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TOPIC:- Group-wise systematic study of p-block elements

Group-13

Hydrides

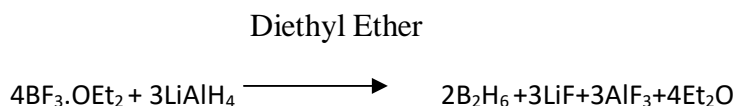
Hydrides

The elements form tri-hydrides (MH_3), the stability decreases on moving down the group. They are electron deficient compounds. Boron forms a series of volatile hydrides called boranes (by analogy with alkanes and silanes). They fall into two series:

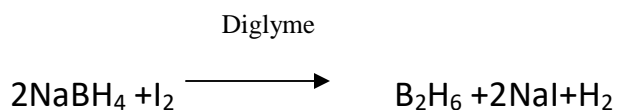


They are named by indicating the number of boron atoms. If two or more boranes have the same number of B atoms, then the H atoms are also specified, e.g. B_5H_9 and B_5H_{11} are named pentaborane – 9 and pentaborane – 11 respectively.

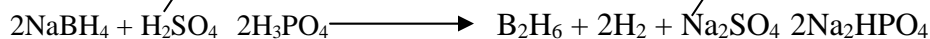
Diborane is the simplest and most extensively studied hydride. It is an important reagent in synthetic organic chemistry. It may be prepared by various ways:



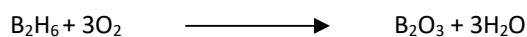
Boron tri-fluoride etherate



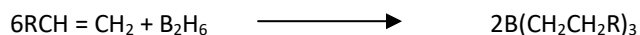
Sodium borohydride



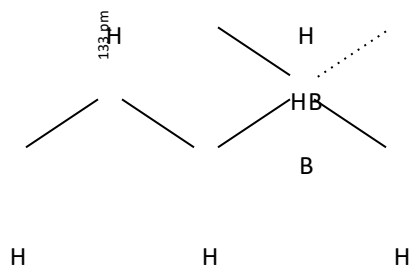
It is a colourless gas, which burns in air and is readily hydrolyzed.



Diborane undergoes addition reaction with alkenes and alkynes in ether at room temperature to form organo-boranes.



This is known as hydroboration reaction. The structure of diborane is of great interest as it is an electron deficient compound having only twelve electrons, which are insufficient to form the required number of bonds. Each boron has three electrons and can form a BH_3 unit each but how will the two units be held together?



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 two B atoms. The structure 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 and by the fact that diborane cannot be methylated beyond the tetramethyl derivative without breaking the molecule into BMe_3 .

The terminal B-H bond distances are the same as in non-electron deficient compounds. These are normal two-centre-two-electron bonds (2c-2e). Electron deficiency is thus associated with the bridge bonds. The four bridge bonds involve only four electrons – a pair of electrons is involved in binding three atoms – B, H and B. These bonds are called three-centre-two-electron-bonds (3c-2e).

Each B atom is sp^3 hybridized giving four sp^3 hybrid orbitals. B has three valence electrons so three orbitals are filled singly. Two of the sp^3 hybrid orbitals on each B overlap with the 1s orbitals of H forming four 2c – 2e bonds.

Then one singly filled sp^3 hybrid orbital on one B atom, and one vacant sp^3 hybrid orbital on another B atom overlap with a singly filled 1s orbital on one H atom to form a bonding orbital shaped like a banana embracing all three nuclei. Another 3c – 2e bond is formed similarly (fig 3)

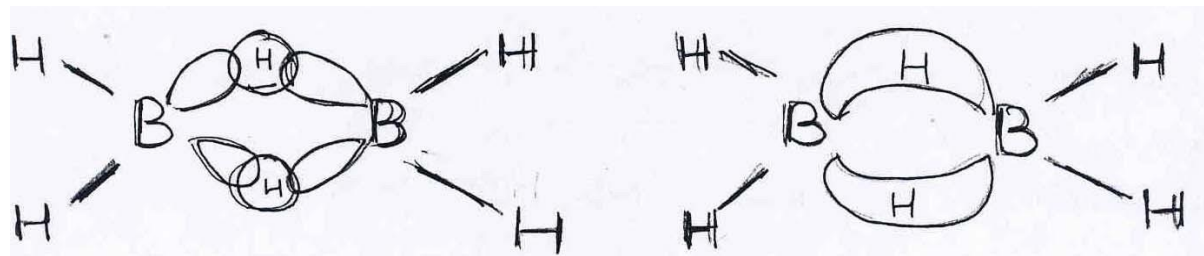


Fig.3: Formation of banana-shaped three-centre-two-electron bond in Diborane

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.

The higher boranes have an open cage structure (fig4). 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.

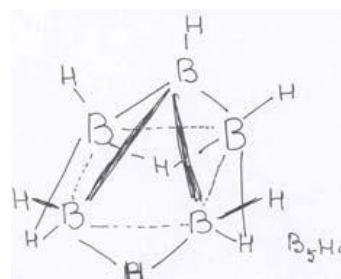
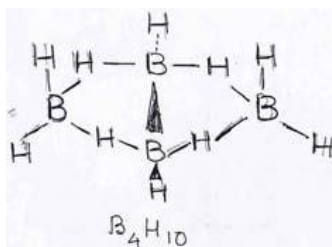
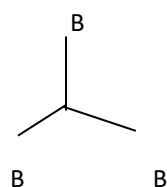


Fig.4: Structures of Some Boranes

Borohydrides

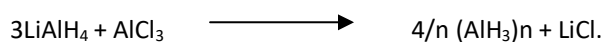
Borohydrides like NaBH_4 , $\text{Al}(\text{BH}_4)_3$ contain the tetrahydroborate (III) anion, BH_4^- . In these compounds boron has a complete octet and thus they are more stable than the boranes. Sodium borohydride is obtained by the reaction between sodium hydride and methyl borate.



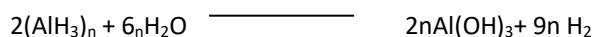
Other borohydrides may be obtained from NaBH_4 . The BH_4^- ion has a tetrahedral structure, NaBH_4 is a useful reagent used in reduction of aldehydes and ketones.

Hydrides of other members

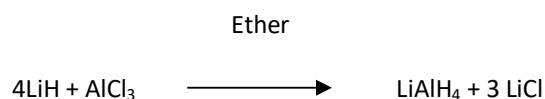
Other members of Group 13 form a few hydrides which are polymeric in nature e.g. $(\text{AlH}_3)_n$, $(\text{GaH}_3)_n$ and $(\text{InH}_3)_n$ and contain M-H-M bridges. Their stability decreases on moving down the group. $(\text{AlH}_3)_n$ is the best known and is prepared by the action of pure H_2SO_4 or AlCl_3 on lithium aluminium hydride in ether.



It is a colourless and thermally unstable solid and reacts violently with water.



A complex hydride of aluminium, lithium aluminium hydride is well known. It is prepared from lithium hydride and aluminium chloride in ether.



It is a powerful reducing agent and is widely used in organic chemistry. The borohydrides of aluminium, beryllium and the transition metals are covalent. In $\text{Al}(\text{BH}_4)_3$ each BH_4^- unit forms two hydrogen bridges while in $\text{Be}(\text{BH}_4)_2$ each BH_4^- unit forms three hydrogen bridges

(Fig 5)

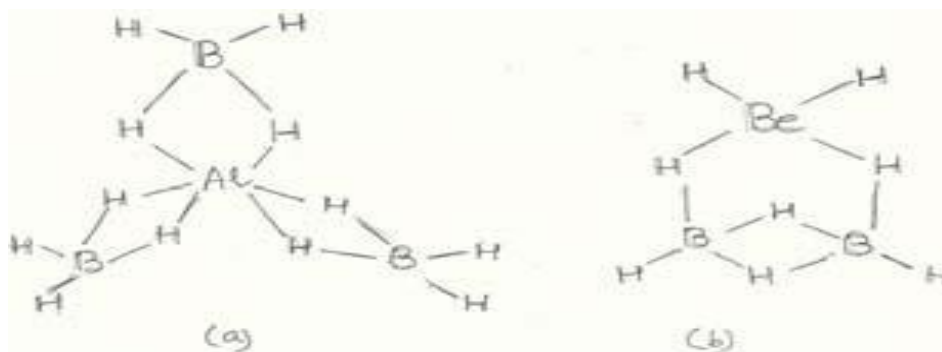


Fig.5: Structures of (a). $\text{Al}(\text{BH}_4)_3$ (b) $\text{Be}(\text{BH}_4)_2$