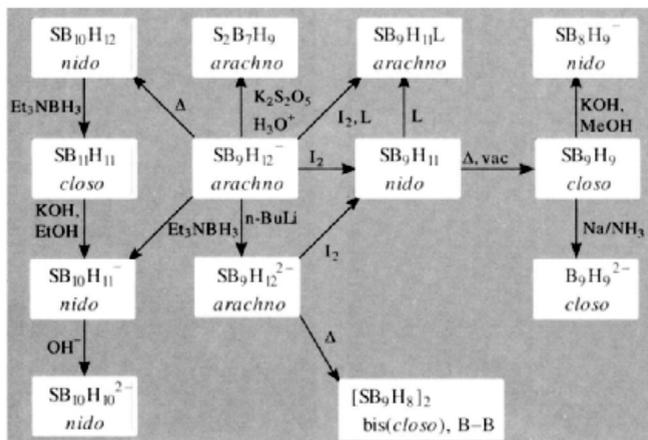
¹³⁰ H. NÖTH, *Z. anorg. allg. Chem.* **555**, 79–84 (1987).

¹³¹ A. M. ARIF, A. H. COWLEY, M. PAKULSKI and J. M. POWER, *J. Chem. Soc., Chem. Commun.*, 889–90 (1986).

¹³² H. V. R. DIAS and P. P. POWER, *Angew. Chem. Int. Edn. Engl.* **26**, 1270–1 (1987); H. V. R. DIAS and P. P. POWER, *J. Am. Chem. Soc.* **111**, 144–8 (1989).

¹³³ G. L. WOOD, E. N. DUESLER, C. K. NARULA, R. T. PAINE and H. NÖTH, *J. Chem. Soc., Chem. Commun.*, 496–8 (1987).

¹³⁴ W. HAUBOLD, W. KELLER and G. SAWITZKI, *Angew. Chem. Int. Edn. Engl.* **27**, 925–6 (1988).



Scheme (for page 215)

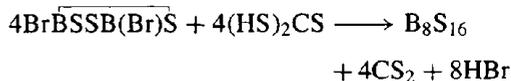
and this can be capped using $\text{Et}_3\text{N}\cdot\text{BH}_3$ in diglyme at 160° to give the *closo*-icosahedral anion $\text{B}_{11}\text{H}_{11}\text{As}^-$ in 51% yield. Other examples include $\text{B}_{11}\text{H}_{11}\text{Sb}^-$, $1,2\text{-B}_{10}\text{H}_{10}\text{Sb}_2$, $1,2\text{-B}_{10}\text{H}_{10}\text{AsSb}$ and the arsenathia- and arsenaselenaboranes $\text{B}_8\text{H}_8\text{As}_2\text{S}$ and $\text{B}_8\text{H}_8\text{As}_2\text{Se}$.⁽¹³⁵⁾

6.10.2 Compounds with bonds to S, Se and Te

The vast array of B–O minerals and compounds (pp. 139–40 and 203–7) finds no parallel in B–S or B–Se chemistry though thioborates of the type $\text{B}(\text{SR})_3$, $\text{R}'\text{B}(\text{SR})_2$ and $\text{R}'_2\text{B}(\text{SR})$ are well documented. There are also a growing number of binary boron sulfides and boron–sulfur anions which feature chains, rings and networks. B_2S_3 itself has been known for many years as a pale-yellow solid which tends to form a glassy phase (cf. B_2O_3 and also B_2Se_3). This absence of a suitable crystalline sample prevented the structural characterization of this compound until as late as 1977. It has now been found that B_2S_3 has a fascinating layer structure which bears no resemblance to the three-dimensionally linked B_2O_3 crystal structure but is slightly reminiscent of BN. The structure (Fig. 6.29a) is made up of planar

B_3S_3 6-membered rings and B_2S_2 4-membered rings linked by S bridges into almost planar two-dimensional layers.⁽¹³⁶⁾ All the boron atoms are trigonal planar with B–S distances averaging 181 pm and the perpendicular interlayer distance is almost twice this at 355 pm. More recently⁽¹³⁷⁾ a monomeric form of B_2S_3 was prepared by matrix-isolation techniques at 10 K and shown by vibrational spectroscopy to be a planar V-shaped molecule, $\text{S}=\text{B}-\text{S}-\text{B}=\text{S}$, with C_{2v} symmetry, the angle subtended at the central S atom by the linear arms being about 120° .

Another boron sulfide, of stoichiometry BS_2 , can be made by heating B_2S_3 and sulfur to 300°C under very carefully defined conditions.⁽¹³⁸⁾ It is a colourless, moisture-sensitive material with a porphine-like molecular structure, B_8S_{16} , as shown in Fig. 6.29b. An alternative route to B_8S_{16} involves the reaction of dibromotrithiadiborolane with trithiocarbonic acid in an H_2S generator in dilute CS_2 solution:



¹³⁶ H. DIERCKS and B. KREBS, *Angew. Chem. Int. Edn. Engl.* **16**, 313 (1977).

¹³⁷ I. R. BEATTIE, P. J. JONES, D. J. WILD and T. R. GILSON, *J. Chem. Soc., Dalton Trans.*, 267–9 (1987).

¹³⁸ B. KREBS and H. U. HURTER, *Angew. Chem. Int. Edn. Engl.* **19**, 481–2 (1980).

¹³⁵ L. J. TODD, Chap. 4 in R. N. GRIMES (ed.) *Metal Interactions with Boron Clusters*, Plenum, New York, 1982, pp. 145–71.

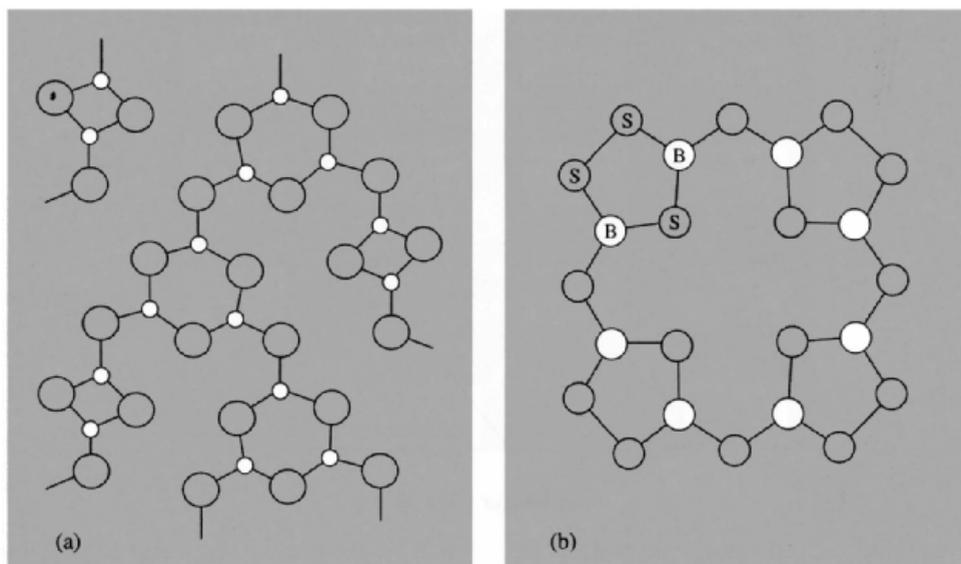
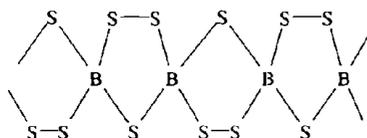


Figure 6.29 (a) Part of the layer structure of B_2S_3 perpendicular to the plane of the layer. (b) Porphine-like structure of the molecule B_8S_{16} .

The monomeric selenium compound BSe_2 has been identified mass-spectrometrically in the vapours formed by reacting solid boron with Se_2 and its thermodynamic properties evaluated.⁽¹³⁹⁾

Another expanding area of B–S chemistry is the synthesis and structural characterization of anionic species. The colourless thioborate $RbBS_3$ was formed by heating the stoichiometric amounts of Rb_2S , B and S at 600° . Its structure, and that of the yellow $TlBS_3$, features polymeric anionic chains that are spirocyclically connected via tetrahedral B atoms as shown schematically below:⁽¹⁴⁰⁾



The sulfur-rich analogue $Tl_3B_3S_{10}$ was likewise prepared as yellow plates from the appropriate stoichiometric mixture of $(3Tl_2S + 6B + 17S)$ at

¹³⁹ M. BINNEWIES, *Z. anorg. allg. Chem.* **589**, 115–21 (1990).

¹⁴⁰ C. PUTTMANN, F. HILTMANN, W. HAMANN, C. BRENDL and B. KREBS, *Z. anorg. allg. Chem.* **619**, 109–16 (1993).

850° and shown to have a similar polymeric anion with the extra S atoms inserted into each third pentatomic heterocycle to make it a hexatomic unit, $>B(S_2)_2B<$. With the smaller cation, Li^+ , similar procedures generate $Li_5B_7S_{13}$ and $Li_9B_{19}S_{33}$ which again have novel polymeric anions. The $\{B_7S_{13}^{5-}\}_\infty$ polymer is formed by sharing B_4S_{10} and $B_{10}S_{20}$ units, i.e. $\{B_4S_6S_{4/2}^{4-}\}$ (cf. P_4O_{10}) and $\{B_{10}S_{16}S_{4/2}^{6-}\}$ both of which are built up from tetrahedral BS_4 subunits, whereas the $\{B_{19}S_{33}^{9-}\}_\infty$ polymer is formed from the conjoining of $\{B_{19}S_{30}S_{6/2}^{9-}\}$ units.⁽¹⁴¹⁾

The structural principles and reaction chemistry of B–S compounds have recently been reviewed.⁽¹⁴²⁾ This includes not only electron-precise 4-, 5- and 6-membered heterocycles of the types described above, but also electron-deficient polyhedral clusters based on *closo*-,

¹⁴¹ F. HILTMANN, P. ZUM HEBEL, A. HAMMERSCHMIDT and B. KREBS, *Z. anorg. allg. Chem.* **619**, 293–302 (1993). For other novel B/S/Se anions from B. Krebs' group see *Z. anorg. allg. Chem.* **620**, 1898–1904 (1994); **621**, 424–30, 1322–9 and 1330–7 (1995).

¹⁴² J. R. BOWSER and T. P. FEHLNER, in H. W. ROESKY (ed.), *Rings, Clusters and Polymers of Main Group and Transition Elements*, Elsevier, Amsterdam, 1989, pp. 1–48.

nido- and *arachno*-boranes. Some typical inter-conversion reactions of thiaboranes are shown in the scheme on p. 213,⁽¹⁴²⁾ and further examples are in references (143) and (144). Seleno- and telluro-derivatives are also known^(135,145) and, like the thiaboranes, have structures that can be rationalized by the normal electron

counting rules, taking the chalcogen atom as a 4-electron donor, e.g. *closo*-B₁₁H₁₁Te, *nido*-B₁₀H₁₂Te, *nido*-B₁₀H₁₁Te⁻, *nido*-B₉H₁₁Te, *nido*-B₉H₉Se₂, *nido*-B₉H₉STe, *arachno*-B₈H₁₀Se₂, [Fe(η^5 -B₁₀H₁₀Te)₂]²⁻ (green) and [Co(η^5 -C₅H₅)-(η^5 -B₁₀H₁₀Te)] (yellow).

There appears to be no end to the structural ingenuity of boron and, whilst it is true that many regularities can now be discerned in its stereochemistry, much more work is still needed to unravel the reaction pathways by which the compounds are formed and to elucidate the mechanisms by which they isomerize and interconvert.

¹⁴³ T. JELINEK, J. D. KENNEDY and B. ŠTÍBR, *J. Chem. Soc., Chem. Commun.*, 1415–6 (1994).

¹⁴⁴ S. O. KANG and L. G. SNEDDON, Chap. 8 in G. A. OLAH, K. WADE and R. E. WILLIAMS (eds.), *Electron Deficient Boron and Carbon Clusters*, Wiley, New York, 1991, pp. 195–213.

¹⁴⁵ G. D. FRIESEN, T. P. HANUSA and L. J. TODD, *Inorg. Synth.* **29**, 103–7, (1992).