# Group 13 (3A) - The Elements - Boron

- Boron is a hard, crystalline, black, semimetal found in borate ores such as borax, $Na_2B_4O_5(OH)_4 \cdot 8H_2O$, found in vast deposits in Death Valley, Nevada & California.

- The element boron has powerful abilities to strengthen, toughen and make fire-resistant glasses, metals, wood, and fibers. It is used in approximately three hundred high-tech products. A few of its uses are as soldering flux, in welding rods, as preservatives for wood and fabric, as fire retardant, in insecticides, in pottery glaze, as antiseptics, in hybrid fuels, and in experimental fuel cells.[1]

- Impure boron is obtained by reduction of the oxide with Mg, followed by washing with alkali, HCl(*aq*), and HF(*aq*).
$$B_2O_3 + 3Mg \xrightarrow{\Delta} 3MgO + 2B \text{ (~95\% pure)}$$

- High purity boron is obtained with difficulty by pyrolysis or reduction of a halide over a hot Ta, W, or BN surface.
$$2BI_3(g) + 3H_2(g) \xrightarrow[\text{800-1000°C}]{\text{Ta}} 2B(s) + 6HI(g)$$

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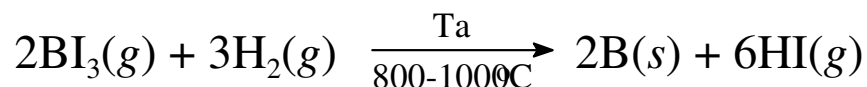
[1]Death Valley National Park website: http://www.nps.gov/deva/faqs.htm

Boron Physical and Chemical Properties

● Boron is very non-reactive and high melting (m.p. = 2300 ºC), making it useful for fire resistant and high-temperature applications.

● Naturally occurring boron consists of two stable isotopes, ^{10}B (19.6%) and ^{11}B (80.4%).

● Boron has several crystal forms, all containing B_{12} icosahedra (I_h).
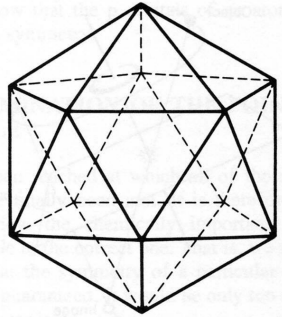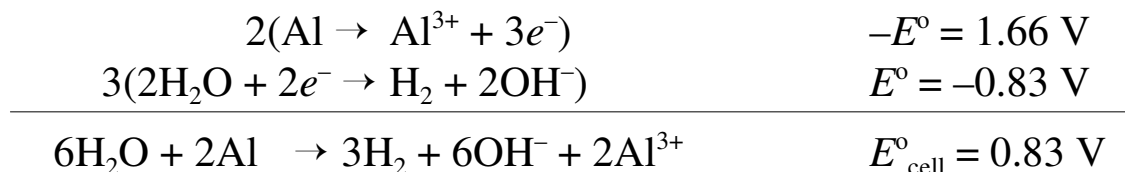

  • Individual icosahedra are linked by $3c$-$2e$ bonds.

● Boron, boron nitride (BN), and carborundum (BC), have hardness approaching diamond.
    Mohs scale: diamond = 10, BC = 9.3

● BN has forms isomorphous with diamond and graphite, but it resists oxidation up to 800 ºC.
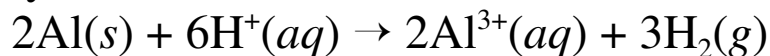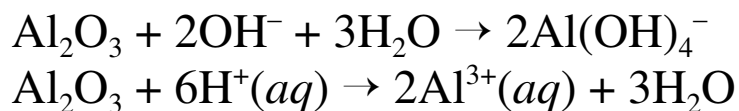
Group 13 (3A) - The Elements - Aluminum

● Aluminum is the third most abundant element and the most abundant metal.
  • Samples of it were rare before the Hall-Héroult process.

● Charles M. Hall in 1886 developed a technique for electrolyzing poorly conductive fused bauxite (Al_2O_3) by dissolving in molten cryolite (K_3AlF_6).

$$Al_2O_3 \xrightarrow[K_3AlF_6/elect.]{1000ºC} 4Al + 3O_2$$
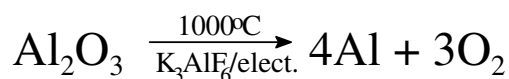
  • Canada is the principal source of bauxite for American use.

● Al is an active metal.

$$\begin{array}{ll} 2(Al \rightarrow Al^{3+} + 3e^-) & -E^o = 1.66 \text{ V} \\ 3(2H_2O + 2e^- \rightarrow H_2 + 2OH^-) & E^o = -0.83 \text{ V} \\ \hline 6H_2O + 2Al \rightarrow 3H_2 + 6OH^- + 2Al^{3+} & E^o_{cell} = 0.83 \text{ V} \end{array}$$

● Aluminum in contact with air immediately forms an amphoteric oxide coating that passivates the metal.
  • In acid or base the coating dissolves and the metal becomes reactive.

$$Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2Al(OH)_4^-$$
$$Al_2O_3 + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O$$

  • With the oxide coating removed, Al shows typical active-metal reactivity with acid.

$$2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$$

● The very exothermic heat of formation of Al_2O_3 ($\Delta H^o_f = -1670$ kJ/mol) is the driving force of the Goldschmidt or thermite reaction.

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe \qquad \Delta H^o = -849 \text{ kJ/mol}$$

Group 13 (3A) - The Elements - Gallium, Indium, Thallium

● Ga, In, and Tl are rare elements.

● All are soft, white, lustrous, and reactive metals with long liquid ranges.
  - Ga has longest known liquid range: m.p. = 30 °C, b.p. = 2071 °C.
  - Ga(l) wets glass, like H_2O, and expands below its m.p.

● Obtained by electrolysis of aqueous solutions of their salts.

Ion	Ga^{3+}	In^{3+}	Tl^{3+}	Tl^{+}
E^{o} (V) $M^{n+}{\rightarrow}M$	–0.549	–0.3382	0.741	–0.3363

$$E(H_2O) = -0.42 \text{ V @ pH 7}$$

  - Ga^{3+} can be reduced from aqueous solution, despite an unfavorable E^{o}, because of a high hydrogen over-voltage on Ga.

Group 13 Bonding

Ionic Radii of Group 13 Elements

	B	Al	Ga	In	Tl
r^+ (pm)	—	—	113	132	140
r^{3+} (pm)	20	50	62	81	95

● The group-characteristic oxidation state is +3, but +1 becomes more important down the group.
  • The stable state of thallium is +1.

$$Tl^{3+} + 2e \rightarrow Tl^+ \qquad\qquad E° = +1.247 \text{ V}$$
$$Tl^+ + e \rightarrow Tl^0 \qquad E° = -0.336 \text{ V}$$

  • Tl^+ has an ionic radius intermediate between K^+ (133 pm) and Rb^+ (148 pm), resulting in very similar ionic chemistry.

● In the +3 state, all have high charge density, so compounds have significant covalent character.

● All boron compounds are covalent, although some (e.g., BF_3) have very polar bonds.
  • The B–F bond is the strongest known single bond ($D = 757$ kJ/mol).
  • There is no ionic boron chemistry.

● Only Al_2O_3 and AlF_3 are considered ionic among Al compounds.

Oxidation State and the "Inert Pair Effect"

● Increasing stability of the lower state for heavier group elements in group 13 and succeeding groups is sometimes called the "inert pair effect" for the reluctance to lose the ns^2 pair.

$$Tl\ [Hg^{2+}]6s^26p^1 \quad \rightarrow \quad Tl^+\ [Hg^{2+}]6s^2 \quad \rightarrow \quad Tl^{3+}\ [Hg^{2+}]$$
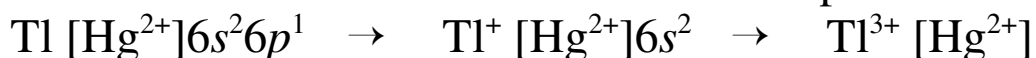
● Increasing stability of the lower state is the result of rapidly declining bond strength and less rapidly declining ionization energy going down the group.
  • Poor shielding by filled $(n-1)d^{10}$ subshell makes ionization energies of Ga, In, Tl comparable to Al.
  • Very poor shielding of $4f^{14}$ subshell makes ionization energies of Tl greater than In, despite larger size.

Ionization Enthalpies (kJ/mol)

	B	Al	Ga	In	Tl
$M\rightarrow M^+$	800.6	577.5	578.8	558.3	589.4
$M\rightarrow M^{3+}$	6885	5139	5521	5083	5439

Mean Bond Enthalpies (kJ/mol)[2]

|	H	F	Cl	Br	I
B	334	757	536	423	220
Al	284	664	511	444	370
Ga	274	577	481	444	339
In	243	506	439	414	331
Tl	188	445	372	334	272

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[2]Data from P. Atkins, T. Overton, J. Rourke, M. Weller, and F. Armstrong, *Inorganic Chemistry*, 4th ed., Freeman, NY, 2006, p. 289.

Ions in Solution

- In aqueous solution, all M^{3+} ions are acidic, although $B^{3+}(aq)$ does not exist.

Ion	K_a
$[B(H_2O)_3^{3+}]$	$>>10^{+3}$ (?)
$Al(H_2O)_6^{3+}$	1.12×10^{-5}
$Ga(H_2O)_6^{3+}$	2.5×10^{-3}
$In(H_2O)_6^{3+}$	2.0×10^{-4}
$Tl(H_2O)_6^{3+}$	$\sim 1 \times 10^{-1}$

- Greater acidity of heavier ions is due to poor shielding by underlying d subshells (Ga^{3+}, In^{3+}, Tl^{3+}) and $4f$ subshell (Tl^{3+}).

- If $B(H_2O)_3^{3+}$ existed it would immediately hydrolyze to form boric acid, $B(OH)_3$.

$$B(H_2O)_3^{3+} + 3H_2O \rightarrow B(OH)_3 + 3H_3O^+$$
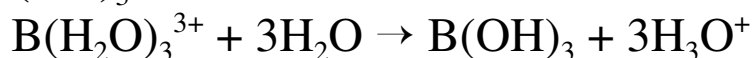
Boric Acid

● Orthoboric acid (boric acid) is unique in its acid hydrolysis, acting as a hydroxide acceptor, rather than a proton donor.

$$B(OH)_3 + 2H_2O \rightleftharpoons B(OH)_4^- + H_3O^+ \qquad pK_a = 9.3$$
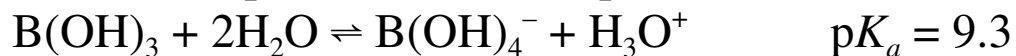
● Made in vast quantities commercially by acidification of borax.
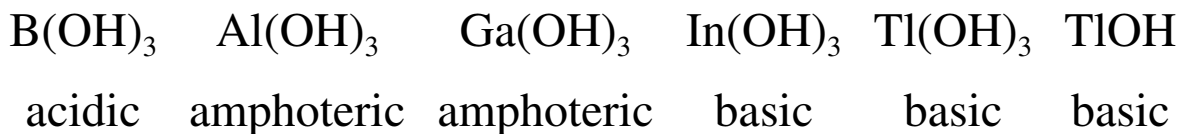
● Individual $B(OH)_3$ molecules are planar, C_{3h}.
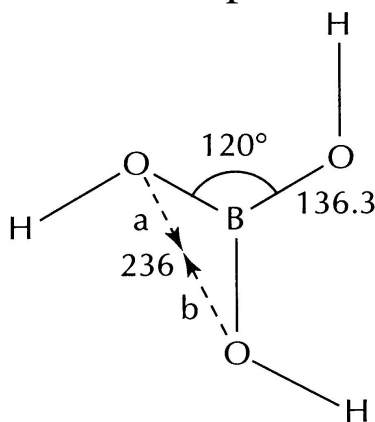
● In the solid, molecules are linked together in sheets by asymmetric hydrogen bonds, with large separation between sheets (318 pm), similar to graphite.

● $B(OH)_3$ is the expected hydrolysis product of many boron compounds, rather than the hydrated ion as with the other group 13 elements.
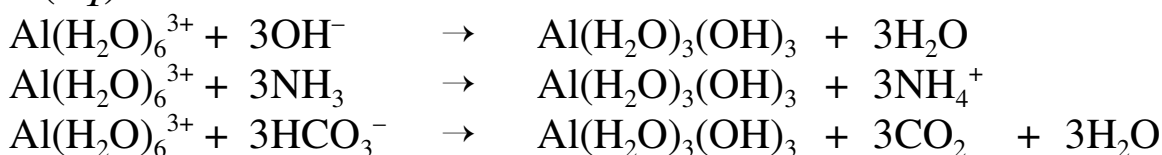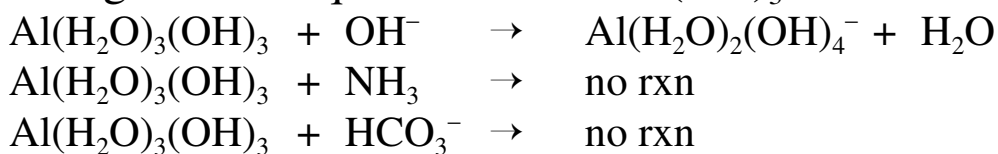
$$BCl_3 + 3H_2O \rightarrow B(OH)_3 + 3HCl$$
$$Al_2Cl_6 + 12H_2O \rightarrow 2Al(H_2O)_6^{3+} + 6Cl^-$$
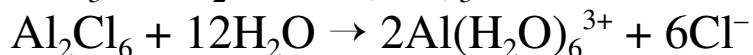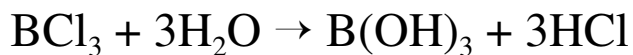
Group 13 Hydroxides

● As charge density declines, the hydroxides go from acidic to amphoteric and then to basic.

$$B(OH)_3 \quad Al(OH)_3 \quad Ga(OH)_3 \quad In(OH)_3 \quad Tl(OH)_3 \quad TlOH$$

    acidic   amphoteric amphoteric   basic   basic   basic

● Hydrated $Al(OH)_3$ is precipitated as a gelatinous solid whenever $Al^{3+}(aq)$ is treated with a base:

$$Al(H_2O)_6^{3+} + 3OH^- \quad \rightarrow \quad Al(H_2O)_3(OH)_3 + 3H_2O$$
$$Al(H_2O)_6^{3+} + 3NH_3 \quad \rightarrow \quad Al(H_2O)_3(OH)_3 + 3NH_4^+$$
$$Al(H_2O)_6^{3+} + 3HCO_3^- \quad \rightarrow \quad Al(H_2O)_3(OH)_3 + 3CO_2 + 3H_2O$$

● A strong base is required to make $Al(OH)_3$ behave as an acid:

$$Al(H_2O)_3(OH)_3 + OH^- \quad \rightarrow \quad Al(H_2O)_2(OH)_4^- + H_2O$$
$$Al(H_2O)_3(OH)_3 + NH_3 \quad \rightarrow \quad \text{no rxn}$$
$$Al(H_2O)_3(OH)_3 + HCO_3^- \quad \rightarrow \quad \text{no rxn}$$

● Treating solutions of $In^{3+}(aq)$ or $Tl^{3+}(aq)$ with base only gives the hydroxide:

$$In(H_2O)_6^{3+} + 3OH^- \quad \rightarrow \quad In(H_2O)_3(OH)_3 + 3H_2O$$
$$In(H_2O)_3(OH)_3 + OH^- \quad \rightarrow \quad \text{no rxn}$$
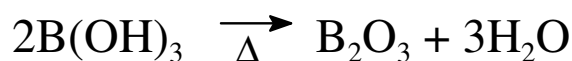
● $Tl(H_2O)_6^{3+}$ (D_{4h}) is so acidic that the hydrous oxide precipitates even at pH 1 – 2.5.

Boron Oxygen Compounds

- Boron has a large and complex chemistry, including boron-oxygen compounds.

- The oxide is formed by fusing boric acid:

$$2B(OH)_3 \xrightarrow{\Delta} B_2O_3 + 3H_2O$$

  - B_2O_3 is a glass-like substance with random B_3O_3 rings connected by bridging oxygen atoms.
  - Similarity to SiO_2 structure makes it possible to mix B_2O_3 in glass to make borosilicate glass (Pyrex®).

- Oxoanions contain BO_4 and BO_3 units.
  - The simplest oxoanion is $B(OH)_4^-$, the conjugate base of $B(OH)_3$.
  - In concentrated solutions $B(OH)_4^-$ polymerizes to form a variety of ions, predominated by $B_3O_3(OH)_4^-$.
  - The anion in borax, $Na_2B_4O_5(OH)_4 \cdot 8H_2O$, is $B_4O_5(OH)_4^{2-}$:
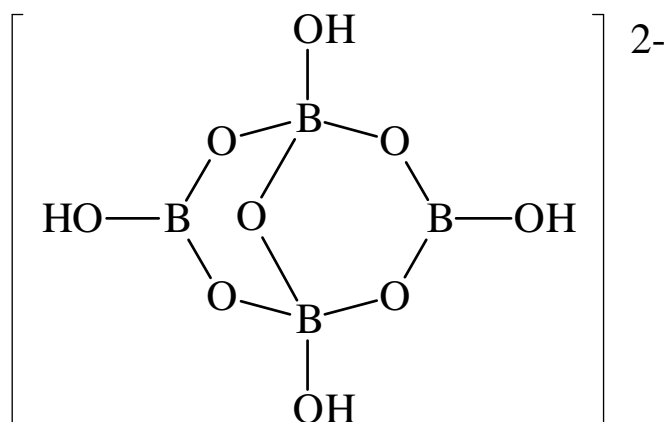
Boron Trihalides

● All trihalides, BX_3 (X = F, Cl, Br, I), have a trigonal planar structure (D_{3h}).

    • The VB model has B with sp^2 hybrids with an "empty" p_z orbital that serves as a site of nucleophilic attack by a Lewis base when BX_3 functions as a Lewis acid.
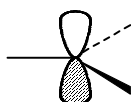
    • In the MO model, the LUMO is $\pi^*(a_2'')$, which involves overlap of B $2p_z$ with the A_2'' SALC formed from np_z orbitals on the three X atoms.
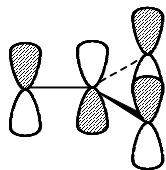
● Lewis acid strength increases in the order $BF_3 \ll BCl_3 < BBr_3 < BI_3$.

    • With small amounts of water BF_3 forms Lewis acid-base adducts $BF_3 \cdot H_2O$ and $BF_3 \cdot 2H_2O$, but it does not readily hydrolyze.

    • When small amounts of $BF_3(g)$ are passed through water, a solution of fluoroboric acid results:
$$4BF_3 + 6H_2O \rightarrow 3H_3O^+ + 3BF_4^- + B(OH)_3$$

    • The others hydrolyze completely and vigorously (BI_3 explodes!).
$$BX_3 + 3H_2O \rightarrow B(OH)_3 + 3HX \qquad X = Cl, Br, I$$
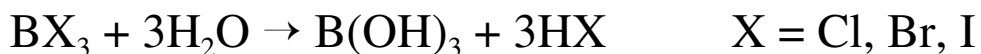
Lewis Acid Strength of BX₃ Compounds

- The order of the BX_3 Lewis acid strengths, $BF_3 << BCl_3 < BBr_3 < BI_3$, is contrary to expectations based on steric or electronegativity arguments.

- The "classic" explanation for the order of Lewis acid strengths is the effectiveness of pi bonding as an inhibition to forming CN4 coordination about the boron atom.
  - Calculations suggest that the order of pi-bond strength is $BF_3 > BCl_3 > BBr_3 > BI_3$.
  - Adduct formation of the type $BX_3 + :Y \rightarrow BX_3Y$ results in tetrahedral coordination about B, which precludes effective pi bonding.

- Size alone is not the principal factor, because BF_4^- is quite stable, but BCl_4^- and BBr_4^- can only be stabilized with large cations such as Cs^+ and $N(CH_3)_4^+$.

- Low BF_3 acid strength may have more to do with the strength of the B–F bond and the unfavorable thermodynamics to lengthen it in forming tetrahedrally coordinated B in adducts.

- There is no single explanation that is completely satisfying!

Borazines

- Borazines are B–N analogues of benzene.

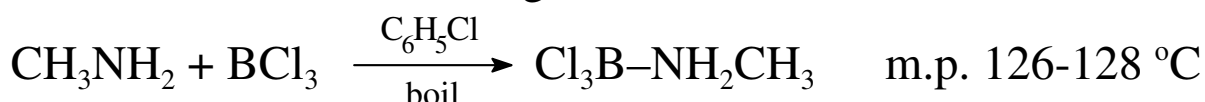- B-trichloroborazine, $B_3N_3H_3Cl_3$, can be synthesized by refluxing NH_4Cl and BCl_3 in chlorobenzene:

$$3NH_4Cl + 3BCl_3 \xrightarrow[\text{140-150°C}]{C_6H_5Cl} \quad + \quad 9HCl$$
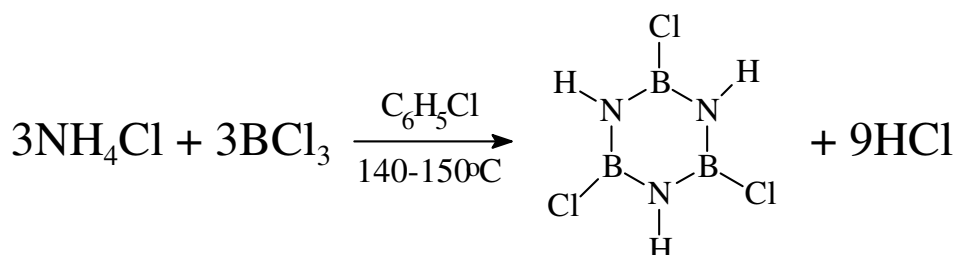
- Borazine, $B_3N_3H_6$ (b.p. 55°), is formed by reaction of $B_3N_3H_3Cl_3$ with $NaBH_4$.

$$4B_3N_3H_3Cl_3 + 3NaBH_4 \rightarrow 4B_3N_3H_6 + 3NaBCl_4$$
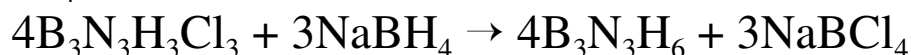
- B-trimethylborazine, $B_3N_3H_3(CH_3)_3$, is formed from $B_3N_3H_3Cl_3$ by reaction with methyl magnesium bromide.
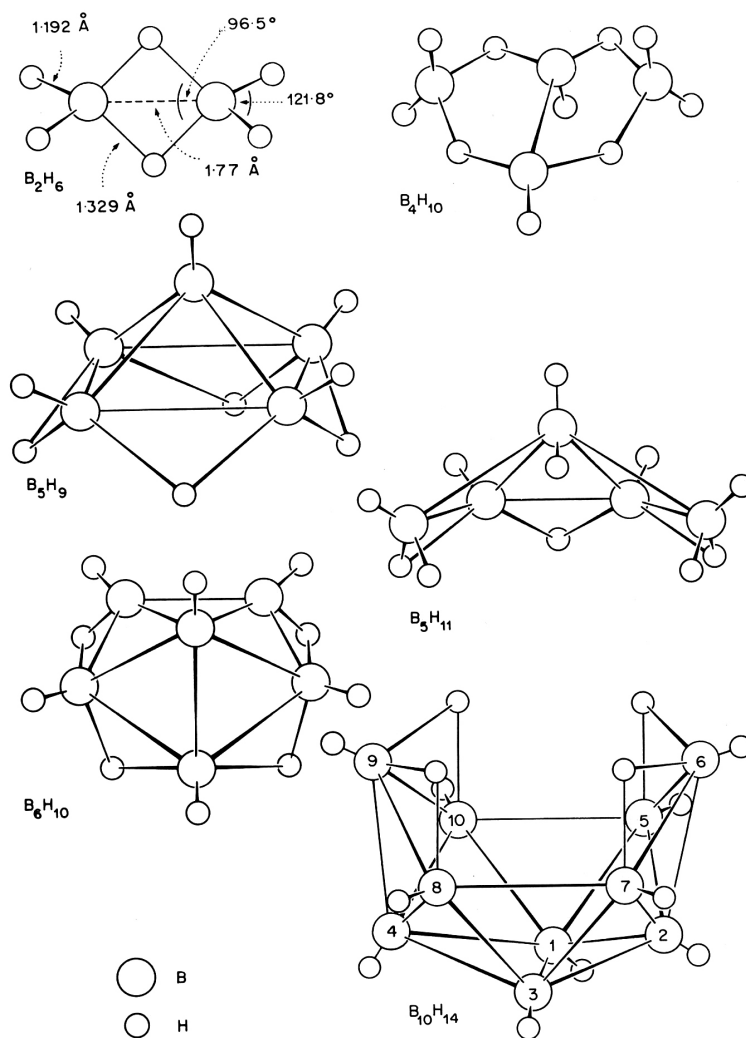
$$B_3N_3H_3Cl_3 + 3CH_3MgBr \rightarrow B_3N_3H_3(CH_3)_3 + 3MgBrCl$$
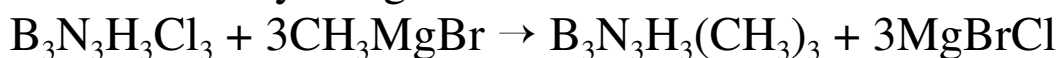
- Aminoboranes are ethane analogues:

$$CH_3NH_2 + BCl_3 \xrightarrow[\text{boil}]{C_6H_5Cl} Cl_3B–NH_2CH_3 \quad \text{m.p. 126-128 °C}$$

- Polarity of the B–N bond favors addition over substitution:

$$B_3N_3H_6 + 3HCl \rightarrow B_3N_3H_9Cl_3$$

B-trichlorocycloborazine
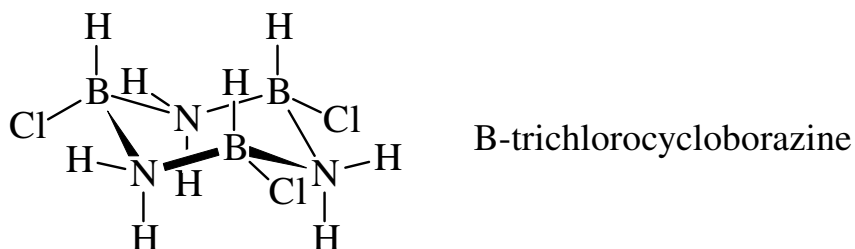
Boranes

- Boranes are boron hydrides, which were first prepared by Alfred Stock in the period 1912-1936, using acidification of MgB_2 to yield a mixture of boranes.
  - Most boranes are flammable, so Stock developed glass vacuum-line apparatus and techniques to do the work.

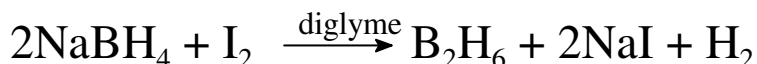1·192 Å   96·5°

B_2H_6 121·8°

1·329 Å   1·77 Å

B_4H_{10}

B_5H_9

B_5H_{11}

B_6H_{10}

9 10 6 5 8 7 4 1 2 3

$B_{10}H_{14}$

B

H

- Air flammability decreases with molecular weight, becoming stable at B_6H_{10}, and $B_{10}H_{14}$ is very stable.

- Most are liquids, but B_2H_6 is a flammable gas, and $B_{10}H_{14}$ is a white solid (m.p 99.7 °) stable in air.
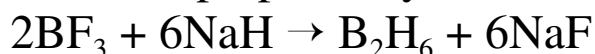
Synthesis of Boranes

- The simplest isolable borane is diborane(6), B_2H_6, which can be made in quantitative yield in ether at room temperature in a vacuum line:

$$3NaBH_4 + 4BF_3 \xrightarrow{\text{ether}} 2B_2H_6 + 3NaBF_4$$
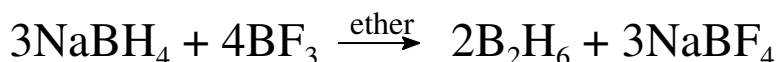
  - A convenient laboratory synthesis[3] is

$$2NaBH_4 + I_2 \xrightarrow{\text{diglyme}} B_2H_6 + 2NaI + H_2$$
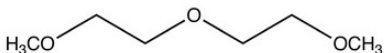
  - Industrial quantities are prepared by the following reaction:

$$2BF_3 + 6NaH \rightarrow B_2H_6 + 6NaF$$

- It mixes well with air and easily forms explosive mixtures. Diborane will ignite spontaneously in moist air at room temperature. Diborane is used in rocket propellants, as a reducing agent, as a rubber vulcanizer, as a catalyst for hydrocarbon polymerization, as a flame-speed accelerator, and as a doping agent.[4]

- Thermal decomposition of B_2H_6, resulting in transient BH_3, leads to higher boranes.

$$2B_2H_6 \xrightarrow{\Delta} [BH_3] + B_3H_9 \rightarrow \text{higher boranes}$$

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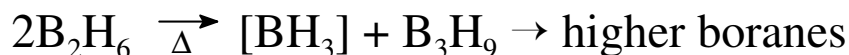
[3]Diglyme = diethylene glycol dimethyl ether =

[4]U.S. Department of Health and Human Services, Public Health Service Agency for Toxic Substances and Disease Registry, http://www.atsdr.cdc.gov/toxfaqs/tfacts181.pdf
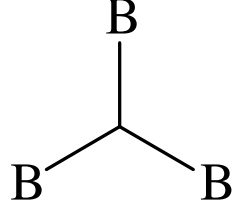
Bonding in Boranes

- Bonding in boranes defies simple VB modeling.

- The following bond types are used to describe borane structures:

  Terminal $2c$-$2e$ boron-hydrogen bond   B–H

  $3c$-$2e$ Hydrogen bridge bond

  $2c$-$2e$ boron-boron bond   B–B

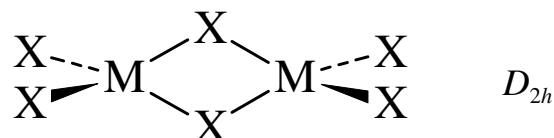 Open $3c$-$2e$ boron bridge bond

  Closed $3c$-$2e$ boron bond

- Complete description requires an MO approach for each compound.

Compounds of Al, Ga, In, Tl

● All trihalides are known, but TlI_3 is $[Tl^+][I_3^-]$.

● Trihalides of Al, Ga, and In are more stable than those of Tl.
  • Fluorides are ionic $[M^{3+}][X^-]_3$.
  • Other trihalides are dimeric with normal $2c$-$2e$ bridge bonds.

$$X\cdots M \underset{X}{\overset{X}{<}} M \cdots X \quad D_{2h}$$

M = Al, Ga, In; X = Cl, Br, I

● Hydrides are limited to simple tetrahedral species; e.g., AlH_4^-, GaH_4^-, $R_3N{:}AlH_3$.

● Allane, AlH_3 may exist in the gas phase, but the solid is polymerized $(AlH_3)_n$.
  • Failure to form analogues to the boranes results from weaker M–M bonds and greater size, which precludes M–H–M bridge bonds.

● Only important organometallic compounds are those of aluminum.
  • With simple R groups, these are dimeric Al_2R_6, with a C of the R group making $3c$-$2e$ bridge bonds.

$$R\cdots M \underset{R}{\overset{R}{<}} M \cdots R \quad D_{2h}$$
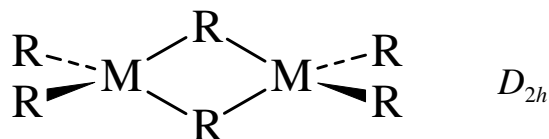
R = CH_3, C_6H_5, cyclo-C_3H_5, $H_2C{=}CH_2$

  • Bonding in Al_2R_6 is similar to polymeric $Be(CH_3)_2$.