

metal atoms and the structure represents a transition between the puckered layer structures of MB_2 and the cubic MB_6 .

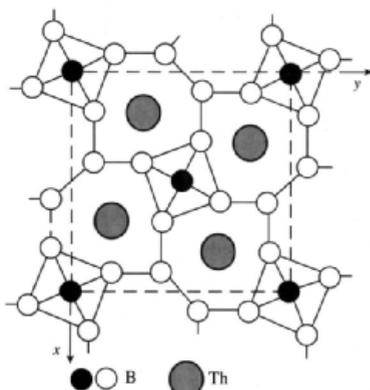


Figure 6.11 Structure of ThB_4 .

The structure and properties of many borides emphasize again the inadequacy of describing bonding in inorganic compounds as either ionic, covalent or metallic. For example, in conventional terminology LaB_6 would be described as a rigid, covalently bonded network of B_6 clusters having multicentred bonding within each cluster and 2-centre covalent B–B bonds between the clusters; this requires the transfer of up to 2 electrons from the metal to the boron sublattice and so could be said also to involve ionic bonding ($La^{2+}B_6^{2-}$) in addition to the covalent inter-boron bonding. Finally, the third valency electron on La is delocalized in a conduction band of the crystal (mainly metal based) and the electrical conductivity of the boride is actually greater than that of La metal itself so that this aspect of the bonding could be called metallic. The resulting description of the bonding is an *ad hoc* mixture of four oversimplified limiting models and should more logically be replaced by a generalized MO approach.⁽⁸⁾ It will also be clear from the preceding paragraphs that a classification of borides according to the periodic table does not result in the usual change in stoichiometry from one group to the next; instead, a classification

in terms of the type of boron network and the size and electropositivity of the other atoms is frequently more helpful and revealing of periodic trends.

6.4 Boranes (Boron Hydrides)^(1,9)

6.4.1 Introduction

Borane chemistry began in 1912 with A. Stock's classic investigations,⁽¹⁰⁾ and the numerous compounds prepared by his group during the following 20 y proved to be the forerunners of an amazingly diverse and complex new area of chemistry. During the past few decades the chemistry of boranes and the related carboranes (p. 181) has been one of the major growth areas in inorganic chemistry, and interest continues unabated. The importance of boranes stems from three factors: first, the completely unsuspected structural principles involved; secondly, the growing need to extend covalent MO bond theory considerably to cope with the unusual stoichiometries; and finally, the emergence of a versatile and extremely extensive reaction chemistry which parallels but is quite distinct from that of organic and organometallic chemistry. This efflorescence of activity culminated (in the centenary year of Stock's birth) in the award of the 1976 Nobel Prize for Chemistry to W. N. Lipscomb (Harvard) "for his studies of boranes which have illuminated problems of chemical bonding".

Over 50 neutral boranes, B_nH_m , and an even larger number of borane anions $B_nH_m^{x-}$ have been characterized;⁽¹¹⁾ these can be classified

⁹ E. L. MUETTERTIES (ed.), *Boron Hydride Chemistry*, Academic Press, New York, 1975, 532 pp.

¹⁰ A. STOCK, *Hydrides of Boron and Silicon*, Cornell University Press, Ithaca, New York, 1933, 250 pp.

¹¹ N. N. GREENWOOD, Boron Hydride Clusters, in H. W. ROESKY (ed.) *Rings, Clusters and Polymers of Main Group and Transition Elements*, Elsevier, Amsterdam, 1989, pp. 49–105.

according to structure and stoichiometry into 5 series though examples of neutral or unsubstituted boranes themselves are not known for all 5 classes:

closo-boranes (from Greek κλωβός, *clovos*, a cage) have complete, closed polyhedral clusters of n boron atoms;

nido-boranes (from Latin *nidus*, a nest) have non-closed structures in which the B_n cluster occupies n corners of an $(n + 1)$ -cornered polyhedron;

arachno-boranes (from Greek ἀράχνη, *arachne*, a spider's web) have even more open clusters in which the B atoms occupy n contiguous corners of an $(n + 2)$ -cornered polyhedron;

hypho-boranes (from Greek ὑφή, *hyphē*, a net) have the most open clusters in which the B atoms occupy n corners of an $(n + 3)$ -cornered polyhedron;

conjuncto-boranes (from Latin *conjuncto*, I join together) have structures formed by linking two (or more) of the preceding types of cluster together.

Examples of these various series are listed below and illustrated in the accompanying structural diagrams. Their interrelations are further discussed in connection with carborane structures 51–81.

Closo-boranes:

$B_nH_n^{2-}$ ($n = 6-12$) see structures 1–7. The neutral boranes B_nH_{n+2} are not known.

Nido-boranes:

B_nH_{n+4} , e.g. B_2H_6 (8), B_5H_9 (9), B_6H_{10} (10), $B_{10}H_{14}$ (11); B_8H_{12} also has this formula but has a rather more open structure (12) which can be visualized as being formed from $B_{10}H_{14}$ by removal of B(9) and B(10).

$B_nH_{n+3}^-$ formed by removal of 1 bridge proton from B_nH_{n+4} , e.g. $B_5H_8^-$, $B_{10}H_{13}^-$; other anions in this series such as $B_4H_7^-$ and $B_9H_{12}^-$ are known though the parent boranes have proved too

fugitive to isolate; BH_4^- can be thought of as formed by addition of H^- to BH_3 .

$B_nH_{n+2}^{2-}$, e.g. $B_{10}H_{12}^{2-}$, $B_{11}H_{13}^{2-}$.

Arachno-boranes:

B_nH_{n+6} , e.g. B_4H_{10} (13), B_5H_{11} (14), B_6H_{12} (15), B_8H_{14} (16), *n*- B_9H_{15} (17), *i*- B_9H_{15} .

$B_nH_{n+5}^-$, e.g. $B_2H_7^-$ (18), $B_3H_8^-$ (19), $B_5H_{10}^-$, $B_9H_{14}^-$ (20), $B_{10}H_{15}^-$.

$B_nH_{n+4}^{2-}$, e.g. $B_{10}H_{14}^{2-}$ (21).

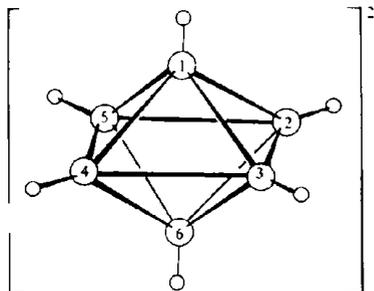
Hypho-boranes:

B_nH_{n+8} . No neutral borane has yet been definitely established in this series but the known compounds B_8H_{16} and $B_{10}H_{18}$ may prove to be *hypho*-boranes and several adducts are known to have *hypho*-structures (pp. 171–2).

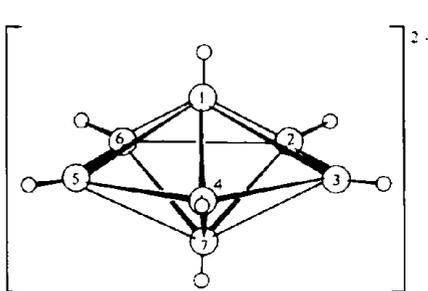
Conjuncto-boranes:

B_nH_m . At least five different structure types of interconnected borane clusters have been identified; they have the following features:

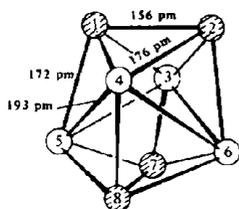
- fusion by sharing a single common B atom, e.g. $B_{15}H_{23}$ (22);
- formation of a direct 2-centre B–B σ bond between 2 clusters, e.g. B_8H_{18} , i.e. $(B_4H_9)_2$ (23), $B_{10}H_{16}$, i.e. $(B_5H_8)_2$ (3 isomers) (24), $B_{20}H_{26}$, i.e. $(B_{10}H_{13})_2$ (11 possible isomers of which most have been prepared and separated), (e.g. 25a, b, c); anions in this subgroup are represented by the 3 isomers of $B_{20}H_{18}^{4-}$, i.e. $(B_{10}H_9^{2-})_2$ (26);
- fusion of 2 clusters via 2 B atoms at a common edge, e.g. $B_{13}H_{19}$ (27), $B_{14}H_{18}$ (28), $B_{14}H_{20}$ (29), $B_{16}H_{20}$ (30), *n*- $B_{18}H_{22}$ (31), *i*- $B_{18}H_{22}$ (32);
- fusion of two clusters via 3 B atoms at a common face: no neutral borane or borane anion is yet known with this conformation but the solvated complex $(MeCN)_2B_{20}H_{16}$.MeCN has this structure (33);
- more extensive fusion involving 4 B atoms in various configurations, e.g. $B_{20}H_{16}$ (34), $B_{20}H_{18}^{2-}$ (35).



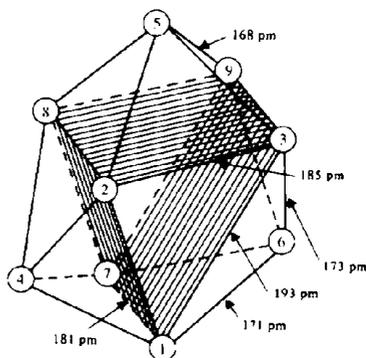
(1) The $B_4H_6^{2-}$ anion. The relationship to the structure of the B_4 network in CaB_4 and the boron cluster in B_4H_4 should be noted.



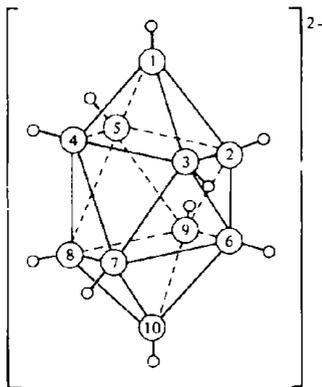
(2) Probable D_{3h} pentagonal bipyramidal structure of the anion $B_5H_5^{2-}$ in solution.



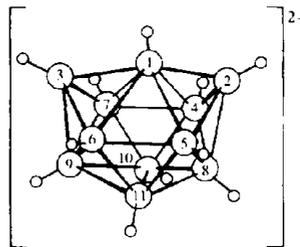
(3) The D_{2d} configuration of the boron atoms in $B_5H_5^{2-}$ showing the two structurally non-equivalent sets of 4 boron atoms.



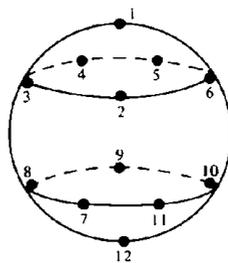
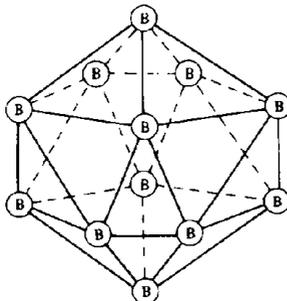
(4) Structure of the boron cluster in $B_6H_6^{2-}$ (interatomic distances ± 1.5 pm). The four unique B-H distances are 107, 110, 127 and 144 ± 15 pm.



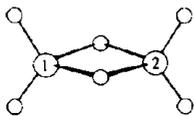
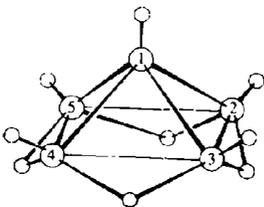
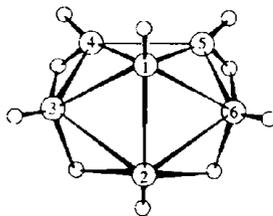
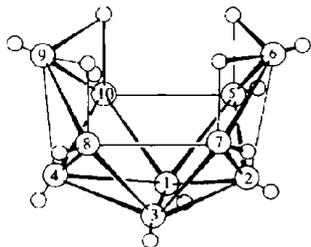
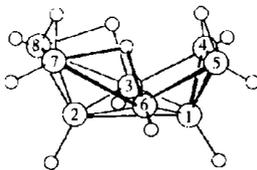
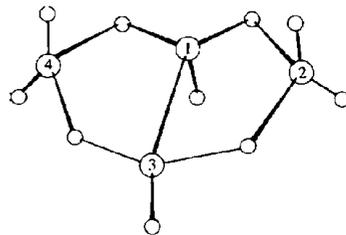
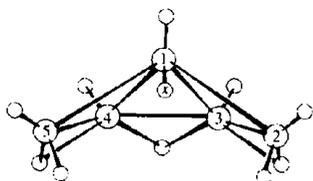
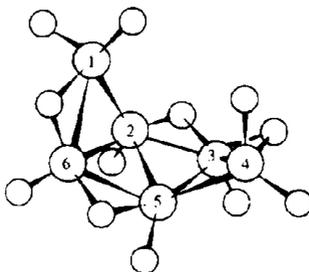
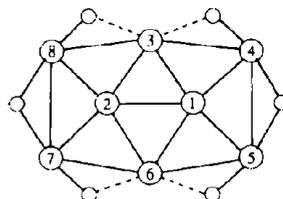
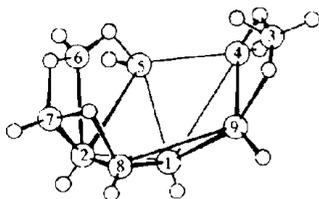
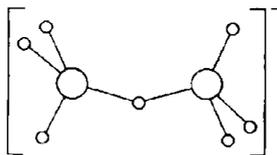
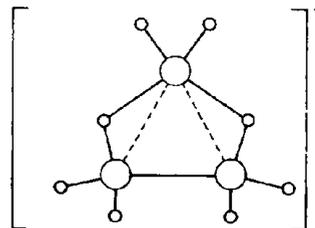
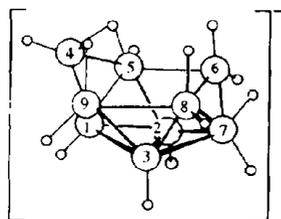
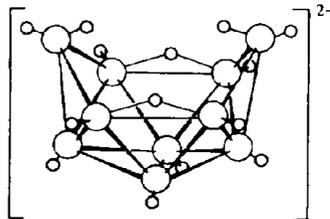
(5) $B_{10}H_{10}^{2-}$: decahydro-closo-decaborate ($2-$)

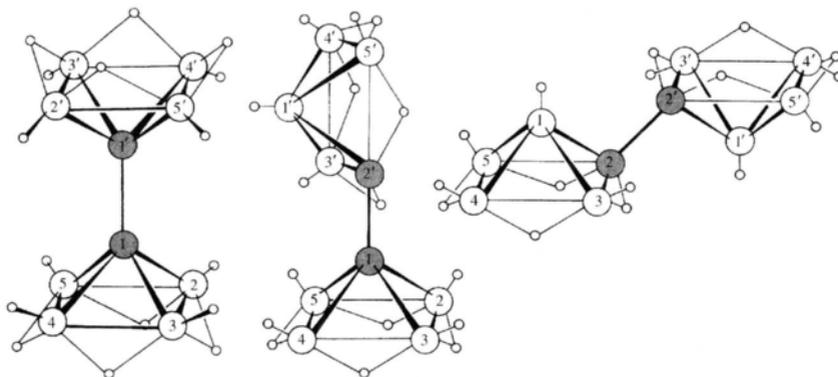
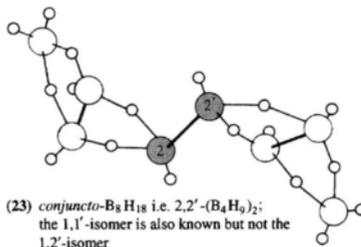
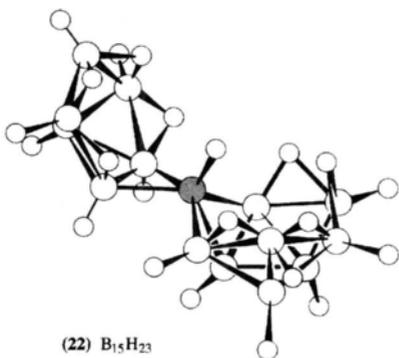


(6) $B_{11}H_{11}^{2-}$

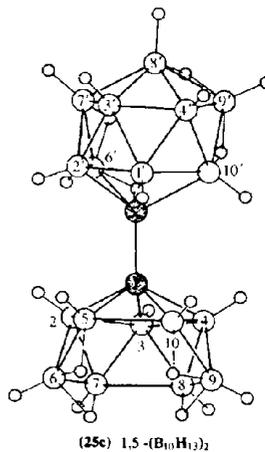
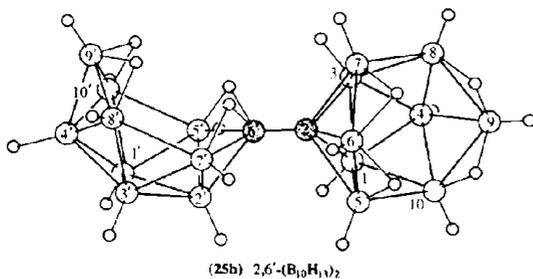
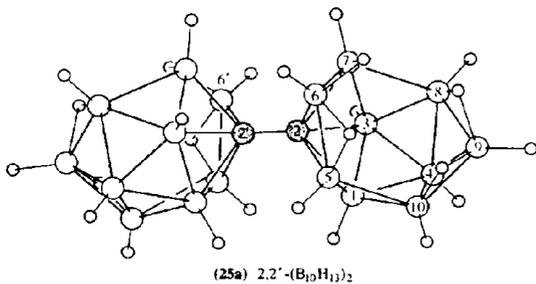


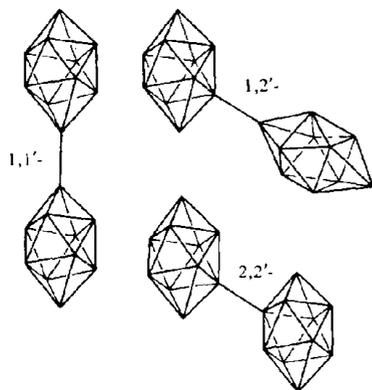
(7) Position of boron atoms and numbering system in the icosahedral borane anion $B_{12}H_{12}^{2-}$. The hydrogen atoms, which are attached radially to each boron atom, are omitted for clarity. There are six B-B distances of 175.5 pm and 24 of 178 pm.

(8) B_2H_6 (9) B_5H_9 (10) B_6H_{10} (11) B_7H_{14} (12) B_8H_{12} (13) B_4H_{10} (14) B_5H_{11} (15) B_6H_{12} (16) Proposed structure for B_8H_{14}
(terminal H atoms omitted)(17) $n-B_5H_{15}$ (18) $B_2H_7^-$ (19) $B_3H_8^-$ (20) B_7H_{14} (21) $B_{10}H_{14}^{2-}$

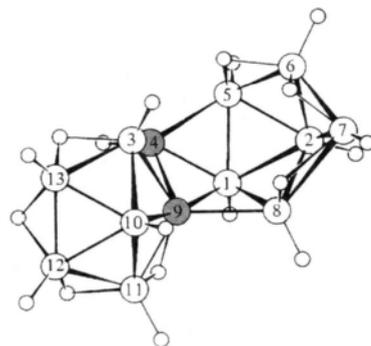


(24) Structures of the three isomers of $B_{10}H_{16}$. The $1,1'$ isomer comprises two pentaborane(9) groups linked in eclipsed configuration via the apex boron atoms to give overall D_{2h} symmetry, the B-B bond distances are 174 pm for the linking bond, 176 pm for the slant edge of the pyramids, and 171 pm for the basal boron atoms

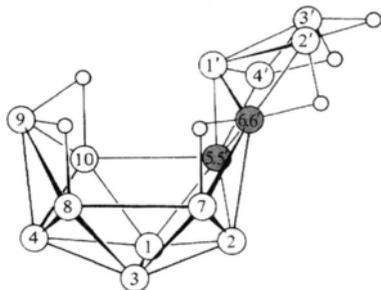




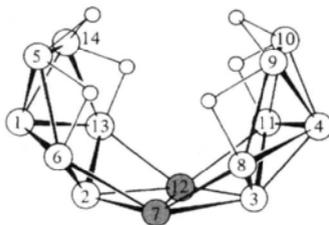
(26) Proposed structures for the three isomers of $[B_{10}H_{10}]^{4-}$; terminal hydrogen atoms omitted for clarity. (See also p. 180)



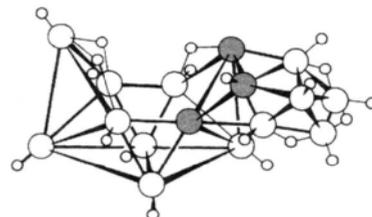
(27) $B_{13}H_{19}$



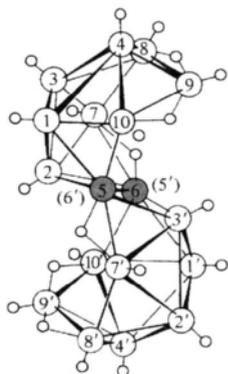
(28) Proposed structure of $B_{14}H_{18}$, omitting terminal hydrogen atoms for clarity



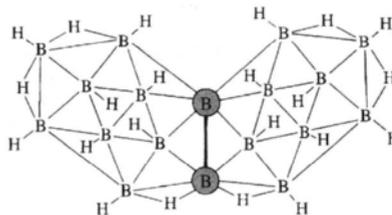
(29) $B_{14}H_{20}$
Terminal hydrogen atoms have been omitted for clarity



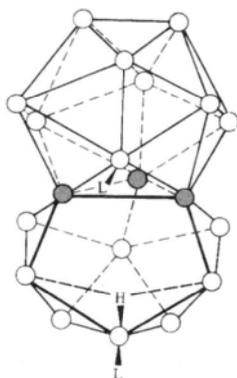
(30) $B_{16}H_{20}$



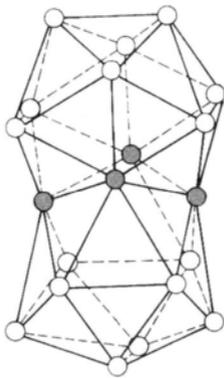
(31) $n-B_{18}H_{22}$ (centrosymmetric)



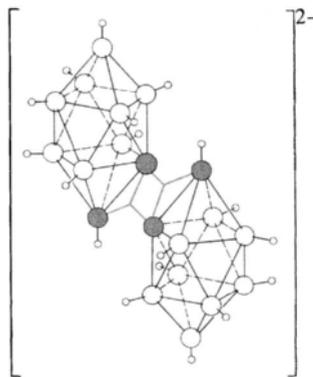
(32) Plane projection of the structure of $i-B_{18}H_{22}$.
The two decaborane units are fused at the 5(7') and 6(6') positions to give a non-centrosymmetric structure with C_2 symmetry



(33) Molecular structure of $(\text{MeCN})_2\text{B}_{20}\text{H}_{16}$ as found in crystals of the solvate $(\text{MeCN})_2\text{B}_{20}\text{H}_{16}\cdot\text{MeCN}$ (see text)



(34) The boron atom arrangement in *closo*- $\text{B}_{20}\text{H}_{16}$. Each boron atom except the 4 "fusion borons" carries an external hydrogen atom and there are no BHB bridges



(35) Structure of the $\text{B}_{20}\text{H}_{18}^{2-}$ ion. The two 3-centre BBB bonds joining the $2\text{B}_{10}\text{H}_9^-$ units are shown by broad shaded lines

Boranes are usually named⁽¹²⁾ by indicating the number of B atoms with a latin prefix and the number of H atoms by an arabic number in parentheses, e.g. B_5H_9 , pentaborane(9); B_5H_{11} , pentaborane(11). Names for anions end in "ate" rather than "ane" and specify both the number of H and B atoms and the charge, e.g. B_5H_8^- octahydropentaborate(1-). Further information can be provided by the optional inclusion of the italicized descriptors *closo*-, *nido*-, *arachno*-, *hypho*- and *conjuncto*-, e.g.:

$\text{B}_{10}\text{H}_{10}^{2-}$: decahydro-*closo*-decaborate(2-)
[structure (5)]

$\text{B}_{10}\text{H}_{14}$: *nido*-decaborane(14) [structure (11)]

$\text{B}_{10}\text{H}_{14}^{2-}$: tetradecahydro-*arachno*-
decaborate(2-) [structure (21)]

$\text{B}_{10}\text{H}_{16}$: 1,1'-*conjuncto*-decaborane(16)
[structure (24a)]
[i.e. 1,1'-bi(*nido*-pentaboranyl)]

The detailed numbering schemes are necessarily somewhat complicated but, in all other respects, standard nomenclature practices are followed.⁽¹²⁾

Derivatives of the boranes include not only simple substituted compounds in which H has been replaced by halogen, OH, alkyl or aryl groups, etc., but also the much more diverse and numerous class of compounds in which one or more B atom in the cluster is replaced by another main-group element such as C, P or S, or by a wide range of metal atoms or coordinated metal groups. These will be considered in later sections.

6.4.2 Bonding and topology

The definitive structural chemistry of the boranes began in 1948 with the X-ray crystallographic determination of the structure of decaborane(14); this showed the presence of 4 bridging H atoms and an icosahedral fragment of 10 B atoms. This was rapidly followed in 1951 by the unequivocal demonstration of the H-bridged structure of diborane(6) and by the determination of the structure of pentaborane(9). Satisfactory theories of bonding in boranes date from the introduction of the concept of the 3-centre 2-electron B-H-B bond by H. C. Longuet-Higgins in 1949; he also extended the principle of 3-centre bonding and multicentre bonding to the higher boranes. These ideas have been extensively developed and

¹² G. J. LEIGH (ed.), *Nomenclature of Inorganic Chemistry: Recommendations 1990* (The IUPAC "Red Book"), Blackwell, Oxford, 1990, Chap. 11, pp. 207-37.

refined by W. N. Lipscomb and his group during the past four decades.⁽¹³⁾

In simple covalent bonding theory molecular orbitals (MOs) are formed by the linear combination of atomic orbitals (LCAO); for example, 2 AOs can combine to give 1 bonding and 1 antibonding MO and the orbital of lower energy will be occupied by a pair of electrons. This is a special case of a more general situation in which a number of AOs are combined together by the LCAO method to construct an equal number of MOs of differing energies, some of which will be bonding, some possibly nonbonding and some antibonding. In this way 2-centre, 3-centre, and multicentre orbitals can be envisaged. The three criteria that determine whether particular AOs can combine to form MOs are that the AOs must (a) be similar in energy, (b) have appreciable spatial overlap, and (c) have appropriate symmetry. In borane chemistry two types of 3-centre bond find considerable application: B–H–B bridge bonds (Fig. 6.12) and central 3-centre BBB bonds (Fig. 6.13). Open 3-centre B–B–B bonds are not now thought to occur in boranes and their anions though they are still useful in describing the bonding in carbaboranes and other heteroatom clusters (p. 194). The relation between the 3-centre bond formation for B–H–B, where the bond angle at H is $\sim 90^\circ$ and the 3-centre bond formation for approximately linear H bonds A–H \cdots B is given on pp. 63–4.

Localized 3-centre bond formalism can readily be used to rationalize the structure and bonding in most of the non-*closo*-boranes. This is illustrated for some typical *nido*- and *arachno*-boranes in the following plane-projection diagrams which use an obvious symbolism for normal 2-centre bonds: B–B \bigcirc — \bigcirc , B–H_t \bigcirc — \bullet , (t = terminal), central 3-centre bonds , and B–H_μ–B bridge bonds . It is particularly important

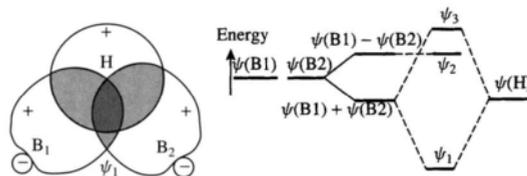


Figure 6.12 Formation of a bonding 3-centre B–H–B orbital ψ_1 from an sp^x hybrid orbital on each of B(1), B(2) and the H 1s orbital, $\psi(H)$. The 3 AOs have similar energy and appreciable spatial overlap, but only the combination $\psi(B1) + \psi(B2) + \psi(H)$ has the correct symmetry to combine linearly with $\psi(H)$.

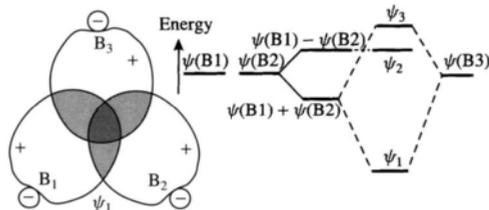
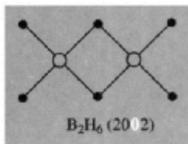


Figure 6.13 Formation of a bonding, central 3-centre bond ψ_1 and schematic representation of the relative energies of the 3 molecular orbitals ψ_1 , ψ_2 and ψ_3 .

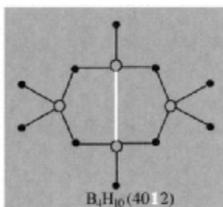
to realize that the latter two symbols each represent a single (3-centre) bond involving one pair of electrons. As each B atom has 3 valence electrons, and each B–H_t bond requires 1 electron from B and one from H, it follows that each B–H_t group can contribute the remaining 2 electrons on B towards the bonding of the cluster (including B–H–B bonds), and likewise each BH₂ group can contribute 1 electron for cluster bonding. The overall bonding is sometimes codified in a 4-digit number, the so-called *styx* number, where *s* is the number of B–H–B bonds, *t* is the number of 3-centre BBB bonds, *y* the number of 2-centre BB bonds, and *x* the number of BH₂ groups.⁽¹³⁾ Examples are on p. 159.

Electron counting and orbital bookkeeping can easily be checked in these diagrams: as each B has 4 valency orbitals (*s* + 3*p*) there should be 4 lines emanating from each open circle; likewise, as each B atom contributes 3 electrons in all and each H atom contributes 1 electron, the total

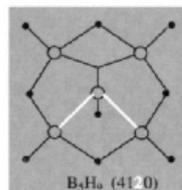
¹³ W. N. LIPSCOMB, Chap. 2 in ref. 9, pp. 30–78. W. N. LIPSCOMB, *Boron Hydrides*, Benjamin, New York, 1963, 275 pp. W. N. LIPSCOMB, Nobel Prize Lecture, *Science* **196**, 1047–55 (1977).



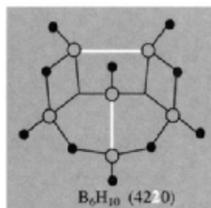
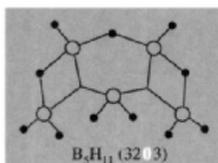
Each terminal BH_2 group and each (bridging) H_u contributes 1 electron to the bridging; these 4 electrons just fill the two B-H-B bonds.



Each of the 4 B and 4 H_u contribute 1 electron to the B-H-B bonds, i.e. 4 pairs of electrons for the 4 (3-centre) bonds. The 2 "hinge" BH_2 groups each have 1 remaining electron and 1 orbital which interact to give the 2-centre B-B bond.



In B_5H_9 the bonding can be thought of as involving the structure shown and 3 other equivalent structures in which successive pairs of adjacent basal B atoms are combined with the apex B in a 3-centre bond.

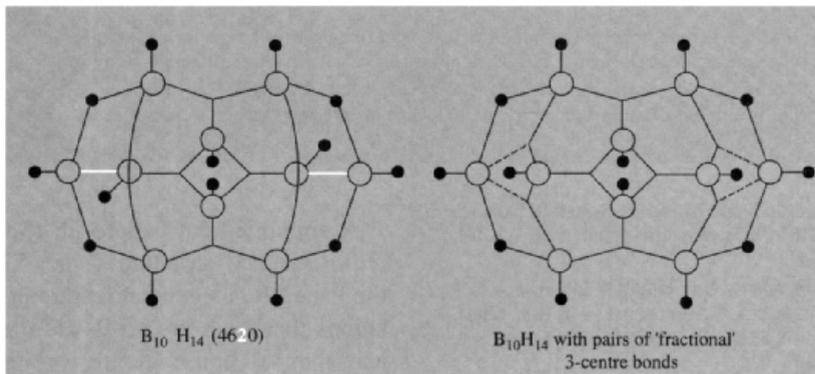


number of valence electrons for a borane of formula B_nH_m is $(3n + m)$ and the number of bonds shown in the structure should be just half this. It follows, too, that the number of electron-pair bonds in the molecule is n plus the sum of the individual *styx* numbers (e.g. 13 for B_5H_{11} , 14 for B_6H_{10}) and this constitutes a further check.[†] An appropriate number of additional electrons should be added for anionic species.

For *closo*-boranes and for the larger open-cluster boranes it becomes increasingly difficult to write a simple satisfactory localized orbital structure, and a full MO treatment is required. Intermediate cases, such as B_5H_9 , require several "resonance hybrids" in the localized orbital

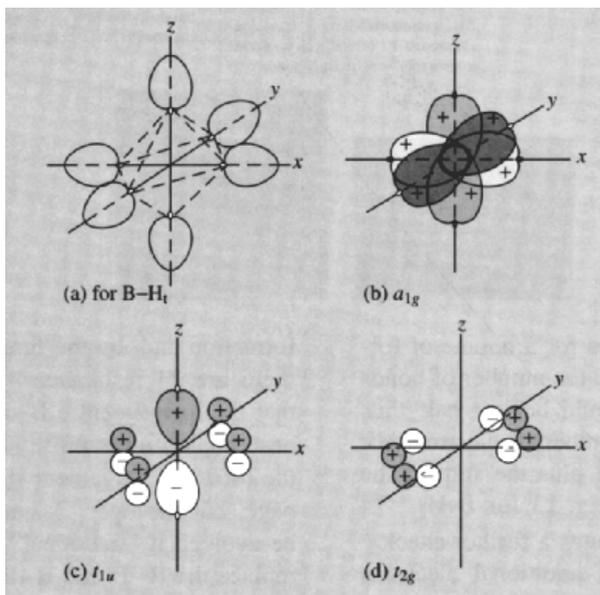
formation and, by the time $B_{10}H_{14}$ is considered there are 24 resonance hybrids, even assuming that no open 3-centre B-B-B bonds occur. The best single compromise structure in this case is the (4620) arrangement shown at the foot of the page, but the open 3-centre B-B-B bonds can be avoided if "fractional" central 3-centre bonds replace the B-B and B-B-B bonds in pairs:

[†] Further checks, which can readily be verified from the equations of balance, are (a) the number of atoms in a neutral borane molecule = $2(s + t + y + x)$, and (b) there are as many framework electrons as there are atoms in a neutral borane B_nH_m since each BH group supplies 2 electrons and each of the $(m - n)$ "extra" H atoms supplies 1 electron, making $n + m$ in all.



MO Description of Bonding in *closo*-B₆H₆²⁻

Closo B₆H₆²⁻ (structure 1) has a regular octahedral cluster of 6 B atoms surrounded by a larger octahedron of 6 radially disposed H atoms. Framework MOs for the B₆ cluster are constructed (LCAO) using the 2s, 2p_x, 2p_y, and 2p_z boron AOs. The symmetry of the octahedron suggests the use of sp hybrids directed radially outwards and inwards from each B along the cartesian axes (see figure) and 2 pure p orbitals at right angles to these (i.e. oriented tangentially to the B₆ octahedron). These sets of AOs are combined, with due regard to symmetry, to give 24 MOs as follows: the 24 AOs on the 6 B combine to give 24 MOs of which 7 (i.e. *n* + 1) are bonding framework MOs, 6 are used to form B-H_i bonds, and the remaining 11 are antibonding.



Symmetry of orbitals on the B₆ octahedron. (a) Six outward-pointing (sp) orbitals used for σ bonding to 6 H_i. (b) Six inward-pointing (sp) orbitals used to form the a_{1g} framework bonding molecular orbital. (c) Components for one of the t_{1u} framework bonding molecular orbitals — the other two molecular orbitals are in the *yz* and *zx* planes. (d) Components for one of the t_{2g} framework bonding molecular orbitals — the other two molecular orbitals are in the *yz* and *zx* planes.

The diagrams also indicate why neutral *closo*-boranes B_{*n*}H_{*n*+2} are unknown since the 2 anionic charges are effectively located in the low-lying inwardly directed a_{1g} orbital which has no overlap with protons outside the cluster (e.g. above the edges or faces of the B₆ octahedron). Replacement of the 6 H_i by 6 further B₆ builds up the basic three-dimensional network of hexaborides MB₆ (p. 150) just as replacement of the 4 H_i in CH₄ begins to build up the diamond lattice.

The diagrams, with minor modification, also describe the bonding in isoelectronic species such as *closo*-CB₅H₆⁻, 1,2-*closo*-C₂B₄H₆, 1,6-*closo*-C₂B₄H₆, etc. (pp. 181–2). Similar though more complex, diagrams can be derived for all *closo*-B_{*n*}H_{*n*+2}⁻ (*n* = 6–12); these have the common feature of a low lying a_{1g} orbital and *n* other framework bonding MOs; in each case, therefore (*n* + 1) pairs of electrons are required to fill these orbitals as indicated in Wade's rules (p. 161). It is a triumph for MO theory that the existence of B₆H₆²⁻ and B₁₂H₁₂²⁻ were predicted by H. C. Longuet-Higgins in 1954–5,⁽¹⁴⁾ a decade before B₆H₆²⁻ was first synthesized and some 5 y before the (accidental) preparation of B₁₀H₁₀²⁻ and B₁₂H₁₂²⁻ were reported.^(15,16)

¹⁴ H. C. LONGUET-HIGGINS and M. DE V. ROBERTS, *Proc. R. Soc. A*, **230**, 110–19 (1955); see also *idem ibid.* A, **224**, 336–47 (1954).

¹⁵ J. L. BOONE, *J. Am. Chem. Soc.* **86**, 5036 (1964).

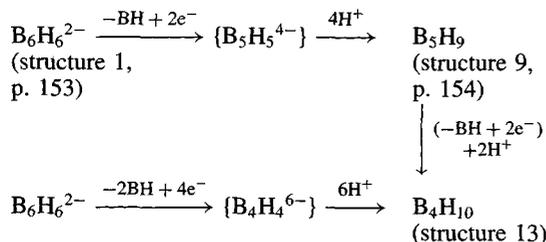
¹⁶ M. F. HAWTHORNE and A. R. PITTOCHELLI, *J. Am. Chem. Soc.* **81**, 5519 (and also 5833–4) (1959); *J. Am. Chem. Soc.* **82**, 3228–9 (1960).

A simplified MO approach to the bonding in *closo*-B₆H₆²⁻ (structure 1, p. 153) is shown in the Panel. It is a general feature of *closo*-B_{*n*}H_{*n*+2}⁻ anions that there are no B-H-B or BH₂ groups and the 4*n* boron atomic orbitals are always

distributed as follows:

- n in the $n(\text{B}-\text{H}_t)$ bonding orbitals
- $(n + 1)$ in framework bonding MOs
- $(2n - 1)$ in nonbonding and antibonding framework MOs

As each B atom contributes 1 electron to its $\text{B}-\text{H}_t$ bond and 2 electrons to the framework MOs, the $(n + 1)$ framework bonding MOs are just filled by the $2n$ electrons from $n\text{B}$ atoms and the 2 electrons from the anionic charge. Further, it is possible (conceptually) to remove a BH_t group and replace it by 2 electrons to compensate for the 2 electrons contributed by the BH_t group to the MOs. Electroneutrality can then be achieved by adding the appropriate number of protons; this does not alter the number of electrons in the system and hence all bonding MOs remain just filled.



The structural interrelationship of all the various *closo*-, *nido*- and *arachno*-boranes thus becomes evident; a further example is shown at the foot of the page.

These relationships were codified in 1971 by K. Wade in a set of rules which have been

extremely helpful not only in rationalizing known structures, but also in suggesting the probable structures of new species.⁽¹⁷⁾ Wade's rules can be stated in extended form as follows:

closo-borane anions have the formula $\text{B}_n\text{H}_n^{2-}$; the B atoms occupy all n corners of an n -cornered triangulated polyhedron, and the structures require $(n + 1)$ pairs of framework bonding electrons;

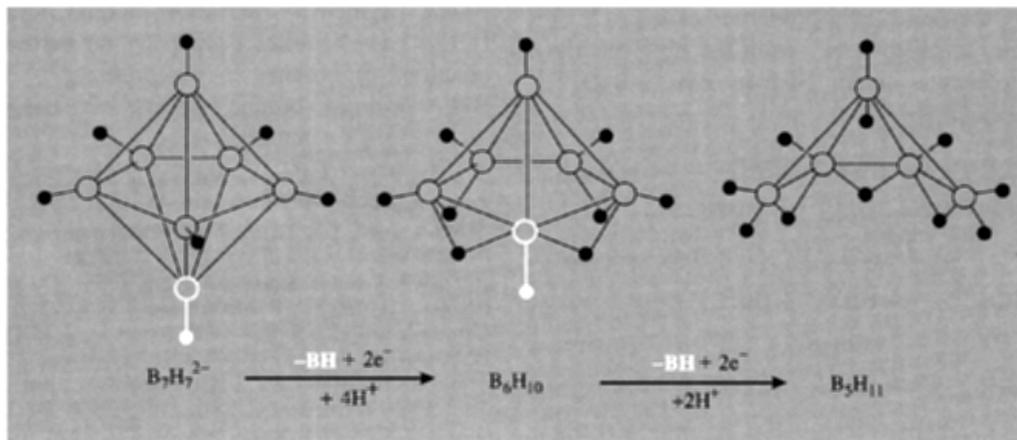
nido-boranes have the formula B_nH_{n+4} with B atoms at n corners of an $(n + 1)$ cornered polyhedron; they require $(n + 2)$ pairs of framework-bonding electrons;

arachno-boranes: B_nH_{n+6} , n corners of an $(n + 2)$ cornered polyhedron, requiring $(n + 3)$ pairs of framework-bonding electrons;

hypho-boranes: B_nH_{n+8} : n corners of an $(n + 3)$ cornered polyhedron, requiring $(n + 4)$ pairs of framework-bonding electrons.

The rules can readily be extended to isoelectronic anions and carboranes ($\text{BH} \equiv \text{B}^- \equiv \text{C}$) and also to metalloboranes (p. 174), metalocarbaboranes (p. 194) and even to metal clusters themselves, though they become less reliable the further one moves away from boron in atomic size, ionization energy, electronegativity, etc.

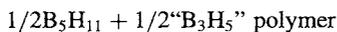
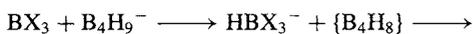
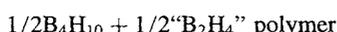
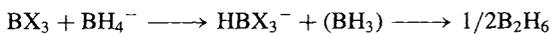
¹⁷ K. WADE, *Adv. Inorg. Chem. Radiochem.* **18**, 1-66 (1976).



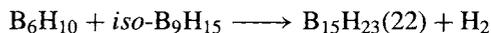
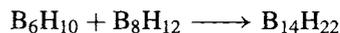
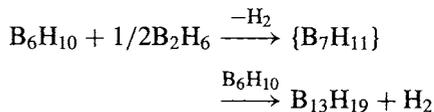
More sophisticated and refined calculations lead to orbital populations and electron charge distributions within the borane molecules and to predictions concerning the sites of electrophilic and nucleophilic attack. In general, the highest electron charge density (and the preferred site of electrophilic attack) occurs at apical B atoms which are furthest removed from open faces; conversely the lowest electron charge density (and the preferred site of nucleophilic attack) occurs on B atoms involved in B-H-B bonding. The consistency of this correlation implies that the electron distribution in the activated complex formed during reaction must follow a similar sequence to that in the ground state. Bridge H atoms tend to be more acidic than terminal H atoms and are the ones first lost during the formation of anions in acid-base reactions.

6.4.3 Preparation and properties of boranes

Earlier methods for preparing the boron hydrides were tedious and inefficient⁽¹⁰⁾ but have now been superseded by modern high-yield routes.^(11,18) The first great advance was to replace the reaction between protonic hydrogen and negative boride clusters by the reaction of hydridic species such as LiH or LiAlH₄ with boron halides or alkoxides which contain more positive boron centres. Subsequently, S. G. Shore and his group developed a systematic synthesis by using the Lewis acid properties of BX₃ (X = F, Cl, Br) to abstract H⁻ from the now readily available borane anions such as BH₄⁻, B₃H₈⁻ etc. For example:⁽¹⁹⁾



The perception by R. Schaeffer that *nido*-B₆H₁₀ (structure 10, pp. 154, 159) could act as a Lewis base towards reactive (vacant orbital) borane radicals has led to several new *conjuncto*-boranes, e.g.:⁽²⁰⁾



A useful route to B-B bonded *conjuncto*-boranes involves the photolysis of parent *nido*-boranes. Thus, ultraviolet irradiation of B₅H₉ (9) yields the three isomers of *conjuncto*-B₁₀H₁₆ (24) and similar treatment of B₁₀H₁₄ (11) yields a mixture of 1,2'- and 2,2'-(B₁₀H₁₃)₂ (25a). High-yield catalytic routes to specific B-B coupled *conjuncto*-boranes (using PtBr₂) have been developed by L. G. Sneddon and his group⁽²¹⁾, e.g. B₅H₉ gave 1,2'-(B₅H₈)₂ (24), B₄H₁₀ gave 1,1'-(B₄H₉)₂ (i.e. *conjuncto*-B₈H₁₈, of which the 2,2'-isomer is shown in 23), and a mixture of B₄H₁₀ and B₅H₉ yielded 1,2'-(B₄H₉)(B₅H₈), i.e. *conjuncto*-B₉H₁₇. When applied to a mixture of B₂H₆ and B₅H₉ in decane at room temperature, the method gave the first authenticated neutral heptaborane, B₇H₁₃, in which one of the bridging H atoms in diborane has been replaced by a basal B atom of the B₅ unit, i.e. 1,2-μ(2-B₅H₈)B₂H₅.

The synthesis of *closo*-borane dianions B_nH_n²⁻ (1-7) relies principally on thermolysis reactions of boranes in the presence of either BH₄⁻ or amino-borane adducts.^(9,11) The yields

¹⁸ R. W. PARRY and M. K. WALTER, in W. L. JOLLY (ed.), *Preparative Inorganic Reactions* **5**, 45-102 (1968).

¹⁹ M. A. TOFT, J. B. LEACH, F. L. HIMPSL and S. G. SHORE *Inorg. Chem.* **21**, 1952-7 (1982).

²⁰ J. RATHKE and R. SCHAEFFER, *Inorg. Chem.* **13**, 3008-11 (1974); J. RATHKE, D. C. MOODY and R. SCHAEFFER, *Inorg. Chem.* **13**, 3040-2 (1974); J. C. HUFFMAN, D. C. MOODY and R. SCHAEFFER, *Inorg. Chem.* **20**, 741-5 (1981).

²¹ E. W. CORCORAN and L. G. SNEDDON, *J. Am. Chem. Soc.* **106**, 7793-7800 (1984); **107**, 7446-50 (1985); L. G. SNEDDON, *Pure Appl. Chem.* **59**, 837-46 (1987).

Table 6.2 Properties of some boranes

Nido-boranes				Arachno-boranes			
Compound	mp	bp	$\Delta H_f^\circ/\text{kJ mol}^{-1}$	Compound	mp	bp	$\Delta H_f^\circ/\text{kJ mol}^{-1}$
B ₂ H ₆	-164.9°	-92.6°	36	B ₄ H ₁₀	-120°	18°	58
B ₅ H ₉	-46.8°	60.0°	54	B ₅ H ₁₁	-122°	65°	67 (or 93)
B ₆ H ₁₀	-62.3°	108°	71	B ₆ H ₁₂	-82.3°	~85° (extrap)	111
B ₈ H ₁₂	Decomp	above -35°	—	B ₈ H ₁₄	Decomp	above -30°	—
B ₁₀ H ₁₄	99.5°	213°	32	n-B ₉ H ₁₅	2.6°	28°/0.8 mmHg	—

are very sensitive to conditions (solvent, pressure and temperature) and mixtures are often obtained. A more recent variant is the thermolysis of Et₄NBH₄ at 175–190°C for about 12 hours, which yields a mixture of *closo*-B₉H₉²⁻, B₁₀H₁₀²⁻, B₁₂H₁₂²⁻ and *nido*-B₁₁H₁₄⁻. The smaller *closo*-dianions ($n = 6, 7, 8$) can then be obtained (in smaller yield) by the oxidative (air) degradation of B₉H₉²⁻ salts in the presence of EtOH, thf or 1,2-dimethoxyethane.

Boranes are colourless, diamagnetic, molecular compounds of moderate to low thermal stability. The lower members are gases at room temperature but with increasing molecular weight they become volatile liquids or solids (Table 6.2); bps are approximately the same as those of hydrocarbons of similar molecular weight. The boranes are all endothermic and their free energies of formation ΔG_f° are also positive; however, their thermodynamic instability results from the exceptionally strong interatomic bonds in both elemental B and H₂ rather than any weakness of the B–H bond. In this the boranes resemble the hydrocarbons. Likewise, the remarkable chemical reactivity of the boranes and their ready thermolytic interconversion (p. 164) should not be taken to imply that the bonds holding the boranes together are inherently weak. Indeed, the opposite is the case; the B–B and B–H bonds are among the strongest 2-electron bonds known, and the great reactivity of the boranes is to be sought rather in the availability of alternative structures and vacant orbitals of similar energies. Some comparative data are in Table 6.3⁽²²⁾ which

shows that the bond enthalpies E for the 2-centre B–B bond in boranes and for the C–C bond in C₂H₆ are essentially identical and that the value for the 3-centre 2-electron BBB bond in boranes is very similar to that for the B–C bond in BMe₃.

Table 6.3 Some enthalpies of atomization (ΔH_f° , 298 K) and comparative bond-enthalpy contributions, E

$\Delta H_f^\circ/\text{kJ mol}^{-1}$	$E/\text{kJ mol}^{-1}$	$E/\text{kJ mol}^{-1}$
H(g) 1/2 × 436	B–B (2c,2e) 332	C–C 331
B(g) 566	BBB(3c,2e) 380	B–C 372
C(g) 356	B–H (2c,2e) 381	C–H 416
	BHB(3c,2e) 441	H–H 436

Boranes are extremely reactive compounds and several are spontaneously flammable in air. *Arachno*-boranes tend to be more reactive (and less stable to thermal decomposition) than *nido*-boranes and reactivity also diminishes with increasing mol wt. *Closo*-borane anions are exceptionally stable and their general chemical behaviour has suggested the term “three-dimensional aromaticity”.

Boron hydrides have proved to be extremely versatile chemical reagents but the very diversity of their reactions makes a general classification unduly cumbersome. For this reason, the range of behaviour will be illustrated by typical examples taken from the chemistry of the boranes and their anions, arranged approximately according to the size of the borane cluster being discussed. Nearly all boranes are highly toxic when inhaled or absorbed through the skin though they can be safely and conveniently handled with relatively minor precautions.

²²N. N. GREENWOOD and R. GREATREX, *Pure Appl. Chem.* **59**, 857–68 (1987).