Chem 241

Lecture 31

Announcement

__**Reminder ** Friday, April 23: EXAM 3!!!__

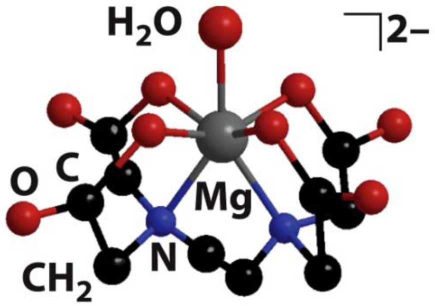
Holiday - Patriot's Day Monday April 19

Recap

Mg
Ca
Sr
Ba
Ra
Hydrides
Halides
Structures and Solvation
Oxides and Hydroxides
Carbides
Carbonates and Bicarbonates
Sulfates

Group II: Alkaline earths

- III. Coordination Compounds and Organometallics
  - A. Coordination compounds
    - 1. In general, the coordination compounds of GpII are more stable than those of GpI, reflecting the higher charge and increased covalent character of the coordinate bonds.
    - 2. Classified as hard acids, the most stable complexes are formed with polydentate charged ligands such as EDTA.



K_f M(EDTA): $Ca^{2+} > Mg^{2+} > Sr^{2+} > Ba^{2+}$

the Mg(EDTA) complex has CN = 7, with one water molecule, and the Ca complex is either 7 or 8 coordinate with 1 – 2 aqua ligands.

3. Only Be forms stable complexes with simple ligands (*e.g.*, unidentate ligands).

Organometallics

- 1. Be
  - Be organometallics are pyrophoric, and unstable in water. Can be made by transmetallation of Be metal with HgR_2, reaction of $BeCl_2$ with RLi or with Grignard reagents, RMgCl.
  - Structures are similar to hydrides, polymeric with 3c,2e bonds in solid, dimers with large R, CN=2 only in vapor or with large R.
- 2. Mg
  - Grignard reagents are important in organic synthesis; serve as a source of R-.
  - Synthesis: $Mg(s) + RBr \rightarrow RMgBr$; usually requires activation to overcome passivating oxide layer. (a little I_2 or Br_2 can be added to make the soluble halide which dissolves and presents a fresh reactive surface.)
  - The structure of a Grignard reagent is complicated.
    - CN = 2 only exists in solution for large R groups. Usually tetrahedral solvate of Mg^{2+} with R- and Cl- counterions
- 3. Ca, Sr, Ba form analogs of Grignards that are ionic and unstable.

Homework

- Finish Reading Chapter 11
- Start Reading Chapter 12
- Exercises Chapter 11:

2, 3, 5, 6, 7, 9, 11

General features of the Elements

- A. Electron configuration ns^2np^1. First group in "p-block."
  - 1. all have compounds with +3 oxidation state.
  - 2. the heavier congeners also exhibit the +1 oxidaiton state, which is the most common ox. st. for Tl. (an example of the inert pair effect).
  - 3. Neutral compounds are electron deficient and thus good Lewis acids.
- B. Metal character increases top to bottom. Boron is a non-metal; the rest (Al, Ga, In, Tl) are metals. Al has some properties that are like metalloids (*e.g.,* amphoteric oxide).

  1. Transition from covalent compound to ionic compounds can be rationalized in terms of increase in atomic radius and decrease in IE down the group.
  - 2. However, Ga is more electronegative than Al because the intervening 3d series is poorly shielding.

Group 13

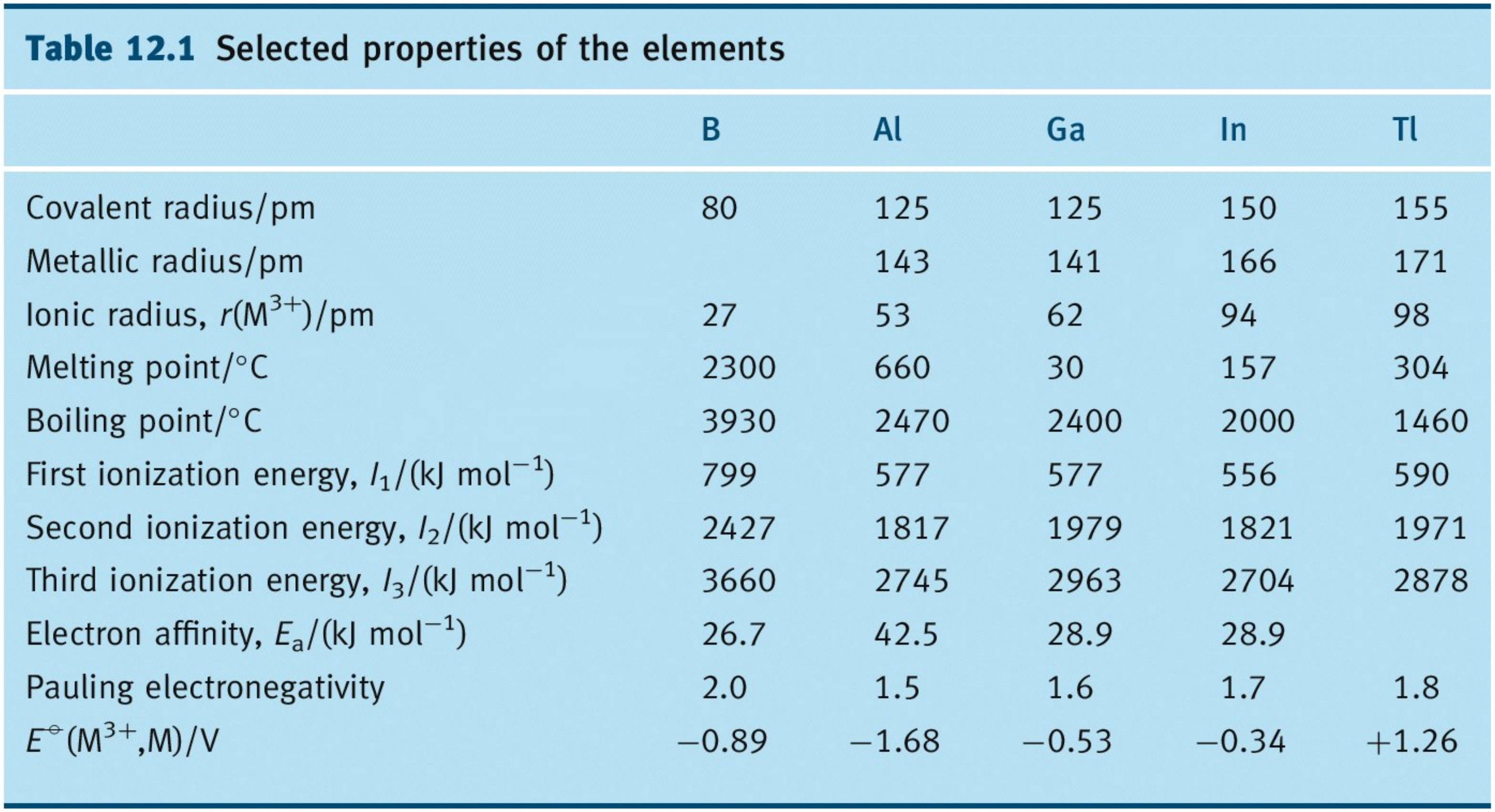


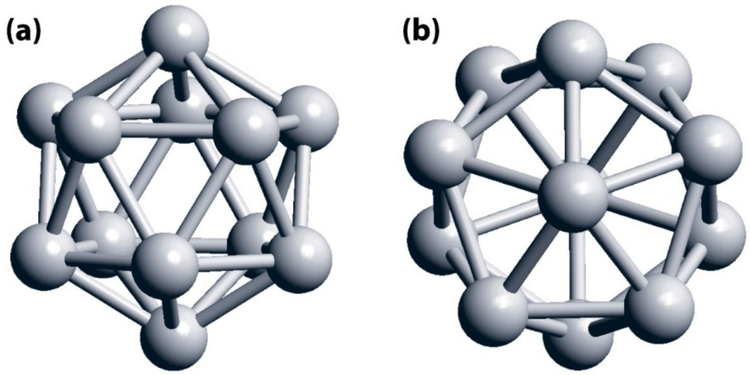
Table 12.1 Selected properties of the elements

	B	Al	Ga	In	Tl
Covalent radius/pm	80	125	125	150	155
Metallic radius/pm		143	141	166	171
Ionic radius, $r(M^{3+})$/pm	27	53	62	94	98
Melting point/°C	2300	660	30	157	304
Boiling point/°C	3930	2470	2400	2000	1460
First ionization energy, $I_1/(\mathrm{kJ\ mol^{-1}})$	799	577	577	556	590
Second ionization energy, $I_2/(\mathrm{kJ\ mol^{-1}})$	2427	1817	1979	1821	1971
Third ionization energy, $I_3/(\mathrm{kJ\ mol^{-1}})$	3660	2745	2963	2704	2878
Electron affinity, $E_a/(\mathrm{kJ\ mol^{-1}})$	26.7	42.5	28.9	28.9	
Pauling electronegativity	2.0	1.5	1.6	1.7	1.8
$E^{\ominus}(M^{3+},M)$/V	−0.89	−1.68	−0.53	−0.34	+1.26

Table 12-1
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Boron

- A. Elemental Boron exists in several hard and refractory allotropes. Three (four inc. a high pressure phase) solid phases for which crystal structures are available contain icosahedral (20 faces) B_{12} unit.



- B. Boron and Si have a diagonal relationship
  - 1. B and Si have acidic oxides
  - 2. B and Si form many polymeric oxides
  - 3. B and Si have flammable gaseous covalent hydrides.

Group 13.

- C. Boron occurs in nature as borax, $Na_2B_4O_5(OH)_4 \cdot 8H_2O$, and kernite, $Na_2B_4O_5(OH)_4 \cdot 2H_2O$.
    - 1. isolation from minerals is by conversion to boric acid, $B(OH)_3$, then to boron oxide, B_2O_3. The oxide is reduced with Mg, and washed with alkali and then HF.
    - 2. Highly pure B is made by reduction of BBr_3 vapor with H_2:

$$2\ BBr_3 + 3\ H_2 \rightarrow B + 6\ HBr$$

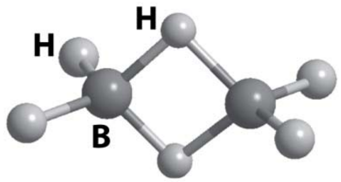
- D. Uses
    - 1. Borosilicate glass & fiberglass.
    - 2. Borax is used as a water softener, cleaner, mild pesticide
    - 3. Boric acid is a mild antiseptic
    - 4. Essential nutrient in plants

Compounds of Boron

- 1. Hydrides. Boron forms a large number of neutral and anionic hydrides with cage-like structures called Boranes.
  - a. boranes are air-sensitive compounds, some of which ignite explosively, that burn with a green flame.
  - The observation of a green flame associated with a Soviet rocket launch in the 1950s spurred a great deal of research on boranes and at least one Nobel Prize (H.C. Brown, Purdue University).

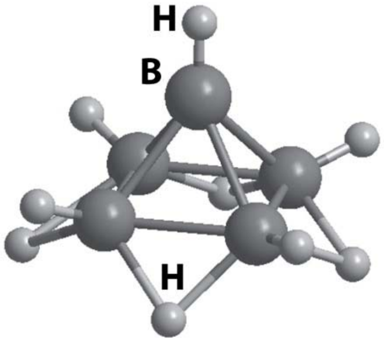
    $B_2H_6 + 3O_2 \rightarrow 2\ B(OH)_3$
  - Synthesis: Simplest is diborane (a gas at STP):

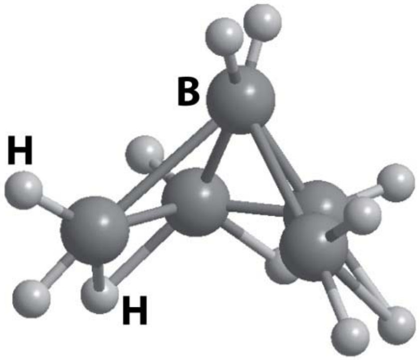
    $3\ LiBH_4 + 4\ BF_3 \rightarrow 2\ B_2H_6 + 3\ LiBF_4$
  - Diborane decomposes very slowly at RT and forms higher boron hydrides and a nonvolatile yellow solid consisting of $B_{10}H_{14}$ and polymer, BH_n.



Boranes

- b. first prepared by Alfred Stock (German) in 1912
  - Stock prepared 6 different boron hydrides and had evidence for a 7th.
- c. Two classes
  - B_nH_{n+4} and B_nH_{n+6} (less stable)
    - *e.g.*, diborane, pentaborane(9), B_5H_9
  - B_nH_{n+6} (less stable)
    - *e.g.*, pentaborane(11), B_5H_{11};
    - tetraborane(10), B_4H_{10}





d. All are colorless and diamagnetic; low mol. Wt. are gases (e.g., diborane) and are more reactive than the higher Mol. Wt (B_5H_9 is a liquid; $B_{10}H_{14}$ is a sublimable solid).

- e. hydrolysed by water (particularly low MW).

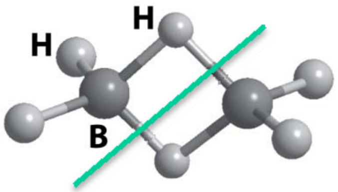
$$B_2H_6 + 6H_2O \rightarrow 2\ B(OH)_3 + 6\ H_2$$

Lewis acidity

Lewis acidity

- Two cleavage patterns:

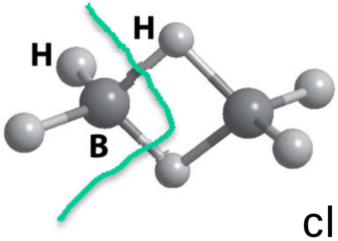
  symmetric



$+ \quad 2\ \mathrm{N(Me)_3} \rightarrow 2\ \mathrm{H_3B\text{-}N(Me)_3}$

products are isoelectronic with hydrocarbons

unsymmetrical



$+ \quad 2\mathrm{NH_3} \rightarrow \mathrm{BH_2(NH_3)_2}^+ + \mathrm{BH_4}^-$

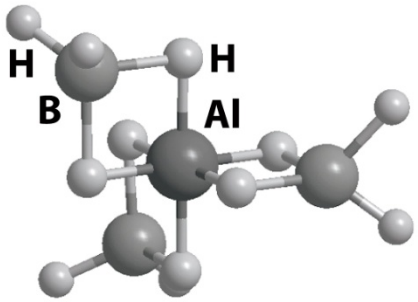
cleavage gives ionic products. Typical of low temperature rxns with small, strong bases.

Reactions

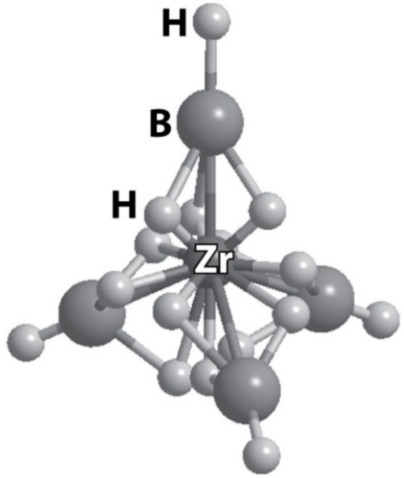
g. hydroboration (addition of HB across a multiple bond)

$H_3B\text{-}OR_2 + H_2C{=}CH_2 \rightarrow CH_3CH_2BH_2 + R_2O$

useful in the preparation of organoboranes



5 $Al(BH_4)_3$



6 $Zr(BH_4)_4$

- h. BH_4^-, tetrahydroborate
  - $B_2H_6 + 2\ LiH \rightarrow 2\ LiBH_4$
  - Can be viewed as a Lewis acid/base complex between BH_3 and H-.
  - Isoelectronic with CH_4 and NH_4^+

    Basic → neutral → acidic
  - Useful as a source of H- or as a reducing agent

    while unstable in water, kinetics of hydrolysis are slow under basic conditions.
  - Reduces Ni(II) or Cu(II) to the metal

Halides

Halides

- a. Preparation: With the exception of BI_3, prepared by direct reaction of the elements.
  - Preferred method for BF_3:
  - B_2O_3 + 3 CaF_2 + 6 H_2SO_4 → 2 BF_3 + 3 $[H_3O]\{HSO_4]$ + 3 $CaSO_4$
- b. Structure: Trigonal planar (D_{3h})
- c. BF_3 and BCl_3 are gases, BBr_3 is a liquid, BI_3 is a solid.
- d. Electron deficient, and thus good Lewis acids.
- e. Proteolysis occurs in protic solvents (water, alcohols, etc)

  BCl_3 + 3 H_2O → $B(OH)_3$ + 3 HCl
- f. $[BF_4]^-$ is a good anion
- g. Useful for making boron alkyls:
  - BF_3 + 3 MeMgI → $B(Me)_3$ + MgX_2;
  - BF_3 + 4MeLi → $Li[BMe_4]$ + 3LiF

Boron-oxygen compounds

a. B_2O_3 is the most important oxide.

prepared by dehydration of boric acid

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

b. Boric acid is an acid because of its Lewis acidity:

$$B(OH)_3 + 2H_2O \rightleftharpoons [H_2O\text{-}B(OH)_3] \rightleftharpoons H_3O^+ + B(OH)_4^-$$

$pK_a = 9.2$

c. Polyborates

d. Fusion of $Na[B(OH)_4)$ with silica (SiO_2) leads to the formation of borosilicate glasses (e.g., Pyrex)

Nitrogen compounds

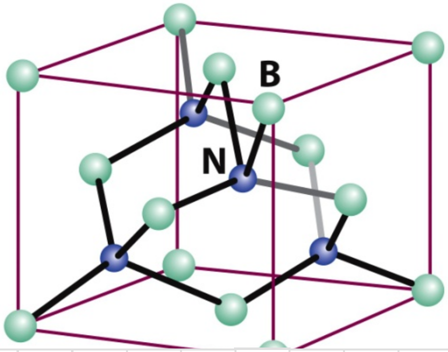
- a. BN, boron nitride
  - Synthesis:

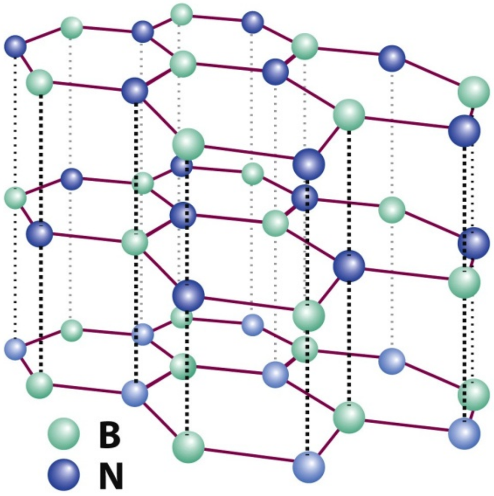
$$B_2O_3 + NH_3 \xrightarrow[1200\ C]{} 2BN + 3H_2O$$

Structure: planar sheets (like graphite, but with sheets stacked directly over each other).

electrical insulator, colorless, slippery material used as lubricant.

at high T and P (60 kbar; 2000 C) forms cubic crystalline analog of diamond.

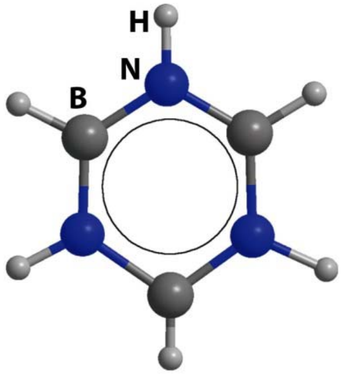




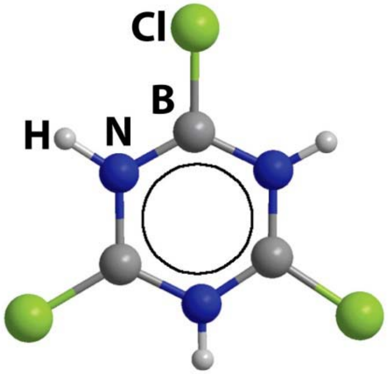
Borazines

- Borazines (isoelectronic with benzene)
  synthesis and structure

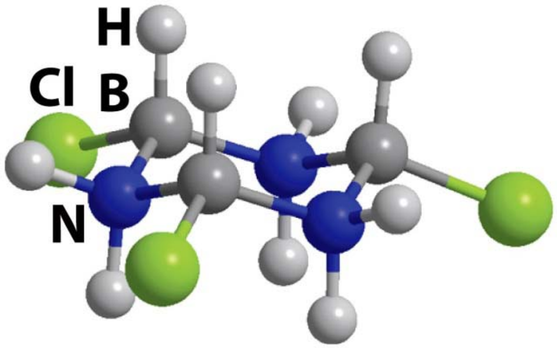
$3\ B_2H_6 + 6\ NH_3 \rightarrow B_3N_3H_6$



$3\ NH_4Cl + BCl_3 \rightarrow B_3N_3H_3Cl_3$



$3\ HCl + B_3N_3H_6 \rightarrow B_3N_3H_9Cl_3$



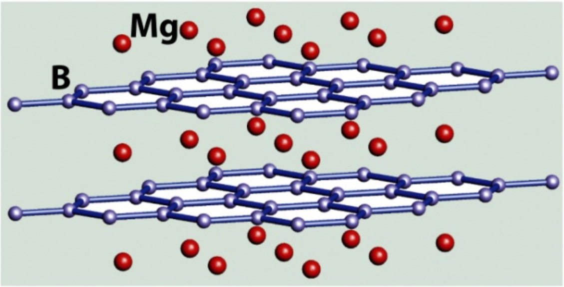
Boron clusters

- a. Metal Borides
  - 1. synthesis: Direct reaction of elements

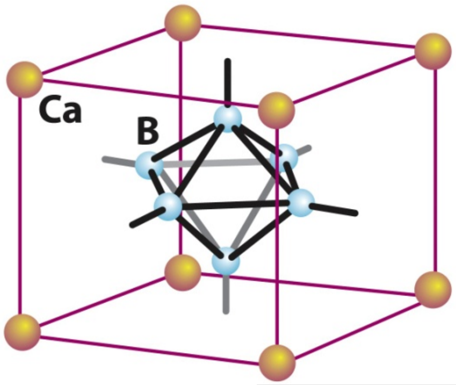
    $Ca + 6B \rightarrow CaB_6$
  - 2. Structures
    - Metal rich contain B^{3-} anions, M_2B
    - Hexagonal rings of B, MB_2, mostly with electropositive metals (Mg, Al, early d-block)

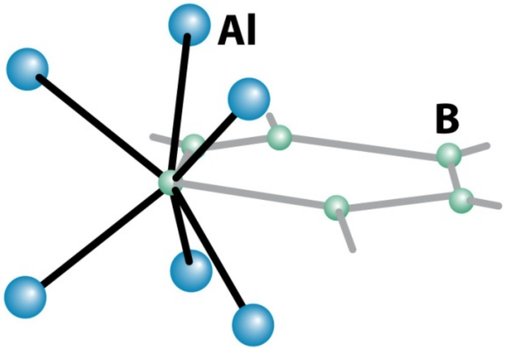
      MgB_2 becomes supercond., T_c = 38K
    - Boron-rich, MB_6 (Na, K, Ca, Ba),

      MB_{12} (e.g., f-block)



B12.1 MgB_2





Group 13

- b. Higher Boranes and Borohydrides
  - Wade's Rules

-apply to deltahedra (polyhedra made up of triangular faces

-can be used to predict the general shape of molecular and anionic boranes from the formula.

-Step 1. Determine the number of skeletal electrons

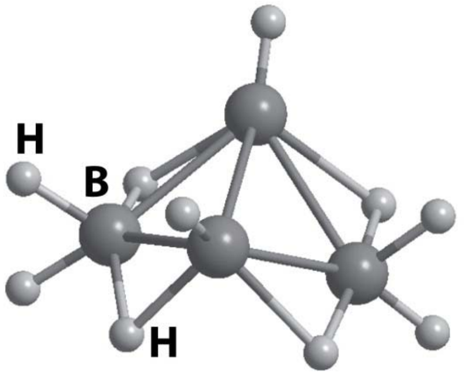
B-H groups contribute 2 skeletal electrons (there are 4 e-, but the 2 e- in the B-H bond are not skeletal electrons.) Additional H atoms contribute 1 e- each.

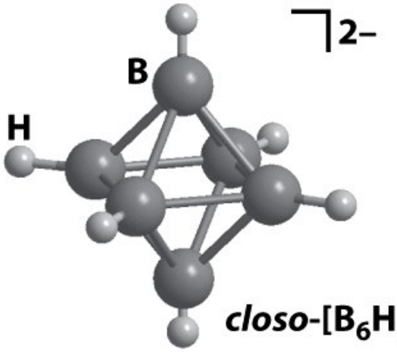
(In B_4H_{10} there are 4B-H + 6 additional H (8 + 6 = 14 skeletal electrons). Charges count as skeletal e-.

-Step 2. Assign the cluster type. species with the formula $B_nH_n^{2-}$ and n+1 pairs of skeletal electrons have a "**closo**" (cage) structure consisting of a closed deltahedron and no B-H-B 3c, 2e- bonds. (*e.g.*, $B_5H_5^{2-}$, $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$).

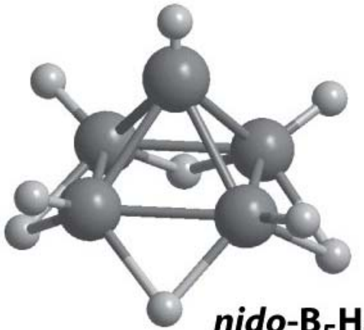
Clusters with the B_nH_{n+4} and n+2 pairs of e- have the **nido** (nest) structures. Look like closo structures without one vertex, but have B-H-B and B-B bonds.

(*e.g.* B_5H_9, 10 + 4 = 14 (7 pairs, nido structure)



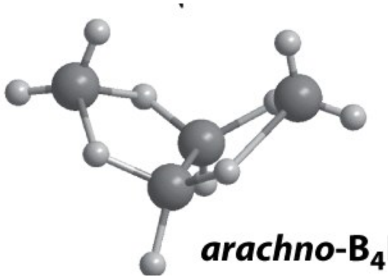


closo-$[B_6H_6]^{2-}$



nido-B_5H_9

Group 13



arachno-B_4H_{10}

Clusters with the formula, B_nH_{n+6} and n+3 pairs of skeletal electrons have an **arachno** (spider) structure, corresponding to a closo missing two vertices, and must have B-H-B bonds (*e.g.*, B_5H_{11}; 5 B-H + 6 = 16 skeletal electrons, 8 pairs).

- Can be used to predict reactivity:

  closo < nido < arachno

- Wade's rules work because they describe the population of M.O.s

Synthesis

Pyrolysis of diborane to generate BH_3, and condensation, sometimes with quench.

$B_2H_6 \rightarrow 2\ BH_3$

$BH_3 + B_2H_6 \rightarrow B_3H_7 + H_2$

$BH_3 + B_3H_7 \rightarrow B_4H_{10}$ ...

- Reactions

Reaction with a Lewis base can cleave BH_n group, abstraction of one or more H^+, and cluster enlargement.

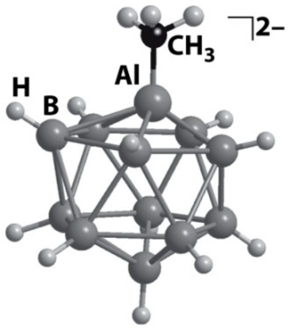
Deprotonations usually occur at B-H-B groups, 3c, 2e- bonds, and result in B-B bond formation.

The Brønsted acidity of clusters increases approx. with size.

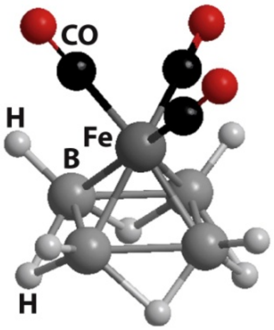
$B_4\ 10_{10} < B_5 10_9 < B_{10} 10_{14}$

Group 13

- c. Metallaboranes and Carboranes
  - One class have M-H bonds (*e.g.,* the intermediates in reductions and hydride formation with BH_4^-), but more stable clusters have M-B bonds, and take the postion of a vertex in the cluster.

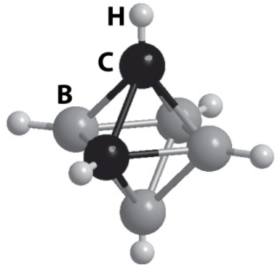


24 *closo*-$[B_{11}H_{11}AlCH_3]^{2-}$



25 $[Fe(CO)_3B_4H_8]$

  - Carboranes are derived by substituting BH- vertices with CH, with which it is isoelectronic and isolobal, but reduces the (-) charge by one for each CH. Thus, $B_6H_6^{2-}$ and $B_4C_2H_6$ are isoelectronic, and isostructural, and obey Wade's rules.

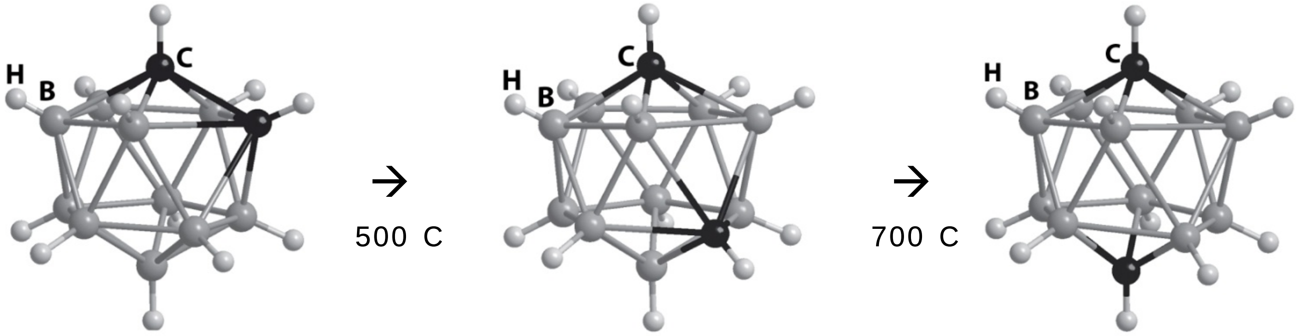


28 *closo*-1,2-$B_4C_2H_6$

Synthesis Carboranes

$B_{10}H_{14} + 2\ SEt_2 \rightarrow B_{10}H_{12}(SEt_2)_2 + H_2$...

$B_{10}H_{12}(SEt_2)_2 + C_2H_2 \rightarrow 1,2\text{-}B_{10}C_2H_{12} + 2\ SEt_2 + H_2$



29 *closo*-1,2-$B_{10}C_2H_{12}$ **30** *closo*-1,7-$B_{10}C_2H_{12}$ **31** *closo*-1,12-$B_{10}C_2H_{12}$

The C-H protons are mildly acidic, and so can be lithiated and used in synthesis like LiR reagents, where R is a carborane.

$B_{10}C_2H_{12} + 2\ LiBu \rightarrow 1,2\text{-}B_{10}C_2H_{10}Li_2 + 2\ C_4H_{10}$

Homework

Finish Reading Chapter 12
Exercise 1, 2, 5, 6, 7, 8, 10, 12, 15