

Chapter 12

BORON

12-1 Introduction

The principal ores of boron are borates such as:



The structures of borate minerals are complex and diverse, but they characteristically contain trigonal BO_3 or tetrahedral BO_4 units in large boron–oxygen anions. Some oxygen atoms in borate minerals are monoprotonated to give hydroxyl groups, while others are diprotonated to give waters of hydration. The cations in such minerals are usually alkali or alkaline earth cations. The structure of the borate anion in borax is shown in Structure 5-XXVII. Borax occurs in large deposits in the Mojave desert of California, which is the major source of boron.

No ionic compounds involving simple B^{3+} cations are formed because the ionization enthalpies for boron are so high that lattice energies or hydration enthalpies cannot offset the energy required for formation of a cation. Boron does form three covalent bonds using sp^2 hybrid orbitals in a trigonal plane. All such BX_3 compounds are coordinatively unsaturated and act as strong Lewis acids; interaction with Lewis bases (molecules or ions) gives tetrahedral adducts such as $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$, BF_4^- , and $\text{B}(\text{C}_6\text{H}_5)_4^-$. The formation of such Lewis acid–base adducts requires a change to sp^3 hybridization for boron.

Another major feature of boron chemistry is the preponderance of compounds consisting of boron atoms in closed polyhedra or in open, basketlike arrangements. Often the structures are seen to be derivatives or fragments of the icosahedron. The frameworks of such molecules may include atoms other than boron (e.g., carbon) and many of those with carbon (the carboranes) form complexes with transition metals.

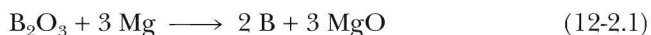
Among the Group IIIB(13) elements, it is the chemistry of boron that is unique. The chemistry of boron has only a few features in common with that of aluminum. The main resemblances to silicon and differences from the more metallic aluminum are as follows:

1. The oxide B_2O_3 and $\text{B}(\text{OH})_3$ are acidic. The compound $\text{Al}(\text{OH})_3$ is a basic hydroxide, although it shows weak amphoteric properties by dissolving in strong NaOH .
2. Borates and silicates are built on similar structural principles with sharing of oxygen atoms so that complicated chain, ring, or other structures result.

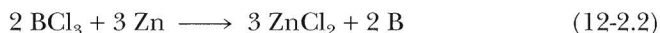
3. The halides of B and Si (except BF_3) are readily hydrolyzed. The Al halides are solids and only partly hydrolyzed by water. All act as Lewis acids.
4. The hydrides of B and Si are volatile, spontaneously flammable, and readily hydrolyzed. Aluminum hydride is a polymer, $(\text{AlH}_3)_n$.

12-2 Isolation of the Element

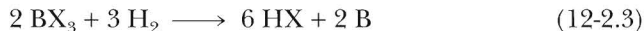
Boron forms a number of allotropes that are difficult to purify because of the high melting points of the solids (e.g., 2250 °C for the β -rhombohedral form) and because of the corrosive nature of the liquid. Boron is made in 95–98% purity as an amorphous powder by reduction of the oxide B_2O_3 with Mg



followed by washing of the powder with NaOH, HCl, and HF. Other electropositive metals may be used in place of Mg. Purer forms of the element are available from the reductions of boron trihalides with zinc at 900 °C, as in Reaction 12-2.2



or from reductions with hydrogen over hot tantalum metal as a catalyst, as in Reaction 12-2.3



The several allotropes of crystalline boron all have structures built up of B_{12} icosahedra (Structure 8-II), one form differing from another by the manner in which these icosahedra are packed into the unit cell.

Crystalline boron is very inert and is attacked only by hot concentrated oxidizing agents. Amorphous boron is more reactive. With ammonia for instance, amorphous boron at white heat gives $(\text{BN})_x$, a slippery white solid with a layer structure resembling that of graphite, but with hexagonal rings of alternating B and N atoms.

12-3 Oxygen Compounds of Boron

Almost all of the naturally occurring forms of boron are the oxygen-containing borate minerals, which are mentioned in the introduction to this chapter and in Section 5-4. In addition, there are many types of organic derivatives containing boron–oxygen bonds, the chief examples being those containing trigonal boron: the orthoborates, $\text{B}(\text{OR})_3$; the acyl borates, $\text{B}(\text{OCOR})_3$; the peroxo borates, $\text{B}(\text{OOR})_3$; and the boronic acids, $\text{RB}(\text{OH})_2$, all of which are best considered to be derivatives of boric acid. We consider first the borate-containing compounds.

Crystalline Borates

Many borates occur naturally, usually in hydrated form. Anhydrous borates may

be made by fusion of boric acid and metal oxides. The hydrated borates may be precipitated from aqueous solution. The stoichiometries of borates (e.g., $\text{KB}_5\text{O}_8 \cdot 4 \text{H}_2\text{O}$, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$, CsB_2O_4 , and $\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$) give little idea of the structure of the anions in these substances. The main structural principles of the borates are similar to those for silicates: cyclic or linear polyoxo anions, formed by the linking together of BO_3 and/or BO_4 units shared by oxygen atoms.

In crystalline borates, the most common structural units are those shown in Fig. 12-1. Notice that the skeletal boron–oxygen units may be protonated to varying degrees, and that the boron atoms are either tetrahedral or trigonal. Recall also the structure of the borate anion in borax, Structure 5-XXVII. The largest discrete borate anion known is $\text{B}_{10}\text{O}_{21}^{12-}$, which consists of two tetraborate units linked by two BO_3 triangles.

In *anhydrous borates*, the BO_3^{3-} and $\text{B}_3\text{O}_6^{3-}$ ions are common, as is the infinite chain anion $(\text{BO}_2)_n^{n-}$, which occurs in $\text{Ca}(\text{BO}_2)_2$. Planar BO_3 units are linked in three dimensions in the mineral tourmaline. Also common in minerals are networks of $\text{B}_6\text{O}_{12}^{6-}$ and $\text{B}_3\text{O}_6^{3-}$ linked by shared oxygen atoms.

Hydrated borates contain polyoxo anions in the crystal, with the following important structural features.

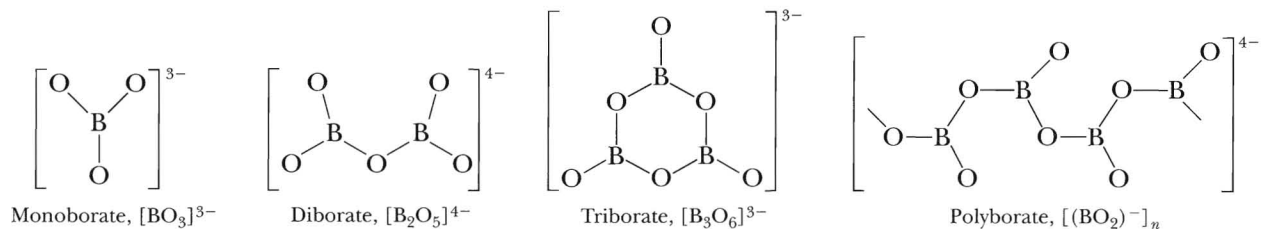
1. Both BO_3 and tetrahedral BO_4 groups are present, the number of BO_4 units being equal to the charge on the anion. Thus $\text{KB}_5\text{O}_8 \cdot 4 \text{H}_2\text{O}$ has one BO_4 and four BO_3 , whereas $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 7 \text{H}_2\text{O}$ has four BO_4 and two BO_3 groups.
2. Anions that do not have BO_4 groups, such as metaborate, $\text{B}_3\text{O}_6^{3-}$, or metaboric acid, $\text{B}_3\text{O}_3(\text{OH})_3$, hydrate rapidly and lose their original structures. Also, although certain complex borates can be crystallized from solution, this does not constitute evidence for the existence of these ions in solution, since other less complex polyoxo anions can readily combine during the crystallization process.
3. Certain discrete as well as chain-polymer borate anions can be formed by the linking of two or more rings by shared tetrahedral boron atoms.

Examples of many of these structural features are illustrated in Fig. 12-1.

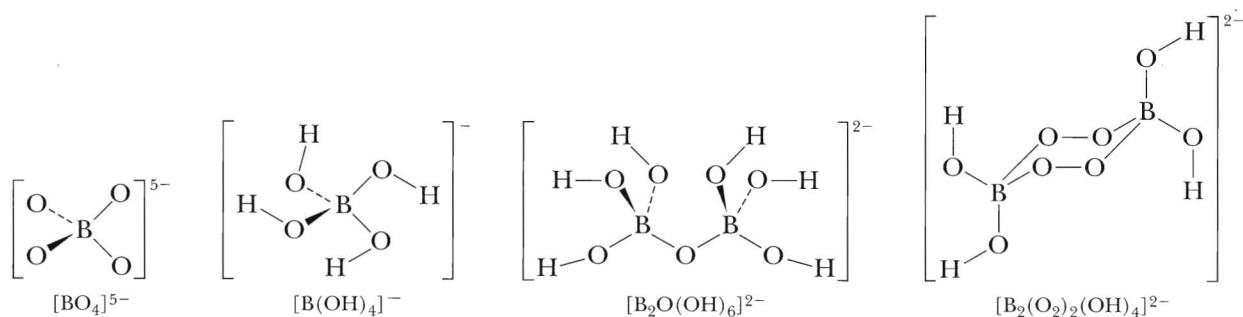
Boric Acid

The acid $\text{B}(\text{OH})_3$ can be obtained as white needles either from borates, or by hydrolysis of boron trihalides. The $\text{B}(\text{OH})_3$ units are linked together by hydrogen bonds to form infinite layers of nearly hexagonal symmetry. The layers are 3.12 Å apart, and the crystals are readily cleaved along interlayer planes. Some reactions of boric acid are given in Fig. 12-2.

When heated, boric acid loses water stepwise to form one of three forms of metaboric acid, HBO_2 . If $\text{B}(\text{OH})_3$ is heated below 130 °C, the so-called form-III is obtained, which has a layer structure in which B_3O_3 rings are joined by hydrogen bonding. On continued heating of form-III of HBO_2 , between 130 and 150 °C, HBO_2 -II is formed. This compound has a more complex structure containing both BO_4 tetrahedra and B_2O_5 groups in chains linked by hydrogen bonds. Finally, on heating of form-II above 150 °C, cubic HBO_2 (form-I) is obtained, in which all boron atoms are four coordinate. Complete fusion of boric acid gives the oxide B_2O_3 as a glass. The melt readily dissolves metal oxides to give borate glasses. It also reacts with silica to give the borosilicate glass known as Pyrex.



(a)



(b)

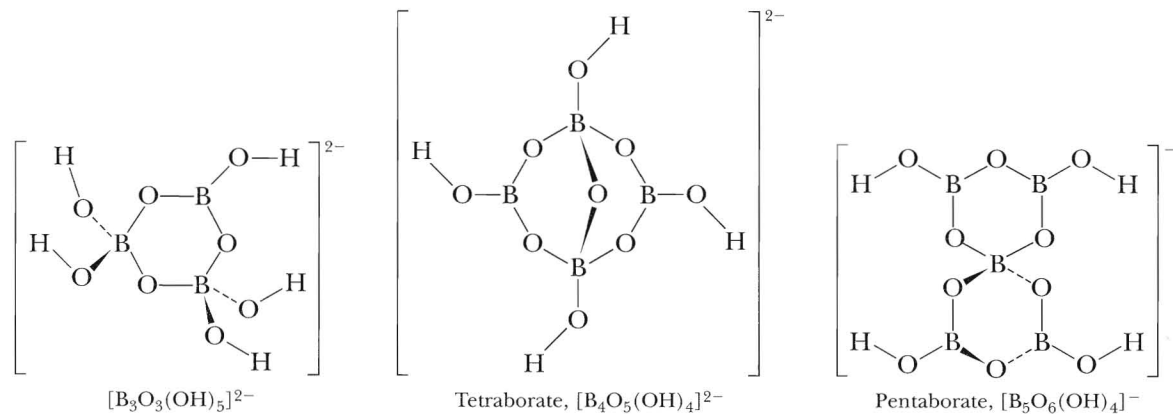


Figure 12-1 The structure of borate anions in boron-containing minerals. (a) Anions containing boron in planar BO_3 units. (b) Anions containing boron in tetrahedral BO_4 units. (c) Anions containing boron in both planar BO_3 and tetrahedral BO_4 units.

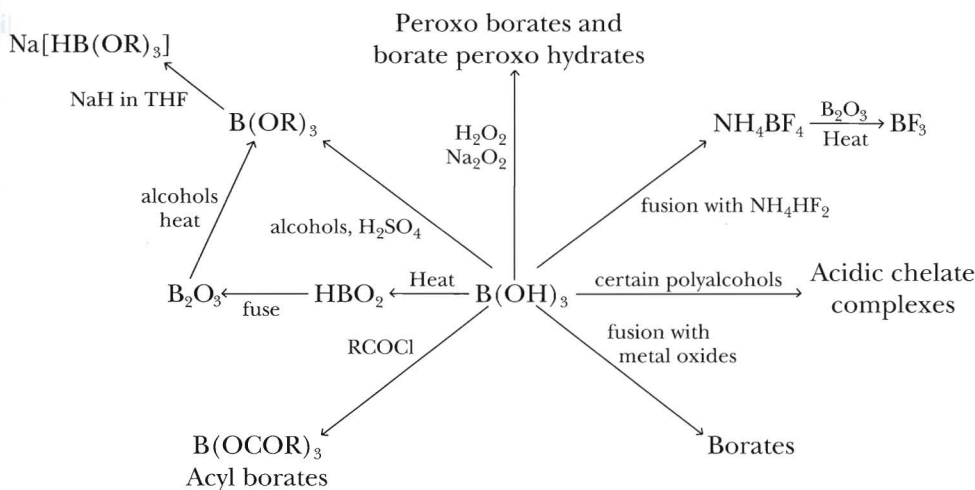
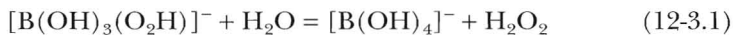


Figure 12-2 Some reactions of boric acid.

Boric acid is readily converted to alkyl or aryl orthoborates, $B(OR)_3$, by condensation with alcohols in the presence of sulfuric acid. These compounds are usually colorless liquids that are converted, in ether solvents, by alkali metal hydrides to the very useful reducing agents $[HB(OR)_3]^-$. The reactivity and selectivity of the latter as reducing agents can be controlled by changing the R groups.

Treatment of boric acid with sodium peroxide leads to peroxoborates, variously formulated as $NaBO_3 \cdot 4 H_2O$ or $NaBO_2 \cdot H_2O_2 \cdot 3 H_2O$, which are extensively used in washing powders because they afford H_2O_2 in solution. For example, in solution there is the equilibrium shown in Reaction 12-3.1:

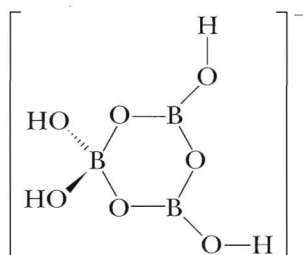


Boric Acid and Borate Ions in Solution

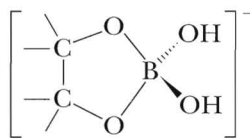
Boric acid is moderately soluble in water, where it acts as a weak Lewis acid towards OH^-



The $B(OH)_4^-$ ion occurs in many borate-type minerals, but most borates (especially those formed by fusion of boric acid with metal oxides) have complex structures such as the ring anion (Structure 12-I). Boric acid and borates form very stable complexes with 1,2-diols, as in Structure 12-II.

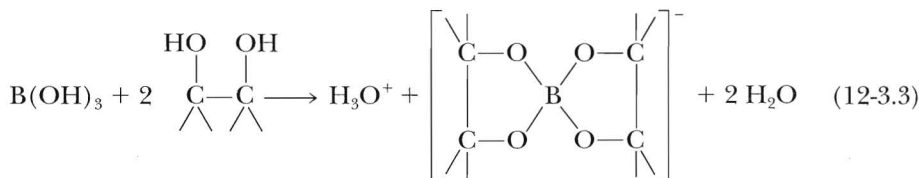


12-I



12-II

The concentration of boric acid can be determined by complexation with a diol such as glycerol (Reaction 12-3.3)



followed by titration with NaOH.

As noted previously, in concentrated solutions of boric acid, polyoxo borate anions are also present. These are formed, for example, as in equilibrium 12-3.4.



Equilibria between various borate anions is rapidly established in aqueous solution, as shown by rapid exchange between B(OH)_3 labeled with ^{18}O and borates. The larger polyoxo anions $\text{B}_5\text{O}_6(\text{OH})_4^-$ and $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ are formed at higher pH. In dilute solutions, however, depolymerization to the mononuclear species occurs. Thus when borax is dissolved in dilute solution, $\text{B(OH)}_4^-(\text{aq})$ is formed.

12-4 The Halides of Boron

Trihalides

Boron trifluoride is a pungent, colorless gas (bp -101°C) that is obtained by heating B_2O_3 with NH_4BF_4 , or with CaF_2 and concentrated H_2SO_4 . It is commercially available in tanks.

Boron trifluoride is one of the strongest Lewis acids known and reacts readily with most Lewis bases, such as ethers, alcohols, amines, or water to give adducts, and with F^- to give the tetrafluoroborate ion, BF_4^- . The diethyletherate, $(\text{C}_2\text{H}_5)_2\text{OBF}_3$, a viscous liquid, is available commercially. Unlike the other halides, BF_3 is only partially hydrolyzed by water:

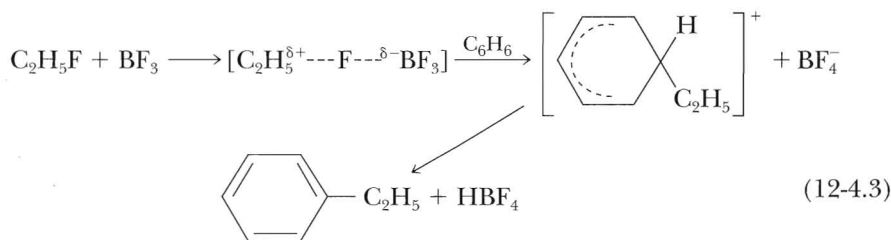


Because of this, and its potency as a Lewis acid, BF_3 is widely used to promote various organic reactions. Examples are

1. Ethers or alcohols + acids \rightarrow esters + H_2O or ROH .
2. Alcohols + benzene \rightarrow alkylbenzenes + H_2O .
3. Polymerization of alkenes and alkene oxides such as propylene oxide.
4. Friedel-Crafts-like acylations and alkylations.

In (1) and (2) the effectiveness of BF_3 must depend on its ability to form an adduct with one or both of the reactants, thus lowering the activation energy of the rate-determining step in which H_2O or ROH is eliminated by breaking of $\text{C}-\text{O}$ bonds. In reactions of type (4), intermediates may be characterized at low temperatures. Thus the interaction of benzene and $\text{C}_2\text{H}_5\text{F}$ proceeds as in

Reaction 12-4.3. It is clear that BF_3 is not actually a catalyst, since it must be present in stoichiometric amount and is consumed in removing HF as HBF_4 .

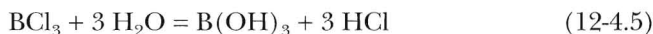


Fluoroboric acid solutions are formed on dissolving $\text{B}(\text{OH})_3$ in aqueous HF



The commercial solutions contain 40% acid. Fluoroboric acid is a strong acid and cannot, of course, exist as HBF_4 . The ion is tetrahedral and fluoroborates resemble the corresponding perchlorates in their solubilities and crystal structures. Like ClO_4^- and PF_6^- , the anion has a low tendency to act as a ligand toward metal ions in *aqueous* solution. In nonaqueous media, there is evidence for complex formation.

Boron trichloride (bp 12 °C) and the *bromide* (bp 90 °C) are obtained by direct interaction at elevated temperatures. They fume in moist air and are violently hydrolyzed by water.



The rapid hydrolysis supports other evidence that these halides are stronger Lewis acids than BF_3 .

Reactions of the Trihalides of Boron

As already mentioned, the boron trihalides are Lewis acids, and they readily react with Lewis bases to form adducts. Two other important reactions that we shall consider are halide exchange among the trihalides themselves, and the elimination of HX from adducts of the trihalides when an acidic hydrogen is available.

Formation of Adducts with Lewis Bases

Even the weakest of bases will form adducts with the trihalides of boron. Ethers, amines, phosphines, alcohols, anions, carbon monoxide, and the like all form adducts by donation of an electron pair to boron. The rehybridization of boron that accompanies adduct formation results in a loss in BX double-bond character, as shown in Fig. 12-3. When the Lewis donor is trimethylamine, the enthalpy change for adduct formation, as in Reaction 12-4.6,



is most negative for BBr_3 and least negative for BF_3 . We would expect that the higher electronegativity of fluorine should enhance the stability of the trimethyl-

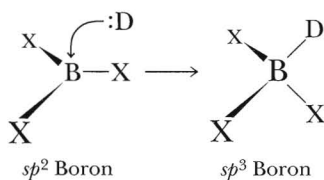


Figure 12-3 The reaction of a trigonal trihalide of boron with a Lewis base (:D) to give a tetrahedral adduct. The rehybridization of boron that is required when :D disrupts the B—X π bond in the BX_3 reactant.

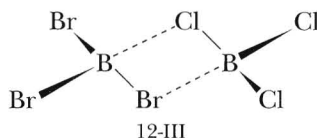
amine adduct with BF_3 . Since the enthalpy of adduct formation is least favorable with BF_3 , however, it is concluded that the loss in BX double-bond character upon rehybridization to form an adduct is greater with BF_3 than in the other trihalides. From this we can conclude that the double-bond character in the trihalides follows the order $\text{BF}_3 > \text{BCl}_3 > \text{BBr}_3$, a trend opposite to that expected from the electronegativities of the halides. (Recall that the double bond in BX_3 results from donation of π -electron density from X into an empty $2p$ atomic orbital of an sp^2 -hybridized boron atom. The π -bond system in these sorts of molecules was discussed in Section 3-6.) Evidently the π -bond system in BF_3 is especially strong because of effective overlap between the boron $2p$ and the fluorine $2p$ atomic orbitals—overlap that is effective because of the closely matched energies and sizes of the orbitals. The $3p$ and $4p$ atomic orbitals of Cl and Br have the proper symmetry for π overlap with the $2p$ atomic orbital of B in the compounds BX_3 , but the π overlap is less effective because the energies and sizes of the π -donor orbitals ($3p$ for chlorine and $4p$ for bromine) are not well matched to those of the π -acceptor ($2p$) orbital of boron.

Halide Exchange Reactions Among the Boron Trihalides

Mixtures of two different trihalides of boron undergo exchange of halide as illustrated in Reaction 12-4.7.



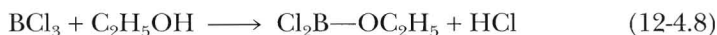
The position of equilibrium in Reaction 12-4.7 lies mostly to the left, but small amounts of the exchange products can be detected spectroscopically. The trifluoride undergoes halide exchange less readily than BBr_3 and BCl_3 . No intermediates have been detected, but it is reasonable to propose that the exchange involves the type of dimeric structure shown in Structure 12-III. Such a dimer would be similar to Al_2Cl_6 (Structure 6-I).



Equilibria of the type illustrated by Reaction 12-4.7 are established rapidly, and only small amounts of the exchange products can be detected. Attempts to isolate the exchange products from such systems are not successful because of the facile nature of the equilibria. Thus, no pure mixed halide of boron is known. A concerted mechanism, as illustrated in Structure 12-III, would be consistent with all of the facts as long as the new, bridging BX bonds that form the dimer are weak.

Elimination Reactions of BX_3 Adducts

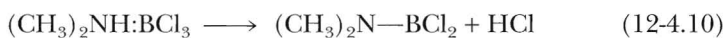
When an acidic hydrogen is present in an adduct of BX_3 , elimination of HX is possible, as illustrated in the following reactions. Solvolysis of BCl_3 by alcohols involves adduct formation followed by elimination of HCl as in Reaction 12-4.8.



Stepwise addition and elimination eventually leads to complete solvolysis as in Reaction 12-4.9:



The dimethylamine adduct of BCl_3 undergoes elimination of HCl to give an aminoborane as in Reaction 12-4.10.



Aminoboranes, and in particular, the nature of the BN bond in aminoboranes, will be discussed in Section 12-6.

Subhalides of Boron

A number of interesting subhalides of boron, in which the proportion of halogen to boron is less than 3:1, are known. The best characterized are

1. The gaseous monohalides BF and BCl.
2. The so-called monohalides of Cl, Br, and I: B_nCl_n ($n = 8, 9, 10,$ or 11); B_nBr_n ($n = 7, 8, 9,$ or 10); and B_nI_n ($n = 8$ or 9).
3. The diboron tetrahalides, B_2X_4 , $X = F, Cl, Br,$ or I , although the last one has been little studied.
4. Certain other fluorides: B_3F_5 , B_8F_{12} , and $B_{14}F_{18}$.

All of these require special synthetic techniques to avoid reactions with air, water, and even hydrocarbon or silicone greases. For instance, the diboron tetrahalides are pyrophoric, water sensitive, and thermally unstable either at room temperature (B_2F_4 , B_2Cl_4 , or B_2Br_4) or at the melting point (B_2I_4). The compounds have been characterized by mass spectrometry, and by IR and Raman spectroscopies in the solid, liquid, and gas. In some cases (see below), structures have been determined by X-ray crystallography.

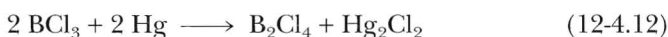
Boron monochloride, BCl, is produced when B_2Cl_4 is passed rapidly through a quartz tube at $1000^\circ C$. It is also obtained by electric discharge of B_2Cl_4 at a copper electrode, at liquid nitrogen temperature. Boron monofluoride, BF, is produced by passing BF_3 gas over boron at $1950-2000^\circ C$.

Diboron tetrafluoride (B_2F_4) is made by fluorination of B_2Cl_4 with either SbF_3 or TiF_4 . Also, condensation of BF together with BF_3 converts about 25% of the BF to B_2F_4 . Triboron pentafluoride (B_3F_5) is obtained by condensing BF with B_2F_4 . Disproportionation of liquid B_3F_5 at $-30^\circ C$ gives B_8F_{12} , as in Reaction 12-4.11:

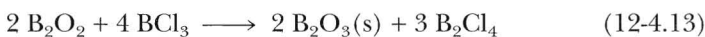


which may then be separated from B_2F_4 by fractional distillation.

Diboron tetrachloride (B_2Cl_4) is made from BCl_3 by radiofrequency discharge in the presence of mercury, as in Reaction 12-4.12.



This compound can also be made by condensation of gaseous B_2O_2 with BCl_3 at $-196^\circ C$, as in Reaction 12-4.13.

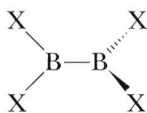


Condensation of BCl with BCl_3 at $-196^\circ C$ gives B_4Cl_4 . Boron monochloride is produced when B_2Cl_4 is rapidly passed through a quartz tube at $1000^\circ C$. It is also obtained from B_2Cl_4 by electric discharge from copper electrodes at liquid nitrogen temperatures. The thermal decomposition of B_2Cl_4 at temperatures between 100 and $450^\circ C$ gives a mixture of B_nCl_n compounds in which $n = 8, 9, 10$, or 11 , from which the individual compounds may be separated. The relative amounts of the various compounds produced by this method depend on the temperature used. Recently, B_9X_9 molecules ($X = H, Cl, Br$, or I , but not F) have been prepared by oxidation of $B_9X_9^{2-}$ ions using sulfuryl chloride in CH_2Cl_2 , starting with the salts $[n-Bu_4N]_2[B_9X_9]$.

Diboron tetrabromide (B_2Br_4) is made by radiofrequency discharge of $BBr_3(g)$ in the presence of Hg, or by treating B_2Cl_4 with excess BBr_3 . It decomposes readily at room temperature to produce B_7Br_7 , B_9Br_9 , and $B_{10}Br_{10}$. Reaction of B_8Cl_8 with Al_2Br_6 in BBr_3 solvent at $100^\circ C$ affords B_8Br_8 . Through silent electric discharge, B_2Br_4 gives B_9Br_9 and BBr_3 .

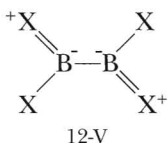
Diboron tetraiodide (B_2I_4) is obtained by radiofrequency discharge of BI_3 . It is also produced (among other compounds) by reacting I_2 with $Zr(BH_4)_4$ (Fig. 12-7). Above its melting point ($92-94^\circ C$), B_2I_4 decomposes to give B_9I_9 and B_8I_8 .

In the low-temperature crystal, both B_2F_4 and B_2Cl_4 are planar, with XBX angles close to 120° . In the case of B_2Cl_4 , the planarity in the crystal is evidently due to crystal packing forces that overcome the steric considerations that would otherwise favor a staggered conformation. This can be deduced from the fact that in the liquid and the gas, the staggered conformation (Structure 12-IV) is preferred, with a barrier to rotation about the B—B bond of $1.85 \text{ kcal mol}^{-1}$. There has been some disagreement over the liquid and gas phase structures of B_2F_4 , but recently Raman and IR analysis suggested that it is planar in the liquid and gas too, with an exceedingly small barrier ($< 1.1 \text{ kcal mol}^{-1}$) to rotation about the B—B bond. This is in agreement with theoretical calculations.



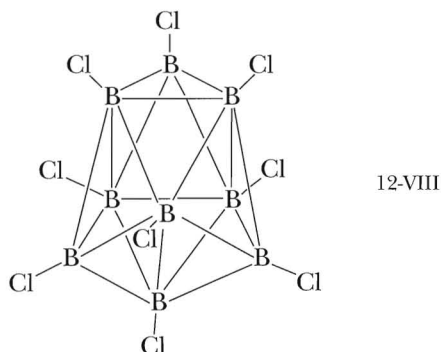
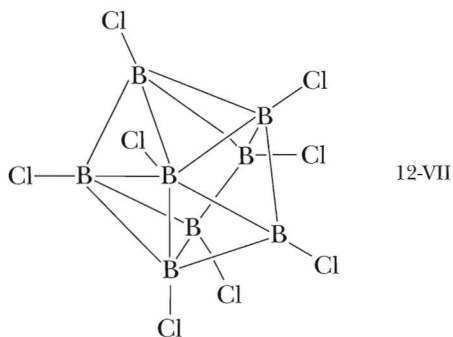
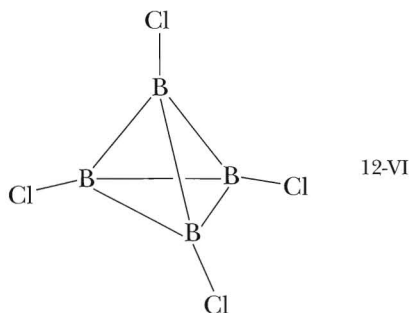
12-IV

In both B_2Cl_4 and B_2F_4 , the B—X bonds are somewhat shorter than is expected from the sum of the single-bond covalent radii. This suggests a delocalized π -bond system as in Structure 12-V.



Such a π -bond system, when conjugated across the B—B bond, should favor planar geometry. Evidently, in the case of B_2Cl_4 (though not for B_2F_4), this is outweighed by steric considerations that should favor the staggered form.

The tetrahedral structure of B_4Cl_4 (Structure 12-VI) has been determined by X-ray crystallography and by IR and Raman spectroscopy in the gas phase. Similarly, a dodecahedron forms the basis for the structure of B_8Cl_8 (Structure 12-VII), whereas B_9Cl_9 (Structure 12-VIII) is based on a tricapped trigonal prism.



12-5 The Hydrides of Boron

Boranes

Boron forms an extensive series of molecular hydrides called *boranes*. Typical boranes are B_2H_6 , B_4H_{10} , B_9H_{15} , $B_{10}H_{14}$, and $B_{20}H_{16}$. Boranes were first prepared between 1912 and 1936 by Alfred Stock who developed vacuum line techniques to handle these reactive materials. Stock's original synthesis (the reaction of Mg_3B_2 with acid) is now superseded for all but B_6H_{10} . Most syntheses now involve thermolysis of B_2H_6 under varied conditions, often in the presence of hydrogen.

The properties of some boranes are listed in Table 12-1. The nomenclature that is used for boranes is straightforward: the number of boron atoms is indicated by the prefix, and the number of hydrogen atoms is indicated parenthetically. For example, B_4H_{10} is *tetraborane(10)*.

Diborane(6)

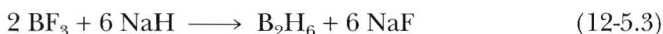
Diborane(6) (B_2H_6) is a gas (bp $-92.6^\circ C$) that is spontaneously flammable in air and instantly hydrolyzed by H_2O to H_2 and boric acid. It is obtained virtually quantitatively in ether, at room temperature, by the reaction of sodium borohydride with BF_3 , as in Reaction 12-5.1.



Laboratory quantities may be prepared by oxidation of sodium borohydride by iodine in diglyme, as in Eq. 12-5.2.



Industrial quantities are prepared at high temperatures by reduction of BF_3 with sodium hydride.



Borane (BH_3) has only a transient existence in the thermal decomposition of diborane.



Reactions of diborane are discussed later in Section 12-5. Note that diborane is an extremely versatile reagent for the synthesis of organoboranes, which in turn are very useful intermediates in organic synthesis. Diborane is also a powerful reducing agent for some functional groups, for example, aldehydes and organic nitriles.

Higher Boranes

The heavier boranes (e.g., B_6H_{10}) are mainly liquids whose flammability in air decreases with increasing molecular weight. One of the most important is decaborane ($B_{10}H_{14}$), a solid (mp $99.7^\circ C$) that is stable in air and only slowly hydrolyzed by water. It is obtained by heating B_2H_6 at $100^\circ C$ and is an important starting material for the synthesis of the $B_{10}H_{10}^{2-}$ anion and carboranes discussed later.

Table 12-1 Important Properties of Some Boranes

Formula	Name	Melting Point (°C)	Boiling Point (°C)	Reaction with Air (at 25°C)	Thermal Stability	Reaction with Water
B ₂ H ₆	Diborane(6)	-164.85	-92.59	Spontaneously flammable	Fairly stable at 25 °C	Instant hydrolysis
B ₄ H ₁₀	Tetraborane(10)	-120	18	Not spontaneously flammable if pure	Decomposes fairly rapidly at 25 °C	Hydrolysis in 24 h
B ₅ H ₉	Pentaborane(9)	- 46.6	48	Spontaneously flammable	Stable at 25 °C; slow decomposition 150°C	Hydrolyzed only on heating
B ₅ H ₁₁	Pentaborane(11)	-123	63	Spontaneously flammable	Decomposes very rapidly at 25 °C	Rapid hydrolysis
B ₆ H ₁₀	Hexaborane(10)	- 62.3	108	Spontaneously flammable	Slow decomposition at 25 °C	Hydrolyzed only on heating
B ₆ H ₁₂	Hexaborane(12)	- 82.3	80-90	—	Liquid stable few hours at 25 °C	Quantitative, to give B ₄ H ₁₀ , B(OH) ₃ , H ₂
B ₈ H ₁₂	Octaborane(12)	- 20	—	—	Decomposes above -20 °C	—
B ₈ H ₁₈	Octaborane(18)	—	—	—	Unstable	—
B ₉ H ₁₅	Enneaborane(15)	2.6	—	Stable	—	—
B ₁₀ H ₁₄	Decaborane(14)	99.7	213 (extrap.)	Very stable	Stable at 150 °C	Slow hydrolysis

Structure and Bonding in the Boranes

The structures of the boranes are unlike those of other hydrides, such as those of carbon, and are unique. A few of them are shown in Fig. 12-4. Observe that in none are there sufficient electrons to allow the formation of conventional two-electron bonds between all adjacent pairs of atoms ($2c-2e$ bonds). There is thus the problem of electron deficiency. It was to rationalize the structures of boranes that the earliest of the various concepts of multicenter bonding (Chapter 3) were first developed.

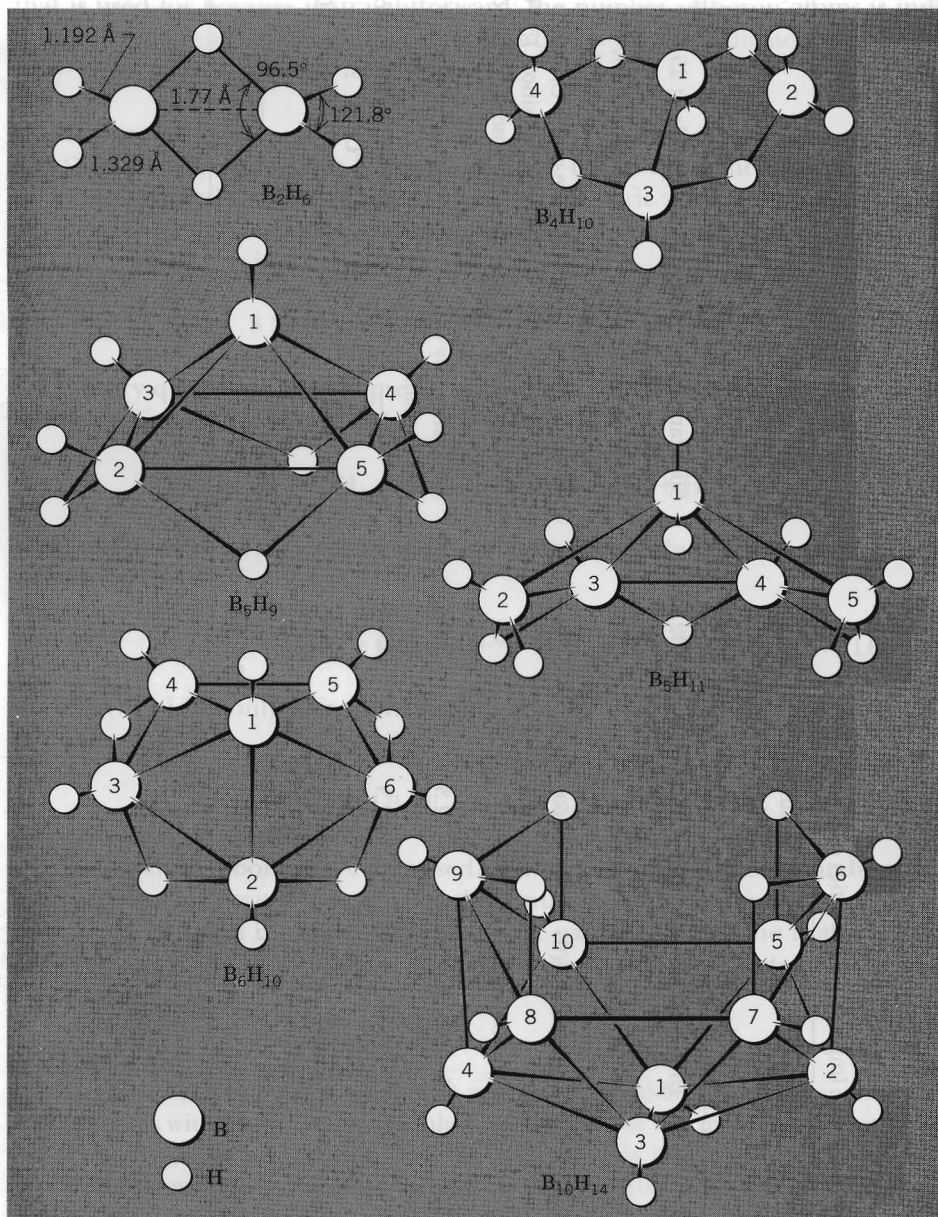
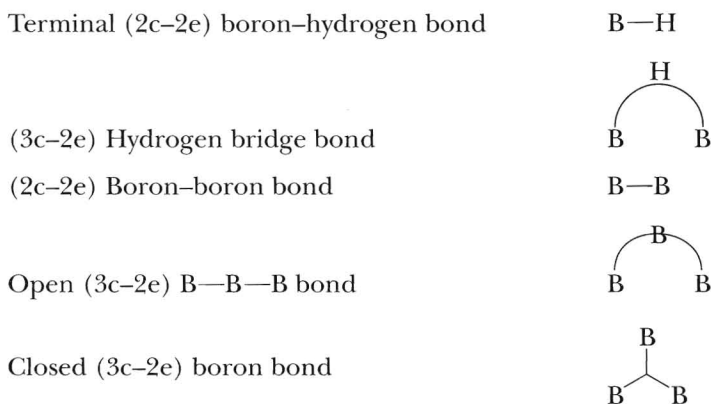


Figure 12-4 The structures of some boranes.

For diborane itself ($3c-2e$) bonds are required to explain the B—H—B bridges. The terminal B—H bonds may be regarded as conventional ($2c-2e$) bonds. Thus, each boron atom uses two electrons and two roughly sp^3 orbitals to form ($2c-2e$) bonds to two hydrogen atoms. The boron atom in each BH_2 group still has one electron and two hybrid orbitals for use in further bonding. The plane of the two remaining orbitals is perpendicular to the BH_2 plane. When two such BH_2 groups approach each other, as is shown in Fig. 12-5, with hydrogen atoms also lying in the plane of the four empty orbitals, two B—H—B ($3c-2e$) bonds are formed. The total of four electrons required for these bonds is provided by the one electron carried by each H atom and by each BH_2 group.

We have just seen that two structure-bonding elements are used in B_2H_6 , namely, ($2c-2e$) BH groups and ($3c-2e$) BHB groups. To account for the structures and bonding of the higher boranes, these elements, as well as three others, are required. The three others are ($2c-2e$) BB groups, ($3c-2e$) open BBB groups, and ($3c-2e$) closed BBB groups. These five structure-bonding elements are conveniently represented in the following way:



By using these five elements, W. N. Lipscomb was able to develop “semi-topological” descriptions of the structures and bonding in all of the boranes. The scheme is capable of elaboration into a comprehensive, semipredictive tool for correlating all the structural data. Figure 12-6 shows a few examples of its use to depict known structures.

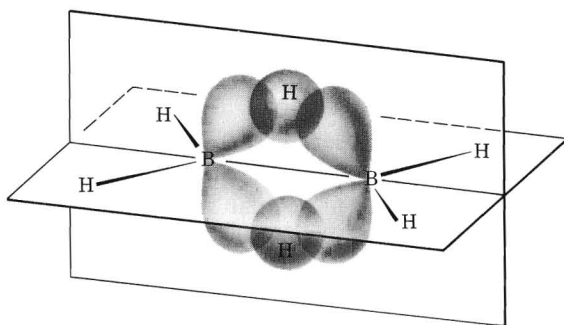


Figure 12-5 A diagram showing the formation of two bridging ($3c-2e$) B—H—B bonds in diborane.

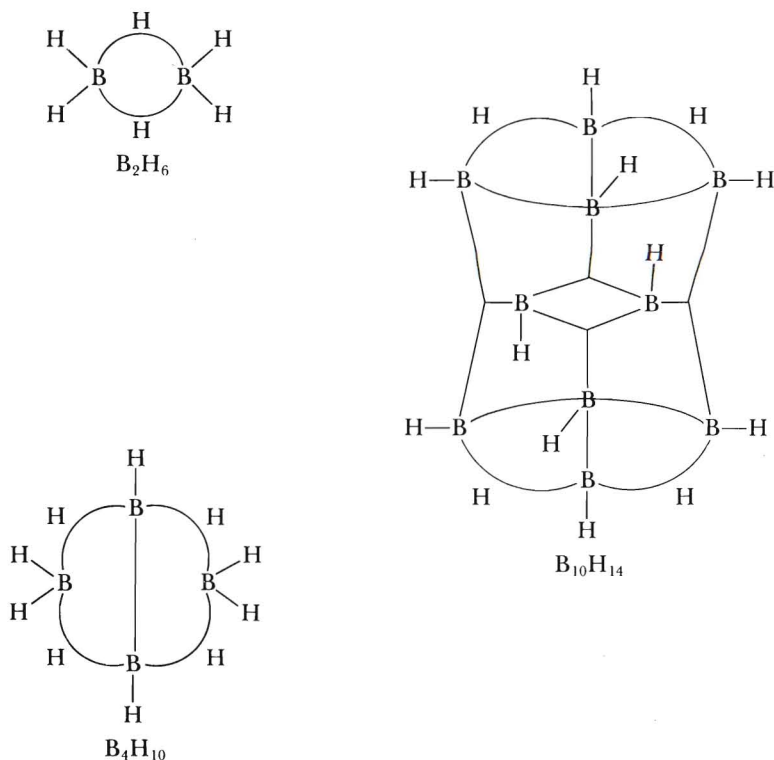
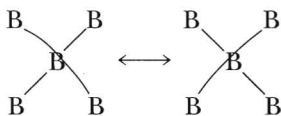


Figure 12-6 Valence descriptions of some electron deficient boranes using Lipscomb's "semitopological" scheme.

The semitopological scheme does not always provide the best description of bonding in the boranes, and related species such as the polyhedral borane anions and carboranes we shall discuss later. Where there is symmetry of a high order it is often better to think in terms of a highly delocalized MO description of the bonding. For instance, in B_5H_9 (Fig. 12-4), where the four basal boron atoms are equivalently related to the apical boron atom, it is *possible* to depict a

resonance hybrid involving the localized $\begin{array}{c} \text{B} \\ \diagup \quad \diagdown \\ \text{B} \quad \text{B} \end{array}$ and B—B elements, namely,



but it is neater and simpler to formulate a set of seven five-center MO's with the lowest three occupied by electron pairs. When one approaches hypersymmetrical species such as $B_{12}H_{12}^{2-}$, use of the full molecular symmetry in an MO treatment becomes the only practical course.

Reactions of the Boranes

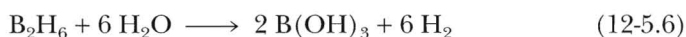
The boranes undergo an impressive variety of reactions including oxidations to oxides, pyrolysis to higher boranes, attack by nucleophiles and electrophiles,

reduction to borane anions, and reactions with bases such as OH^- and NH_3 . In some cases it is useful to view at least the substitutions as being either reactions of terminal BH groups or of bridging BHB groups. We shall restrict our attention to three illustrative systems: diborane(6), B_2H_6 ; pentaborane(9), B_5H_9 ; and decaborane(14), $\text{B}_{10}\text{H}_{14}$.

Diborane(6), B_2H_6 . Controlled pyrolysis of diborane leads to most of the higher boranes. Reaction with oxygen is extremely exothermic.



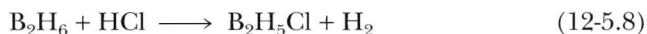
Reaction of diborane with water is instantaneous.



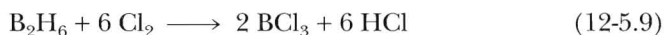
Diborane is also hydrolyzed by weaker acids (e.g., alcohols), as in Reaction 12-5.7.



Reaction with HCl replaces a terminal H with Cl



and reaction with chlorine gives the trichloride, as in Reaction 12-5.9.



The electron deficient $3c-2e$ BHB bridges are sites of nucleophilic attack. Small amines such as NH_3 , CH_3NH_2 , and $(\text{CH}_3)_2\text{NH}$ give unsymmetrical cleavage of diborane, as in Reaction 12-5.10.



The boronium ion products, $[\text{H}_2\text{BL}_2]^+$, are tetrahedral, and can undergo substitution by other bases, as in Reaction 12-5.11.

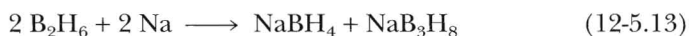


Large amines, such as $(\text{CH}_3)_3\text{N}$ and pyridine, give symmetrical cleavage of diborane, as in Reaction 12-5.12.



The amine borane products from symmetrical cleavage of diborane are Lewis base adducts of BH_3 . Amine boranes will be discussed more in Section 12-6.

Reduction of diborane can be accomplished with sodium



or with sodium borohydride

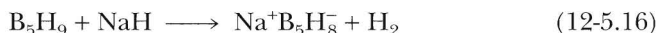


Reductions of diborane with sodium borohydride can also lead to higher borane anions, as in Reaction 12-5.15.

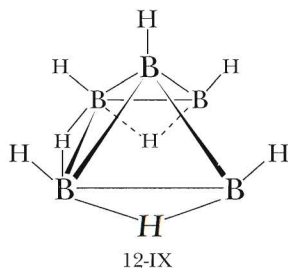


The polyhedral borane anion $\text{B}_{12}\text{H}_{12}^{2-}$ has icosahedral geometry. Other polyhedral borane anions and carboranes will be discussed shortly.

Pentaborane(9), B_5H_9 . Pentaborane(9) has the structure shown in Fig. 12-4. The apical boron is bonded to a single terminal hydrogen atom, while each of the four basal borons is bonded to one terminal hydrogen atom and to two bridging hydrogen atoms. The relative electron deficiency in the basal plane is illustrated by reaction of B_5H_9 with base, as in Reaction 12-5.16.



Higher boranes are even more acidic than B_5H_9 . The anionic product of Reaction 12-5.16 (Structure 12-IX) is fluxional (Section 6-6) due to rapid cycling

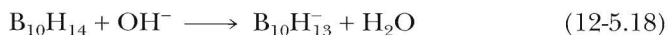


of bridging hydrogen atoms. Thus the basal boron atoms are indistinguishable using NMR techniques, as are the bridging hydrogen atoms.

The relatively electron-rich apical BH group of pentaborane(9) is susceptible to attack by electrophiles, as in Reaction 12-5.17.

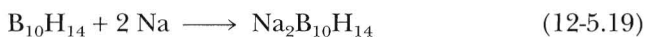


Decaborane(14), $\text{B}_{10}\text{H}_{14}$. The structure of decaborane(14) is shown in Fig. 12-4. Four electron deficient bridging BHB groups cap the top of this icosahedral fragment, making this part of the molecule the preferred site for attack by nucleophiles. As for pentaborane(9), it is the bridging hydrogen atoms that are acidic.

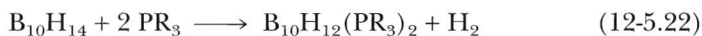
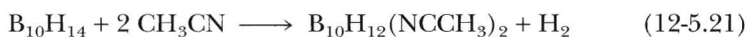
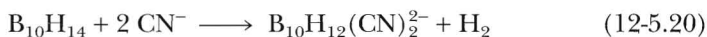


Reduction by sodium converts two of the bridging hydrogen atoms at the top of

the molecule to terminal hydrogen atoms.



Nucleophiles react to give 6,9-disubstituted products as in Reactions 12-5.20 to 12-5.22:



In contrast to reactions with nucleophiles, decaborane(14) reacts with electrophiles to give 2,4- or 1,3-disubstituted products. An example is shown in Reaction 12-5.23.

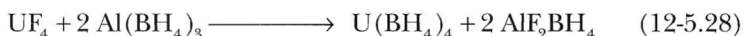
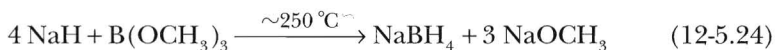


Charge distribution calculations using MO theory indicate that considerable excess negative charge should be assigned to boron atoms 1, 2, 3, and 4, with positive charge assigned to the electron deficient positions elsewhere in the molecule. It is thus gratifying that experiments show consistently that only positions 1, 2, 3, and 4 can be substituted electrophilically.

The Tetrahydroborate Ion (BH_4^-)

The tetrahydroborate ion (BH_4^-) is the simplest of a number of borohydride anions. This ion is of great importance as a reducing agent and as a source of H^- ion both in inorganic and organic chemistry; derivatives such as $[\text{BH}(\text{OCH}_3)_3]^-$ and $[\text{BH}_3\text{CN}]^-$ are also useful, the latter because it can be used in acidic solutions.

Borohydrides of many metals have been made and some representative syntheses are:



The most important salt is NaBH_4 . This is a white crystalline solid, which is stable in dry air, and nonvolatile. It is insoluble in diethyl ether but dissolves in H_2O , THF, and ethyleneglycol ethers from which it can be crystallized.

Many borohydrides are ionic, containing the tetrahedral BH_4^- ion. However, BH_4^- can serve as a ligand, interacting more or less covalently with metal ions, by bridging hydrogen atoms. Thus in $(\text{Ph}_3\text{P})_2\text{CuBH}_4$ there are two $\text{Cu}-\text{H}-\text{B}$ bridges, whereas in $\text{Zr}(\text{BH}_4)_4$, each BH_4 forms three bridges to Zr, as shown in Fig. 12-7. These $\text{M}-\text{H}-\text{B}$ bridges are (3c-2e) bonding systems.

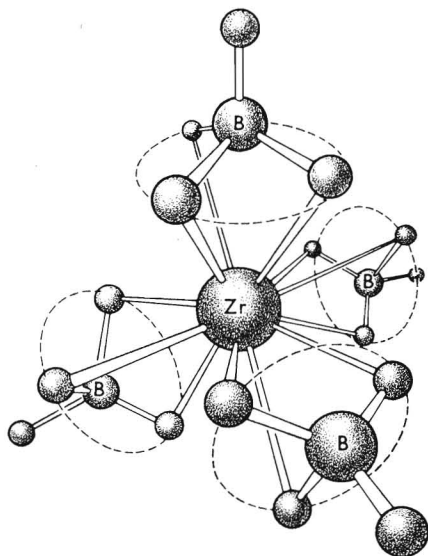


Figure 12-7 The structure of $\text{Zr}(\text{BH}_4)_4$. [Taken from Bird, P. H. and Churchill, M. R., *J. Chem. Soc., Chem. Commun.*, 1967, 403. Used with permission.]

Polyhedral Borane Anions and Carboranes

The polyhedral borane anions have the formula $\text{B}_n\text{H}_n^{2-}$. The carboranes may be considered to be *formally* derived from $\text{B}_n\text{H}_n^{2-}$ by replacement of BH^- by the isoelectronic and isostructural CH . Thus two replacements lead to neutral molecules ($\text{B}_{n-2}\text{C}_2\text{H}_n$). Carboranes or derivatives with $n = 5$ to $n = 12$ are known, in some of which two or more isomers may be isolated. Sulfur and phosphorus derivatives can also be obtained, with PH^+ , for example, replacing CH or BH^- .

Geometrically, there are three broad classes of boranes or carboranes.

1. Those in which the boron or boron-carbon framework forms a regular polyhedron. These are called *closo* (Greek for cage) compounds.
2. Those in which the boron or boron-carbon framework has the structure of a regular polyhedron with one vertex missing. These are called *nido* (nest) compounds.
3. Those in which the boron or boron-carbon framework has the structure of a regular polyhedron with two vertices missing. These are termed *arachno* (spider web) compounds.

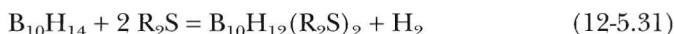
A systematic method for counting electrons and for organizing structures in these and other classes of compounds will be presented in Section 12-7. For now, examples of some important *closo* and *nido* borane anions and carboranes are presented in Fig. 12-8. Structures of some other *nido* and *arachno* compounds have already been presented, for example *nido*- B_5H_9 and *arachno*- B_4H_{10} in Fig. 12-4.

$\text{B}_n\text{H}_n^{2-}$ Ions. The most stable and best studied ions are $\text{B}_{10}\text{H}_{10}^{2-}$ and $\text{B}_{12}\text{H}_{12}^{2-}$, which can be synthesized by the reactions



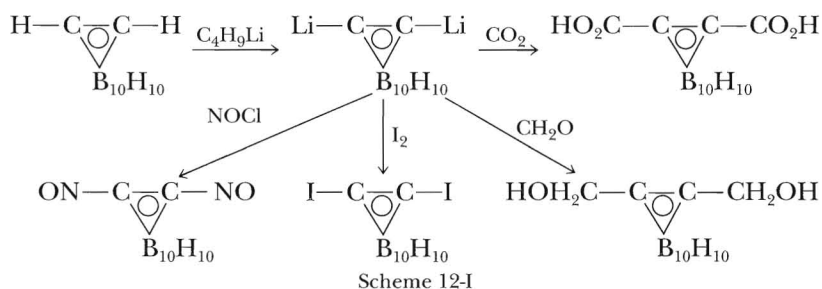
The most important general reaction of the anions is attack by electrophilic reagents such as Br^+ , $\text{C}_6\text{H}_5\text{N}_2^+$, and RCO^+ , in strongly acid media. The $\text{B}_{10}\text{H}_{10}^{2-}$ ion is more susceptible to substitution than $\text{B}_{12}\text{H}_{12}^{2-}$.

$\text{B}_{n-2}\text{C}_2\text{H}_n$ Carboranes. The most important carboranes are 1,2- and 1,7-dicarba-*closo*-dodecaborane ($\text{B}_{10}\text{C}_2\text{H}_{12}$) and their C-substituted derivatives. The 1,2 isomer may be obtained by the reactions



On heating at 450°C the 1,2 isomer rearranges to the 1,7 isomer.

Derivatives may be obtained from $\text{B}_{10}\text{C}_2\text{H}_{12}$ by replacement of the CH hydrogen atoms by Li. The dilithio derivatives react with many other reagents (Scheme 12-1) where a self-explanatory abbreviation is used for $\text{B}_{10}\text{H}_{10}\text{C}_2$.



An enormous number of compounds has been made, one of the main motives being the incorporation of the thermally stable carborane residues into high polymers, such as silicones, in order to increase the thermal stability. Chlorinated carboranes can be obtained directly from $\text{B}_{10}\text{C}_2\text{H}_{10}\text{R}_2$.

$\text{B}_9\text{C}_2\text{H}_{13-n}^-$ Carborane Anions. When the 1,2- and 1,7-dicarba-*closo*-dodecaboranes are heated with alkoxide ions, degradation occurs to form isomeric *nido*-carborane anions ($\text{B}_9\text{C}_2\text{H}_{12}^-$).

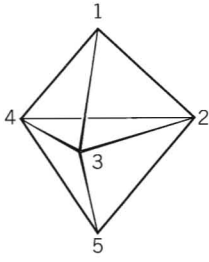


This removal of a BH^{2+} unit from $\text{B}_{10}\text{C}_2\text{H}_{12}$ may be interpreted as a nucleophilic attack at the most electron-deficient boron atoms of the carborane. Molecular orbital calculations show that the C atoms in carboranes have considerable electron-withdrawing power. The most electron-deficient B atoms are those adjacent to carbon. In 1,2- $\text{B}_{10}\text{C}_2\text{H}_{12}$ these will be in positions three and six while in 1,7- $\text{B}_{10}\text{C}_2\text{H}_{12}$ they will be at positions two and three.

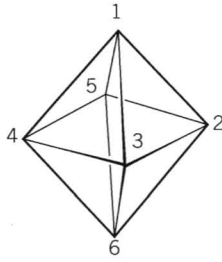
While alkoxide ion attack produces only $\text{B}_9\text{C}_2\text{H}_{12}^-$, use of the very strong base NaH forms the $\text{B}_9\text{C}_2\text{H}_{11}^{2-}$ ions.



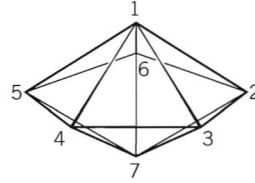
The structures of the isomeric $\text{B}_9\text{C}_2\text{H}_{11}^{2-}$ ions are shown in Fig. 12-9. The $\text{B}_9\text{C}_2\text{H}_{11}^{2-}$



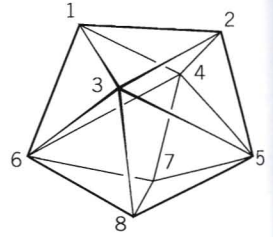
$B_5H_5^{2-}(B_3C_2H_5)$



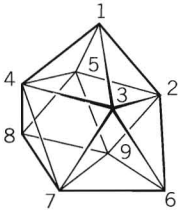
$B_6H_6^{2-}(B_4C_2H_6)$



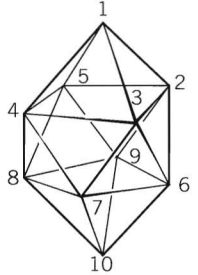
$B_7H_7^{2-}(B_5C_2H_7)$



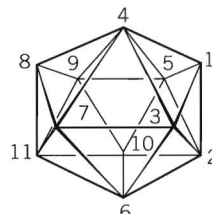
$B_8H_8^{2-}(B_6C_2H_8)$



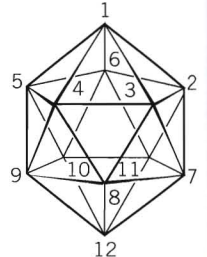
$B_9H_9^{2-}(B_7C_2H_9)$



$B_{10}H_{10}^{2-}(B_8C_2H_{10})$

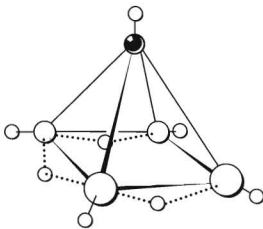


$B_{11}H_{11}^{2-}(B_9C_2H_{11})$

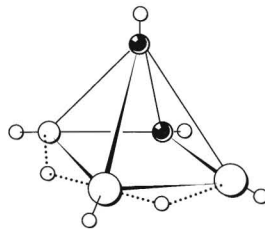


$B_{12}H_{12}^{2-}(B_{10}C_2H_{12})$

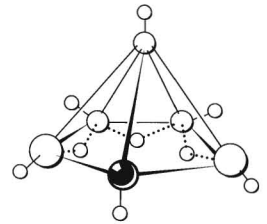
(a)



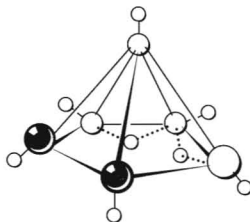
CB_4H_8



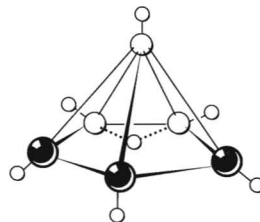
$C_2B_3H_7$



CB_5H_9



$C_2B_4H_8$



$C_3B_3H_7$

(b)

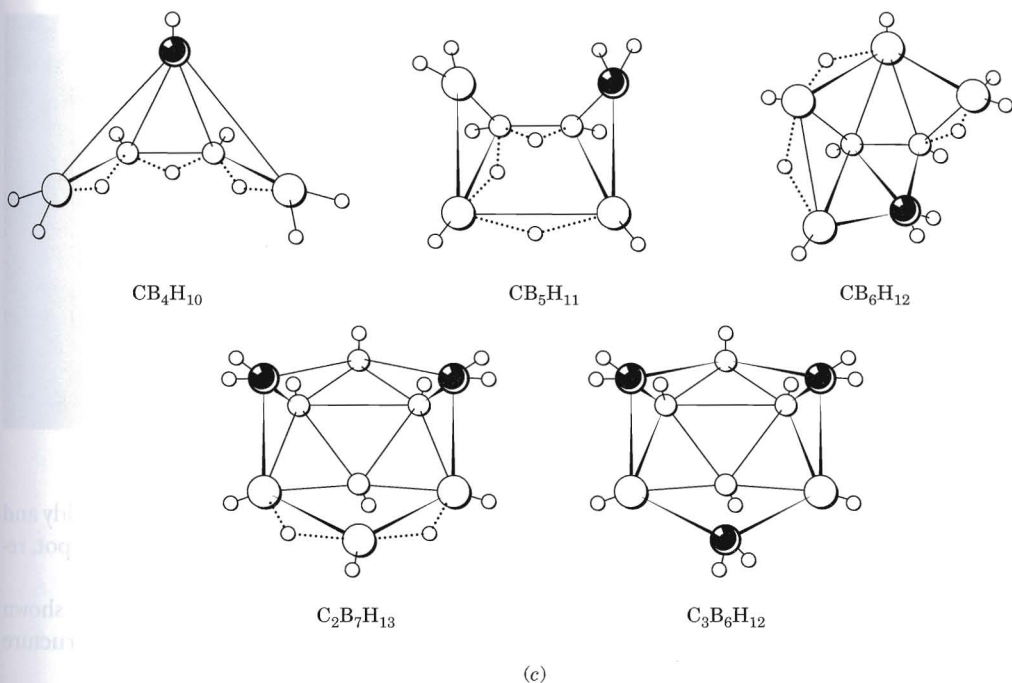
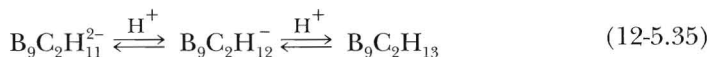


Figure 12-8 The structures of selected boranes and carboranes. (a) The triangulated regular polyhedra, which serve as the framework structures for the *closo* borane anions, $B_nH_n^{2-}$, and for the neutral, isoelectronic carboranes, $C_2B_{n-2}H_n$. Conventional numbering schemes are indicated. Each vertex B or C atom is bonded to a terminal H atom, which is not shown. (b) Selected *nido* carboranes. Note the presence of both terminal B—H (or C—H) groups and bridging B—H—B groups in these *nido* carboranes, as well as in the *nido* boranes shown in Fig. 12-4. (c) Selected *arachno* carboranes. Note, for the *arachno* carboranes shown here, as well as for the *arachno* boranes shown in Fig. 12-4, the additional presence of boron atoms bound to two terminal H atoms, namely, BH_2 groups.

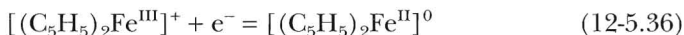
ions are very strong bases and readily acquire H^+ to give $B_9C_2H_{12}^-$. These, in turn, can be protonated to form the neutral *nido*-carboranes $B_9C_2H_{13}$, which are strong acids.



Heating $B_9C_2H_{13}$ gives yet another *closo*-carborane ($B_9C_2H_{11}$) with loss of hydrogen.

Metal Complexes of Carborane Anions. The open pentagonal faces of the $B_9C_2H_{11}^{2-}$ ions (Fig. 12-9) were recognized by M. F. Hawthorne in 1964 to bear a strong resemblance structurally and electronically to the cyclopentadienyl ion ($C_5H_5^-$). The latter forms strong bonds to transition metals, as we discuss in Chapter 29.

Interaction of $Na_2B_9C_2H_{11}$ with metal compounds such as those of Fe^{2+} or Co^{3+} thus leads to species isoelectronic with ferrocene, $(C_5H_5)_2Fe$, or the cobalticinium ion, $(C_5H_5)_2Co^+$, namely, $(B_9C_2H_{11})_2Fe^{2-}$ and $(B_9C_2H_{11})_2Co^-$, respectively. The iron complex undergoes reversible oxidation like ferrocene:



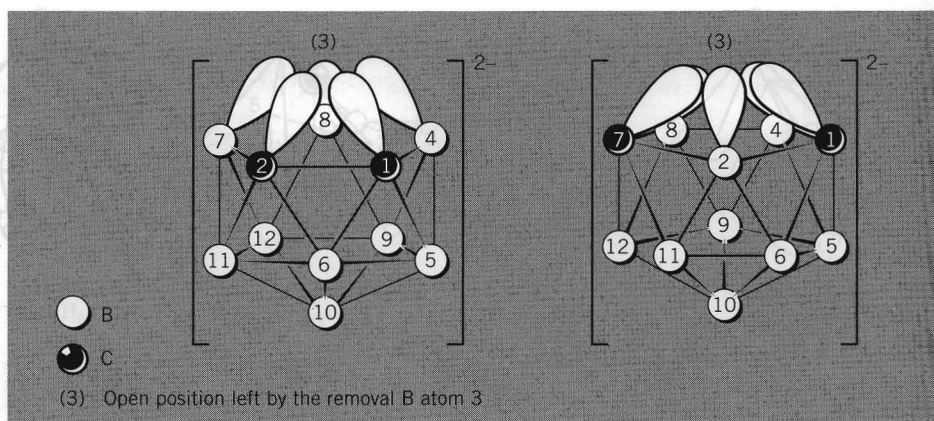


Figure 12-9 The isomeric *nido*-1,2- and *nido*-1,7-carborane anions ($B_9C_2H_{11}^{2-}$).

The formal nomenclature for the $B_9C_2H_{11}^{2-}$ ion and its complexes is unwieldy and the trivial name “dicarbollide” ion was proposed (from the Spanish *olla* for pot, referring to the potlike shape of the B_9C_2 cage).

The structures of two types of bis(dicarbollide) metal complexes are shown in Fig. 12-10. While some complexes have a symmetrical “sandwich” structure [Fig. 12-10(a)] others have the metal disposed unsymmetrically.

Finally, comparable with $\eta^5-C_5H_5Mn(CO)_3$ (Chapter 29), there are mixed complexes with only one dicarbollide unit and other ligands such as CO, $(C_6H_5)_4C_4$, and C_5H_5 [Fig. 12-10(b)].

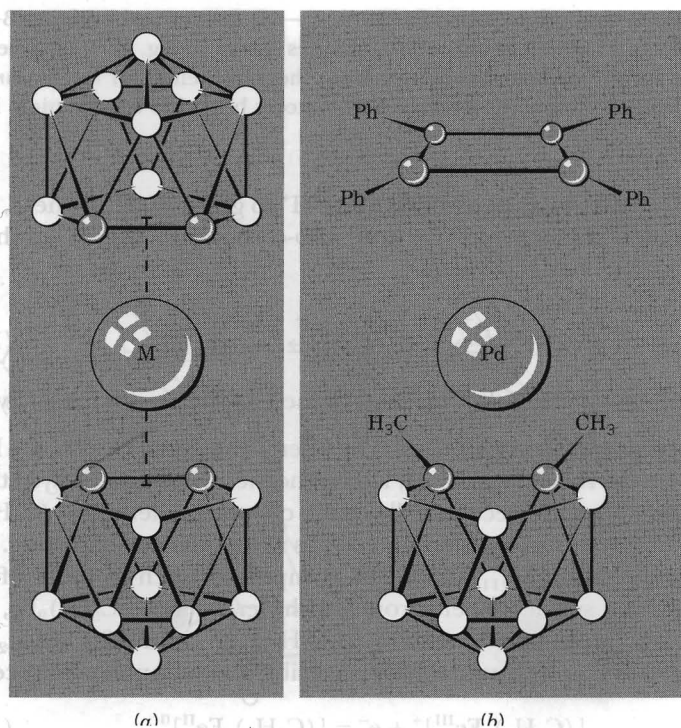


Figure 12-10 (a) The general structure of bis(dicarbollide) metal complexes. (b) An example of a mono(dicarbollide) complex of palladium.

12-6 Boron-Nitrogen Compounds

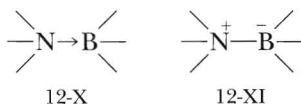
Here we describe three types of B—N compounds, each of which is analogous to C—C compounds, but with some differences. Since the covalent radius and the electronegativity of carbon are each intermediate between those of B and N, it is to be expected that C—C compounds will be similar to, but less polar than, their isoelectronic B—N counterparts. We shall consider amine boranes (analogous to alkanes), aminoboranes (analogous to alkenes), and borazines (analogous to benzenes).

Amine Boranes

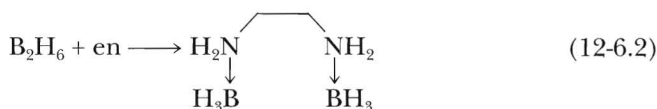
Amine boranes are Lewis acid–base adducts containing a boron–nitrogen donor bond. Both boron and nitrogen are typically tetrahedral, and the B—N bond length is comparable to the C—C bond lengths found in simple alkanes such as ethane. Amine boranes are formed by symmetrical cleavage of diborane or by reaction of ammonium salts as in Reaction 12-6.1.



The B—N bond strength varies from one adduct to another. The weakest B—N bonds are represented as in Structure 12-X, where an arrow indicates a slight donor \rightarrow acceptor interaction. More complete sharing of nitrogen electrons with boron is represented by Structure 12-XI, which is expected to be polar.



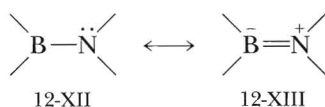
Steric hindrance can prevent the formation of some adducts, for example, 2,6-dimethylpyridine with trimethylborane. Diadducts can be obtained, as in Reaction 12-6.2.



The chief reaction of amine boranes is elimination either of HX or of RH, to give aminoboranes.

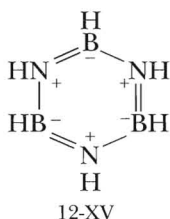
Aminoboranes

Aminoboranes are B—N compounds that are analogous to alkenes. Boron is trigonal in aminoboranes, and the three substituents at boron are planar, or very nearly so. Two resonance forms may be written, Structures 12-XII and 12-XIII.

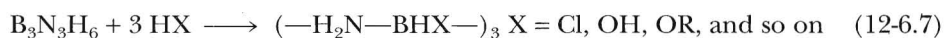


Borazines

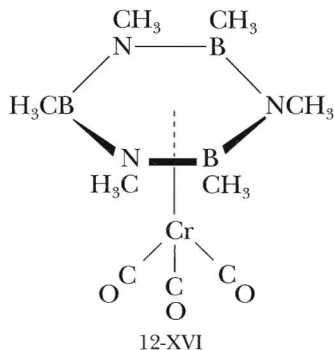
One of the most interesting B—N compounds is *borazine*, $B_3N_3H_6$ (Structure 12-XV).



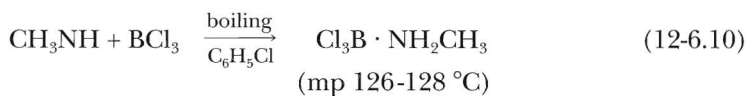
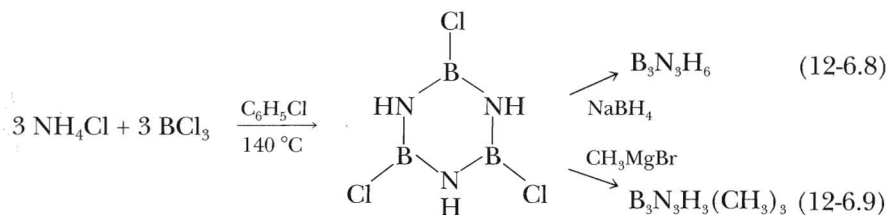
It has an obvious formal resemblance to benzene, and the physical properties of the compounds are similar. However, borazine is much more reactive than benzene and readily undergoes addition reactions, as in Reaction 12-6.7:

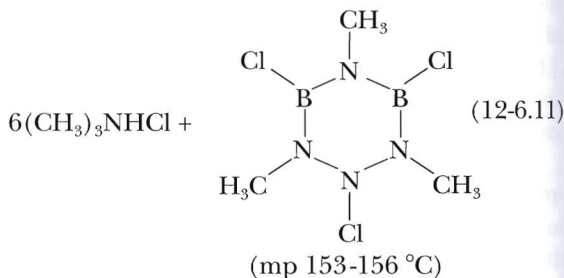
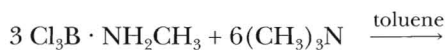


which do not occur with benzene. Borazine also decomposes slowly and may be hydrolyzed to NH_3 and boric acid at elevated temperatures. As with benzene, π complexes with transition metals may be obtained (Chapter 29); thus hexamethylborazine gives compound 12-XVI:



Borazine and substituted borazines may be synthesized by reactions such as 12-6.8 to 12-6.11.





12-7 Electron Counting for Boranes and Other Framework Substances: Wade's Rules

It is now instructive to review the structures of the numerous boranes and carboranes, which, as noted earlier, fall into the *closo*, *nido*, and *arachno* categories. The type of structure adopted by a particular compound has been shown to be related to the number of electrons that are available in the compound for bonding within the polyhedral framework, that is, the number of "framework electrons." A way of correlating the number of framework electrons with structure was first articulated by K. Wade, hence the name "Wade's rules."

Wade's Rules as Applied to Boranes and Carboranes

We start by defining the quantity F , the number of electrons available for framework bonds, as in Eq. 12-7.1:

$$F = 3b + 4c + h + x - 2n \quad (12-7.1)$$

where

b = the number of boron atoms

c = the number of carbon atoms

h = the number of hydrogen atoms

x = the amount of **negative** charge on the ion

n = the number of vertices, that is, $b + c$

Note that x is defined so as to be a positive quantity for anions. Thus the number of valence electrons available for the framework bonds (F) is the number that remains after providing for n exo-framework ($2c-2e$) terminal B—H or C—H bonds.

RULE 1 When the value of F is equal to the quantity $(2n + 2)$, the substance should have a *closo* structure, that is, the framework geometry is based on an n vertex, triangulated, regular polyhedron. This result is obtained for all of the borane dianions ($\text{B}_n\text{H}_n^{2-}$), for the carborane anions ($\text{CB}_{n-1}\text{H}_n^-$), and for the neutral carboranes ($\text{C}_2\text{B}_{n-2}\text{H}_n$), since substitution of a BH^- group by the isoelectronic CH unit does not change the value of F as defined in Eq. 12-7.1.

Two examples readily illustrate this result. For $\text{B}_6\text{H}_6^{2-}$, the value of F is $3 \times 6 + 4 \times 0 + 6 + 2 - 2 \times 6 = 14$. Since the quantity $(2n + 2)$ is also equal to 14, we have identified a *closo* situation. Similarly, for the carborane $\text{C}_2\text{B}_4\text{H}_6$, we have $F = 3 \times 4 + 4 \times 2 + 6 + 0 - 2 \times 6 = 14$. The structure for both $\text{B}_6\text{H}_6^{2-}$ and $\text{C}_2\text{B}_4\text{H}_6$

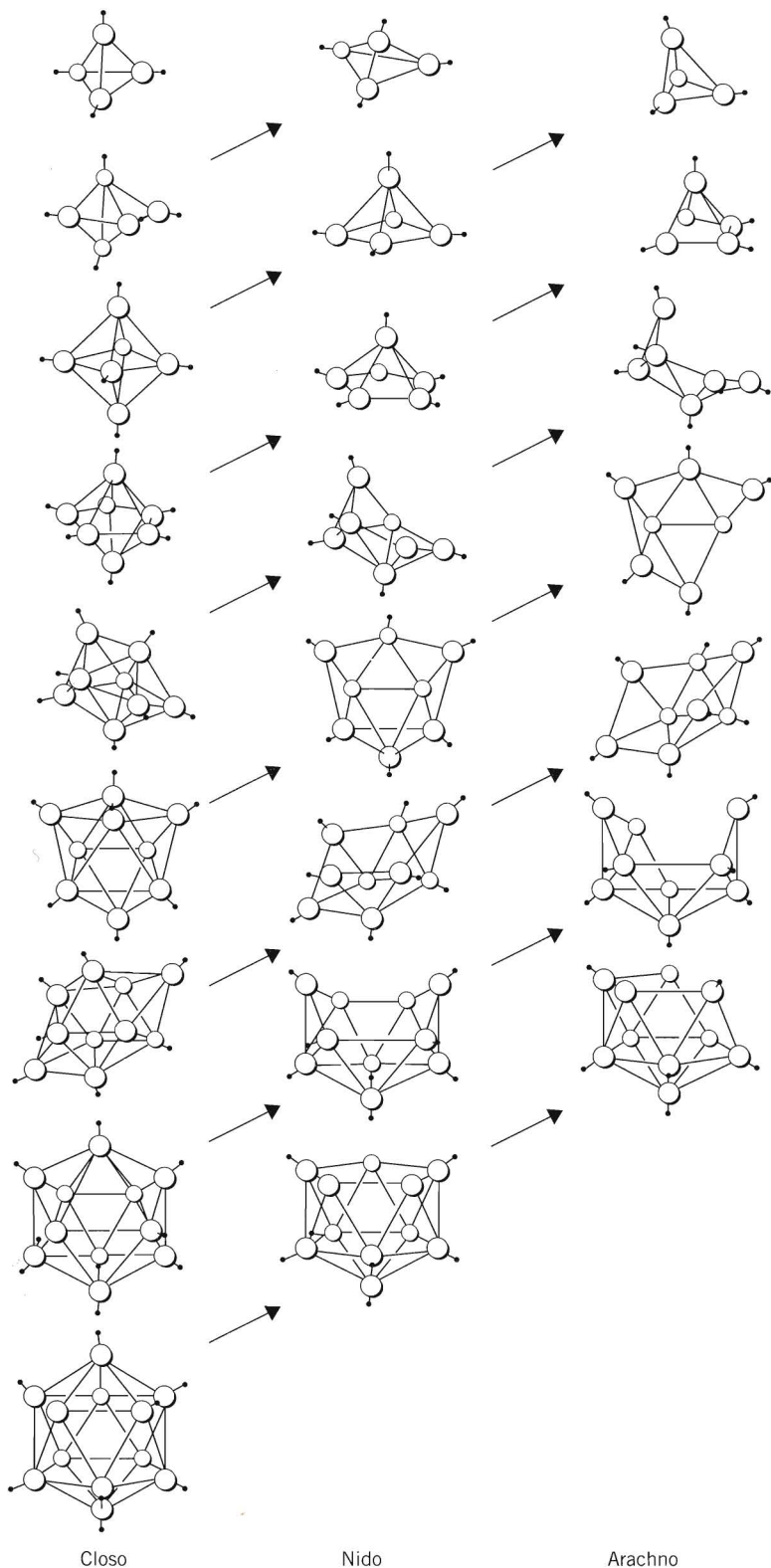


Figure 12-12 The conversion of *closo* polyhedral borane and heteroborane frameworks to *nido* and *arachno* structures by removal of one or two vertices, respectively. Bridge hydrogen atoms are not shown in the *nido* and *arachno* structures, and BH_2 groups are not distinguished from $B-H$ groups in the *arachno* structures. The lines linking boron atoms are meant merely to illustrate cluster geometry. [Reprinted with permission from R. W. Rudolph, *Acc. Chem. Res.*, 9, 446 (1976). Copyright © (1976) American Chemical Society.]

is thus a six vertex polyhedron (namely, the octahedron), as shown in Figs. 12-8(a) and 12-12. In *closo* compounds, the bonds to hydrogen are only of the terminal-type B—H or C—H, 2c–2e bonds.

RULE 2 When the value of F is equal to the quantity $(2n + 4)$, the substance should have the *nido* structure, that is, an $(n + 1)$ vertex polyhedron, with one vertex missing, as illustrated in Fig. 12-12.

For example, for B_5H_9 , the quantity F is equal to $3 \times 5 + 4 \times 0 + 9 + 0 - 2 \times 5 = 14$. Since this is equal to the quantity $(2n + 4)$, the structure of B_5H_9 (Fig. 12-4) is that of an $(n + 1) = 6$ vertex polyhedron, with one vertex missing. This structure is well illustrated in Fig. 12-12. A similar result is obtained for $C_2B_3H_7$. In *nido* compounds, there are B—H—B bridge bonds at those edges left open by the missing vertex atom. The other hydrogen atoms are bonded in the 2c–2e terminal fashion. It is characteristic, then, of *nido* compounds that we find two types of groups: n terminal B—H hydrogen atoms, and B—H—B bridges for the remainder.

RULE 3 When the value of F is equal to the quantity $(2n + 6)$, the compound falls into the *arachno* category, and the preferred structure is that of the $(n + 2)$ vertex polyhedron, with two vertices missing.

The compound B_4H_{10} and the ion $B_9H_{14}^-$ provide useful examples. For B_4H_{10} , the quantity F is equal to $3 \times 4 + 4 \times 0 + 10 + 0 - 2 \times 4 = 14$. This is equal to the quantity $(2n + 6)$ and, as shown in Fig. 12-4, the structure is based on an $(n + 2)$ vertex polyhedron, with two adjacent vertices missing (Fig. 12-12). For $B_9H_{14}^-$, the value of F is $3 \times 9 + 4 \times 0 + 14 + 1 - 2 \times 9 = 24$, which is equal to $(2n + 6)$. The same value is obtained for CB_8H_{14} . Both have a structure (Fig. 12-12) based on a $(9 + 2) = 11$ vertex polyhedron, with two adjacent vertices missing. It is characteristic of *arachno* compounds that we find hydrogen bound in three ways: B—H or C—H terminal bonds, B—H—B bridge bonds, and BH_2 groups. The compound B_5H_{11} (Fig. 12-4) provides another example.

12-8 Descriptive Summary of Reactions

As a study aid, and as a means of summarizing the chemistry of this chapter, we present Figs. 12-13(a–c), which illustrate some of the key reactions for $B(OR)_3$, $B(OH)_3$, B_2H_6 , BCl_3 , and BF_3 . The student should also note Fig. 12-2, as well as Study Question 12-3, in part B.

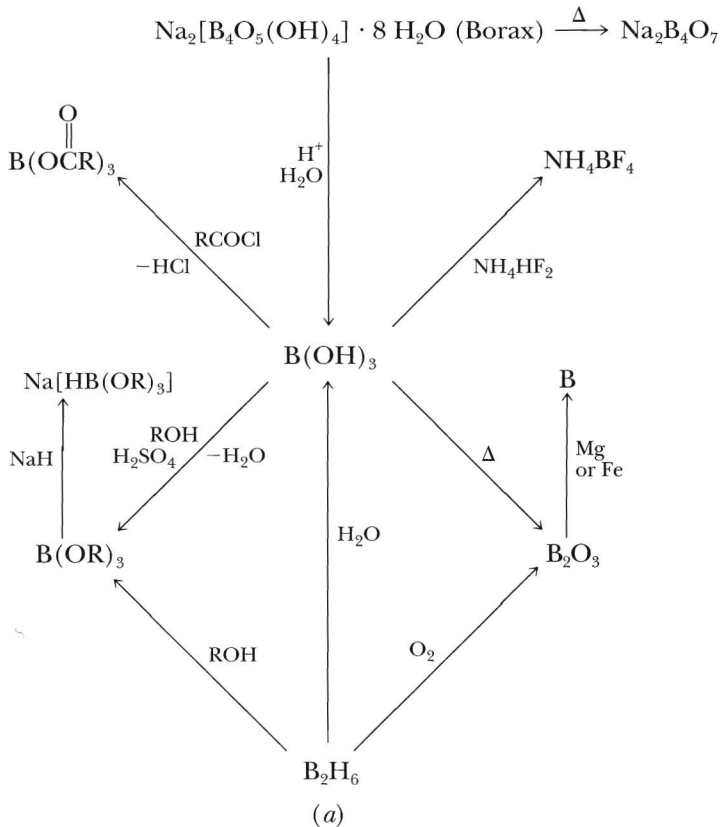
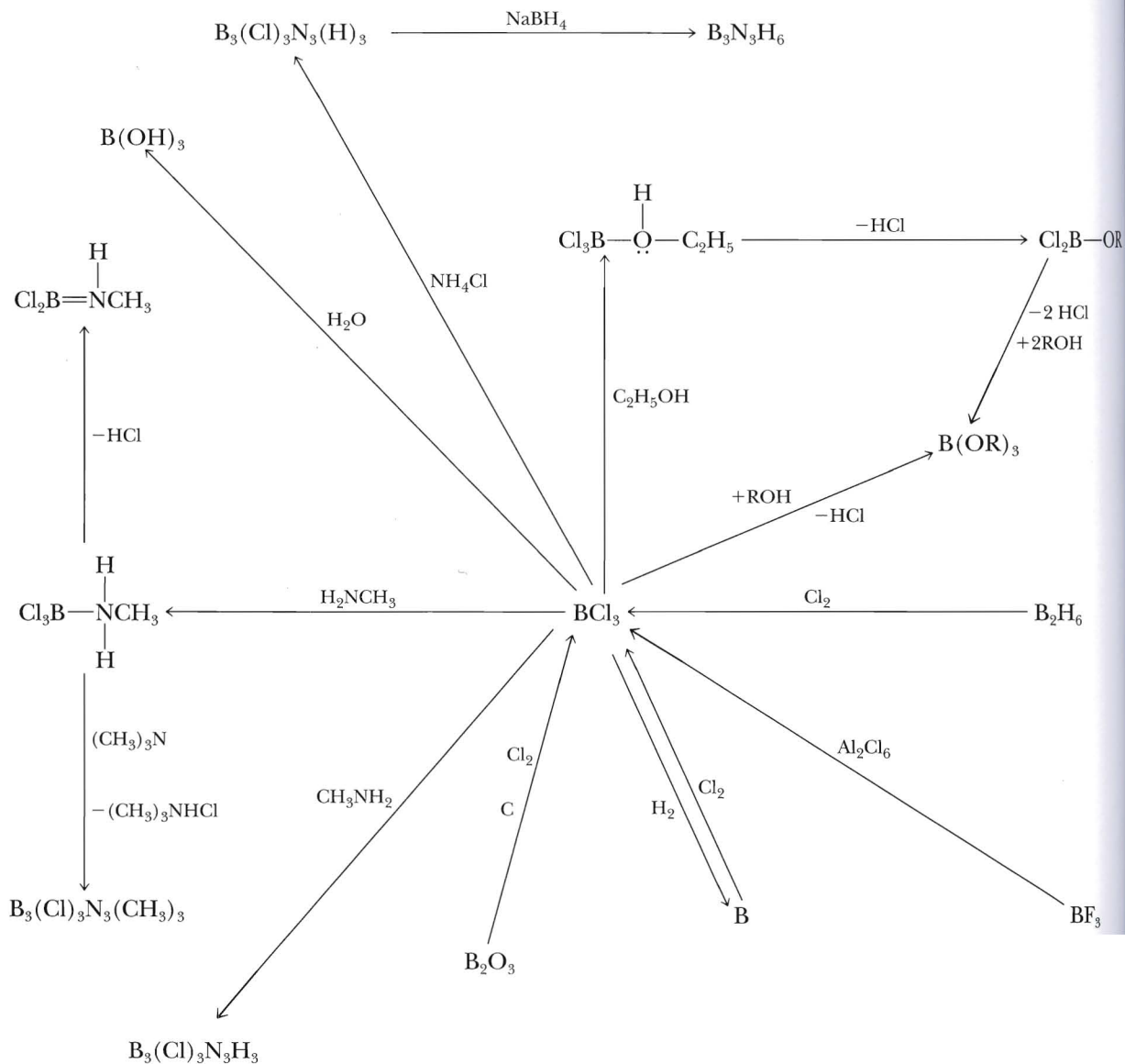


Figure 12-13a



(b)

Figure 12-13b

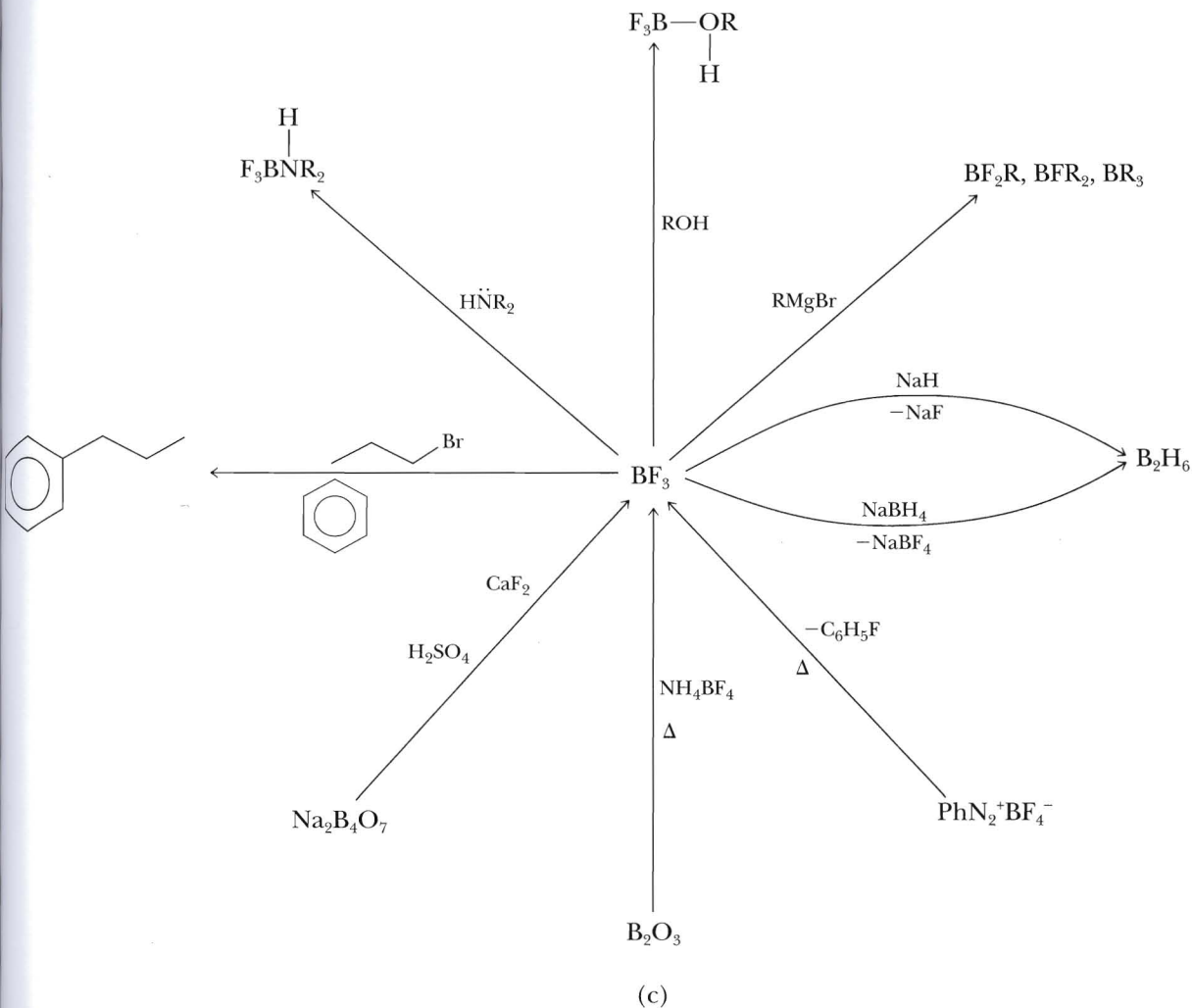


Figure 12-13c

STUDY GUIDE

Study Questions

A. Review

1. Draw the structure of the B12 unit that is found in elemental boron.
2. Draw the structures of the cyclic borate anion in $\text{K}_3\text{B}_3\text{O}_6$ and the chain borate anion in $\text{Mg}_2\text{B}_2\text{O}_5$. Indicate the hybridization at each atom in these borate anions.
3. How does boric acid ionize in water? How strong an acid is it?
4. Why is the activity of boric acid increased by the addition of glycerol?
5. How would one best prepare BF_3 in the laboratory?
6. Why is BBr_3 a better Lewis acid than BF_3 ?

7. Draw the structure of diborane and describe its bonding.
8. Give equations for one useful synthesis of diborane(6).
9. How is sodium borohydride (or tetrahydroborate) prepared?

B. Additional Exercises

1. Review each of the structures of the boron hydrides that have been presented in this chapter and decide which can properly be thought of as a fragment of the icosahedron.
2. The borate anion, $[\text{B}_5\text{O}_6(\text{OH})_4]^-$, has one tetrahedral boron and four trigonal boron atoms, and has two six-membered rings. Draw the structure.
3. Review the reactions of diborane and prepare the same sort of "reaction wheel" for it that has already been prepared for boric acid (Fig. 12-2).
4. Explain why the barriers to rotation around the B—N bond in the following aminoboranes display the trend $\text{H}_2\text{B}(-\text{NR}_2) > \text{HB}(-\text{NR}_2)_2 > \text{B}(-\text{NR}_2)_3$.
5. Propose a structure for the anion B_3H_8^- featured in Reactions 12-5.13 and 12-5.14.
6. Draw the structure of the disubstituted product from the reaction of decaborane(14) with CN^- .
7. What are the hybridizations and the geometries of the C and O atoms in the organic derivatives $\text{B}(\text{OR})_3$, $\text{B}(\text{OCOR})_3$, and $\text{B}(\text{OOR})_3$?
8. What is the structure of the anion formed upon deprotonation of decaborane(14)? Which are the acidic hydrogens in decaborane(14) and why?
9. Predict the products of the following reactions:

(a) $\text{BF}_3 + \text{OEt}_2$	(b) $\text{BF}_3 + \text{H}_2\text{O}$
(c) $\text{BCl}_3 + \text{ROH}$	(d) $\text{B}_2\text{H}_6 + \text{HCl}$
(e) $\text{B}_{10}\text{H}_{14} + \text{NR}_3$	(f) $\text{B}_{10}\text{H}_{14} + \text{I}_2$
(g) $\text{LiH} + \text{B}_2\text{H}_6$	(h) $\text{NH}_4\text{Cl} + \text{LiBH}_4$
(i) $(\text{CH}_3)_2\text{N}-\text{BCl}_2 + \text{C}_6\text{H}_5\text{MgBr}$	(j) $\text{B}_3\text{N}_3\text{H}_6 + \text{H}_2\text{O}$
(k) $\text{B}_3\text{N}_3\text{H}_6 + \text{HBr}$	(l) $(\text{Cl}-\text{B})_3(\text{NH})_3 + \text{C}_2\text{H}_5\text{MgBr}$
10. Suggest a series of reactions for the synthesis of
 - (a) Borazine, beginning with boron trichloride.
 - (b) Decaborane(14), starting with diborane.
 - (c) $[\text{H}_2\text{B}(\text{NMe}_3)_2]^+$, starting with diborane.
 - (d) Diethylaminodichloroborane, starting with BCl_3 .
 - (e) *B*-Trichloro-*N*-trimethylborazine, starting with BCl_3 .
11. Suggest a reason for the greater reactivity of borazine than benzene towards addition of HX.
12. Draw the structure of $(\text{Ph}_3\text{P})_2\text{CuBH}_4$. Carefully show the geometry at P, Cu, and B.
13. Consider the semitopological diagram of $\text{B}_{10}\text{H}_{14}$ in Fig. 12-6. Account for all of the electrons in the molecule by listing the number of each that is involved in (a) terminal BH groups, (b) bridging BHB groups, (c) open BBB bridge groups, (d) two-electron BB bonds, and (e) closed BBB bonds.
14. Use Wade's rules to classify each of the following.

(a) $\text{B}_6\text{H}_6^{2-}$	(j) B_8H_{14}
(b) $\text{C}_2\text{B}_4\text{H}_6$	(k) $\text{C}_2\text{B}_7\text{H}_{11}$
(c) B_5H_9	(l) $\text{B}_{10}\text{H}_{14}^{2-}$
(d) $\text{C}_2\text{B}_3\text{H}_7$	(m) $\text{B}_7\text{H}_7^{2-}$
(e) B_4H_{10}	(n) $\text{C}_2\text{B}_8\text{H}_{10}$

- (f) $B_9H_{14}^-$ (o) $C_2B_8H_{12}$
 (g) $B_{10}H_{14}$ (p) $C_2B_9H_{11}$
 (h) B_5H_{11} (q) B_6H_{12}
 (i) B_6H_{10} (r) B_9Cl_9 and $B_9Cl_9^{2-}$
15. The spectrum of B_3F_5 suggests the presence of two types of F atoms in a ratio of 4:1 and two types of B atoms in a ratio of 2:1. Suggest a possible structure for this compound using trigonal boron atoms only.
16. The compound B_8F_{12} has four trigonal boron atoms and four tetrahedral atoms. Furthermore, there appears to be four terminal BF_2 groups and two bridging BF_2 groups. Suggest a plausible structure.
17. Write equations for each of the following reactions.
- Reaction of diborane with ammonia.
 - Reaction of diborane with HCl.
 - Reduction of boron oxide by Fe.
 - $B(OH)_3 + CH_3COCl$
 - Reduction of BF_3 with NaH.
 - Reaction of $B_{10}H_{14}$ with I_2 .
 - Hydrolysis of B_5H_9 .
 - $B_2H_6 + O_2$
 - Hydrolysis of BCl_3 .
 - Condensation of boric acid with ethanol.
 - Reaction of boron with chlorine.
 - Reduction of diborane with sodium.
 - Hydrolysis of diborane.
 - Reaction of BCl_3 with ethanol.
 - Thermolysis of boric acid.
 - $B(OH)_3 + NH_4HF_2$
18. Write out a stepwise synthesis, starting with borax, of $Cl_2B-OC_2H_5$.
19. Show how to make the following compounds from the given starting materials.
- B_2H_6 from BF_3
 - $[ClB-NH]_3$ from BCl_3
 - $B(OCH_3)_3$ from $B(OH)_3$
 - B_2F_4 from B_2Cl_4
 - B_2Cl_4 from BCl_3
 - B_4Cl_4 from BCl_3
 - B_9Cl_9 from B_2Cl_4
 - $B(OC_2H_5)_3$ from B_2H_6
 - BCl_3 from BF_3
 - $NaBH_4$ from B_2H_6
 - $B_3N_3H_6$ from BCl_3

C. Problems from the Literature of Inorganic Chemistry

- Consider the paper by R. W. Parry, R. W. Rudolph, and D. F. Shriver, *Inorg. Chem.*, **1964**, *3*, 1479–1483.
 - Write balanced equations for the symmetrical and unsymmetrical cleavage reactions of tetraborane(10) by a general nucleophile, L.
 - Write balanced equations for the symmetrical and unsymmetrical cleavage reactions of tetraborane(10) by $NaBH_4$.
 - Write the balanced equations for the symmetrical and unsymmetrical cleavage of tetraborane(10) by $NaBD_4$, and account for the predicted percentage of D label in the products for each case.

- (d) Why have the authors so carefully argued against "exchange" in such reactions or among the reaction products?
- (e) What are the products of the cleavage of tetraborane(10) by NH_3 ?
2. Consider the comparison of amine boranes and borazines made by O. T. Beachley, Jr., and B. Washburn, *Inorg. Chem.*, **1975**, *14*, 120–123.
- (a) Write balanced chemical equations to represent the reactions that were employed to synthesize
- (i) $\text{H}_2\text{ClB}\cdot\text{N}(\text{CH}_3)_3$ and $\text{H}_2\text{BrB}\cdot\text{N}(\text{CH}_3)_2\text{H}$
- (ii) $\text{H}_2\text{CH}_3\text{B}\cdot\text{N}(\text{CH}_3)_3$ and $\text{H}_2\text{CH}_3\text{B}\cdot\text{N}(\text{CH}_3)_2\text{H}$
- (iii) $\text{H}_2(\text{CN})\text{B}\cdot\text{N}(\text{CH}_3)_3$ and $\text{H}_2(\text{CN})\text{B}\cdot\text{N}(\text{CH}_3)_2\text{H}$
- (b) Draw the Lewis diagram for each adduct mentioned in (a).
- (c) What reaction takes place between HgBr_2 and (i) $\text{H}_3\text{B}\cdot\text{N}(\text{CH}_3)_3$; (ii) $\text{H}_3\text{B}_3\text{N}_3\text{H}_3$?
- (d) What reaction takes place between AgCN and (i) $\text{H}_3\text{B}_3\text{N}_3\text{H}_3$ at 0°C (ii) $\text{H}_3\text{B}\cdot\text{N}(\text{CH}_3)_3$ at 130°C ?
- (e) What mechanistic interpretation do the authors give to the facts in (c)?
- (f) How do π - and σ -bond effects combine in the borazine ring to make the BH group sufficiently hydridic to react with HgCl_2 ?
- (g) What suggestion do the authors make to explain the facts in (d)?
3. Methylation at boron of the *closo*-carborane, $2,4\text{-C}_2\text{B}_5\text{H}_7$, has been studied by J. F. Ditter, E. B. Klusmann, R. E. Williams, and T. Onak, *Inorg. Chem.*, **1976**, *15*, 1063–1065.
- (a) When methylation was performed with methylchloride in the presence of an excess of AlCl_3 , which boron atom(s) was methylated to give (i) $\text{CH}_3\text{C}_2\text{B}_5\text{H}_6$ via monomethylation (ii) $(\text{CH}_3)_2\text{C}_2\text{B}_5\text{H}_5$ via dimethylation (iii) $(\text{CH}_3)_3\text{C}_2\text{B}_5\text{H}_4$ via trimethylation?
- (b) What do the facts in (a) suggest about the relative availability of electrons (as judged by readiness to react with electrophilic reagents) at the different boron atoms in $\text{C}_2\text{B}_5\text{H}_7$?
- (c) How does its position in the cage influence the electron availability at a boron atom, according to these authors?
4. Although borazine, the inorganic analog of benzene, was known as early as 1926, a similar B—P cyclic trimer was not reported until 1987. Read the subsequent account of the compound by H. V. Rasika Dias and P. P. Power, *J. Am. Chem. Soc.*, **1989**, *111*, 144–148, and answer the following questions.
- (a) What synthetic method was used for the title compounds?
- (b) What mechanisms are proposed for formation of the compounds?
- (c) For the compound $(\text{MesB—PC}_6\text{H}_5)_3$, what is the significance of the planarity of the ring atoms and the six substituent carbon atoms?
- (d) What other structural data suggest a considerable amount of B—P double-bond character in the rings?
5. Read the article on synthesis of $\text{B}_5\text{H}_9^{2-}$ and B_5H_{11} by J. R. Wermer and S. G. Shore, *Inorg. Chem.*, **1987**, *26*, 1644–1645.
- (a) Write equations for the syntheses reported here of $\text{B}_5\text{H}_9^{2-}$ and B_5H_{11} , starting with B_5H_9 .
- (b) Use Wade's rules to classify the structures of the above three compounds.
- (c) How do the structure and chemistry of $\text{B}_5\text{H}_9^{2-}$ compare with those of B_5H_8^- ?
6. Read the article by T. Davan and J. A. Morrison, *Inorg. Chem.*, **1986**, *25*, 2366–2372.
- (a) What is the overall stability order found for the polyhedral boron chlorides?

- (b) How does this stability order differ from that for the polyhedral borane anions, $B_nH_n^{2-}$?
- (c) What difference is there between the two classes of compounds as far as Wade's rules are concerned?

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