

Boranes

Boranes are compounds composed solely of boron and hydrogen (and sometimes a cation) and may be neutral or anionic. They have considerable significance in the development of the understanding of unusual bonding modes.

History: The chemistry of the boranes was first studied systematically by Alfred Stock and his research group beginning in 1912 and continuing for almost 25 years. His initial work involved the reaction of acids with magnesium boride, although better routes have been developed since then. Because these compounds are exceedingly air-sensitive (they instantaneously burn in air) he developed the glass vacuum line and techniques for using it. As much of the inorganic chemistry done today involves oxygen and moisture sensitive compounds this development permitted advances in a wide range of fields beyond boranes. Another giant in the field of boranes is W.N. Lipscomb of Harvard Univ. whose work on the theory of bonding within boranes (*vide infra*) led to his being awarded the Nobel Prize in Chemistry in 1976. Furthermore, H.C. Brown (Purdue) shared the 1979 Nobel prize for synthetic work in organic chemistry utilizing boranes.

Nomenclature: Boranes are named as follows:

- a) The Latin prefixes mono-, di-, tri-, etc. are used before "borane" to indicate the number of boron atoms in the compound.
- b) Immediately following the "e" in "borane" the number of hydrogen atoms is placed in parentheses using Arabic numerals.

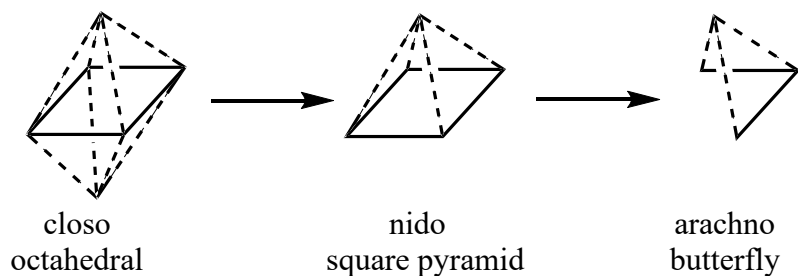
Example: B_5H_{11} is pentaborane(11).

Structure: Boranes fall into 6 structure categories, the 3 most important of which are:

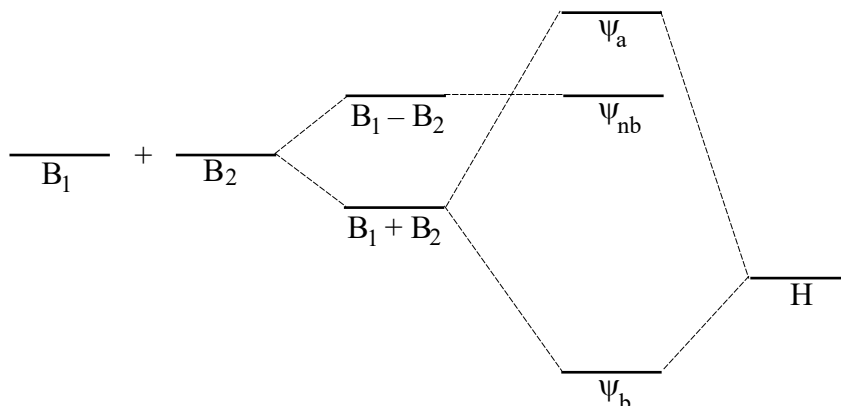
- a) *closo* - B_nH_{n+2} b) *nido* - B_nH_{n+4} c) *arachno* - B_nH_{n+6}

These are prefixes that can be given to the borane designation above. However they are not necessary because each structure type has only one general formula, thus the formula gives the structure.

The boron atoms will form a shape by occupying vertices on a polyhedron (e.g. for 4 B atoms the polyhedron can be a tetrahedron), whether or not the boron atoms are actually bound to each other. This arrangement is frequently called a "cage." *Closo*- refers to the most symmetrical possible arrangement, a closed polyhedron (e.g. 6 B atoms form an octahedron, see figure below). *Nido*- comes from the next higher *closo*- polyhedron with the most highly connected boron vertex removed (e.g. for 5 B atoms, an octahedron less any one vertex to yield a square pyramid). *Arachno*- comes from the next higher *nido*- structure with the most highly connected boron vertex on the open face removed (e.g. for 4 B atoms, a square pyramid less any basal vertex to yield a butterfly structure). The words *closo*-, *nido*-, and *arachno*- are derived from words meaning "closed" (Greek), "nest" (Latin), and "spider's web" (Greek). A large number of examples are shown on p. 799 of Huheey, Keiter, and Keiter.



In this bonding arrangement there are 2 boron sp^3 hybrids overlapping 1 hydrogen 1s orbital.



$$\Psi_b = \frac{1}{2}\psi_{B1} + \frac{1}{2}\phi_{B2} + \frac{1}{\sqrt{2}}\phi_H$$

$$\Psi_{nb} = \frac{1}{2}\phi_{B1} - \frac{1}{2}\phi_{B2}$$

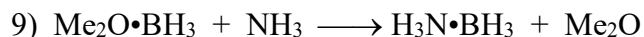
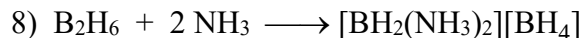
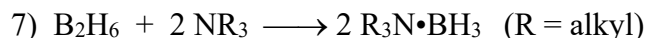
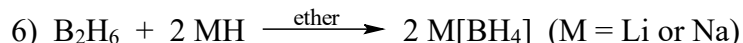
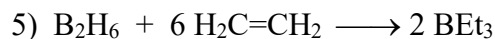
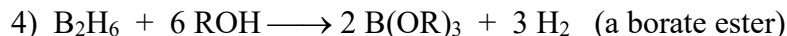
$$\Psi_a = \frac{1}{2}\phi_{B1} + \frac{1}{2}\phi_{B2} - \frac{1}{\sqrt{2}}\phi_H$$

Reactions of Diborane

Diborane, like all boranes, is thermodynamically unstable with respect to its component elements. They owe their existence to kinetic factors. That is, in an anaerobic, anhydrous environment, no pathway for decomposition exists with an accessible energy barrier at room temperature.



Note: This is a very exothermic reaction, $\Delta H \cong 2100 \text{ kJ/mol}$ compared with $\Delta H \cong 1000 \text{ kJ/mol}$ for burning ethane. This reaction also begins on contact with oxygen, as is the case for all boranes.



The last 3 reactions illustrate an interesting feature of diborane chemistry. Soft Lewis bases induce symmetrical cleavage of diborane (Figure 1), while hard Lewis bases induce asymmetrical cleavage (Figure 2).

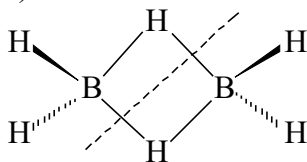


Figure 1

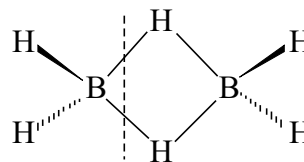


Figure 2

