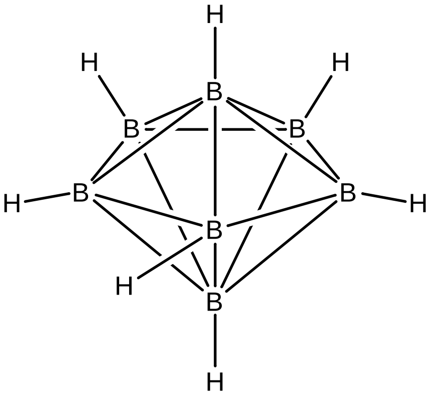
CHE 514, Descriptive Inorganic Chemistry
Spring, 2005
Problem Set 4 Key

1. (32) Sketch the structures of these boron compounds. Classify each as *closo, nido* or *arachno* and tell which polyhedron is the basis of each shape. [If you're interested, try to describe the simpler compounds by according to Lipscomb's semitopological model.

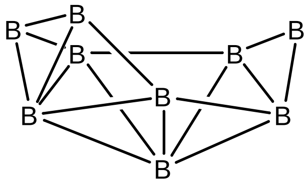
a. $B_7H_7^{2-}$

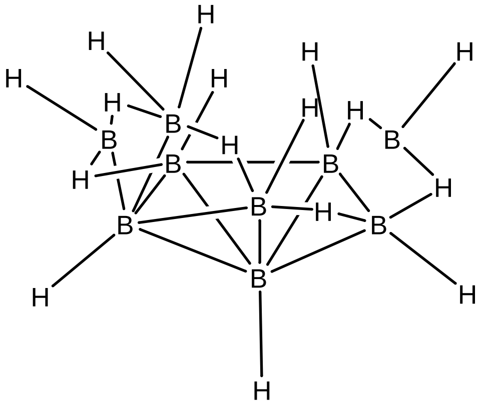
Closo, pentagonal bipyramid



b. B_9H_{15}

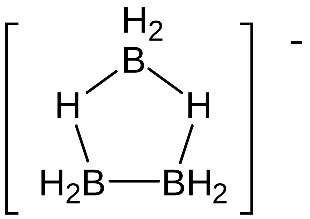
Equivalent to $B_9H_9^{6-}$, so *arachno* based on octadecahedron (2 adjacent vertices missing usually)





framework only if you want to tackle H positions, they'll mostly be on the open edges

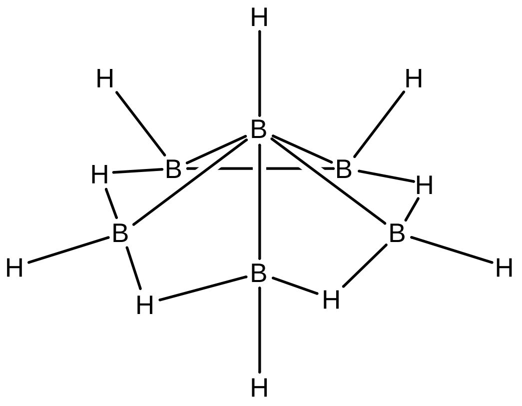
c. $B_3H_8^-$



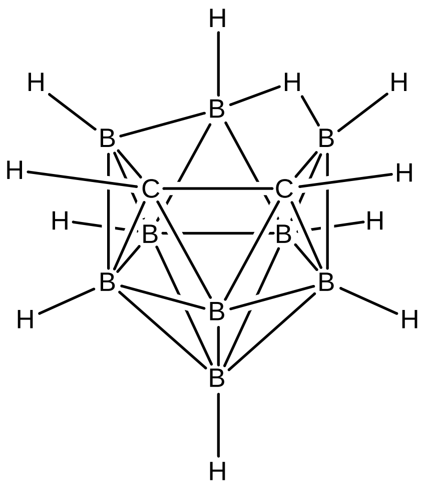
arachno, trigonal bipyramid with 2 missing vertices

d. B_6H_{10}

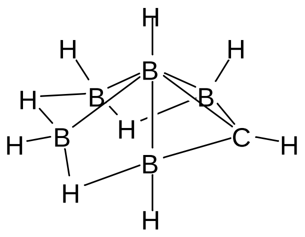
Nido, pentagonal bipyramid with one missing vertex



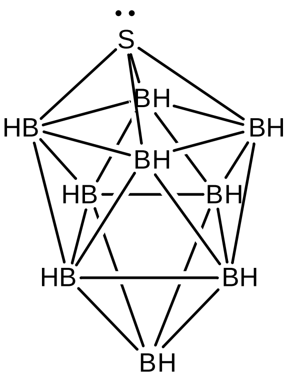
e. $1,7\text{-}C_2B_9H_{12}^-$
equivalent to $B_{11}H_{11}^{4-}$, *nido* dodecahedron (1,7 numbering is from Greenwood)



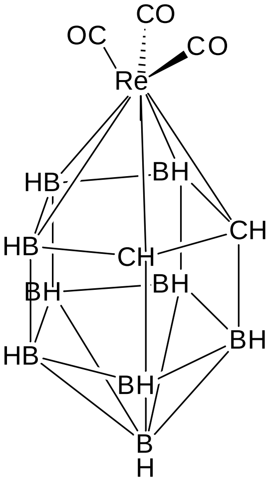
f. CB_5H_9
equivalent to $B_6H_9^-$ or $B_6H_6^{4-}$, *nido* pentagonal bipyramid (you get to choose which isomers; 2- CB_5H_9 is shown here)



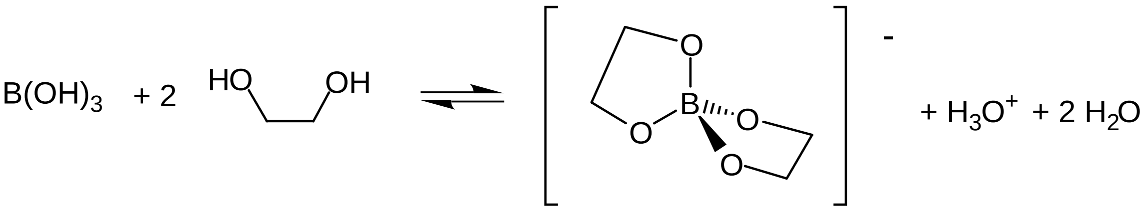
g. $1\text{-}SB_9H_9$
S contributes 4 electrons to cluster bonding like BH^{2-}; one lone pair is exo to the cluster, so equivalent to $B_{10}H_{10}^{2-}$, *closo* bicapped square antiprism (1-position means that S is at one of the caps)



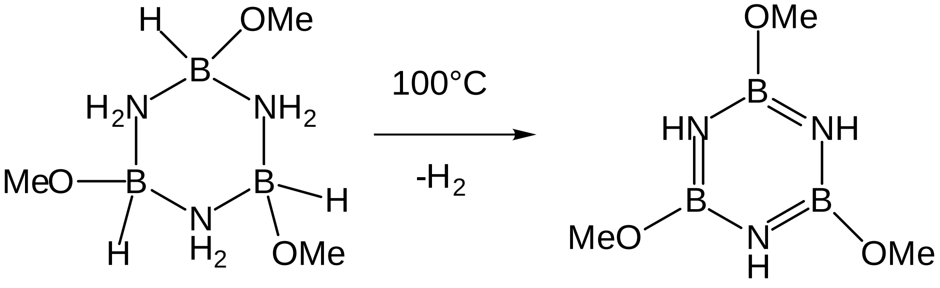
h. $[3\text{-}\{Re(CO)_3\}\text{-}1,2\text{-}C_2B_9H_{11}]^-$
equivalent to $B_{12}H_{12}^{2-}$, *closo* icosahedron (negative sign was missing from problem set but corrected in class and on www; numbering tells you that the 2 C and one Re are in adjacent positions)



2. (10) What are the products of these reactions?
a. $B(OH)_3$ + excess $HOCH_2CH_2OH$ ⟶ H^+ + ?



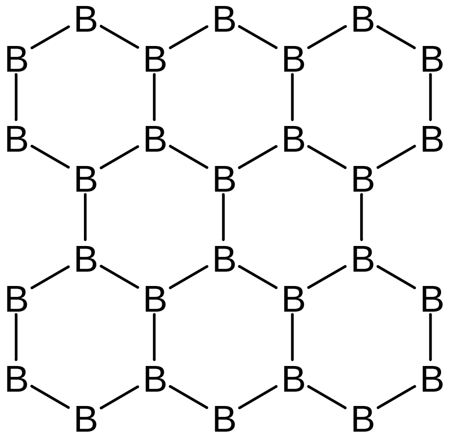
b. $B_3N_3H_6$ + 3 MeOH →



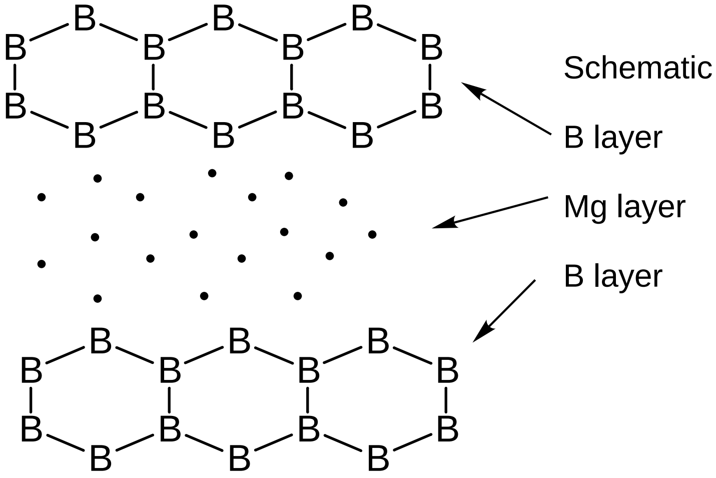
Depends on conditions -- either answer is OK.

3. (10) Describe and sketch (idealized) three-dimensional structures of MgB_2 and ScB_{12}, emphasizing the arrangement of the boron building blocks.

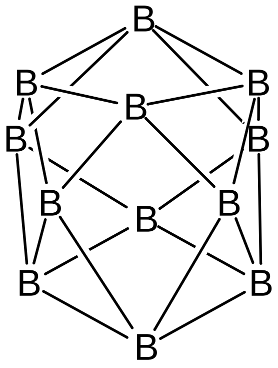
MgB_2 consists of anionic, planar, hexagonal nets of B atoms with layers of Mg^{2+} ions between the nets. The magnesium ions adopt a close-packed geometry, but the closest contacts are really between Mg and B.



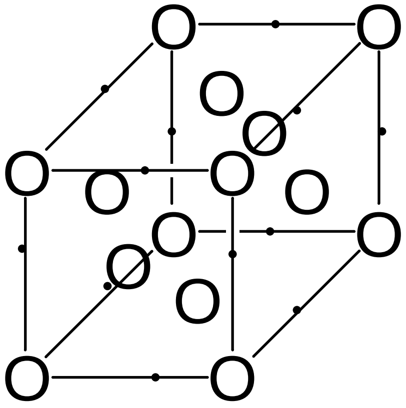
Hexagonal net of boron atoms



ScB_{12} consists of a NaCl - like lattice with Sc on the Na positions and B_{12} cubooctahedra on the Cl positions.



B_{12} cubooctahedron



Cubic close-packed array of B_{12} units (O) with Sc in the octahedral holes

4. (10) Describe the solution composition of aqueous Al^{3+} as the pH is gradually raised from below 2 to above 12.

At low pH, acidic $[Al(H_2O)_6]^{3+}$ dominates the solution. As the pH is raised, H^+ dissociates from water ligands.

$[Al(H_2O)_6]^{3+} \leftarrow\rightarrow [Al(OH)(H_2O)_5]^{2+} + H^+$
$pK_a = 4.95$

The resulting hydroxy complexes aggregate to polynuclear aluminate species form at higher pH until ultimately $Al(OH)_3$ precipitates at intermediate pH.

$[Al(OH)(H_2O)_5]^{2+} \rightarrow [(H_2O)_4Al(\mu\text{-}OH)_2Al(H_2O)_4]^{4+}$

$\rightarrow [AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+} \rightarrow Al(OH)_3{\cdot}(H_2O)_n$ gel

In strong base, anionic aluminates begin to redissolve aluminum hydroxide.

$Al(OH)_3 + OH^- \rightarrow [Al(OH)_4(H_2O)_2]^-$

$[Al(OH)_4(H_2O)_2]^-$ is the principal species in solution at high pH, but there are probably other –ate complexes between pH about 8 and 12.

Greenwood mentions this but does not give many details. Some details about the aggregates are found in J. Chem. Soc. *Dalton Trans.* **1988**, 1347. Any reasonably formulated Al^{3+} species of increasing size and complexity are acceptable if you could not find any data in the literature.

5. (15) What is spinel? Describe the coordination environments around the Mg^{2+} and Al^{3+} ions in spinel, and explain why the ions are arranged in these environments. Use this structure to explain the magnetic behavior of Fe_3O_4.

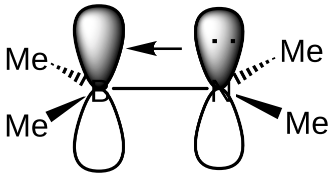
Spinel itself is $MgAl_2O_4$. The general formula AB_2O_4 describes a common class of mixed-metal oxides in which the sum of the A and 2B ionic charges is 8+. Commonly A is a 2+ ion and B is a 3+ ion.

The lattice of many spinels can be described approximately as a close-packed oxide lattice with two octahedral sites occupied for every one tetrahedral site. In spinel itself, Mg^{2+} occupies the tetrahedral site surrounded by 4 oxygen atoms, and Al^{3+} occupies the octahedral sites surrounded by 6 oxygen atoms. This is contrary to expectations based on size. The *overall lattice energy* is apparently more favorable with the more strongly polarizing Al^{3+} ion in the octahedral site *despite* its smaller size.

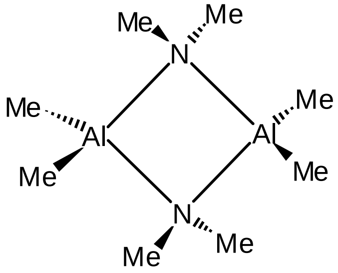
Fe_3O_4.adopts the inverse spinel structure $[Fe^{III}]_{tetrahedral}$ $[Fe^{II}\ Fe^{III}]_{octahedral}$ $[O^{2-}]_4$. The driving force for putting $[Fe^{III}]$ into a smaller tetrahedral site is size – Fe^{3+} is smaller than Fe^{2+}. Crystal field stabilization energy favors placing d^6 Fe^{2+} in an octahedral site ($t_{2g}^4\ e_g^2$), whereas d^5 Fe^{3+} has no CFSE preference. Its higher charge favors placing Fe^{3+} in an octahedral site.
To explain the magnetism, Fe^{3+} has a d^5 electron configuration. In an O_6 environment, the ion is high spin, i.e., $t_{2g}^3\ e_g^2$; in an O_4 environment, the ion is also high spin, i.e., $e^2\ t^3$ with five unpaired electrons in either case. Strong antiferromagnetic coupling between octahedral and tetrahedral sites "cancels out" the two S = 5/2 spins. The magnetic moment is dominated by the four unpaired electrons of the octahedral Fe^{2+} ($t_{2g}^4\ e_g^2$) ion that are "canceled out". Fe_3O_4 (magnetite) is overall ferrimagnetic, and it can maintain a permanent magnetic moment at room temperature.

6. (10) Show how the compounds with empirical formula Me_2ENMe_2 with E = B and Al differ from one another. Why are they so different?

$Me_2B–NMe_2$ is a monomer isoelectronic with $Me_2C=CMe_2$; B is small enough for effective $p\pi$-$p\pi$ overlap to occur. Hypothetical cyclic $[Me_2B–NMe_2]_2$ with a structure like the Al compound below would probably be quite strained, as is cyclobutane, and would dissociate.



The monomeric structure is correct. See *J. Chem. Soc. (A)* **1970**, 992.
Greenwood's figure on p 209 refers to $Me_2BN\underline{H}_2$.
$Me_2Al–NMe_2$ is a dimer with Me_2N bridging the Al atoms; Al is too large for effective $p\pi$-$p\pi$ donation from N. Al atoms are also too large to be satisfied with 3-coordinate, trigonal geometry like B adopts.



7. (15) a. Explain why thallium forms TlX and TlX_3 for all four halides (F, Cl, Br and I), whereas this is not true of the other group 13 elements.
All 8 Tl halides, i.e., TlF, TlCl, TlBr, TlI, TlF_3, $TlCl_3$, $TlBr_3$, and "TlI_3" are stable.
Tl has a much more stable +1 oxidation state than the other group 13 elements. This can be explained by the "inert lone pair effect", or simply by the fact that E-X bond enthalpies (or lattice enthalpies) decrease from small B to large Tl, so the 2nd and 3rd ionization enthalpies are not overcome by the formation of 3 rather weak Tl-X bonds. Thus only Tl forms stable monohalides. However, for B the B_nX_n clusters are known and pretty stable for x = 8, 9. AlX disproportionates to Al and AlX_3. Tl^{3+} is a weak enough oxidant that it can coexist with F^- and Cl^-. (For Br^- and I^- see parts b and c.)

b. Comment on the existence of TlI_3. [Hint: are there three I^- anions?]

TlI_3 is really thallium (I) triiodide $Tl^+ [I\text{-}I\text{-}I]^-$.
Tl^{3+} is a strong enough oxidant to oxidize iodide to iodine:

Half-reaction	ε° (V)
$Tl^{3+} + 2e^- \rightarrow Tl^+$	1.25
$3\, I^- \rightarrow I_3^- + 2\, e^-$	-0.55
	+0.70 V

c. Explain the curious thermal behavior of TlX_3: TlF_3 is stable to about 500°C; $TlCl_3$ loses Cl_2 at about 40°C to give an insoluble white salt; $TlBr_3$ loses bromine just above room temperature to give first "$TlBr_2$", then an insoluble pale yellow solid.

TlF_3 is stable to about 500°C because Tl-F "bond" (i.e., lattice enthalpy) is strong enough to overcome the 2nd and 3rd ionization enthalpies of Tl; F^- is much too difficult to oxidize for Tl^+.
$TlCl_3$ loses Cl_2 at about 40°C to give an insoluble white salt
$TlCl_3 \rightarrow TlCl\,(s) + Cl_2\,(g)$
is driven by the irreversible (in an open system) evolution of chlorine gas.
$TlBr_3$ loses bromine just above room temperature to give first "$TlBr_2$", then an insoluble pale yellow solid.

$TlBr_3 \rightarrow$ "$TlBr_2\,(s)$" $+ 1/2\, Br_2\,(l) \rightarrow TlBr\,(s) + 1/2\, Br_2\,(l)$

$TlBr_2$ is really the mixed valent compound $Tl^{I+}\ [Tl^{III}Br_4]^-$
The decomposition reactions become more favorable in the order
$TlF_3<TlCl_3<TlBr_3<$"TlI_3"
both because of the lower bond (lattice) enthalpies for the heavier halogens, and because the increasing ease of oxidation of the halogens
for $X_2 + 2\, e^- \rightarrow 2\, X^-$

	ε° (V)
F	2.87
Cl	1.40
Br	1.09
I	0.62

therefore Cl^- doesn't reduce Tl^{3+} under equilibrium conditions.