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 tetrahedral chains of B₆ – B₂.
The Boron Hydrides

- **closo** – Closed $B_n$ “deltahedra” – $B_nH_n^{2-}$
- **nido** – “nest”, **closo** minus one apical boron, $B_{n-1}H_{n+1}^{+4}$, $B_{n-1}H_{n+2}^{+3}$
- **arachno** – “spider web”, **closo** minus a B-B, $B_nH_{n+2}^{+3}$$B_{n-1}H_{n+5}^{+3}$
- **hypho – closo** minus a B$_3$ deltahedra, rare. $B_nH_{n+8}^{+3}$, examples $B_8H_{16}^{+3}$, $B_{10}H_{18}^{+3}$
- **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.
Bonding in the closo-Hydridoboranes, B₆H₆²⁻

- Sigma bonding
- Strongly bonding
- Weakly antibonding
- Lowest energy MO

Exocyclic B-H bonding

Relationship of closo- to nido-Hydridoboranes

- BH⁺ + 4 H⁺ → nido-B₃H₅
Relationship of nido- to arachno-Hyridoboranes

Chemistry of Pentaborane-9; nido-B_5H_9

Electrophilic methods cause apical substitution.

Nucleophilic methods and rearrangement using bases cause equatorial substitution.

Chemistry of Pentaborane-9; nido-B_5H_9

"Soft" base attack, not a strong nucleophile

A hypso-borane adduct results.
Chemistry of Pentaborane-9; *nido*-B$_5$H$_9$

A fluxional anion, equatorial hydrogens & bridge hydrogens are equivalent on nmr timescale.

Anion behaves as a formal 2e donor ligand & synthon.

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

Cluster Expansion Reactions

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

- $\text{B}_2\text{X}_4$ are planar in the solid state, only $\text{B}_2\text{F}_4$ remains planar in the gas phase. The formation of an “extended π system” is more important than steric effects for the small F.

- $\text{B}_4\text{Cl}_4$ – Regular tetrahedron;
- $\text{B}_n\text{X}_n$; n = 8-12 X = Cl; n = 7-10 X = Br. All are closo- and hyper electron deficient.

Boron - Oxygen – Boric Acid – A Lewis Acid

$$\text{H}_2\text{O} \rightleftharpoons \text{B} \left(\text{OH}\right)_{\text{OH}} + 2 \text{H}_2\text{O} \quad \text{H}_2\text{O}^+ + \text{B} \left(\text{OH}\right)_{\text{OH}} \quad pK_a = 9$$

$$\text{H}_2\text{O} \rightleftharpoons \text{B} \left(\text{OH}\right)_{\text{OH}} + 2 \text{CH}_2\text{CH}_2\text{OH} \quad \text{CH}_3\text{O}^+ + \text{B} \left(\text{OH}\right)_{\text{OH}} \quad pK_a = 5$$

A chelating alcohol, glycol, or sugar can increase the acidity by 104.
Boron – Oxygen: Borates & Silicates

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

Compare with:

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

Bonding Elements:

- \( \text{B—O} \)
- \( d = 120 \text{ pm} \)
- \( d = 128 \text{ to } 143 \text{ pm} \) may be planar or 3D
- \( d = 143 \text{ to } 155 \text{ pm} \) tetrahedral, \( T_d \)

Aminoboranes – Alkene Mimics

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

Borazine Organometallics

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