Metallocene and Metal-carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts

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Lecture 14

Bonding and Electronic Nature in Bent Metallocene (Contd.)

Okay, so welcome once again, let us continue our discussion as lecture 14 bonding and electronic nature in bent metallocene in the last class, remember, we discussed what are the parameters for the bent metallocene and what are the structural variations in bent metallocene. So, now, we will try to understand that what is the difference in orbitals and the electronic nature between the parallel and the bent metallocene.

As I told that understanding of orbitals in bent metallocenes is very important to understand the mechanism and the reactivities associated with bent metallocene, because, our the catalysts are actually the bent metallocene. So, this is very important to understand.

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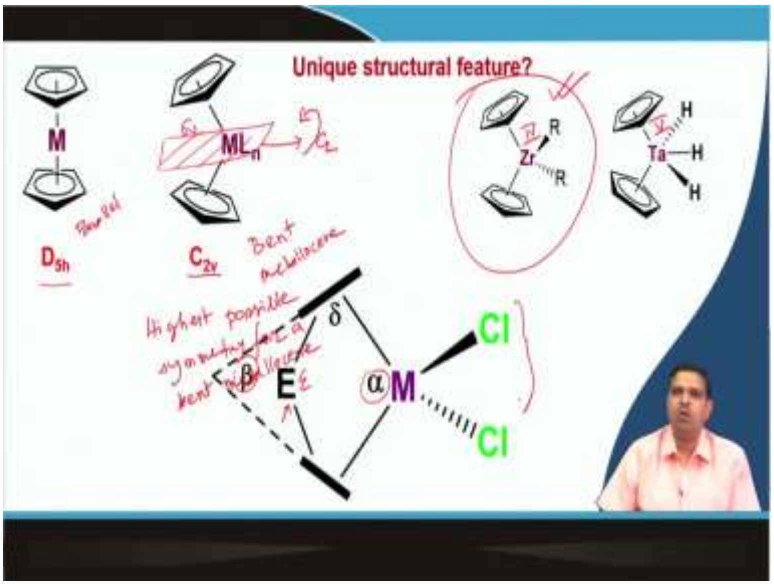

Unique structural feature?

So, let us try to understand this. So, this is you will see that this is the D 5h that is the eclipsed form as example ferocene, where 2 Cp ligands are parallel and these are is the this is the your bent metallocene. So, this is the parallel and this is the bent metallocene and you see that the point group is C 2V, C 2V is the actually highest possible symmetry for a bent metallocene.

So, we will discuss okay we will try to understand the emos with the most symmetric bent metallocene system. In the last class, we discussed that how it is C 2V so, you will see the if this is your C 2V and then this is your the sigma V plan this is sigma V and this is your C 2 axis. So, it is easy to understand why it is C 2V. So, there are a lot of examples on this kind of bent metallocene as example like zirconium, tantalum. So, this is your pulp 4 oxidation state this is 5 oxidation state particularly we are very interested to understand the emos and electronic nature for the zirconium that is a good for metallocene, because most of the metallocene catalysts for olefin polymerations are actually based on this, but we have to design okay, our catalyst to get the desired polymer with desired tacticity that we will understand.

So, let us discuss now, we in the last class, I mentioned that some of the structural parameters which actually is used which are helpful to quantify how much bent the metallocene is as example this alpha angle, this beta angle also this angle. So, these are very important when and these parameters will be useful to design a new catalyst. Suppose, I need a lower beta angle or higher beta angle.

So, accordingly I will choose my, the bridging atoms or number of bridging atoms. So, these are very important because as I told that depending on the beta angle, the opening nest of here this case opening nest of the metallocene will also be changed.

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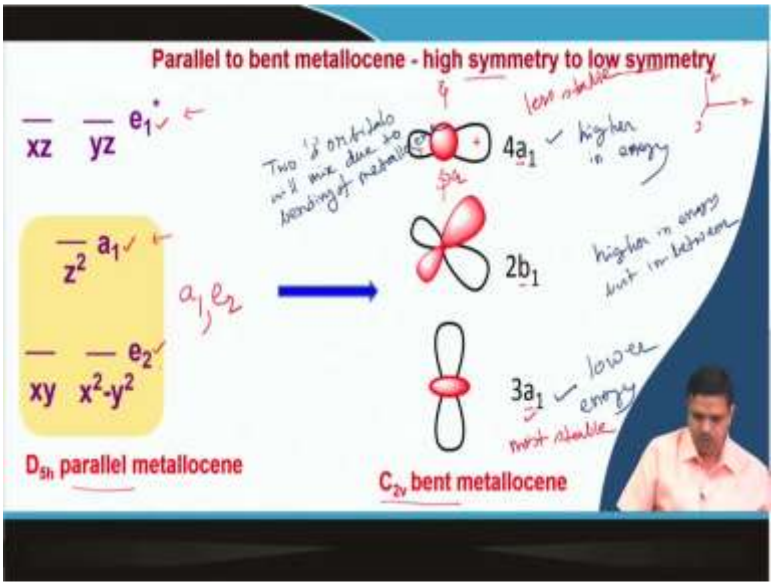

Parallel to bent metallocene - high symmetry to low symmetry

So, let us try to understand what will happen for the molecular orbitals, if you remember that the for the molecular orbitals of the parallel ferocene. So these 2 these 3 set of orbitals are very important. So, this e 2 involved the d x y and d x square minus y square orbitals. So, if we see the axis okay here okay this is I think this is fine. So, this is I think we I should mention the axis so, z x y the Cartesian coordinate.

So, here you will see that depending on the number of electrons filling up the electrons in e 2 a 1 and in e 1 star for parallel metallocene actually the structural and reactivity will also vary. As an example, like for ferocene we saw in the last classes that all the bonding orbitals are filled it up. So, for ferocene up to this one is filled it up. So, all the bonding orbitals filled up and that is why very stable.

If we can put electron here okay then we are putting electron to anti bonding orbitals then obviously, the system will be destabilized however, as I told many times that here although you are (())(6:24) the antibonding e 1, but the antibonding nature is comparatively less for e 1 star for the metallocene.

And similarly, for a 1 e 2 the bonding character is relatively less and we discussed that one. Now, what will happen if the symmetry changes from the D 5h parallel metallocene to the C 2V bent metallocene. I will try to discuss in a very qualitative way I am not going to use the group theory here very qualitatively, so that everybody can understand.

So, and also I am considering the most symmetric bent metallocene that is the C 2V. Now, what will happen here what will happen that these are the field d orbitals, generally, so, out of these 3 two field orbitals, we will mix it up due to the bent mix it up and it will be effort in energy. So, they will mix up and so, this is so two orbitals out of these 3 d orbitals. So, two field d orbitals will mix due to bending of metallocene and it will be one component that is the a 1 will be in higher in an energy this one and one component will be lower in energy, that means you will see that from here.

So, 1 component the symmetry was e 2 and another a 1. So, from here one will be the 4 a 1 and another will be the 3 a 1. So, one will be higher in energy higher in energy and one will be in lower in energy and the third orbital. That is the that is the one component of the e 2 will be also higher in energy and but it will be in between 4 a 1 and 3 a 1. But in between I am very qualitatively I am discussing.

So, you probably have seen that that I have used a and b here, a and b if you have taken a group theory or if you can recall the (())(9:39) symbols we used you used to use that a and b actually comes for that is for the small smaller case a and b comes for the orbitals. And these are basically to identify whether upon rotating through a axis whether the phase is changing or not.

So, here you see that if we change through if we rotate through C 2 axis okay you will see that you are here plus here plus So, again here plus if we consider this is plus and this is the plus. So, if I rotate the phase will not change, but here you will see if I rotate here okay through C 2. So, initially this the minus that is red, now, if we rotate the phase of the lobes will change. So, in that case it is b so, if it is symmetric with respect to a, axis rotation then it is a and if it is not symmetric with respect to a, axis rotation then it is b.

Similarly, for d z square it is falls in the a symmetry. So, now what will happen you see that a 1 and e 2 okay, a 1 and e 2 now splits into 3 orbitals, that is the a 1, b 1 and a 1 and where you see that d z square resembling orbitals is in the lowest in energy between these 3 d orbitals and the a 1 and 2 b 1, are a 1 is the highest in energy and the b 1 is the in the middle. So, it will also gain in energy but not as a 1, 4 a 1.

So 2 b 1 will be in between the 4 a 1 and 3 a 1. So, this is the most 3 a 1 is the most stable. Most stable means among these 3 orbitals, and this is the less stable., so, you see when I am changing the symmetry D 5h to C 2V. So, what I am doing I am doing high symmetry to the low symmetry. So, then you will see that my 3 set of the 3d orbitals further splitting and one is going in high energy and one is going in low energy and one is in between. So, I am getting now 3 orbitals with different energy.

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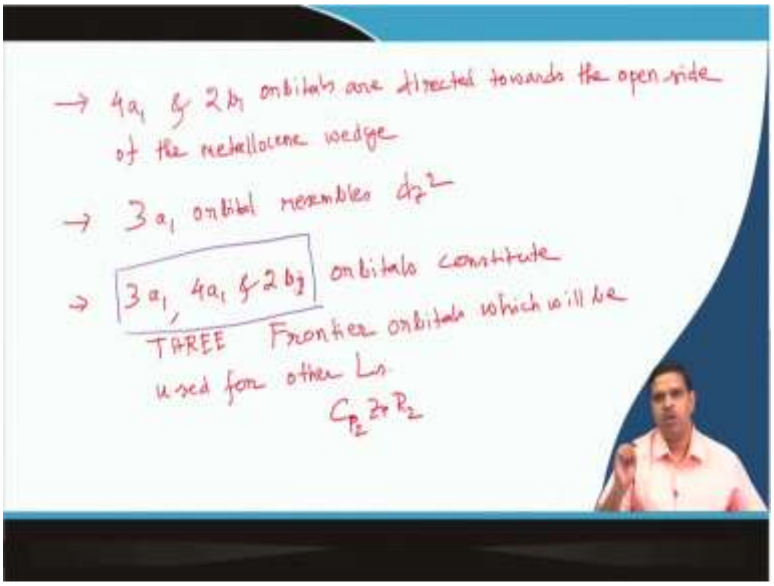
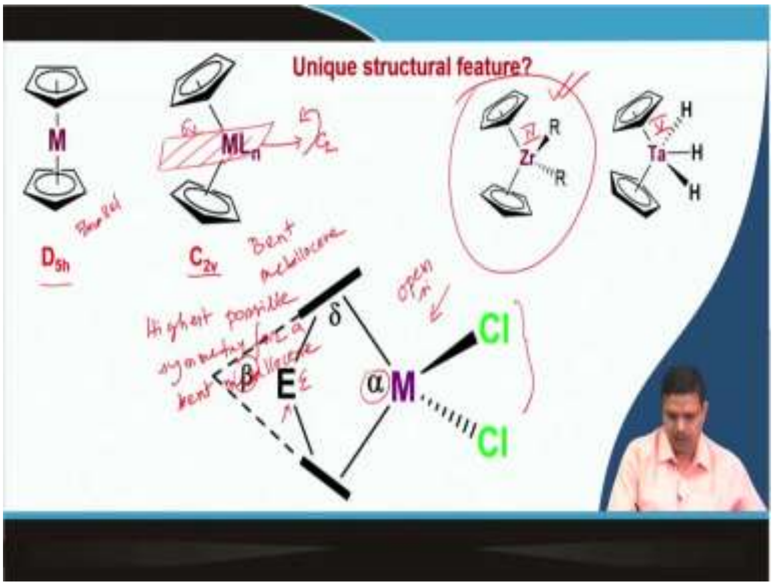


→ $4a_1$ & $2b_1$ orbitals are directed towards the open side of the metallocene wedge

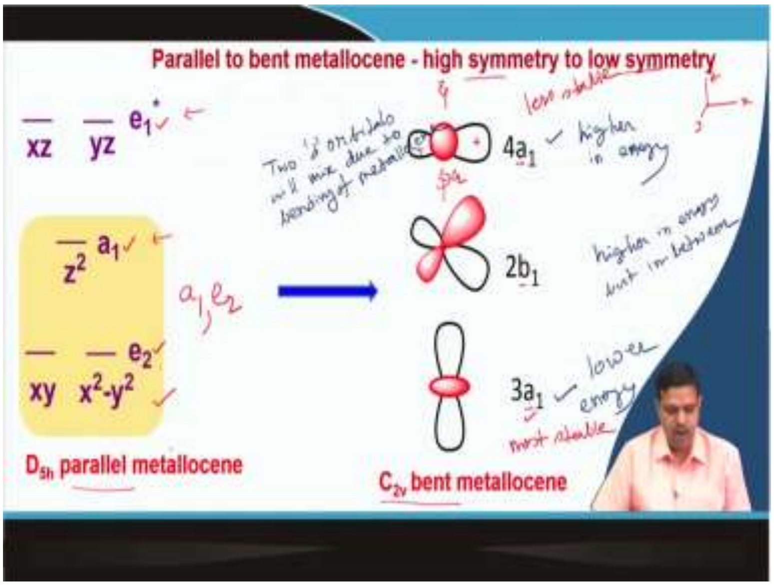
→ $3a_1$ orbital resembles d_{z^2}

→ $\boxed{3a_1,\ 4a_1 \ \& \ 2b_1}$ orbitals constitute THREE Frontier orbitals which will be used for other Ls

Cp_2ZrR_2



Unique structural feature?



Parallel to bent metallocene - high symmetry to low symmetry

Now, we will try to understand with some specific examples. So, here you will see, I just point out some of the important criteria what I what will be needed for my future discussion. So, you will see here 4 a 1 that is the 4 a 1 and 2 b 1. So, 4 a 1 and 2 b 1 that is what are the 4 a 1 and 2 b 1. So, these 4 a 1 2 b 1 basically the d x y and d x square minus y square is coming from the d x y and d x square minus y square orbitals. So, 2 b 1 is actually x y and 4 a 1 is actually the d x square minus y square.

So, this if you see the lobes and if you consider this coordinate, then the 4 a 1 and 2 b 1 orbitals are directed towards the open side of the metallocene wedge, open side means I am telling this side this side, this is the open side.

Now you will see that same 3 a 1 so 3 a 1 orbitals resembles d z square orbitals it is very obvious. So the 3 a 1, 4 a 1 and 2 b 1 orbitals in metallocene constitute three frontier orbitals which will be used for other ligands. So which will be used for bonding to other ligands, I am writing L so what I am telling that Cp 2 Zr we know but it is a plus 4 oxidation state. So I will have other groups R 2 that R Maybe X maybe halides, aryl, alkyl okay so this three set of orbitals that one is very important these actually your okay will dictate the bonding and reactivities of the bent metallocene.

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So let us try now by taking a particular system. So this is a perfect example okay, how this will vary, so, what we have done here, very systematic way okay. So that it is easy, it will be very clear to you. So, this one you know that these are all the bent metallocene. So, all are bent metallocene, but L is different. If you consider like Cp 2 M and L 3 category, so here, L is equal to 1 2 3. Is it clear?

Now, here, let us say this is the rhenium. So this is the D 4 case. And this one, we will so this is for molybdenum and tungsten, there are the same group. And this here metal is the niobium and tantalum. So metals are different. And here oxidation state is 3, here 4 and here 5. So this is 3, this is 4 and this is 5, and this is d 0 case. So there is no D electron.

And here, so, we will see, okay, after understanding the molecular orbitals, that it has 2 lone pair, do not worry, we will discuss how the 2 lone pairs are coming. I am just writing, that what how many lone pairs are there? Now we will try to understand that how the 2 lone pairs exist in this kind of bent metallocene.

Now, here you will see that 1 lone pair very interesting and it is very important to understand. And here you will see the no lone pairs and what is the consequence for the no lone pair. Let us understand.

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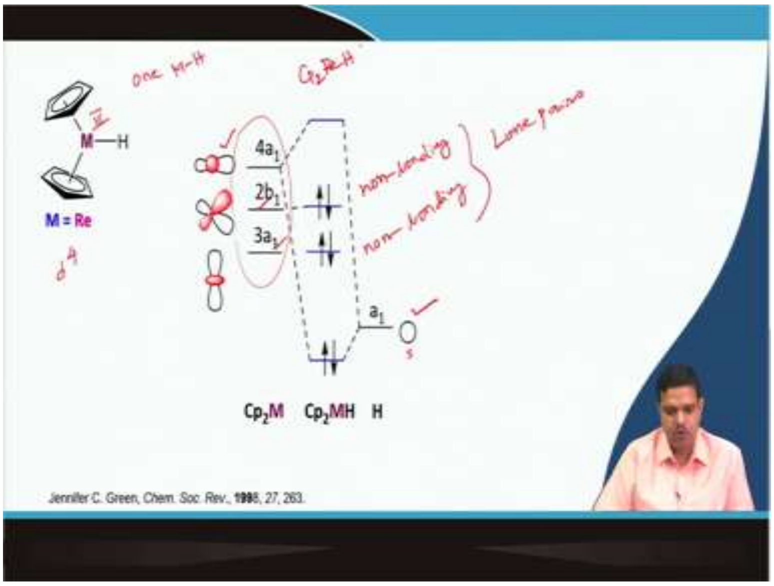

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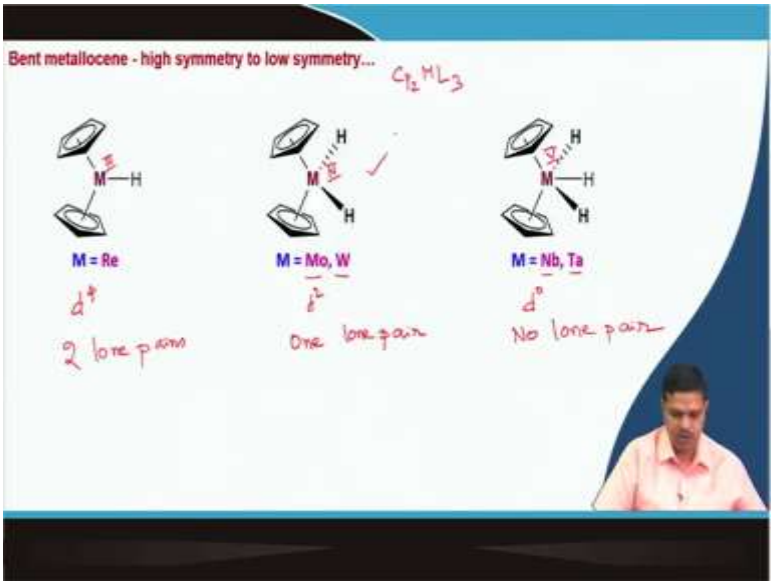

Bent metallocene - high symmetry to low symmetry...

So now I am coming to the first case where I told that there should be 2 lone pairs. Now, you see that this is the d 4 cases d 4 and this is my class 3 oxidation state and the metal is rhenium.

Now, I am now I want one bond, okay, let us covalent bond that is with the hydrate MH. So, one MH bond. That means one s atom then again, I am again doing the same approach as we constructed the molecule orbitals for the ferocene. So here you will see these are the resultant molecular orbitals for the bent metallocene, so, these are.

Now, I am now considering the one hydrogen bond that one MH so, this is my s orbital of the H, now what will happen this a 1 and this a 1 that is the 4 a 1 you see that this s orbitals and this s orbitals and this d orbitals the 4 a 1 orbitals, that is the d x square minus y square can interact and form again one the bonding and one the antibonding, like molecular orbitals.

And this a 1 and b 1 will be nonbonding and here nonbonding. So, your this is 2 b1 is the here HOMO, highest occupied molecular orbitals. So, this is the 2 b1 with highest energy which have the fully occupied electrons. So, here you will see that the 2 nonbonding molecular orbitals. So, these basically are the lone pairs, for this Cp 2 MH, that is the one example like Cp 2 ReH. Now, what will happen if I go to the next system that is the this one okay. Let us see.

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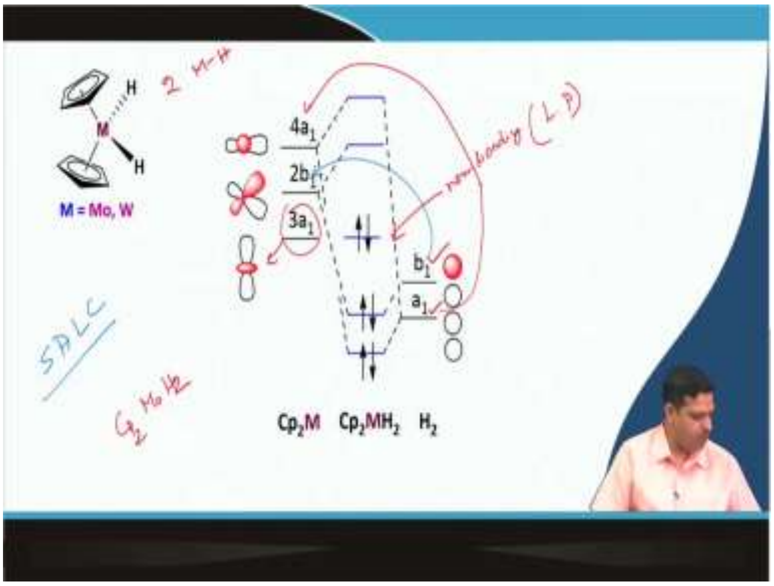

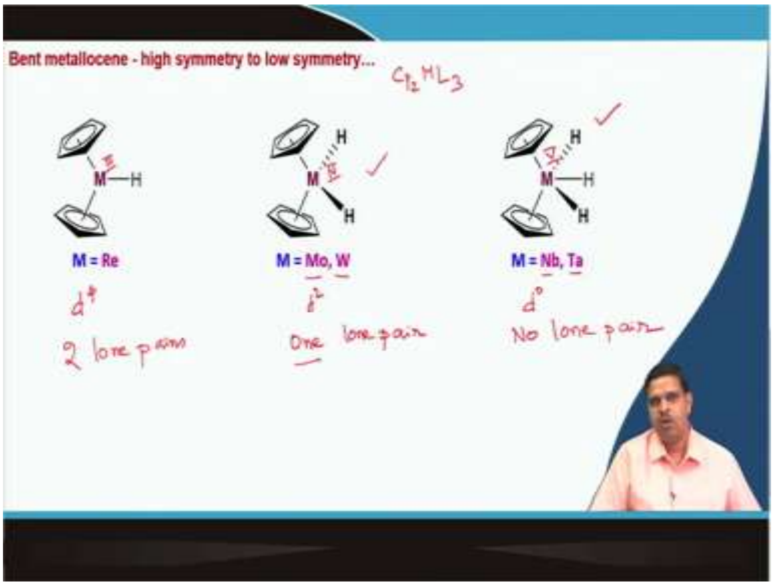
Bent metallocene - high symmetry to low symmetry...

So, here I have now 2 MH. So, we have to consider the 2H. So, now, one is a bonding and one is the anti-bonding, possible. Now, here you see that I have an a 1 and I have a b 1. So, this a 1 will interact with the this one, because symmetry is matching and this b 1 again is interacting with the b 1 symmetry of the d orbitals. So, because symmetry is matching. So, this is you will see that how the symmetry is allowing to understand the interaction between the, between the LGOs of ligands and the molecular orbitals of the bent metallocene.

So, as I told that this approach is called the SALC that is the symmetry adducted linear combination approach. Now, here you will see now, this is my nonbonding So, this is the nonbonding so, that means, this is my lone pair, so, you will see that this will have one lone pair I wrote here, so, one lone pair and due to this scenario that this molybdenum Cp 2 H2 have one lone pair and in which orbitals, these lone pair are, this is in the 3 a 1 that 3 a 1 that is the one d z square type of in orbital the lone pair is housed. Now it is clear, very easy. Now, let us see what will happen in the next system this one Cp 2 tantalum 3 hydrates. Let us see what happens okay.

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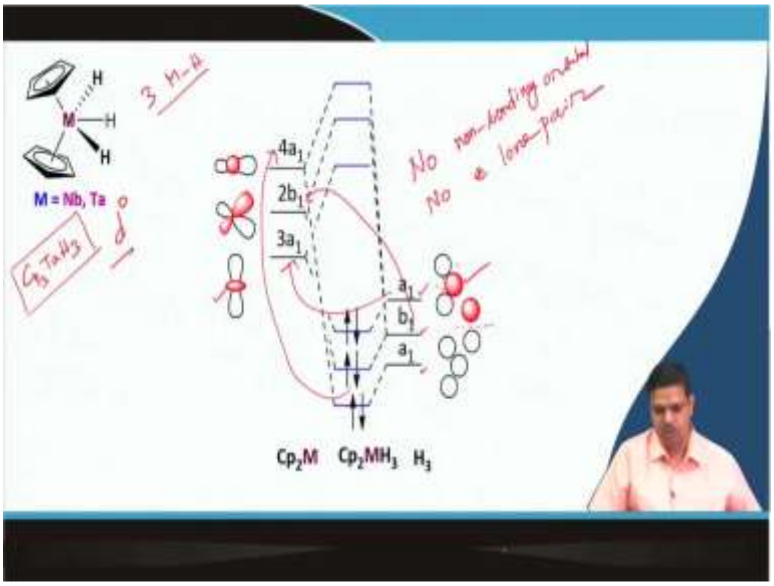

So here are 3 MH so, you know that this is very famous catalyst. We will discuss in the next class. Very famous catalyst for to make the (())(24:31) aryl compounds. So here you will see that I have now 3 hydrogen, so we have to this is the nodal plane, this is the nodal plane. Now I have a 1. Now I have b 1 and I have another a 1.

Now if you match with the symmetry, again through the ACLC approach, so what did happen? The b1 is matching with this one. Now, this a 1 is matching with this one okay and this a 1 is matching with this one okay this a 1. So, this one this one is matching with this one. So, what will happen no nonbonding orbital, no lone pair.

So, for tantalum this is the d 0 you will see there is no lone pair okay because all are in a bonding situation. So, this approach is very easy, very qualitatively I have discussed to understand the electronic nature of the bent metallocene okay because all are very important category of the bent metallocene which have lots of applications in synthesis in organic synthesis and also in polymer synthesis.

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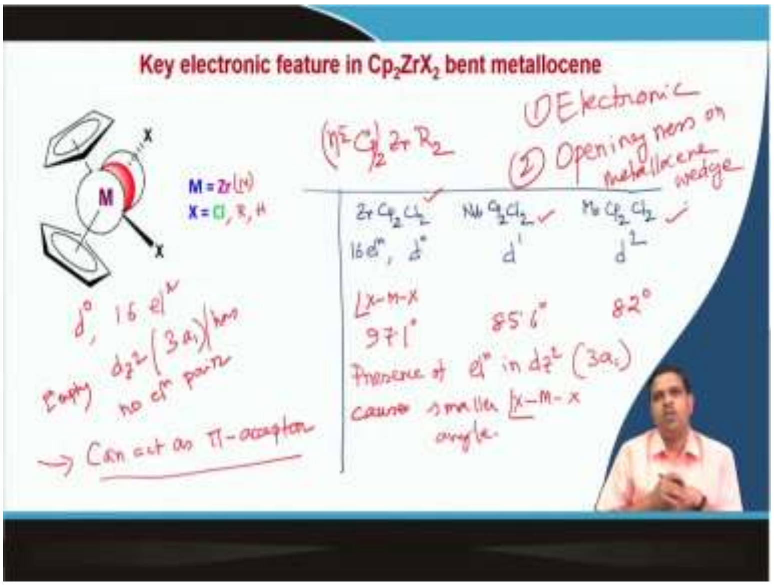


Key electronic feature in Cp_2ZrX_2 bent metallocene

$(\eta^5\text{-}Cp)_2ZrR_2$

① Electronic

② Openingness on metallocene wedge

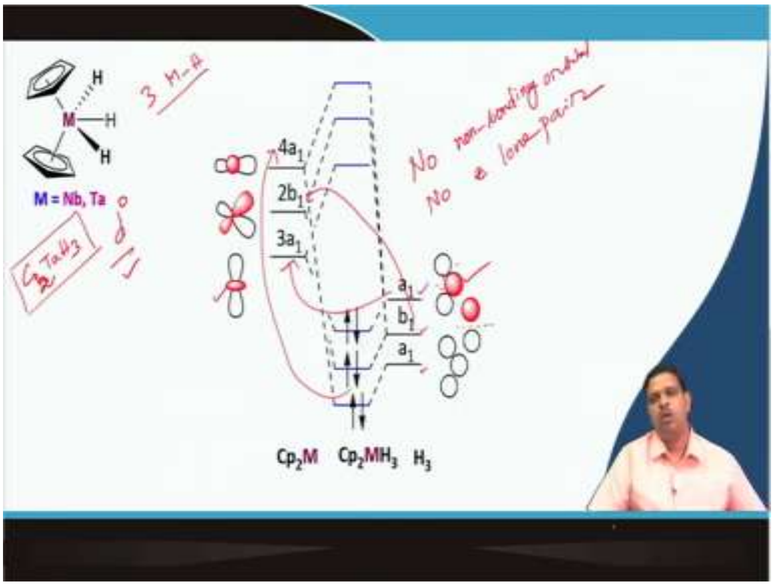
d^0, 16 e⁻

Empty d_{z^2} $(3a_1)$ has no e⁻ pair

→ Can act as π-acceptor

$ZrCp_2Cl_2$	$NbCp_2Cl_2$	$MoCp_2Cl_2$
16 e⁻, d^0	d^1	d^2
∠X–M–X 97.1°	85.6°	82°

Presence of e⁻ in d_{z^2} $(3a_1)$ causes smaller ∠X–M–X angle.



3 M–H

Cp_2TaH_3

d^0

No non-bonding orbital

No e lone pair

We will understand now that we have what we have done so, far we have tried to understand with a series of bent metallocene where we saw that I have increased the metal ligand that is the here in this case metal hydrogen from 1 to 3 numbers with of course with different metal centers now, with this knowledge we will try to understand what will be the scenario for the Zr Cp 2 because these are our main interest.

So, students here Cp means eta 5 when I will not write anything it is actually the eta 5. Now, here you will see that what scenario will fall here. So, here it is again d 0 and this is 16 electron system sorry d 0 16 electron system. So, here it is Zirconium it is in plus 4 oxidation state and this X maybe as Cl or R or H. So, both are hydride both are Cl both are R.

So, in this case again you see that there is no so, if we see if we do the similar. So, here also you it will be like your Cp 3 sorry here Cp 2 tantalum H 3. So, in this case also you will see that your the d z square orbitals that is which is actually the 3 a 1. So, this is the 3 a 1, the 3 a 1 is actually resembling to d z square orbitals. So, these d z square orbital is empty has no electron pair. So, this is important to understand why it is like that.

So, you have the empty d z square has no electron pair. So, that is why this one can act as pi acceptor now, if it is a pi acceptor, because the d z square is now empty. So, this can act as a acceptor for a ligands which have pi orbitals as example for can you guess what maybe the ligand yes it is alkyne. So, it can interact with alkyne.

Now, can you understand what we have why we have discussed so much. Because, yes, because these kind of compounds the metallocene compound bent metallocene are actually the catalysts for olefin polymerization as example ethelene. Now, why it reacts with ethelene, this you have to understand the fundamental question how okay because for that you have to understand this molecular orbital theory.

So, from here you saw that this d it has a empty d z square type of orbitals that is actually 3 a 1 orbitals and this orbitals can act as a pi acceptor for the ligands like ethelene. So, that is very important to understand and for to understand this we discussed in a systematic way using the molecular orbitals or SALC approach.

Now, one very interesting another interesting aspect I will discuss very shortly with again some a series of compounds. So, here I am Zr Cp 2 Cl 2 okay Nb that is Nabium Cp 2 Cl 2 and I am writing the MoCp 2, Mo means molybdenum. Now, this is we know 16 electron and this is you know the d 0 system this is the d 1 system and this is the d 2 system.

Now, if we see the angle okay, because from the angle you can understand the electronic nature of the, this kind of metallocene complexes that is why I am trying to understand. So, if you, if I see the angle. Here, you will see that this is 97 1 degree this is the experimental angle from the single (())(32:27), this is a 85.6 degree and this is 82 degree.

So, can you, can you know correlate that what is the relation between this angle that is the chloride metal chloride angle and the electronic nature of that d z square orbitals. Can you correlate, yes you are right that presence of electron in d z square like orbitals that is the here 3 a 1 orbital causes smaller X-M-X angle. So, this is also important, fine.

So, if there is a electron if there is electron in the d z square orbital, it has a two impact why I am discussed, one is the electronic and one is the opening ness on metallocene wedges. So, here you will see that in this case of Zirconium analog this angle is more 97.1 degree that is the Cl M Cl that means, the opening ness that is the it substrate can easily approach. But when we have electrons in the these 3 a 1 orbital as example for the nibium Cp 2 Cl 2 the angle is reducing like 85 degree, if you have molybdenum, where two electrons in this 3 a 1 orbital it is further reducing.

So, here you will see that in this case of zirconium analog. This is the perfect system, both in view of the electronic nature and also the view of the angle or opening ness in the metallocene wedge site.

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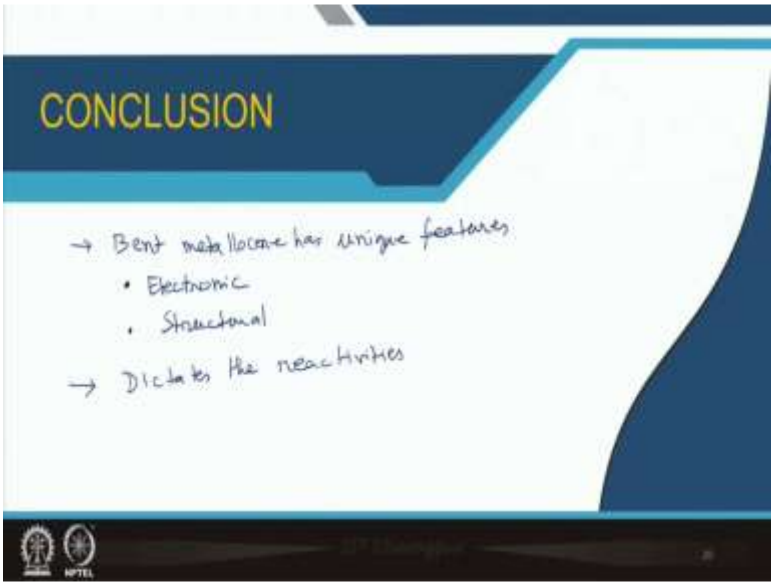

CONCLUSION

→ Bent metallocene has unique features
  - Electronic
  - Structural

→ Dictates the reactivities

So, in conclusion we discussed in this class that bent metallocene has unique features electronic, structural and this unique features is actually dictates the reactivities. So, in the next class we will take some of the bent metallocene and we will highlight. We will discuss the key reactivities and the properties before going to the polymerization reaction.

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REFERENCES

- The Organometallic chemistry of the transition metals by Crabtree, Wiley, Sixth edition, 2014
- Organotransition metal chemistry from bonding to catalysis by John Hartwig, University science books, 2010

So, these are the reference books you can consult for the last two classes discussion, the Crabtree or Hartwig are also you can also see the Wiley book. So, thank you and see you in the next class.