Main Group Chemistry
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Lecture – 26
Chemistry of Group 13 Elements

Welcome to MCB lecture series on main group chemistry. In my previous lecture I was discussing about methods of extraction of boron and aluminium from their respective minerals and let me start the discussion on chemistry of boron and aluminium compounds. To begin with let me consider discussion on hydrides of boron the simplest hydride of boron is gaseous diborane.

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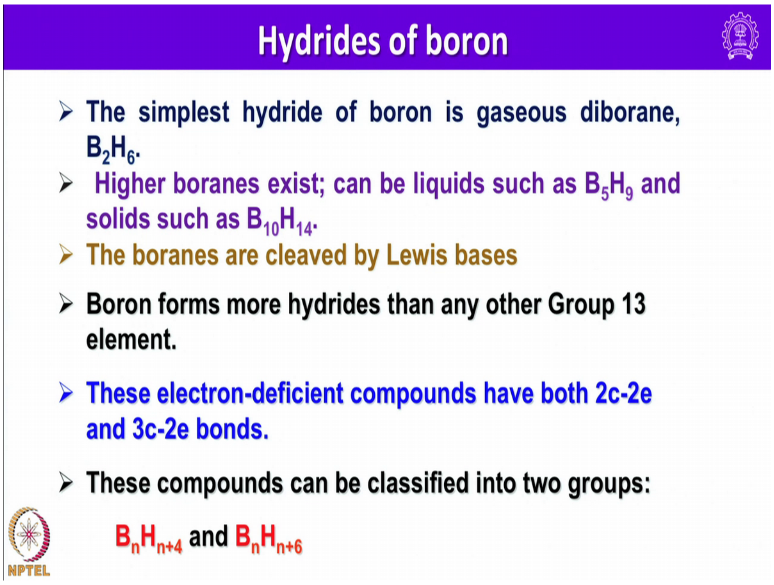

Hydrides of boron

- The simplest hydride of boron is gaseous diborane, B_2H_6.
- Higher boranes exist; can be liquids such as B_5H_9 and solids such as $B_{10}H_{14}$.
- The boranes are cleaved by Lewis bases
- Boron forms more hydrides than any other Group 13 element.
- These electron-deficient compounds have both 2c-2e and 3c-2e bonds.
- These compounds can be classified into two groups:

B_nH_{n+4} and B_nH_{n+6}

Of course the simplest one should have been B H 3 it does not have an independent existence and it dimerises readily as a result for all practical purpose we can consider the simplest hydride of boron as B 2 H 6. Higher borons to exist they can be liquid such as B 5 H 9 and solid such as B 10 H 14. Of course, we have numerous examples of boron hydrides both neutral as well as an ionic. I shall give more details on those things when I consider wades rules for explaining structures. In boron hydrides the borons are essentially cleaved by Lewis bases because they have electron deficient B H B bridging bonds. So, one can expect them to readily cleave in presence of stronger Lewis bases.

Boron form more hydrates than any other group 13 elements of course, perhaps after carbon boron is the second element among p-block elements to form largest number of hydrides. Majority of this boron hydrides or electron deficient compounds; that means, they have both 2 centred 2 electron bonds and 3 centred 2 electron bonds; that means, most of the boron hydrides have a few terminal B H bonds which are 2 centred to electron and some of them are bridging B H B where we come across 3 centre 2 electron bonds. These compounds can be classified into two groups one is B n H n plus 4 and B n H n plus 6, two types of boron hydrides we come across.

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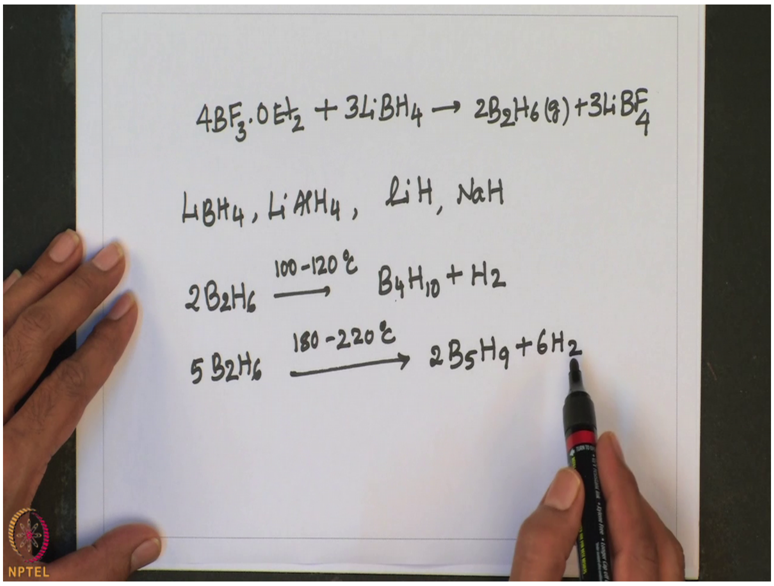

$4BF_3.OEt_2 + 3LiBH_4 \rightarrow 2B_2H_6(g) + 3LiBF_4$

$LiBH_4, LiAlH_4, LiH, NaH$

$2B_2H_6 \xrightarrow{100-120°C} B_4H_{10} + H_2$

$5B_2H_6 \xrightarrow{180-220°C} 2B_5H_9 + 6H_2$

Of course, one can prepare diboron starting from metathesis reaction for example, one can consider boron trifluoride etherate, simply reacting this one with lithium borohydride in at ether solvent such as diethyl ether or tetrahydrofuran. And in case of lithium boro hydride and lithium aluminium hydride if you consider lithium borohydride and lithium aluminium hydride, similar to lithium hydride are good reagents for the transfer of H minus, but they are generally preferred over lithium hydride and sodium hydride because they are soluble in ethers. So, that is a reason in organic chemistry where ever we want to transfer hydrogen we prefer lithium boro hydride or lithium aluminium hydride simply because they solubility in organic solvents such as ethers. So, they are preferred over lithium hydride or sodium hydride.

So, higher boron hydrides contain the same structural features as that of B 2 H 6 where we come across 3 centre 2 electron bonds and how to prepare higher boron hydrides. It is simply by taking diboron and heating at different temperature one can get higher boron hydrides. For example, B 2 H 6 on heating at temperature 100 to 120 degree centigrade leads to the formation of B 4 H 10 plus H 2, instead if di-boron is heated to a temperature of 180 to 220 at least the formation of B 5 H 9.

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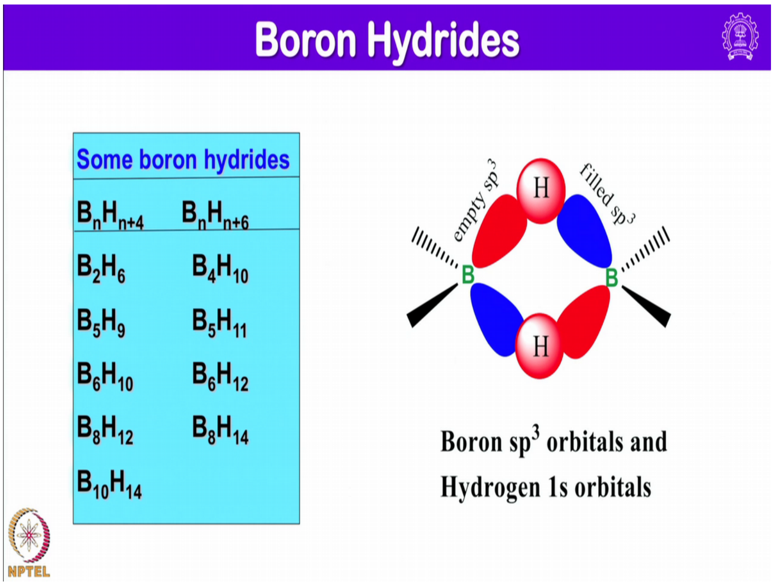

Boron Hydrides

Some boron hydrides

B_nH_{n+4}	B_nH_{n+6}
B_2H_6	B_4H_{10}
B_5H_9	B_5H_{11}
B_6H_{10}	B_6H_{12}
B_8H_{12}	B_8H_{14}
$B_{10}H_{14}$	

Boron sp^3 orbitals and Hydrogen 1s orbitals

So, some boron hydrides I have listed here you can see under B n H n 4 plus we have I have listed few examples here for example, B 2 H 6, B 5 H 9, B 6 H 10, B 8 H 12, B 10 H 14 under B n H n plus 6 series I have listed a few examples there B 4 H 10, B 5 H 11, B 6 H 12, B 8 H 14 and all of them invariably have some terminal B H points and some bridging B H b. So, in B H B one can expect 3 centred 2 electron bonds a typical of di-boron. You can see here in case of boron before prior to the formation of say B H 3 it promotes one of the electron to the p and then it undergoes sp 3 hybridisation to have 3 sp 3 orbitals having one electron and one sp 3 with no electron.

So, they arrange in this fashion and they interact with one s electron of hydrogen to form a central like this, this 2 are terminal where we have to electron each. Here we have no electron here we have 2 electrons. So, as a result it becomes 3 centred B H B 3 centred 2 electron bond. So, similarly we have one here. Similar type of bonds you can anticipate wherever we have hydrogen bridging 2 electron deficient boron atoms in all most of boron hydrides.

So, all the boron hydrides are flammable and several of the lighter ones including diborone reacts spontaneously with air and often with explosive violence and a green flash emission from a from an excited state of the reaction intermediate involving a species such as B O the final product of the reaction is the essentially the hydrated oxide. For example, if we expose it to oxygen the product one can see here.

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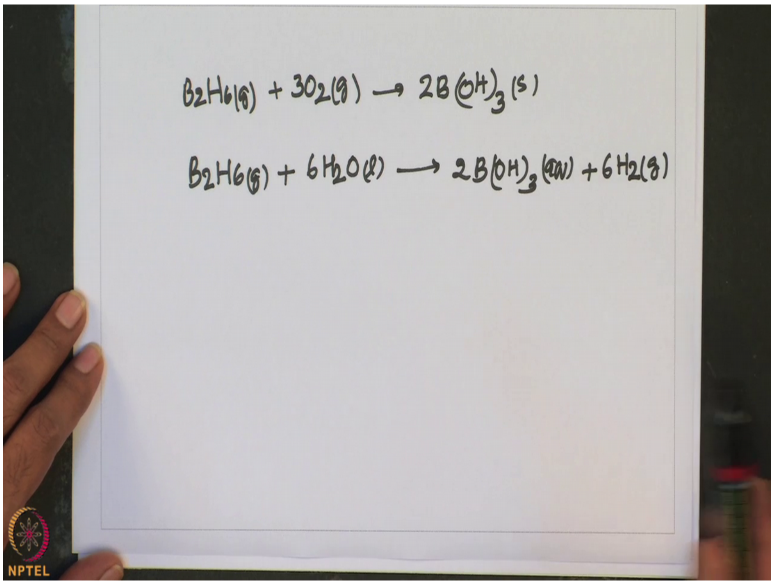

$$B_2H_6(g) + 3O_2(g) \rightarrow 2B(OH)_3(s)$$

$$B_2H_6(g) + 6H_2O(l) \longrightarrow 2B(OH)_3(aq) + 6H_2(g)$$

For example if you take B 2 H 6 on exposure to oxygen it can give. So, if you expose B 2 H 6 2 moisture. So, one has to be extremely careful while handling boron hydrides strictly they have to be handled under inert atmosphere and moisture and air should be excluded and also whenever we are using solvents organic solvents all these reactions has to be carried out in non aqueous medium and in super dry organic solvents preferably ether such as a higher ethers such as diglymer triglyme.

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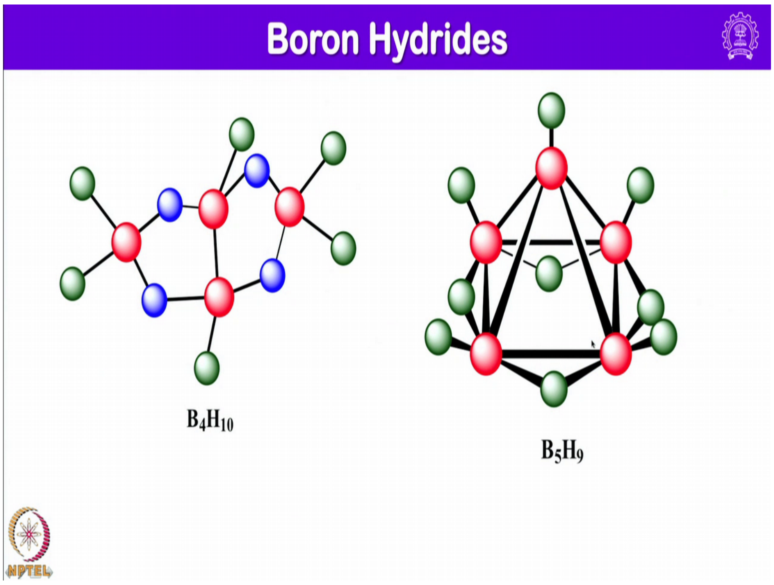

Boron Hydrides

So, some structures I am showing you here for example, B 4 H 10 this how it looks like and B 5 H 9 they are all originated from these structures from regular polyhedron. And of course, when I describe wades rule for depicting the structure of boron hydrides I elaborate more on this aspect and I will show you all kind of polyhedron we come across from how and how to derive the boron hydride structures starting from regular polyhedron.

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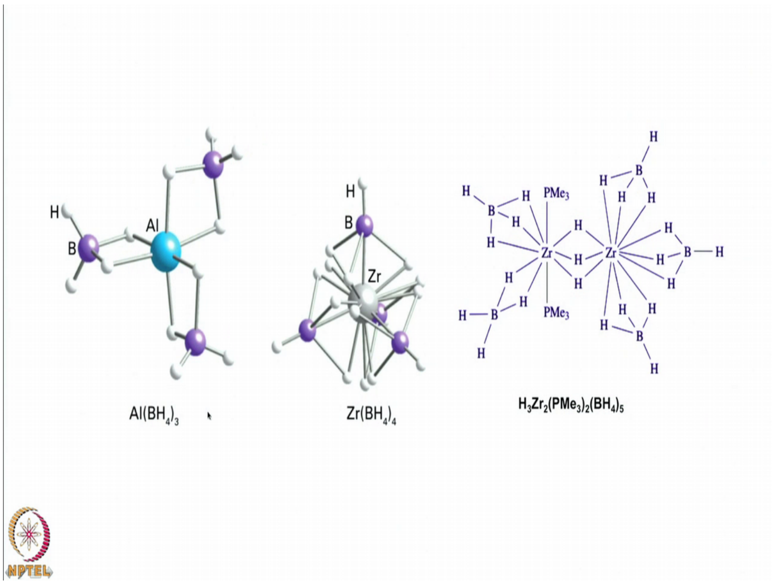

These are couple of examples of homonyptic boron hydride compounds for example, Al B H 3, 3 times you can see here Al B H 3 times in which 2 hydrogen atoms are acting as bridging were as 2 we have terminal. So, aluminium is octahedraly surrounded by 6 hydrogen atoms. So, similarly we have tetra kis boron hydride zirconium. So, here we have essentially surrounding zirconium 8 we have, as a result zirconium is at the centre of anti square prismatic geometry. And one can also see here zirconium having as many as 8 coordination couple of them are trimethyl phosphine and rest of them are tribridging a boron hydrides in this way.

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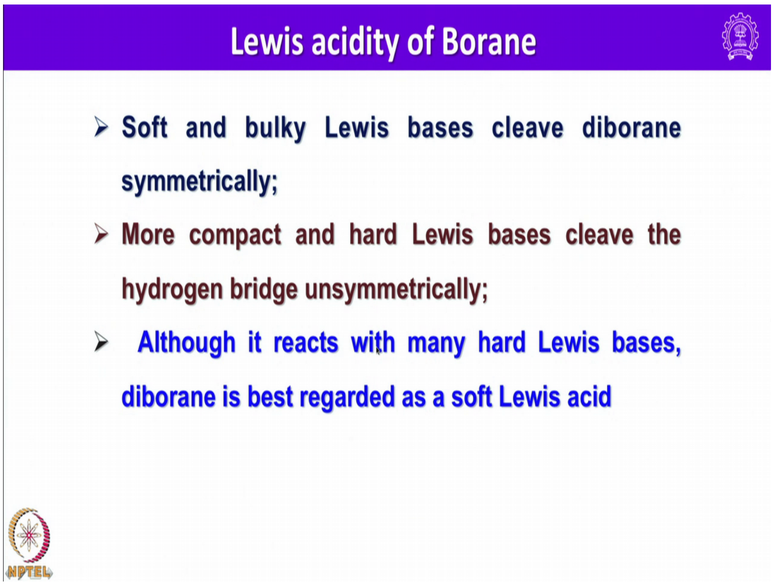

Lewis acidity of Borane

- Soft and bulky Lewis bases cleave diborane symmetrically;
- More compact and hard Lewis bases cleave the hydrogen bridge unsymmetrically;
- Although it reacts with many hard Lewis bases, diborane is best regarded as a soft Lewis acid

So, let us look into the properties of this borons. So, these borons are Lewis acids because of electron deficiency and they are soft and bulky Lewis bases; that means, whenever we take borons and treat them with soft and bulky Lewis bases cleave di-boron symmetrically. If I use the term symmetrically you can think that there are 2 ways of cleaving this borons one is symmetrical cleaving and another one is unsymmetrical cleaving, unsymmetrical cleaving. Soft and bulky Lewis bases cleave di-boron symmetrically and more compact and hard Lewis spaces cleave the hydrogen bridge unsymmetrically. Although they react with many hard Lewis bases di-boron is best regarded as a soft Lewis acid ok.

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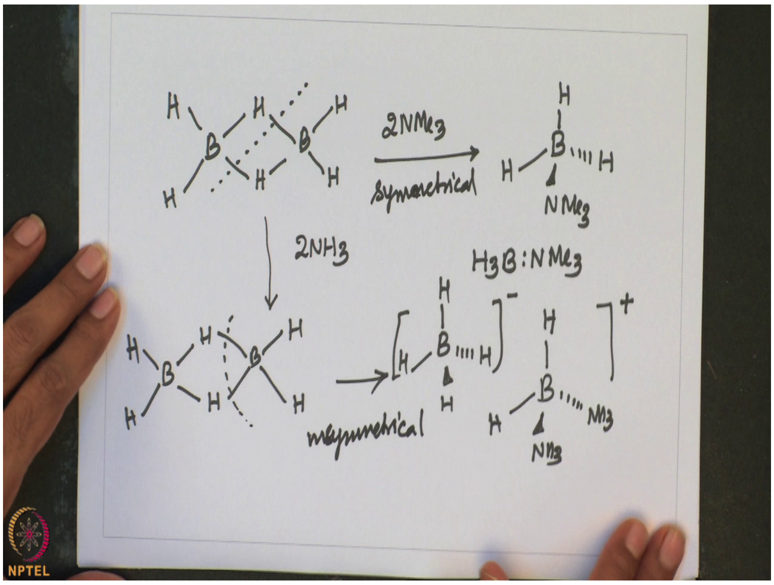

So, I will show you those symmetrical as well as unsymmetrical cleaving. For example, di boron is treated with trimethylamine, if it is treated with 2 equivalents of trimethylamine. So, it can cleave this one symmetrically like this. So, in this one it results in the formation of course, one can also write conveniently this one as this is the standard practice. It indicates boron is tetrahedraly surrounded by 3 hydrogen atoms and one NMe 3 and NMe 3 lone pair is going towards boron.

So, in case of unsymmetrical let me consider here. For example, if I treat this one with the 2 equalents of ammonia it unsymmetrically cleaves the bond. So, usymmetrically wing here. So, this leads to essentially minus and then we have another one plus. So, this shows symmetrical and this is unsymmetrical. So, soft bulky, amines, cleaves, symmetrically and hard simple Lewis bases cleave unsymmetrical.

Let us look into a one more important reaction we come across with boron hydrides that is the hydroboration.

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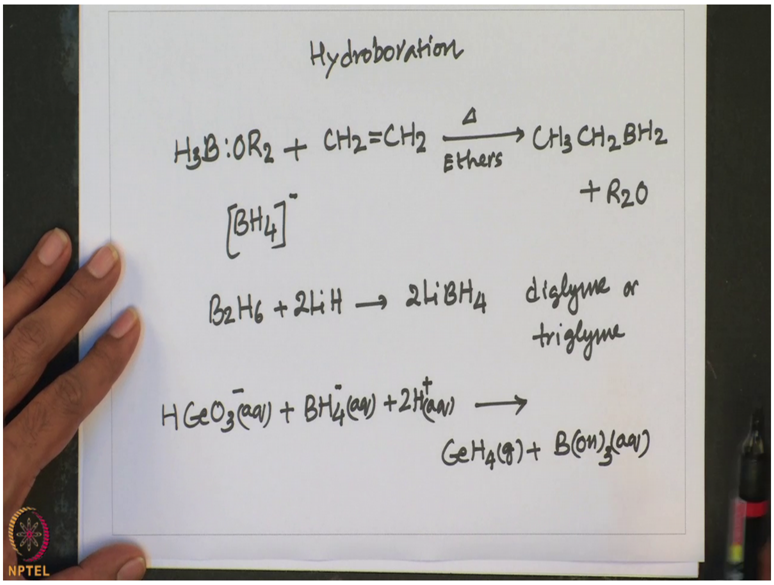

Hydroboration

$H_3B{:}OR_2 + CH_2{=}CH_2 \xrightarrow[\text{Ethers}]{\Delta} CH_3CH_2BH_2 + R_2O$

$[BH_4]^-$

$B_2H_6 + 2LiH \rightarrow 2LiBH_4$ diglyme or triglyme

$HGeO_3^-(aq) + BH_4^-(aq) + 2H^+(aq) \longrightarrow GeH_4(g) + B(OH)_3(aq)$

So, hydroboration is nothing but the reaction of diboron with alkenes in ether solvent to produce organoborones. I repeat again hydroboration reaction is nothing, but the reaction of diborane with alkenes in ether solvent to produce organoboranes. So, organoboranes are very useful intermediates in synthetic organic chemistry for example, you can use diborane or one can also use borane ether adduct. For example, one can use adduct here when it is treated with an alkene preferably in ether solvents ethers. So, it forms CH 3 CH 2 BH 2 plus R 2 O comes out.

So, the B C bond here in the primary product of hydroboration is an intermediate stage in the stereo specific formation of CH or COH bond; that means, further if you carry out this reaction one can make CH bond or one can also make COH bond from the inorganic chemistry point of you the reaction this hydroboration reaction is a very convenient method for the preparation of a wide variety of organo boranes.

Let us look into another interesting ion B H 4. So, this is also called as tetrahydrido borate ion. Of course, here if you have sodium we call sodium borohydride and if you have lithium here we can call lithium borohydride and simply this ion can be termed as tetrahydrido borate ion. So, this ion is an useful intermediate for the preparation of metal hydride complexes and a variety of borane adducts diborane reacts with alkali metal hydrides to produce salts containing B H 4 minus. So, because of the sensitivity of diborane and lithium hydride one should not carry out this reactions in water or under atmosphere. So, this reactions has to be carried out as I had mentioned already in non aqueous medium using very very dry organic solvents. So, here simply one can take B 2 H 6 treat with a 2 equivalents of lithium hydride to generate very useful this lithium borohydride.

So, this reaction is essentially carried out in diglyme or triglyme they are higher or high boiling ethers. So, although this B H 4 minus ion is thermodynamically unstable with respect to hydrolysis the reaction is very slow at high p H and some synthetic applications have been devised in water as well for example, germane that is GeH 4 can be prepared by dissolving germanium oxide and potassium tetrahydro borate in aqueous potassium hydroxide and then acidifying the solution.

For example, here I will show you that reaction how one can conveniently carry out in aqueous medium as well. So, this how one can do, but these reactions are very rear not often we come across this kind of situation where boron hydride can be used in aqueous medium. Just let me give some reactions showing the formation of higher boron hydrides starting from diborane.

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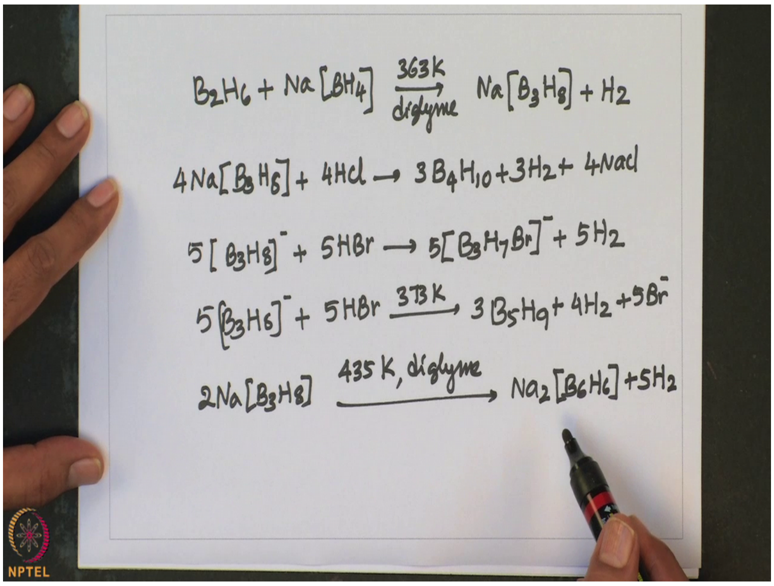

$$B_2H_6 + Na[BH_4] \xrightarrow[\text{diglyme}]{363\text{K}} Na[B_3H_8] + H_2$$

$$4Na[B_3H_6] + 4HCl \rightarrow 3B_4H_{10} + 3H_2 + 4NaCl$$

$$5[B_3H_8]^- + 5HBr \rightarrow 5[B_3H_7Br]^- + 5H_2$$

$$5[B_3H_6]^- + 5HBr \xrightarrow{373\text{K}} 3B_5H_9 + 4H_2 + 5Br^-$$

$$2Na[B_3H_8] \xrightarrow{435\text{K, diglyme}} Na_2[B_6H_6] + 5H_2$$

For example, B 2 H 6 when it is treated with sodium borohydride at 363 Kelvin in a diglyme it gives an ionic boron hydride Na B 3 H 8 plus H 2. Similarly one can start from an ionic boron hydride the same that is generated right now this is when it is treated with hydrochloric acid it gives neutral boron hydride B 4 H 10. So, one can see whether the equation is balanced or not. When B 3 H 8 minus is treated with 5 equivalents of H Br it gives B 3 H 7 Br minus plus 5 equivalents of H 2 will be liberated.

The same reaction when it is carried out at elevated temperature a 100 degree centigrade for example, 373 Kelvin it gives a different boron hydride B 5 H 9 plus 4 H 2 plus 5 Br minus.

One more example I will give you let us take B 3 H 8 anine an ion and I heat this one at 435 Kelvin in diglyme it gives Na 2 B 6 H 6 plus 5 H 2. The structure of this one is very similar to planar benzene molecule. So, I was using this terms diglyme triglyme. So, let us see what are those they are I said acyclic poly ethers. So, let me write the structure for diglyme.

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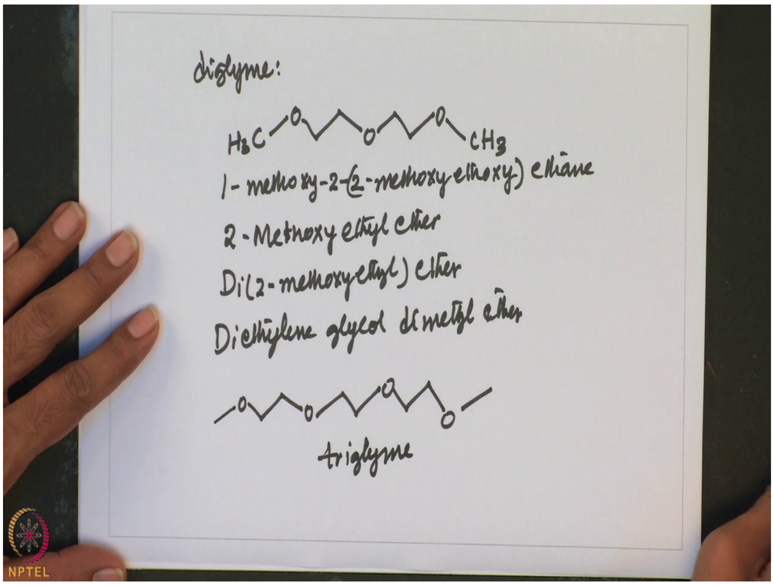

diglyme:

1-methoxy-2-(2-methoxyethoxy) ethane

2-Methoxy ethyl ether

Di(2-methoxyethyl) ether

Diethylene glycol dimethyl ether

triglyme

So, now make an attempt to name this ether of course, one can write several names for them 1 methoxy 2 2 methoxy ethoxy ethoxy ethane. So, this is one way of mentioning or simply one can write 2 methoxy ethyl ether this is the another way of writing or one can also write its name di 2 methoxy ethyl ether ether or another name is there di diethylene diethylene glycol dimethyl ether. So, this is essentially they are high boiling ethers wherever you required to go for higher temperature one can conveniently use this ethers.

Triglyme is this one. So, this is triglyme in the same fashion you make an attempt to name this one as well. So, as I mentioned diborane finds lot of you know applications in organic synthesis. Let me write a few reactions here.

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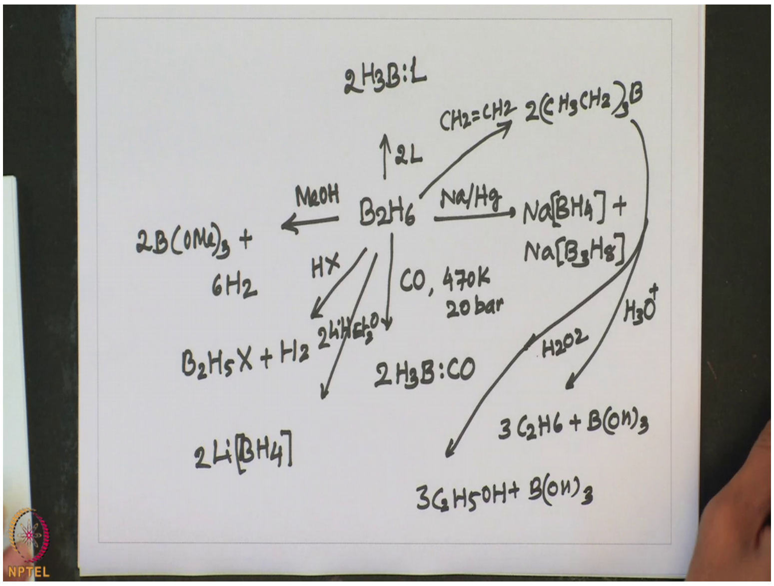

Already I showed you the reaction with the ammonia. What would happen if it is treated with sodium mercury alloy or sodium amalgam it forms sodium borohydride plus B 3 H 8. So, one can get these 2 and if we react this one with CO carbon monoxide at 470 Kelvin, CO is 20 bar you can simply get the adduct. If it is treated with methanol it will give of course, I did not balance it, you can always balance by look into how many molecules of methanol is needed.

So, in general if you use soft bulky Lewis acids what you get is L. So, adduct if you treat this one with H X what you get is B 2 H 5 X plus H 2 that also I showed you and if you treat with lithium aluminium hydride in ether you can get lithium boro hydride suppose you take here you get this one.

So, what would happen if you treat this one with of course, I already showed you this hydroboration reaction if you take this one what you get is 2 CH 3 CH 2 whole thrice boron. This you get it. Of course, here I will go further if you take here we add H 3 O; that means, H plus what should can give is 3 C 2 H 6 plus B OH thrice. What would happen if you add here H 2 O 2 at this stage? What you can get is 3 C 2 H 5 alcohol you will get ethanol plus same B OH thrice. I think this will do of course, if you want more example always you can go to any organic chemistry book and look into the chapter on hydroboration, you will come across several such reactions.

Let me stop here and let me continue in my next lecture on aluminium hydrides. Thank you very much and have a very wonderful inorganic chemistry reading.

Thank you.