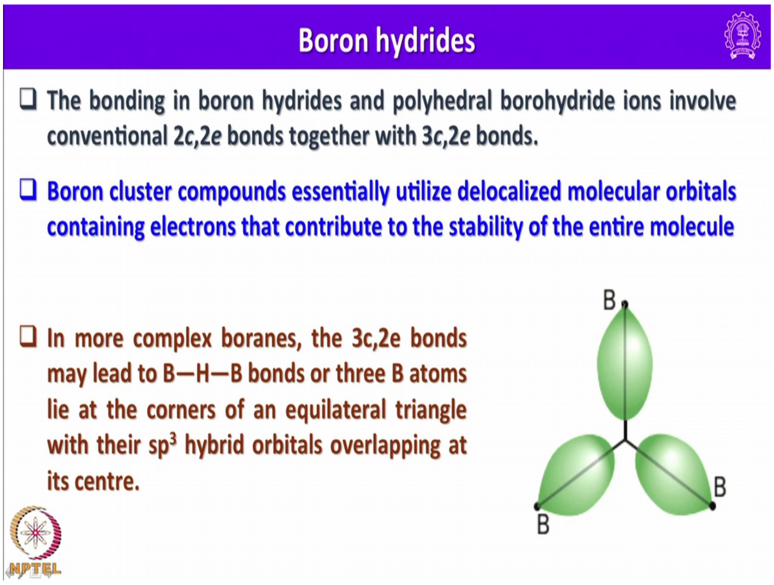
Main Group Chemistry
Prof. M. S. Balakrishna
Department of Chemistry
Indian Institute of Technology, Bombay

Lecture – 30
Wades Rules

Welcome to MSB lecture series on Main Group Chemistry. In my previous lecture I was discussing about the chemistry of group 13 elements.

(Refer Slide Time: 00:39)



While discussing the chemistry of boron hydrides I had mentioned that I would give more details about wades rules to explain, structure and geometry of boron hydrides. Today let me do that one. So, let us consider the utility of wades rule in explaining structures of boron hydrides, the bonding in boron hydrides, and also polyhedral borohydrate ions essentially involve a conventional 2 centre 2 electron bond; that is normal, so every bond requires 2 electrons. Along with 3 centred 2 electron bonds.

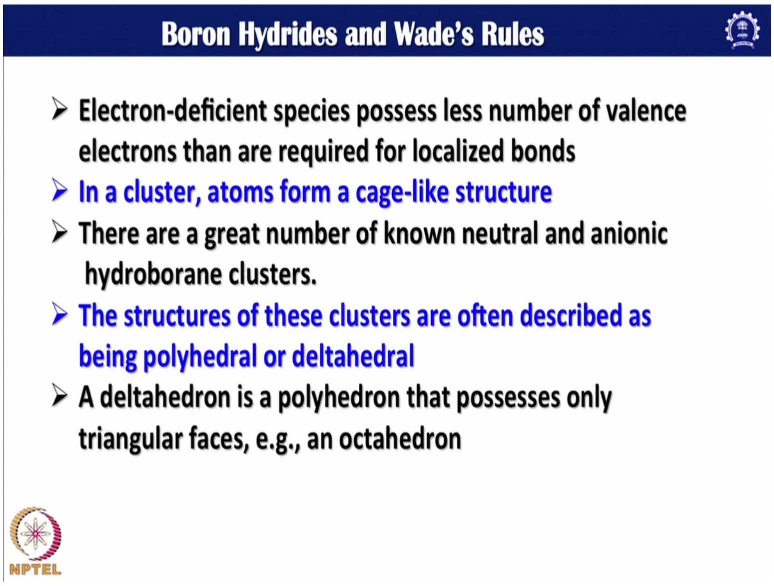
Since group 13 elements are in particular boron being for having s 2 p 1 electronic configuration. In order to have a stable tetrahedral geometry with coordination number four there in short of 2 electrons, so they are electron deficient and most of the electron deficient molecules tend to have some bonds similar to 3 centre 2 electron bonds. So, boron cluster compounds essentially utilise delocalised molecular orbitals containing these electrons that contribute to the stability of the entire molecule. So I repeat again:

boron cluster compounds essentially utilise delocalized molecular orbitals containing electrons that contribute to the stability of the entire molecule. So, after setting aside the number of electrons that are required to make 2 centre 2 electron bond remaining electrons are essentially utilised in building the cluster involving 3 centred 2 electron bonds depending upon how many hydrogen atoms are there that are going to bridge two boron atoms.

So in more complex boranes, 3 centre 2 electron bonds may lead to a B-H-B bond; as I had mentioned or three boron atoms lie at the corners of an equilateral triangle with their sp 3 hybrid orbitals overlapping at its centre. So, let me show you that one in this diagram you can see here. Let us say, a each boron atom is having one sp 3 empty sp 3 orbital and two others have one electron each so they overlap in this fashion to have a bonding of this type; this also essentially 3 centre 2 electron bond.

So, let us look into more details about wades rules.

(Refer Slide Time: 03:31)

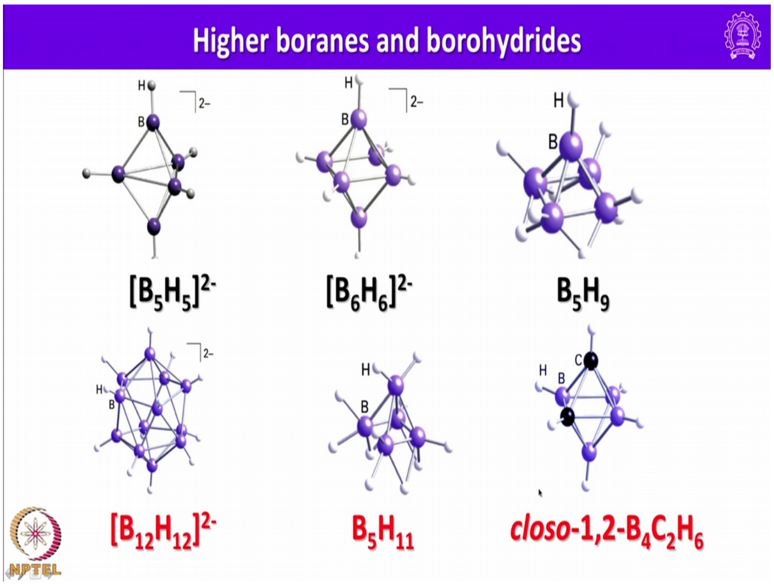


So, electron deficient species posses less number of valence electrons as I had mentioned, then are required for localised bonds. So, in a cluster atoms form a cage like structure. So, there are a great number of known neutral and anionic hydroborane clusters. The structures of these clusters are often described as being polyhedral or deltahedral. A deltahedron is a polyhedron that possesses only triangular faces; triangular triangular means equilateral triangle equilateral triangles.

For example, let us consider octahedron. If you take octahedron; so if you just look into this one; it is one face made up of equilateral triangle we have four such triangle shear forces triangles here that is the reason it is called octahedron. So, this is one of the example for deltahedron. I would give you more details about other deltahedron.

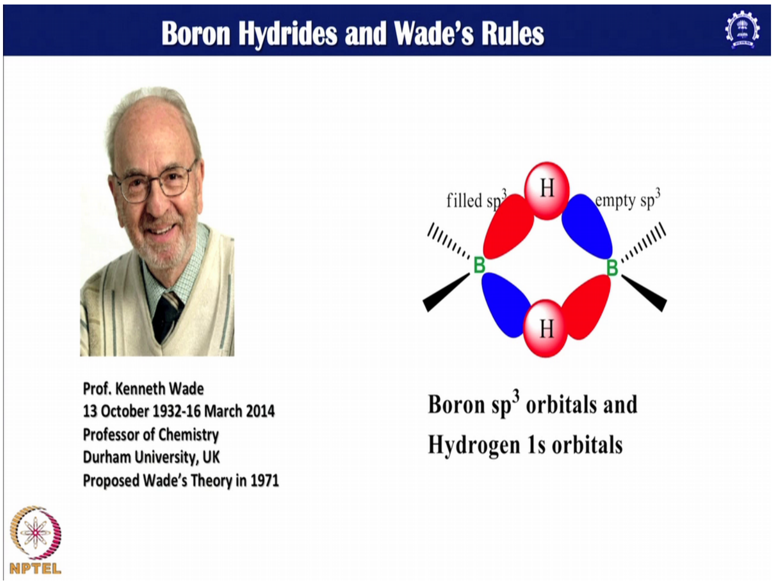
So, for example, you consider here B 5 H 5.

(Refer Slide Time: 04:38)



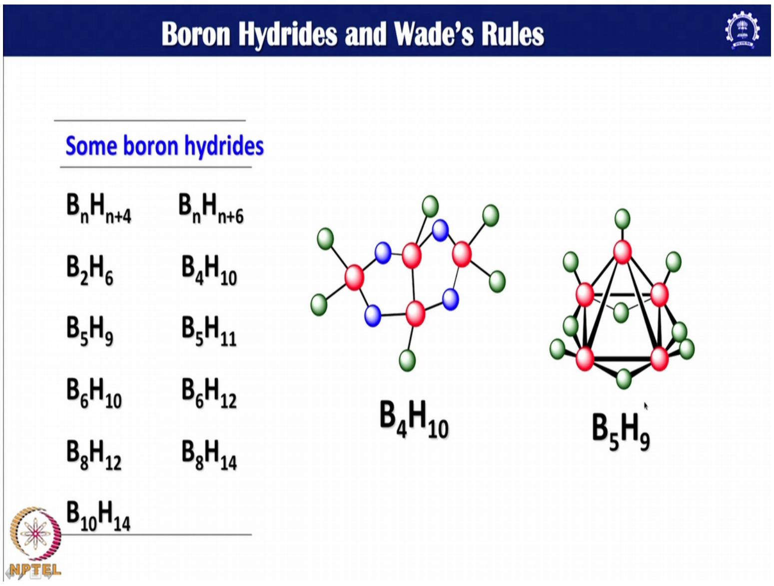
We have 5 vertices are there occupied by boron atoms. And in similarly if you look into B 6 H 6 2 minus, so we have six boron atoms occupying 6 vertices of a regular octahedron. Similar here we have B 5 H 9: so one of the actual position of octahedron is missing. And then we have this one B 12 H 12 2 minus; here in this case the structure is called icosahedrons. I will show you this structures later. And also similarly we have B 5 H 11. And also we have some prefix here closo 1, 2 B 4 C 2 H 6 it is a carborane. What is this closo is all about I will be elaborating when I start discussing on wades rules again.

(Refer Slide Time: 05:31)



So Professor Kenneth Wades proposed this theory to explain bonding in boron hydrides and similar type of clusters of main group elements as well as metal carbonates. And here you can see a earlier when you are looking to the structure of diborane that is B 2 H 6 we proposed this kind of 3 centre to electron bonds were filled sp 3 of boron interacts with 1 s 1 electron of hydrogen with an empty sp 3 of another boron to form 3 centre 2 electron bonds like this. And of course, here if you look into terminal one they are conventional 2 centre 2 electron bonds.

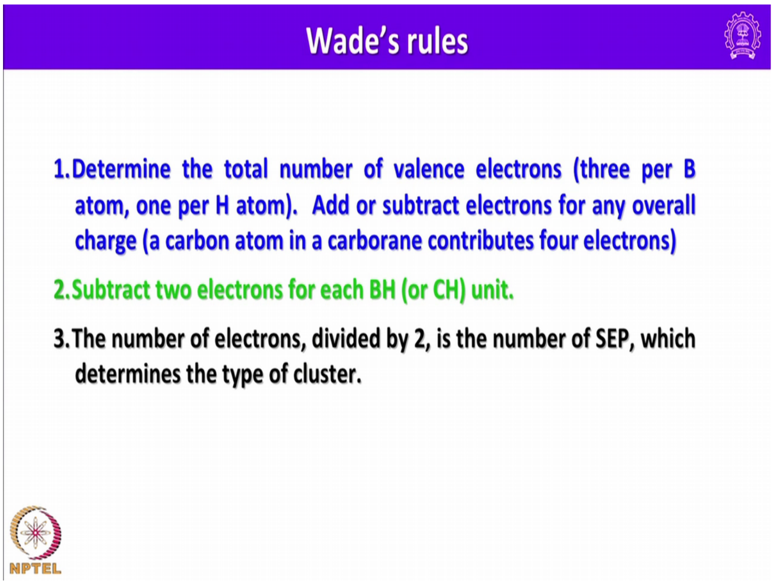
(Refer Slide Time: 06:22)



Now, let us look into the types again the type of boron hydrides we have we have two series one is B n H n plus 4, and another one is B n H n plus 6 series. And some examples I have given here in case of B n H n plus 4: so B 2 H 6, B 2 B 5 H 9, B 6 H 10, B 8 H 12, B 10 H 14, and similarly in this series we have B 4 H 10. So, essentially by just counting the number of boron atoms and hydrogen atom you should be able to tell whether it belongs to B n H n plus 6 or B n H n plus 4 series. So, some examples shown here: so B 4 H 10 belongs to B n H n plus 6 series and this one B 5 H 9 belongs to B n H n plus 4 series.

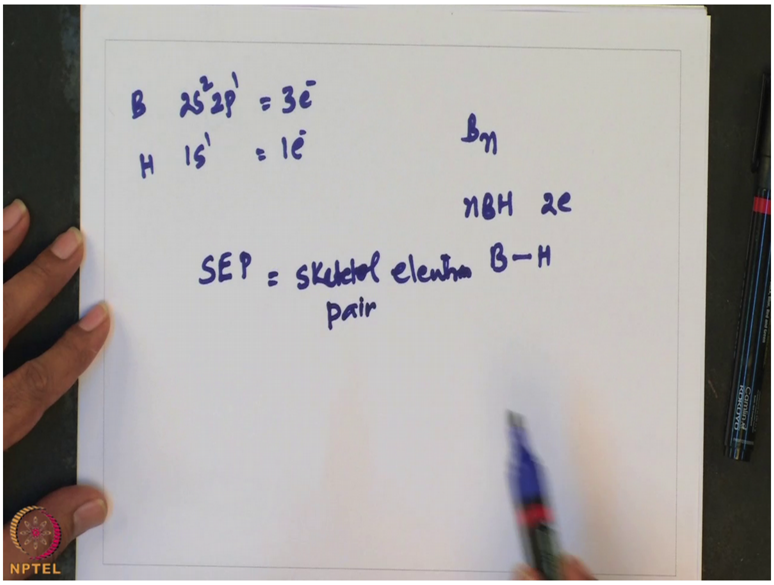
Now, let us look into the wades rules.

(Refer Slide Time: 07:18)



First what we should do is determine the total number of valence electrons present in a particular boron hydride. So, for example we know that boron has S 2 P 1 electronic configuration.

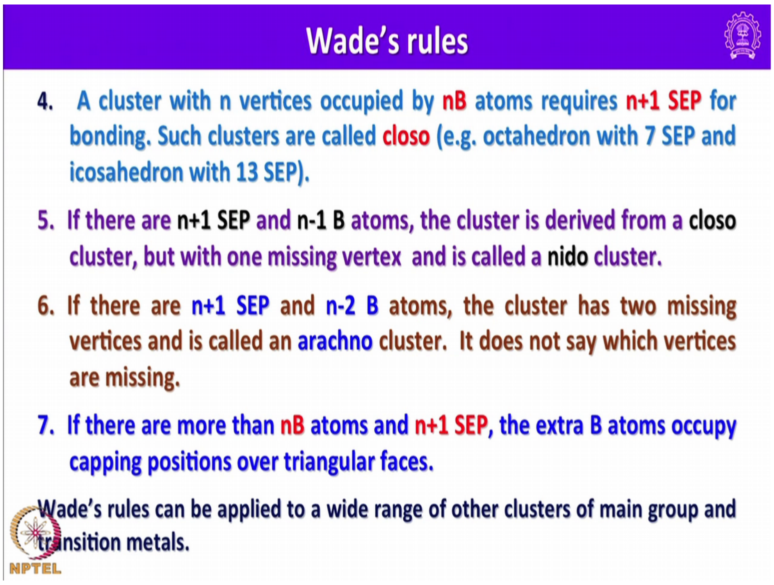
(Refer Slide Time: 07:32)



So, we have 2S 2 2p 1; so totally we have 3 electrons in its valence shell similarly hydrogen 1s 1 we have one electron is there; that means, each boron will give 3 electrons and 1 hydrogen will give an electron. So, in this way what we should do is: in a given boron hydride we have to count total number of valence electrons that are coming from boron as well as hydrogen, add or subtract electrons for any overall charge. If positive charge is there subtract 1 or if negative charge is there you add 1, and depending upon how many charges are there.

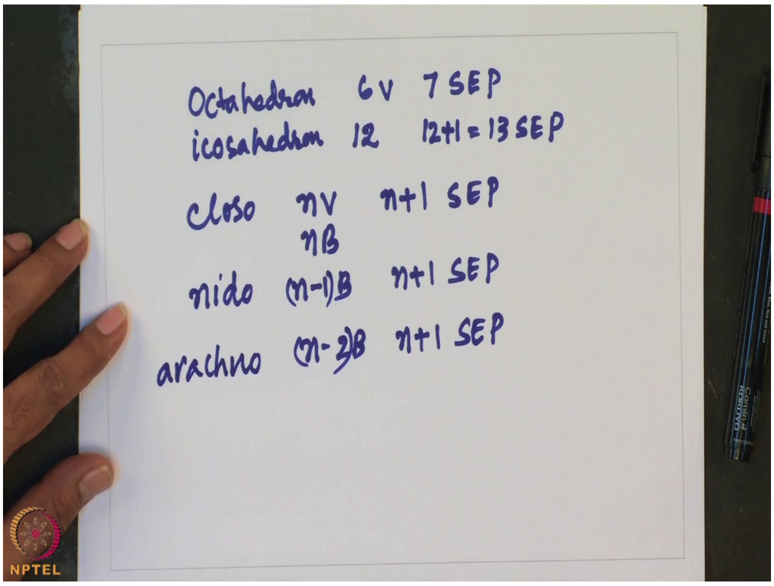
And now after counting and totalling all the valence electrons coming from boron as well as hydrogen we have to subtract 2 electrons for each BH bond. For example, if we have say B n boron hydride, so n BH terminal bonds will be there. So, in a B n poly hydride we will be having n BH bonds they are essentially they involve 2 electrons. So, it is a BH bond. That means, after determining just subtract 2 electrons for each BH unit or CH unit if it is a carborane the number of electrons remaining electrons if you divide by 2 we get a number that is called Sep; this is called Skeletal Electron Pair.

(Refer Slide Time: 09:27)



So, you can see here I have given these details. So, a cluster with n vertices occupied by n boron atoms requires n plus 1 skeletal electron pairs for bonding such clusters are called closo. Example: octahedron will require 7 skeletal electron pairs and icosahedron would require 13 skeletal electron pairs.

(Refer Slide Time: 09:56)



In case of octahedron we have 6 vertices are there. So, we need n plus 1 means 7 skeletal electron pairs. If we look into icosahedron we have 12 vertices are there. So, here 12 plus

1 that is 13 skeletal electron pairs are required. So, this is how one should be able to decide the type of cluster.

If there are n plus 1 skeletal electron pairs are there; that means for closo; so n vertices and n plus 1 skeletal electron pairs. For example, if we have n plus 1 skeletal electron pairs and n minus 1 boron atoms. So, this is n vertices means essentially n boron atoms ok. And then in case if we have n plus 1 skeletal electron pair and we have n minus 1 boron atoms; so then it is called nido. Similarly if we have n plus 1 skeletal electron pairs and we have n minus 2 boron atoms that is called arachno.

So, this is how we can classify boron hydrides clusters. If there are more than n B atoms and n plus 1 skeletal electron pair the extra boron atom occupy capping position over triangular faces. You should remember, if there are more than n b atoms and n plus 1 skeletal pairs the extra boron atoms occupy capping positions over triangular faces. For example, octahedron is there it becomes capped octahedron. So, wades rules can also be applied to a wide range of other clusters of main group as well as transmittals. That I would discuss later.

So, let us look into the type of clusters whatever I showed here.

(Refer Slide Time: 12:12)

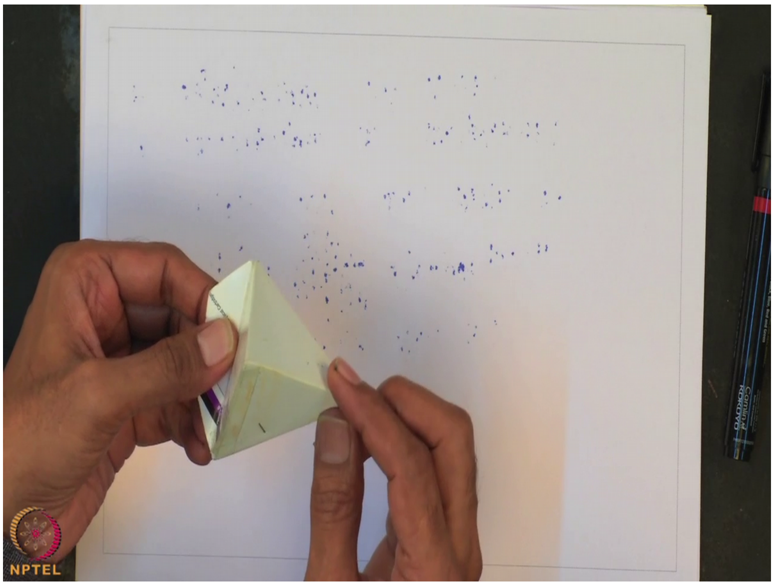
Classification and electron count of boron hydrides

Type	Formula*	Skeletal electron pairs	Examples
Closo	$[B_nH_n]^{2-}$	$n + 1$	$[B_5H_5]^{2-}$ to $[B_{12}H_{12}]^{2-}$
Nido	B_nH_{n+4}	$n + 2$	B_2H_6, B_5H_9, B_6H_{10}
Arachno	B_nH_{n+6}	$n + 3$	B_4H_{10}, B_5H_{11}
Hypho†	B_nH_{n+8}	$n + 4$	None‡

So closo, n plus 1 skeletal electron pairs will be there. And then n number of vertices or n boron atoms will be there. So, in here when we have n plus 2 skeletal electron pairs are there or n pus 1 skeletal electron pairs are the n minus 1 boron atoms will be there that is naido. Similarly n minus 2 boron atoms will be arachno. And if we have n minus 3 boron atoms that is called hypo; so we do not have any example among boron hydrides for hypo type structures.

So, I was telling about deltahedra. So, deltahedral cages with 5 to 12 vertices are the parent cages used in conjunction with wades rule; wades rules to rationalize borane cluster structures. Borane cluster structures as a general rule when removing the vertices from these cages to generate naido framework, remove vertex connectivity 3 from the trigonal bipyramid. So, for example let us look into a trigonal bipyramid. So, this is a typical trigonal bipyramid.

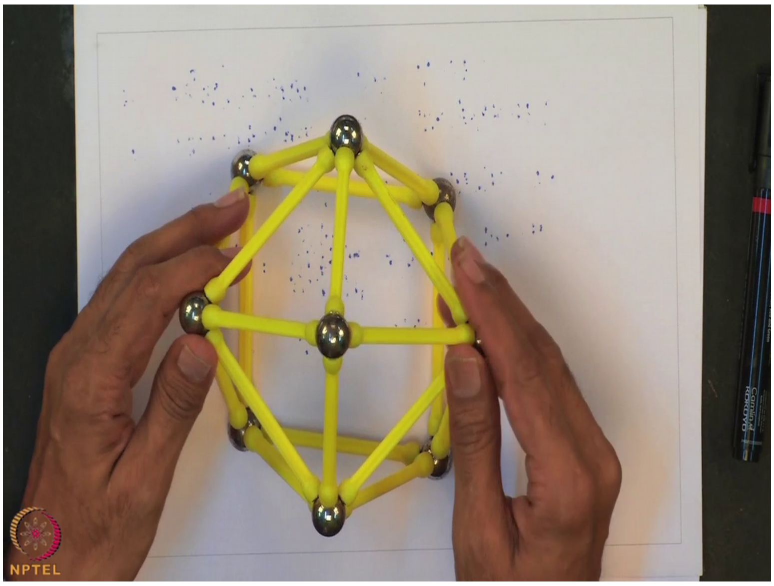
(Refer Slide Time: 13:25)



So, for example this has now, if you just look into it you have 1 2 3 4 5; 5 vertices are there. And from this one if you have to generate a naido structure we have to take out the vertices that makes three connections here; 1 2 3 connection either this one or this one can be taken out; this makes four connection this should not be taken out. So, just take out this. If you take out this one it would be something like this. So, we will get a tetrahedral structure. So, this is a naido; so this is how it is.

And similarly one cap from the one from the octahedron or icosahedron you capped form this one we have to take out this cap. So this one, we have to take out it becomes square pyramidal. For example, if we take out this one it becomes like this. Or in case of icosahedron you have to take out one of the caps here. In this one we have 5 here, 5 here, and 10, 11, 12 is there so we have to take out 1. And of course, from square antiprism, this is square antiprism. So, this square antiprism is this one. This is the square antiprism

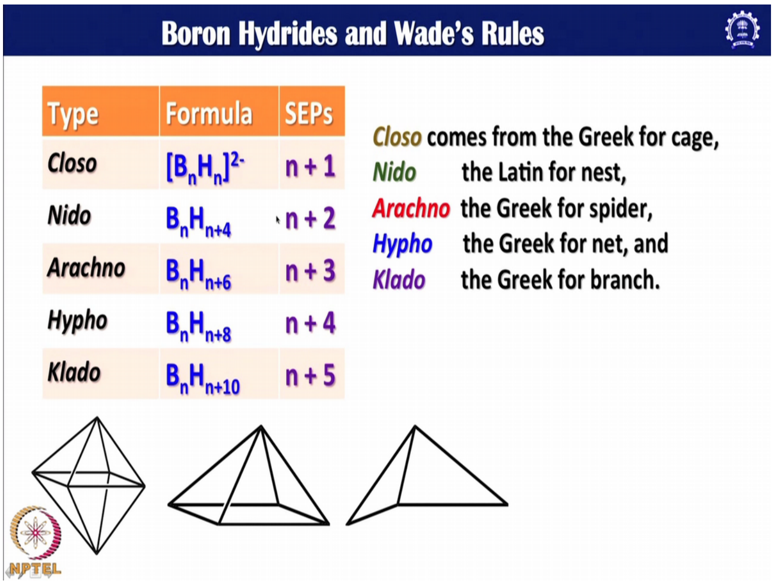
(Refer Slide Time: 14:44)



Basically a cube if you just turn it and make it staggered one of the face it becomes and then connect them with triangular faces it becomes square antiprism. And this one if you put here one more vertices with mono capped one if I put one more here it is by capped one; so it is something like this. So, something like this; this is mono capped one. Similarly one can I can put here it becomes by capped square antiprism, and from this one you have to take out this for 8; for 9 also you can take out one for 8 you have to take out both of them ok.

So, here again I am showing you the details.

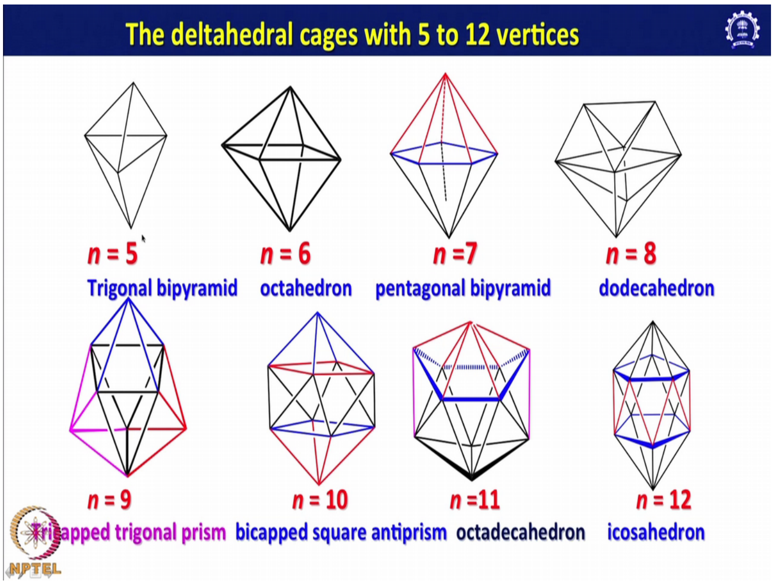
(Refer Slide Time: 15:31)



Closo will have n plus 1 skeletal electron pairs and naido would have n plus 2 skeletal electron pairs and arachno will have n plus 3 skeletal electron pairs. Or if you have n plus 1 skeletal electron pairs we have n minus 2 boron atoms in case of arachno or if you have n plus 1 skeletal electron pairs and n minus 1 boron atom that is naido or if you have n plus 1 skeletal electron pairs and n boron atom that is called closo. And hypo and klado are rare where you have n minus 3 boron atoms for n plus 1 skeletal electron pairs and n minus 4 boron atoms for n plus 1 skeletal electron pairs are essentially called as hypo and klado. They are rare, we do not have any examples some of boron hydrides for these two cases.

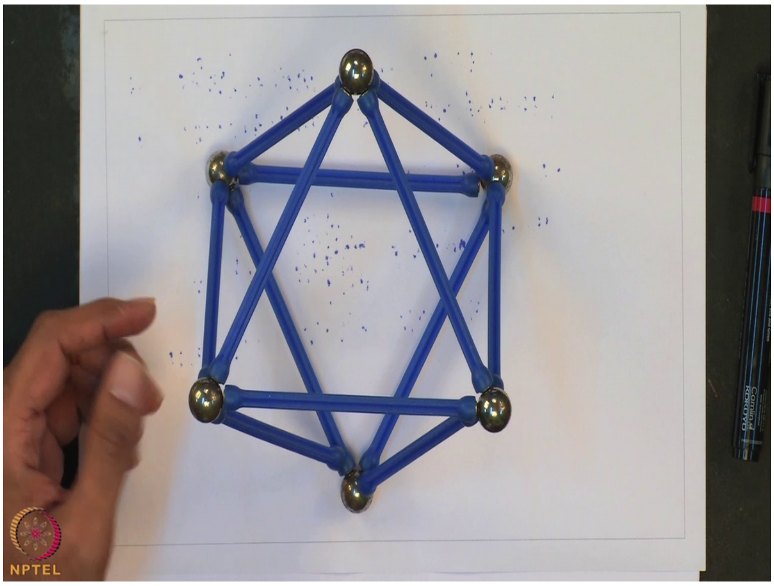
So, essentially some of this terms are coming from Greek or Latin. Closo comes from Greek for cage, naido the Latin for nest, and arachno in Greek for spider, hypo Greek for net again, and klado the Greek for branch. So, this is how the prefix have been included to different type of boron hydride clusters.

(Refer Slide Time: 16:49)



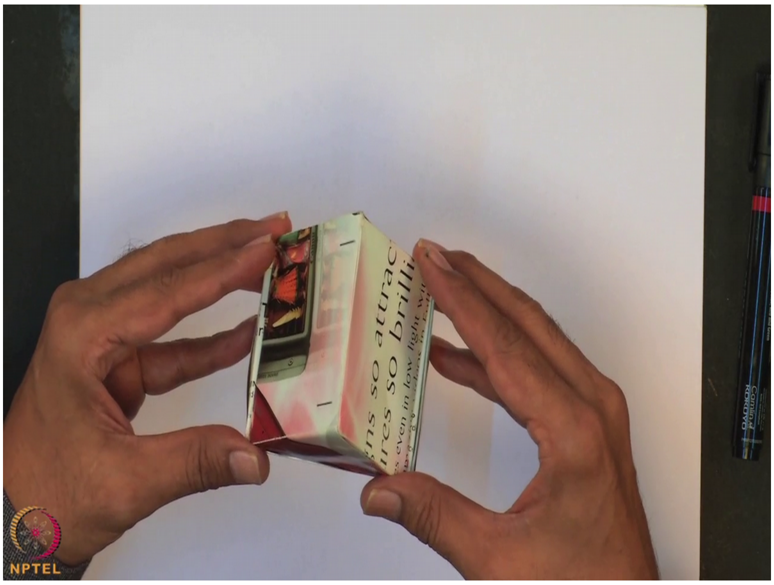
So, I have shown here with n equals 5 this is trigonal bipyramidal. So, n equals 5 this is trigonal bipyramidal. And n equals 6 this is octahedron.

(Refer Slide Time: 17:02)



So, this is octahedron. N equals 7, of course you can imagine pentagonal bipyramidal. N equals 8 dodecahedron; it is very simple to imagine two decahedron.

(Refer Slide Time: 17:15)

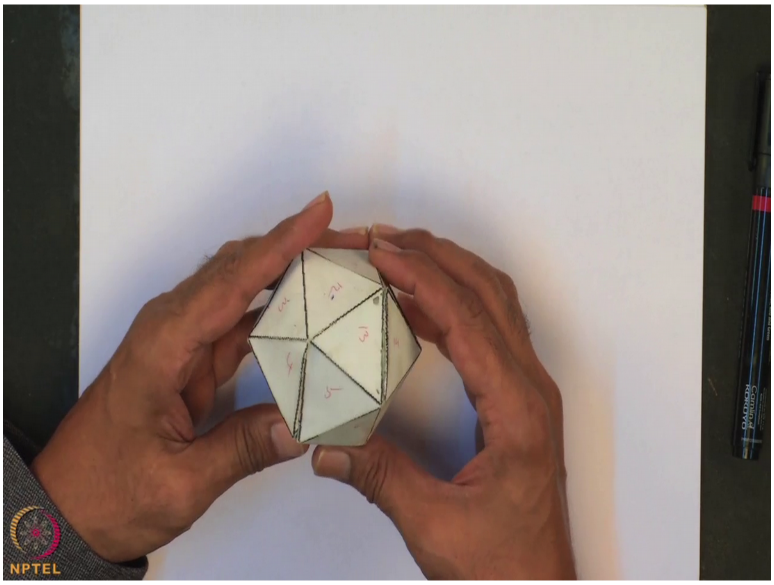


So, this will give rise to a dodecahedron. So, this is a trigonal prism this another trigonal prism; connect them this way not this way if you connect this way and if you see this will have 2 4 6 plus 2 8 vertices are there; so n equals 1 2 3 4 5 6 7 8; this is dodecahedron. And what we have next is tricapped trigonal prism.

For trigonal prism you can take this a trigonal prism; you start capping this positions here you put one connect four and similarly here is mono capped this bicapped and here it is tricapped. We can take like this here and you can connect this way here something like this. So, it is mono capped. And similarly I can put one more here its bicapped and if I put one here tri capped this is for n equals 9. This is the symmetric polyhedron for vertices if 9; if 9 boron atoms are there this is the structure for closo.

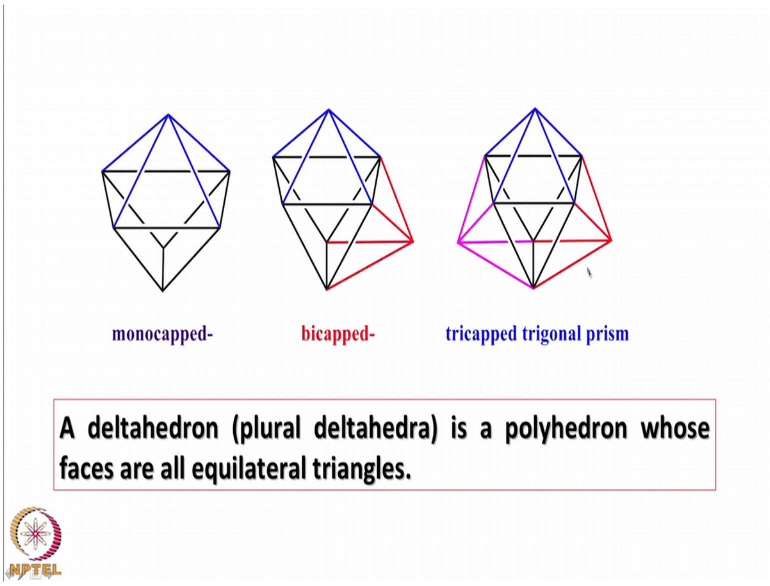
And similarly bicapped square antiprism; bicapped square antiprism as I mentioned we can take this one and if I put one more here. So, this is now; if you see here mono capped bicapped this bicapped square antiprism. And also we have next one is for n equals 11 octa decahedron, and then for 12 its icosahedrons.

(Refer Slide Time: 19:15)



I showed you this is icosahedron we have 5 here and another 5 here and then 1 10 11 and 12; we have 12 vertices this is icosahedrons. Of course, you can see delta hedron.

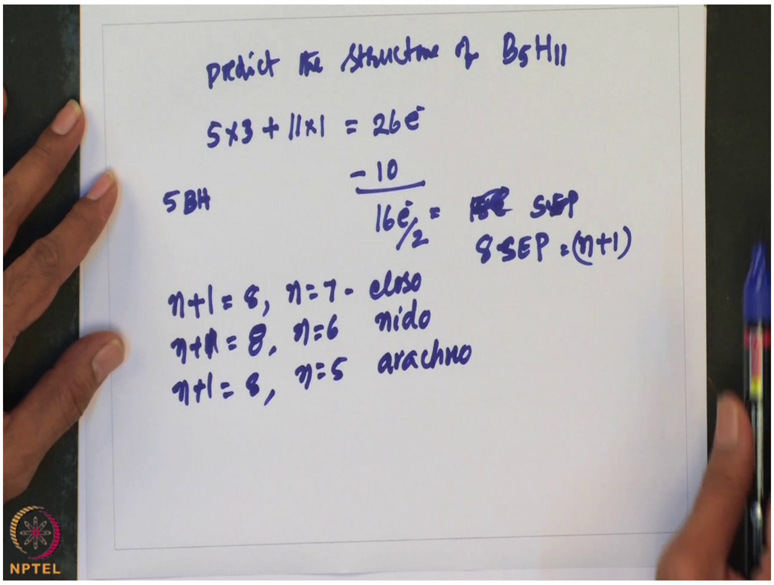
(Refer Slide Time: 19:26)



And this is a mono capped this is bicapped and this is tricapped. A delta hedron is plural is a polyhedron whose faces or all equilateral triangles. If you just look into it there are equilateral triangles and all faces should be equilateral triangles.

And let us now predict the structures of some boron clusters using wades rules. Now let us predict the structure of; let me look into a problem.

(Refer Slide Time: 20:10)



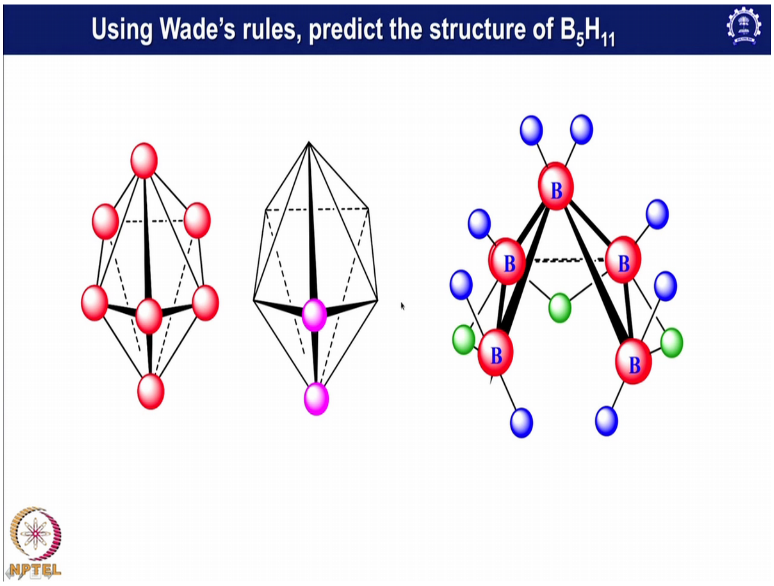
If you learn chemistry through problem chemistry is not a problem. So, predict the structure of B 5 H 11. As I had mentioned we should start counting the electrons from boron and hydrogen. We have 5 boron atoms are there, so 5 into each 1 will give 3 electron S 2 P 1 when only we have to count only valence shell electrons. So, each boron has 3 valence electrons 3 into 4, plus we have 11 hydrogen atoms; so 11 into 1. So, totally we have 15 plus 11 26 electrons are there. Out of 26 electrons we have to subtract 2 electrons per boron atom to make a BH bond.

So, we have here in this case we have at least minimum of 5 BH bonds and each one will require 2 electron, so we should take 10 electrons from this one. And then remaining electrons will be utilised in cluster building. So, we have about 16 electrons here. And 16 electrons divided by 2. So, here it is 8 skeletal electron pairs. This is essentially equal to n plus 1 if you consider closo. If it is n plus 1 equals 8. So, n equals 7 should be closo. And then if n plus 1 equals 8 n equals 6 it is naido. If n plus 1 equals 8 n equals 5 it is arachno.

So, now, we have only 5 boron atoms; that means essentially n minus 2 boron atoms are there. So, as a result this is arachno structure. So, arachno structure should be derived from the closo. Closo means here vertices should be 7. For vertices 7, polyhedron we can consider is pentagonal bipyramidal. From pentagonal bipyramidal what we should do is we have to take out 2 vertices. So, let me show you how we can array about the structure.

See now, we are taking a pentagonal bipyramidal here because the closo for that one is vertices are 7; from this one we have to take out 2 vertices.

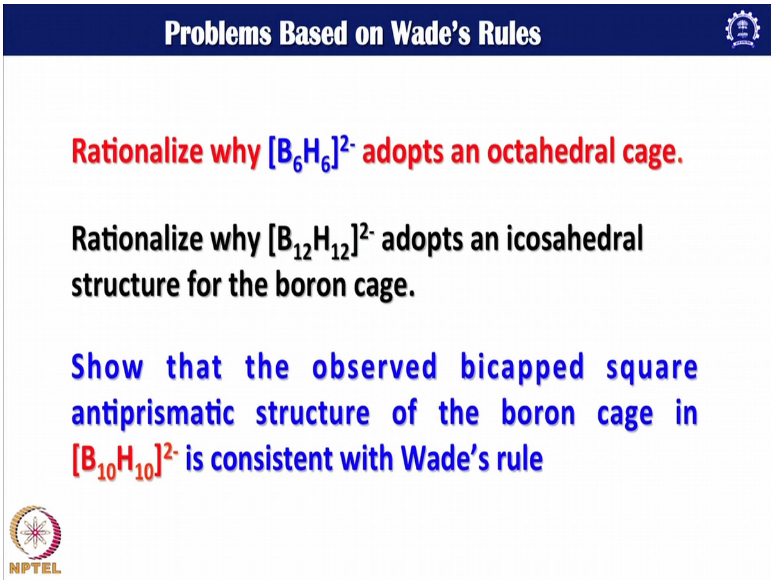
(Refer Slide Time: 23:01)



And this is the closo structure. This should have been ideal if we had 7 boron atoms. So, we do not have 7 boron atoms we have now 5 boron atoms, so we have to choose which one has to be taken. So, these two has to be taken out; first what one from the capping one and next one from the plane. So, this has to be taken out. Once if we take out this one this is the skeletal will be left with 5 boron atoms, this represents the skeleton of B 5 H 11. And now put all the hydrogen atoms this how it looks like. So, this is the structure of B 5 H 11 predicted using wades rules. I hope you have understood this one.

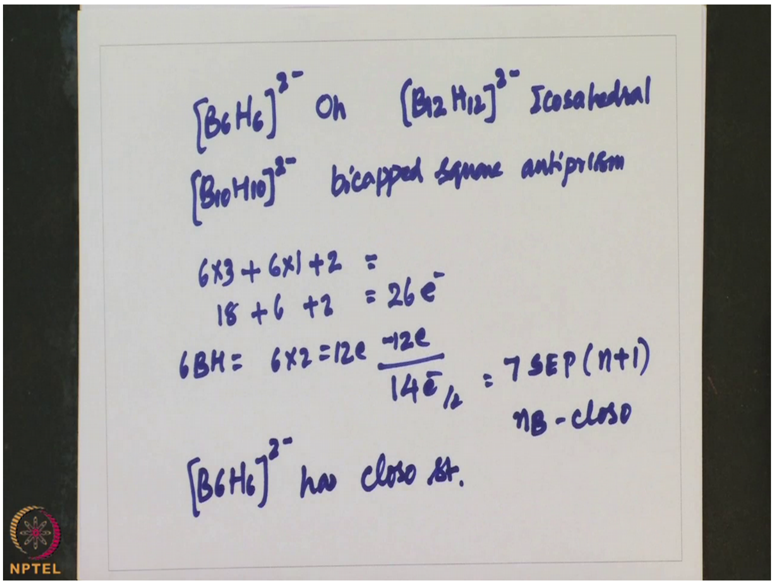
Let me do more examples to make it clear. Now, I have three more problems here: the first one look into it.

(Refer Slide Time: 23:54)



Rationalize why B 6 H 6 2 minus adopts an octahedral cage.

(Refer Slide Time: 24:02)

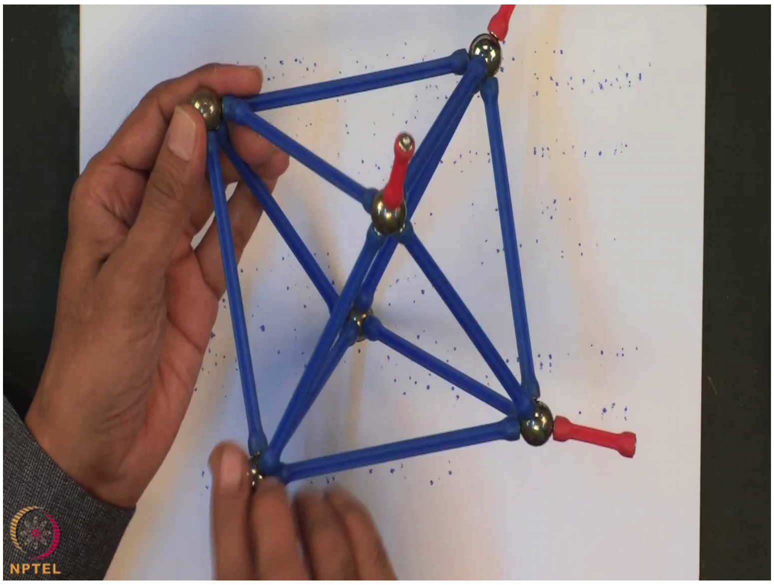


So, here we should prove that B 6 H 6 2 minus has octahedral geometry. And similarly B 12 H 12 2 minus has icosahedron structure. And another one is B 10 H 10 2 minus that shows bicapped square antiprism. So, let us look into this three problems one at a time to make you familiar with wades rules.

Let me start with B 6 H 6 let us start counting electrons in B 6 H 6. So, 6 boron atoms are there so each one is giving see. As a result 6 into 3 and plus 6 hydrogen atoms are there each one will give 1 plus 2 charges are there negative should be added. So, what we have is 18 plus 6 plus 2; that means, essentially 18 plus 6 24 plus 2 26 electrons are there. Out of 26 electrons we have at least 6 BH bonds, so 6 BH bond would require each one requires 2 electrons. So, requires 6 into 2 equal to 12 electrons. So, remove 12 electrons from here minus 12, so it will give you 14 electron. So, 14 electron divided by 2 will be 7, 7 skeletal electron pair and this is n plus 1. If it is n plus 1, so we should have n boron atoms. So, if you have n boron atoms this is called closo.

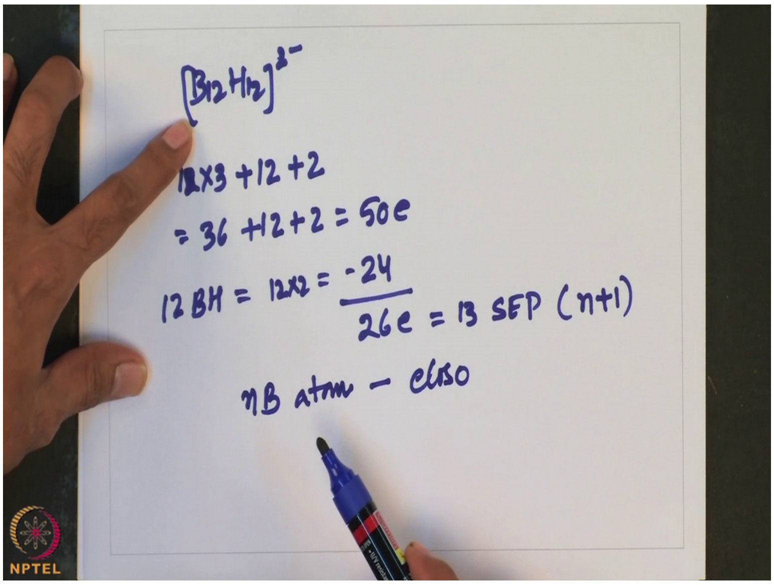
So, since we have 6 boron atoms are there. So, it is a B 6 H 6 2 minus has closo structure. So, it has a closo structure that means it is something like this.

(Refer Slide Time: 26:38)



And this one what we have is each one has one BH bond which is something like this one can add. So, here we can add here. So, this is your BH bond. So, that this is a structure of B 6 H 6 2 minus. We should put 1 2 3 here; 1 2 3 here. So, we have B 6 H 6 2 minus. Similarly let me look into B 12 H 12 2 minus.

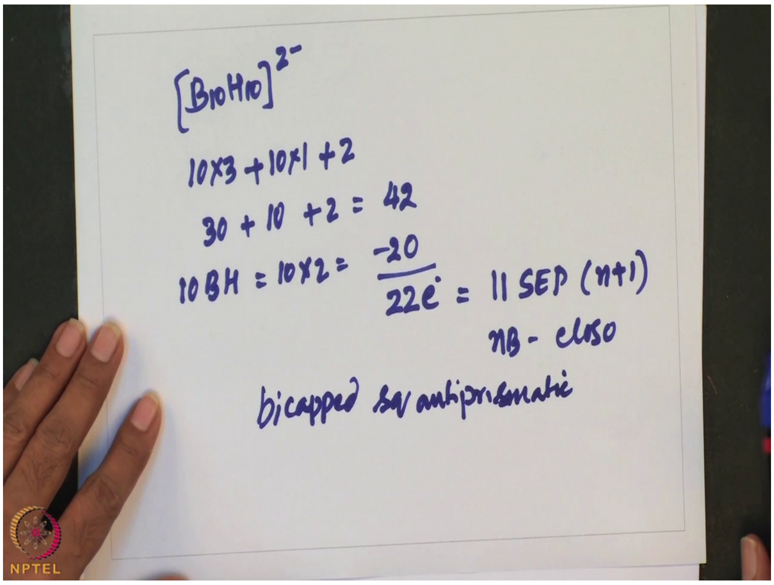
(Refer Slide Time: 27:10)



So, B 12 H 12 2 minus, so 12 into 3 plus 12 plus 2 charge; so 12 into 3 is 36 plus 12 plus 2. So, total we have 50 electrons are there. Out of 50 what we need is we have to deduct 24 electrons for 12 BH bond. So, 12 into 2 equals 24. So, then we have 26 electrons are there. This will be 13 skeletal electron pairs, this is n plus 1. So, in order to have a closo structure we should have n boron atoms; n boron atoms will give a closo structure. So, we have n boron atoms 12 boron atoms are there so that means, the structure is icosahedron.

So, structure will be something icosahedron and at each vertices a boron atom sits and each boron makes a BH bond. So, this is how we can explain.

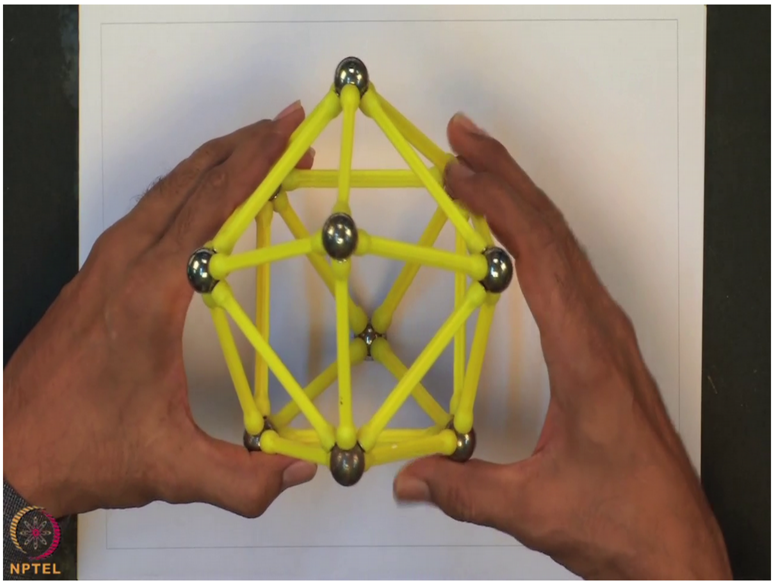
(Refer Slide Time: 28:23)



So, about B 10 H 10 2 minus in the same fashion we can count each boron is giving 3 electrons to 10 into 3 and plus here 10 into 1 and plus charge. So, here 30 plus 10 40 plus 2; so 42 electrons are there. Out of 42 electrons we have to deduct for 10 BH bonds 20 electrons 10 into 2. So, remaining 22 electrons are there. If 22 electrons are there it will be 11 skeletal electron pairs, this will be n plus 1.

So then, if we have n boron atoms this will be closo, so we have n boron atoms we have n is 10. So, this has a closo structure and this closo structure will be having bicapped anti square prismatics geometry. So, you can see here, I can say here bicapped square anti prismatic geometry. So, you can see here this is the one, ok.

(Refer Slide Time: 29:49)



So, this is one you can see here; so 4 here, and 4 here 8 9 and 10. So, this is bicapped anti square prismatic for B 10 H 10 2 minus. So, this is how we can derive the structures usually for a neutral or anionic boron hydrides. So, in my next lecture I will be give you more details, and also application of wades rule to other main group clusters.

Thank you very much, and have a very pleasant reading of inorganic chemistry and understanding of wades rules.