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Lecture – 31 Chemistry of Group 13 Elements

Welcome to MSB lecture series on main group chemistry, in my previous lecture I was discussing about wades rules and how to use wades rules to elucidate the structures of boron hydride clusters. And I had mentioned about the type of clusters we have and all those things let me continue from where I had stopped. So, I will show you now, how a naido and arachno cages can be a derived from the parent closo cage with n equals 6 that is having 6 vertices.

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For example you consider a octahedron having 6 vertices, and from this one if you remove one of the capping positions and it becomes naido. And once after removing one from capped we should not make an attempt to remove another from cap, in that case what happens we will be left with 4 born atoms in one plane, in that case what happens we know that each boron atom has a tetrahedral geometry, and arriving a tetrahedral geometry when they are in plane will be difficult as a result instead of removing to arrive at arachno structure, instead of removing the actual one we have to take out one from the plane and this how it is. So, remove one vertex from the plane so that leads to the

formation of arachno. So, this rule we should follow, the first one especially trigonal planar I had mentioned the one that makes 3 connectivity is essentially this one, you can see here this makes 3 connections this should be taken out to make naido of course, from naido if you remove one more it becomes trigonal planar. So, we do not have the those kind of examples.

So, never the less one should remember, first one has to be taken out from the capping positions or axial one, the next one should be preferably from the plane. So, you can see here I have given n plus 1 skeletal electron pairs and n boron atom octahedral, and from this one when we take out one essentially one of this one we are taking out here one of the axial position, and that leads to n minus 1 boron atoms having a naido structure from this naido structure, one can arrive at arachno structure by removing one more from this this is taken out here. So, once you take out this one this one is taken out you will be having a situation like this here n minus 2 boron atoms.

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This for B 4 Cl 4 tetrahedron is looks like this one and also B 9 Cl 9 trichapped trigonal prism will have a structure like this of course, you can see how it is made. So, this is a trigonal prism will have a structure like this of course, you can see how it is made. So, this is a trigonal prism and you have to place 3 boron atoms and then connect them with this 4 to complete the structure like this. So, this is tricapped trigonal prism for vertices 9

are having 9 boron atoms and now you connect them with hydrogen atoms or if in this case it is chlorine. So, essentially you have terminal 9 BCl bonds BH bonds.

So, what would happen if we replace one or more boron atoms with main group elements. So, many such boron hydrides are known in which one or more boron atoms are being replaced by main group elements.

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	Boror	1 Hydrides and \	Wade's Rules		٢			
*	Many derivativ atoms are also	es of boranes co known.	ntaining other i	main group				
*	These heteroboranes may be classified by formally converting the heteroatom to a BH _x group having the same number of valence electrons.							
	Heteroatom	Replace with						
	C, Si, Ge, Sn	BH						
	N, P, As	BH2						
	S, Se	BH3						
	L							

So, these heteroboranes may be classified by formally converting the heteroatoms to a BH x group having the same number of valence electrons; that means, we should remember now for example, boron is coming from group 13 having s 2 p 1 electronic configuration, in case of group 14 such as carbon silicon and germanium and tin we have s 2 p 2 electronic configuration; that means, if one carbon is replacing boron then that should replace 1 BH unit, because 4 electrons will be compensated. Similarly if you are adding an heteroatom from group 15 having s 2 p 3 electronic configuration so; that means, in order to add one nitrogen phosphorus arsenic we have to take out 1 BH 2. In case of carbon silicon germanium or tin we have to take out 1 BH whereas, in case of nitrogen phosphorus and arsenic we have to take out a BH 2 unit and in case of sulphur and selenium having s 2 p 4 electronic configuration we have 3 electrons more, as a result we have to take out a BH 3 unit to incorporate one sulphur or selenium. So, this we should remember. So, s 2 p 1 is for boron if you are replacing one boron and then if you are adding carbon. So, one electron will be added as a result along with boron one h also

should be taken out, similarly in case of nitrogen phosphorus arsenic when they are coming into the borane. So, each for each incorporation of each group 15 element, 1 BH 2 unit has to be taken out similarly for incorporation of each element from group 16 1 BH 3 unit has to be taken out . So, that the number of valence electrons remains same for the cluster formation ok.

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Problems Based on Wade's Rules Classify the following polyhedral heteroboranes according to their valence electron count:					
C ₂ B ₂ H ₁₂	Heteroatom	Replace with			
2 / 13	C, Si, Ge, Sn	вн			
SB ₉ H ₁₁	N, P, As	BH ₂			
CPB ₁₀ H ₁₁	S, Se ,	BH ₃			
(*)					

So, now 3 questions are there classify the following polyhedral heteroboranes according to their valence electron count. So, now, basically if you just look into the first one, what we have is 2 carbon atoms are there along with boron; that means, here vertices are 7, and in case of this one SB 9 H 11 vertices are 10, and in this one vertices are 12, let us see what kind of polyhedral we can assign for this and of course, we should remember here carbon, silicon, germanium and tin would replace 1 BH unit whereas, from group 15 they replace 1 BH 2 unit and in case of sulphur and selenium we have to take out 1 BH 3 unit here 1 BH 2 and here 1 BH 3.

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24 e = 12 SEP (1+1) ,1 mido

So, C 2 B 7 H 13. So, here you should remember if you have n boron atoms n BH bonds will be there for which we have to take out 2 electrons. So, essentially each boron atom is contributing 2 electrons towards making a BH covalent bond, and since we are counting all the electrons of hydrogen for all practical purpose we can consider only one electron from boron towards cluster formation. So, in that case what happens? Your carbon will be giving 2 electrons. So, 2 4 plus boron will be give only 7 electrons and then this will be 13.

So, we have 24 electrons. So, that is 12 skeletal electron pair will be n plus 1 vertices will be closo and if you have 10 vertices it will be naido, and if you have 9 vertices it will be arachno. So, since we have 7 plus 2 b 9. So, it is arachno structure we have. So, this has an arachno structure and now let us look into SB 9 H 11. So, in this case what we can do is, we can consider 4 from sulphur and 9 from 9 boron atoms and we have 11 here. So, it will be 24 will be 12 pairs. So, 12 pairs this is n plus 1 if you for this one 11 is closo, and then if it is 10 this is naido. So, structure of this one will be naido.

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And similarly we can consider this one CPB 10 H 11. So, in this one carbon is giving 2 phosphorus giving 3 plus we have 10 from this one and 11 from this one. So, we have 21 plus 5 26. So, 26 electrons will be equivalent to 13 skeletal electron pairs, this is n plus 1 and then if you have n. So, and n should be 12; 12 n should be closo and so, we have here 10 11 12 we have. So, this has a closo structure. So, here 10, 11, 12. So, 12 vertices are occupied by 10 boron atoms one phosphorous one carbon. So, it has a closo structure and the structure will be icosa hedron. So, this is how you can count and arrive at the structures of mixed boron hydrides.

So, wades rule can also be applied to a wide range of other clusters of main group entrance metals, and then another thing is both BH and MCO 3 moieties is with C 3 v symmetry have 3 frontier orbitals with matching symmetries and the same number of electrons are available.

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So; that means, for example, if we have B 6 H 6 2 minus and R u 6 CO 18 2 minus, we can consider both of them having similar structure B 6 H 6 2 minus is a n plus 1 skeletal electron pairs are there, 6 plus 6 12 plus 2 14 electrons are there 14 electrons means essentially here I am counting 6 from boron 6 from hydrogen, because I already I have deducted 12 electrons for BH bond formation. So, I am taking only one electron from boron as a result 6 plus 6 12 plus charge 14, 14 electron means 7 skeletal electron pairs and if n plus 1 is 7, n should be 6. So, we have n 6 vertices are there closo structure similarly R u 6 CO 12, 2 minus is also a closo structure with octahedral cage, but how did we arrive at this structure.

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I will show you here you can see this is the C 3 v structure, if the C 3 any molecule having a unit which has C 3 v structure then that can be compared with 1 BH unit so; that means, such that 3 electrons are coming from that one.

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Cluster fragment	Group 6: Cr, Mo, W	Group 7: Mn, Tc, Re	Group 8: Fe, Ru, Os	Group 9: Co, Rh, Ir
M(CO) ₂	-2	-1	0	1
$M(CO)_3$	0	1	2	3
$M(CO)_4$	2	3	4	5
$M(\eta^5 - C_5 H_5)$	-1	0	1	2
$M(\eta^6 - C_6 H_6)$	0	1	2	3
$M(CO)_{2}(PR_{2})$	0	1	2	3

So, here I have given for different groups that cluster fragment and the number of electrons coming towards the cluster formation. You can see MCO 2 for group 6 minus 2; that means, you have to deduct that many electrons and group 7 minus 1 electron are group 8 iron ruthenium osmium 0 electron, and group 9 cobalt rhodium iridium one

electron comes, for MOCO 3 0 contribution and one contribution from group 7, and 2 electrons should be considered from group 8 and 3 from group 9. Similarly MCO 4 units are there we should have 2 electrons 3 electrons 4 electrons and 5 electrons. So, it goes like that if I have a arene eta 6 coordinated arene, we should consider 0 in case of group 6 elements and one in case of manganese technetium and rhenium, an in case of group 8 such as iron ruthenium osmium we should consider 2 electrons for each such unit and 3 from here ok.

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So, and here we do some corrections we cannot use directly. So, for that correction the formula is given here x equals meu plus n minus 12, where x is number of cluster bonding electrons that are available. So, meu is essentially number of valence electrons from the metal atom, and n equals number of valence electrons provided by the ligand. So, let us look into at least one here example R h 4 CO 12, we shall see how many electrons are coming for cluster building are from each unit here R h 4 CO 12 is there we can think of each unit having R h CO 2 o 3. So, let me see whether we can arrive at this one ok.

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 $\begin{bmatrix} Rh_{4}(C0)n \end{bmatrix} \quad X = 1 + n - 12 \\ Rh = d^{7}s^{2} = 9 = 9 + 6 - 12 = 3\hat{e}$ 4×3= 120 = 65EP= 9+1 4 Rh((0); 57 : CLOSO TBP

So, in case of R h 4 CO 12 we have rhodium of course, rhodium we have 7 plus 2 9 electrons are coming it is rhodium we have is d 7 s 2 cobalt rhodium iridium. So, cobalt has d 9 3 d 7 s 2 it is 4 d 7 s 2 rhodium. So, we have 9 electrons are coming. So, equation given is x equals meu plus n minus 12. So, here essentially what we are getting is 9 and CO 3 unit we have here 4 R h CO 3 units each CO is giving 6 electrons and 12. So, essentially here it is we have to consider how many electrons, we have to consider 3 electrons if you consider 3 electrons for this one. So, then we have essentially R h is 4 such units are there, 4 into 3 we have 12 electrons are there and for this one 6 skeletal electron pair which is equal to n plus 1 so; that means, n vertices should be your closo and now n closo that should be n should be 5, this should be TBP trigonal bipyramidal and then here we have 4. So, n minus 1 vertices are there n minus 1 rhodium atoms are there it should be removal of one so; that means, essentially we start with a closo; closo structure of trigonal bipyramidal.

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And remove one on this one then we have a tetrahedral structure, where each rhodium will be occupying this 4 corners with having 3 carbon hill groups on each one. So, that you can see here.

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So, same thing is to case of iridium 4 also. So, brakes into 4 MCO 3 and each one will give 3 electrons towards cluster. So, essentially 12 electrons are coming, and 12 electrons I showed you how 12 electrons are coming and 6 electron pairs totally, that is n plus 1. So, n equals 5 is closo, we do not have we have once less. So, it is n minus 1 rhodium

atoms we have it has a nido structure. So, it has a naido structure and this how rhodium atoms are arranged in a tetrahedral fashion and with each one having some bridging and all those things. So, the core structure can be determined using wades rules.

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And let us look into some of this array and c l here germanium 4, tin 4, lead 4 are given and if you see here tricapped trigonal prismatic geometry we have, and in this one we have monocapped square antiprismatic geometry; in one of this case I would show you for example, let us consider Sn 5 2 minus.

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2×5= 10+2= +2=20e 10 SE

Simply s; I will consider s n 5 2 minus and let us try to predict the geometry of this one. So, in case of Sn 5 this function carbon group; carbon group what we have is S 2 P 2 electronic configuration as I mentioned 2 electrons you can simply take out for making Sn bonds with the neighbouring 2 Sn atoms. So, we consider only 2 electrons if you are considering only 2 electrons 2 into 5 will be 10 plus 2, 12 electrons are there and 6 is the skeletal electron pair that is equal to n plus 1. So, now, n will be 5; n equals 5 will be closo. So, it has a trigonal bipyramidal geometry. So, you can see here it has trigonal bipyramidal geometry same thing is too in case of P b 5 2 minus. So, this is how you can consider so; that means, essentially what you should do is, just leave the s 2 electrons for making 2 Sn bonds and consider only the electrons that are coming from p orbital for the cluster building. That is the thumb rule you can ignore the s electrons consider only from the p orbital no matter which group it belongs to.

Let us look into one more example here G e 9 2 minus; germanium is also essentially coming below silicon. So, we have getting 2 electrons. So, 9 into 2 plus 2 charge equals 20 electrons, 20 electrons will be 10 skeletal electron pairs this is n plus 1. So, if you have n then this is closo n vertices will should be 9 that is n equals 9. So, we have nine. So, this should be a tricapped trigonal prismatic geometry. So, that we are arriving at the right structure, so that you can use this one in this fashion to understand the structures.

So, before I conclude let me give the uses of some of the group 13 elements ok.

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So, magnesium diboride is used in superconductors. So, magnesium diboride that is M g B r 2 is a cheap compound that has been known in the laboratory for over 50 years in 2001, this simple compound was found to have superconducting properties. Jun Akimitsu and his co-workers discovered by chance that MgB 2 loses its electrical resistance when cooled, and MgB 2 has a simple structure in which the boron atoms are arranged in graphite like planes with alternating layers of magnesium atoms, you recall I showed you that one so, this is how it is there.

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Red one shows boron layer and the grey one shows the magnesium layer. So, alternately they are arranged magnesium sheet and boring sheet, and with the composition of MgB 2. And this high quality MgB 2 can be synthesized by heating fine boron and magnesium powders together around 950 degree centigrade under high pressure. So, thin films wires and tapes have since been formed, that have potential for applications of superconducting magnets microwave communication and power applications in super conducting magnets microwave communications and power applications.

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A new form of radiotherapy for brain tumors involves irradiation of boron compounds with low energy neutrons. So, boron neutron capture therapy also knows BNCT, it involves injecting the patient with a 10 boron labelled boron compound, which preferentially binds to tumour cells and when irradiated with neutrons that 10 boron undergoes nuclear fission and produces a helium nucleus as shown below, and 7 lithium plus nucleus and liberates approximately 2.4 MeV of energy. So, here you can see this is the reaction that happens. The most promising boron containing compound for this application have been polyhedral boron hydrides having the composition such as N a 2 B 12 H 11 SH or N a 2 B 12 H 12 ok.

And boron carbide is also important and it is in use in nano particles. So, these nano particles of boron carbide are introduced into a sample of the patients bone tumor cells, which are then injected back into the patient where the travel to the tumor and deliver the nano particles. The nano particles have also been coated with a peptide that improves cell uptake and labelled with a fluorescent dye, that enables the nanoparticles to be tracked within the body.

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So, this is another important application and of course, I have a couple of questions here and predict the outcome of the following reactions. You can see here of course, here you should remember the relative strengths of the Lewis acidity of various boron halides, and here if you see BF 3 n m e 3 adduct when it is reacted with BCl 3 you can anticipate the replacement of BF 3 by BCl 3 simply because BCl 3 is a stronger Lewis acid compared to BF 3. So, reaction occurs here and then in case of BCl 3 n m e three. So, this already a strong adduct BF 3 being a weaker Lewis acid compare to BCl 3 there is no reaction in this case again NMe 3 being a stronger Lewis base compare to SMe 2 replaces and SMe 2 comes out whereas, in this one's Me 2 is a weaker Lewis base compared to NMe 3 there will be no reaction. So, essentially you can see a in first case reaction occurs, in second case no reaction here reaction occurs and here no reaction.

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And borazine reacts with 3 equivalents of HCl to give a material of composition B 3 N 3 H 9 Cl 3. So, write the structure of the compound and how does it react with HCl. So, you should remember in borazine B-N bonds are polarized with boron carrying plus charge and nitrogen carrying negative charge like this I have shown here and then so; that means, once you polarize you can notice where exactly Cl will be going on where H will be going.

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So, since B plus is there, C l minus will be coming and N plus see their H will be N has lone pair. So, H will be coming here, and you form a compound of this type. So, this is the product of the reaction of borazine with HCl you can see here.

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You can see charges here. So, automatically you know where HCl is there and it goes and you get that product.

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Ask a Question	Ŵ
yourself	
(a) BCI₃ + EtOH →	
(b) BF ₃ + EtOH	
(c) $BCI_3 + PhNH_2$	
(d) BF ₃ + KF	
(*)	
NPTEL	

So, in this one you can also write the product here in the reaction I showed here we should be able to write the product.

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 $\begin{array}{rcl} BU_{3}+3 \mbox{Eton} & \rightarrow & B(0\mbox{Et})_{3}+3 \mbox{H}U\\ BF_{3}+ \mbox{Eton} & \rightarrow & \mbox{Eton}.BF_{3}\\ BU_{3}+3 \mbox{PhNN}_{2} & \rightarrow & B(\mbox{NNPh})_{3}+3 \mbox{H}U\\ BF_{3}+ \mbox{KF} & \rightarrow & \mbox{KBF4}(\mbox{ionic sall}) \end{array}$

So, let me complete this reactions. So, BCl 3 plus 3 E t o h will give BO Et thrice plus 3 HCl yeah BF 3 plus Et o h gives adduct there is no nucleophilic substitution, it gives only the adduct and BCl 3 plus 3 P h NH 2 gives BNHPh. So, n nucleophilic substitution plus 3 HCl comes out and BF 3 plus KF gives KBF 4 say ionic salt. So, we should be able to do that one.

Or in this cases we can also add a base. So, that if you add triethylamine, triethylamine hydrochloric precipitate reaction will be much faster.

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So, last question BCl 3 is a volatile liquid suggest a way in which it can be more conveniently handled. So, if it is liquid and its volatile its more reactive its very difficult to handle, what we can do is we can make an adduct with for example, SMe 2 we should make an adduct in such a way that we should not use a stronger Lewis base for example, we can make an adduct with dimethyl sulphide and an adduct of dimethly sulphide is a crystalline solid which is very easy to handle, and it is less sensitive towards hydrolysis than BCl 3. So, that we can have weighing al those things we can do it easily.

All though f is more electronegative than Cl, why BCl 3 stronger lewis acid that BF 3 I already discussed with you. So, no there is no need to repeat the answer for this one again.

So, let me summarise the chemistry what we learnt about group 13 elements, except for boron other elements such as aluminium to thallium have electro negativity value and all are metals ok.

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Plus 3 oxidation dominates the chemistry of group 13 elements, inert pair effect appears for the first time among p block elements, the plus 1 of state for thallium is moderately stable. So, I did not give much emphasis to explain inert pair when I was discussing group 13 elements; however, I will explain you in detail the inert pair effect when I start the chemistry of group 14 elements as well as group 15 elements. So, boron forms a large number of neutral and ionic boron hydride clusters, as a result of its electron deficiency. All boron tri halides are very strong Lewis acids and NaBH 4 sodium borohydride and lithium aluminium hydride find application has very useful reducing agents in inorganic as well as organic synthesis. So, with this one I am concluding the chemistry of group 13 elements, have a nice time reading in organic chemistry.

Thank you.