Chem 241

Lecture 32

Announcement

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

Bring calculator

Bring Pencil

- Model Kit -

Recap

Coordination Compounds of Alkaline Earth Metals
Organometallics
Group 13
Boron
Compounds

Homework

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

Aluminum

- 1. Occurrence

a. Most abundant element in Gp 13, it is the most abundant metal in the Earth's crust.

b. Found in clays and aluminosilicates, the commercial source of Al is bauxite, a hydrated aluminum oxide/hydroxide.

c. Al is extracted by the **Bayer** process as $Al(OH)_3$. The ore is dissolved in hot aqueous NaOH, which dissolves Al_2O_3 and SiO_2, but leaves Fe_2O_3. The mix is cooled to precipitate $Al(OH)_3$. In the **Hall-Heroult** process, the hydroxide is dissolved in molten cryolite, Na_3AlF_6, and electrolyzed using a cell with a steel cathode and graphite anode.

$$2\ Al_2O_3 + 3C \rightarrow 4\ Al + 3\ CO_2$$

Aluminum

- 1. Uses

  a. Most important element commercially in Gp 13

  It is light and corrosion resistant because of a tough oxide layer, and its uses include: cans, foils, aircraft alloys.

  b. Construction

  c. Heat sinks

  2. Health Concerns

  a. Competes with Calcium

  b. Alzheimer's disease

Gallium

- Ga chemistry is similar to Al, but with tendencies toward the chemistry of the heavier metals in Gp13.
  - 1. Ga_2O_3 occurs as an impurity in bauxite, and is recovered in Al manufacture. Like Al, the element is prepared by electrolysis. The element has a low melting point (30 C) but has a normal bp (2070 C), and thus the widest liquid range of any known substance.

Indium

Soft malleable metal

Indium Tin Oxide – clear elctrode → solar energy, LCD and touchscreens

Thallium

Thallium compounds are found in flue dusts from roasting sulfide ores (*e.g.*, of Zn and Pb). Great abundance but not commercially extractable.

Poisonous “poisoner’s poison”

Photomultiplier tubes

Hydrides

-AlH_3 is a salt with H- in the lattice.

-Alkyl Al hydrides are molecular compounds that contain Al-H-Al 3c, 2e- bonds. They are used to react with alkenes as in hydroboration, adding Al-H across the double bond.

-$LiAlH_4$ is an important source of H- in synthesis

Direct reaction of Li, Al and H_2 yields either $LiAlH_4$ or Li_3AlH_6.

The former is more conveniently prepared from $AlCl_3$:

$$4\ LiH + AlCl_3 \rightarrow LiAlH_4 + 3\ LiCl$$

-Unlike BH_4^-, AlH_4^- reacts violently on contact with water (more hydridic).

-Useful in metathesis reactions, where H- migrates to more electroneg. element:

$$LiAlH_4 + SiCl_4 \rightarrow LiAlCl_4 + SiH_4$$

Halides

-synthesis: Direct reaction with X_2 gives AlX_3, but will also react with HCl or HBr:

$$2\ Al + 6\ HCl \rightarrow 2\ AlCl_3 + 3H_2$$

- reactions: The fluorides are relatively unreactive and good Lewis acids, although AlF_3 will add F- to form AlF_6^{3-}, as in cryolite. The rest are trigonal planar molecules only in the gas phase, and form Al_2X_6 dimers in solution. In the solid, X = Br, I are dimers, X= Cl- has a layer structure.

- Lewis acids

- Lower valent halides are unstable → disproportionation:

$$3\ AlX \rightarrow 2\ Al + AlX_3$$

-Friedl-Craft reaction

- Tl(I) and Gallium(I)/(II) careful

Oxides

- Al_2O_3 (α-alumina) is a very hard refractory material. The structure is hcp in oxide anions with Al(III) in 2/3 of the O_h holes.

- Al_2O_3 (γ-alumina) is formed by dehydration of $Al(OH)_3$ at temperatures below 900 C. → solid phase in chromatography and as a hetergeneous catalyst.

- Gallium oxide, Ga_2O_3 → vapor deposition

- Indium oxide, In_2O_3

- Thallium oxide, Tl_2O or Tl_2O_3 → superconductor/ semiconductor

Sulfides

Sulfides

- Only sulfide of Al, Al_2S_3, is prepared by direct reaction of the elements at elevated T. It is rapidly hydrolyzed in aqueous solution:

$$2\ Al + 3\ S \rightarrow Al_2S_3$$

$$Al_2S_3 + 6\ H_2O \rightarrow 2\ Al(OH)_3 + 3\ H_2S$$

Group 15

Wide variety of semiconductors with group 13 – isoelectronic with silicon.

Reactive must be kept inert

Organometallics

Boron, electron deficient, Lewis acids

$$B_2H_6 + 6\ CH_2{=}CH_2 \rightarrow 2B(CH_2{=}CH_3)_3$$

$$BPh_3 + NaPh \rightarrow Na^+\ [BPh_4]^-$$

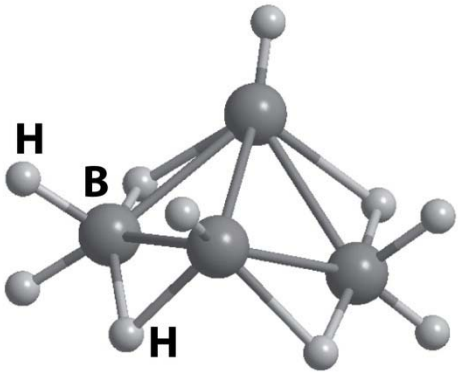
Aluminum

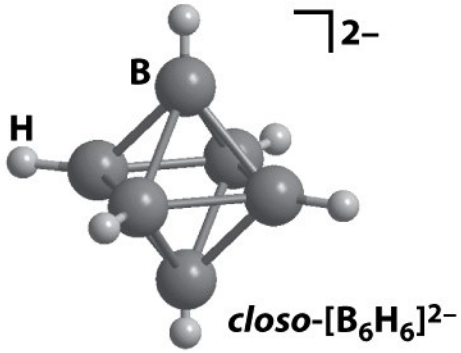
$$2\ Al + 3\ Hg(CH_3)_2 \rightarrow Al_2(CH_3)_6 + 3\ Hg$$

$$2\ Al + 3H_2 + 6\ CH_2{=}CH_2 \rightarrow Al_2(CH_2CH_3)_6 \quad @\ ht,\ hp$$

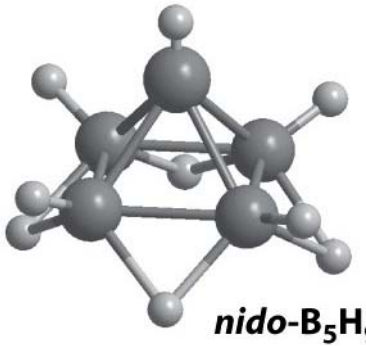
Group 13

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





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



nido-B_5H_9

-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.

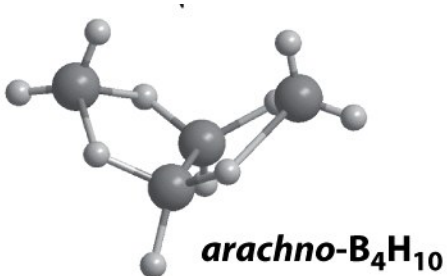
(In B_4H_{10} there are 4B-H + 6 additional H (8 + 6 = 14 skeletal electrons). Charges count as skeletal e-.

-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)

Group 13



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.

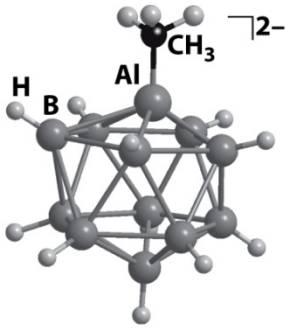
Deprotonations usually occur at B-H-B groups, 3c, 2e- bonds, and result in B-B bond formation.

The Brønsted acidity of clusters increases approx. with size.

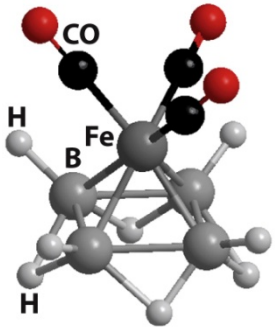
$B_4\ 10_{10} < B_5 10_9 < B_{10} 10_{14}$

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.

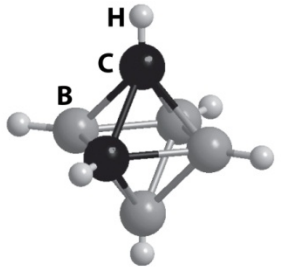


24 *closo*-$[B_{11}H_{11}AlCH_3]^{2-}$



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.

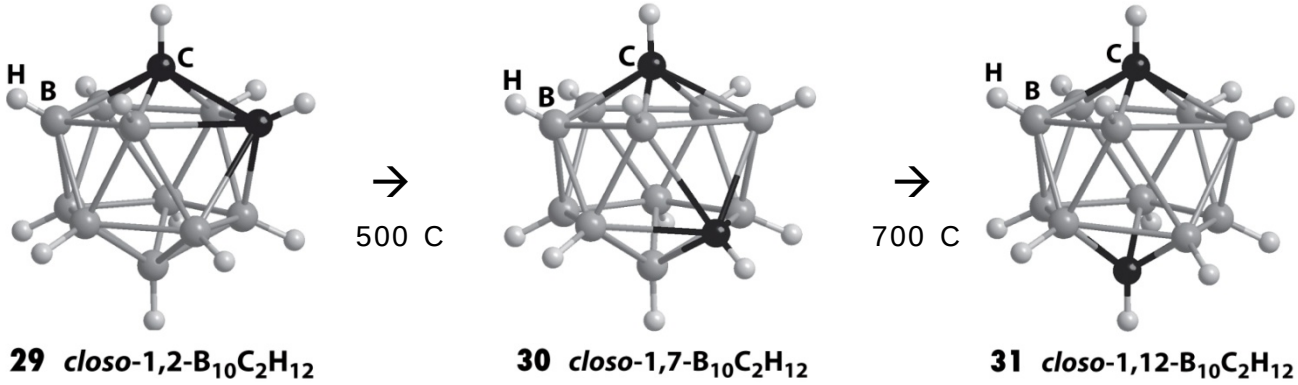


28 *closo*-1,2-$B_4C_2H_6$

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.

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