

Greenwood & Earnshaw

2nd Edition

Chapter 6

Boron

Elemental Boron

➤ Many complex structures, little tendency to form B=B or B=C, strong affinity for oxygen, fluorine. Strong resemblance to silicon. Unreactive to air in bulk, but unoxidized powders pyrophoric.

➤ Four valence orbitals but only three valence electrons. Adept at multi-center bonding, coordination numbers of 1-8 known. Catenates extensively by two- and three-center bonding and multi-center bonding.

➤ Reacts with oxygen, nitrogen, carbon at high temperatures producing intractable mixtures.

Boron Rich Borides - Cubic MB₆

➤ Group 1 metals – Borides are insulators, the metal electrons are localized in the B₆ octahedra.

➤ Group 2 metals – Borides are semi-conductors, B₆ octahedra are just satisfied.

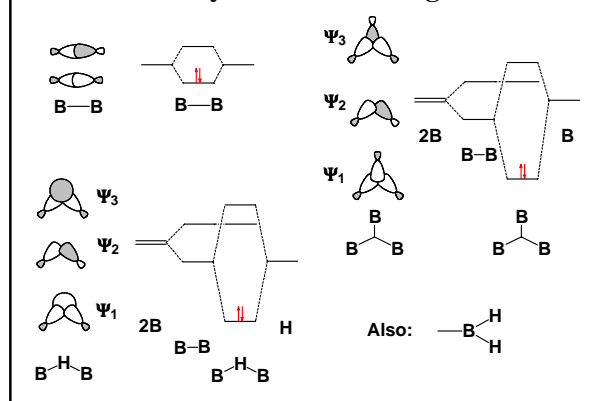
➤ Group 3, lanthanide & early transition metals are metallic conductors, additional metal electrons go into delocalized metallic bonding.

➤ The later, smaller lanthanide metals (Ho, Er, Tm, Lu) are too small for the 24-coordinate metal site and form the tetragonal MB₄, chains of B₆ – B₂.

The Boron Hydrides

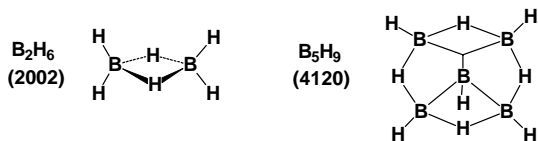
- *closo* – Closed B_n “deltahedra” – $B_nH_n^{2-}$
- *nido* – “nest”, *closo* minus one apical boron, B_nH_{n+4} , $B_nH_{n+3}^-$, $B_nH_{n+2}^{2-}$
- *arachno* – “spider web”, *closo* minus a B-B, B_nH_{n+6} , $B_nH_{n+5}^-$, $B_nH_{n+4}^{2-}$
- *hypho* – *closo* minus a B_3 deltahedra, rare. B_nH_{n+8} , examples B_8H_{16} , $B_{10}H_{18}$
- *conjuncto* – B-B bonded combinations of the above structures, same or mixed.

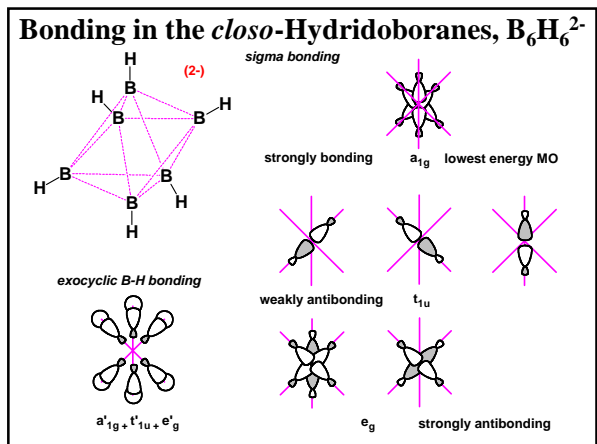
The Boron Hydrides – Bonding Elements

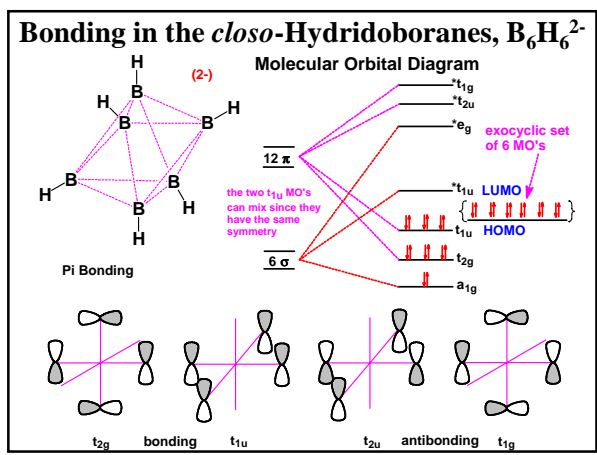


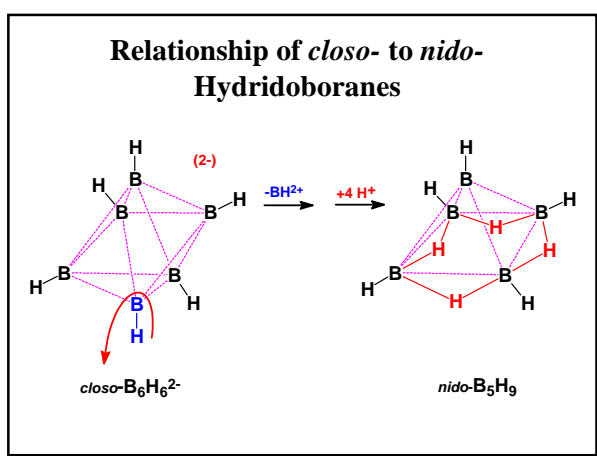
Bonding Topology – The STYX Numbers

- **S** – The number of B-H-B 3c-2e bonds.
- **T** – The number of closed B_3 3c-2e bonds.
- **Y** – The number of B-B 2c-2e bonds.
- **X** – The number of BH_2 groups; 2 2c-2e bonds.

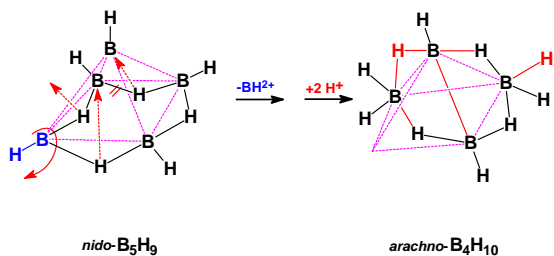




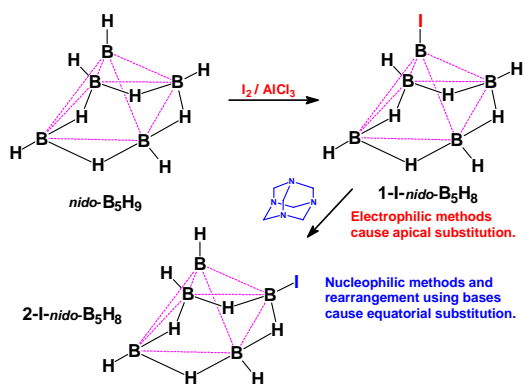




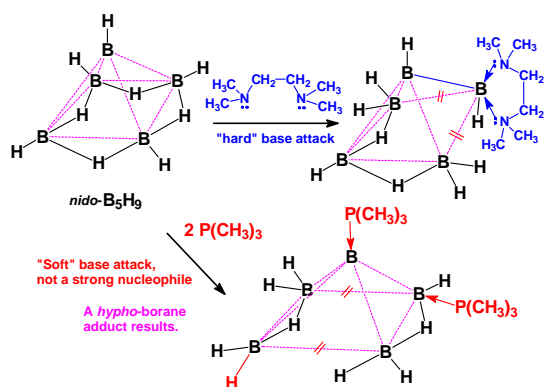
Relationship of *nido*- to *arachno*-Hydridoboranes



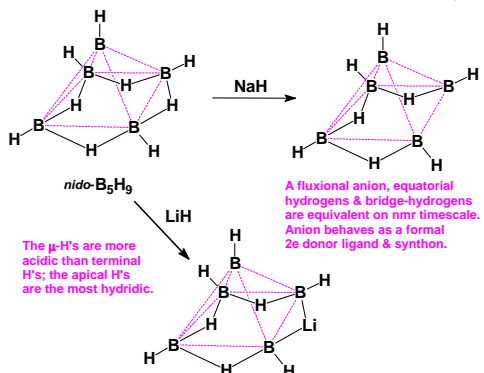
Chemistry of Pentaborane-9; *nido*- B_5H_9



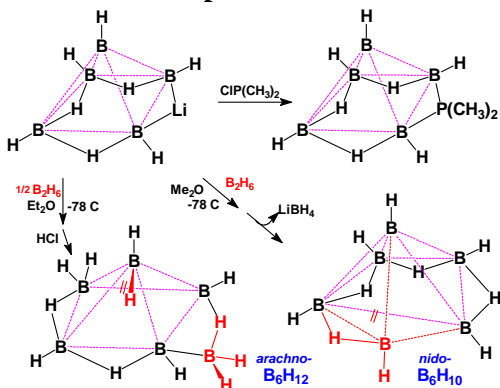
Chemistry of Pentaborane-9; *nido*- B_5H_9



Chemistry of Pentaborane-9; *nido*-B₅H₉



Cluster Expansion Reactions



Boron Halides

➤ BF₃, BCl₃, BBr₃, BI₃ are all monomeric. Mixtures will scramble halogens by bridging intermediates.

➤ BX₄⁻ will not scramble unless BX₃ is present.

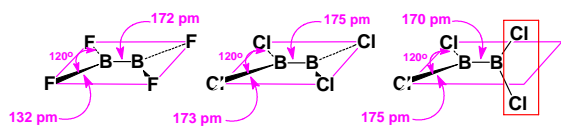
➤ B-F bond is much shorter than the single bond covalent radii predict. Dative π delocalization of the fluorine lone pairs to the vacant p orbital of boron. Effect is much reduced for Cl, Br, and I.

➤ Dative π bonds occur for oxygen and nitrogen.

➤ BX₃, X = halogen are "hard" acids. BH₃ is a "soft" acid forming stronger adducts with P, As, S...

Boron Subhalides

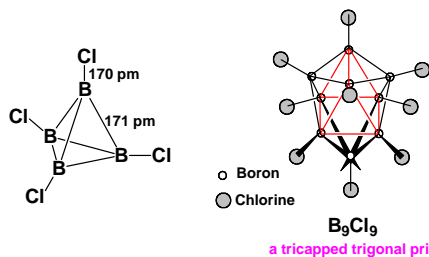
➤ B_2X_4 are planar in the solid state, only B_2F_4 remains planar in the gas phase. The formation of an “extended π system” is more important than *steric* effects for the small F.



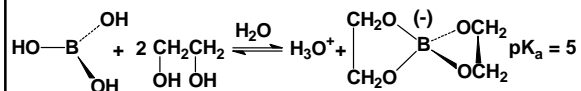
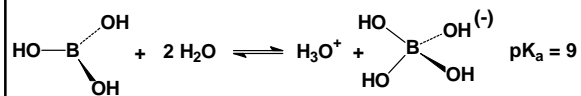
Boron Subhalides – Clusters

➤ B_4Cl_4 – Regular tetrahedron;

➤ B_nX_n ; n = 8-12 X = Cl; n = 7-10 X = Br. All are *closo*- and hyper electron deficient.

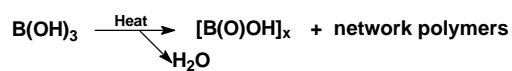


Boron - Oxygen – Boric Acid – A Lewis Acid

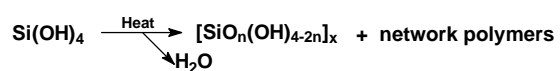


A chelating alcohol, glycol, or sugar can increase the acidity by 10⁴.

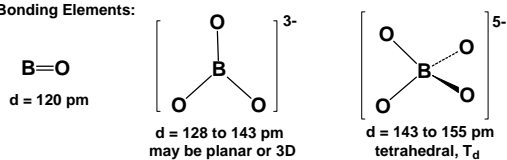
Boron – Oxygen : Borates & Silicates



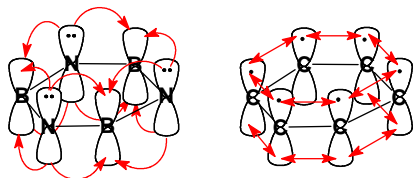
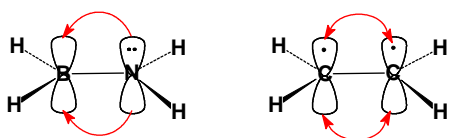
Compare with:



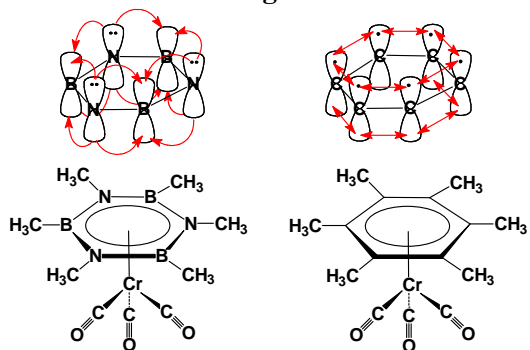
Bonding Elements:



Aminoboranes – Alkene Mimics



Borazine Organometallics



Crystal structures are quite similar, but the borazine complex is slightly puckered in solution. The hexaethylborazine shows puckering in the crystal.
