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.**

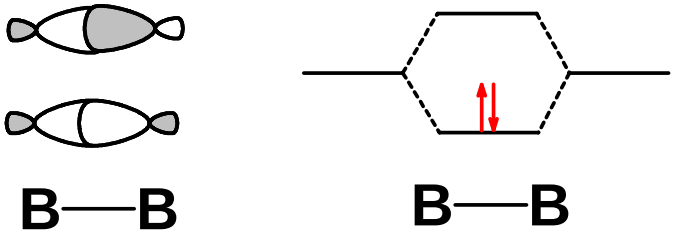
Boron Rich Borides - Cubic MB_6

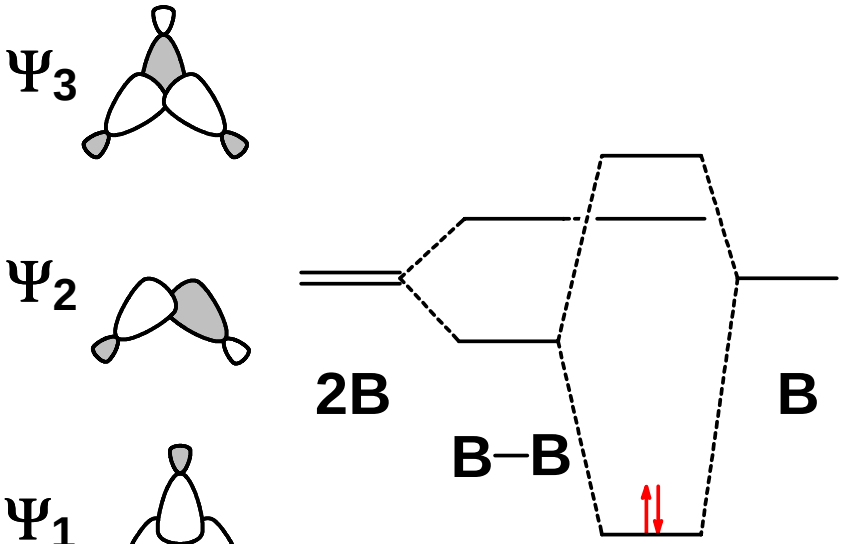
- **Group 1 metals – Borides are insulators, the metal electrons are localized in the B_6 octahedra.**
- **Group 2 metals – Borides are semi-conductors, B_6 octahedra are just satisfied.**
- **Group 3, lanthanide & early transition metals are metallic conductors, additional metal electrons go into delocalized metallic bonding.**
- **The later, smaller lanthanide metals (Ho, Er, Tm, Lu) are too small for the 24-coordinate metal site and form the tetragonal MB_4, chains of $B_6 – B_2$.**

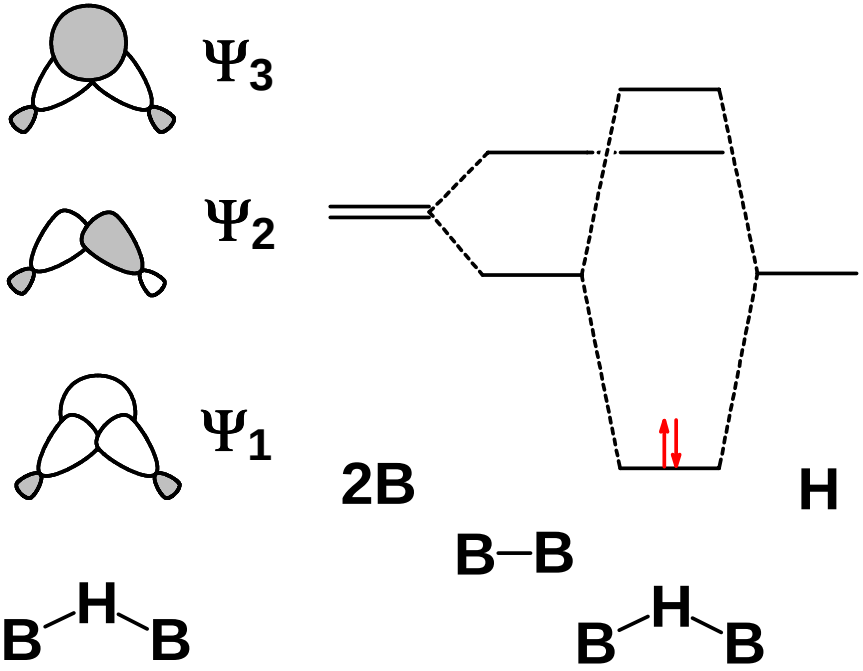
The Boron Hydrides

- ***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







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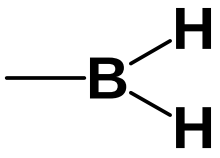
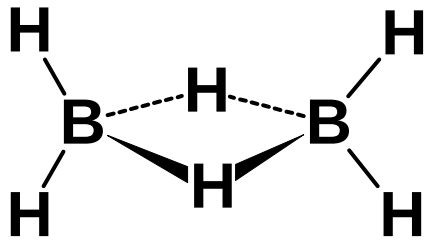


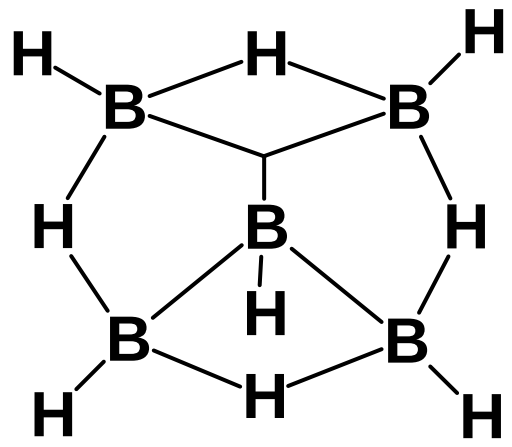
Bonding Topology – The STYX Numbers

- **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.**

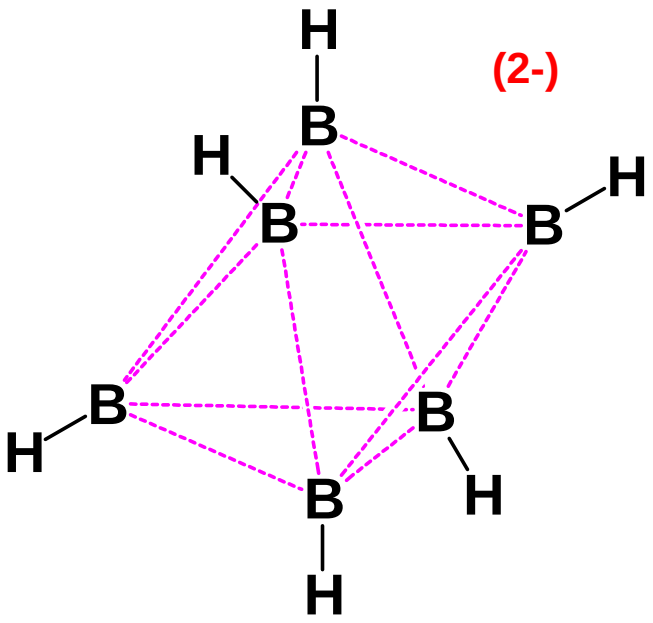
B_2H_6
(2002)



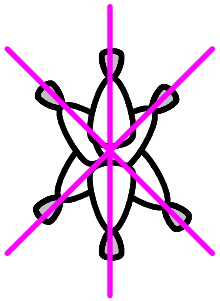
B_5H_9
(4120)



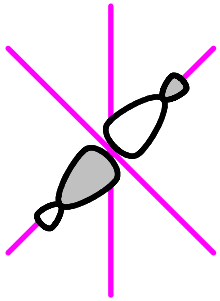
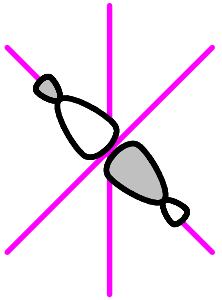
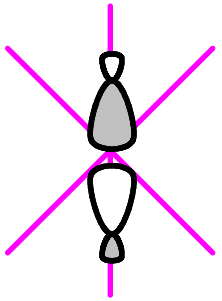
Bonding in the *closo*-Hydridoboranes, $B_6H_6^{2-}$



sigma bonding

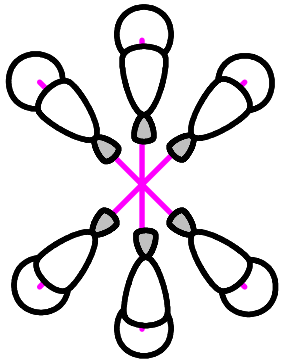


strongly bonding a_{1g} lowest energy MO

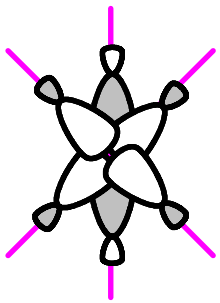
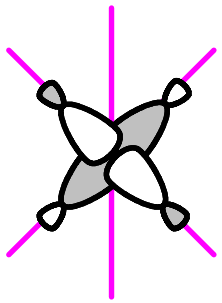




weakly antibonding t_{1u}

exocyclic B-H bonding

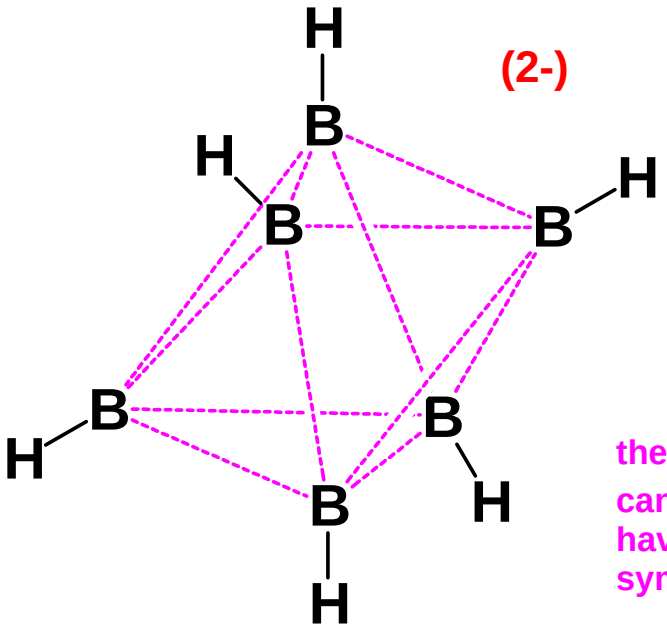


$a'_{1g} + t'_{1u} + e'_g$

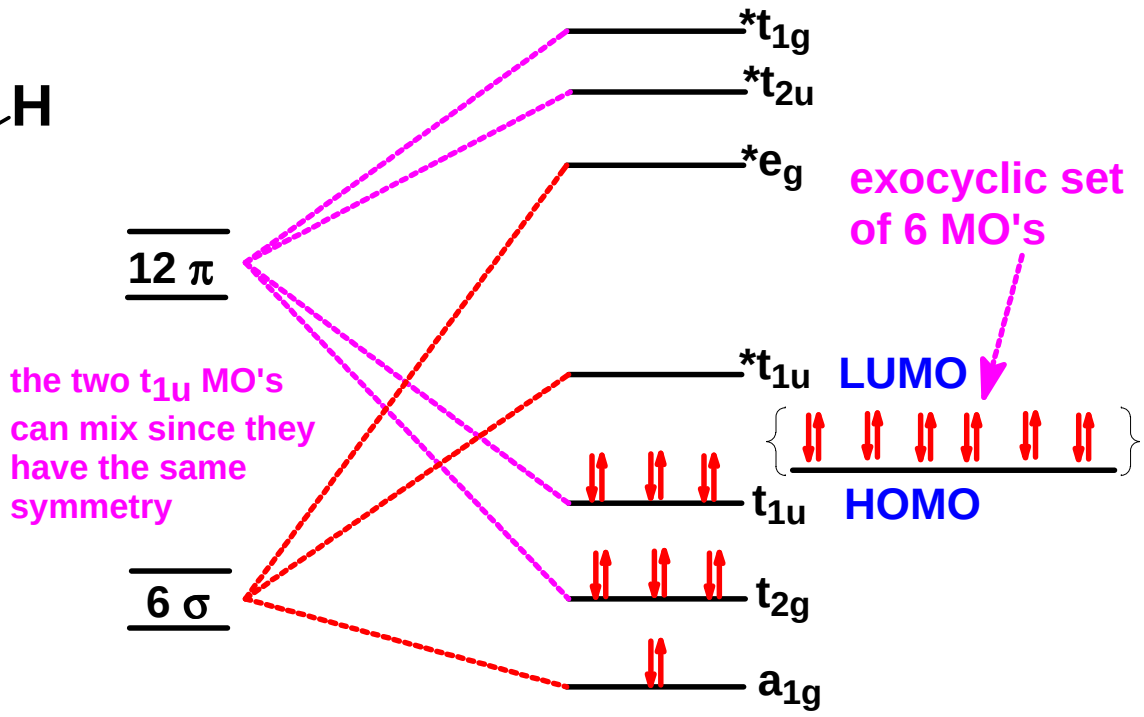
e_g strongly antibonding

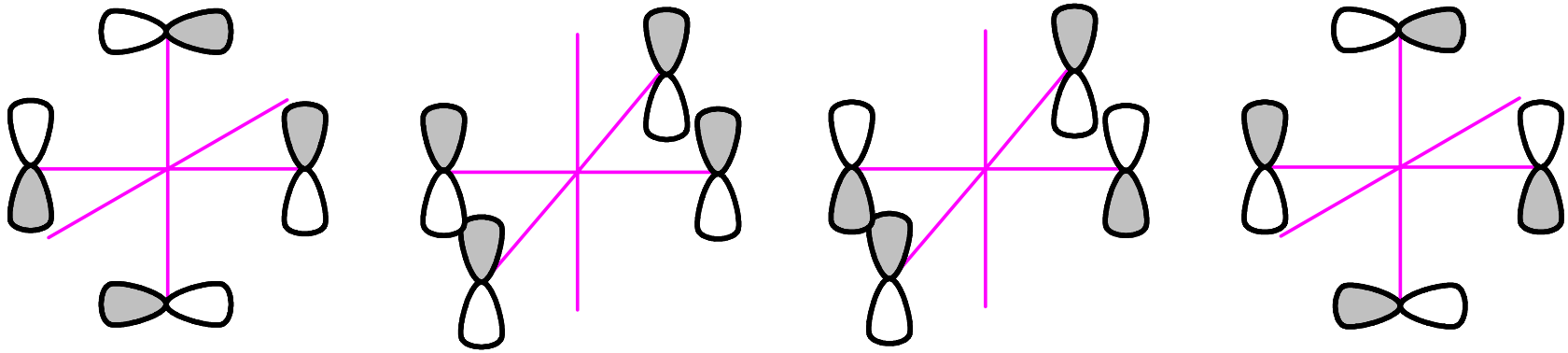
Bonding in the *closo*-Hydridoboranes, $B_6H_6^{2-}$



Pi Bonding

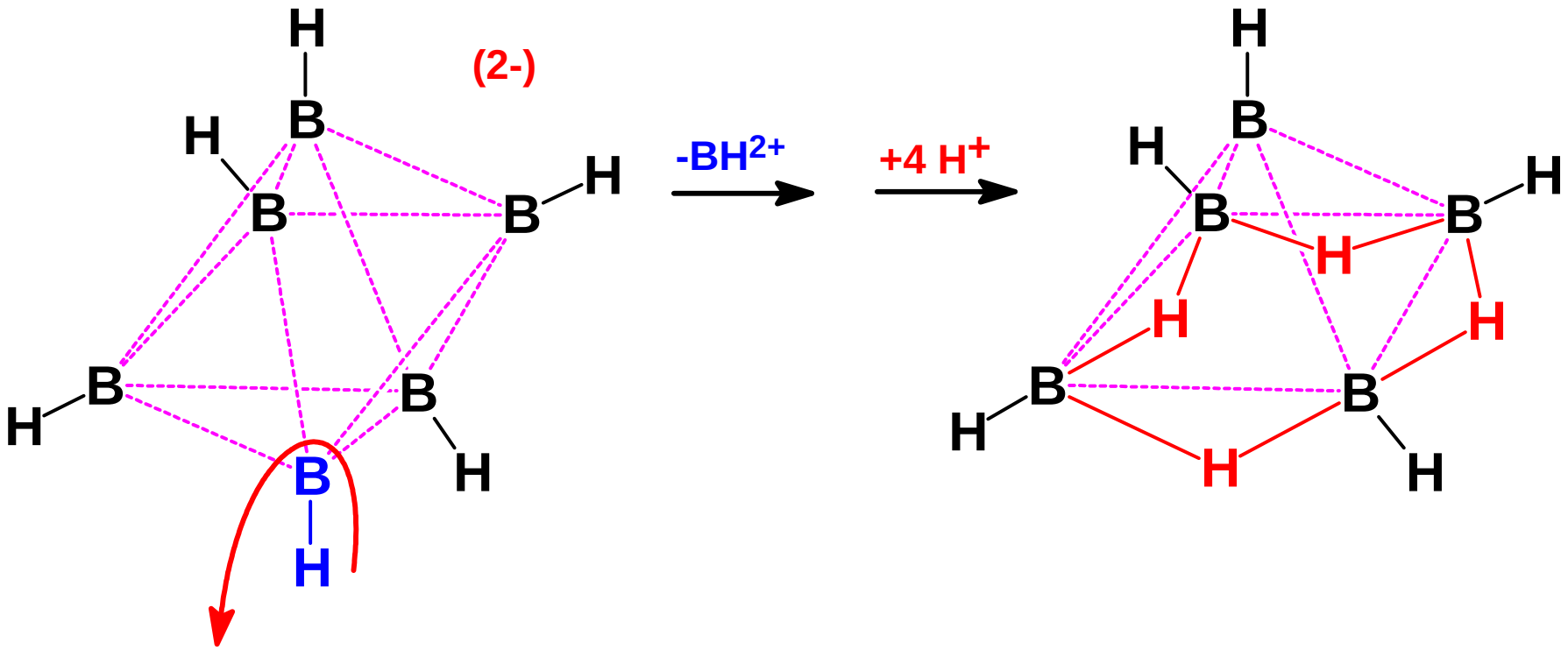
Molecular Orbital Diagram





t_{2g} bonding t_{1u} t_{2u} antibonding t_{1g}

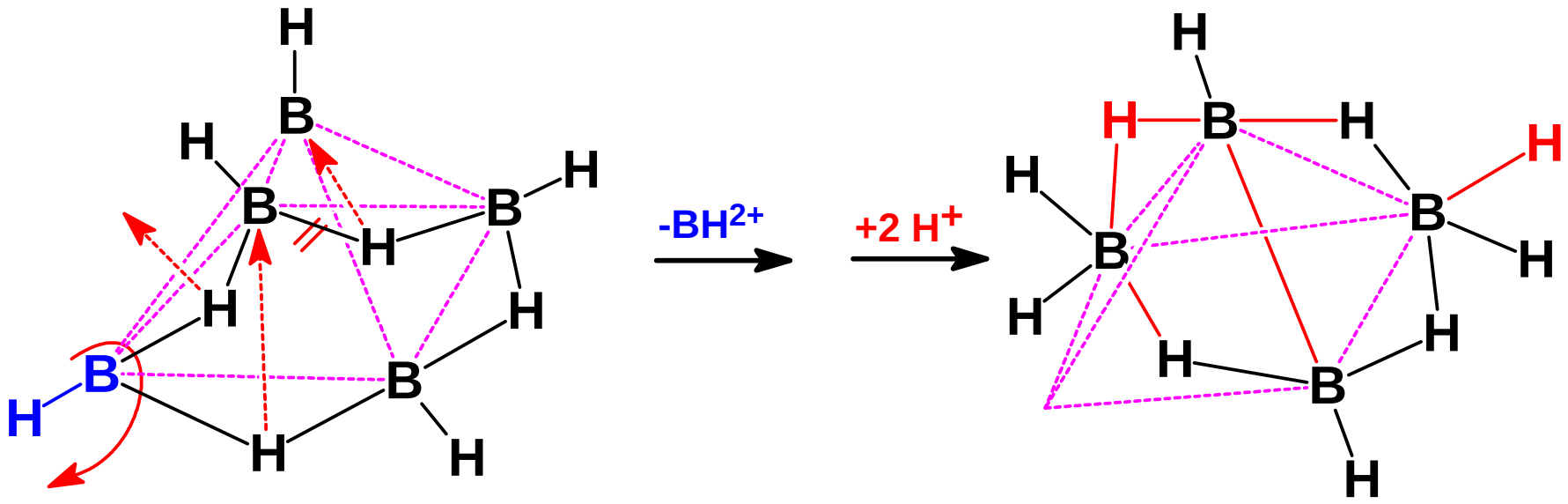
Relationship of *closo*- to *nido*-Hydridoboranes



closo-$B_6H_6^{2-}$

nido-B_5H_9

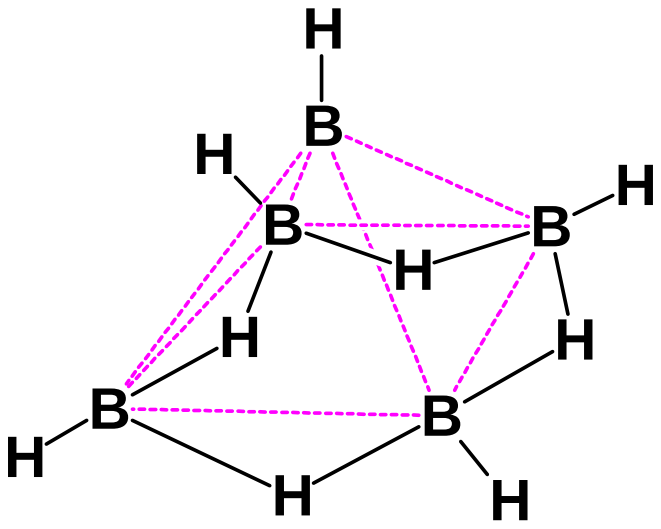
Relationship of *nido*- to *arachno*- Hydridoboranes



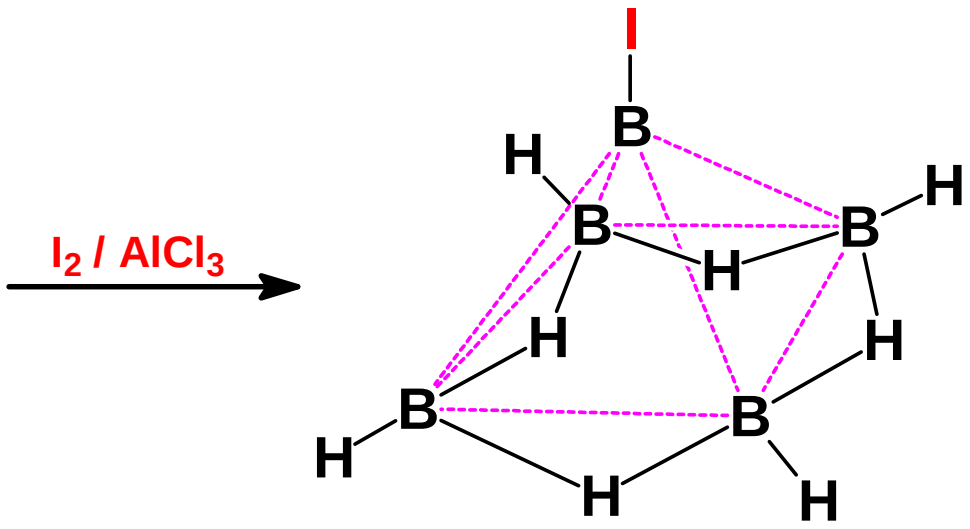
nido-B_5H_9

arachno-B_4H_{10}

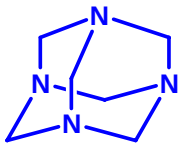
Chemistry of Pentaborane-9; *nido*-B_5H_9



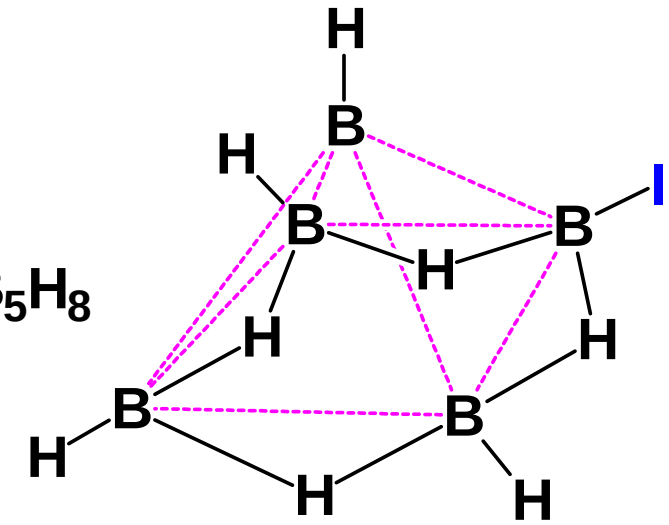
nido-B_5H_9



1-I-*nido*-B_5H_8



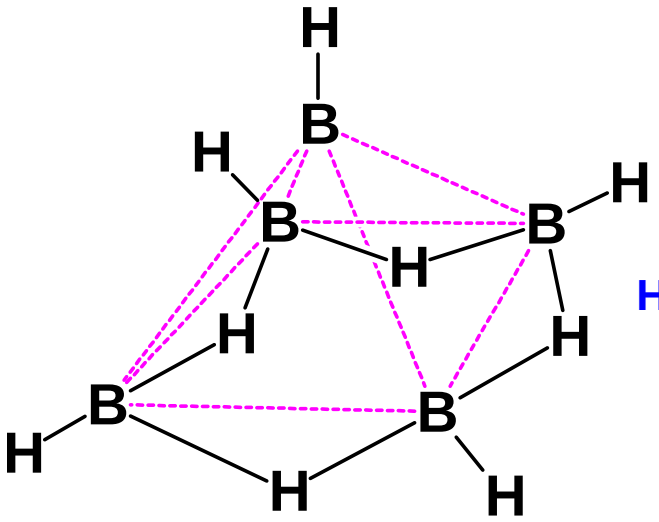
Electrophilic methods cause apical substitution.



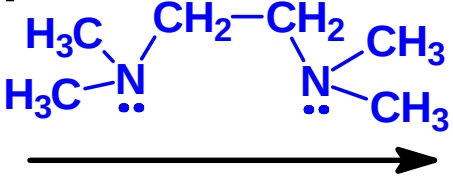
2-I-*nido*-B_5H_8

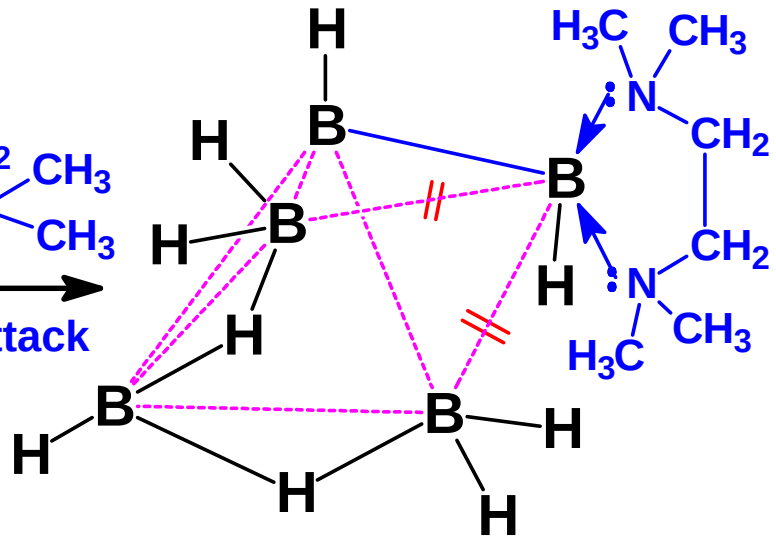
Nucleophilic methods and rearrangement using bases cause equatorial substitution.

Chemistry of Pentaborane-9; *nido*-B_5H_9



nido-B_5H_9

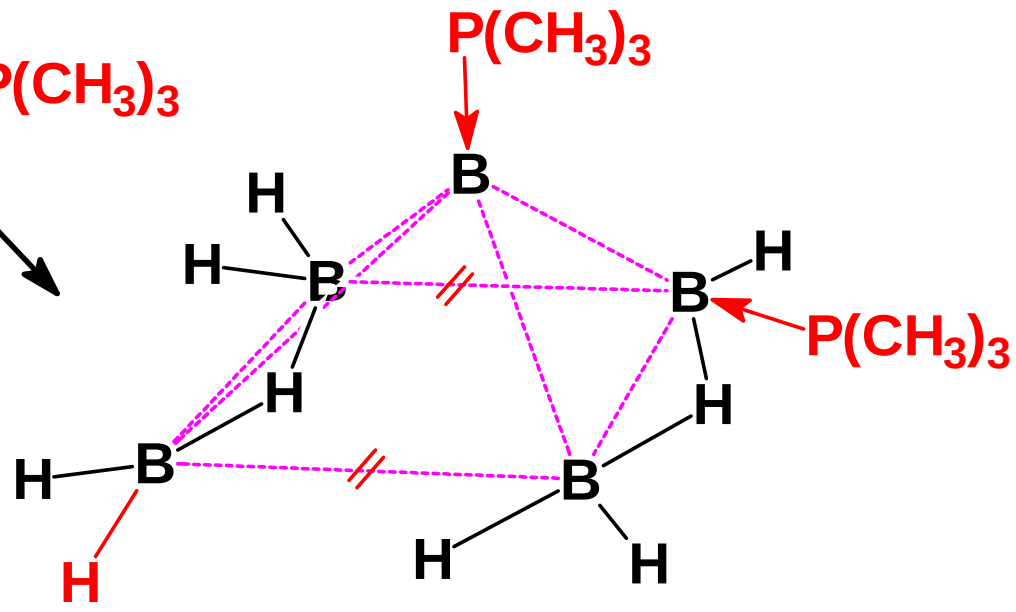




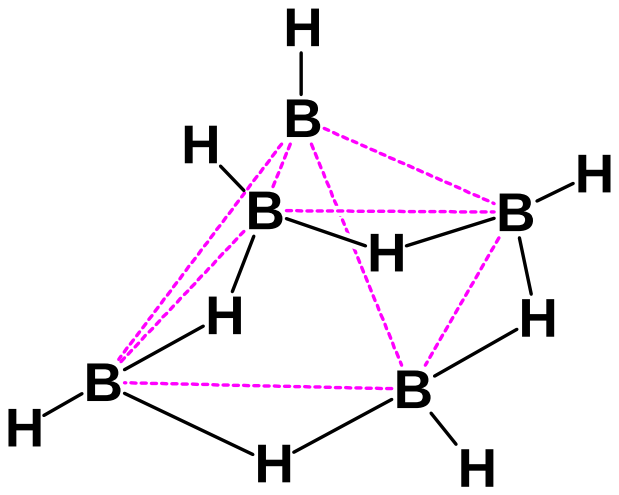
"Soft" base attack,
not a strong nucleophile

2 $P(CH_3)_3$

A *hypho*-borane
adduct results.

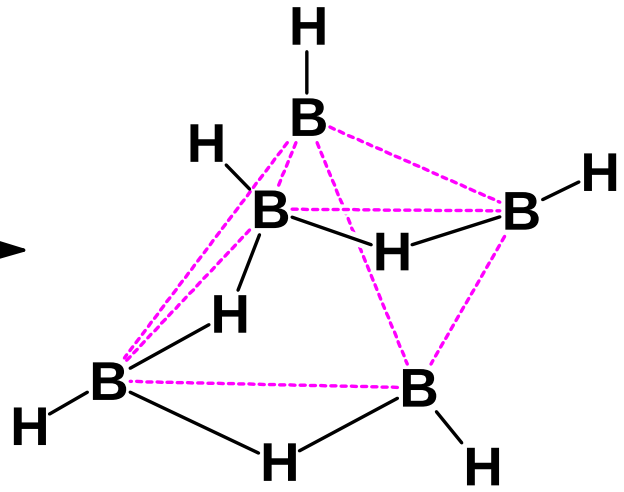


Chemistry of Pentaborane-9; *nido*-B_5H_9



nido-B_5H_9

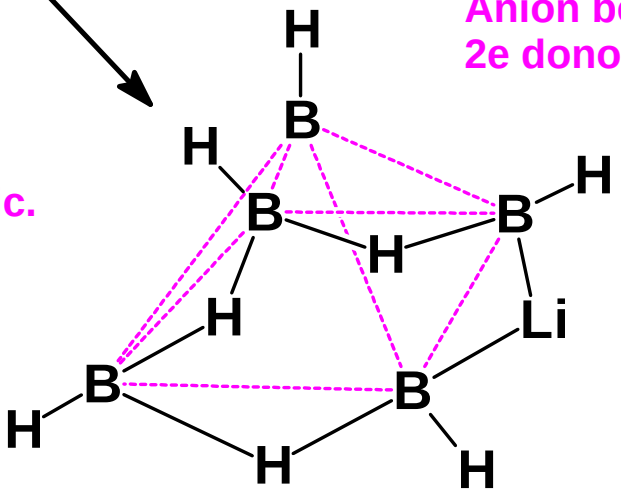
NaH



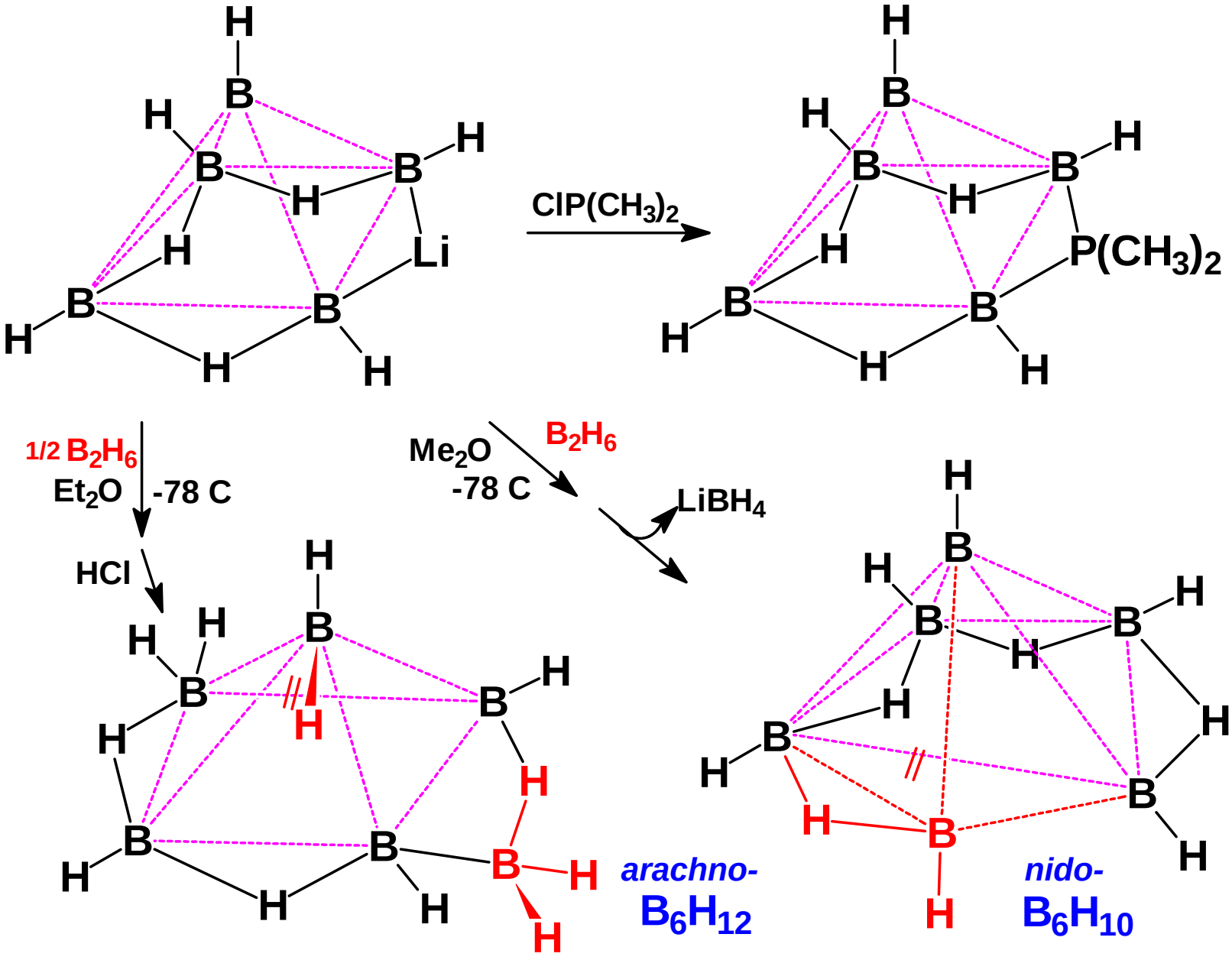
A fluxional anion, equatorial hydrogens & bridge-hydrogens are equivalent on nmr timescale. Anion behaves as a formal 2e donor ligand & synthon.

LiH

The μ-H's are more acidic than terminal H's; the apical H's are the most hydridic.



Cluster Expansion Reactions

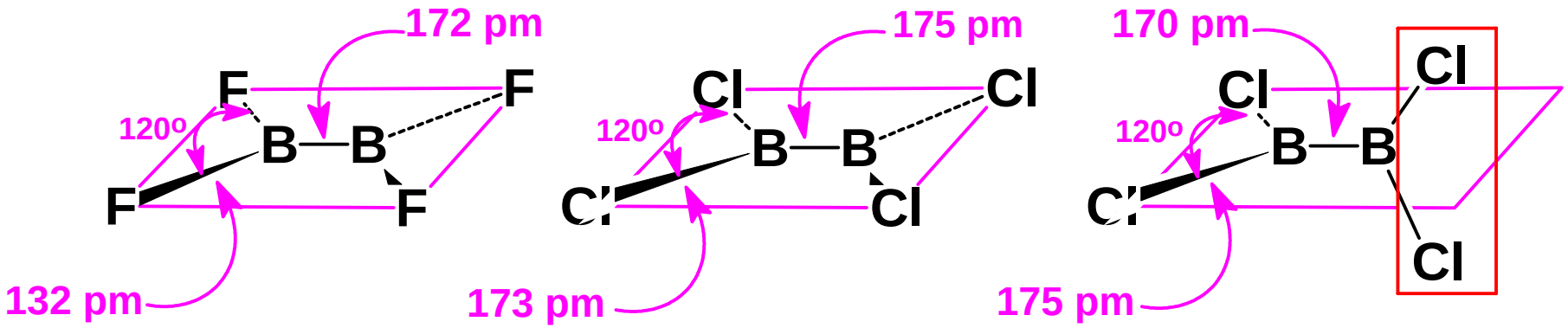


Boron Halides

- **BF_3, BCl_3, BBr_3, BI_3 are all monomeric. Mixtures will scramble halogens by bridging intermediates.**
- **BX_4^- will not scramble unless BX_3 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.**
- **BX_3, X = halogen are "hard" acids. BH_3 is a "soft"acid forming stronger adducts with P, As, S...**

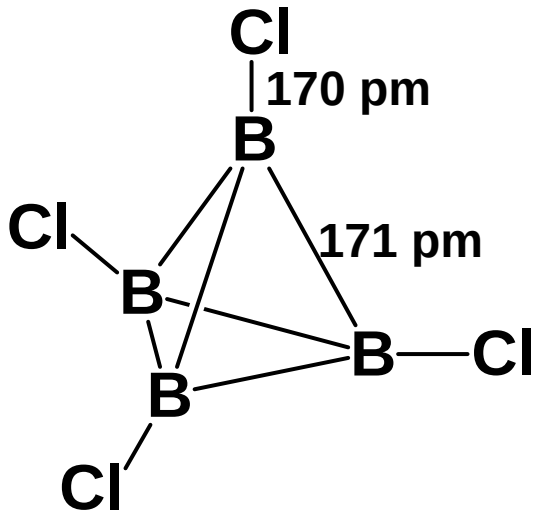
Boron Subhalides

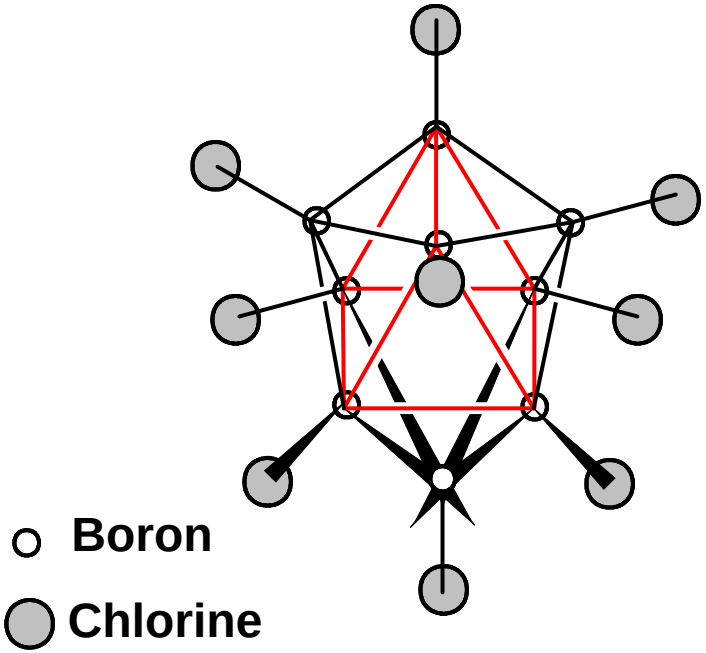
➢ B_2X_4 are planar in the solid state, only B_2F_4 remains planar in the gas phase. The formation of an "extended π system" is more important than *steric* effects for the small F.



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.

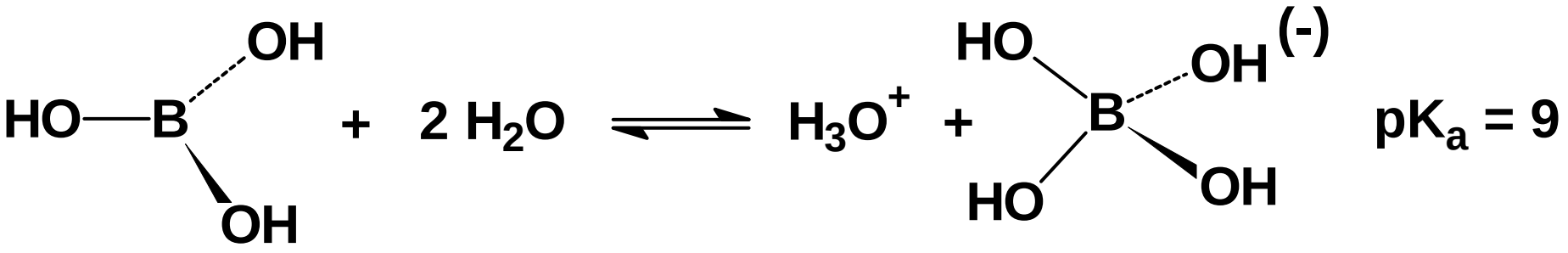


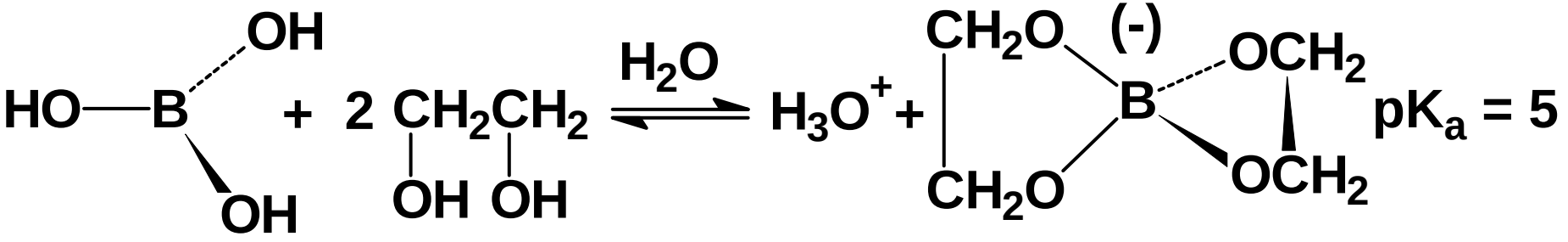


B_9Cl_9

a tricapped trigonal prism

Boron - Oxygen – Boric Acid – A Lewis Acid





A chelating alcohol, glycol, or sugar can increase the acidity by 10^4.

Boron – Oxygen : Borates & Silicates

$B(OH)_3 \xrightarrow{\text{Heat}} [B(O)OH]_x + \text{network polymers}$

H_2O

Compare with:

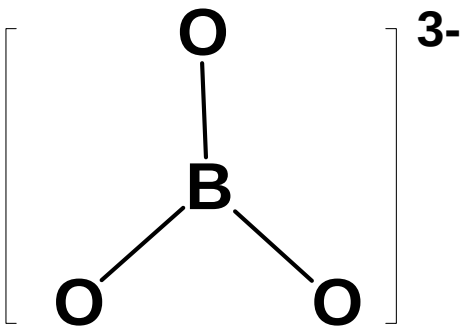
$Si(OH)_4 \xrightarrow{\text{Heat}} [SiO_n(OH)_{4-2n}]_x + \text{network polymers}$

H_2O

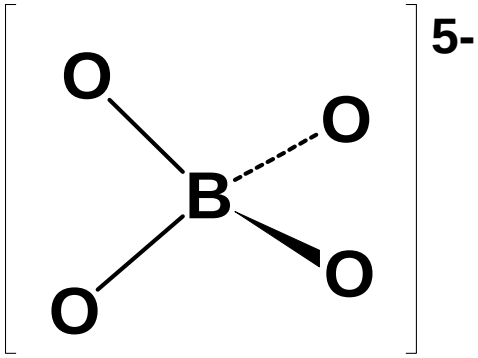
Bonding Elements:

B═O

d = 120 pm

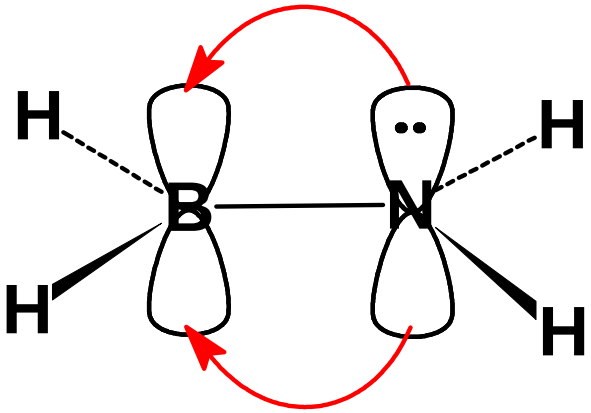


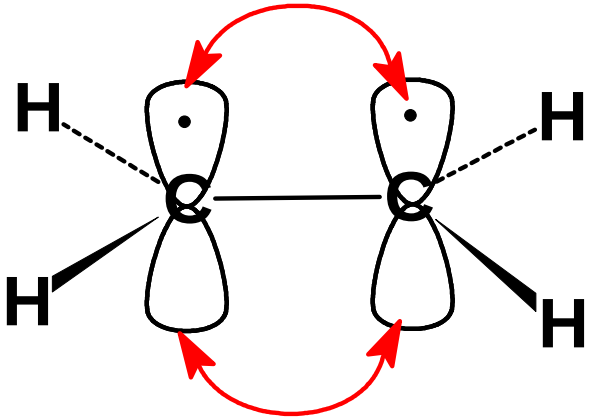
d = 128 to 143 pm
may be planar or 3D

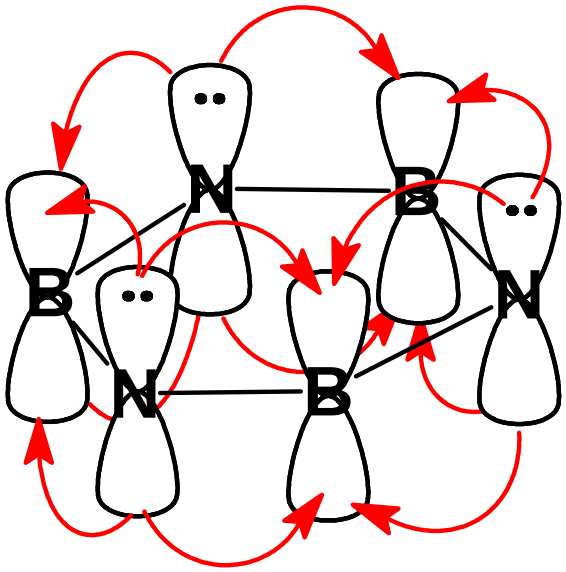


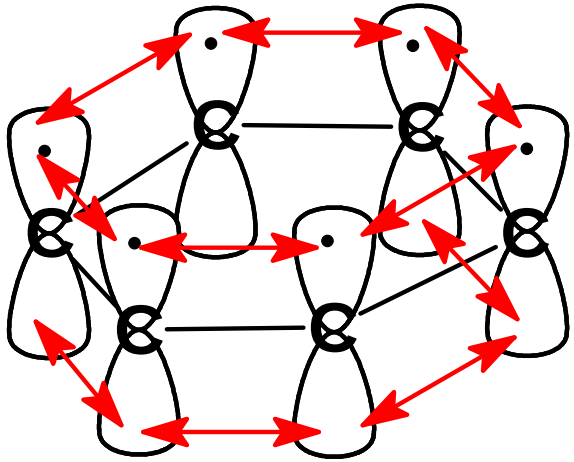
d = 143 to 155 pm
tetrahedral, T_d

Aminoboranes – Alkene Mimics

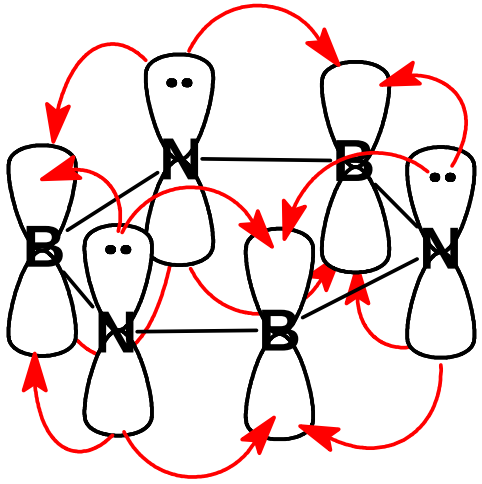


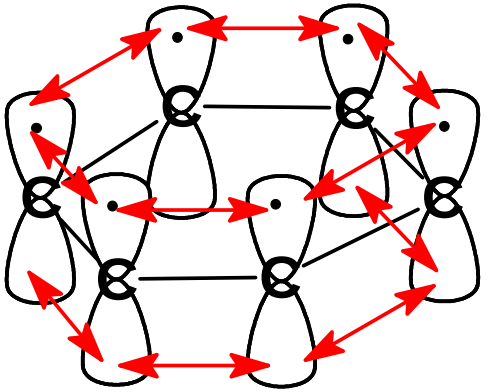


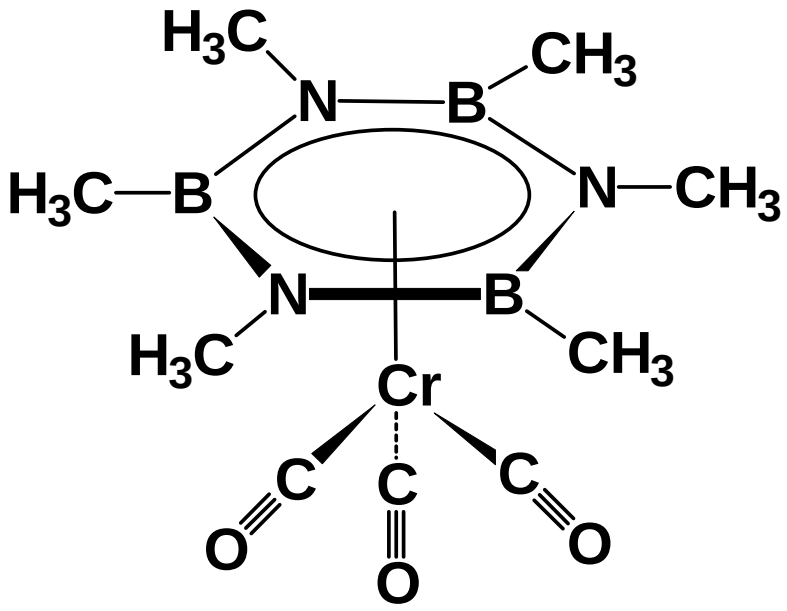


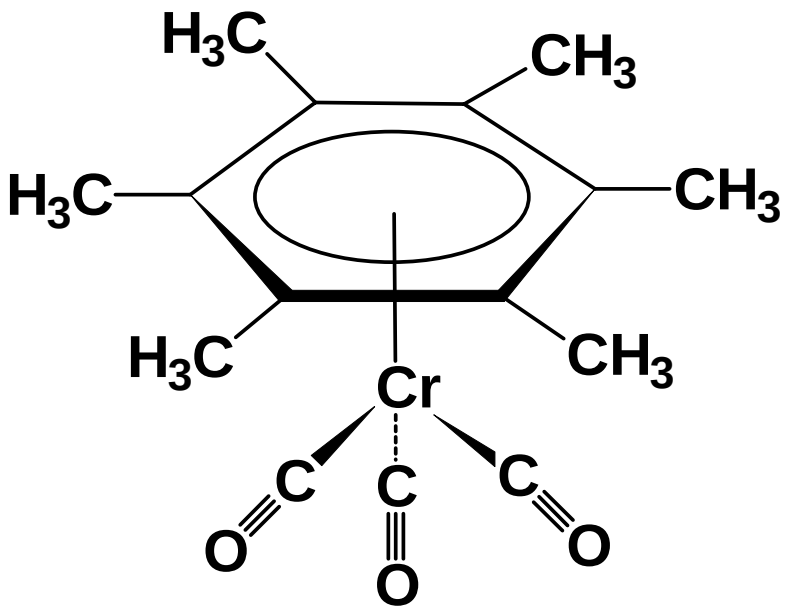


Borazine Organometallics









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