

13
5 <b>B</b> 10,811
13 <b>Al</b> 26,9815
31 <b>Ga</b> 69,72
49 <b>In</b> 114,82
81 <b>Tl</b> 204,37

# Entering the p-block...

The Group 13 ...and the things become complicated

# Occurrence

- Occur only in minerals (never in elemental state)

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31 <b>Ga</b> 69,72
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*Buraq* (Arab.) borax, 9 ppm (Earth Crust)

*Alum* =  $\text{MAI}(\text{SO}_4)_2$ , double salts, 83 000 ppm

*Gallia* (lat.) = France, 19 ppm

*Indigo* = the colour of spectral line, 0.24 ppm



*Thallos* (gr.) = green twig (spec. line), 0.70 ppm



*Alum crystal*  
( $M = K$ )

Data from J. Emsley 'The Elements' Oxford: Clarendon Press, 1989

# Isolation

13
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Treatment of borax ( $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \times 8\text{H}_2\text{O}$ ) with a strong acid gives  $\text{B}(\text{OH})_3$  which on heating gives  $\text{B}_2\text{O}_3$ , and  $\text{B}_2\text{O}_3$  is further reduced with Mg.

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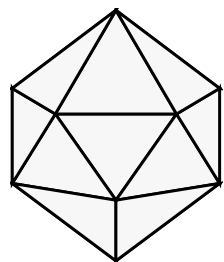
From bauxite (a rock), electrolysis of bauxite solution in molten cryolite ( $\text{Na}_3\text{AlF}_6$ ) using graphite electrodes (requires a lot of energy).

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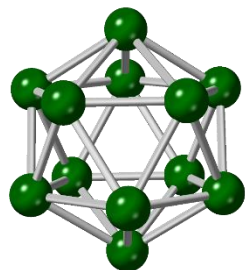
By-products in extraction of other metals (Al, Zn, Cu and Pb).

# The Structures of Elements: Boron

- Boron, the only non-metallic element in the group, has several allotropes (**Allotropes** are different structural modifications of an element.)
- The simplest structure of elemental boron consists of covalently bonded  $B_{12}$  icosahedra:

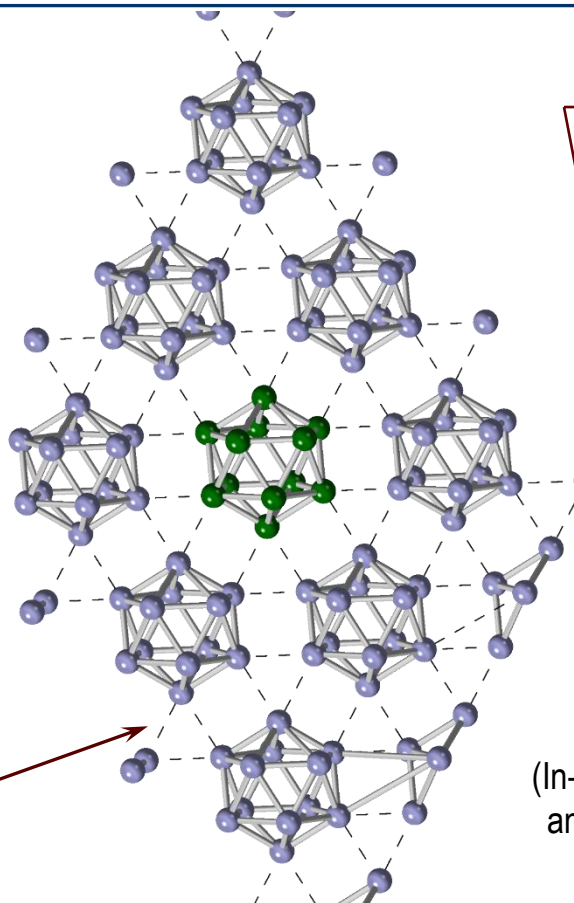


**Icosahedron** consists of 20 identical equilateral triangular faces, 30 edges and 12 vertices

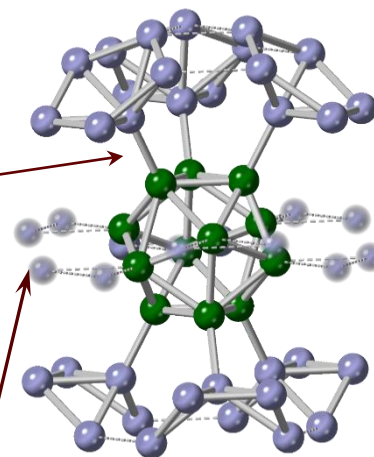


One  $B_{12}$  icosahedron with B atom on each vertex (electrons are delocalized inside each icosahedron) Note that the sticks here do not represent typical bonds!

In a most stable allotrope ( $\alpha$ -rhombohedral), each  $B_{12}$  is surrounded by six other  $B_{12}$  clusters, connected through weak 3c bonding (dashed triangles)...



...and then further to three  $B_{12}$  in plane above and three in plane below via 2c bonds

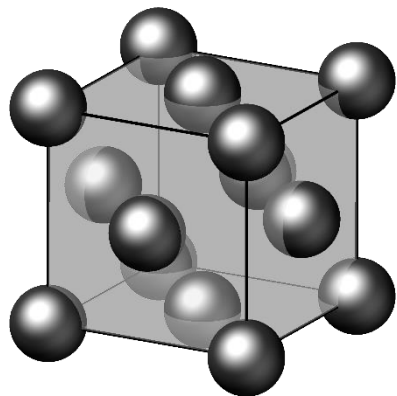


(In-plane bonds and B atoms)

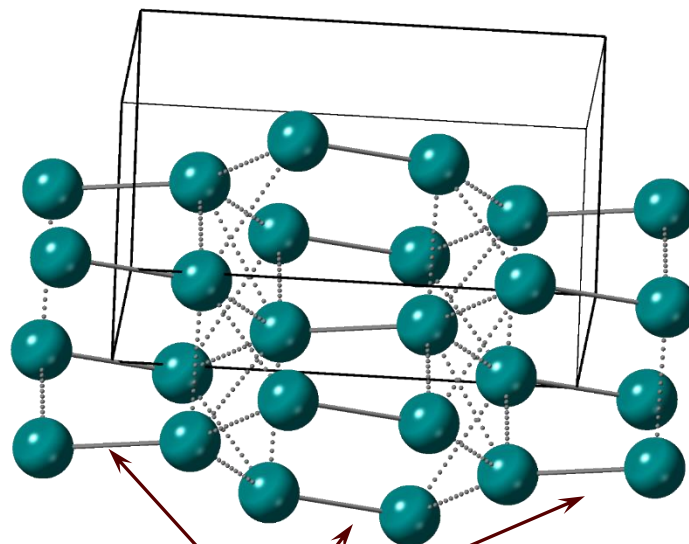
**This clustering of born atoms is an important aspect of boron chemistry!**

# The Structures of Elements: Aluminum and Gallium

**Aluminum**, a typical metal has a face-centered cubic structure (based on ccp; solid state lecture)



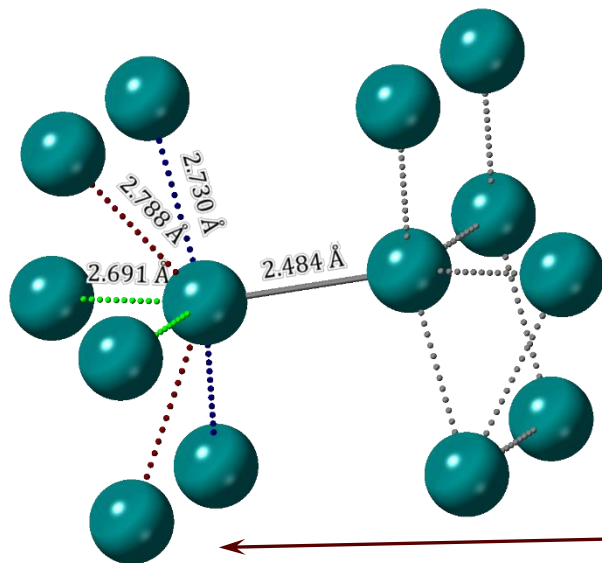
**Gallium** has a very unique structure:



Each Ga has one very close neighbor at 248 pm distance...

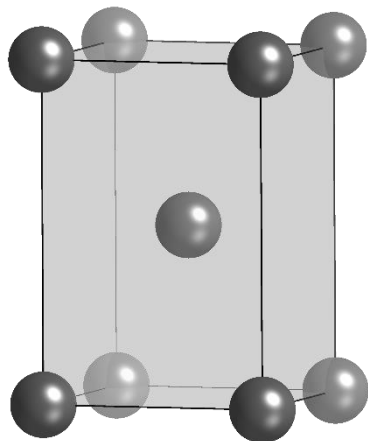
...and then six more Ga atoms at greater distances that come in pairs.

Atom	Nº	d [Å]
Ga1	11	2.4840
Ga1	17	2.6907
Ga1	9	2.6907
Ga1	7	2.7299
Ga1	16	2.7299
Ga1	15	2.7883
Ga1	6	2.7883

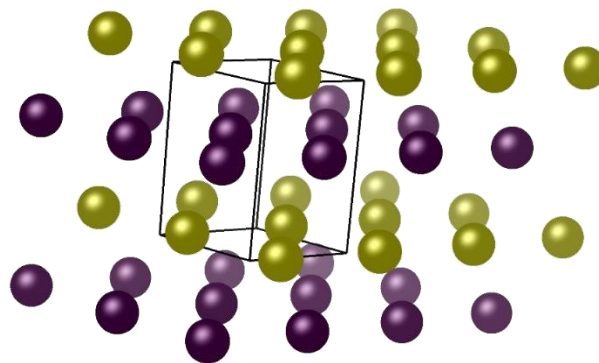
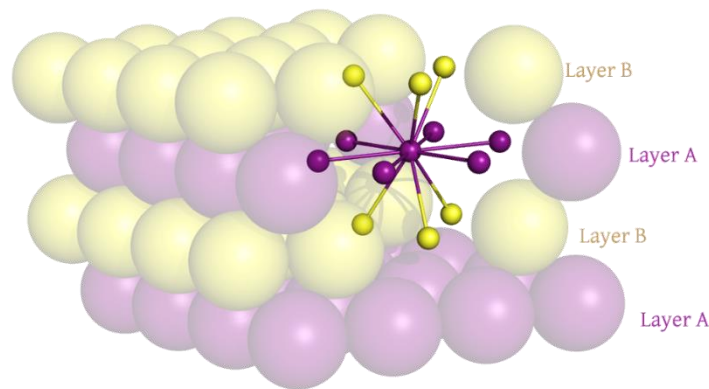


# The Structures of Elements: Indium and Thallium

**Indium** has a body-centered  
*tetragonal* structure



**Thallium** has a hexagonal structure  
(based on hcp, solid state lecture)



# General reactivities

- The presence of p orbitals introduces new patterns in reactivities, both for elements and their compounds (3 electrons but 4 orbitals – one s and three p), heavier members (Ga, In, Tl) have filled (n-1)d orbitals and Tl has additional 4f<sup>14</sup> set as core electrons.
- B ( $\chi_P = 2.0$ ) is a non-metallic element and forms covalent bonds with majority of other elements, no evidence for B<sup>3+</sup> cation under normal chemical conditions (too high charge density). It is a rather inert element reacting under normal conditions only with F<sub>2</sub> and HNO<sub>3</sub>.
- Al ( $\chi_P = 1.6$ ) is strongly reducing, is readily oxidized on air but is passivated; it reacts easily with dilute acid solutions.
- Ga, In & Tl react with dilute acids as well.
- B and Al form very strong bonds with oxygen, heavy Group 13 elements prefer S and P.

# Physical properties of the elements

- Bulk physical properties (particularly mp and bp) are difficult to compare due to the differences in bonding and structure

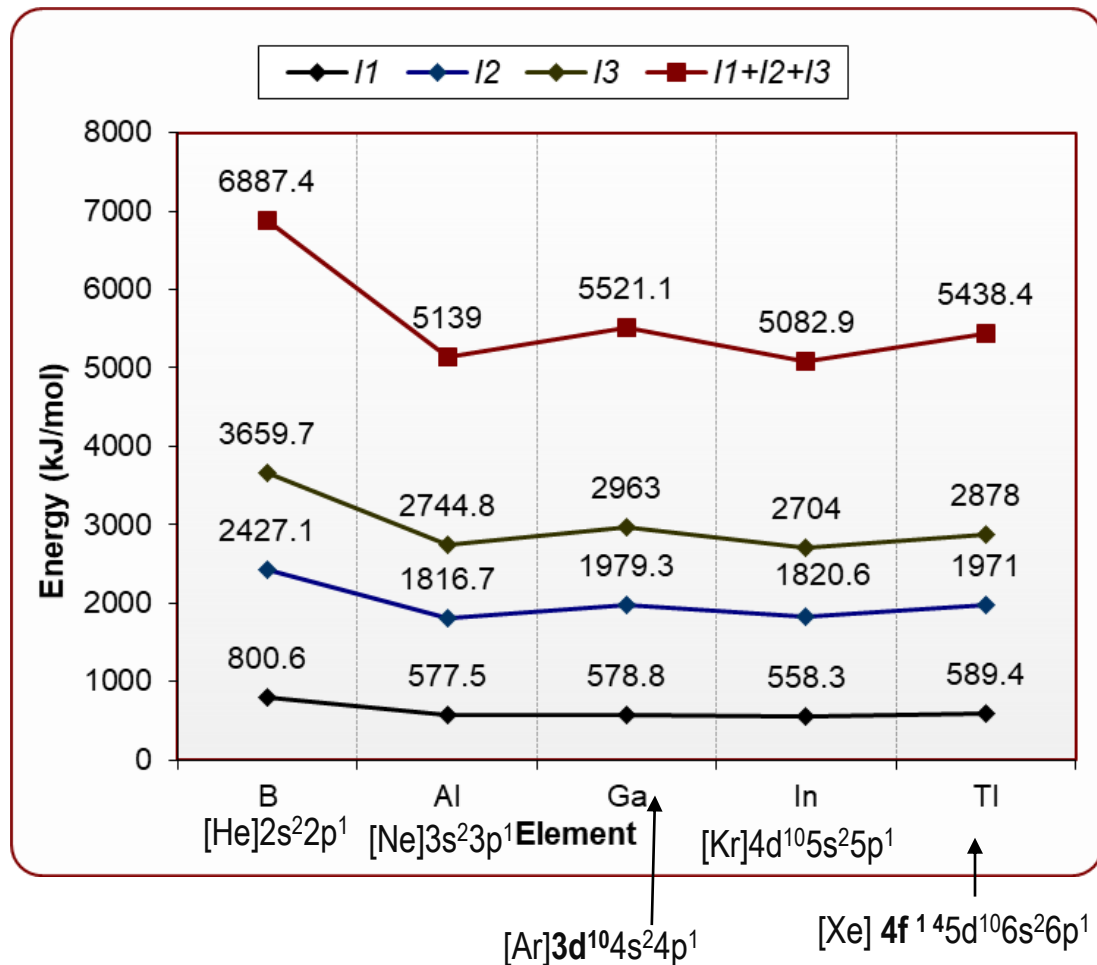
Property	B	Al	Ga	In	Tl
Melting point (°C)	2092	660	29.8	156	303
Boiling point (°C)	4000	2520	2205	2073	1473
$\Delta_{\text{sub}} H^\circ$ (kJ/mol) <sup>a)</sup>	560	329.7	286.2	243	182.2
Metallic radius (pm)	—	143	125-135	167	170
Ionic radius (pm) for +1	—	—	120	140	150
Ionic radius (pm) for +3	“27”	53.5	62	80	88.5
$E^\circ_{\text{M}^+/ \text{M}}$ (V)	—	+0.55	−0.79	−0.18	−0.336
$E^\circ_{\text{M}^{3+}/ \text{M}}$ (V)	—	−1.676	−0.529	−0.338	+1.26

a) Sublimation to monoatomic gas!



# Physical properties of the elements (cont.)

- Important to look at are ionization potentials:



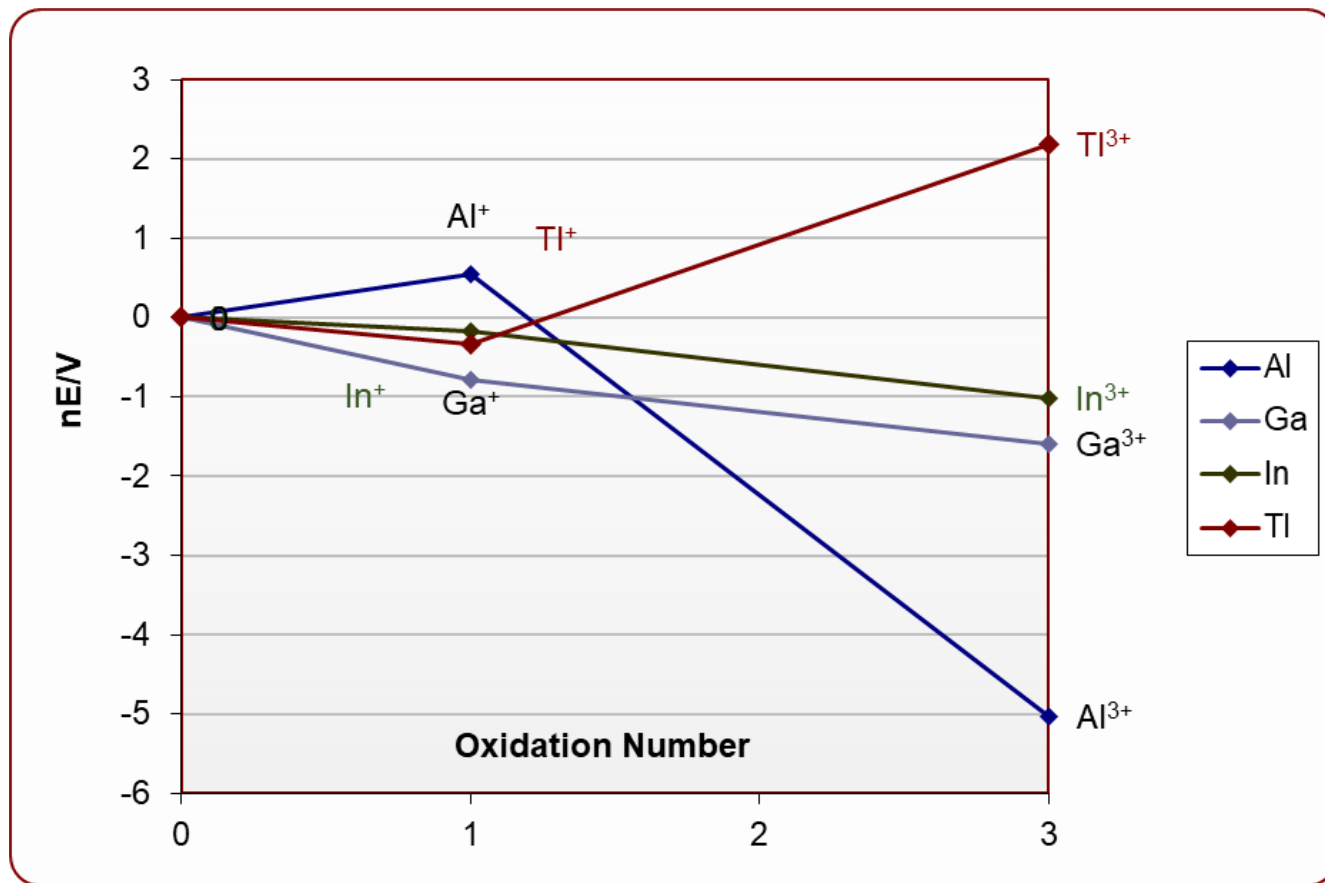
**First:** a very high ionization energies for boron—no wonder B likes to share electrons not loose them!

**Second:** the decrease in ionization potential from B to Al is not followed by the expected, further decrease to Ga. The d<sup>10</sup> electrons that transition metals add do not shield the extra 10 positive charges added—a property of D electrons that simple Slater rules *do not* account for!

**Third:** A decrease from In to Tl due to f electrons and lanthanide contraction!

# Chemical properties: Oxidation Numbers

*The Frost diagram for Al, Ga, In & Tl in aq. solution, pH=0*



13	Al	26,9815
31	Ga	69,72
49	In	114,82
81	Tl	204,37

Stability of max. O.N. decreases!

- There is a steady decrease in stability of O.N. +3 from Al to Tl
- Boron's aqueous chemistry is significantly different:



# Chemical properties & reactivities

- The most stable oxidation number for this group is +3 *except* for thallium which prefers +1.
- The 'Tl anomaly' can be explained using theory of relativity
  - Consider the following equations:

$$m = \frac{m_0}{\sqrt{1 - \left(\frac{v}{c}\right)^2}}$$

*The Einstein's theory of relativity: **increase** in mass as the velocity **increases**!*

$$v = \frac{Ze^2}{2\varepsilon_0 n\hbar}$$

*Velocity of an electron in the Bohr atomic model: increase in Z **increases** electron velocity (consequently, **increase** in Z **increases** the electron mass)*

$$r = \frac{Ze^2}{4\pi\varepsilon_0 m v^2}$$

*Radius of el. orbit in the Bohr model: increase in both velocity and mass **decreases** the radius – electrons come closer to the nucleus and are stabilized – **the case of 6s electrons in Tl.***

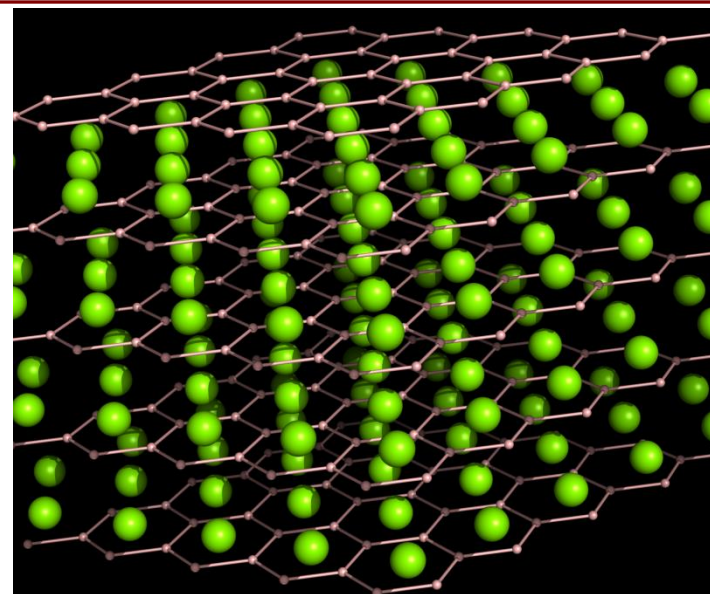
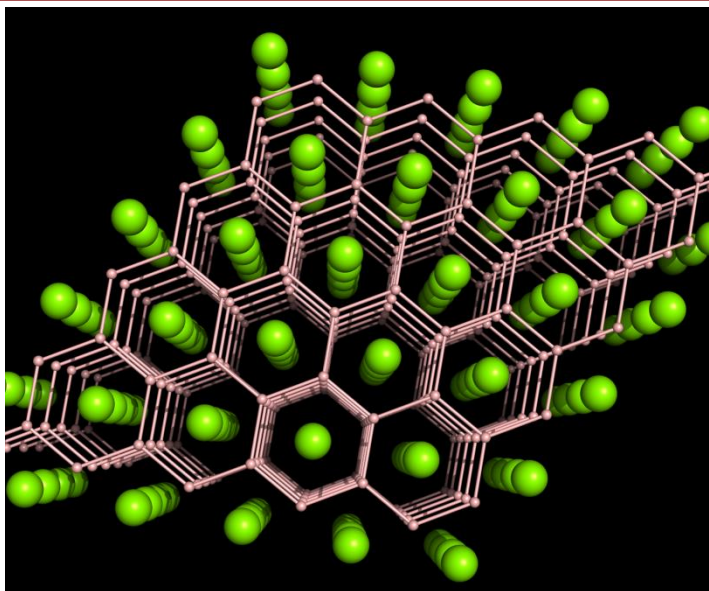
# Metal Borides

- Binary compounds with a general formula  $M_xB_y$  (where M is a metal).
- Boron has a negative oxidation number, but the *exact* value is commonly difficult to assign (see formulas below).
- Very important materials because of their physical properties: durability, hardness, electrical conductivity and ability to withstand stress and corrosion.
- Two classes:
  - **Boron rich** (more B than M):  $MB_3$ ,  $MB_4$ ,  $MB_6$ ,  $MB_{10}$ ,  $MB_{12}$ ,  $M_2B_5$  and  $M_3B_4$  (typical for s, p and f block metals)
  - **Metal rich** (more M than B):  $M_3B$ ,  $M_4B$ ,  $M_5B$ ,  $M_3B_2$  and  $M_7B_3$  (d block metals)
- Most common methods of synthesis:
  - From elements:  $Cr + nB \xrightarrow{\sim 1150^\circ C} CrB_n$
  - From oxides in the presence of a reducing agent (i.e. carbon):
$$V_2O_5 + B_2O_3 + 8C \xrightarrow{\sim 1500^\circ C} 2VB + 8CO$$
  - From M-oxide and boroncarbide:  $Eu_2O_3 + 3B_4C \xrightarrow{\sim 1600^\circ C} 2EuB_6 + 3CO$

# Selected boride structures

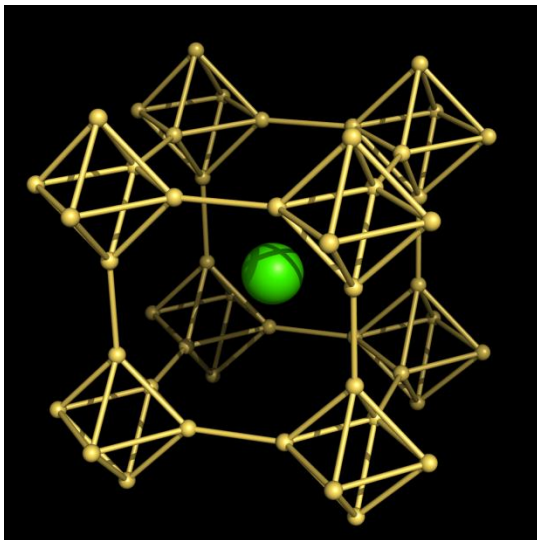
The structure of  $MB_2$   
(M= Mg, Ti, Cr):  
top view (left)  
side view (right)

M is green  
sphere



The Structure of  $MB_6$   
(M= Ca La, Ce):

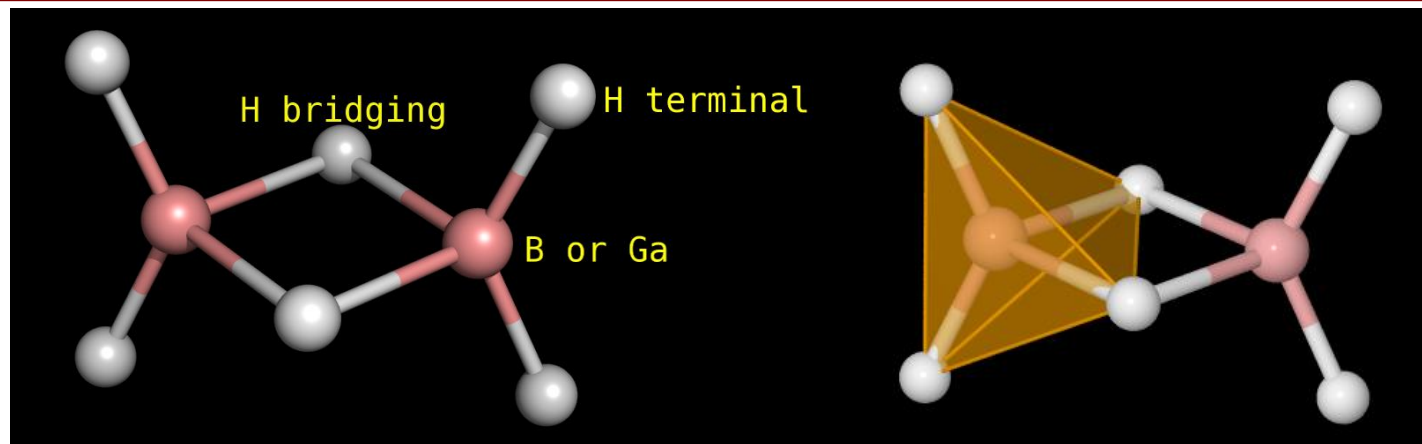
- M is the green sphere
- $B_6^{2-}$  is octahedral
- Do you note a similarity with another, simpler structure?



- M-rich borides have isolated  $B^-$  ( $M_3B$  and  $Mn_4B$ ) or  $B_2^-$  ( $M_3B_2$  and  $Cr_5B_3$ ) ions.
- As the B content increases, B atoms form chains ( $M_3B_4$  and MB single;  $M_3B_4$  double chain), sheets ( $MB_2$  and  $M_2B_5$ ) and clusters.

# Overview of Group 13 Hydrides

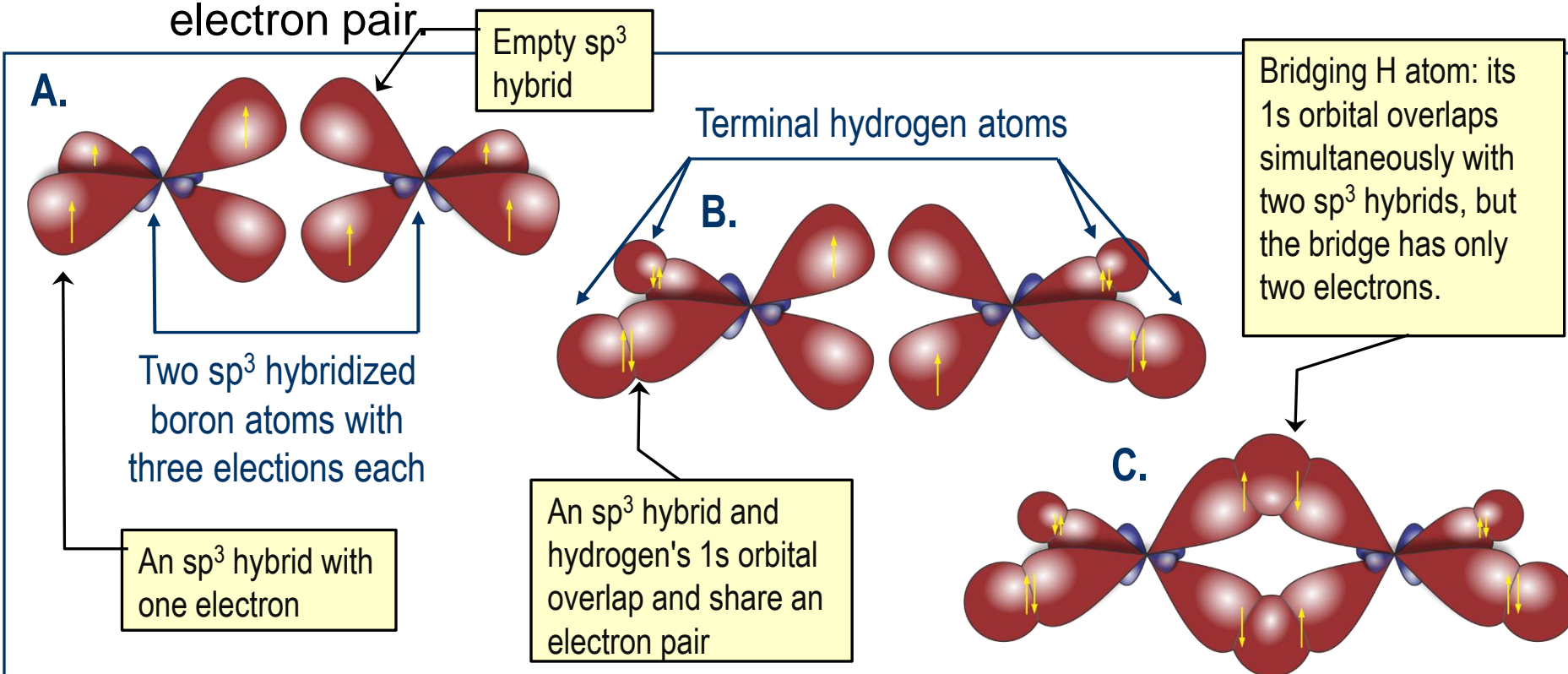
- Only hydrides of B, Al and Ga are well characterized, In and Tl form very unstable species of probable composition  $\text{EH}_3$  ( $\text{E} = \text{In}, \text{Tl}$ ):
  - The hydrides in oxidation number III are the best examples of electron deficient hydrides: they do not exist as monomeric species, rather they form dimers  $\text{E}_2\text{H}_6$  ( $\text{E} = \text{B}, \text{Ga}$ ) or polymeric structures;
  - Boron forms more than 50 compounds with a general formula  $\text{B}_x\text{H}_y$  and around 200 anionic  $\text{B}_x\text{H}_y^{n-}$  complex hydrides;
  - Both dimers and more complex hydrides of this group are examples of compounds containing 3 center–2 electron bonds.



The structure of  
dimeric  $\text{E}_2\text{H}_6$   
( $\text{E} = \text{B}, \text{Ga}$ )

# 3 center–2 electron bonds

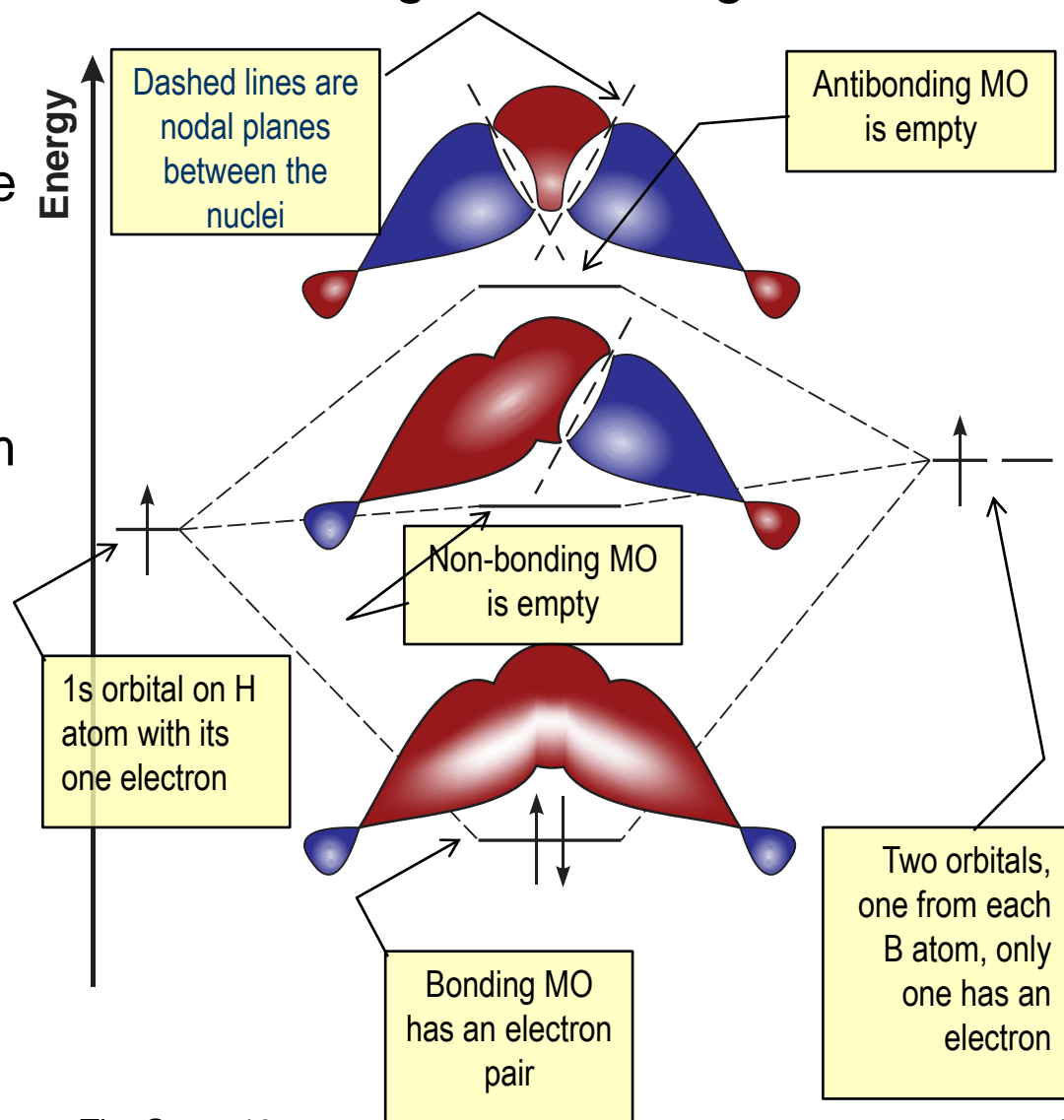
- Applying valence bond (VB) theory to 3c–2e bonds:
  - Boron atom is tetrahedral with  $sp^3$  hybrids: three hybrids have 1 electron; the fourth hybrid orbital remains empty;
  - Two  $sp^3$  hybrids on each B are used for two terminal B–H bonds;
  - Two remaining  $sp^3$  hybrids are overlapping with one 1s orbital on the bridging H atom: this produces two orbital overlaps that share one electron pair





# 3 center–2 electron bonds (cont.)

- Applying molecular orbital (MO) theory: this a *GROSS* approximation, but helpful in understanding the bonding in B–H–B bridges:
  - There are three atomic orbitals (AOs) involved in the bridge formation: two on B atoms & one on H with total of two electrons.
  - From three AOs we can form three molecular orbitals (MOs): bonding (lowest in energy); non-bonding (with energy comparable to the energy of AOs) and anti-bonding orbital (the highest in energy)
  - The two electrons occupy the bonding MO.

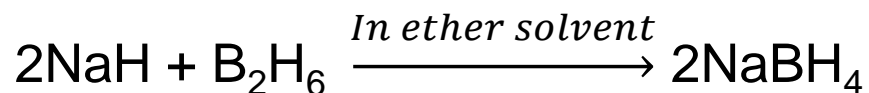




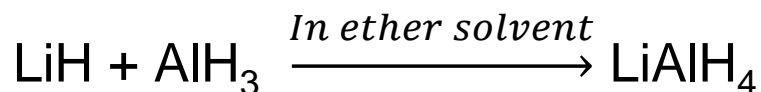
# The $\text{EH}_4^-$ (E = B, Al, Ga) Anions

- Two very common compounds

- sodium tetrahydroborate or sodium borohydride ( $\text{NaBH}_4$ )



- lithium tetrahydroaluminate or lithium-aluminum hydride ( $\text{LiAlH}_4$ )

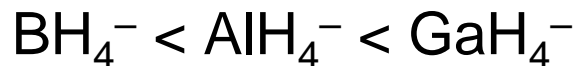


- There is also less frequently used  $\text{GaH}_4^-$ .

- Another method for synthesis of  $\text{GaH}_4^-$  and  $\text{AlH}_4^-$  which we shall encounter later.

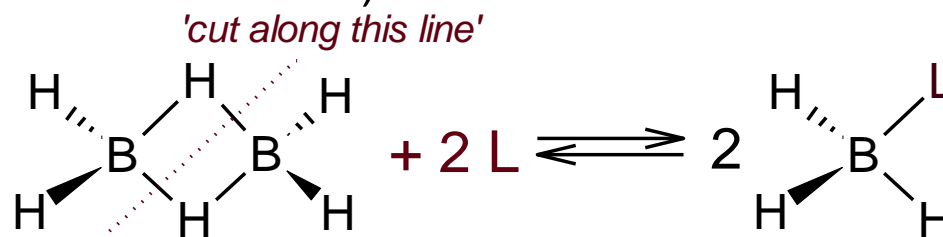
- Tetrahydroborates and tetrahydroaluminates are good sources of hydride anion and are used as reducing agents in organic and inorganic syntheses

- The reactivity and hydridic character increases from B to Ga:

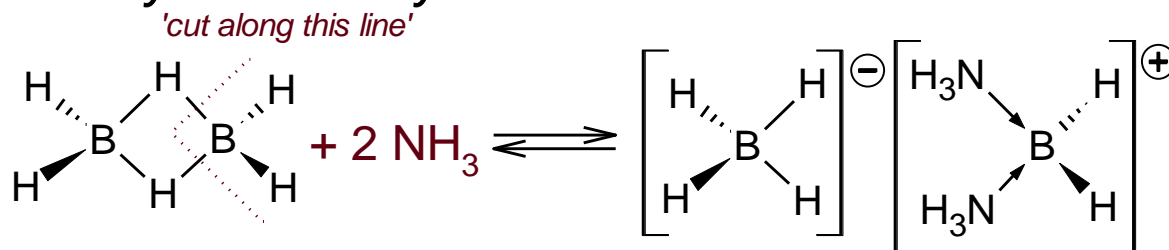


# Further on B<sub>2</sub>H<sub>6</sub> Reactivity

- Electron-deficient B<sub>2</sub>H<sub>6</sub> is a strong Lewis acid that loses the B-H-B bridge when reacting with a Lewis base.
- There are two possibilities:
  - Most commonly the B–H–B bridge is cleaved *symmetrically* (two identical halves are formed):



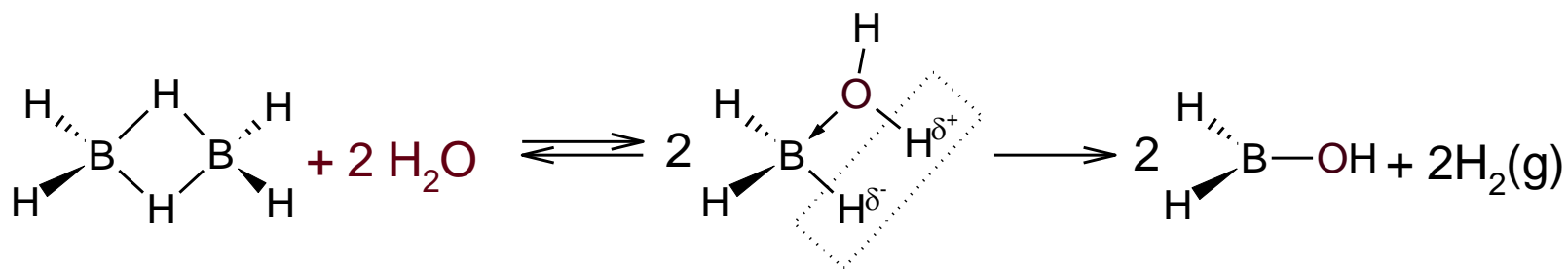
- If the Lewis base L is NH<sub>3</sub>, N(CH<sub>3</sub>)H<sub>2</sub> or N(CH<sub>3</sub>)<sub>2</sub>H the B–H–B bridge is cleaved *asymmetrically*:



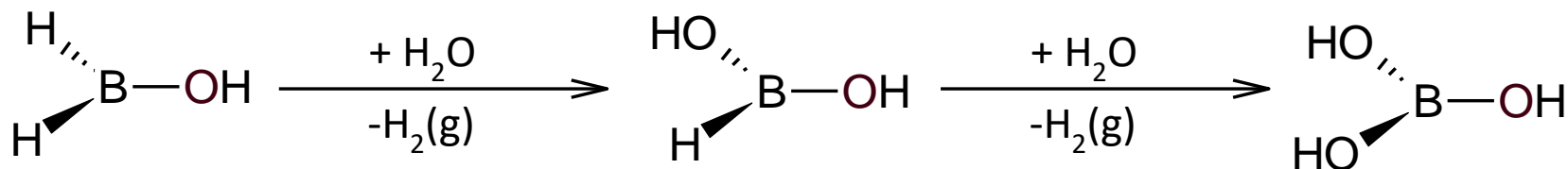
- B<sub>2</sub>H<sub>6</sub> is a gas and is commonly used in a solution (usually in ether-like solvent) in which case the bridge is already cleaved by a solvent molecule.

# Substitution reactions on B<sub>2</sub>H<sub>6</sub>

- If a Lewis base has polar X<sup>δ-</sup>–H<sup>δ+</sup> bonds (for example, Cl–H, O–H, N–H etc), substitution of hydrogen atom with group X usually occurs as a follow-up reaction.
  - These substitutions always involve elimination of H<sub>2</sub> molecule:

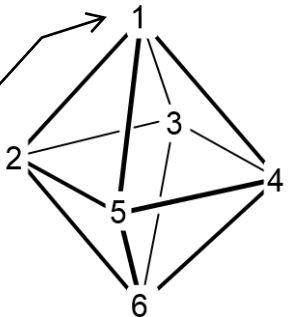
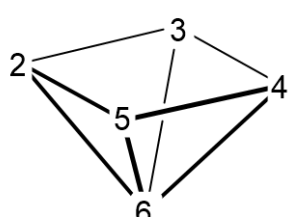
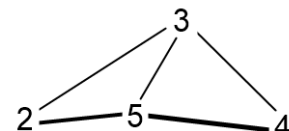
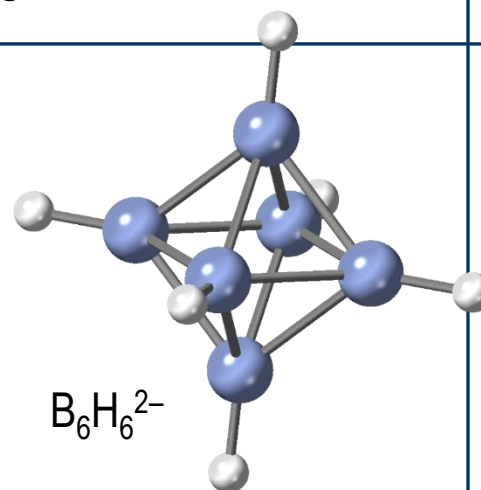
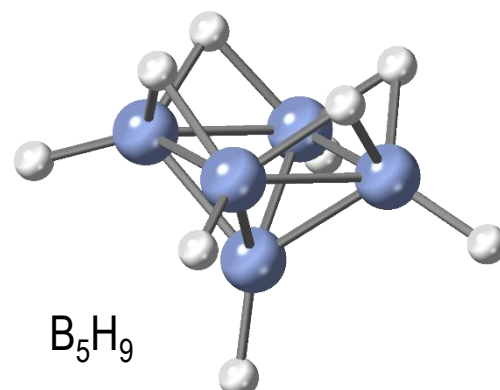
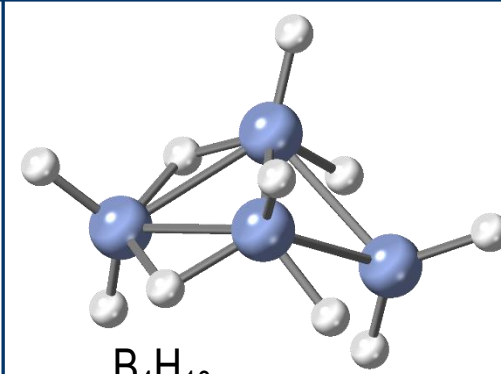


- Further addition/substitution reactions generally follow leading to a fully substituted product:



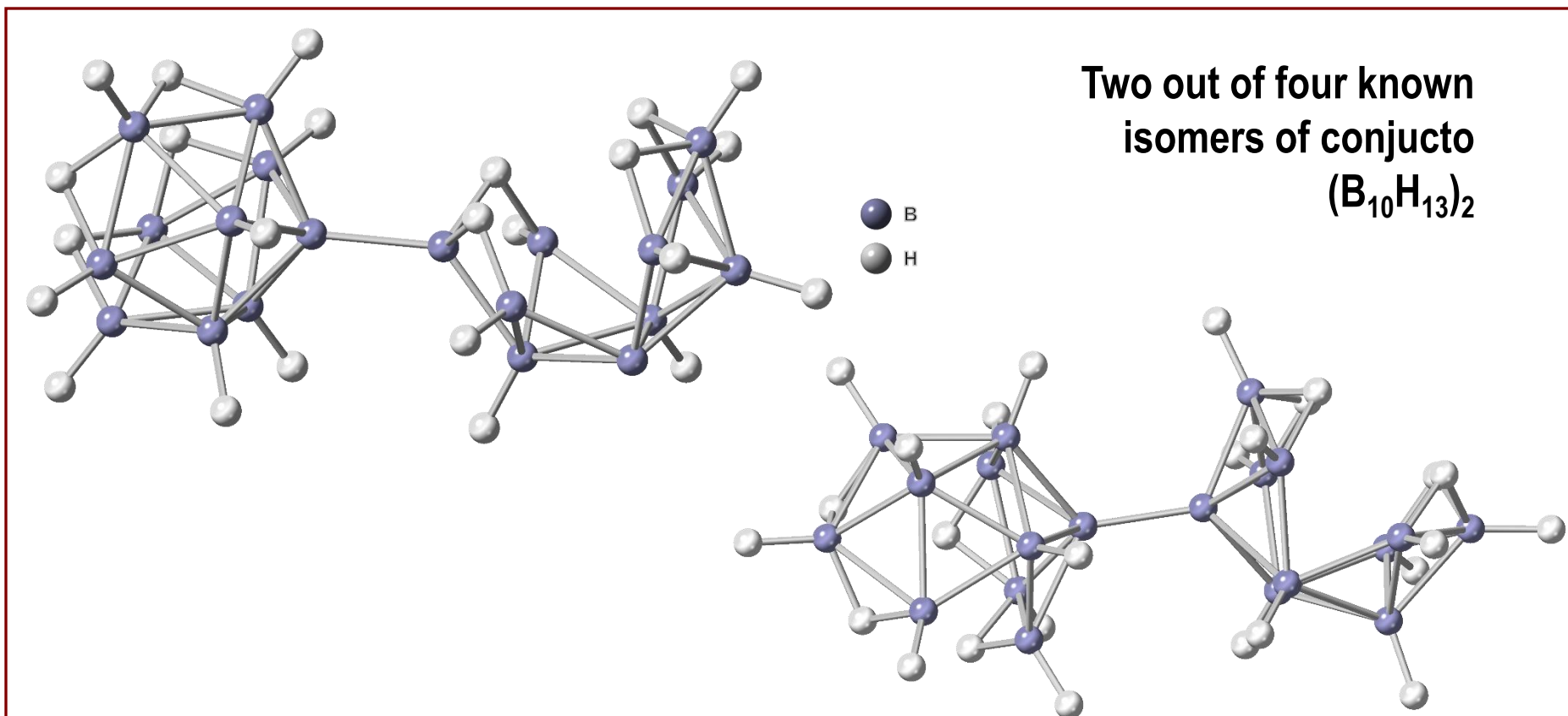
# Boron-hydrogen clusters

- Classification of boron-hydrogen (BH) clusters based on structure:

Type	<i>Closo</i> -clusters	<i>Nido</i> -clusters	<i>Arachno</i> -clusters
	 <p>Remove '1'</p>  <p>Remove '6'</p> 		
Examples	 <p><math>B_6H_6^{2-}</math></p>	 <p><math>B_5H_9</math></p>	 <p><math>B_4H_{10}</math></p>
General formulae	$(B_nH_n)^{2-}$	$B_nH_{n+4}, (B_nH_{n+3})^- \dots$	$B_nH_{n+6}, (B_nH_{n+8})^- \dots$

# Boron-hydrogen clusters (cont.)

- (Only) two more:
  - *Hypo*-clusters: remove one B atom from *arachno* structure (but these are still not characterized well enough)
  - *Conjuncto*-clusters: two or more boron cages connected together via B–B bonds or shared B atom:



# Matching the BH formula with its structure

- Wade's rule: count the number of *skeletal electron pairs* (those *not* involved in B–H bonds) and if the number is ( $n$  = no. of B atoms in the cluster):
  - $n + 1$  the cluster is *closo* type
  - $n + 2$  the cluster is *nido* type
  - $n + 3$  the cluster is *arachno* type &
  - $n + 4$  the cluster is *hypho* type

## ***Calculating number of skeletal electrons for BH clusters:***

- Determine the number of BH units in the structure
- Each BH unit contributes *two* skeletal electrons
- Each 'extra' hydrogen contributes *one* skeletal electron
- Each negative charge contributes *one* skeletal electron

# Wade's rule: Examples

- Determine the type of B cluster in  $B_4H_{10}$ .

- Number of BH units:* the cluster has 4 B atoms and has 4 BH units
- These provide an electron pair each:* 4 electron pairs
- Extra H atoms:* there are  $10 - 4 = 6$  H atoms extra, thus 3 more electron pairs
- No charge*
- Total number of electron pairs:*

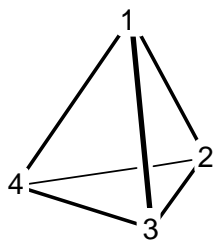
$$4 \text{ (from BH fragments)} + 3 \text{ (from extra H)} = 7$$

*It is  $n+3$  cluster - **arachno***

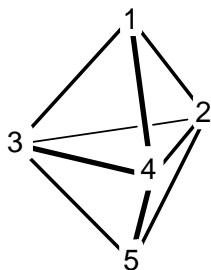
- Determine the type of B cluster in  $B_{12}H_{12}^{2-}$ .

- |                        |   |
|------------------------|---|
| 1. <i>BH = 12</i>      | 4. <i>2- charge: 1 el. pairs</i>                                      |
| 2. <i>12 el. pairs</i> |   |
| 3. <i>None</i>         | 5. <i>Total: <math>12 + 1 \Rightarrow</math> <b>closo</b> cluster</i> |

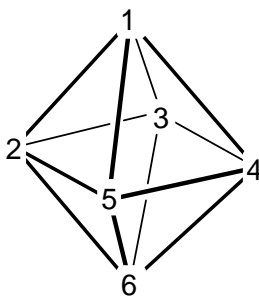
# Parent polyhedrons



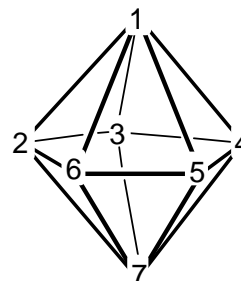
tetrahedron



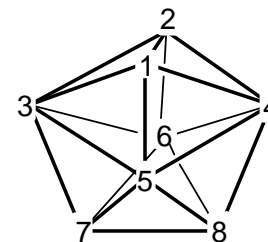
trigonal bipyramid



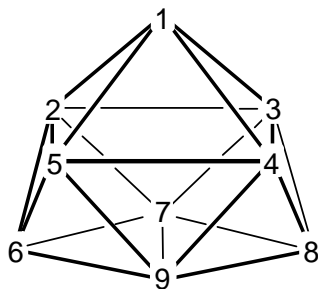
octahedron



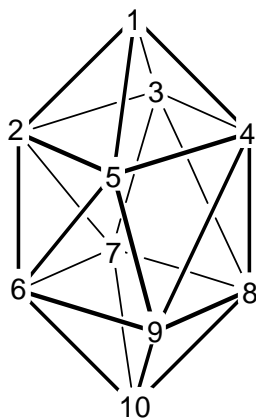
pentagonal bipyramid



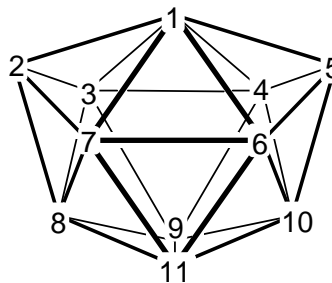
dodecahedron



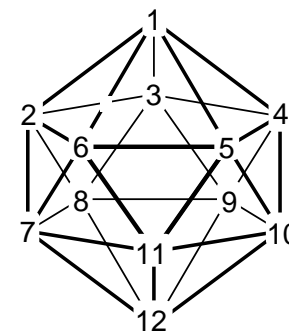
tricapped trigonal prism



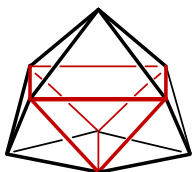
bicapped square antiprism



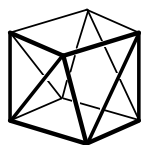
octadecahedron



icosahedron



trigonal prism (red)



square antiprism

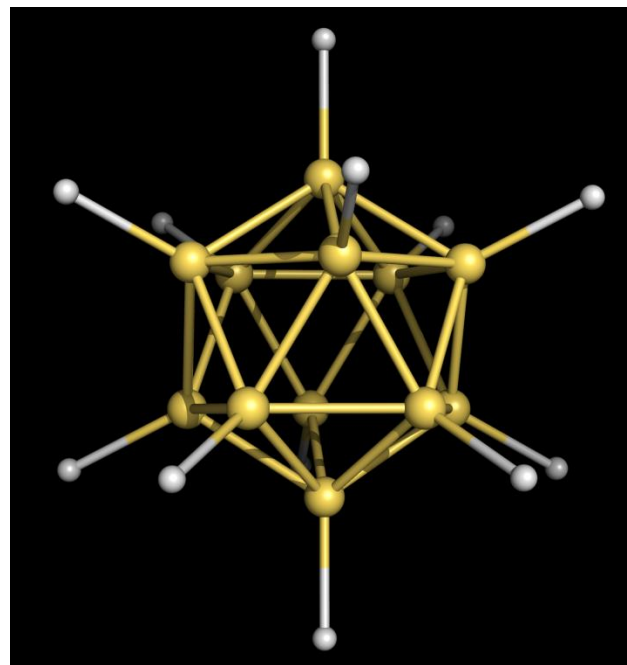
*This is it: no single cage (i.e. non-conjuncto) borane with  $n > 12$  is properly characterized.*



# Suggesting the structure...

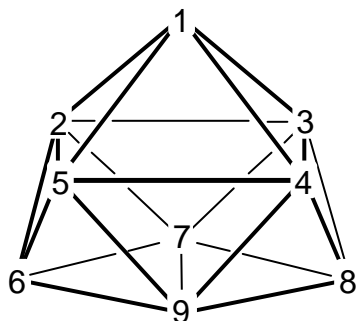
- If you determine *closo* type:
  - Choose the polyhedron that has number of vertices matching number of boron atoms
  - Each vertex = 1 B atom
  - Add an H atom to each B atom
  - Extra H atoms (*very rare for closo structures!*) are added to B atoms of particularly low connectivity

In our case  $(\text{B}_{12}\text{H}_{12})^{2-}$  there are 12 B atoms, and the polyhedron has to have 12 vertices: icosahedron, there are no extra H atoms.

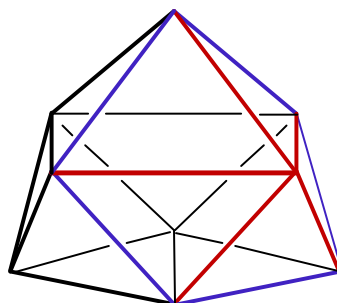


# Suggesting the structure... (cont.)

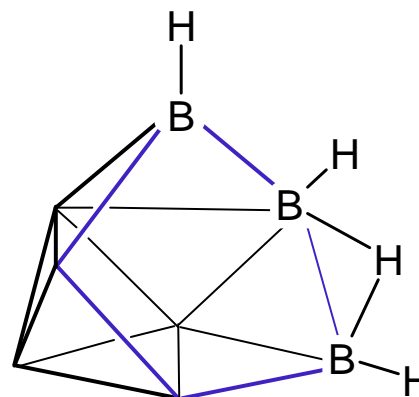
- If you determine *nido* or *arachno* type:
  - Find the *parent* closo polyhedron (the one that has one more B atom than *nido* or two more B atoms than *arachno*) and remove one (for *nido*) or two vertices for *arachno*;
    - *The first removed is usually a vertex of highest connectivity (bonded to the greatest number of neighbours)*
  - Give each B atom its H atom
  - The extra H atoms: first put one as a bridge along each open B–B edge, then (if any H atoms left) as an additional H atom on B of low connectivity



tricapped trigonal prism



*closo*



*nido*

# A full example

- Suggest a possible structure for  $B_7H_{11}$  cluster!

**FIRST** answer – Which type: *closo*, *nido* or *arachno*?

7 BH units = 7 el. Pairs

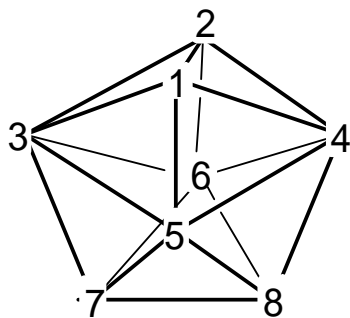
4 extra H = 2 el. Pairs

No charge

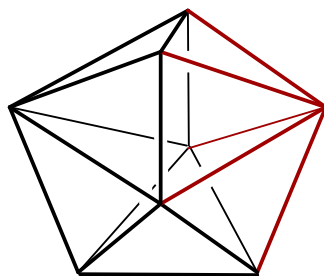
$7 + 2 = 9$  ( $= n + 2 \rightarrow$  *nido* cluster)

**SECOND** answer – Which polyhedron?

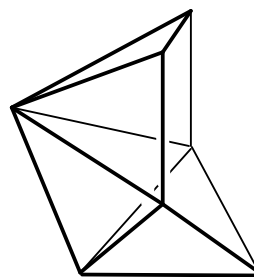
*Nido* = (*closo* – 1 vertex), so we start with polyhedron with 8 vertices or dodecahedron:



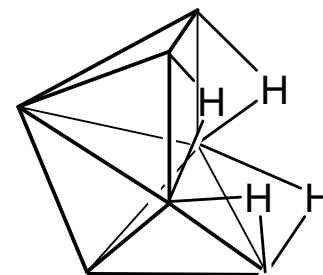
find parent *closo* structure  
dodecahedron



find boron with highest  
connectivity



and remove it

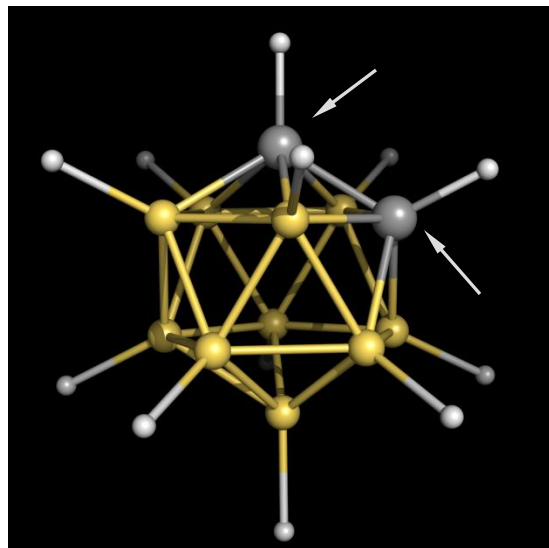
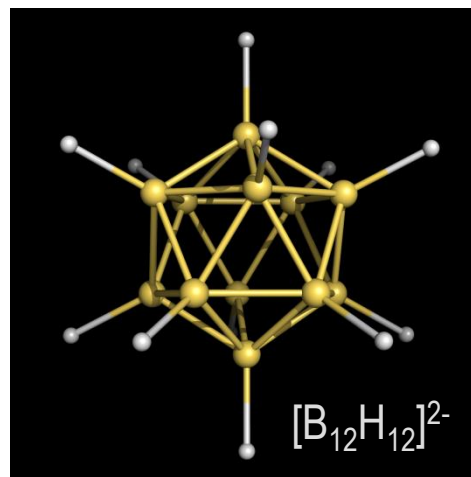
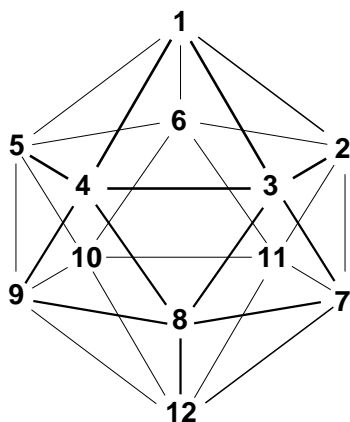


add bridging hydrogens  
along open edges

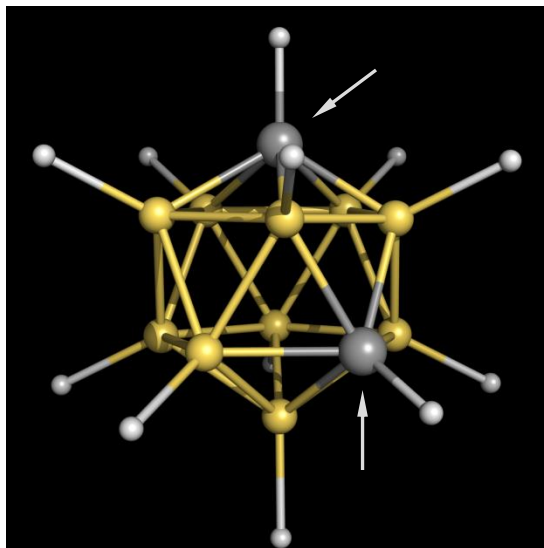
# “Substituted” boranes

- Boron atoms (or B–H groups) can be replaced with carbon (C–H groups) to give *carboranes*:

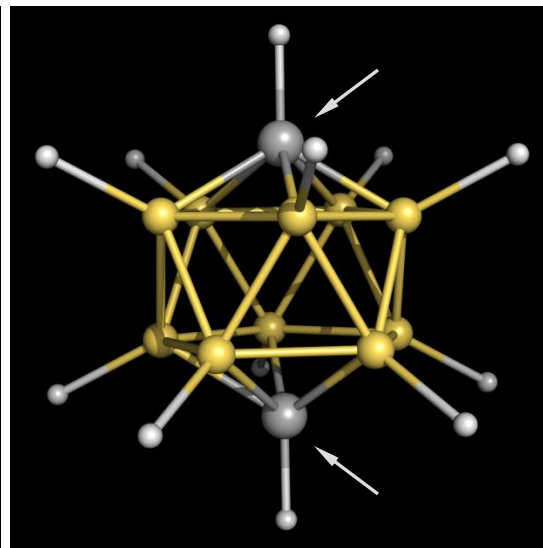
Numbering scheme



*closo*-1,2- $C_2B_{10}H_{12}$



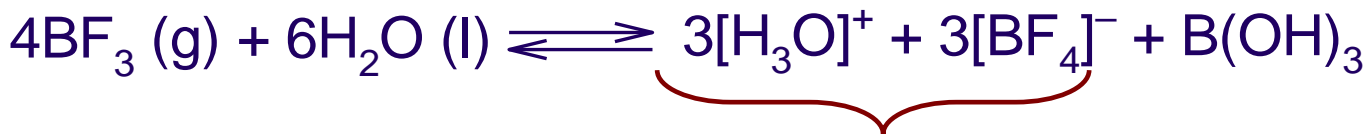
*closo*-1,7- $C_2B_{10}H_{12}$



*closo*-1,12- $C_2B_{10}H_{12}$

# Boron halides (BX<sub>3</sub>)

- All boron halides are known
- Monomeric, volatile trigonal planar molecules
- All are readily decomposed by H<sub>2</sub>O
  - BF<sub>3</sub> with water produces boric acid and tetrafluoroboric acid:



- Other halides produce HX and B(OH)<sub>3</sub>:



- All BX<sub>3</sub> are strong Lewis acids and form Lewis acid-Lewis base adducts L → BX<sub>3</sub> (L = Lewis base)
- The Lewis acidity is not what we would expect based on electronegativity:



# Why the difference in reactivity with H<sub>2</sub>O?



$$\Delta_{\text{rxn}} G^0 = \Sigma[\Delta G^0 \text{ (products)}] - \Sigma[\Delta G^0 \text{ (reactants)}]$$

$$\Delta_{\text{rxn}} G^0 = (\Delta_{\text{f}} G^0[\text{B}(\text{HO})_3] + 3\Delta_{\text{f}} G^0[\text{HX}]) - (\Delta_{\text{f}} G^0[\text{BX}_3] + 3\Delta_{\text{f}} G^0[\text{H}_2\text{O}])$$

**For reaction 1** (reaction with BF<sub>3</sub>): −8.8 kJ/mol

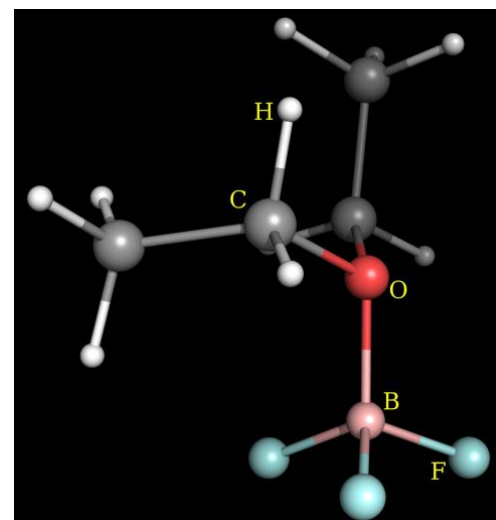
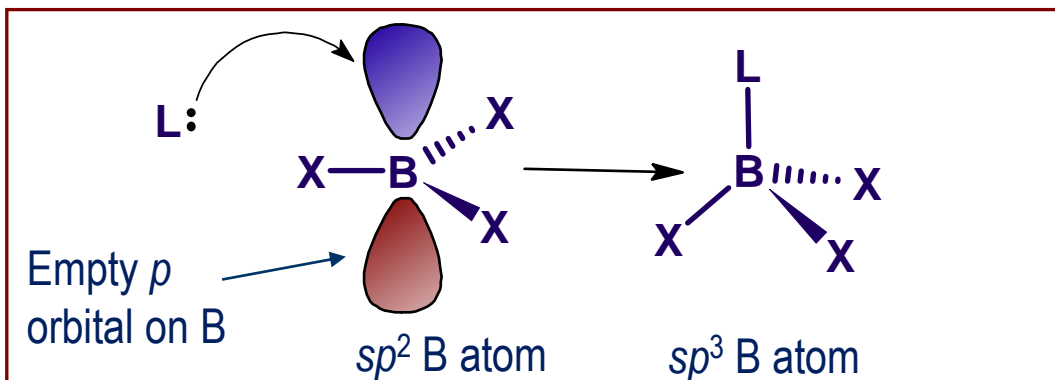
**For reaction 2** (reaction with BCl<sub>3</sub>): −196.5 kJ/mol

Thus, *thermodynamically* reaction 1 is *less* favorable than reaction 2 and for reaction 1 equilibrium is established with considerable amount of reactants still present! *Consequence*: one of the products (HF) reacts further with one of the reactants (BF<sub>3</sub>) and gives H[BF<sub>4</sub>].

The reason for these thermodynamic values is similar strengths of B–F and B–O bonds (rxn 1) and weaker B–Cl bond in comparison to B–O bond.

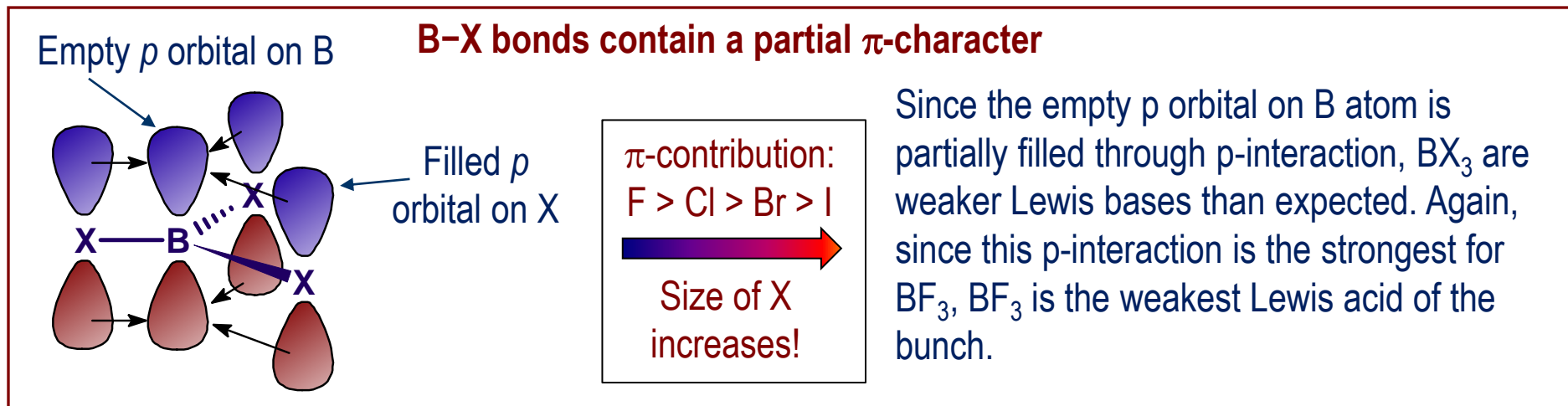
# A Look at Lewis Acidity of $\text{BX}_3$

- Lewis acidity of boron halides ( $\text{BX}_3$ ):



Structure of a  
Lewis acid-  
base adduct:  
 $\text{BF}_3 \cdot \text{OEt}_2$   
Note  
tetrahedral  
boron.

- The B–X bonds are not pure single (sigma) bonds, there is also a  $\pi$  component which makes B–X bonds stronger:

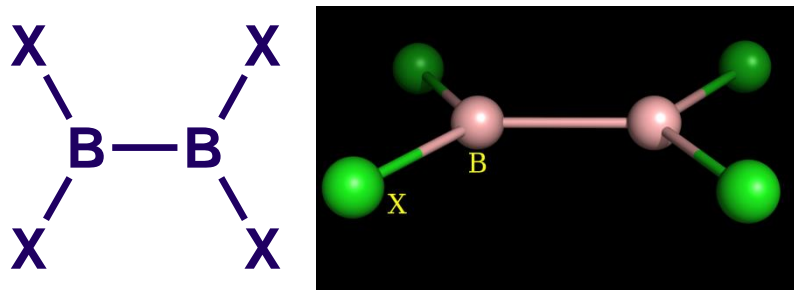


- One evidence for  $\pi$  interaction is B–F bond lengths: in  $\text{BF}_3$  (has  $\pi$  interaction) 130 pm and in  $[\text{BF}_4]^-$  (only  $\sigma$  bonds) is 145 pm.

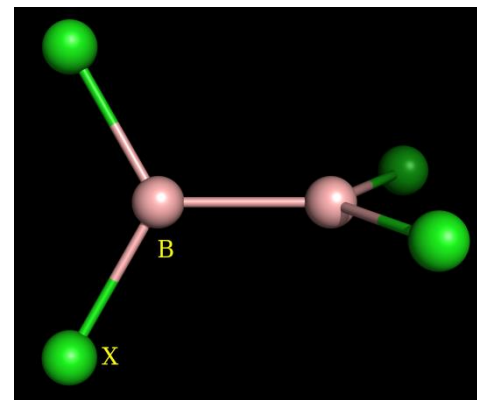
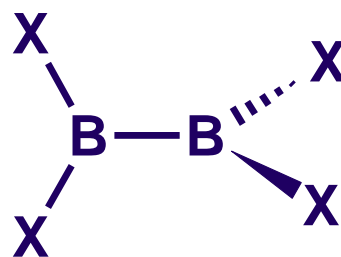
# Other boron halides

- Boron forms a series of unstable, lower halides of which the most important are  $B_2X_4$  with B(II) (*why are there structural differences?*):

$X = F$  (both solid and vapor), Cl (solid only)



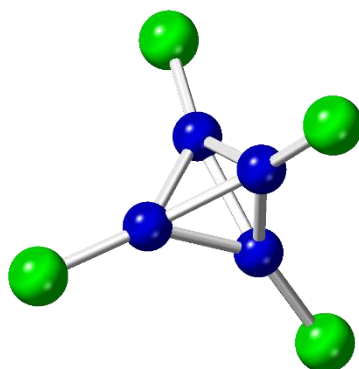
$X = Cl$  (vapor), Br & I (both solid and vapor)



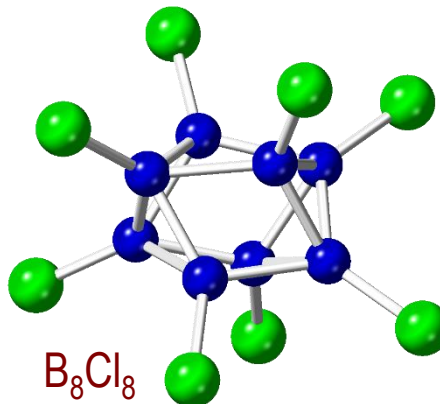
- The stability decreases in order  $B_2F_4 > B_2Cl_4 > B_2Br_4 > B_2I_4$

Another example of lower B halides are boron(I) halides. These halides contain boron clusters in their structures.

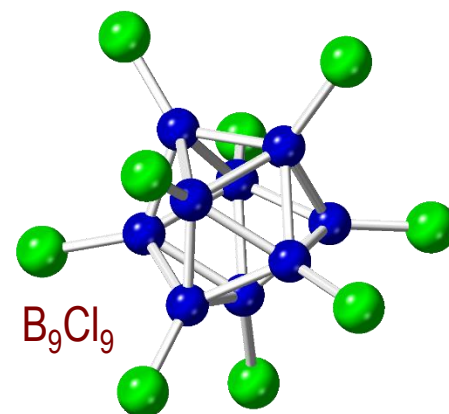
B = blue; Cl = green



$B_4Cl_4$



$B_8Cl_8$



$B_9Cl_9$

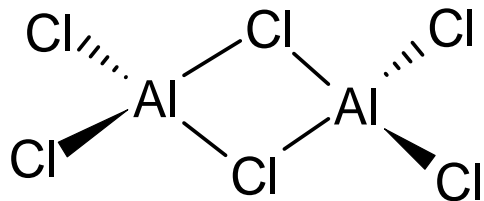


# Halides of Al, Ga, In & Tl

- $\text{MX}_3$ , obtained by direct reaction of M with  $\text{X}_2$
- Tl(III) halides are unstable and easily convert to Tl(I) halide and  $\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ )



- $\text{TlI}_3$  is actually Tl(I) triiodide ( $\text{I}_3^-$ )!



Gas-phase structure of  $\text{Al}_2\text{Cl}_6$

- Unlike  $\text{BX}_3$  (monomeric), gas-phase contains discrete  $\text{M}_2\text{X}_6$  ( $\text{M} = \text{Al}, \text{Ga}$ ) molecules in an equilibrium with small amount of planar monomers, but their solids are polymeric

The  $\pi$ -bonding and  $\pi$ -contributions are stronger in 2<sup>nd</sup> row elements (i.e. B) than the rest, allowing for dimerization and polymerization.

- Tl is the only member of this group with significantly stable TlX halides: TlX are similar to silver and potassium halides

# Lewis acidities of $\text{EX}_3$

- The trifluorides of Al, Ga and In are lousy Lewis acids because they are sparingly soluble.
- For other  $\text{MX}_3$  ( $\text{M} = \text{Al, Ga, In}$ ;  $\text{X} = \text{Cl, Br, I}$ ) the trends are as expected, i.e.  $\text{AlCl}_3 > \text{AlBr}_3 > \text{AlI}_3$ .
- But what is a trend in Lewis acidity for the series  $\text{BCl}_3$ ,  $\text{AlCl}_3$  and  $\text{GaCl}_3$ ?
- The answer depends on the electron-pair donor (Lewis base):
  - For hard donors (i.e. oxygen in  $\text{Et}_2\text{O}$  or nitrogen in  $\text{Me}_3\text{N}$ ) the order is
$$\text{BCl}_3 > \text{AlCl}_3 > \text{GaCl}_3$$
  - For soft donors (i.e. sulfur in  $\text{Me}_2\text{S}$  or phosphorus in  $\text{PMe}_3$ ) the order is inverse
$$\text{GaCl}_3 > \text{AlCl}_3 > \text{BCl}_3$$
- However, in each case the size of L plays an important role as well.

# Compounds with oxygen (ON= +3)

- All  $E_2O_3$  are known (for this oxide is unstable) and can be obtained in direct reaction:  $E + O_2$
- For  $E = B, Al$  the oxides are thermodynamically very stable compounds (very strong E–O bonds!)
- Hydroxides:  $E(OH)_3$  ( $E = B, Al, Ga, In$  but **not** Tl)
- Note change in acidic properties:

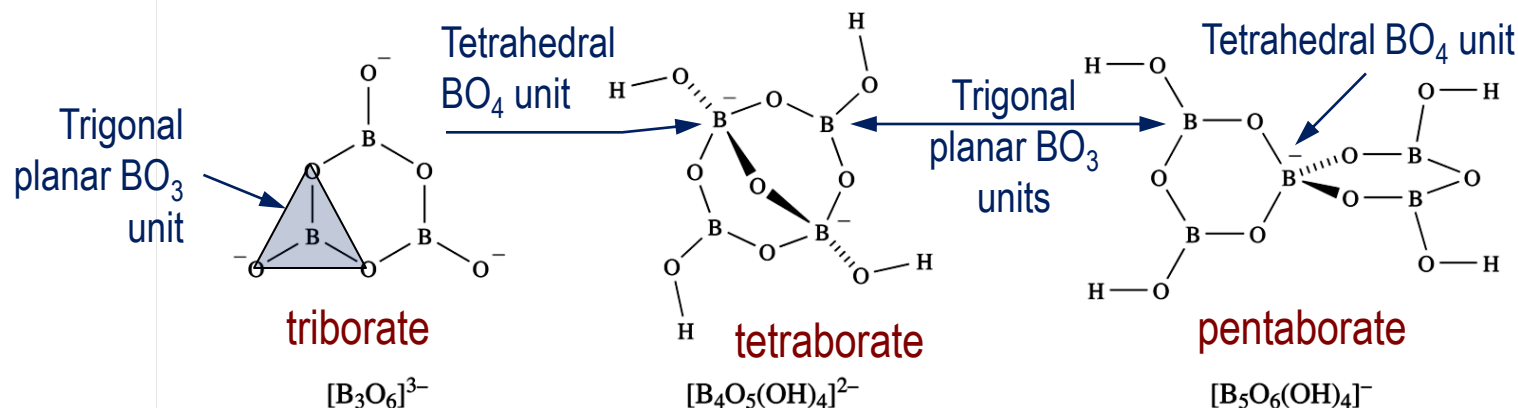
<div>13</div> <div>5</div> <div>B</div> <div>10,811</div>	<div><math>B(OH)_3</math> - acidic</div> <div> <math>B(OH)_3 + 2H_2O \longrightarrow [B(OH)_4]^- + H_3O^+, pK_a = 9.2</math> </div>
<div>13</div> <div>Al</div> <div>26,9815</div>	<div> <math>Al(OH)_3</math> </div> <div> <math>Ga(OH)_3</math> </div> <div>Amphoteric</div> <div> <math>M(OH)_3 + OH^- \longrightarrow [M(OH)_4]^-</math> (acid-like behaviour)                 </div> <div> <math>M(OH)_3 + 3HX \longrightarrow MX_3 + 3H_2O</math> (base-like)                 </div>
<div>31</div> <div>Ga</div> <div>69,72</div>	
<div>49</div> <div>In</div> <div>114,82</div>	<div><math>In(OH)_3</math> - basic</div> <div> <math>In(OH)_3 + 3HX \longrightarrow InX_3 + 3H_2O</math> </div>
<div>81</div> <div>Tl</div> <div>204,37</div>	<div>No <math>Tl^{III}</math> hydroxyde but oxide is basic (<math>TlOH</math> is also basic)</div>

# Boric Acids and Borates

- The chemistry of B–O compounds is extraordinarily diverse and important for geology and technology.
- However, the basics are simple:
  - Most important acid is boric acid,  $\text{B}(\text{OH})_3$ ;
  - When heated this acid loses water to give first  $\text{HBO}_2$  (metaboric acid) and (with further heating)  $\text{B}_2\text{O}_3$ :

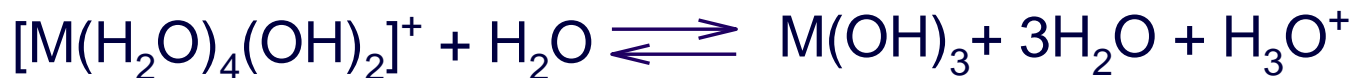
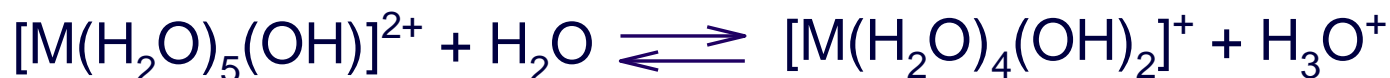


- All other more complex borate anions have structures composed of trigonal planar  $\text{BO}_3$  and/or tetrahedral  $\text{BO}_4$  units sharing a common oxygen atom:

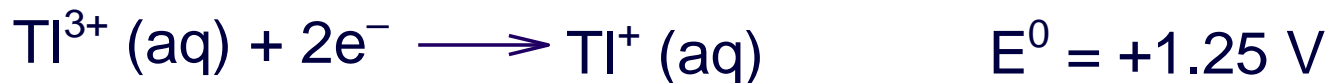


# Aqueous chemistry of $M^{3+}$ and $M^+$ ions

- “ $B^{3+}$ ” does not exist.
- $M^{3+}$  ( $M = Al, Ga, In, Tl$ ) are all hydrated and produce acidic solutions due to hydrolysis (they behave as aqua-acids with acidity decreasing down the group):



- In aqueous solutions,  $Tl(III)$  salts are strong oxidizing agents:

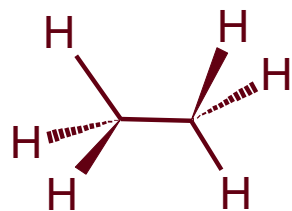


- $M^+$  ( $M = Ga, In$ ) are good reducing agents:



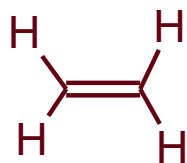
# Boron-nitrogen compounds

- These are inorganic 'organic-like' compounds
- C–C structure is replaced with isoelectronic B–N (or better with B←N) fragment:



ethane

$d_{CC} = 1.54 \text{ \AA}$



ethene

$d_{CC} = 1.33 \text{ \AA}$



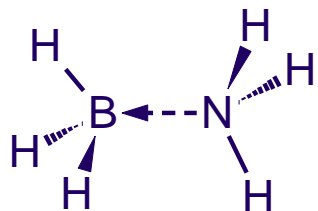
ethyne

$d_{CC} = 1.18 \text{ \AA}$



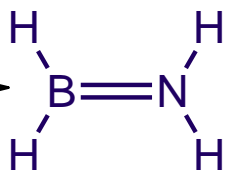
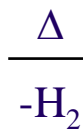
benzene

$d_{CC} = 1.40 \text{ \AA}$



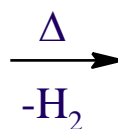
amineborane

$d_{BN} = 1.58 \text{ \AA}$   
(solid, stable)



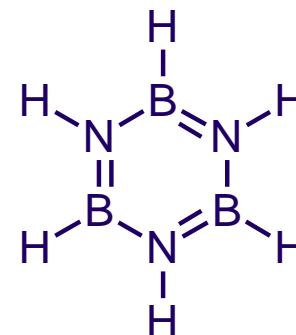
aminoborane

$d_{BN} \sim 1.37 \text{ \AA}$   
(unstable)



iminoborane

$d_{BN} \sim 1.22 \text{ \AA}$   
(unstable)

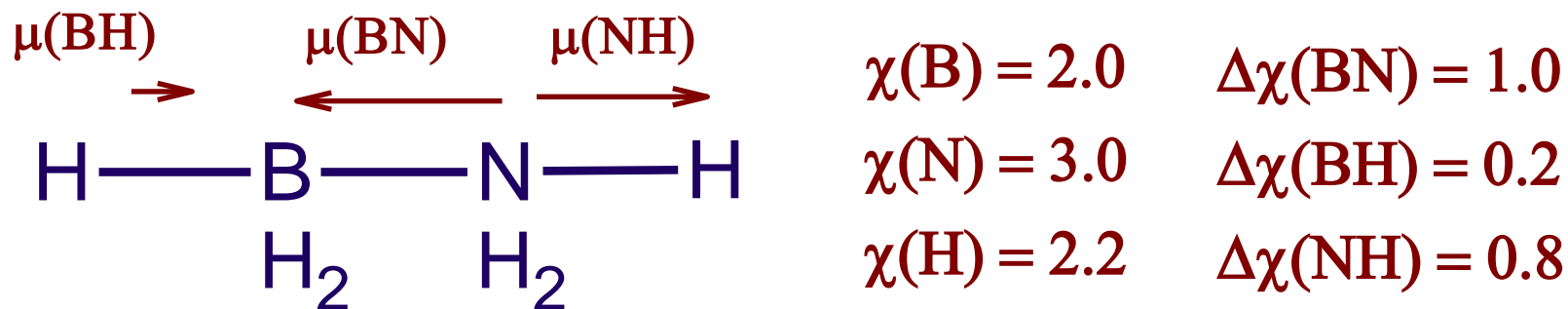


borazine

$d_{BN} = 1.44 \text{ \AA}$   
(liquid)

# Chemistry of B-N compounds

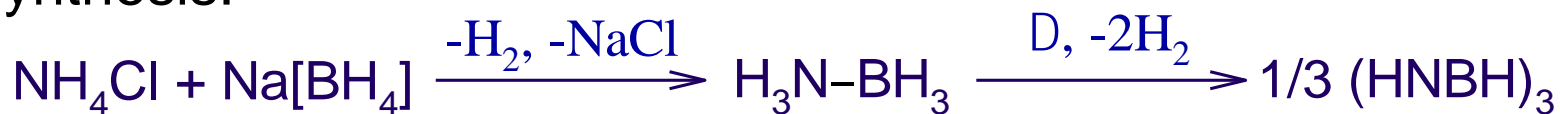
- Unlike C–C bonds, B–N bonds are polar bonds.
- H–B & H–N bonds are more polar than H–C bonds.



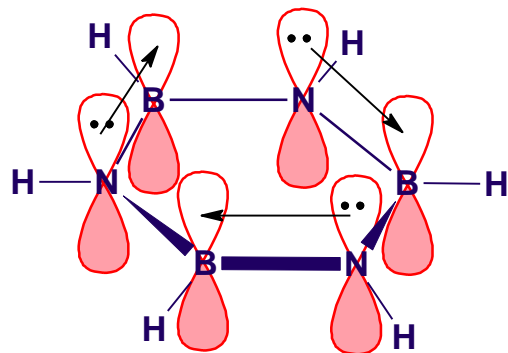
- **Structural vs. chemical similarity:** Although structurally similar, B–N bonds are weaker and more reactive than C–C bonds. As a result, the reaction mechanisms and products can significantly differ between the two groups of compounds.
- Like C-C compounds, hydrogen atoms can be substituted with other groups (for example  $\text{X}_3\text{BNR}_3$ ,  $\text{X}_2\text{BNR}_2$ ,  $\text{XBNR}$  &  $(\text{XBNR})_3$  where X and R = H, OR, halogens, organic groups, etc.).

# Borazene: Inorganic benzene – B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>

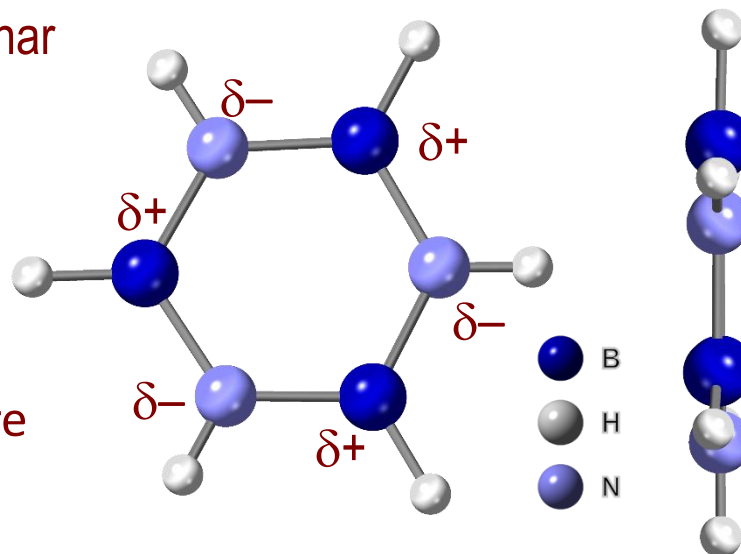
- Synthesis:



Electron delocalization in borazene ring



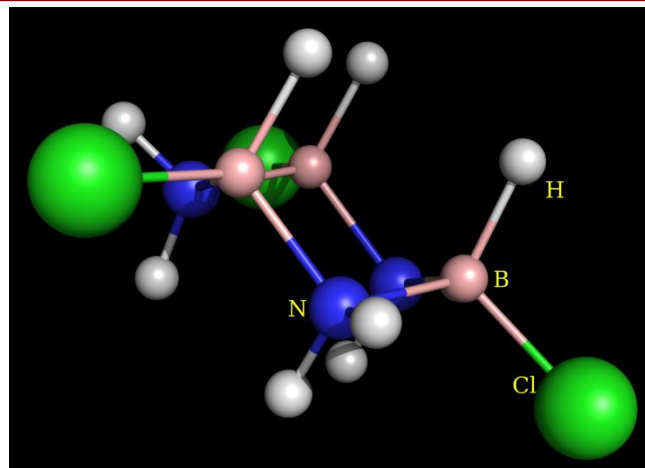
B<sub>3</sub>N<sub>3</sub>H<sub>6</sub> is a planar molecule (as is C<sub>6</sub>H<sub>6</sub>), but B–N bond is polar (unlike C–C bond) making borazene more reactive than benzene



- Additions to (HBNH)<sub>3</sub> are easy:



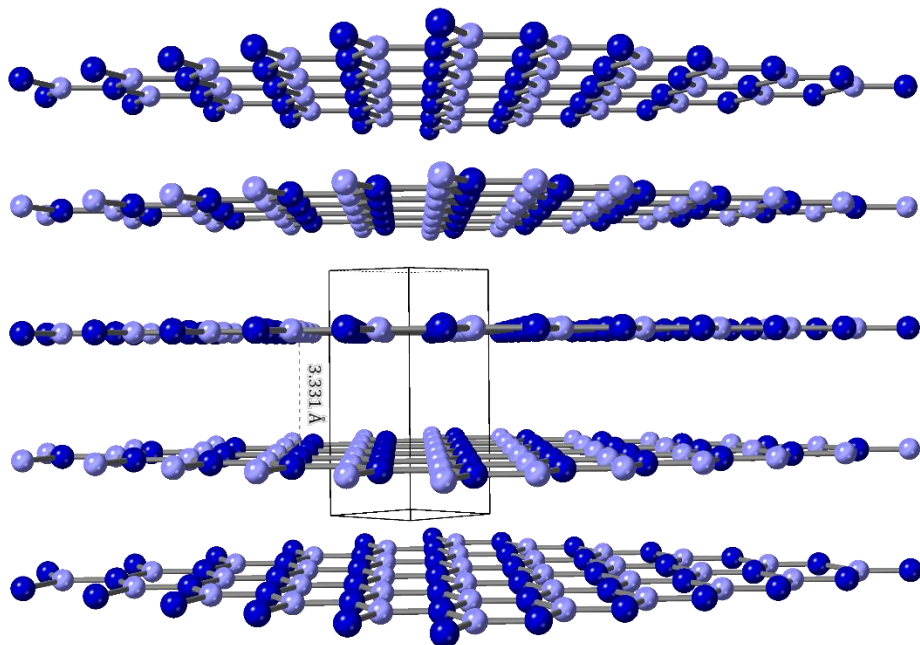
A 1,3,5 –trichlorocyclohexane analogue





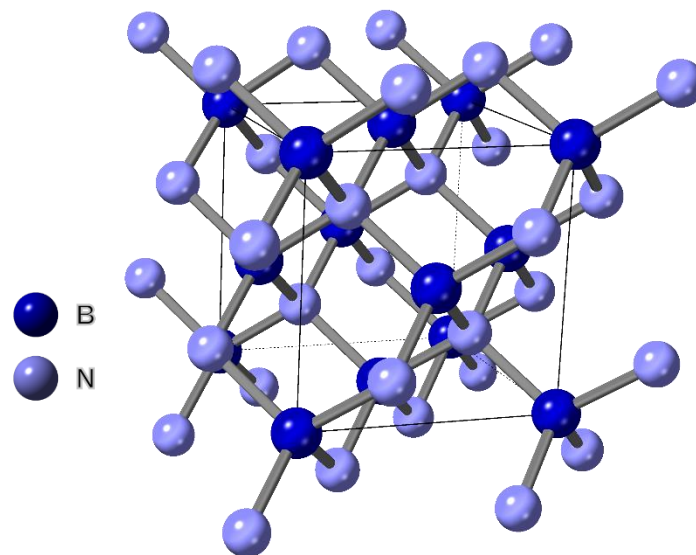
# Hexagonal & cubic BN

- Boron nitride (BN):  $\alpha$ -BN (hexagonal, graphite-like) and  $\beta$ -BN (cubic, diamond-like)



## Layered structure of $\alpha$ -BN (hexagonal):

- Similarity to graphite:* layers composed of six-member hexagonal rings.
- Different from graphite:* layers are stacked above each other (not staggered!) with B atom of one layer exactly above N atom of the other layer.



## Structure of $\beta$ -BN (cubic):

- Identical with the diamond structure (sphalerite for AB type compounds)
- Very hard material but still softer than diamond

# Overview

13
5 <b>B</b> 10,811
13 <b>Al</b> 26,9815
31 <b>Ga</b> 69,72
49 <b>In</b> 114,82
81 <b>Tl</b> 204,37

- The elements
- Thallium and relativistic effects
- Isolation
- Hydrides
  - Structures and 3c-2e bonds ( $\text{B}_2\text{H}_6$  and  $\text{Ga}_2\text{H}_6$ )
  - Reactivity of  $\text{B}_2\text{H}_6$
  - Tetrahydroborates and tetrahydroaluminates
- Halides
  - Lewis acidity and reactions of Group 13 halides
  - Structures of  $\text{BX}_3$  and  $\text{B}_2\text{X}_4$
  - Tl halides
- Oxides and oxoanions
- Aqueous chemistry – hydrolysis in water
- Boron-nitrogen compounds
- Borides
- BH clusters, Wade's rules and carboranes

# Readings and problems

- **Readings**

- **Chapter 13:** The Group 13 – You can skip Section 13.11 parts b) to e) (only part a) is important for us), 13.12 “Metallaboranes and carboranes” and sections 13.17-13.20.

- **Problems**

From 6<sup>th</sup> edition:

- In-text examples and self-tests: 13.2, 13.3, 13.4, 13.5, 13.6, 13.8, 13.10
- End-of-chapter exercises: 13.1, 13.2, 13.4, 13.5, 13.6, 13.9, 13.11(b), 13.14, 13.15, 13.16(a & b parts only), 13.17, 13.18, 13.19, 13.21, 13.23, 13.25, 13.27

From 7<sup>th</sup> edition:

- In-text examples and self-tests: 13.1, 13.2, 13.4, 13.5, 13.6, 13.7, 13.8, 13.10
- End-of-chapter exercises: 13.1, 13.2, 13.4, 13.5, 13.6, 13.7, 13.8, 13.11, 13.12, 13.17(b), 13.20, 13.21(a & b parts only), 13.22, 13.23, 13.26, 13.27, 13.28, 13.31, 13.32, 13.35s

# *Closo, nido and arachno* Relations

