



Paper: CC3

Unit : Chemistry of s and p- Block Elements

Course Instructor: Dr Debopam Sinha

Books:

Inorganic Chemistry- Catherine E. Housecroft And Alan G. Sharpe

Chemistry of the Elements - A. Earnshaw and Norman Greenwood



1	2		13	14	15	16	17	18
H					<i>p</i>			He
Li	Be		B	C	N	O	F	Ne
Na	Mg		Al	Si	P	S	Cl	Ar
K	Ca	<i>d</i> -block	Ga	Ge	As	Se	Br	Kr
Rb	Sr		In	Sn	Sb	Te	I	Xe
Cs	Ba		Tl	Pb	Bi	Po	At	Rn
Fr	Ra							

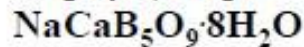
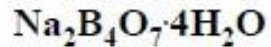
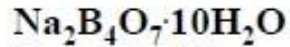


ELEMENT	SYMBOL	ELECTRON CONFIGURATION
Boron	B	$[\text{He}]2s^2 2p^1$
Aluminium	Al	$[\text{Ne}]3s^2 3p^1$
Gallium	Ga	$[\text{Ar}]3d^{10} 4s^2 4p^1$
Indium	In	$[\text{Kr}]4d^{10} 5s^2 5p^1$
Thallium	Tl	$[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^1$

The Elements of the Third Main Group Do Not Exist As Elements, Because of Their High Reactivity (Aluminium Is the Most Abundant Metal of Earth's Crust)

Boron

Mineral: Borax



Borax

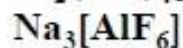
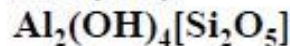
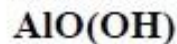
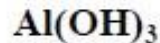
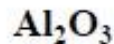
Kernite

Ulexite



Aluminium (alumen)

Lat.: Alaun



Corundum, sapphire, ruby

Hydrargillite

Diaspore, boehmite

Kaolinitic clay

Cryolite



Beryl
 $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$
 Emerald



Gallium (gallia)

Lat.: France

Indium

Indigo spectral line

Thallium (thallus)

Greek: green twig

rare, normally accompanied by other elements, e.g. Zn

→ limited resources

rare, mostly accompanied by Zn (ZnS)

→ limited resources



Lorandite



Sapphire: Intervalence transition between Fe^{2+} and Ti^{4+} replacing Al^{3+} in adjacent octahedral sites

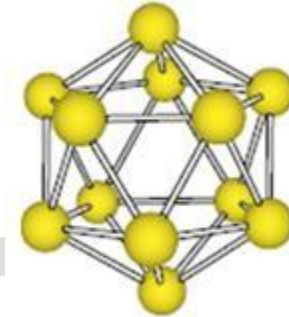
Ruby : Cr^{3+} replacing Al^{3+} in octahedral sites. d-d transition

Emerald : Cr^{3+} replacing Al^{3+} in octahedral sites. d-d transition

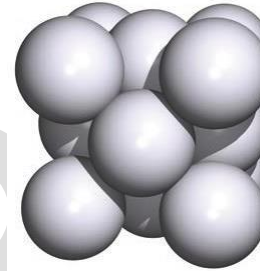
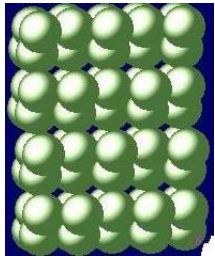


Structure in lattice

Boron \rightarrow B₁₂ (icosahedron) in elemental B

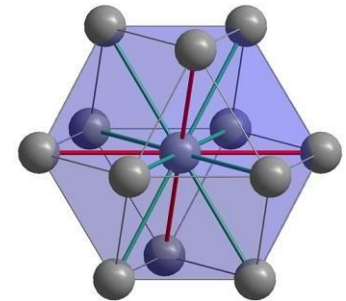


Aluminum \rightarrow fcc (face centered cube, atomic radii 143 pm)

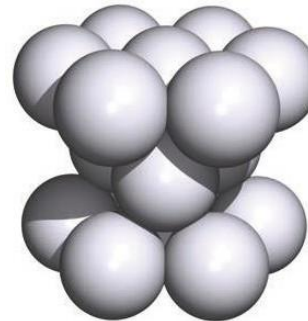


Orthorhombic, each Ga atom has one nearest neighbour at 244 pm, 2 at 270 pm, 2 at 273 pm, 2 at 279 pm

Indium is a slightly distorted face-centered cubic structure, where each indium atom has four neighbours at 324 pm distance and eight neighbours slightly further (336 pm)



Tl adopts hexagonal close packing (hcp) with atomic radii 171 pm



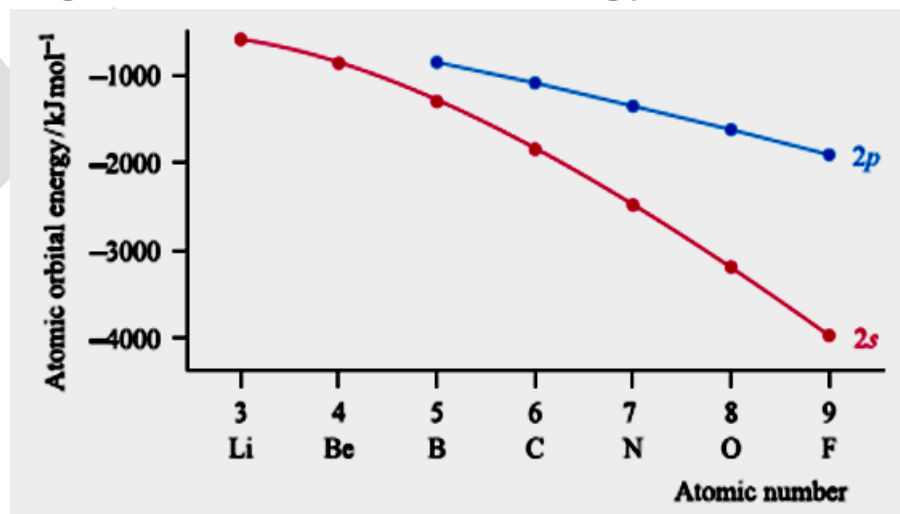


MO Diagram of B₂

Boron is a diatomic molecule and show two electron paramagnetic. The magnetic behaviour can be explained from the Molecular Orbital Theory of B₂ molecule. B₂ molecule has total 10 electrons. And the simple molecular energy level and the molecular orbital electronic configuration (considering no mixing) is as follows:

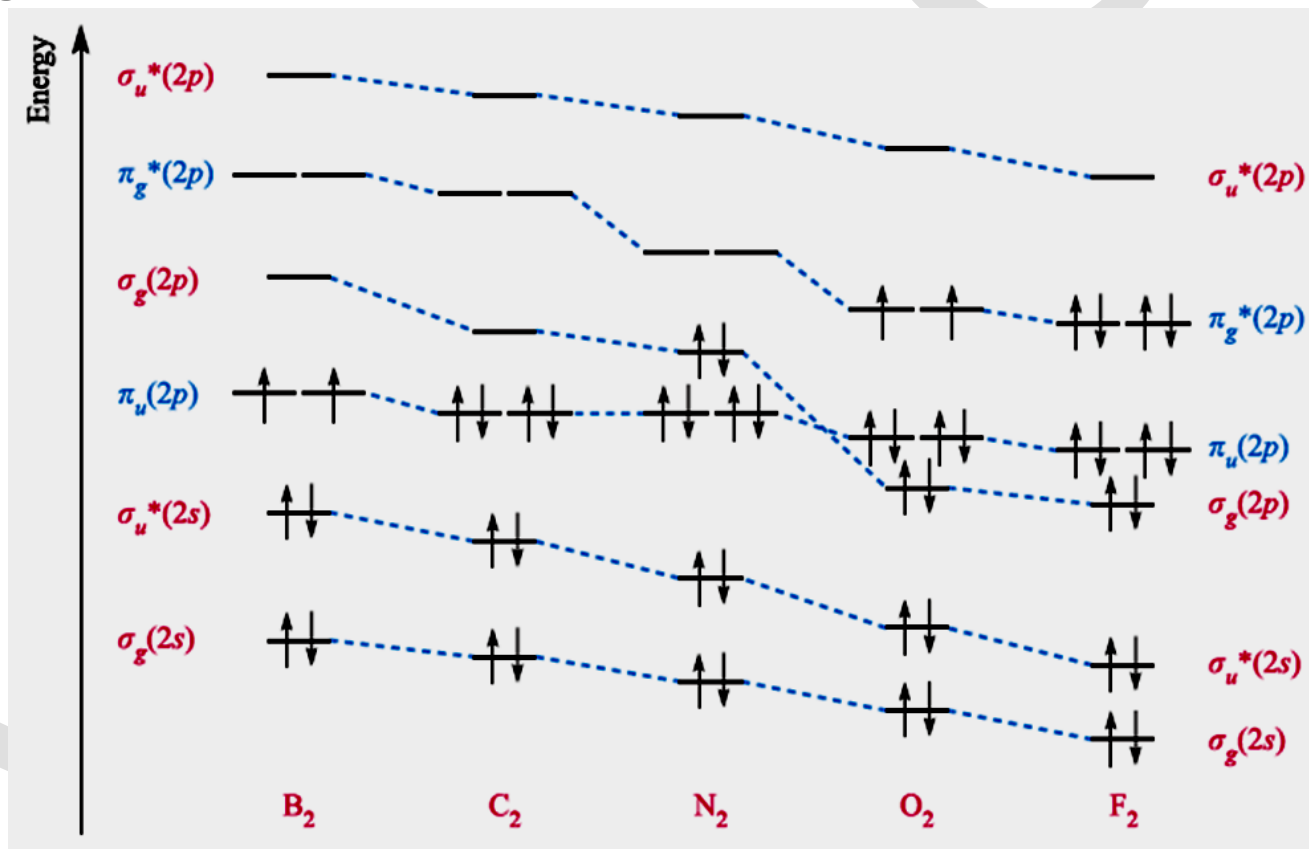
Discussions

The simple MO shows boron is diamagnetic. But B₂ is paramagnetic in nature. This can be explained on the basis of mixing between 2s and 2p orbitals. The extent of mixing depends on the energy separation between 2s and 2p orbital. It is to be noted that the absolute energy of 2s and 2p decreases from Be to F. On the other hand the energy separations between them increases with increasing electronegativity i.e. moving from Be to F.





Thus the degree of mixing decreasing from Be to F. The s-p mixing alter the energy and the energy of $2\sigma_g$ and exceed the energy of $1\pi_u$ upto N_2 and become lower than $1\pi_u$ in case of O_2 and F_2 . A schematic diagram is shown below:



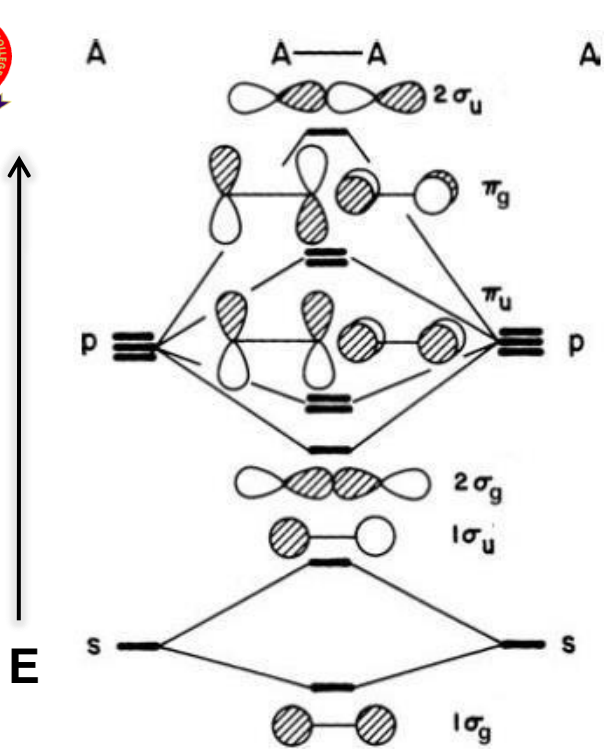
There are two unpaired electron in degenerate (π_u) , hence B_2 paramagnetic



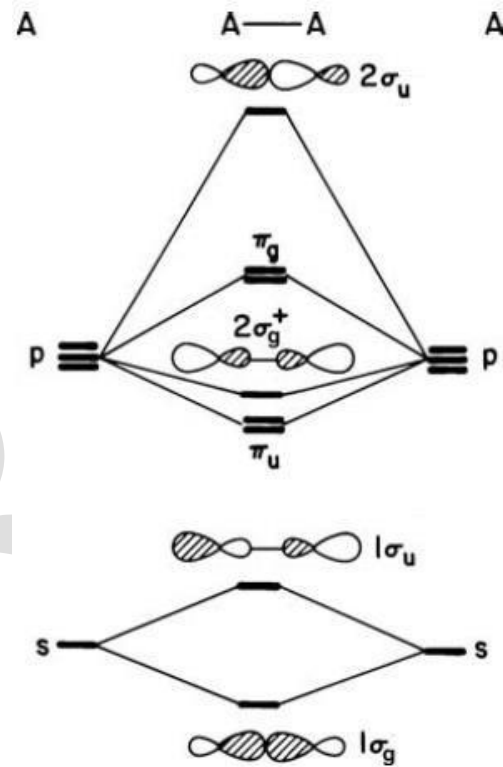
Shapes of MO's considering s-p mixing

s-p mixing is incorporated by the following steps:

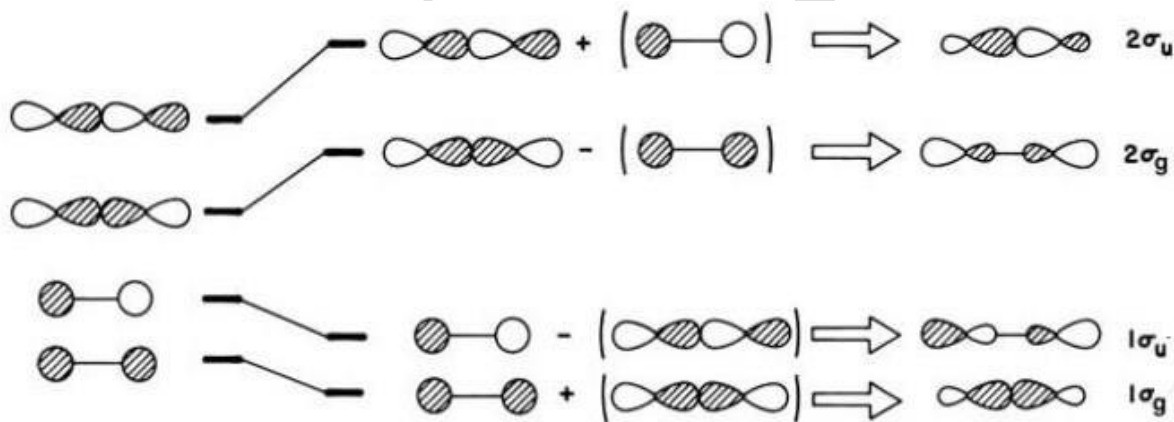
- 1. We at first construct the MOs from the pure (unmixed) AOs in the usual fashion**
- 2. Interaction between the resultant MOs is to be considered following the Non-crossing Rule.**
- 3. Non-crossing Rule: The energies of orbitals of the same symmetry can not cross each other rather mix (interact) and diverge.**



Without s-p mixing Used for O_2 and F_2



With s-p mixing Used for Be_2 , B_2 , C_2 and N_2



Essentially non-bonding orbital with some bonding character

Essentially non-bonding orbital with some anti-bonding character



	B	Al	Ga	In	Tl	
Atomic radius (pm)	85	143	135	167	170	
Ionic radius (pm) M^{3+}	27	53.5	62.0	80.0	88.5	
Density ($g\ cm^{-3}$)	2.35	2.70	5.90	7.31	11.85	
Ionization energy (kJ mol ⁻¹)	I	800	577	578	558	590
	II	2429	1816	1979	1820	1971
	III	3659	2744	2962	1704	2877
Electronegativity	2.0	1.5	1.6	1.7	1.8	
Melting point (K)	2453	933	303	430	576	
Boiling point (K)	3923	2740	2676	2353	1730	

General Physical Characteristic

- Al, Ga, In, and Tl are metals.
- Atomic radius increases suddenly from B to Al.
- This is due to the greater screening effect of electrons present in the penultimate shell.
- The atomic radii of Al and Ga are same. This is because of the poor shielding effect of d-electrons in Gallium
- Density increases from Boron to Thallium.
- The m.p.'s and b.p.'s of IIIA group elements do not show any regular trend. This is due to the difference in their crystal structures.
- Boron has high m.p because it exists as a giant covalent polymer both in liquid and solid.
- Melting points order $B > Al > Tl > In > Ga$
- Boiling points order $B > Al > In > Ga > Tl$
- The most electropositive element in IIIA group is Al.

Anomaly behavior of (i) B (ii) Ga over Al & (iii) Tl vs In

- ◆ The cumulative effects of small size, high electro-negativity and non-availability of d -orbitals for the first member are responsible for differences with the other members
- ◆ The anomalous position of Gallium figures importantly in the chemistry of this element, and is a consequence of the Scandide Contraction. This is reflected in the electron configuration of the element: it is the first in the group to have a set of filled d orbitals preceding the valence p orbitals. The very poor shielding of the d electrons results in a higher-than-expected effective nuclear charge on the valence electrons of Gallium, and hence its anomalous behavior
- ◆ Gallium is liquid as Ga exists as Ga_2 in the lattice.
- ◆ The $6s^2$ electrons are tightly bound (inert pair effect) to the nucleus and act as an inert pair electron due to the very poor shielding of $4f^{14}$ sub shell in case of Tl and hence explain the anomaly behavior of Tl over Indium. (Inert Pair and Relativistic effect)

Ionization potentials for group 13 elements kJ/mol

IP	Boron	Aluminium	Gallium	Indium	Thallium
1st	800.6	577.5	578.8	558.3	589.4
2nd	2427.1	1816.7	1979.3	1820.6	1971
3rd	3659.7	2744.8	2963	2704	2878
(2nd + 3rd)	6086.8	4561.5	4942.3	4524.6	4849

The high ionization potential (IP) (2nd + 3rd) of gallium is explained by d-block contraction, and the higher IP (2nd + 3rd) of thallium relative to indium, has been explained by relativistic effects

The all anomaly behavior can not be explain properly only on the basis of the inert pair effect

Relativistic Effects

The theory of relativistic effects in Chemistry is given here. Einstein's Theory of Special Relativity states that the mass of any moving object changes as its velocity changes:

Qualitative treatment

One of the most important and familiar results of relativity is that the relativistic mass of the electron increases by

$$m_{rel} = \frac{m_e}{\sqrt{1 - (v_e/c)^2}}$$

where m_e , v_e , c are the electron rest mass, velocity of the electron, and speed of light respectively.

It has been proved (found) that the average radial velocity of V_{radial} in atomic unit of electron in 1s shell of an atom is approximately Z , where Z is the atomic number and $C = 137$ speed of light in atomic unit



e.g for Gold (Au) , $Z= 79$. Here, $V_{\text{radial}} / C = 79/137 \approx 0.58$
Thallium (Tl), $Z= 113$; $V_{\text{radial}} / C = 113/137 \approx 0.75$

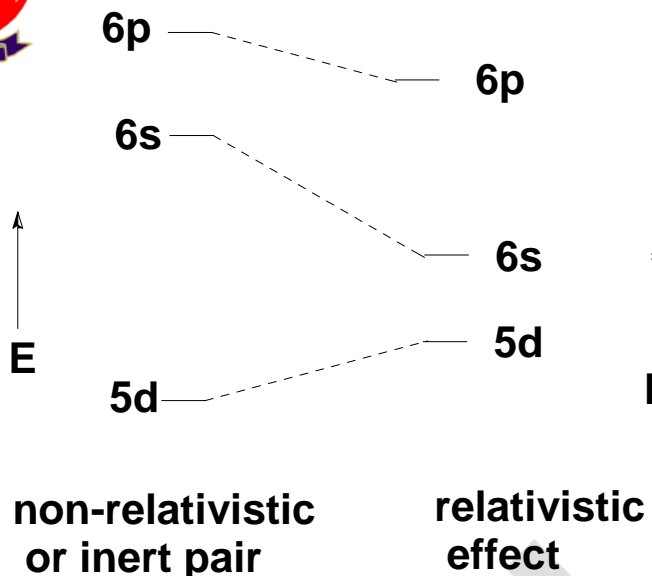
So for heavier elements $m_{\text{rel}} > m_e$

This has a marked effect on the radial distribution of electron, as Borh radius [$r = n^2h^2/4\pi^2me^2Z$] is a function $1/m$. The enhancement of the mass which accompanying the energy stabilization of orbital as the energy [$E = - 2\pi^2me^4Z^2 / n^2h^2$] is a function of mass (m) and subsequent contraction of s-orbital is known as relativistic effect. Although the primary effect operates on the core orbital the mass effects extends up-to the valence shell s- orbital.

- ◆ Small size, high charge density and large energy of summation of three ionization corroborates with covalent compound in +3 State.
- ◆ Similarly the p-orbitals also experienced a smaller effect.
- ◆ Due to the poor shielding effect of 4f and 5d orbitals, the 6s orbital enjoy more nuclear charge resulting the contraction of s-orbital i.e. stabilization of s-electron and destabilization of 5d orbital.



The energy diagram is shown below



Thus the stabilization of s orbital is responsible for high ionization potential and the stabilization +1 state for thallium.

The stabilization of 6s orbitals explain the interesting properties of heavier elements

Oxidation States

- ◆ The group-characteristic oxidation state is +3, but +1 becomes more important down the group.
- ◆ The stable state of thallium is +1
- ◆ Small size, high charge density and large energy of summation of three ionization corroborates with covalent compound in +3 State of boron.
- ◆ The ionic character of the compounds increases down the group



Halides

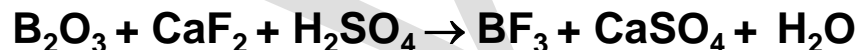
Tri-halides (MX_3) are known for all elements except TlI_3 . Due to inert pair effect and relativistic effect Tl(I) is stable and Tl(III) is oxidizing in nature. It oxidizes iodide to iodine. Thallium (III) chloride and bromide are also unstable. The monohalides MX ($\text{M} = \text{Al, Ga, In, Tl}$ and $\text{X} = \text{F, Cl, Br, I}$) are also known.

The halides of boron are covalent due to small size, high charge density and summation of huge three ionization energy. The Covalent characters of the compounds are decreases down the group.

Boron Halides (BX_3)

Boron halides are mainly synthesized by (i) reaction boron (III) compounds with the HX and (ii) reaction of boron with the halogen.

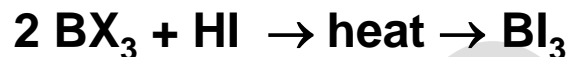
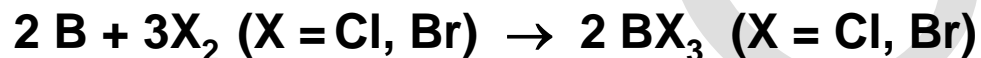
BF_3 is manufactured by the reaction of boron oxides with sulfuric acid and fluorite (CaF_2)



[Typically the HF is produced *in situ* from sulfuric acid and fluorite (CaF_2)].



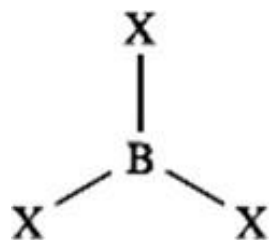
The reactions between B and Cl_2 or Br_2 yield BCl_3 or BBr_3 respectively, while BI_3 is prepared by reaction BCl_3 and HI



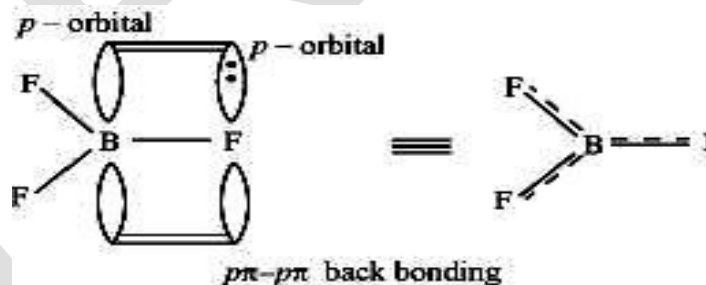
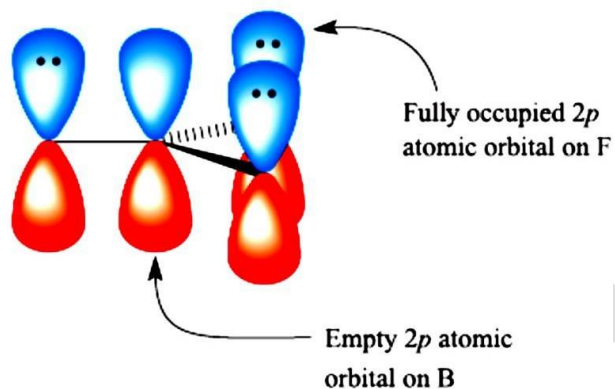
Structure:

Boron trihalide is trigonal planar (D_{3h}), and sp^2 hybridization is appropriate for the B atom. Each of the three B – F σ -interactions arises by overlap of a sp^2 hybrid on the B atom with, for example, a sp^2 orbital on the F atom. After the formation of the σ - bonding framework, the B atom is left with an unoccupied 2p atomic orbital lying perpendicular to the plane containing the BF_3 molecule.

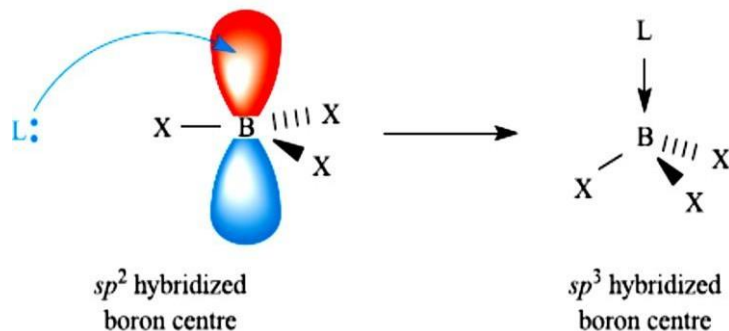
The mononuclear trihalides are electron deficient and acts as a Lewis acid. It has been observed that the B–F distance in $[\text{BF}_4]^-$ is 145 pm which is much less than the B–F distance (131 pm) in BF_3 which clearly indicates that there is π - interaction in BF_3 . Thus the electron deficiency is full filled by accepting the electron from the filled p- orbital of halides.



B – X	
X = F	131 pm
X = Cl	174 pm
X = Br	189 pm
X = I	210 pm



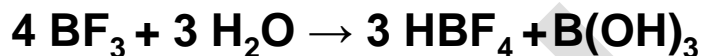
Due to availability of vacant p-orbitals of boron in BX_3 , BX_3 acts a Lewis acid. But the acidity depends on the strength of $p\pi-p\pi$ bonding interaction. The acidity order is reverse of the strength $p\pi-p\pi$ interaction which depends on the size of the $p\pi$ -orbitals and the interaction is maximum for same size of orbitals and decreases gradually with the increasing size of interacting orbital. The degree of interactions are $2p\pi-2p\pi > 2p\pi-3p\pi > 2p\pi-4p\pi \gg 2p\pi-5p\pi$, Thus acid strengths are $\text{BI}_3 \gg \text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$



L = Lewis Base = CO,
Ether, Amine etc

Hydrolysis

Boron trifluoride reacts with water to give boric acid and fluoroboric acid. The reaction commences with the formation of the aquo adduct, H_2O-BF_3 , which then loses HF that gives fluoboric acid with boron trifluoride.



Because of the high acidity of fluoroboric acid, the fluoroborate ion can be used to isolate particularly electrophilic cations, such as diazonium ions, that are otherwise difficult to isolate as solids.

The heavier trihalides do not undergo analogous reactions, possibly due to the lower stability of the tetrahedral ions BX_4^- (X = Cl, Br).

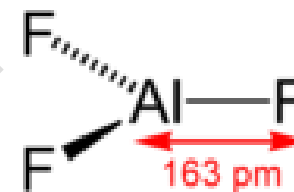
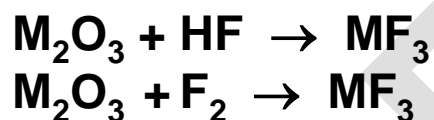
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BCl_3 hydrolyzes readily to give hydrochloric acid and boric acid:



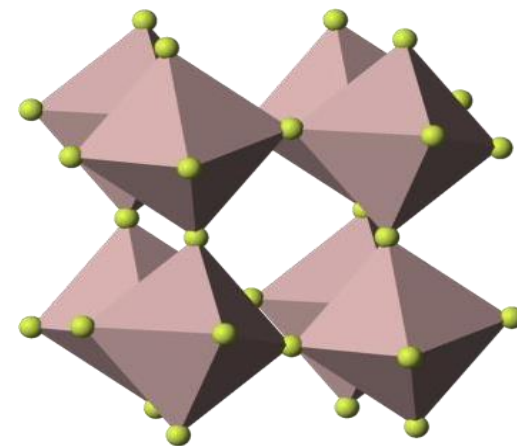
Al(III), Ga(III), In(III) and Tl(III) halides

The trifluorides of Al, Ga, In and Tl are non-volatile solids, best prepared by fluorination of the metal (or one of its simple compounds) with F_2 at high temperature



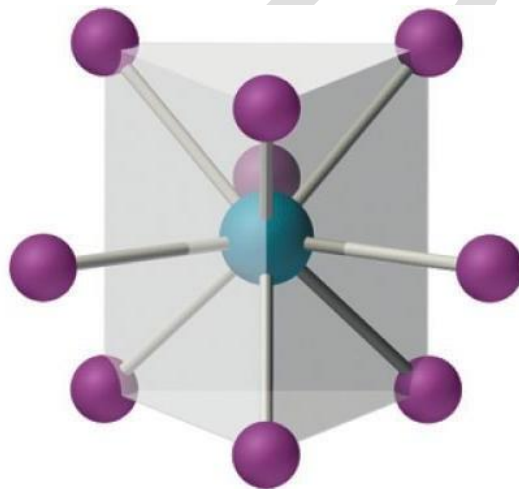
In the gas phase aluminium fluoride exists as trigonal molecules of D_{3h} symmetry. The Al-F bond lengths of this gaseous molecule are 163 pm.

Due to the presence of low lying vacant d-orbital and small size of fluorine atom the metal ion [M (III) = Al(III), Ga(III), In(III)] expand its coordination number and adopt octahedral geometry. In the solid state, AlF_3 adopt the octahedral geometry and the structure is shown.



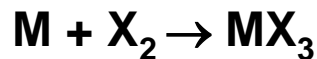


However in case of TlF_3 , due to the presence of low lying vacant d-orbital, f-orbital and small size of fluorine atom the metal ion can expand its coordination number beyond 6. In the lattice the thallium atom is 9 coordinate, (tricapped trigonal prismatic).



Tricapped trigonal prismatic

Compounds MX_3 ($\text{M} = \text{Al, Ga or In}$; $\text{X} = \text{F, Cl, Br or I}$) are obtained by direct combination of the elements.

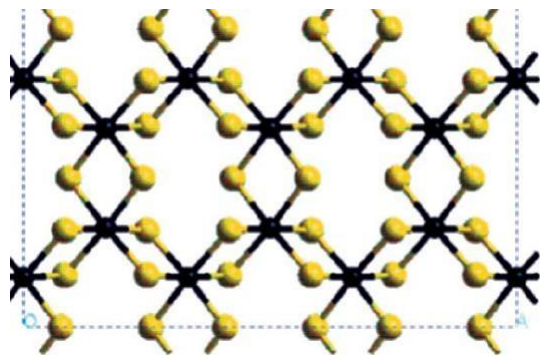


Structure:

MX_3 compound is also an electron deficient compound. However the octets are not full filled by $\text{p}\pi\text{-p}\pi$ bonding in mononuclear MX_3 and this is due to the large size of interacting $\text{p}\pi$ orbital and larger size of M and X. But the octets are full filled by dimerization where the there is $\text{p}\pi\text{-p}\pi$ interaction takes place between the X atom of one molecule interact with M of another atom and vice versa, This situation leads to the formation M_2X_6 structure where the geometry around M is distorted tetrahedral.

They are relatively volatile and in the solid state possess layer structures or structures with coordination number 6 containing dimers M_2X_6 .

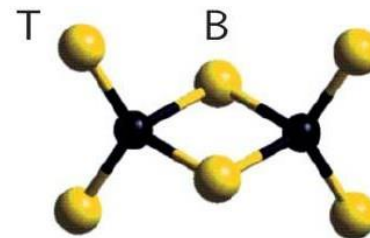
The vapors consist of dimeric molecules and these are also present in solutions of the compounds in inorganic solvents



Layered Al_2Cl_6

Structures of crystalline AlCl_3

Black and yellow balls indicate Al and Cl respectively. T and B indicate terminal and bridging Cl ions.



$\text{Al-Cl (T)} = 221 \text{ pm}$

$\text{Al-Cl (B)} = 206 \text{ pm}$

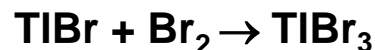
Gas Phase and in liquid phase Al_2Cl_6

AlBr_3 , AlI_3 , GaCl_3 , GaBr_3 , GaI_3 , InCl_3 , InBr_3 , InI_3 also exist as a dimer in the gas phase and have similar structure like Al_2Cl_6

The stabilization of $6s^2$ electron of Tl, due to Inert Pair and Relativistic effect favors the +1 oxidation states over +3.

Thus the thallium trihalides are less stable than their corresponding aluminium, gallium and indium counterparts and chemically quite distinct. The compound TlX_3 ($\text{X} = \text{Cl}, \text{Br}$) are known but the TlI_3 is not known.

TlX_3 ($\text{X} = \text{Cl}, \text{Br}$) can be prepared in by treating a solution of TlX with X_2 gas.



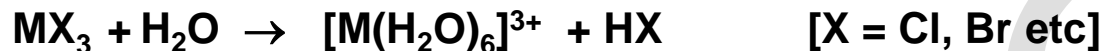
Solid TlCl_3 and TlBr_3 are very unstable and disproportionate at 40°C , losing halogen to give TlX . $\text{TlBr}_3 \rightarrow \text{TlBr} + \text{Br}_2$

Structure of TlX_3 ($\text{X} = \text{Cl}, \text{Br}$) is similar to that of Al_2Cl_6

TlI_3 is a compound of Tl(I), where the compound exist as $[\text{Tl}]^+[\text{I}_3]^-$ isomorphous with NH_4I_3 and CsI_3 , $\text{TlI} + \text{I}_2$ (in ethanol) \rightarrow TlI_3

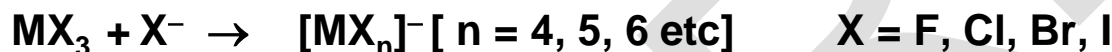
The formation of $[\text{Tl}^+][\text{I}_3]^-$ rather than $[\text{Tl}^{3+}][\text{I}^-]_3$ is consistent with the standard reduction potentials $E^0 (\text{Tl}^{3+}/\text{Tl}^+) = + 1.26 \text{ V}$ and $E^0 (1/2 \text{I}_2/\text{I}^-) = + 0.54 \text{ V}$, reveals that uncomplexed Tl^{3+} is susceptible to rapid and complete reduction to Tl(I) by I^- in acid solution.

Hydrolysis



Anionic Halide Compounds

The trihalides are Lewis Acids and form addition compounds with ligands

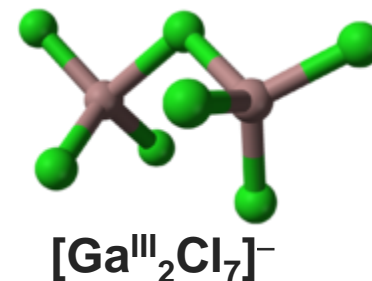


The M-X bond lengths lengthening takes place upon adduct formation, e.g.



Interestingly although TlI_3 is a compound of Tl(I) but TlI_3 reacts with excess I^- to form $[\text{Tl(III)I}_4]^-$. The oxidation of Tl(I) to Tl(III) is not clear, however it is believed that I_2 in I_3^- [$\text{I}_2 + \text{I}^-$] oxidize the Tl(I) to Tl(III) in presence of excess I^-

Intermediate Halide



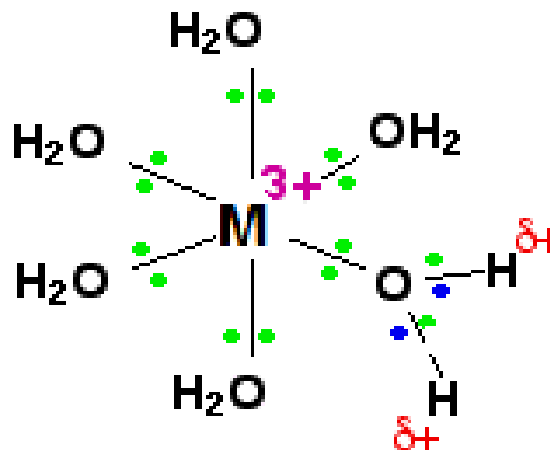


OXIDES, OXOACIDS AND HYDROXIDES

Trioxides of all elements (M_2O_3) are known Thallium forms the monoxide. On moving down the group, the basicity of the oxide increases along with increase in metallic character of the element. Thus B_2O_3 is acidic, Al_2O_3 and Ga_2O_3 amphoteric while In_2O_3 and Tl_2O_3 are basic. Tl_2O is strongly basic; it dissolves in water forming $TlOH$, which is as strong a base as KOH . In aqueous solution, all M^{3+} ($M= Al, Ga, In$ and Tl) ions are acidic

In aqueous solution, all M^{3+} ($M= Al, Ga, In$ and Tl) ions are acidic

Ions	K_a
$[Al(H_2O)_6]^{3+}$	1.12×10^{-5}
$[Ga(H_2O)_6]^{3+}$	2.5×10^{-3}
$[In(H_2O)_6]^{3+}$	2.0×10^{-4}
$[Tl(H_2O)_6]^{3+}$	1.1×10^{-1}

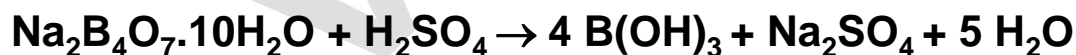
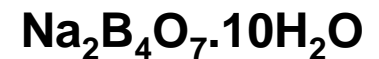
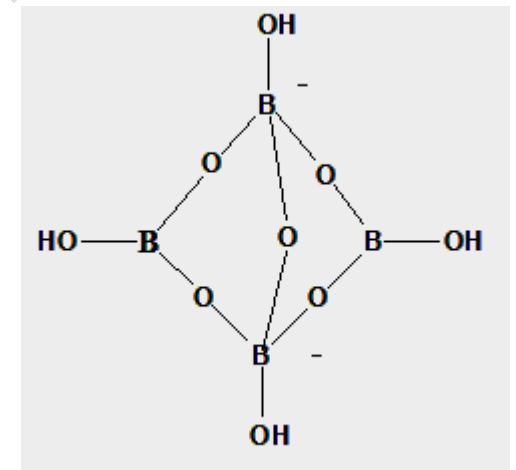
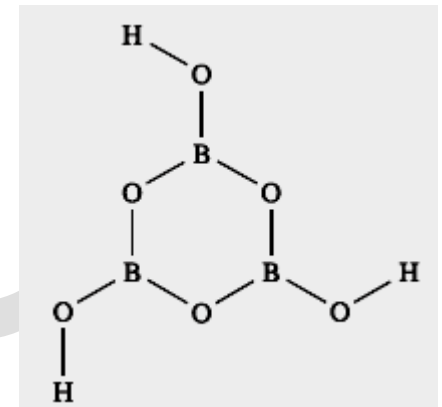


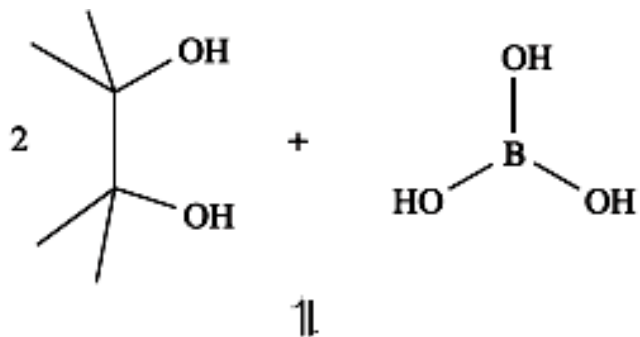
Greater acidity of heavier ions is due to poor shielding by underlying d subshells (Ga^{3+} , In^{3+} , Tl^{3+}) and $4f$ subshell (Tl^{3+})

Boric Acid

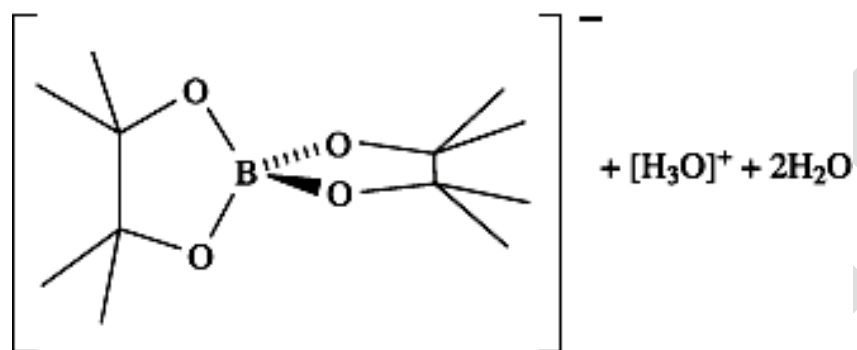
Water is taken up slowly by B_2O_3 giving $B(OH)_3$ (orthoboric or boric acid), but above 1270 K, molten B_2O_3 reacts rapidly with steam to give $B_3O_3(OH)_3$ (metaboric acid).

Industrially, boric acid is obtained from borax and heating $B(OH)_3$ converts it to $B_3O_3(OH)_3$. Both boric acids have layer structures in which molecules are linked by hydrogen bonds. The slippery feel of $B(OH)_3$ and its use as a lubricant are consequences of the layers. In aqueous solution, $B(OH)_3$ behaves as a weak acid, but is a Lewis rather than a Brønsted acid Ester formation with 1,2-diols leads to an increase in acid strength.

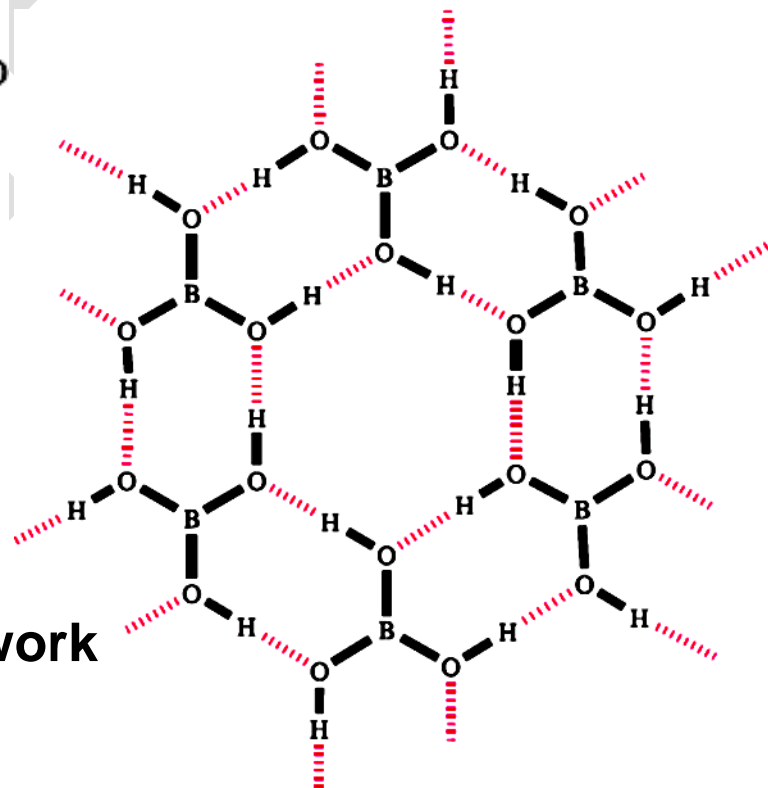




Reaction with 1,2-diol

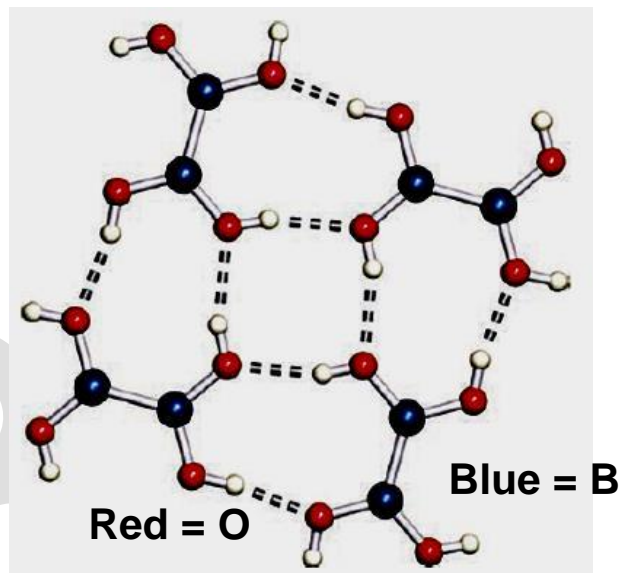


Hydrogen Bonding Network



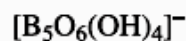
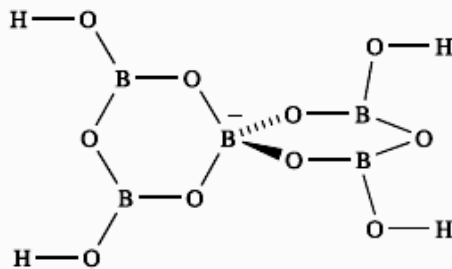
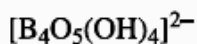
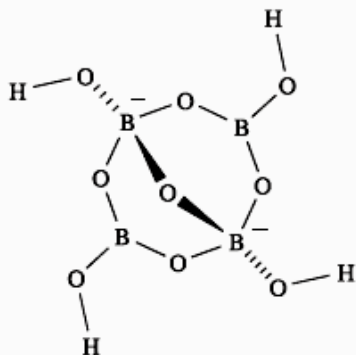
Diboronic acid, $B_2(OH)_4$

Diboronic acid, $B_2(OH)_4$, can be obtained by hydrolysis of B_2Cl_4 . Like boric acid, diboronic acid crystallizes with a layer structure, each layer consisting of hydrogen bonded molecules.

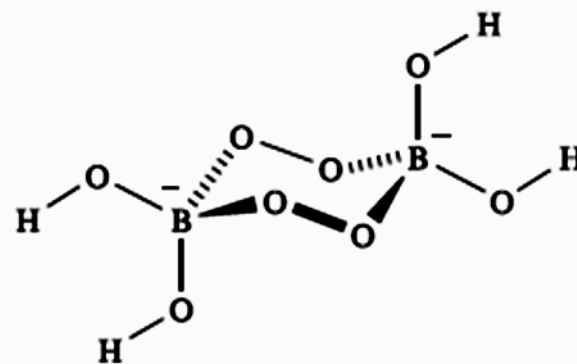


Borate

Many Borate anions exist and metal borates such as *colemanite* ($Ca[B_3O_4(OH)_3] \cdot H_2O$), *borax* ($Na_2[B_4O_5(OH)_4] \cdot 8H_2O$), *kernite* ($Na_2[B_4O_5(OH)_4] \cdot 2H_2O$) and *ulexite* ($NaCa[B_5O_6(OH)_6] \cdot 5H_2O$) occur naturally. The solid state structures of borates are well established, and selected anions are shown. In planar BO_3 groups, $B - O = 136$ pm, but in tetrahedral BO_4 units, $B - O = 148$ pm. This increase is similar to that observed on going from BF_3 to $[BF_4]^-$



The reactions of $\text{B}(\text{OH})_3$ with Na_2O_2 or borates with H_2O_2 , yield sodium peroxoborate (commonly known as sodium perborate). This is an important constituent of washing powders because it hydrolyses in water to give H_2O_2 and so is a bleaching agent. On an industrial scale, sodium peroxoborate is manufactured from borax by electrolytic oxidation. The solid state structure of sodium peroxoborate has been determined by X-ray diffraction and contains anion the compound is formulated as $\text{Na}_2[\text{B}_2(\text{O}_2)_2(\text{OH})_4] \cdot 6\text{H}_2\text{O}$.

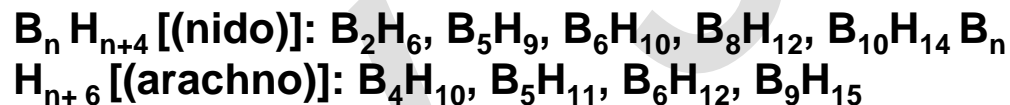




Hydrides

The elements form tri-hydrides (MH_3), the stability decreases on moving down the group. They are electron deficient compounds. The compound either dimerize or polymerize to get stability as well as to full fill their octets as there is no $p\pi-p\pi$ interaction possible in their monomeric form due to the absence of any filled p-electron in hydrogen atom.

Although the existence of BH_3 has been established in the gas phase, its propensity to dimerize means that B_2H_6 [diborane(6)]. Due to small size and electron deficient character of boron, extensive series of neutral boron hydrides are known and commonly these are called boranes (by analogy with alkanes and silanes). These are classified by nido- and arachno-



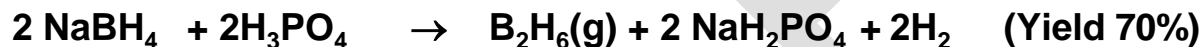
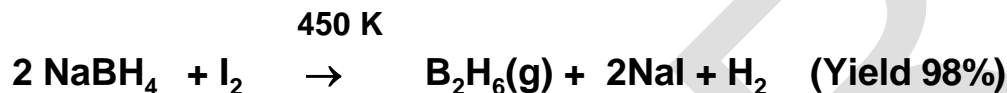
They are named by indicating the number of boron and hydrogen atoms.
e.g. B_5H_9 and B_5H_{11} are named pentaborane – 9 and pentaborane -11 respectively.



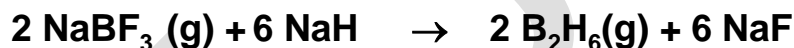
Diborane

Diborane is the simplest and most extensively studied hydride. It is an important reagent in synthetic organic chemistry.

B_2H_6 gas most conveniently be prepared in laboratory by the reaction of I_2 on $NaBH_4$ in diglyme $[(MeOCH_2CH_2)_2O]$ or by the reaction of a solid tetrahydroborate with an anhydrous acid:

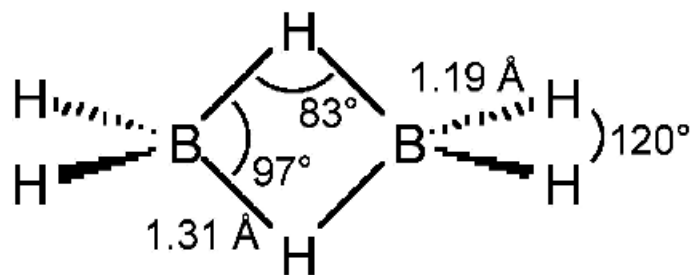


On an industrial scale gaseous BF_3 can be reduced directly with NaH at about 450 K and the product trapped out as it is formed to prevent subsequent pyrolysis:

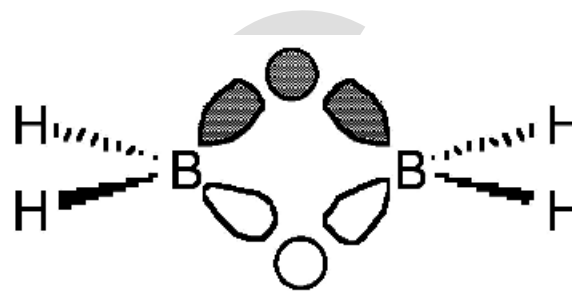


Structure

Diborane is found to have a bridge structure in which each B atom is bonded to two H atoms (called terminal H atom) by regular electron pair bonds. The resulting two BH_2 units are bridged by two H atoms (the bridge H atoms), which are at a plane perpendicular to the rest of the molecule and prevent rotation between the



(a)



(b)

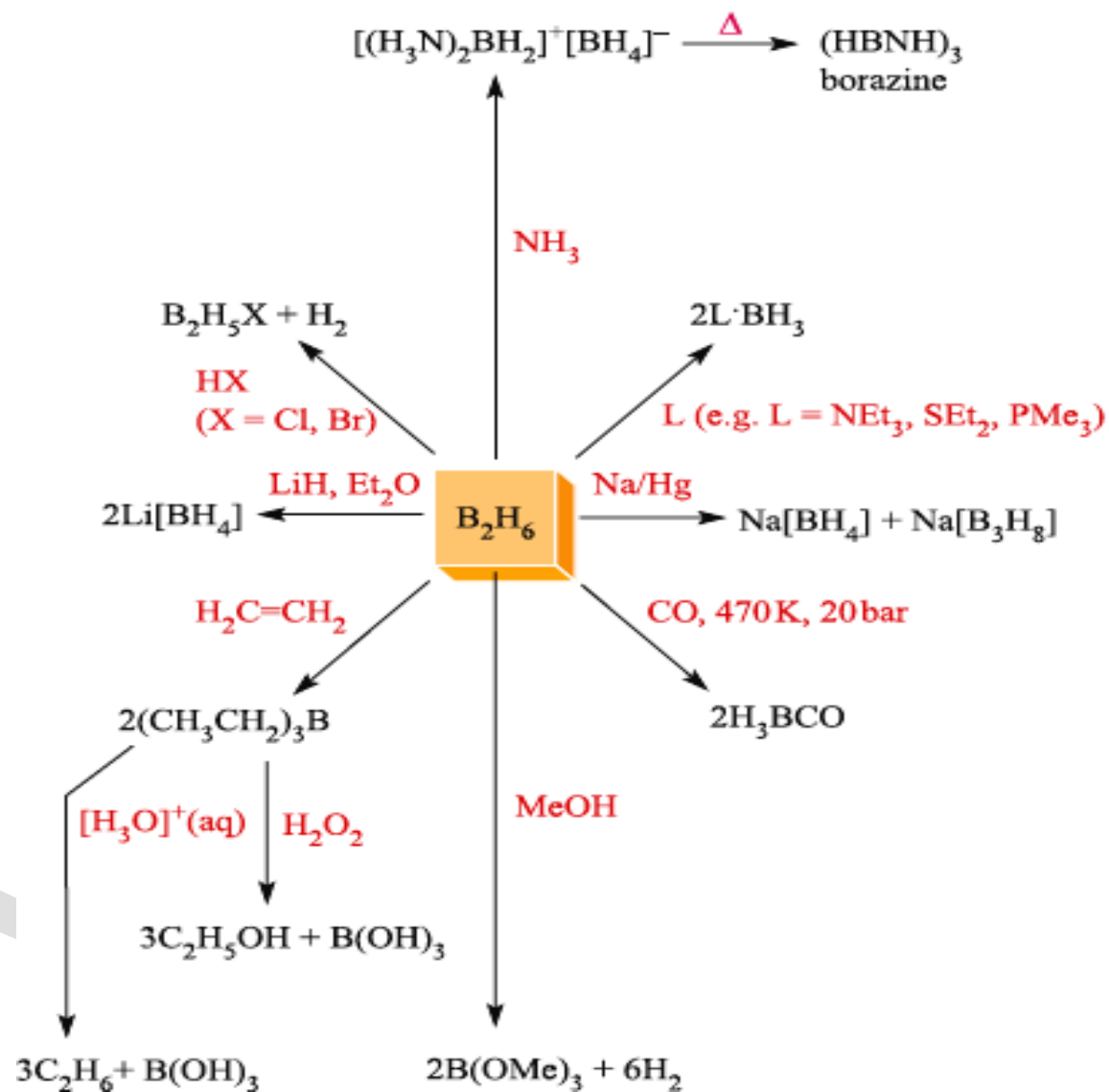
The structure (a) and the typical view of the three-centered two-electron bonds (b) in diborane, B_2H_6 .

The structure (a) has been confirmed by electron diffraction, infrared and Raman spectroscopic methods. Four hydrogen atoms are in an environment different from the other two – this is confirmed by Raman spectra.

The four terminal B-H bonds are normal covalent bonds, however, the bridging B-H-B unit consists of two three-centered two-electron bonds, each ordinarily considered to be formed by the combination of two boron sp^3 orbitals and one hydrogen s orbital (b). However, a consideration of the H-B-H bond angle associated with the terminal hydrides (120°) it is perhaps better to consider the BH_2 fragment to be sp^2 hybridized rather than sp^3 , and the B-H-B bridging unit to be a linear combination of one sp^2 orbital and one p orbital from

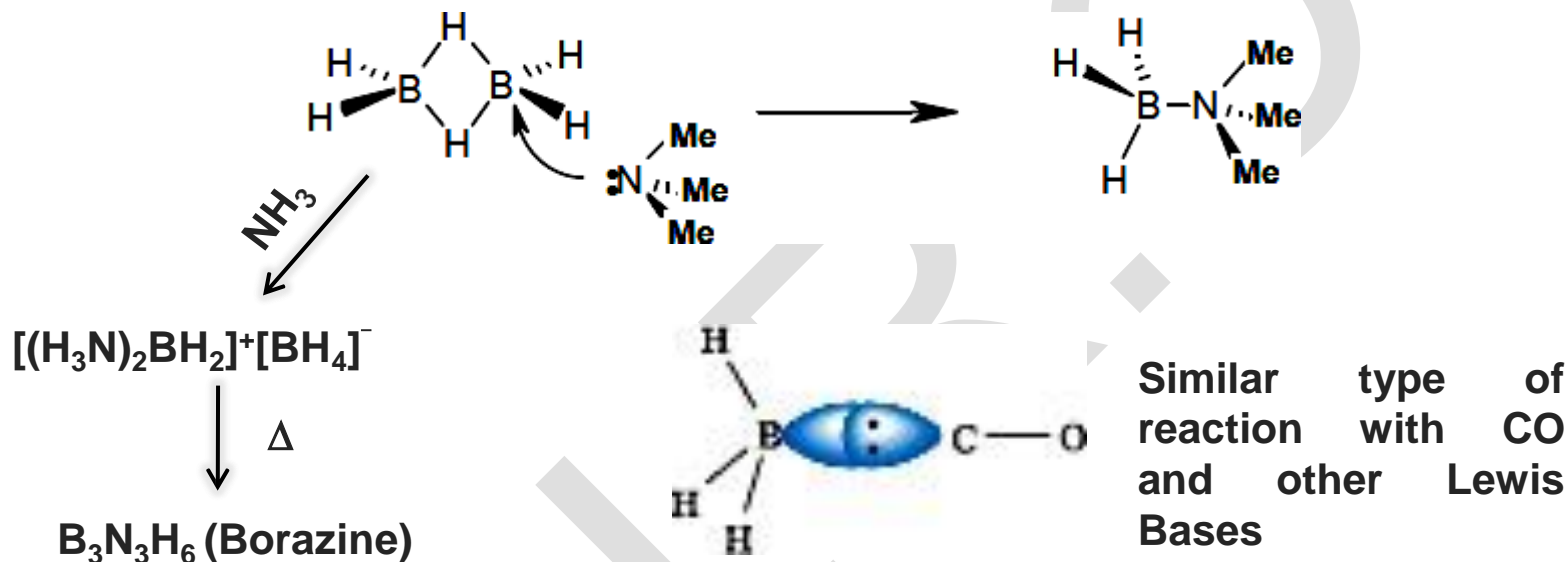
each boron atom with the two hydrogen s orbitals.

V.U.R.C



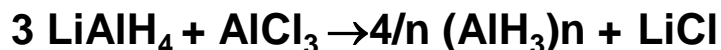
Reactions

Diborane B_2H_6 acts as Lewis acid with tertiary amine to form the adduct.

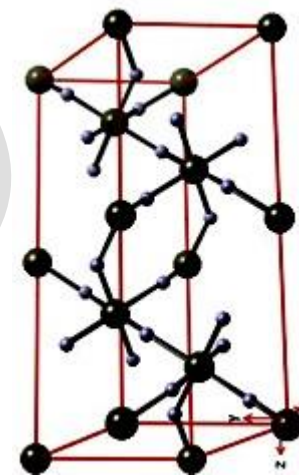


Hydrides of Al, Ga, In and Tl

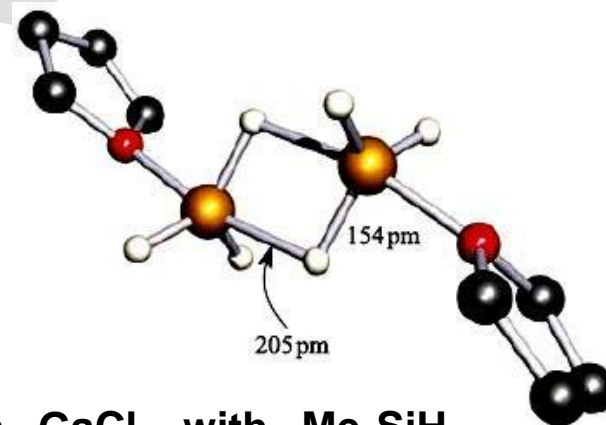
$(AlH_3)_n$ is the best known and is prepared by the action of pure H_2SO_4 or $AlCl_3$ on lithium aluminium hydride in ether.



Monomeric AlH_3 has been isolated at low temperature in a matrix. Evidence for the existence of Al_2H_6 (formed from laser-ablated Al atoms in a solid H_2 matrix at 3.5 – 6.5 K) has been obtained from vibrational spectroscopic data. In the solid state at normal temperatures, X-ray and neutron diffraction data have shown that aluminium hydride consists of a 3-dimensional network in which each Al centre is octahedrally sited, being involved in six Al-H-Al 3c-2e interactions.

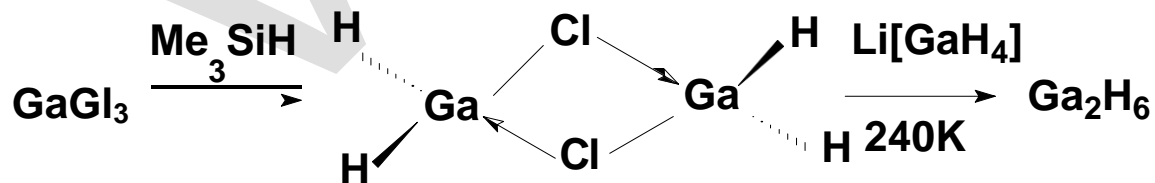


AlH_3 also form adducts with Lewis base, such as THF, NMe_3 . The compound $\text{THF} \cdot \text{AlH}_3$ adduct has been isolated and found the dimeric structure contains two Al-H-Al 3c-2e bond.



DIGALLANE

Digallane, Ga_2H_6 , is prepared by reaction with GaCl_3 with Me_3SiH followed by reduction with $\text{Li}[\text{GaH}_4]$. The product condenses at low temperature as a white solid (mp 223 K) but decomposes above 243 K.

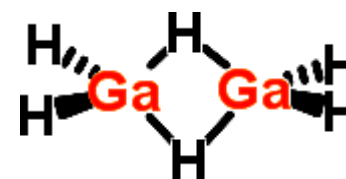
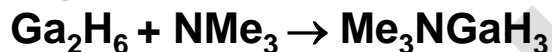




Structure

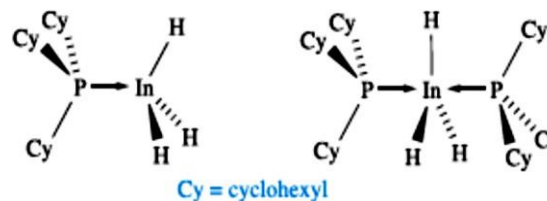
Electron diffraction measurements of the vapour at 255 K established that digallane is structurally similar to diborane with 2 bridging hydrogen atoms (so-called three-center two-electron bonds). The terminal Ga—H bond length is 152 pm, the Ga—H bridging is 171 pm and the Ga—H—Ga angle is 98°. The Ga—Ga distance is 258 pm. The ^1H NMR spectrum of a solution of digallane in toluene shows two peaks attributable to terminal and bridging hydrogen atoms.

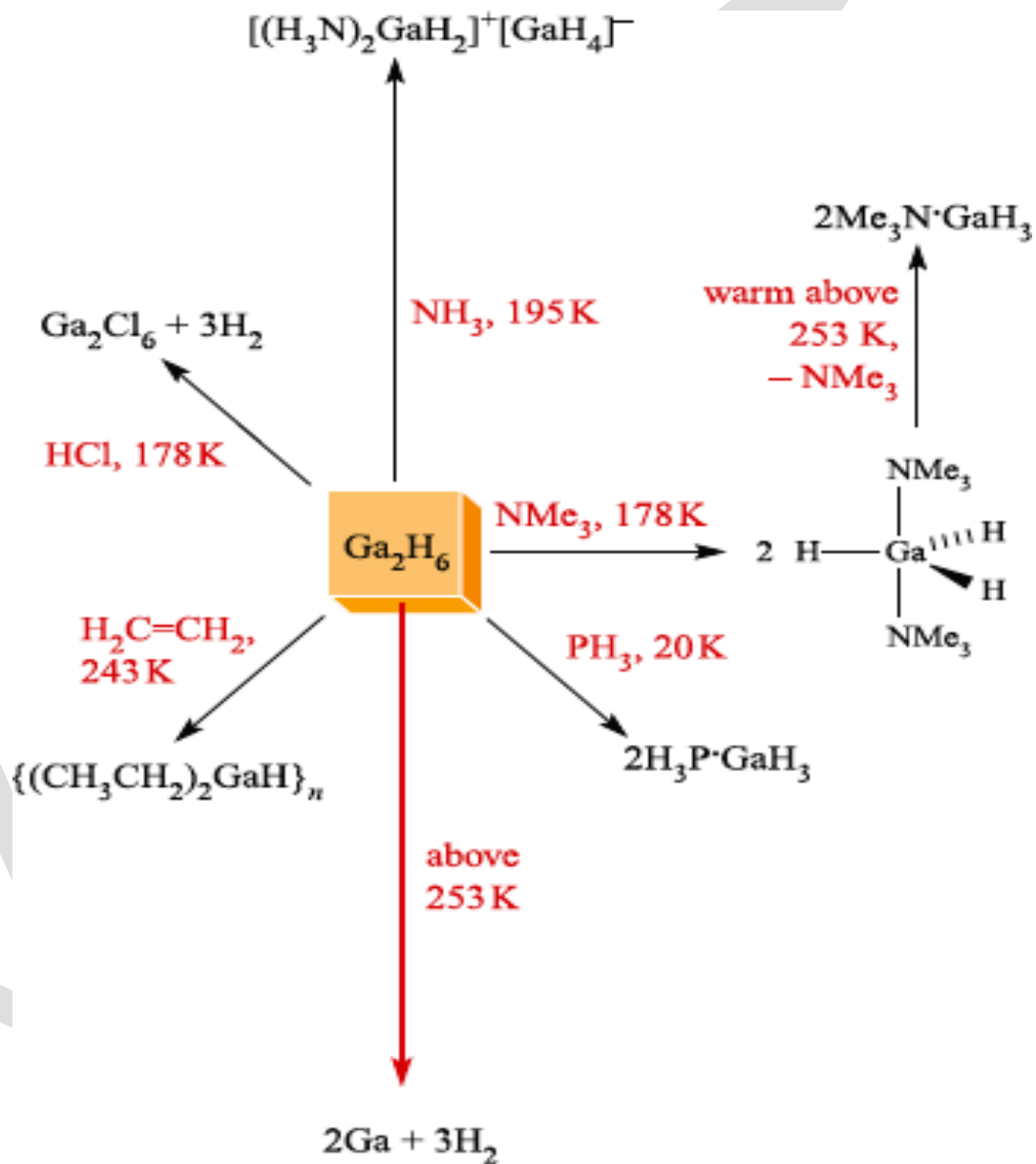
Digallane reacts with Lewis base to form adduct



The existence of InH_3 was confirmed in 2004 (IR spectroscopic data for matrix-isolated InH_3), A number of adducts of InH_3 containing phosphine donors have been isolated, which are stable in the solid state at 298 K, but decompose in solution.

The isolation of TlH_3 remains uncertain.

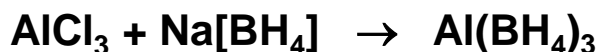




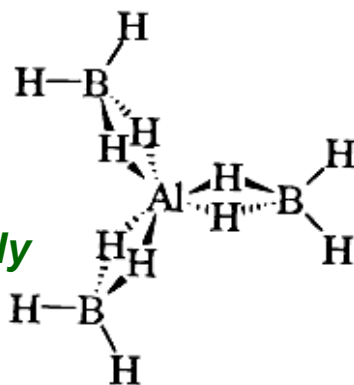
Aluminium Borohydride

Aluminium Borohydride is an extremely useful reducing agent

$\text{Al}(\text{BH}_4)_3$: This is an important compound. This has been synthesized by reacting the AlCl_3 with $\text{Na}[\text{BH}_4]$ or $\text{Li}[\text{BH}_4]$. The X-ray structure reveals that there are 6 numbers 3c-2e bonds



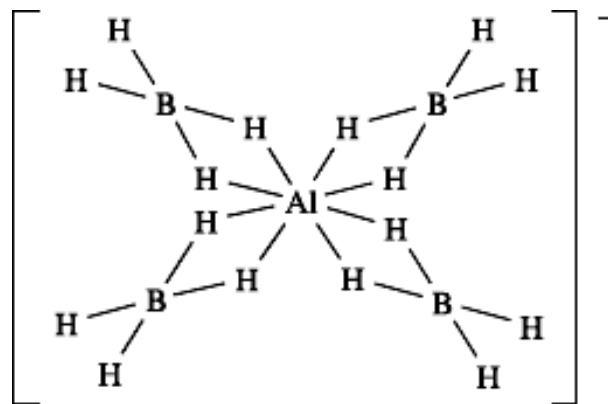
$\text{Al}(\text{BH}_4)_3$ is fluxional molecule at room temperature in solution only one ^1H NMR peak observed



$[\text{Al}(\text{BH}_4)_4]^-$: This is also an important compound. This has been synthesized by reacting the $\text{Al}(\text{BH}_4)_3$ with $\text{Na}[\text{BH}_4]$ or $\text{Li}[\text{BH}_4]$.



The X-ray structure of Triphenylmethylphosphonium Tetrakis(tetrahydroborato)aluminate, $[\text{Ph}_3\text{MeP}][\text{Al}(\text{BH}_4)_4]$ reveals that 8-coordinate $\text{Al}(\text{III})$ bearing eight number 3c-2e bonds.



Borazine

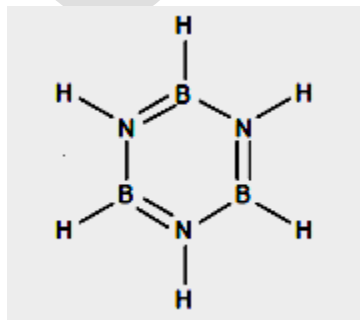
Borazine is a colourless liquid (mp 215 K, bp 328 K) with an aromatic odour and physical properties that resemble those of benzene. Thus it is also called as inorganic benzene.

The compound was reported in 1926 by the chemists Alfred Stock and Erich Pohland by a reaction of diborane with ammonia

Borazine is synthesized from diborane and ammonia in a 1:2 ratio at 250–300 °C with a conversion of 50%.

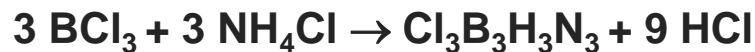


An alternative more efficient route begins with lithiumborohydride and ammonium chloride:

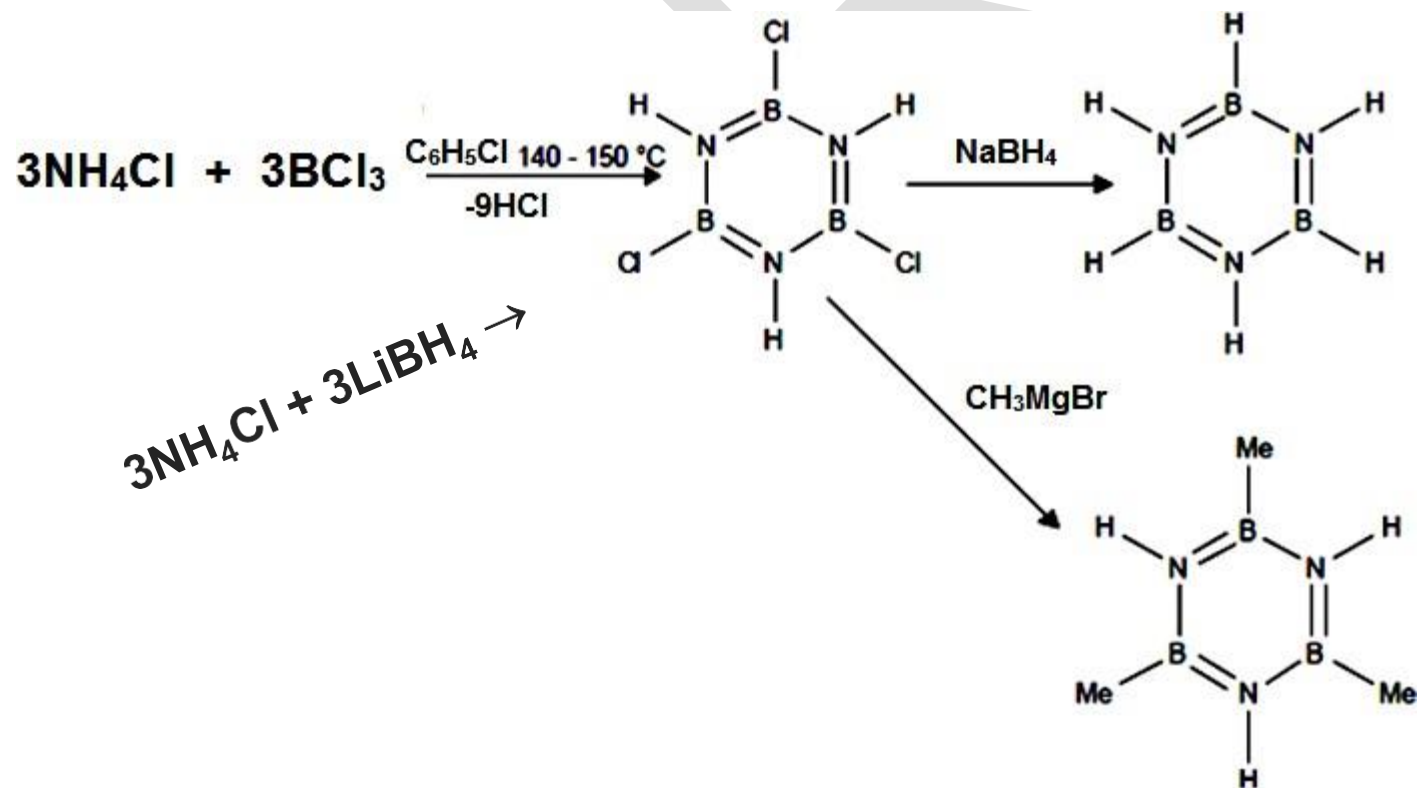




In a two-step process to borazine, boron trichloride is first converted to trichloroborazine. The reaction is carried out in chlorobenzene solvent at 140 - 150 °C



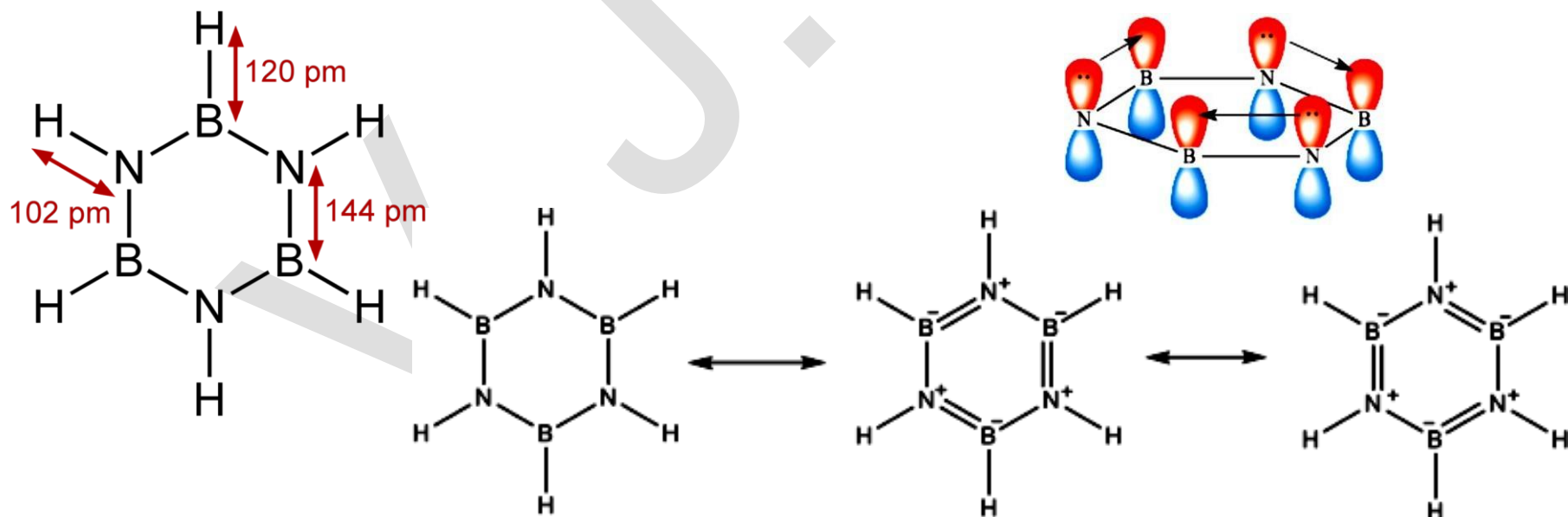
The B-Cl bonds are subsequently converted to B-H bonds or other substituted with suitable reagent





STRUCTURE AND BONDING

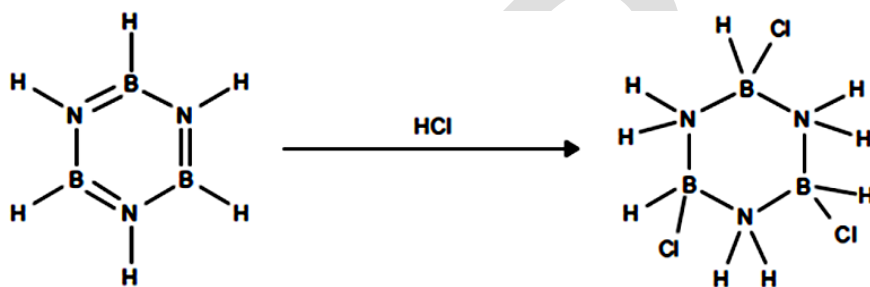
Borazine is isostructural with benzene and BN is isoelectronic with C_2 . Borazine is described by the same type of bonding model as benzene, consisting of a σ - skeleton of sp^2 hybrid orbitals and a set of delocalized π -orbitals. The six B-N bonds have length of 144 pm while the carbon-carbon bond in benzene is shorter length at 139 pm. The short B-N bond distance compared to boron-nitrogen single bond (151 pm) suggests that the presence of π -bonding in BN resulting from overlap between N 2p (occupied) and B 2p (vacant) orbitals orthogonal to the 6-membered rings and this overlap is associated with the alternative mesomer structures for borazine.



Reactivity

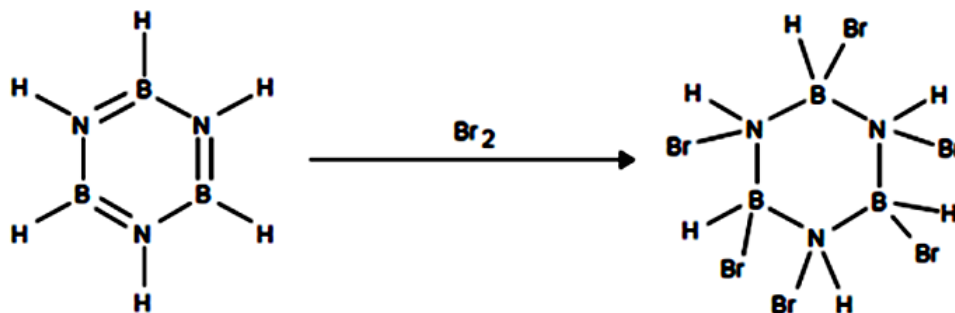
Considering of the relative electronegativities of B (2.0 , Pauling Scale) and N (3.04, Pauling Scale) indicates that B is susceptible to attack by nucleophiles while N attracts electrophiles. The electronegativity difference makes the more reactive than Benzene

(a) Polar addition reactions with HX, X = Cl, OH, OR etc



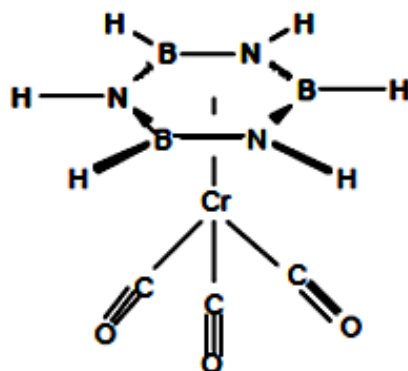
[Benzene does not react with HCl at all]

(b) Reactions with Br₂

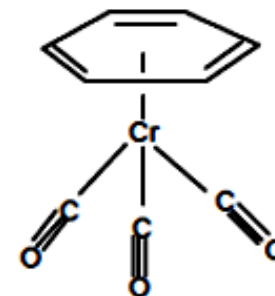


[Benzene undergoes aromatic substitution rather than addition]

(c) Coordination complexes



Cr(0) carbonyl complexes
common to both ligands

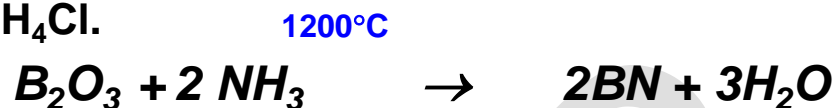


These reactions suggest that there are both similarities and differences between borazine and benzene. The formation of π -sandwich complexes at Cr(0) strongly suggests the presence of a π -system in borazine, as does its odour which is distinctive for aromatic carbon compounds. Yet the reactivity is very different. We need to consider the bonding in these fascinating compounds in more detail to be able to understand the factors involved.

Boron nitride

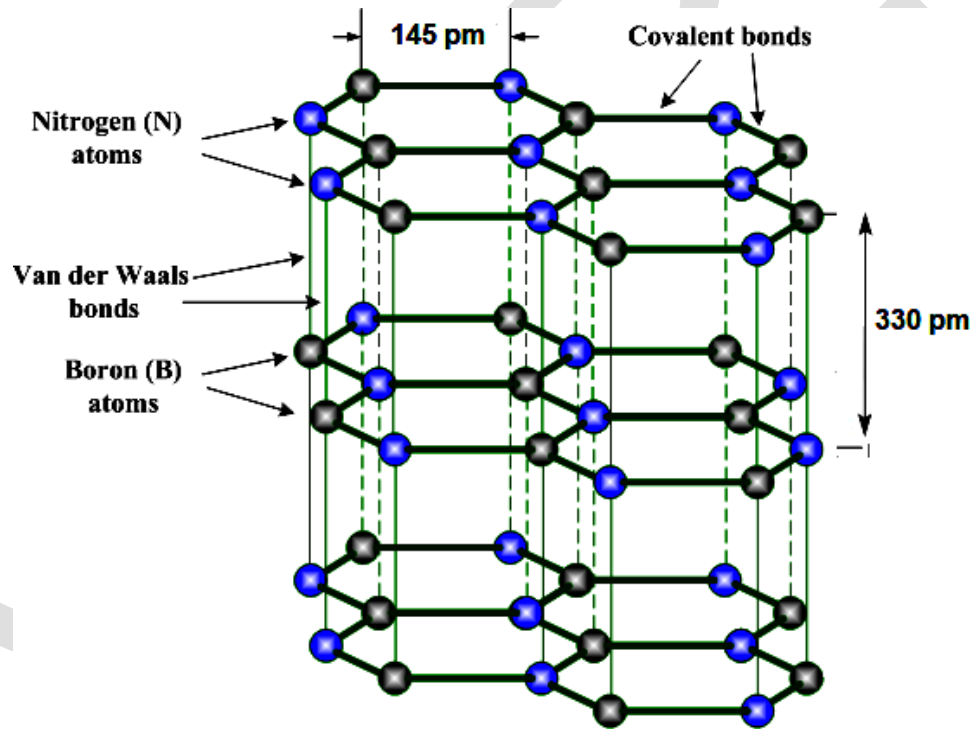


The simplest boron-nitrogen compound is boron nitride Boron nitride (BN). BN, is a robust, chemically rather inert compound. Preparative routes include the high temperature reactions of borax with NH_4Cl , B_2O_3 with NH_3 , and $\text{B}(\text{OH})_3$ with NH_4Cl .

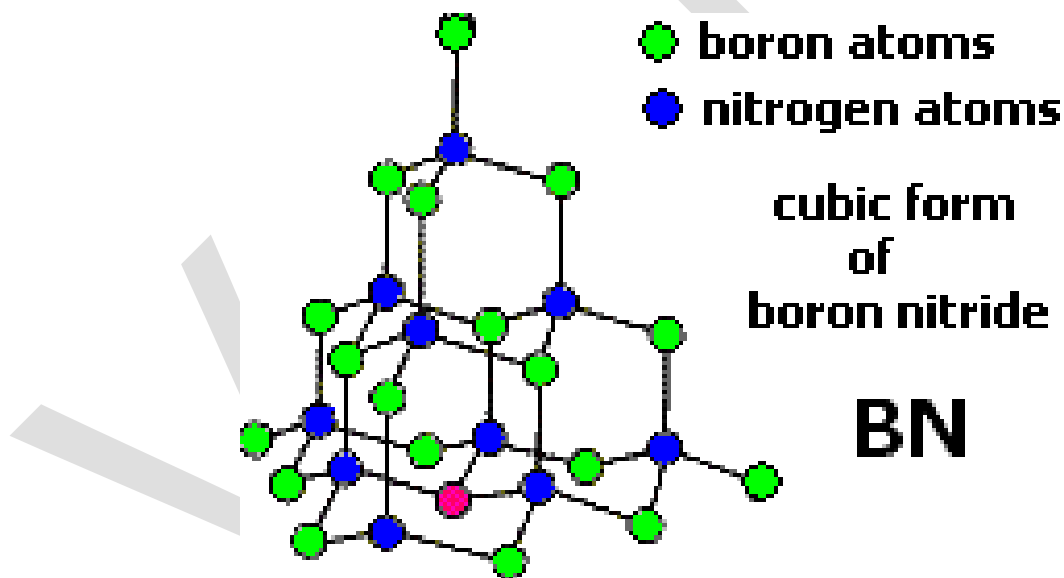


The common form of boron nitride sublimes at 2603 K. It is referred to as hexagonal-BN (or α -BN) and has a layer structure consisting of hexagonal rings. The structure is similar to that of graphite, BN is isoelectronic (and isolobal) with CC and it called inorganic graphite. However, in α -BN, the hexagonal form has one extremely important difference from graphite. In α -BN the layers are arranged so that a B atom in one layer lies directly over an N atom and this contrasts with the staggered arrangement of alternate layers in graphite. The B-N distances within a layer are much shorter than those between layers. The B–N bonds (145 pm) are shorter than in adducts [in $\text{Me}_3\text{N} \cdot \text{BBr}_3$; B-N = 157 pm] and imply the presence of π -bonding in BN resulting from overlap between N 2p (occupied) and B 2p (vacant) orbitals orthogonal to the 6-membered rings.

The interlayer distance of 330 pm is consistent with van der Waals interactions, and α -BN acts as a good lubricant, thus resembling graphite. Unlike graphite, α -BN is white and an insulator. This difference can be interpreted in terms of band theory and the band gap in boron nitride being considerably greater than that in graphite because of the polarity of the B-N bond.



Heating α -BN at $\approx 2000\text{K}$ and >50 kbar pressure in the presence of catalytic amounts of Li_3N or Mg_3N_2 converts it to a more dense polymorph, cubic-BN (or β -BN), with the zinc blend structure. The B–N bond distance in cubic-BN is similar to those in $\text{R}_3\text{N}\cdot\text{BR}_3$ [160 pm] adducts and longer than in hexagonal-BN. This further supports the existence of π -bonding within the layers of the latter. Structurally, the cubic form of BN resembles diamond and the two materials are almost equally hard. Crystalline cubic BN is called **borazon** / **inorganic diamond** and is used as an abrasive.



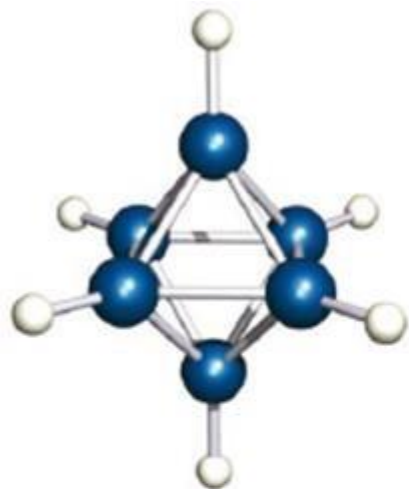


Higher Boron Hydride and Structural Topology

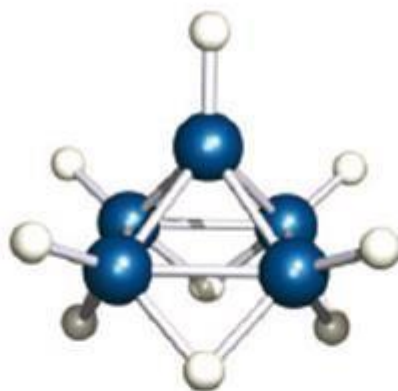
Lipscomb got Nobel Prize in 1976 due to his work in borane with their structural analysis . Most syntheses of the higher boranes involve heating B_2H_6 , sometimes with hydrogen. Most of the higher boranes are liquids but B_6H_{10} and $B_{10}H_{14}$ are solids. They were considered to be potential rocket fuels, but interest in this was soon diverted as it was found that on combustion they formed a polymer, which blocked the nozzles.

Depending on chemical composition of borane and boron hydride ions, the species adopt a particular geometry and classified in several categories

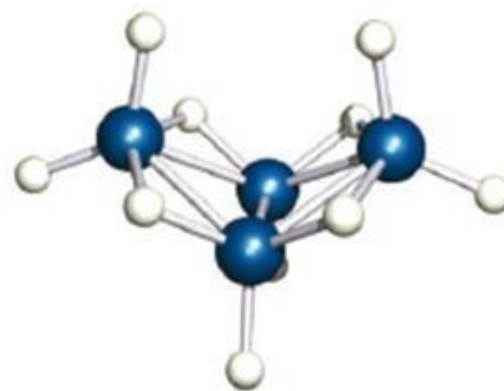
Type	formula	notes
<i>closo-</i> (Close)	$B_nH_n^{2-}$	No neutral B_nH_{n+2} boranes are known. eg $B_6H_6^{2-}$
<i>nido-</i> (nest)	B_nH_{n+4}	hexaborane(B_6H_{10}) and decaborane ($B_{10}H_{14}$)
<i>arachno-</i> (spider's web)	B_nH_{n+6}	Tetraborane(10) B_4H_{10}



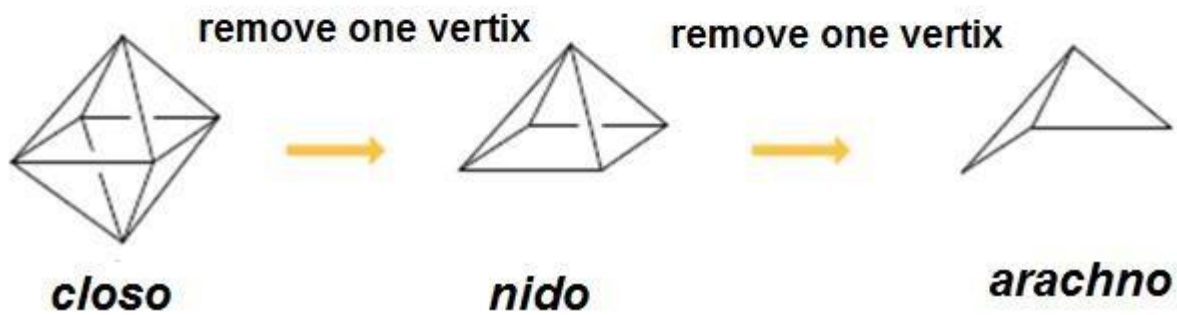
$[B_6H_6]^{2-}$



B_5H_9

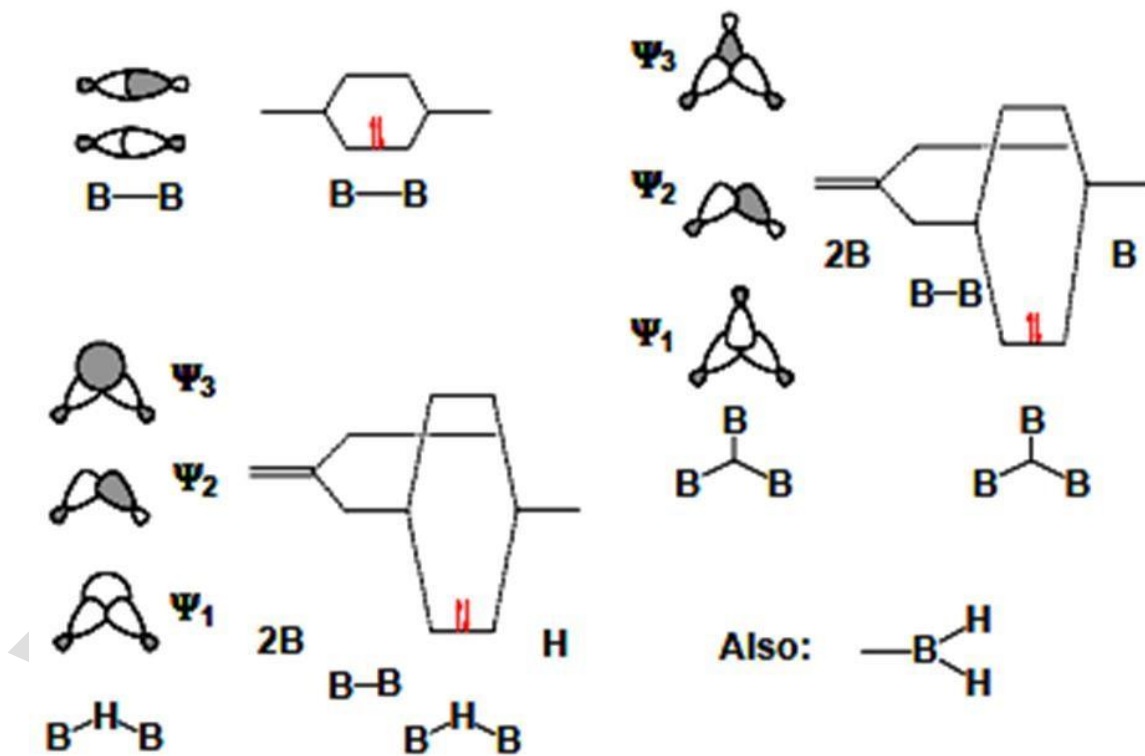


B_4H_{10}



The higher boranes have an open cage structure. The structures involve 2c - 2e bonds between B and H and B - B and 3c - 2e bonds involving B-H-B and B-B-B. Closed 3c-2e bonds of the type are also known. The structure of hydridoboranes are also expressed using this bond type:

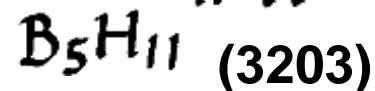
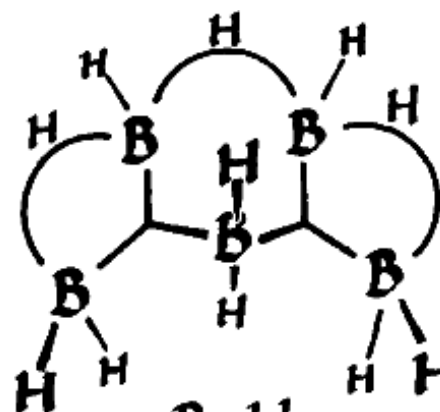
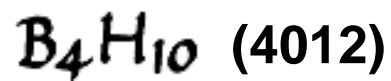
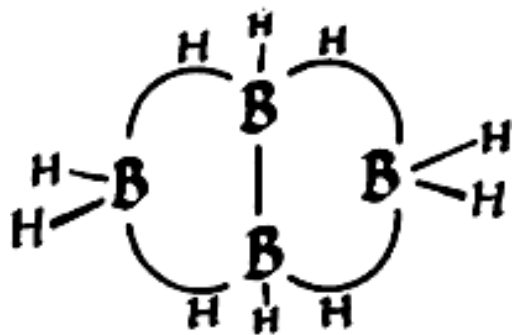
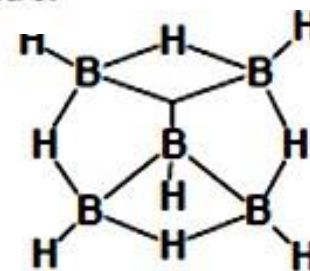
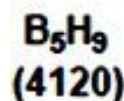
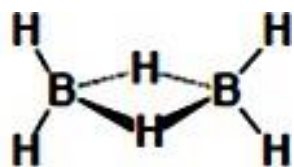
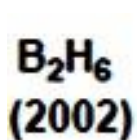
The Boron Hydrides – Bonding Elements



The bond types are expressed in term STYX number.

Bonding Topology – The STYX Numbers

- S – The number of B-H-B 3c-2e bonds.
- T – The number of closed B₃ 3c-2e bonds.
- Y – The number of B-B 2c-2e bonds.
- X – The number of BH₂ groups; 2 2c-2e bonds.





In general the arachno- and nido- boron hydride acts as a Bronsted Acid. and the acidity increase as framework size increases. Within each class of hydrides, the acidity increases with increasing size of the boron framework. It is believed that acidity of bridge hydrogens is related to the extent of electron delocalization in the boron framework.

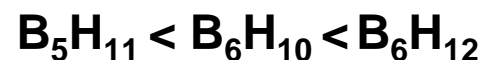
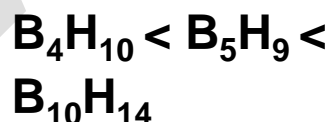
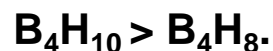
Bases such as ammonia, lithium alkyls, and metal hydrides have been employed. Some examples of laboratory experiments of deprotonation reactions using KH are shown .



The acid strength is as follows

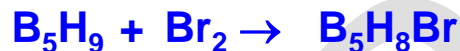


The *arachno* hydrides are more acidic in general than the *nido* hydrides:



Boron Hydrides are generally fluxional molecule

The *boron* hydrides reacts with halogen to form halo substituted hydride



nido- borane



(Asymmetric Cleavage of cage)

arachno- borane



(Asymmetric Cleavage
by a small base)



(Asymmetric Cleavage by
relatively a bulky base)

Metal borides

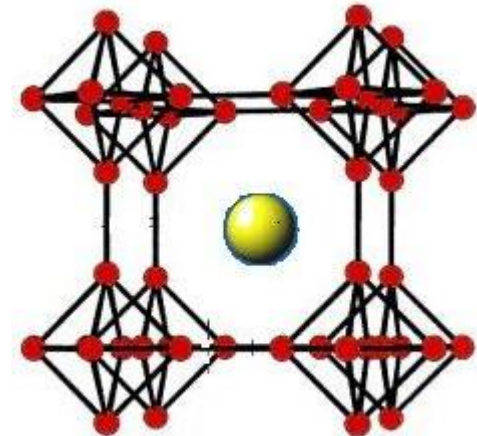
Solid state metal borides are characteristically extremely hard, involatile, high melting and chemically inert materials which are industrially important with uses as refractory materials and in rocket cones and turbine blades, i.e. components that must withstand extreme stress, shock and high temperatures.

Metal borides may be boron- or metal-rich, and general families include MB_3 , MB_4 , MB_6 , MB_{10} , MB_{12} , and M_3B , M_4B , M_5B . The formulae bear no relation to those expected on the basis of the formal oxidation states of boron and metal.

CaB_6

It is an important material due to its high electrical conductivity, hardness, chemical stability, and melting point.

One of the main reactions for industrial production is



Each calcium has 24 nearest-neighbor boron atoms