

	13
5	
B	
10,811	
13	
Al	
26,9615	
31	
Ga	
69,72	
49	
In	
114,82	
81	
Tl	
204,87	

Entering the p-block...

The Group 13 ...and the things become
complicated

Occurrence

- Occur only in minerals (never in elemental state)

	13
5	B
10,811	
13	Al
26,9815	
31	Ga
69,72	
49	In
114,82	
81	Tl
204,87	

Buraq (Arab.) borax, 9 ppm (Earth Crust)



Alum crystal
(M = K)

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

Indigo = the colour of spectral line, 0.24 ppm



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



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

Isolation

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

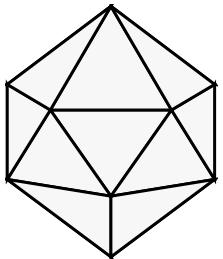
Treatment of borax ($\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \times 8\text{H}_2\text{O}$) with a strong acid gives $\text{B}(\text{OH})_3$ which on heating gives B_2O_3 , and B_2O_3 is further reduced with Mg.

From bauxite (a rock), electrolysis of bauxite solution in molten cryolite (Na_3AlF_6) using graphite electrodes (requires a lot of energy).

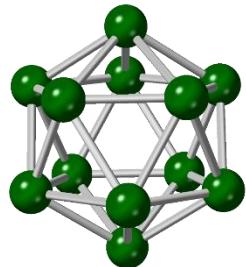
By-products in extraction of other metals (Al, Zn, Cu and Pb).

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:

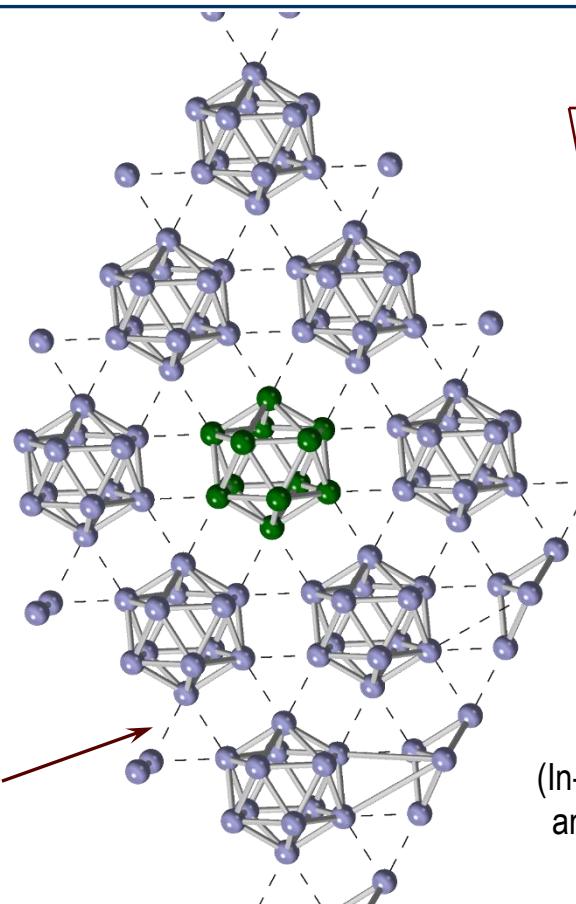


Icosahedron consists of 20 identical equilateral triangular faces, 30 edges and 12 vertices

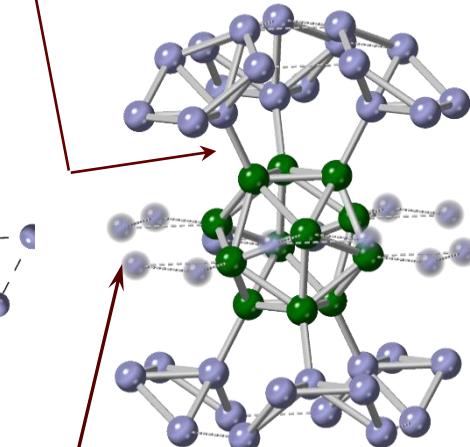


One B_{12} icosahedron with B atom on each vertex (electrons are delocalized inside each icosahedron) Note that the sticks here do not represent typical bonds!

In a most stable allotrope (a-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

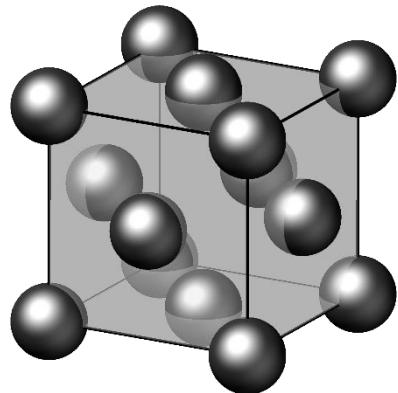


(In-plane bonds and B atoms)

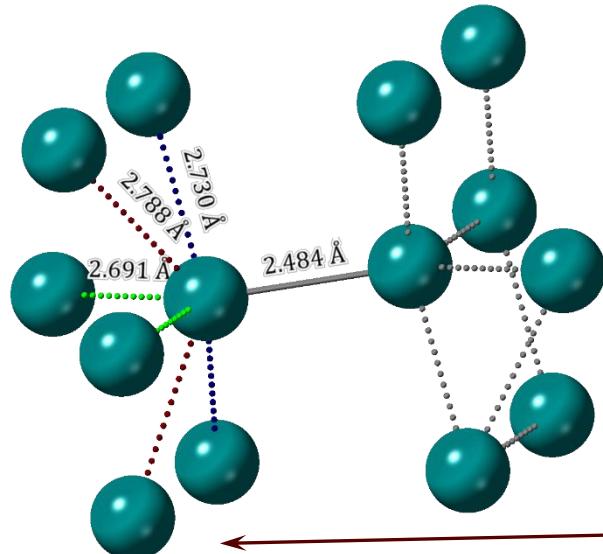
This clustering of born atoms is an important aspect of boron chemistry!

The Structures of Elements: Aluminum and Gallium

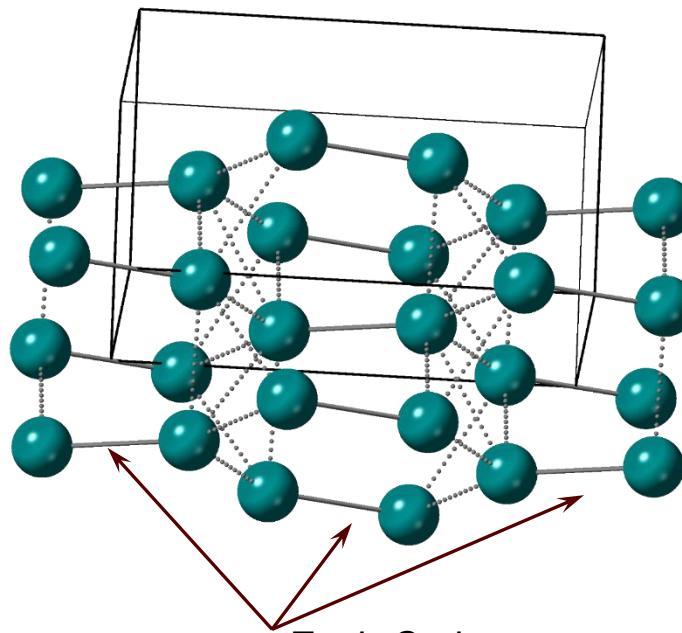
Aluminum, a typical metal has a face-centered cubic structure (based on ccp; solid state lecture)



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



Gallium has a very unique structure:

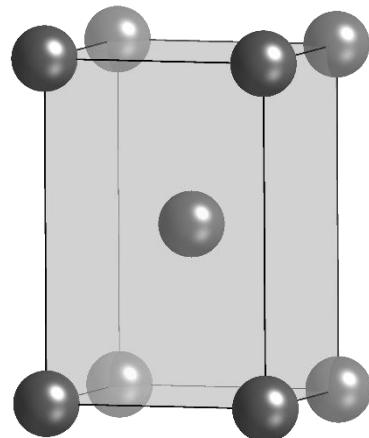


Each Ga has one very close neighbor at 248 pm distance...

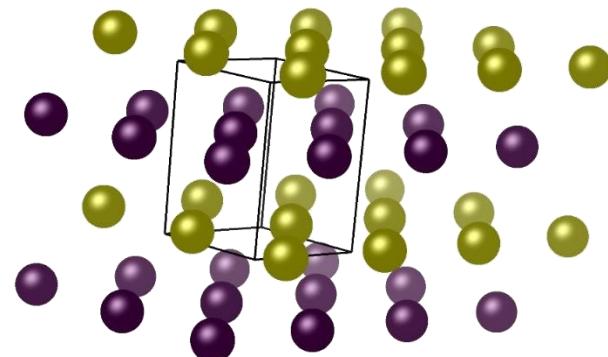
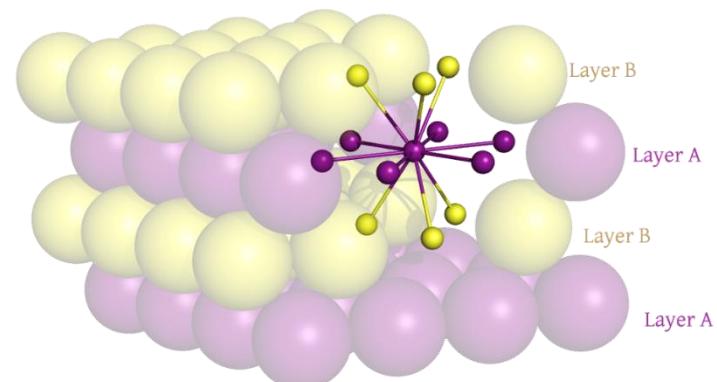
...and then six more Ga atoms at greater distances that come in pairs.

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 $4f^{14}$ 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^{3+} cation under normal chemical conditions (too high charge density). It is a rather inert element reacting under normal conditions only with F_2 and HNO_3 .
- 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

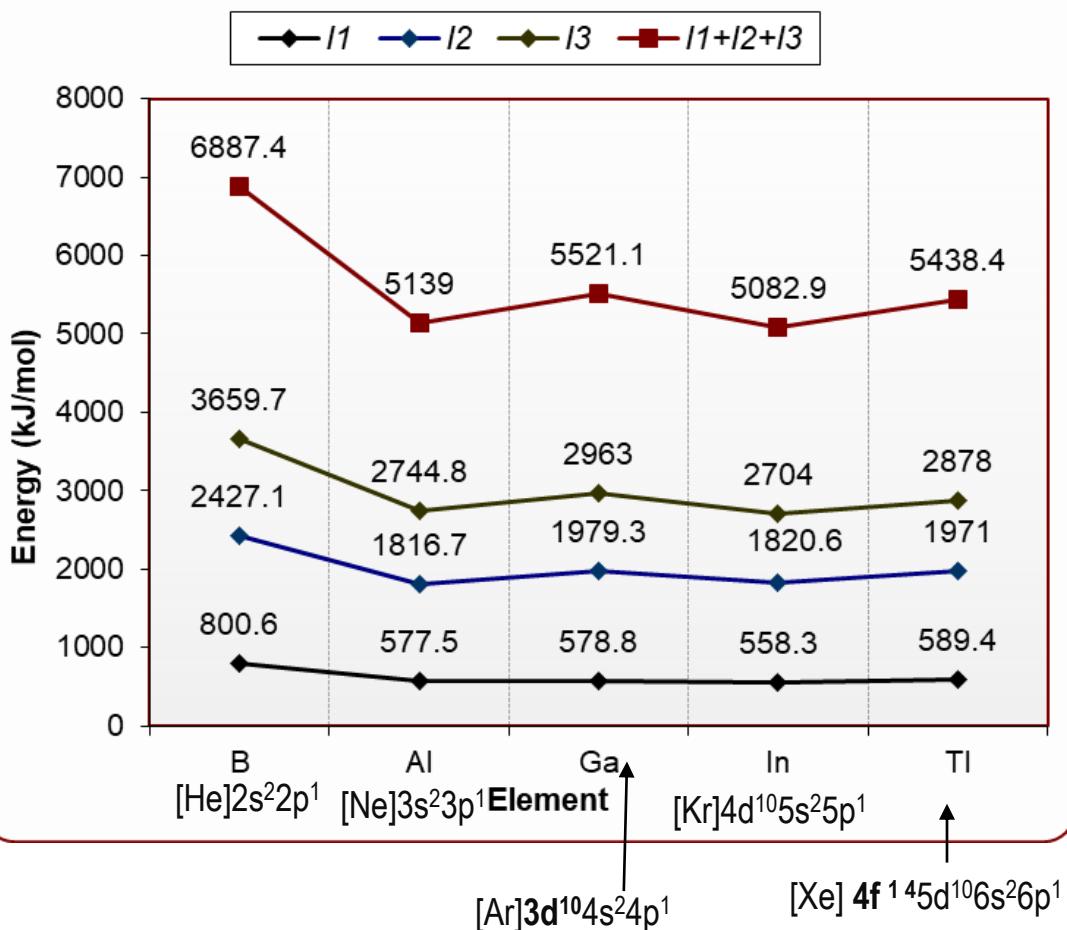
- Bulk physical properties (particularly mp and bp) are difficult to compare due to the differences in bonding and structure

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) ^{a)}	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
$E^\circ_{M+/M}$ (V)	—	+0.55	-0.79	-0.18	-0.336
$E^\circ_{M^{3+}/M}$ (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:



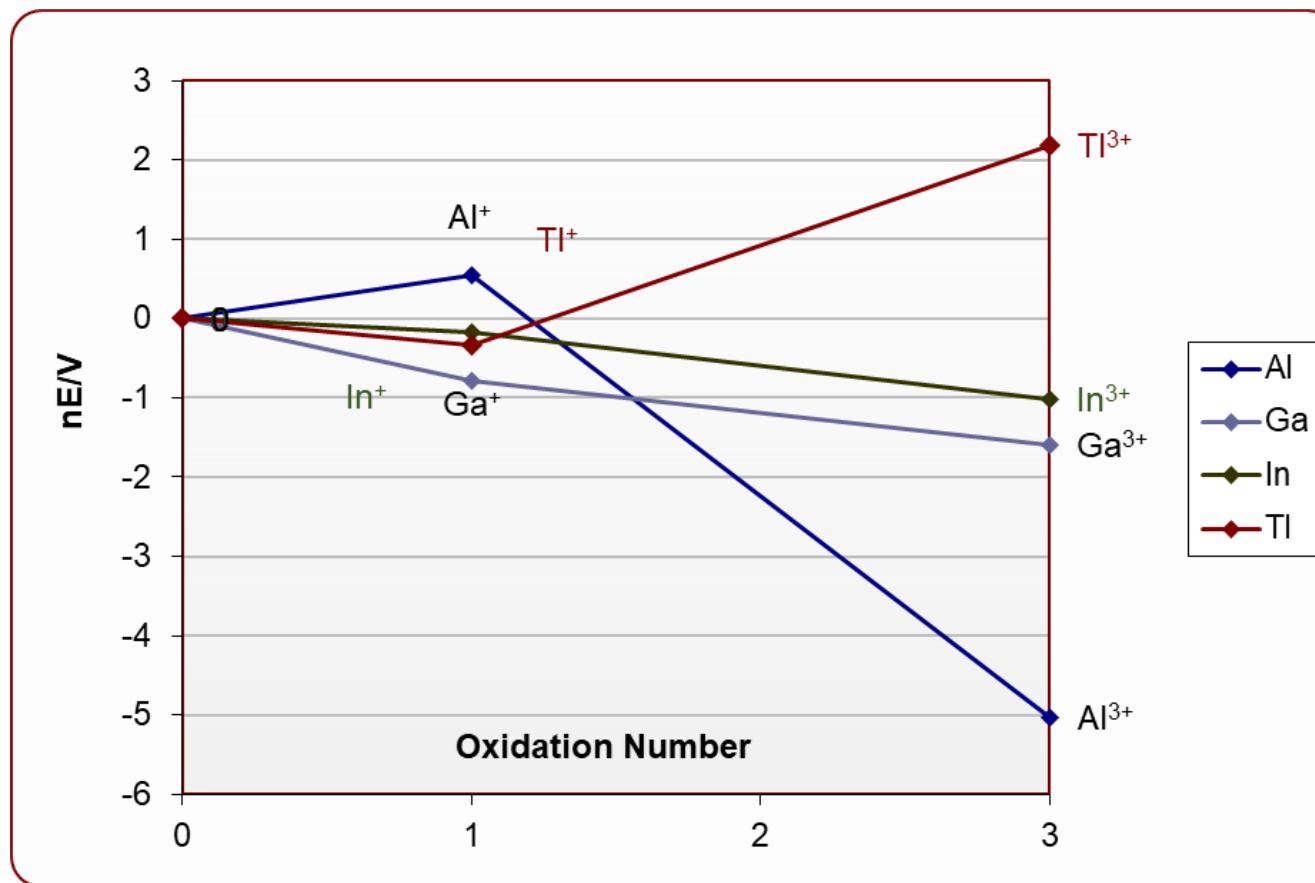
First: a very high ionization energies for boron—no wonder B likes to share electrons not loose them!

Second: the decrease in ionization potential from B to Al is not followed by the expected, further decrease to Ga. The d^{10} 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 form 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	26.9615
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!

$$v = \frac{Ze^2}{2\varepsilon_0 nh}$$

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.**

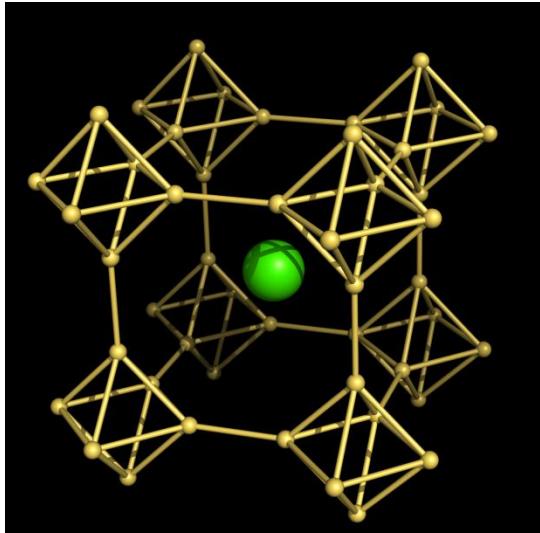
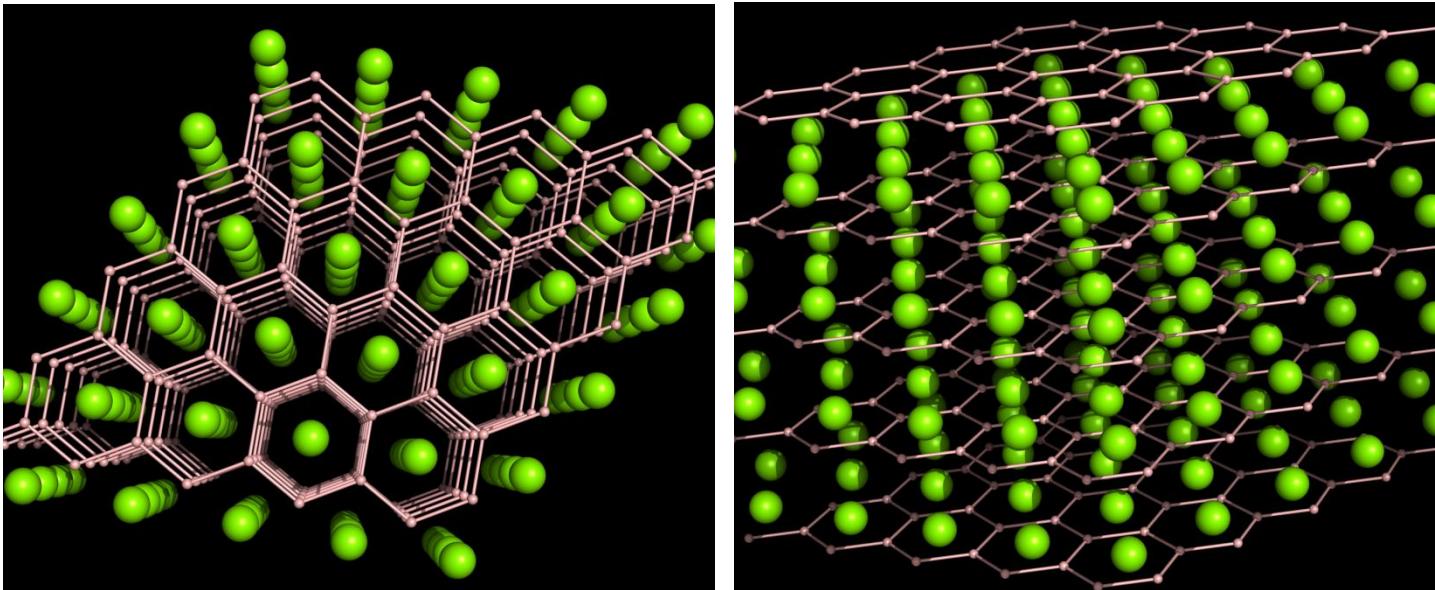
Metal Borides

- 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



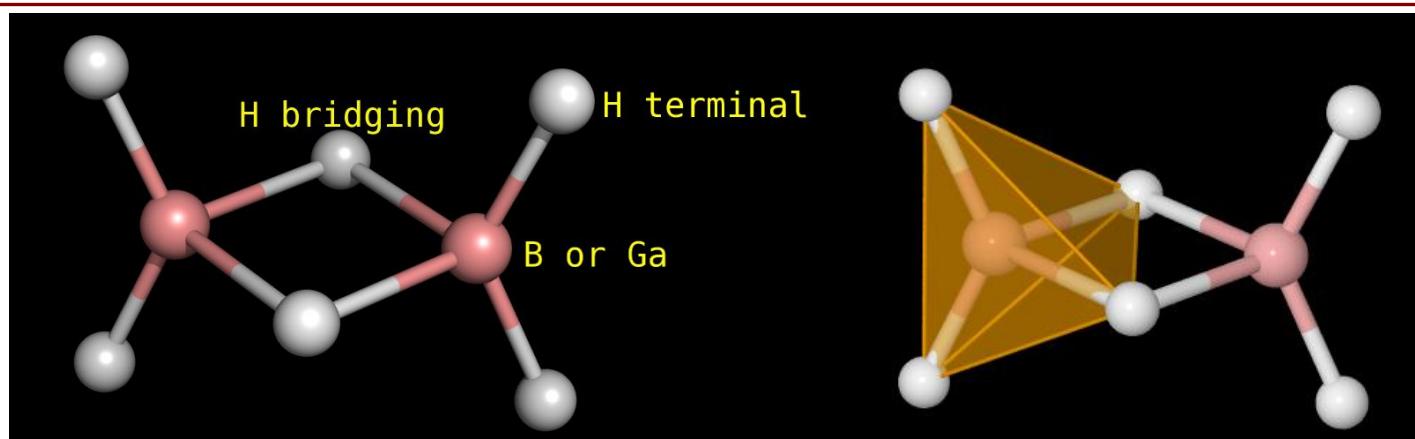
The Structure of MB_6
(M= Ca La, Ce):

- 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.

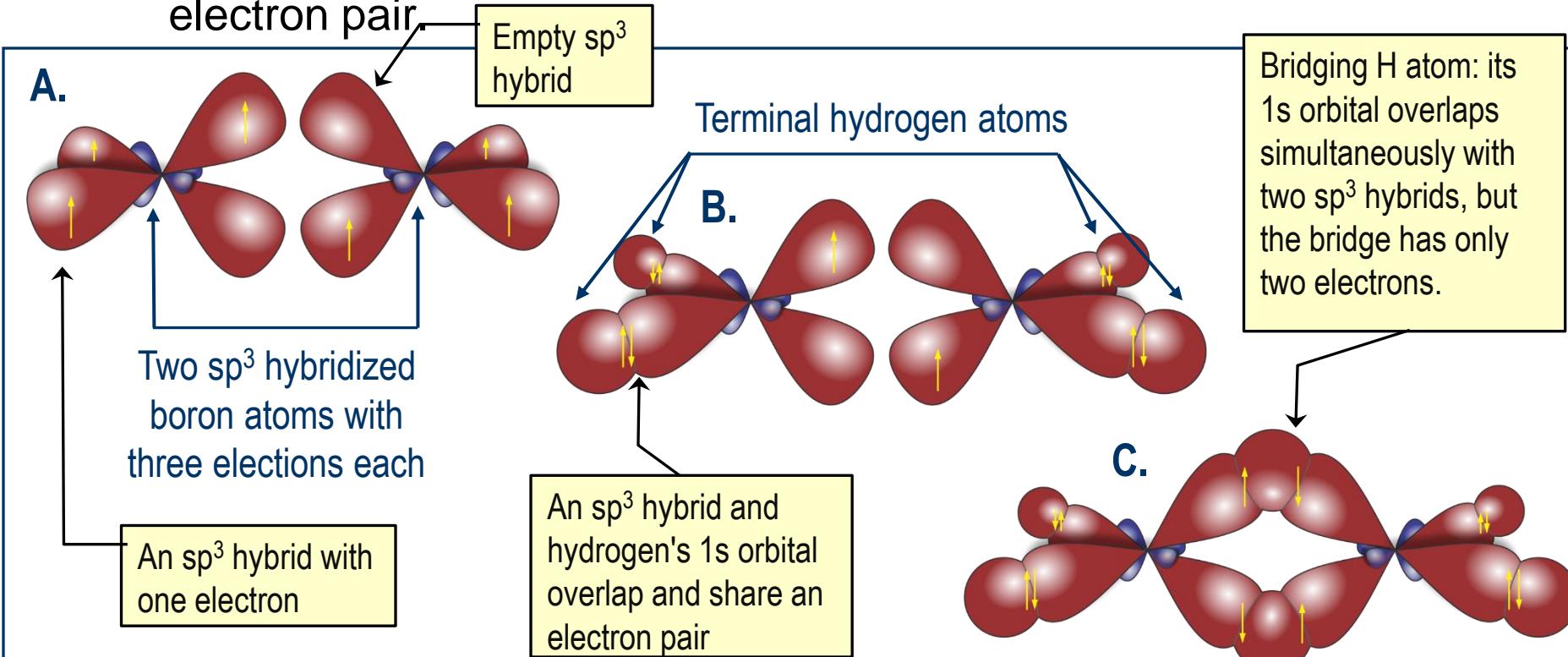
Overview of Group 13 Hydrides

- Only hydrides of B, Al and Ga are well characterized, In and Tl form very unstable species of probable composition 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 E_2H_6 ($\text{E} = \text{B}, \text{Ga}$) or polymeric structures;
 - Boron forms more than 50 compounds with a general formula B_xH_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.



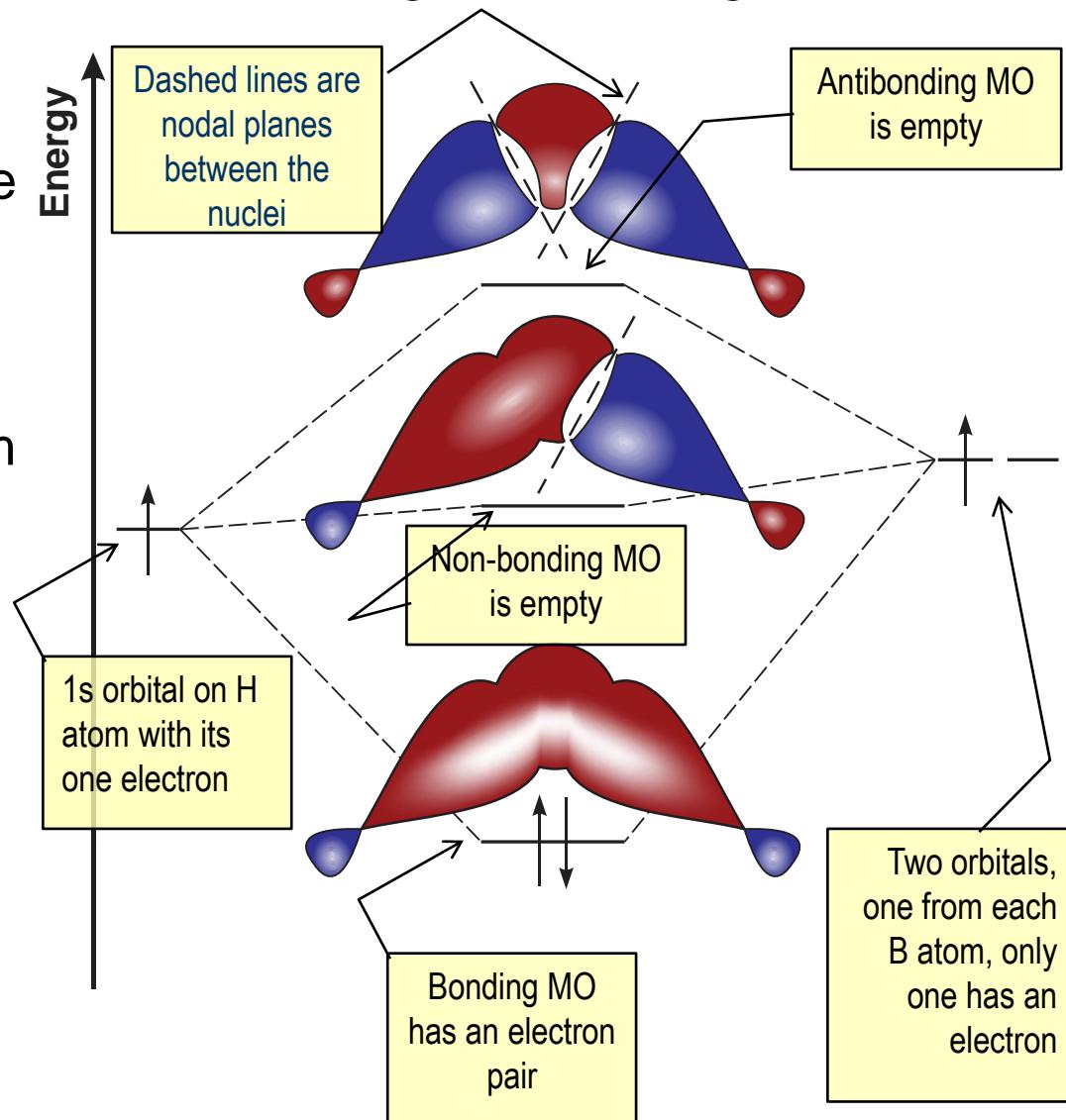
3 center–2 electron bonds

- 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.



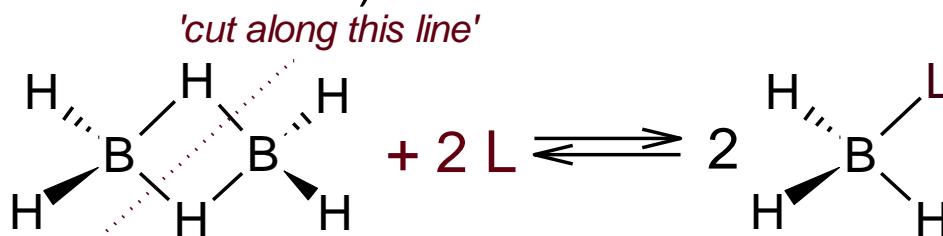
The EH₄⁻ (E = B, Al, Ga) Anions

- Two very common compounds
 - sodium tetrahydroborate or sodium borohydride (NaBH₄)
$$2\text{NaH} + \text{B}_2\text{H}_6 \xrightarrow{\text{In ether solvent}} 2\text{NaBH}_4$$
 - lithium tetrahydroaluminate or lithium-aluminum hidride (LiAlH₄)
$$\text{LiH} + \text{AlH}_3 \xrightarrow{\text{In ether solvent}} \text{LiAlH}_4$$
- There is also less frequently used GaH₄⁻.
 - Another method for synthesis of GaH₄⁻ and AlH₄⁻ which we shall encounter later.
- Terahydroborates 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:

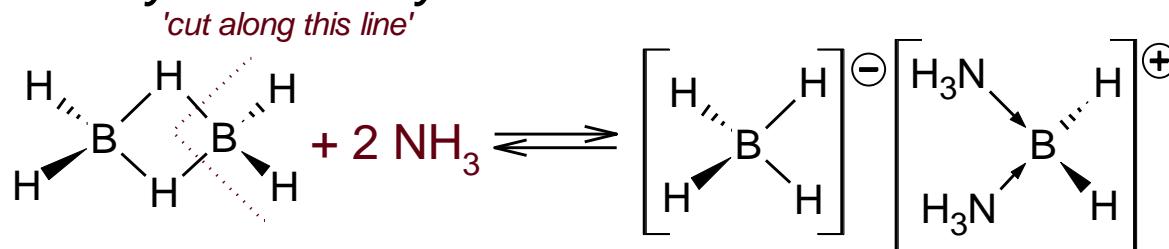


Further on B_2H_6 Reactivity

- Electron-deficient B_2H_6 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):



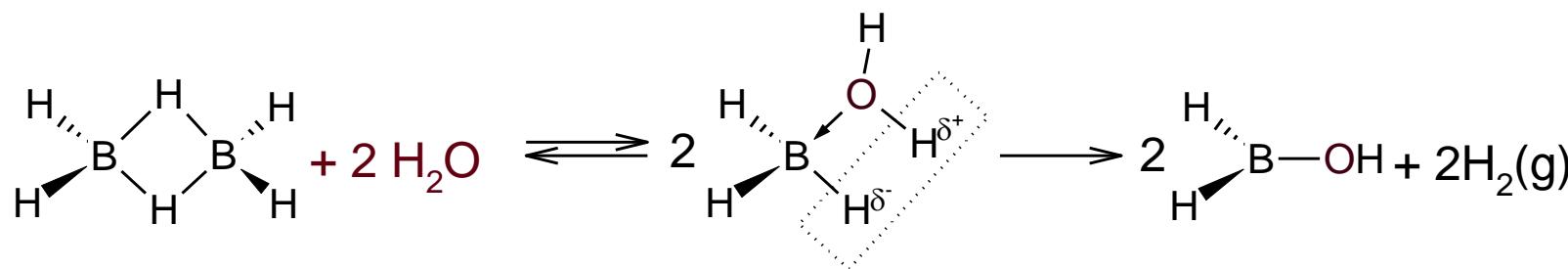
- If the Lewis base L is NH_3 , $\text{N}(\text{CH}_3)\text{H}_2$ or $\text{N}(\text{CH}_3)_2\text{H}$ the B–H–B bridge is cleaved *asymmetrically*:



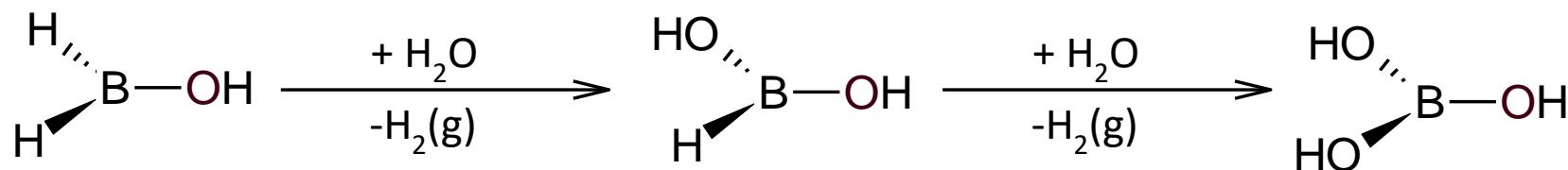
- B_2H_6 is a gas and is commonly used in a solution (usually in ether-like solvent) in which case the bridge is already cleaved by a solvent molecule.

Substitution reactions on B_2H_6

- If a Lewis base has polar $X^{\delta-}\text{--H}^{\delta+}$ 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_2 molecule:



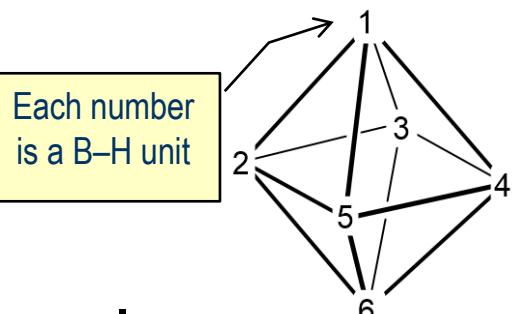
- Further addition/substitution reactions generally follow leading to a fully substituted product:



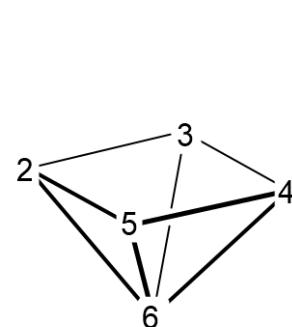
Boron-hydrogen clusters

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

Type	Closo-clusters	Nido-clusters	Arachno-clusters
------	----------------	---------------	------------------

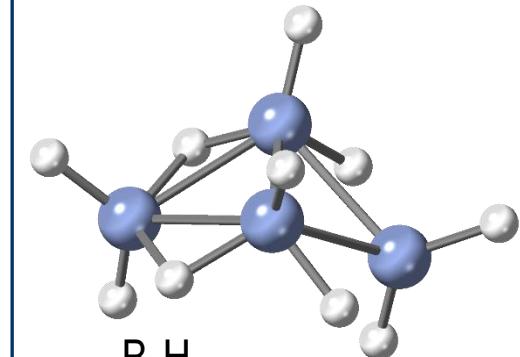
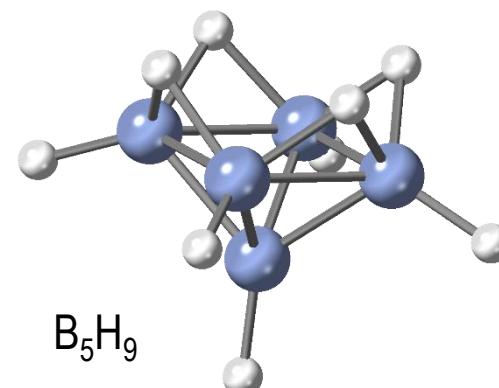
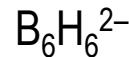
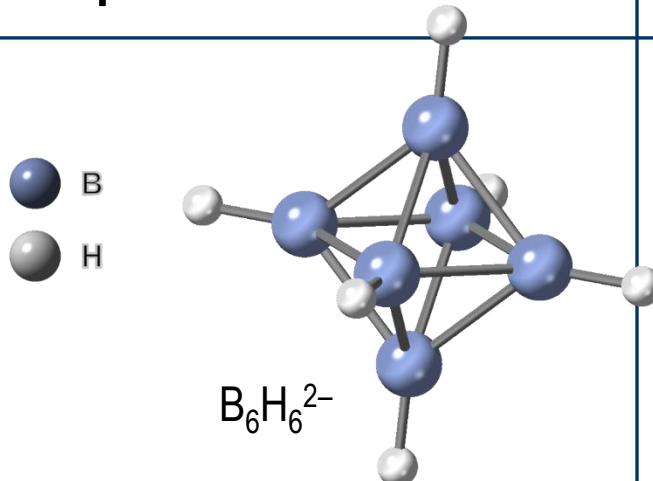


Remove
'1'

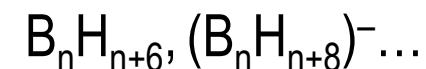
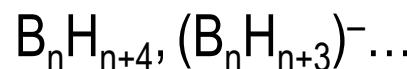


Remove
'6'

Examples

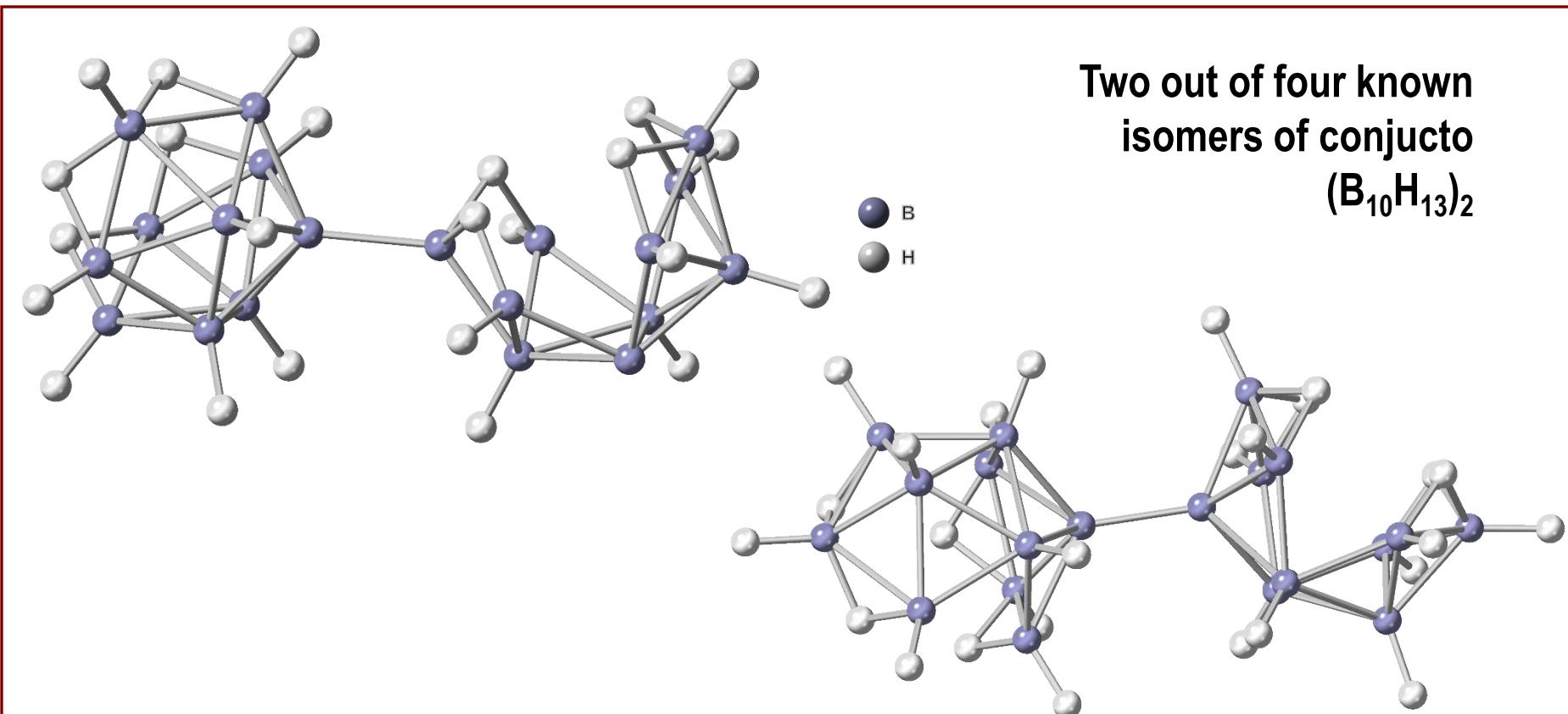


General formulae



Boron-hydrogen clusters (cont.)

- (Only) two more:
 - *Hypo*-clusters: remove one B atom from *arachno* structure (but these are still not characterized well enough)
 - *Conjucto*-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 *closو 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:

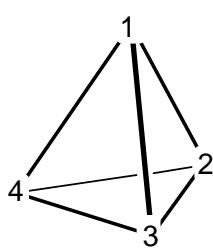
1. Determine the number of BH units in the structure
2. Each BH unit contributes *two* skeletal electrons
3. Each 'extra' hydrogen contributes *one* skeletal electron
4. Each negative charge contributes *one* skeletal electron

Wade's rule: Examples

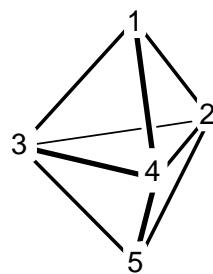
- Determine the type of B cluster in B_4H_{10} .
1. *Number of BH units:* the cluster has 4 B atoms and has 4 BH units
 2. *These provide an electron pair each:* 4 electron pairs
 3. *Extra H atoms:* there are $10 - 4 = 6$ H atoms extra, thus 3 more electron pairs
 4. *No charge*
 5. *Total number of electron pairs:*
 4 (from BH fragments) + 3 (from extra H) = 7
It is $n+3$ cluster - arachno

- Determine the type of B cluster in $\text{B}_{12}\text{H}_{12}^{2-}$.
1. *BH = 12*
 2. *12 el. pairs*
 3. *None*
 4. *2- charge: 1 el. pairs*
 5. *Total: 12 + 1 \Rightarrow closo cluster*

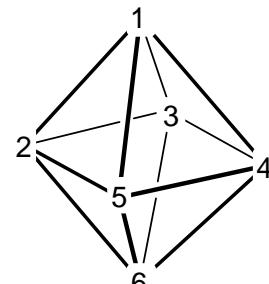
Parent polyhedrons



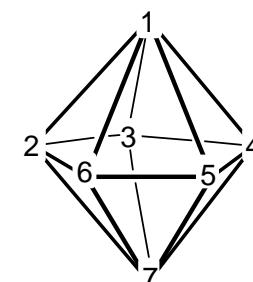
tetrahedron



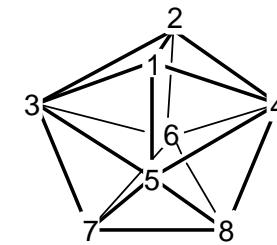
trigonal bipyramid



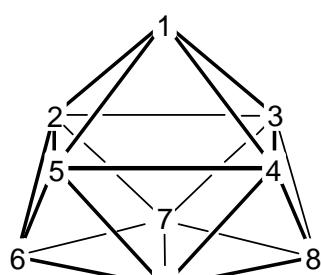
octahedron



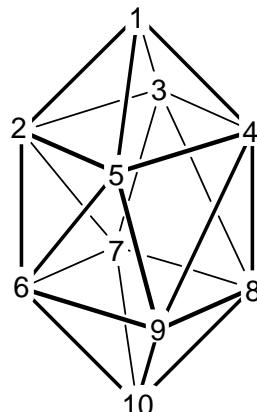
pentagonal bipyramid



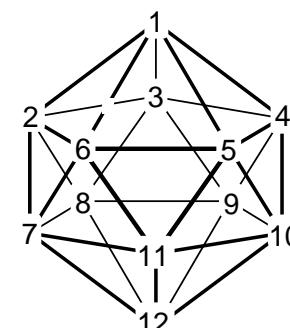
dodecahedron



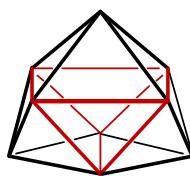
tricapped trigonal prism



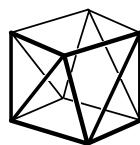
bicapped square antiprism



icosahedron



trigonal prism (red)



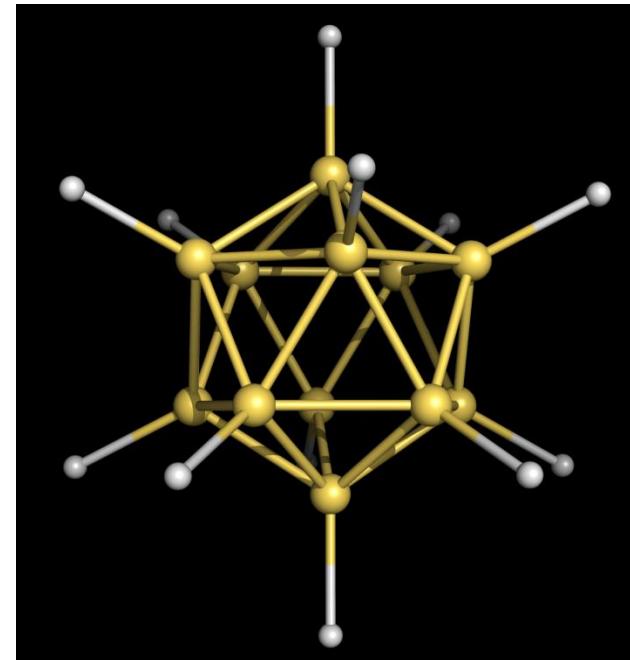
square
antiprism

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

Suggesting the structure...

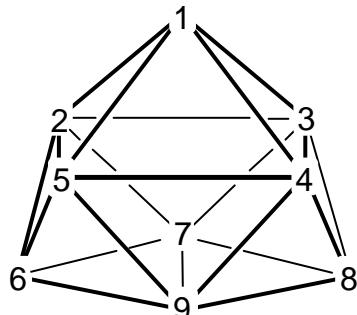
- If you determine *closo* type:
 - Choose the polyhedron that has number of vertices matching number of boron atoms
 - Each vertex = 1 B atom
 - Add an H atom to each B atom
 - Extra H atoms (*very rare for closo structures!*) are added to B atoms of particularly low connectivity

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

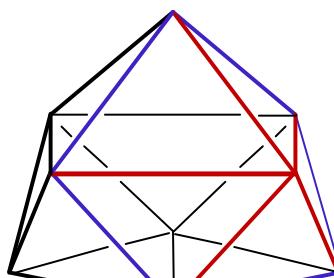


Suggesting the structure... (cont.)

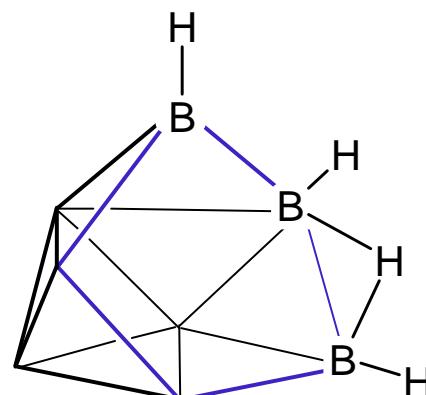
- If you determine *nido* or *arachno* type:
 - Find the *parent* closo polyhedron (the one that has one more B atom than *nido* or two more B atoms than *arachno*) and remove one (for *nido*) or two vertices for *arachno*;
 - *The first removed is usually a vertex of highest connectivity (bonded to 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: *closو*, *nido* or *arachno*?

7 BH units = 7 el. Pairs

4 extra H = 2 el. Pairs

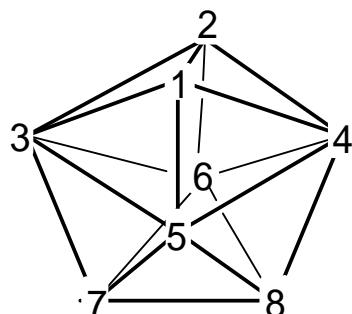
No charge

$7 + 2 = 9 (= n + 2 \rightarrow \text{nido cluster})$

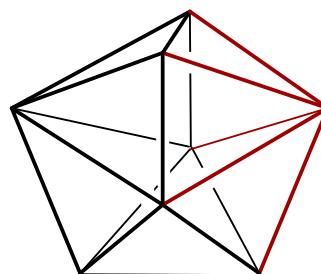
SECOND

answer – Which polyhedron?

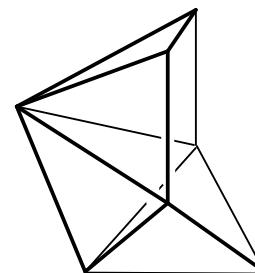
Nido = (*closو* – 1 vertex), so we start with polyhedron with 8 vertices or dodecahedron:



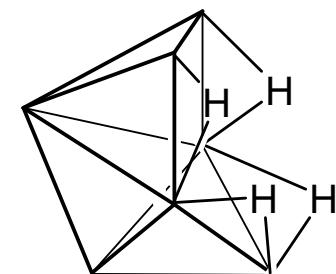
find parent *closو* structure
dodecahedron



find boron with highest
connectivity



and remove it

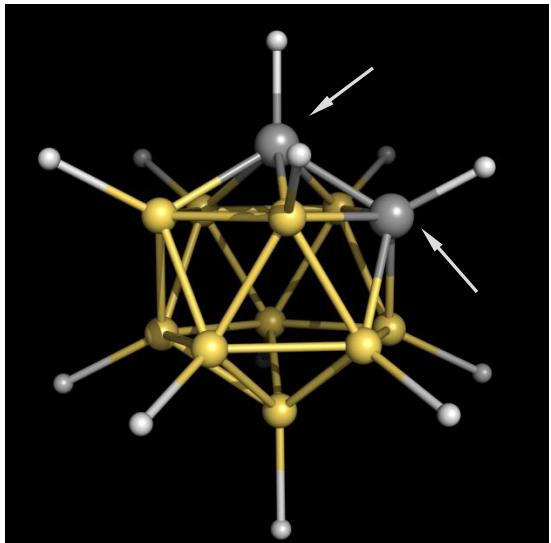
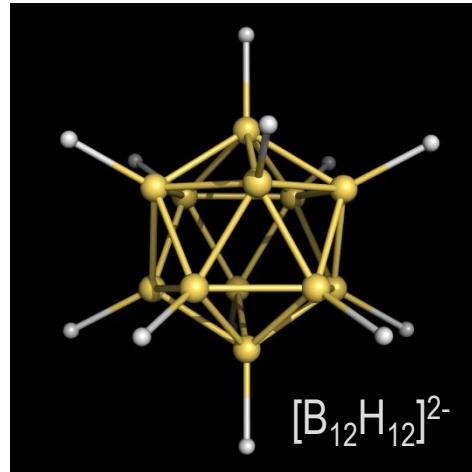
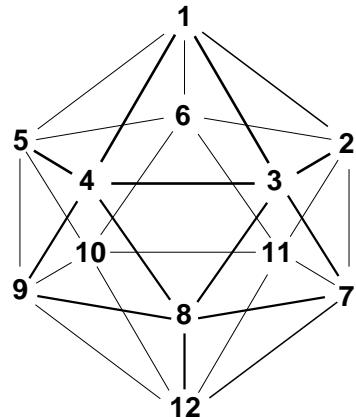


add bridging hydrogens
along open edges

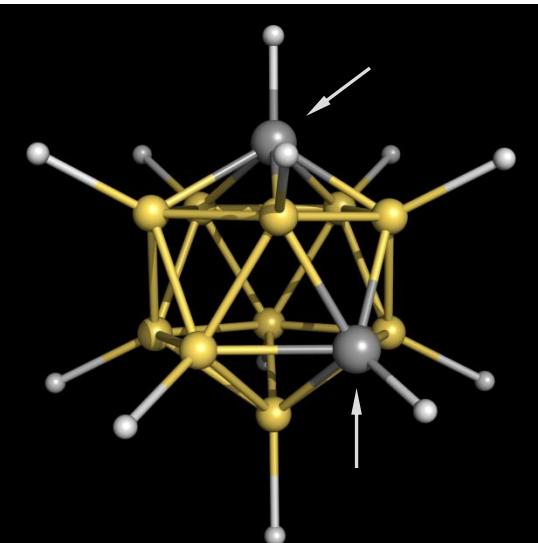
“Substituted” boranes

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

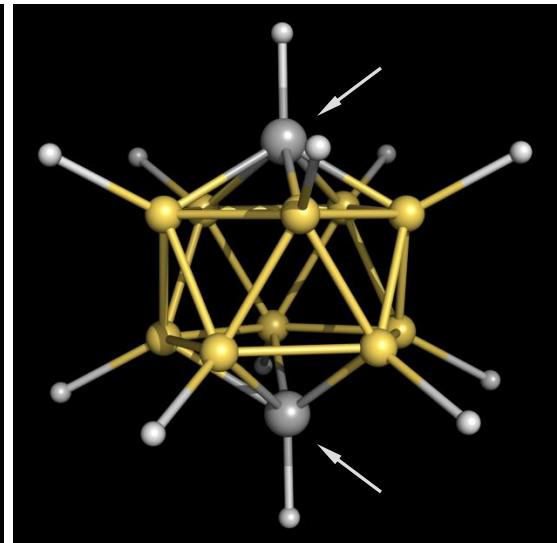
Numbering scheme



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_3)

- All boron halides are known
- Monomeric, volatile trigonal planar molecules
- All are readily decomposed by H_2O
 - BF_3 with water produces boric acid and tetrafluoroboric acid:



$\text{H}[\text{BF}_4]$ is tetrafluoroboric acid, a very strong acid.

- Other halides produce HX and B(OH)_3 :
- $$\text{BX}_3 + 3\text{H}_2\text{O} \rightleftharpoons 3\text{HX} + \text{B(OH)}_3 \quad (\text{X} = \text{Cl}, \text{Br}, \text{I})$$
- All BX_3 are strong Lewis acids and form Lewis acid-Lewis base adducts $\text{L} \rightarrow \text{BX}_3$ (L = Lewis base)
 - The Lewis acidity is not what we would expect based on electronegativity:



Why the difference in reactivity with H₂O?



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

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

For reaction 1 (reaction with BF₃): -8.8 kJ/mol

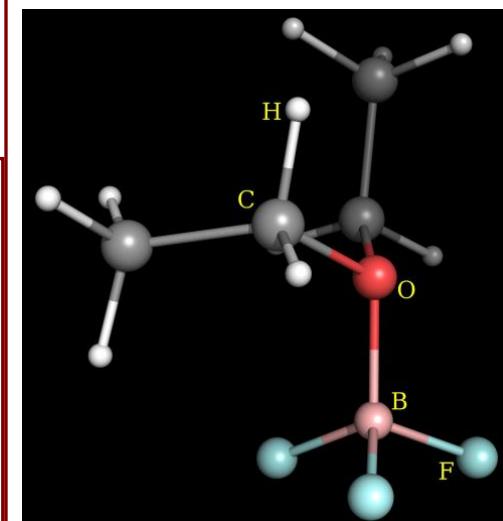
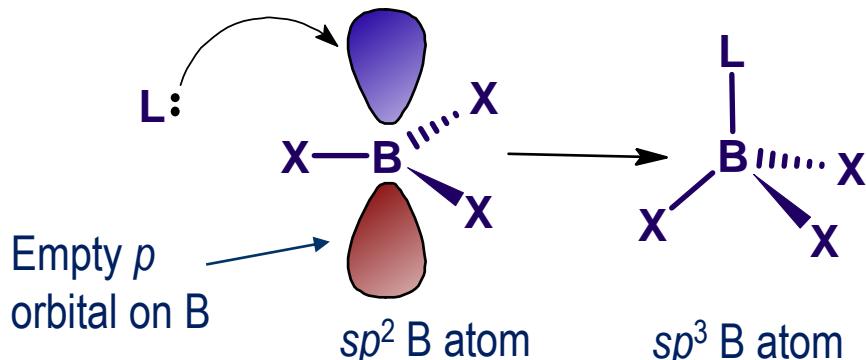
For reaction 2 (reaction with BCl₃): -196.5 kJ/mol

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 (BF₃) and gives H[BF₄].

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 BX_3

- Lewis acidity of boron halides (BX_3):

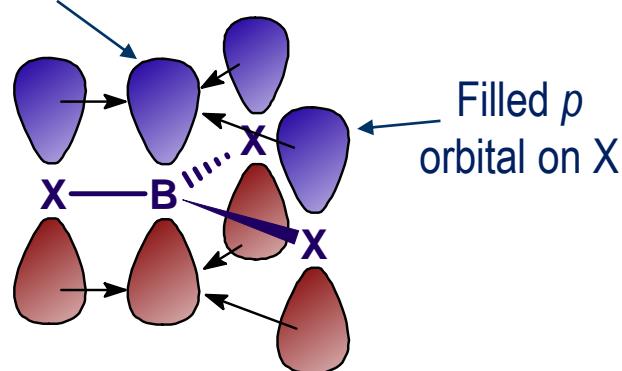


Structure of a Lewis acid-base adduct:
 $\text{BF}_3 \times \text{OEt}_2$
Note tetrahedral boron.

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

Empty p orbital on B

B-X bonds contain a partial π -character



π -contribution:
 $\text{F} > \text{Cl} > \text{Br} > \text{I}$

Size of X increases!

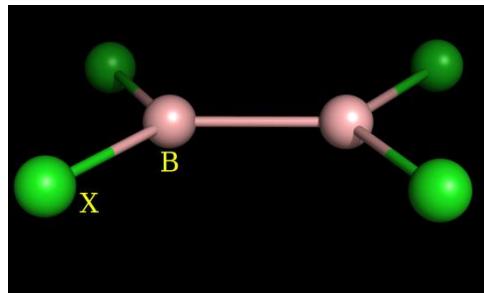
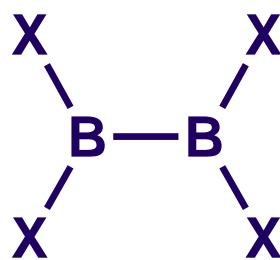
Since the empty p orbital on B atom is partially filled through p -interaction, BX_3 are weaker Lewis bases than expected. Again, since this p -interaction is the strongest for BF_3 , BF_3 is the weakest Lewis acid of the bunch.

- One evidence for π interaction is B-F bond lengths: in BF_3 (has π interaction) 130 pm and in $[\text{BF}_4]^-$ (only σ bonds) is 145 pm.

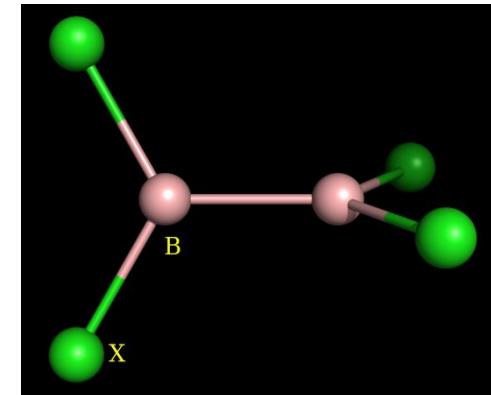
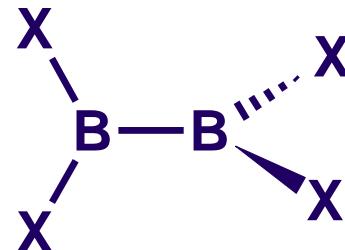
Other boron halides

- 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)



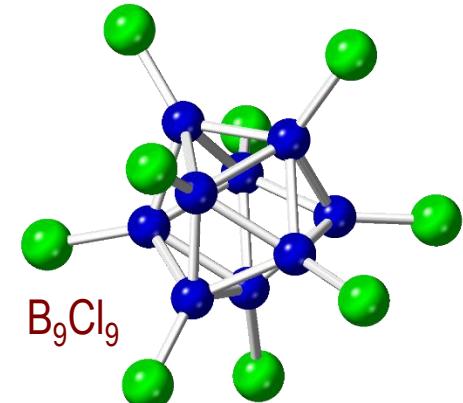
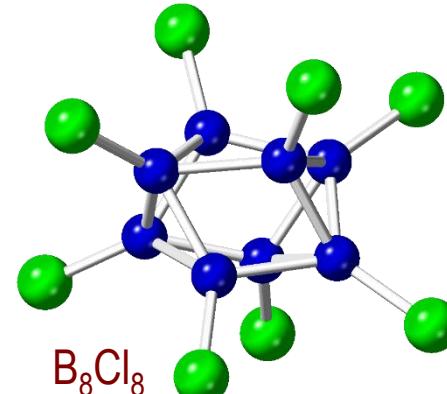
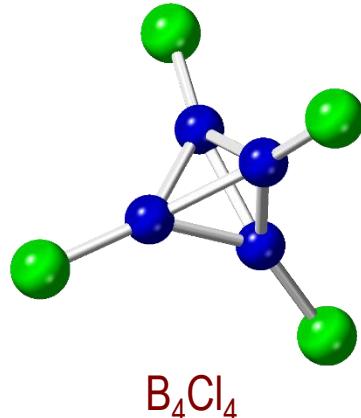
$X = Cl$ (vapor), Br & I (both solid and vapor)



- 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

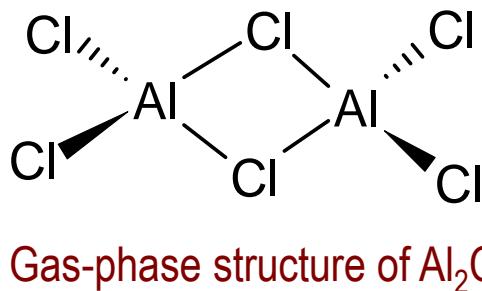


Halides of Al, Ga, In & Tl

- MX_3 , obtained by direct reaction of M with X_2
- Tl(III) halides are unstable and easily convert to Tl(I) halide and X_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)



- TlI_3 is actually Tl(I) triiodide (I_3^-)!



- Unlike BX_3 (monomeric), gas-phase contains discrete M_2X_6 ($\text{M} = \text{Al}, \text{Ga}$) molecules in an equilibrium with small amount of planar monomers, but their solids are polymeric
- The π -bonding and π -contributions are stronger in 2nd 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 EX₃

- The trifluorides of Al, Ga and In are lousy Lewis acids because they are sparingly soluble.
- For other MX₃ (M = Al, Ga, In; X = Cl, Br, I) the trends are as expected, i.e. AlCl₃ > AlBr₃ > AlI₃.
- But what is a trend in Lewis acidity for the series BCl₃, AlCl₃ and GaCl₃?
- The answer depends on the electron-pair donor (Lewis base):
 - For hard donors (i.e. oxygen in Et₂O or nitrogen in Me₃N) the order is
$$\text{BCl}_3 > \text{AlCl}_3 > \text{GaCl}_3$$
 - For soft donors (i.e. sulfur in Me₂S or phosphorus in PMe₃) 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 E₂O₃ are known (for this oxide is unstable) and can be obtained in direct reaction: E + O₂
- 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:

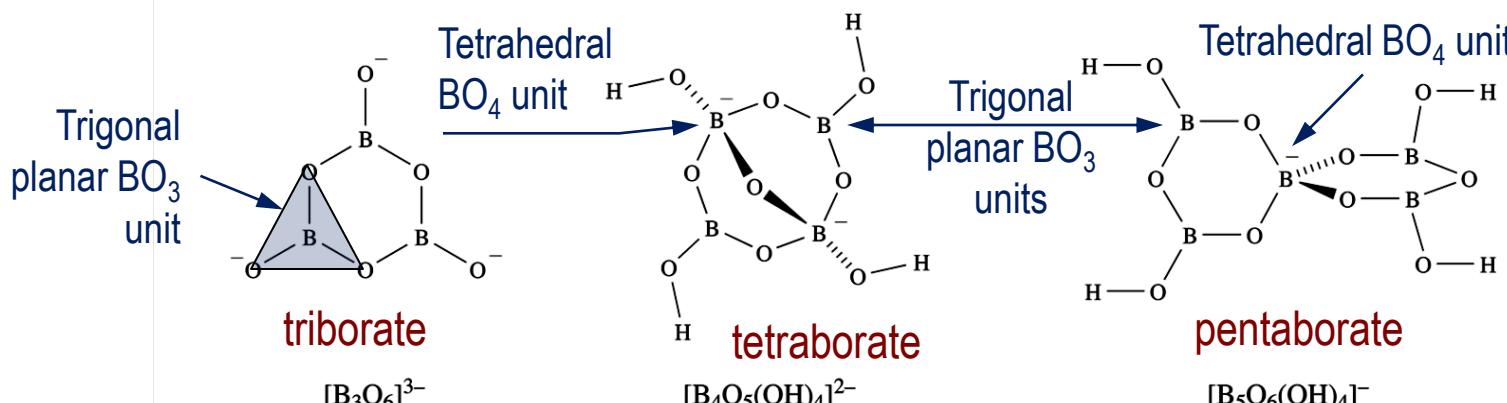
13 5 B 10,811	B(OH) ₃ - acidic	B(OH) ₃ + 2H ₂ O → [B(OH) ₄] ⁻ + H ₃ O ⁺ , pK _a = 9.2
13 13 Al 26,9615	Al(OH) ₃	M(OH) ₃ + OH ⁻ → [M(OH) ₄] ⁻ (acid-like behaviour)
31 31 Ga 69,72	Ga(OH) ₃	M(OH) ₃ + 3HX → MX ₃ + 3H ₂ O (base-like)
49 49 In 114,82	In(OH) ₃ - basic	In(OH) ₃ + 3HX → InX ₃ + 3H ₂ O
81 81 Tl 204,37	No Tl ^{III} hydroxyde but oxide is basic (TlOH is also basic)	

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 HBO_2 (metaboric acid) and (with further heating) B_2O_3 :

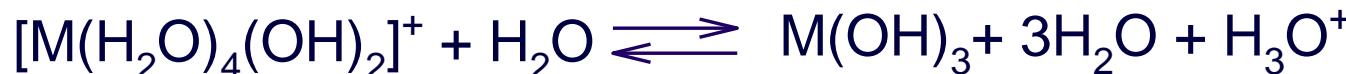
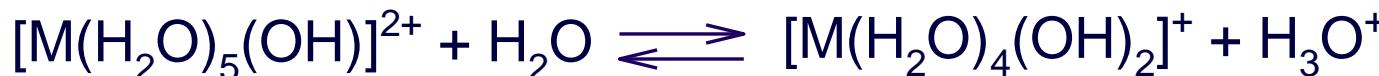


- All other more complex borate anions have structures composed of trigonal planar BO_3 and/or tetrahedral BO_4 units sharing a common oxygen atom:

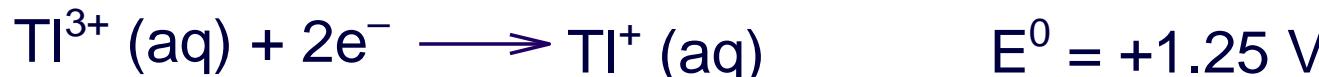


Aqueous chemistry of M³⁺ and M⁺ ions

- “B³⁺” does not exist.
- M³⁺ (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:

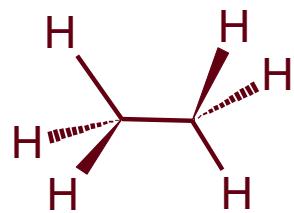


- M⁺ (M = Ga, In) are good reducing agents:

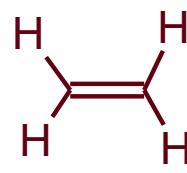


Boron-nitrogen compounds

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



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



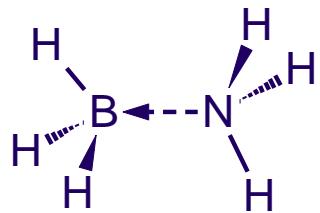
$d_{CC} = 1.33 \text{ \AA}$



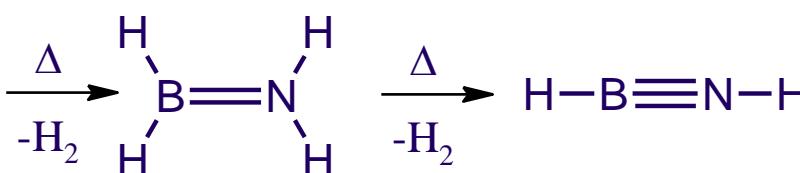
$d_{CC} = 1.18 \text{ \AA}$



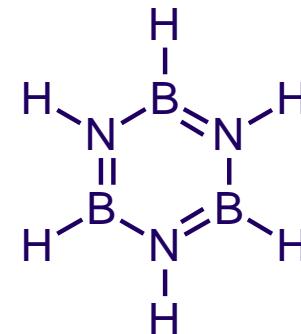
$d_{CC} = 1.40 \text{ \AA}$



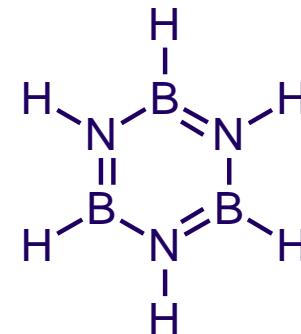
$d_{BN} = 1.58 \text{ \AA}$
(solid, stable)



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



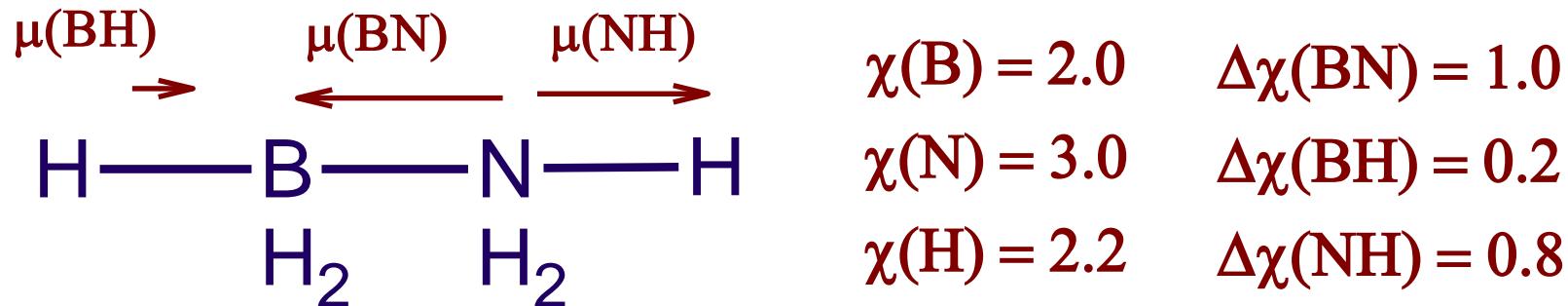
$d_{BN} \sim 1.22 \text{ \AA}$
(unstable)



$d_{BN} = 1.44 \text{ \AA}$
(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.



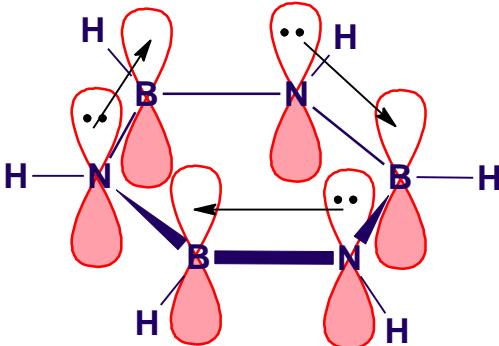
- **Structural vs. chemical similarity:** Although structurally similar, B–N bonds are weaker and more reactive than C–C bonds. As a result, the reaction mechanisms and products can significantly differ between the two groups of compounds.
- Like C-C compounds, hydrogen atoms can be substituted with other groups (for example X_3BNR_3 , X_2BNR_2 , XBNR & $(\text{XBNR})_3$ where X and R = H, OR, halogens, organic groups, etc.).

Borazene: Inorganic benzene – $\text{B}_3\text{N}_3\text{H}_6$

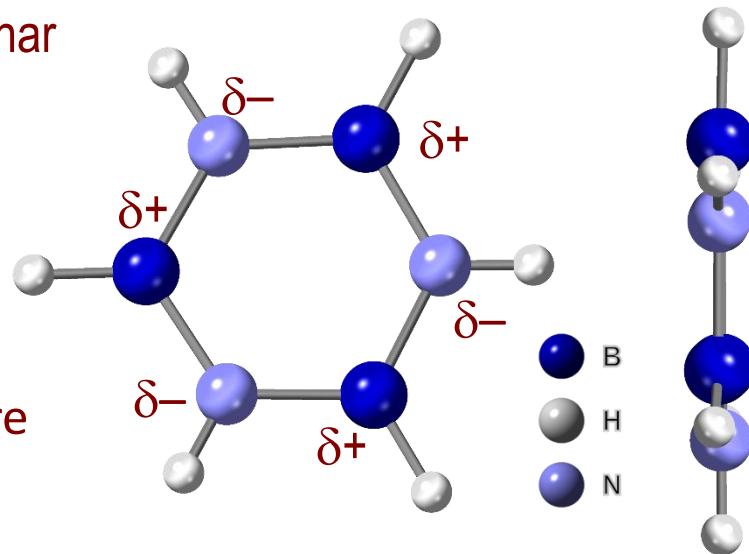
- Synthesis:



Electron delocalization in borazene ring



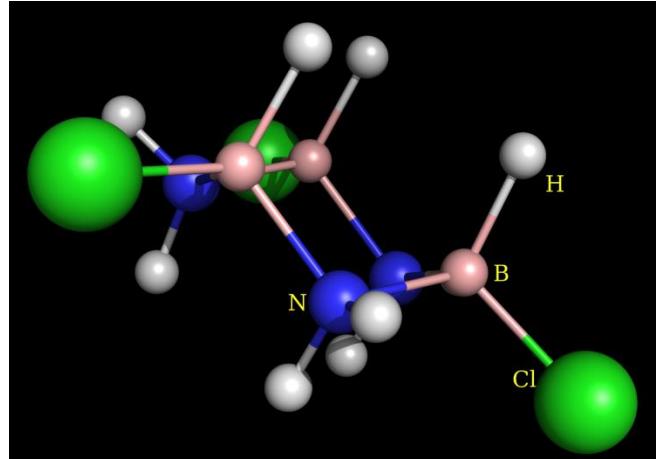
$\text{B}_3\text{N}_3\text{H}_6$ is a planar molecule (as is C_6H_6), but B–N bond is polar (unlike C–C bond) making borazene more reactive than benzene



- Additions to $(\text{HNBH})_3$ are easy:

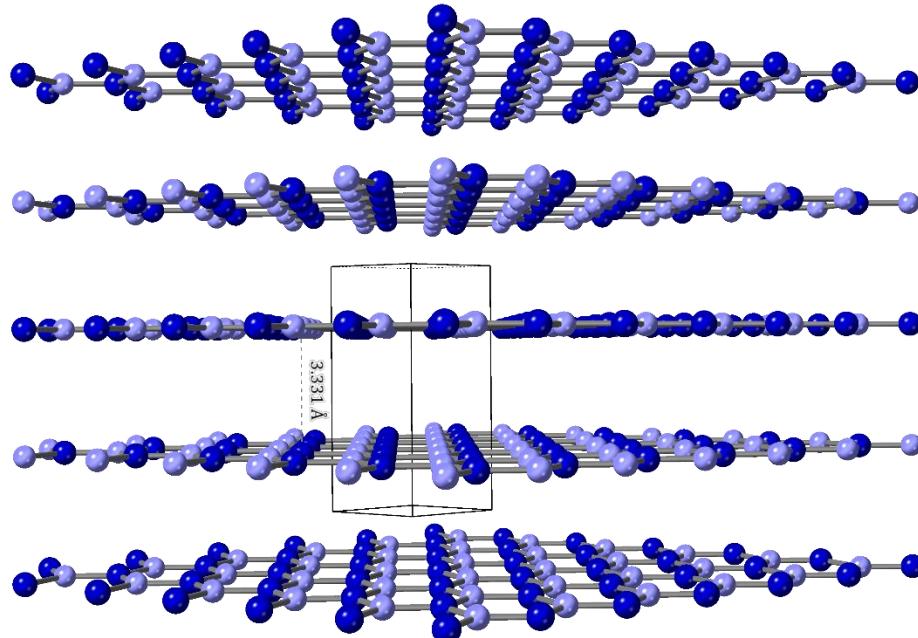


A 1,3,5 –trichlorocyclohexane analogue



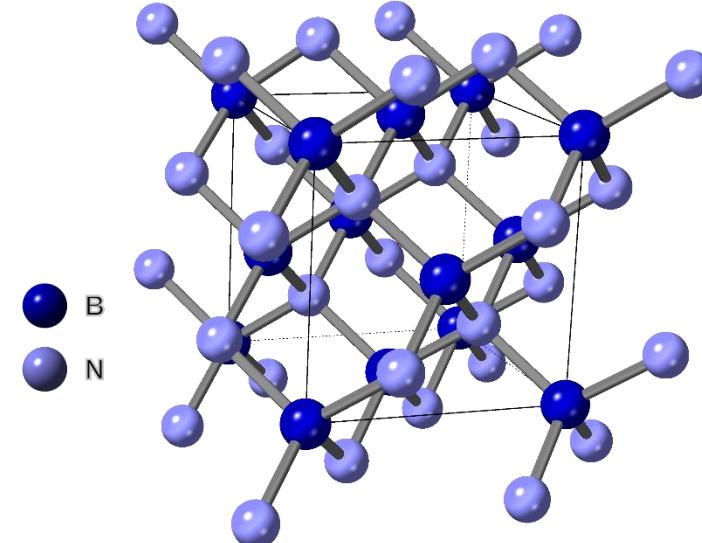
Hexagonal & cubic BN

- Boron nitride (BN): α -BN (hexagonal, graphite-like) and β -BN (cubic, diamond-like)



Layered structure of α -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 β -BN (cubic):

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

Overview

18	B	10,811
13	Al	26,9815
31	Ga	69,72
49	In	114,82
81	Tl	204,37

- The elements
- Thallium and relativistic effects
- Isolation
- Hydrides
 - Structures and 3c-2e bonds (B_2H_6 and Ga_2H_6)
 - Reactivity of B_2H_6
 - Tetrahydroborates and tetrahydroaluminates
- Halides
 - Lewis acidity and reactions of Group 13 halides
 - Structures of BX_3 and B_2X_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 6th 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 7th 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

Closو, nido and arachno Relations

