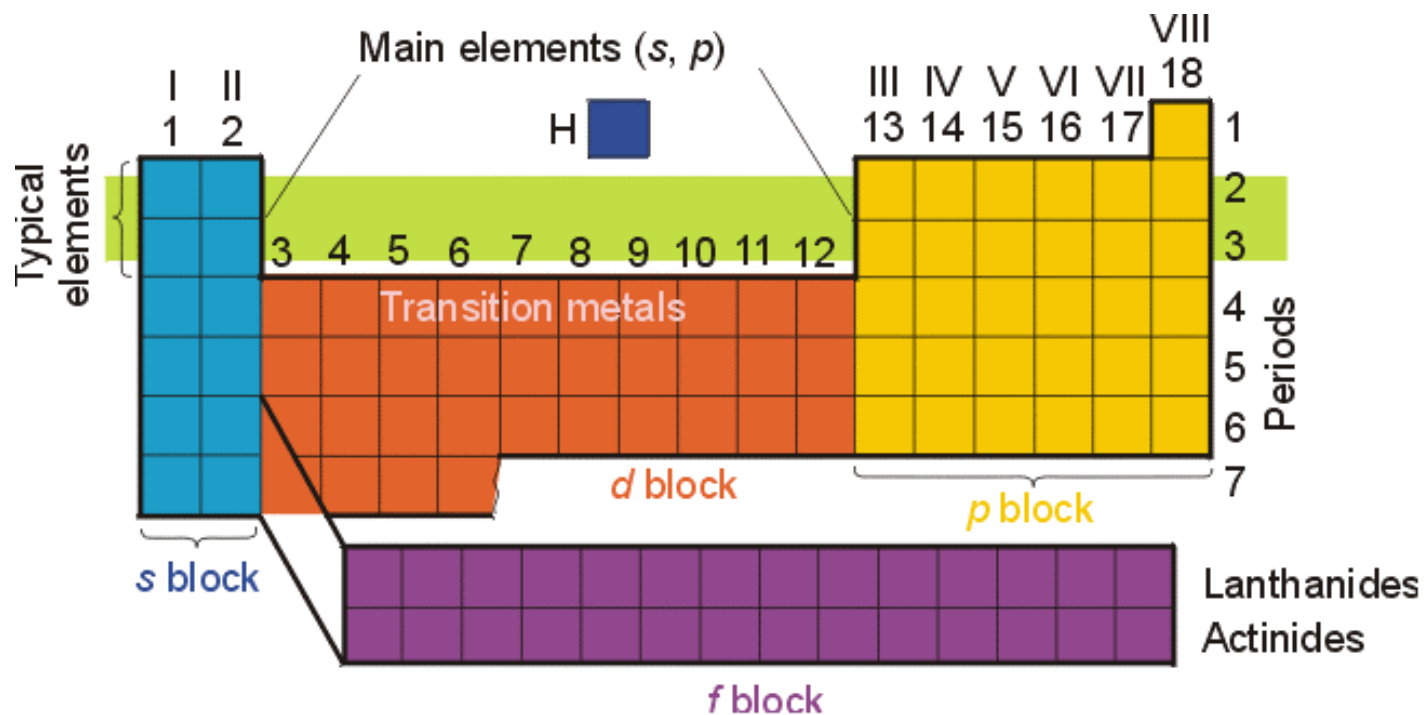
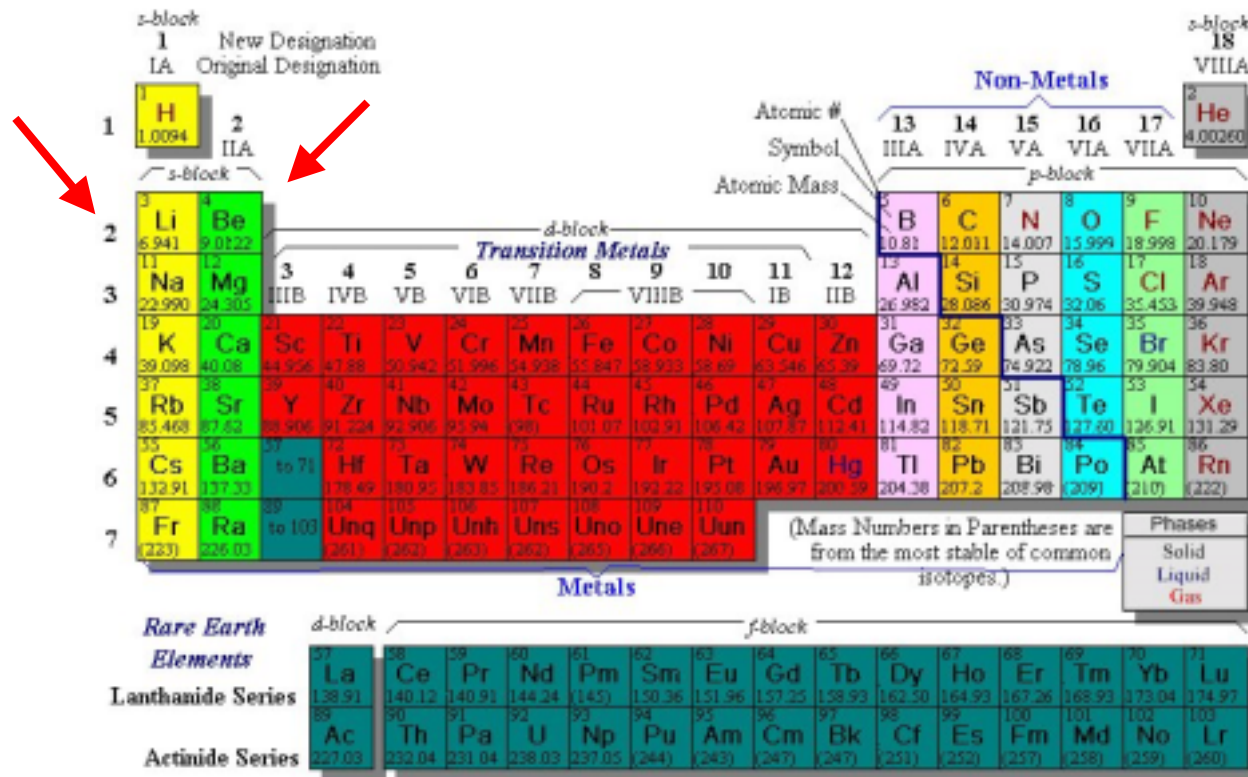


## Selected Aspects of Main Group Chemistry

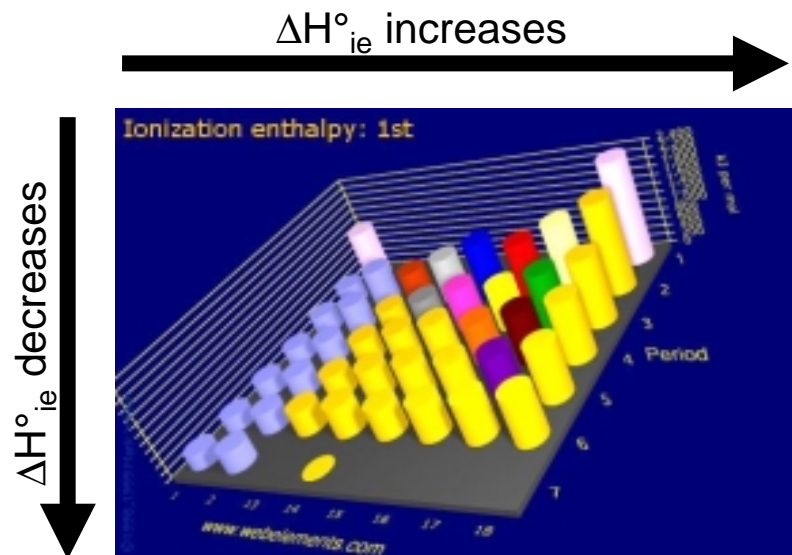
For the rest of the course, we will look at some aspects of the chemistry of main group compounds. The basic principles that you have learned concerning atoms, molecules and bonding (covalent and ionic) can be used to understand the reactivity and structures that are observed for elements and compounds throughout the periodic table. We only have time to look at some examples from the groups that comprise the Main group (the s-block and the p-block elements).





Much of the important chemistry of the alkali and alkaline earth metals can be understood on the basis of their low ionization enthalpies (or electronegativities) and the favourability of ionic bonding.

The s-block elements lose their electrons more easily than the other element in the main group so they are usually strong reducing agents and most tend to form ionic compounds. The stabilization that is provided by the crystal lattice (or hydration) energy of the salts they make helps to favour many reactions.



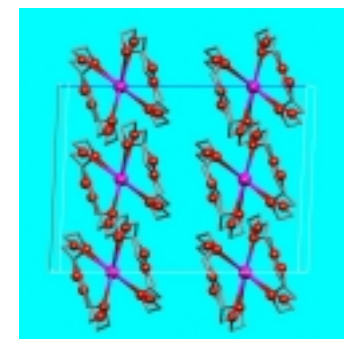
One of the stranger consequences of the low ionization enthalpy is observed when some of the group 1 metals are dissolved in appropriate solvents, such as liquid ammonia:



At low concentration this is a blue solution that contains solvated electrons! If the reaction warms up or is catalyzed, the free electron reacts with the solvent to reduce some of the protons in the solvent to produce hydrogen gas:



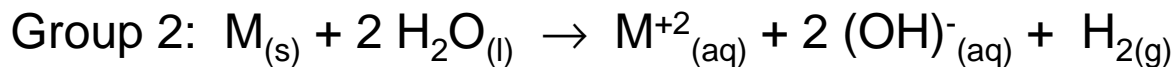
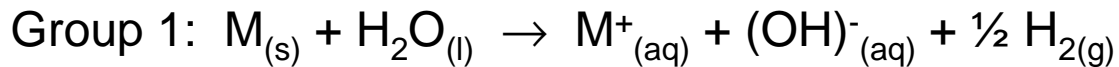
This demonstrates the reducing ability of the alkali metals and is a very common and useful property of these elements.



X-ray crystal structure of  $[\text{Cs}^+\text{L}_2][\text{e}^-]$

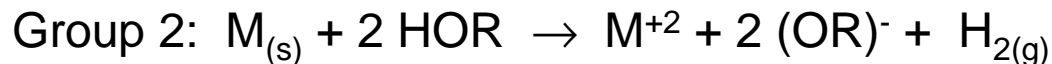
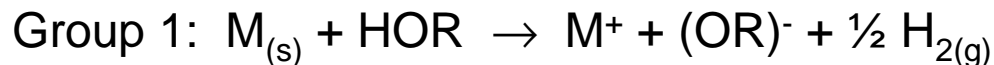
The s-block metals are used as reducing agents for an immense number of different types of compounds.

Reactions of the elements with water:

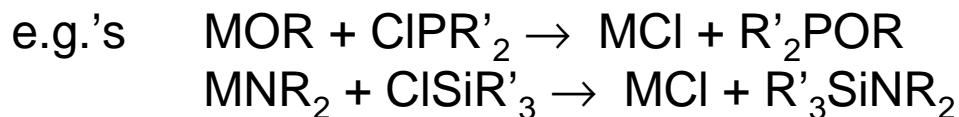


These reactions are very exothermic and increase in violence from the lightest to the heaviest elements in the group (enough to ignite the  $H_2$  for the heavier elements). The non-reversible nature of this reaction means that such metals are very useful for drying many kinds of solvents.

More generally:

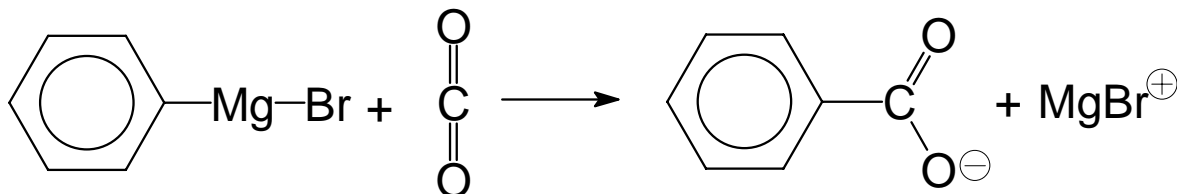
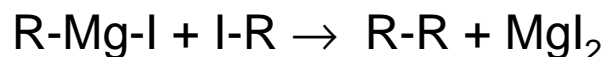
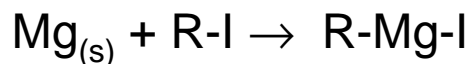


These reactions make metal alkoxides that are very useful for the synthesis of other products using *metathesis* reactions. Metathesis indicates that the reagents exchange ligands with one another. Such reactions are especially favourable when it produces a metal halide because of the large exothermicity provided by the lattice or hydration energies.

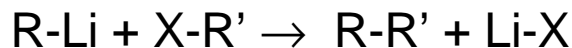
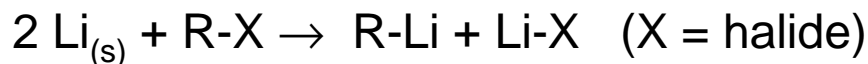




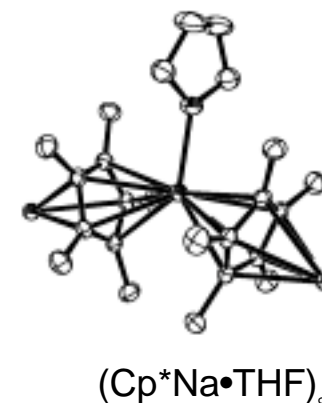
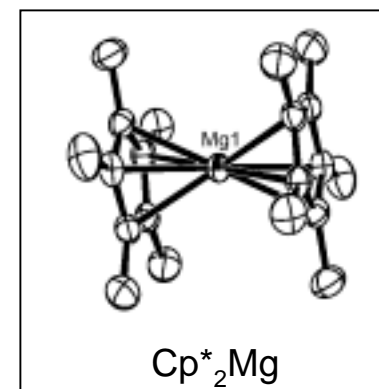
One of the most important discoveries in synthetic chemistry was made by Victor Grignard (Nobel Prize 1912) following the initial work of others. He showed that the reaction of Mg with organic iodides (RI, later applied to other halides) results in the insertion of the Mg into the R-I bond. This provides a reagent of the form R-Mg-I that can be used in nucleophilic or metathesis reactions to make new carbon-carbon bonds.



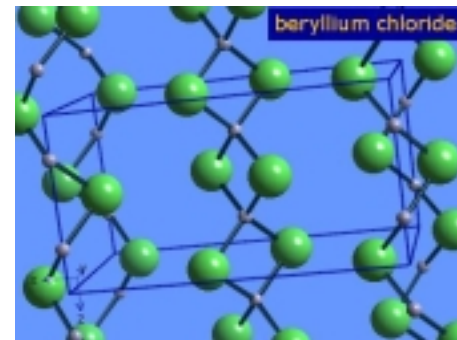
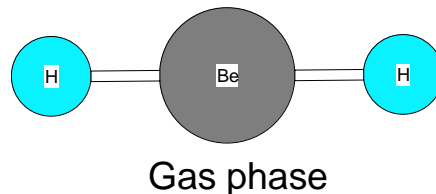
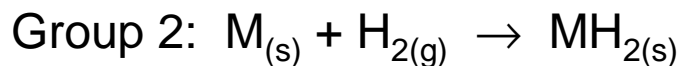
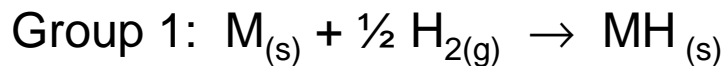
Analogous and more reactive reagents can be made with Li and Na.



Such compounds were among the first that were recognized to contain bonds between metals and carbon. These were thus some of the initial examples of *organometallic* chemistry (one of the most studied branches of inorganic chemistry today).



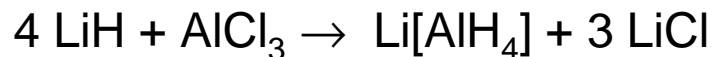
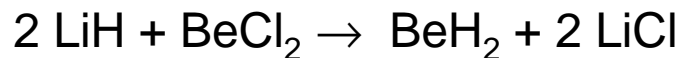
The s-block metal hydrides are also very useful compounds that can usually be made by the reaction of the metal with  $\text{H}_{2(g)}$ ; this does not work for  $\text{BeH}_2$  - you can use a Born-Haber cycle to figure out why. The H atoms are hydrides ( $\text{H}^-$ ), which gives them a totally different kind of chemistry than protons ( $\text{H}^+$ ). All of the s-block hydrides are ionic except for  $\text{LiH}$ ,  $\text{BeH}_2$  and  $\text{MgH}_2$ , which have significant covalent character.



The coordination polymer solid state structure of  $\text{BeH}_2$  is similar to that of  $\text{BeCl}_2$  →

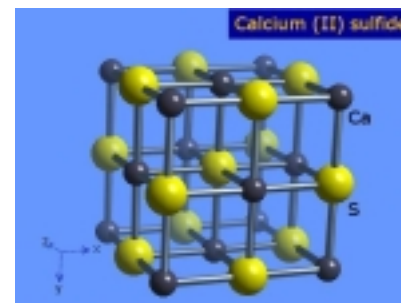
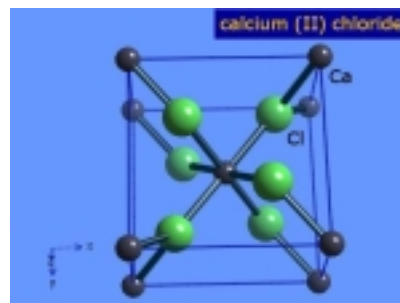
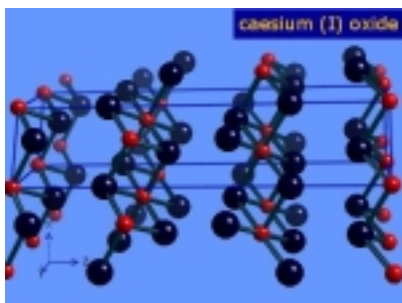
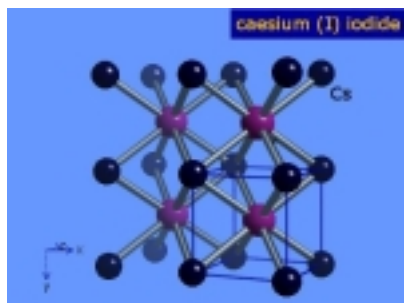
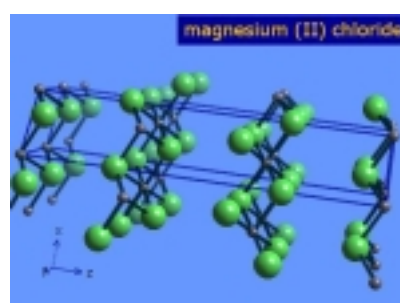
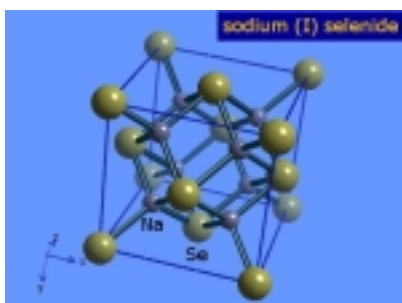
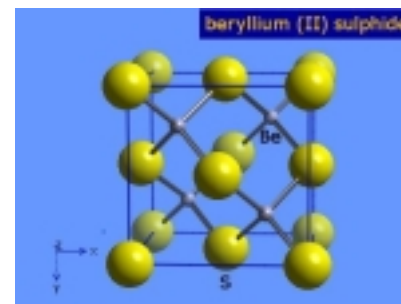
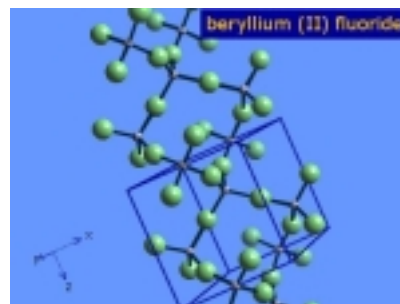
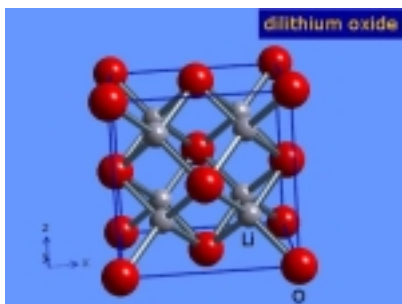
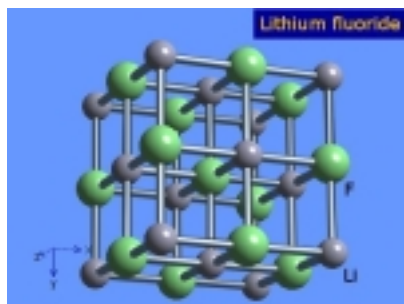
These reagents also react with water in a very exothermic fashion to make gaseous  $\text{H}_2$ . The non-reversible nature of this reaction means that such metal hydrides (especially  $\text{CaH}_2$ ) are also very useful for drying many kinds of solvents.

More importantly, the group 1 and 2 metal hydrides are excellent reagents for putting H atoms onto other elements by metathesis reactions:





Because of their low electronegativities, most of the s-block metal halide or chalcogenide compounds are salts with ionic structures. The lattice (or hydration) energies of such compounds are often used to drive reactions to completion.





# Chem 59-250 Group 13 elements - sometimes called “Earth metals”

Periodic table showing Group 13 elements (Al, Ga, In, Tl) highlighted in pink. A red arrow points to this group. The table includes atomic numbers, symbols, atomic masses, and phase indicators (Solid, Liquid, Gas). The Lanthanide and Actinide series are shown at the bottom.

Atomic #	Symbol	Atomic Mass	Phase
13	Al	26.982	Solid
31	Ga	69.72	Solid
49	In	114.82	Solid
81	Tl	204.38	Solid

**Rare Earth Elements**

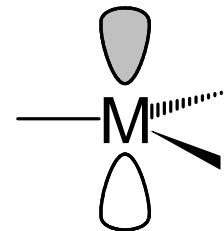
Atomic #	Symbol	Atomic Mass
57	La	138.91
58	Ce	140.12
59	Pr	140.91
60	Nd	144.24
61	Pm	(145)
62	Sm	150.36
63	Eu	151.96
64	Gd	157.25
65	Tb	158.93
66	Dy	162.50
67	Ho	164.93
68	Er	167.26
69	Tm	168.93
70	Yb	173.04
71	Lu	174.97

**Actinide Series**

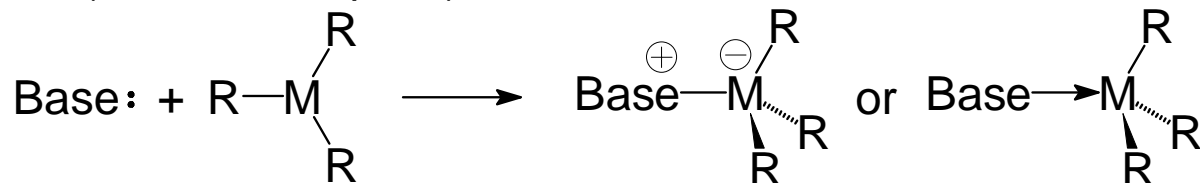
Atomic #	Symbol	Atomic Mass
89	Ac	227.03
90	Th	232.04
91	Pa	231.04
92	U	238.03
93	Np	237.05
94	Pu	(244)
95	Am	(243)
96	Cm	(247)
97	Bk	(247)
98	Cf	(251)
99	Es	(252)
100	Fm	(257)
101	Md	(258)
102	No	(259)
103	Lr	(260)

Much of the important chemistry of the group 13 elements can be understood on the basis of their electronic structure. Since the elements have a  $[\text{core}]ns^2 np^1$  electron configuration, neutral group 13 compounds can form up to three bonds. This only provides for 6 electrons (not a complete octet) around the group 13 atom so such compounds are called “electron-deficient”.

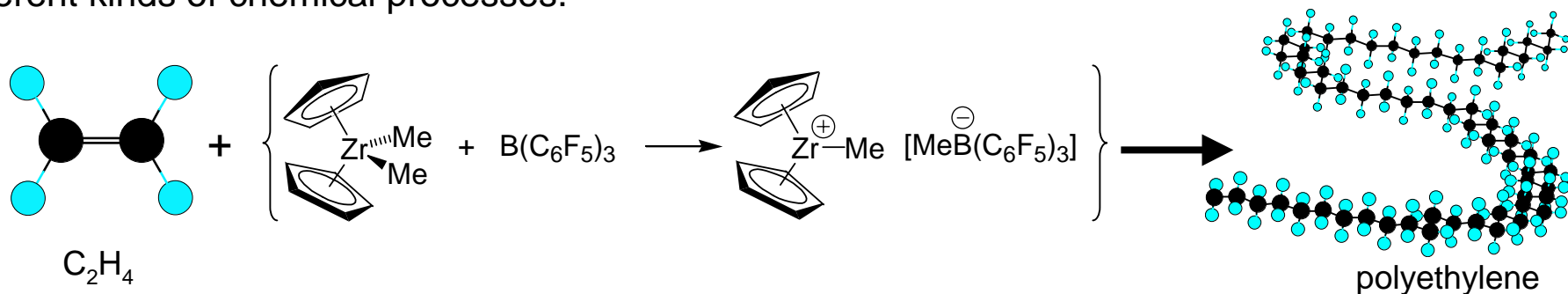




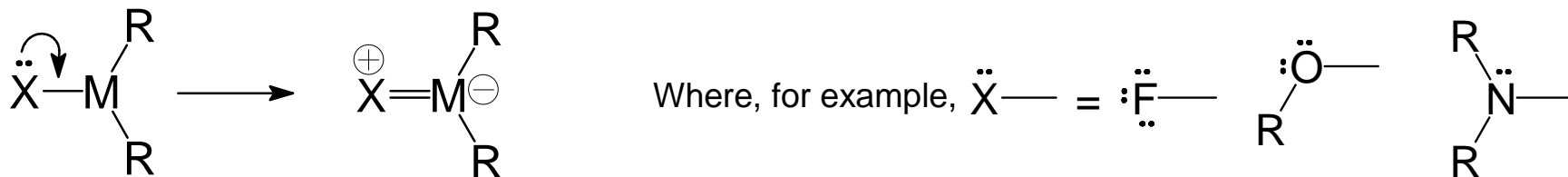
Because of their electron-deficient nature, group 13 compounds containing the element (**M**) in the (+3) oxidation state have a formally vacant  $np_z$  orbital and usually act as Lewis acids (electron acceptors).



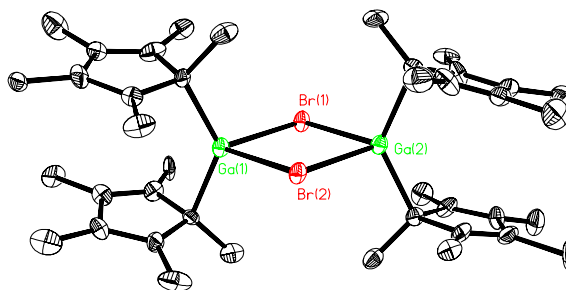
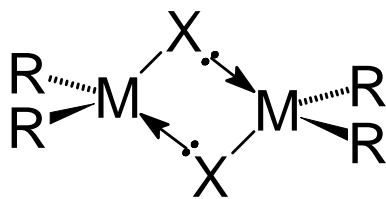
This is probably the most important feature of group 13 reagents and they are used in organic synthesis (e.g. Friedel-Crafts alkylation or acylation) and as catalysts or co-catalysts for many different kinds of chemical processes.



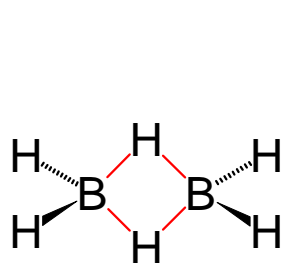
To obtain electron density to fill the empty orbital, group 13 compounds can also form “partial” multiple bonds with terminal atoms that contain lone pairs of electrons. The extent to which this happens depends on the energies of the AO's involved (the empty  $np_z$  orbital and those of the lone pairs) and as you would expect from MO theory it happens mostly for boron.



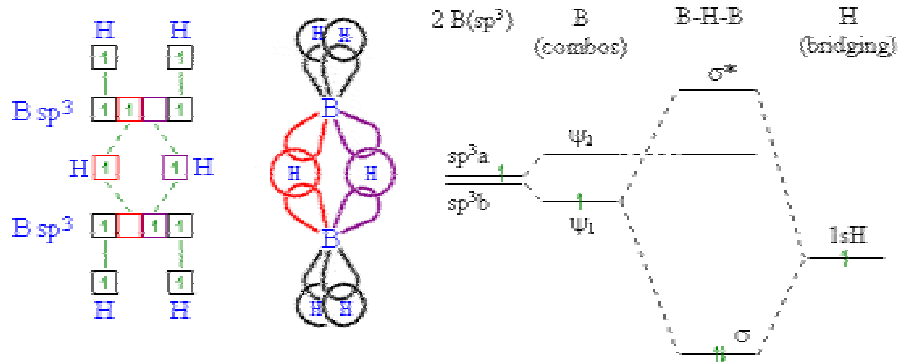
For the heavier elements, “bridging” is often observed if there are no other electron donors to provide electron density to the vacant orbital. If the substituents contain lone pairs of electrons, the bridges can be formed from two two-electron donor-acceptor bonds:



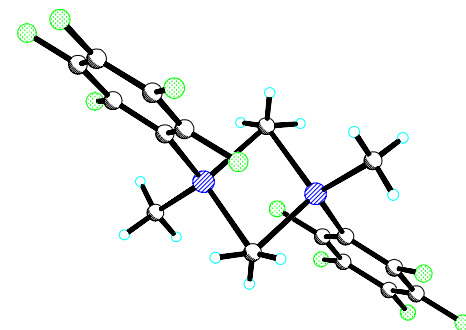
When the substituents do not have any lone pairs of electrons, the bridges can be formed from from three-center-two-electron bonds (sometimes called banana bonds). Such bonds are readily explained by MO theory or a combination of VBT and MO theory:



Diborane

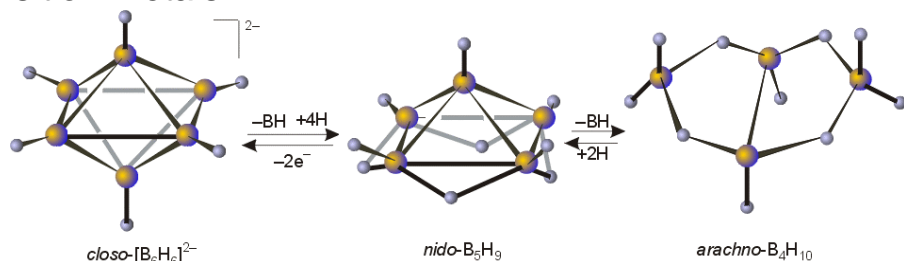


Instead of using pure AO's the SALCs for this MO diagram are two  $sp^3$  hybrids from each B and the two 1s AO's for the bridging H atoms.

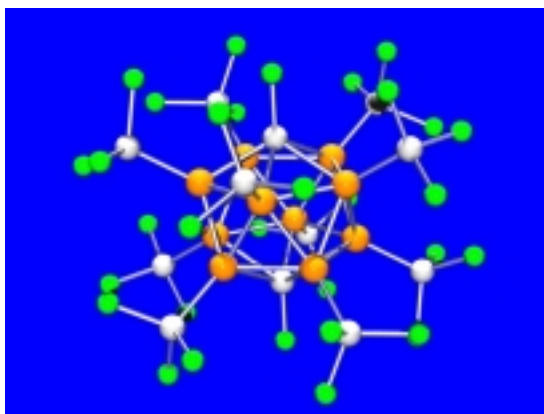


For the even more electropositive element Al, even methyl groups can bridge. e.g.  $[(C_6F_5)AlMe_2]_2$

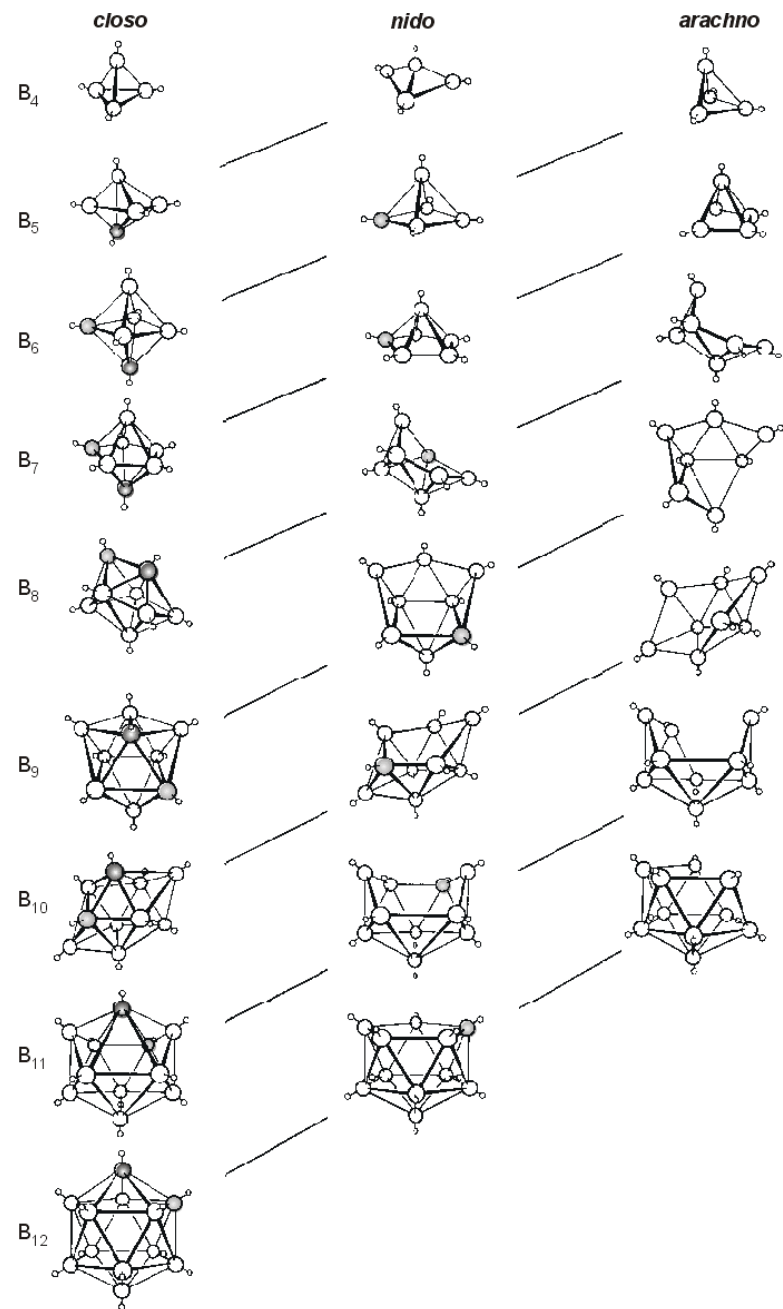
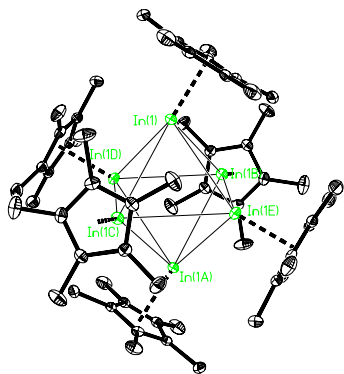
Another consequence of the electron deficiency of the group 13 compounds is that they tend to form clusters under conditions where no other sources of electrons are available. The pyrolysis of  $B_2H_6$  produces a variety of clusters and evolves  $H_2$  gas. Once formed, many of these polyboranes are stable compounds and many other elements can be placed into the skeleton of borane clusters including carbon, other main group elements and transition metals.



Count the number of bonds to the carbon atom (white) in the carborane cluster... the rules of organic chemistry do not apply!




There are rules that allow us to predict the structure and understand the bonding of such clusters, but those will be left for a future course!





# Chem 59-250 Group 14 elements - the group with no name

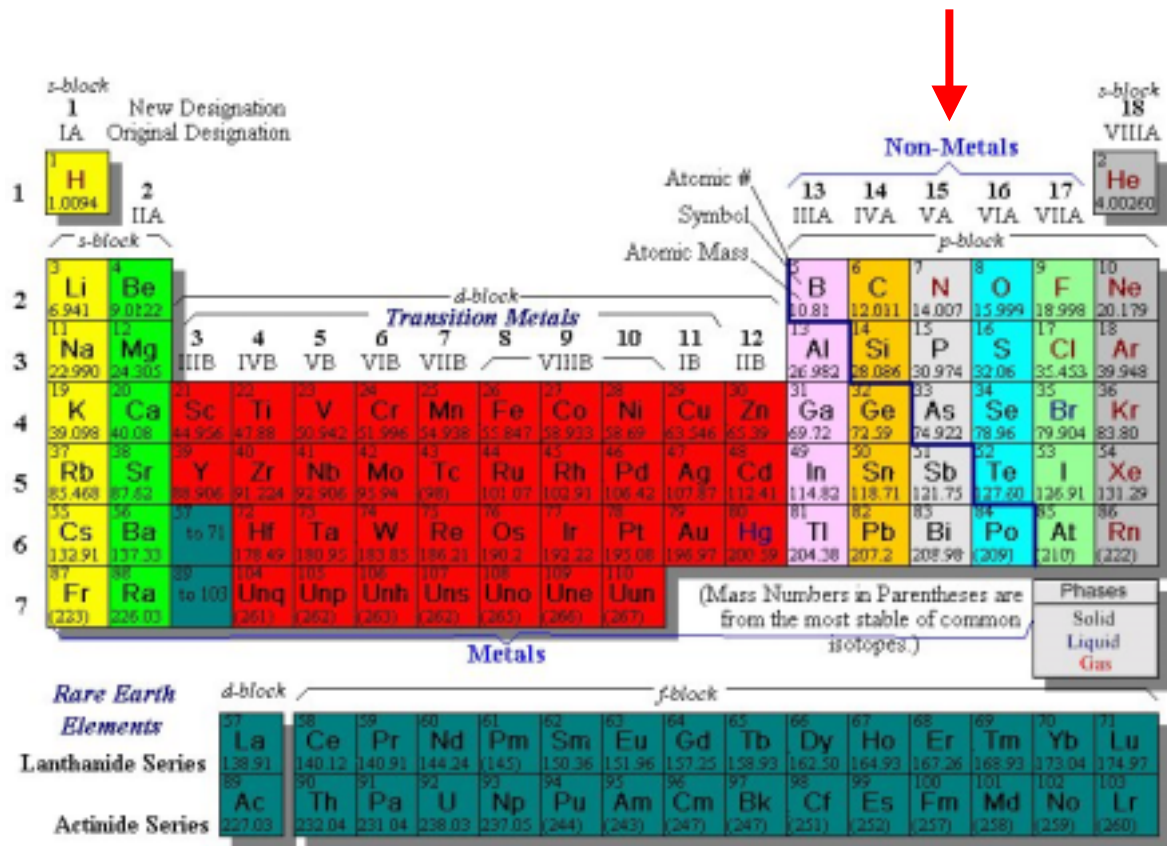


s-block		New Designation										s-block														
1		Original Designation										18														
IA		IIA-VIIA										VIIIA														
1	H 1.008											2	He 4.00260													
s-block		d-block										p-block														
2	Li 6.941	Be 9.0122	Transition Metals										B 10.81	C 12.011	N 14.007	O 15.999	F 18.998	Ne 20.179								
3	Na 22.990	Mg 24.305	3	4	5	6	7	8	9	10	11	12	Al 26.982	Si 28.086	P 30.974	S 32.06	Cl 35.453	Ar 39.948								
4	K 39.098	Ca 40.08	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga 69.72	Ge 72.59	As 74.922	Se 78.96	Br 79.904	Kr 83.80								
5	Rb 85.468	Sr 87.62	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In 114.82	Sn 118.71	Sb 121.75	Te 127.60	I 126.91	Xe 131.29								
6	Cs 132.91	Ba 137.33	to 71	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl 204.38	Pb 207.2	Bi 208.98	Po (209)	At (210)	Rn (222)								
7	Fr (223)	Ra (226.03)	to 103	Unq	Unp	Unh	Uns	Uno	Une	Uun	(Mass Numbers in Parentheses are from the most stable of common isotopes.)								Phases Solid Liquid Gas							
Rare Earth Elements		d-block										f-block														
Lanthanide Series		La 138.91	Ce 140.12	Pr 140.91	Nd 144.24	Pm (145)	Sm 150.36	Eu 151.96	Gd 157.25	Tb 158.93	Dy 162.50	Ho 164.93	Er 167.26	Tm 168.93	Yb 173.04	Lu 174.97										
Actinide Series		Ac 227.03	Th 232.04	Pa 231.04	U 238.03	Np 237.05	Pu (244)	Am (243)	Cm (247)	Bk (247)	Cf (251)	Es (252)	Fm (257)	Md (258)	No (259)	Lr (260)										

Much of the important chemistry of the group 14 elements can be understood on the basis of their electronic structure. Since the elements have a  $[\text{core}]ns^2 np^2$  electron configuration, neutral group 14 compounds usually form up to four bonds. This uses all the electrons and orbitals around the atom (a complete octet) around the group 14 atom so such compounds are called “electron-precise”.



# Chem 59-250 Group 15 elements - sometimes called "Pnictogens"



Much of the important chemistry of the group 15 elements can be understood on the basis of their electronic structure. Since the elements have a [core]ns<sup>2</sup> np<sup>3</sup> electron configuration, neutral group 15 elements can form up to five bonds. This provides for two common oxidation states (+3 and +5) around the group 15 atom so such compounds are called "electron-rich".



# Chem 59-250 Group 16 elements - the Chalcogens

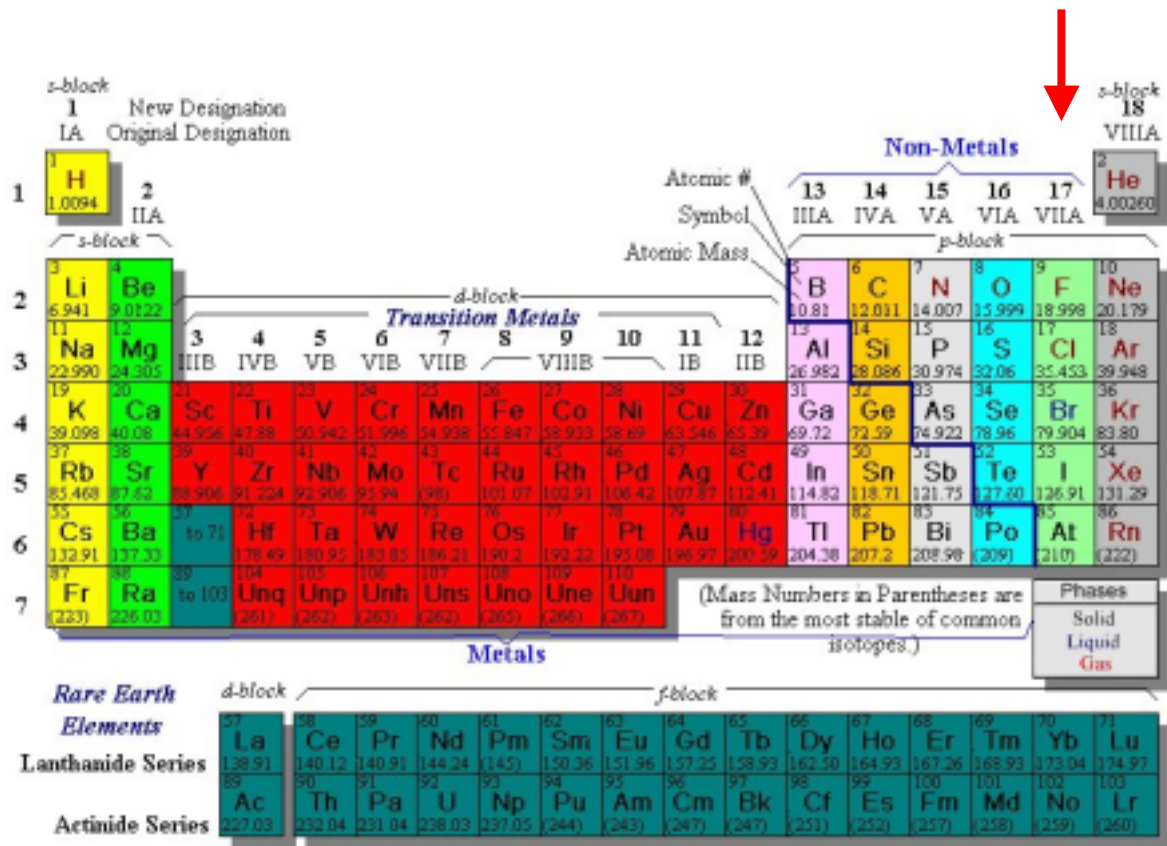
The periodic table shows the following elements in Group 16 (Chalcogens):

Period	Group 16 Element	Atomic #	Symbol	Atomic Mass	Phase
1	Hydrogen	1	H	1.008	Gas
2	Oxygen	8	O	15.999	Gas
3	Sulfur	16	S	32.06	Solid
4	Selenium	34	Se	78.96	Solid
5	Tellurium	52	Te	127.60	Solid
6	Polonium	84	Po	(209)	Solid

The table also includes the Lanthanide Series (La to Lu) and Actinide Series (Ac to Lr) at the bottom.

Much of the important chemistry of the group 16 elements can be understood on the basis of their electronic structure and electronegativity. Since the elements have a  $[\text{core}]ns^2 np^4$  electron configuration, neutral group 16 compounds can form up to six bonds. This provides for common oxidation state from -2 to +6 electrons (with a complete octet) around the group 16 atom so such compounds are also “electron-rich” but the high electronegativities of O and S make them good oxidizing agents.

# Chem 59-250 Group 17 elements - the halogens



Much of the important chemistry of the group 17 elements can be understood on the basis of their electronic structure and electronegativity. Since the elements have a  $[\text{core}]ns^2 np^5$  electron configuration, neutral group 17 compounds can form up to seven bonds. This provides for several possible oxidation states (with a complete octet of electrons around the group 17 atom) although -1 is the most common. The structures of the poly halides are the typical examples used for VSEPR theory.

# Chem 59-250 Group 18 elements - the noble gases

The periodic table shows the following elements in Group 18 (Noble Gases):

Atomic #	Symbol	Atomic Mass	Phase
2	He	4.00260	Gas
18	Ar	39.948	Gas
36	Kr	83.80	Gas
54	Xe	131.29	Gas
86	Rn	(222)	Gas

Other elements shown include H, Li, Be, Na, Mg, Al, Si, P, S, Cl, Br, I, At, Fr, Ra, and the Lanthanide and Actinide series.

The chemistry of the group 18 elements seems to defy their electronic structure. Since the elements have a  $[\text{core}]ns^2 np^6$  electron configuration with a complete octet, one would predict that there would be no chemistry for the noble gases. However, numerous group 18 compounds are known, although they may be very unstable and explosive! Understanding the reactivity of group 18 compounds requires an examination of their ionization potentials.