Metallocene and Metal-Carbene Based Organometallic Compound as Industrially Important Advanced Polyolefin Catalysts

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Lecture 12

Bonding in Metallocene, MOT and Electronic Nature

Hello, welcome once again so to the course, so Metallocene and Metal-carbene based Organometallic Compounds for Application in Polyolefin Catalysts. If you remember in the last class, we discussed about the bonding, started discussion about the bonding in metallocene compounds. And we saw that the CP ligands how they can undergo the pi orbitals of the CP, how it can undergo the LGO to form the set of LGO orbitals of different symmetry which can then interact with the specific DNS and p-orbitals of the metal with the symmetry matching.

So, and that the way we can construct the molecular orbital of the ferrocene, and this is essential to understand the struct, the property and the structure, because the if we understand the bonding very clearly, then it will be very easy to understand the reactivates of that particular metallocene.

So, it is we started discussion with a simple example of a parallel metallocene with a parallel CP ligand which is ferrocene you know that ferrocene we discussed extensively in the last class that in the ferrocene in the c p ligands are like parallel and it can exist as in two forms eclipsed and staggered, in gaseous phase it actually exists as eclipsed and the energy barrier between the Eclipse and staggered is very low, only 4 kilojoules per mole.

So, it can undergo the rotation. And, and that is why you see in even the proton NMR, you see a single signal for, of the c p rings in the ferrocene. So, we will take a simple model of ferrocene, we will discuss with a, with the Eclipse form, and will try to understand that how the molecular orbitals can be constructed.

Let us start and then will discuss with the help of the molecular orbitals, what are the unique properties of the metallocene compounds which is this would be very useful for to understand the mechanism of the metallocene catalyzed polymerization.

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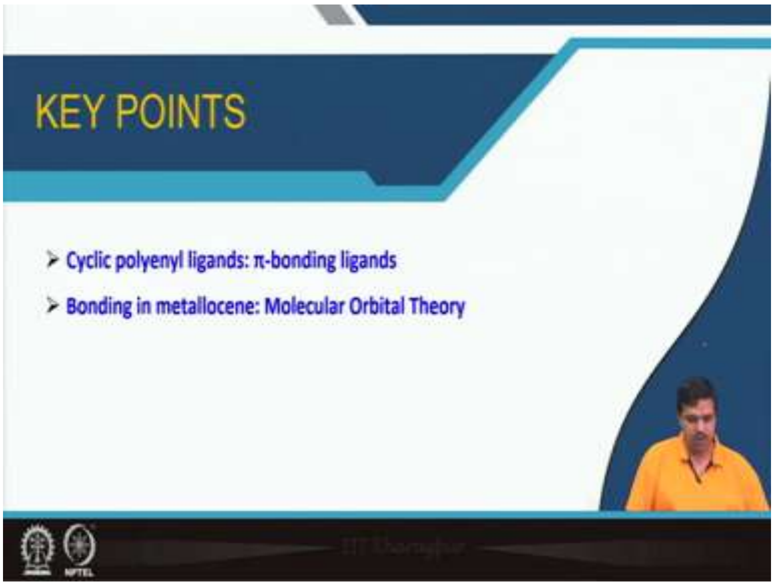
CONCEPTS COVERED

- Ligand group orbitals in cyclic polyenyl ligands (Cp)
- Bonding in metallocene using Molecular orbital theory
- Electronic nature



KEY POINTS

- Cyclic polyenyl ligands: π-bonding ligands
- Bonding in metallocene: Molecular Orbital Theory

The concepts covered we will try to understand the bonding in metallocene using molecular orbital theory. And then will try to understand the electronic nature, the unique properties of the metallocene. So, key points will be the molecular orbital theory and the different polyenyl ligands how they behave.

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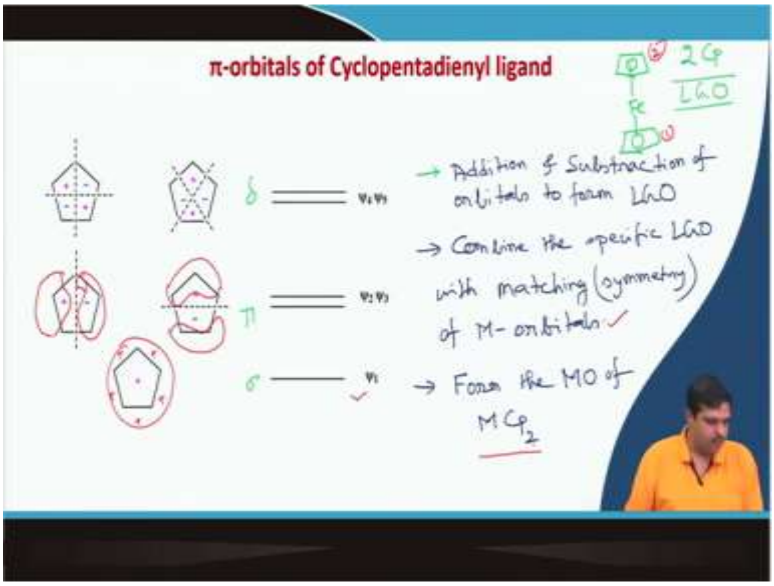

π-orbitals of Cyclopentadienyl ligand

→ Addition & Substraction of orbitals to form LGO

→ Combine the specific LGO with matching (symmetry) of M-orbitals ✓

→ Form the MO of MCp_2

So, this one we started discussion, I will just recap few important points that these are the pi orbitals of the cyclic polyenyl ligands here it is cyclopentadienyl ligands. So, you will see that sigma that is the lowest orbitals, this one, this is where there is no node so this is an little bit at higher energy there will be degenerate system.

Where you will see there is a single nodal plane here you will see this is one, this is zero nodal plane, this is one nodal plane and after that, you will be another there will be a single one degenerate set of orbitals, where you see two nodal planes and then what we will have to do, we have to do the LGO operation that is the way in the case of multiple c p ligands as example, for ferrocene we have a 2 c p ligands 1 and 2.

So, these 2 c p pi orbitals of the 2 c p ligands will undergo the LGO and through the addition and subtraction of the particular symmetry like this one, you will see that this is with the sigma symmetry and how we are, the symmetry or with the basis of that how you are looking from the above to the down so like here another way to draw this one, simple approach.

So, it will be like so here it will be you will see that from the above. How does it look like so you will see plus, plus, plus, plus and from here in this case it will be like that and this case it will be like that. So, plus minus and here also like this one like that and here also it will be like that. So, this is the symmetry with respect to your how we view from the top to down. Now, this is the sigma, this is the pi symmetry, this is the delta symmetry.

Now what we will do, we will do the addition and subtraction of each set of orbital and we will get the LGO orbitals and will try to match with the metal orbitals and then the way we will form the molecular orbitals of the in the metal c p 2 complexes where I am considering here simple system where two cyclopentadienyl ligands are there.

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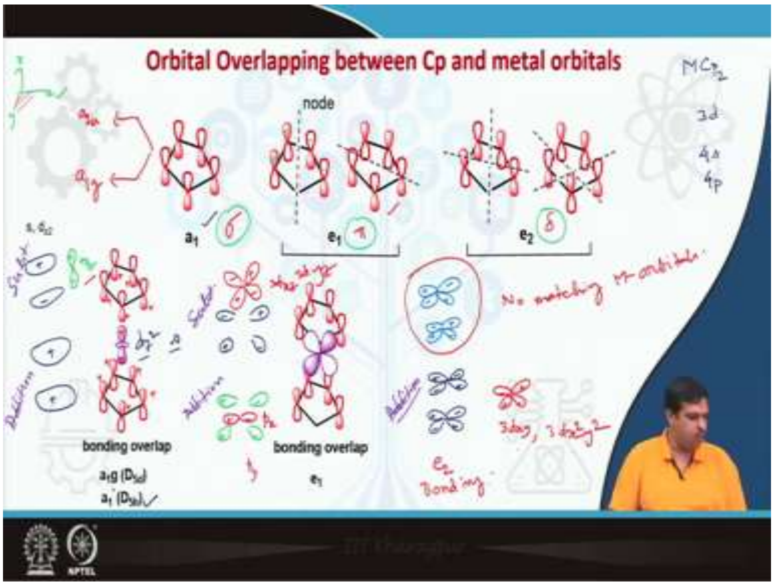
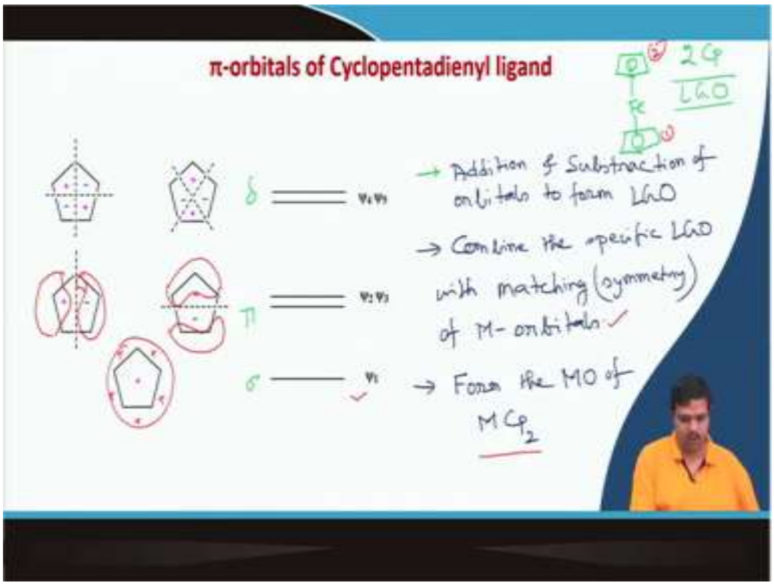


Orbital Overlapping between Cp and metal orbitals



π-orbitals of Cyclopentadienyl ligand

→ Addition & Substraction of orbitals to form LGO

→ Combine the specific LGO with matching (symmetry) of M-orbitals ✓

→ Form the MO of MCp2

Now, let us start it. So, as you know that this a 1 if you do the addition and subtraction of this one, so, I am doing first addition. So, what you will get you will get, two set that is a 1 g, and one set you will get the a 2 u. I am sure that you know that what is a, e, t, a, is basically single orbitals, e means double degenerate, t is triple degenerate, 1 and 2 is based on the symmetry, how does it with respect to principal axis and g u are the parity. So, if you have forgotten you can just take a look how we do the Milliken term symbols and how we use the symbols to designate the orbitals with respect to the symmetry.

So, this one you will see a 1 g, and a 2 u. So, how does it look like if you do a 1 g that means the symmetry you see that the slope let us say this is plus this is plus this is plus this plus this is plus so here also plus so plus. So, if you do the addition then it will look like this one. And this one, you see that this is perfectly can interact with the two orbitals of the metal, can you tell me which those two orbitals will consider in the let us say like, 3d transition metals like this kind of 3d transition metals where metal is let us iron, cobalt, nickel copper, titanium, (())(8:48) like that.

So, here you will have a 3 d, 4 s and 4 p and you all know how this s p d orbital looks like. So, if you can see this one and in more easily we can very simple way we can also draw like this one this the LGO after the addition of this orbital, that is the lowest energy orbitals with sigma symmetry. So, how does it look like it will look like this way. So, this one and you see this one so this is plus this is plus. So, this is the addition of this sigma symmetry pi orbitals.

Now, we can imagine 2 orbitals of the, from the metals, one is the dz square obviously and another one can you guess? Yes, s orbitals so this will be 3d of course and this will be 4s. So, you will see this orbital can interact with and the 3d and 4 s orbital of the middle center. So, one we have how many orbitals 3d 5 orbitals, 4 s 1 orbital, 4 p 3 orbitals.

And what will do now will be basically matching the symmetry no matter the how or what energy it has, that will consider after later that definitely that there is a there is a role because you know that two issues, you have to consider, one is the symmetry matching that is very important and another one is the energy difference between the two orbitals, which will undergo the interaction.

So, if the energies are similar, then definitely there will be go to interaction, if it satisfies the symmetry and if the energy is much difference, then there will be weak interaction. So, the bond strength obviously will be lower. So, that two issues we have to consider first let us say let us consider the symmetry. Now, this is fine so here you will see this is a bonding or overlap. So, this is if we consider the Eclipse.

So, what you are getting you are now I am getting a set of LGO orbitals which can nicely interact with the 3d and the 4 s orbitals. Now, how does it look like if is a subtraction. So, subtraction will look like this one. So, this is my, this one. Now, can you tell me that which metal orbitals it will interact with the symmetry by satisfying the symmetry? Yes, this is so this is if we consider that is the z axis and this is x and this is y then yes definitely. So, this is my p z orbitals so 4 p z orbitals so you will see that these orbital is perfectly matching with p z orbitals, so it is easy, not difficult.

Now, let us go to the another set of orbitals that is this set of orbitals this one this set of orbitals with pi symmetry that is one single nodal pane. Now, here, you first consider the addition so this addition how does it look like what how the LGO the resultant LGO look like? So, let us see the this one if I draw in a very simple way then we can draw it like this.

So, we will draw like so this is this will be minus plus and this will be the lobe phase. Now, you see why I have drawn you see this nodal plane. So, this is the if we consider this is plus and if you this consider is a minus the same will be the bottom also because I am doing first addition. Now, can you tell me that which metal d orbital will be perfect a for this orbital for the interaction can you guess? Yes.

So, this will be nice for the if we consider this is the x axis this is the x axis. So, p x orbital would be fine. So, I will show in a different color so that you can understand easily. So, this will be this is p x that is the 4 p x obviously so you will see that p x orbitals will be perfectly matching now you have the another so 2 orbitals 2 pi orbitals. So, similarly this one also will undergo LGO so another set of LGO will be fine with p y if you see the symmetry, fine.

So, now you will see this e 1 orbital that is the after addition that e 1 set of LGO orbitals will interact with p x and p y orbitals of the metal center. Now, consider how does it look like if there is a subtraction of these orbitals to that is the how will be the resultant LGO? So, we will draw like this simple way and we will do the like that. Now, it is easy to guess that which orbital will be matching which metal orbital will be matching with this LGO orbitals can you guess? Yes. So, this will be fine for the x z orbital.

So, I am drawing in a different color. So, this is the x z orbital so I am writing here so let us say 3 d x z, so you will see that so this e 1 set of LGO orbital will be fine with the 3d x z now, I told that is another orbital in the same set. So, that LGO will be fine with 3 d y z? So, x z and y z gone so you will see that from here my d s orbitals is done.

The d z square done and x z, y z done p x and p y done. Now left over is the 3d x y an 3d x squared minus y squared let us try to find out. So, let us find out the e 2 orbitals and how does it look like with this is with the as I told sigma symmetry this is the pi symmetry and this is the delta symmetry. So, I will this is the sigma symmetry this is important, this is delta symmetry.

Now, how does it look like first we consider the addition and it will look like this is little difficult to imagine and this will be fine. So, this is the addition here in all the cases I have shown it is this is the addition here also addition and here I am showing the subtraction, here also subtraction. So, first is addition. Now, can you tell me that which orbital will be perfectly matching with this symmetry.

So, this one so here you see this plus, plus, minus, minus. So, let us draw the orbitals and this is so this is plus, plus, plus minus. So, if you see that this is the plane x y plane. So, this is the x y plane so this is nothing but the 3 d x y. Now, if you consider the another orbital of the same set so this will be fine with 3 d x square minus y squared. So, now you will see that my 1 2 3 4 5, 5 d orbitals are now done p x, p y two orbital and done.

Now here, d z square here s orbital done and where there 4 p z so 3 orbitals done so 5 3 8 and 1 9 orbitals from the (())(20:32). So, how the subtraction looks like here and you will see there is the subtraction will look like first you draw it like that. Now, here you see and so yes so here you will see that there is a difference here you see plus minus, minus, plus, plus, plus minus, minus.

Now, this is little different this one for this symmetry this LGO no matching orbital, no matching metal orbitals. So, here you will see that this is from the e 2 set, this is the bonding. Now, we now understood that how the metal orbitals can interact with the resultant LGO orbitals, so this is clear now.

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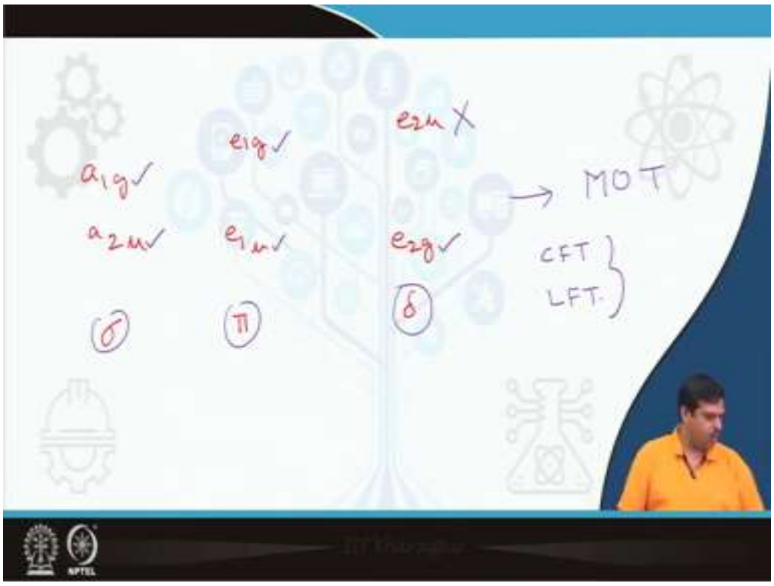

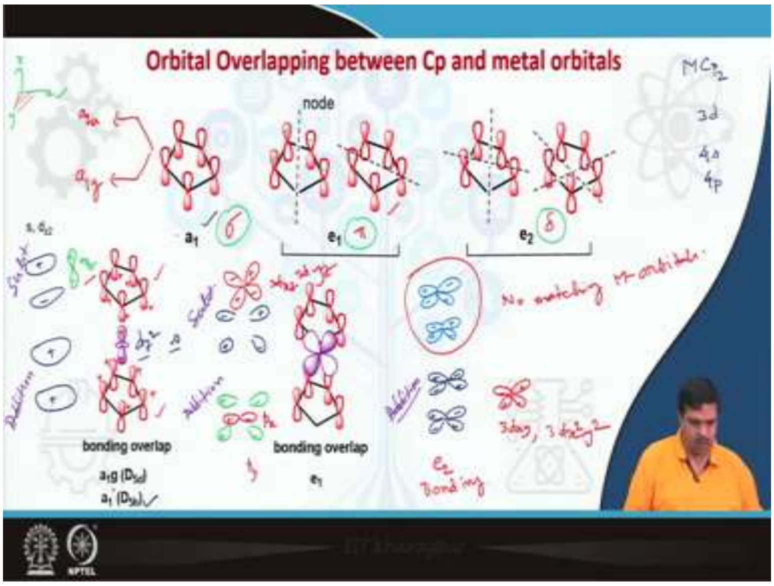

Orbital Overlapping between Cp and metal orbitals

So, we have now a 1 g set, a 1 g set a 2 u set that is a 1 g this is the a 1 g this is the a 2 u. Now, we have the set of e 1 u, e 1 g that is from the, that is from the sigma symmetry LGO that is the pi symmetry LGO and we have the e 2 g and e 2 u that is the delta symmetry orbitals. Now, you will see that from here this is my sigma, this is pi and this is the delta symmetry LGO. So, here you will see for this one we have a metal orbitals, this one we have metal orbitals, this one we have a metal orbitals, but this one there is no matching d orbitals.

Now, let us do to the try to construct the MOT that is the molecular orbital, molecular orbitals with the help of molecular orbital theory, I am sure you know that what is the molecular orbital theory, there is 3 major, main theories to explain the bonding that is the BBT balanced bond theory, one is the molecular orbital theory.

And we also know that in a ligand group orbitals that is also or elliptic legal that is also useful to explain the bonding in transition metal complexes and organometallic compounds. So, let us discuss, so this you all know that we know CFT (())(24:09) theory where we only consider the electrostatic interaction, molecular orbital theory we basically consider the covalent nature and LFT is basically combine the (())(24:25) theory and the molecular orbitals. So, these are the main theories to explain the bonding in transition metal complexes and organometallic compounds fine.

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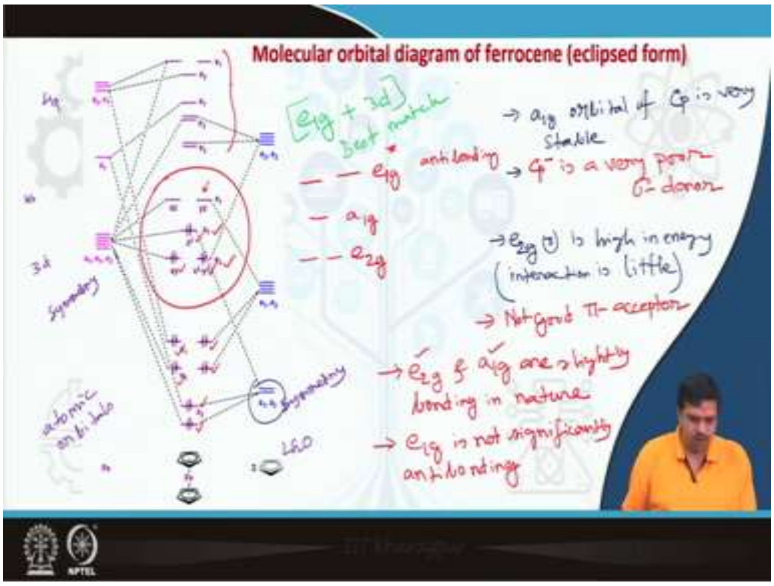


Molecular orbital diagram of ferrocene (eclipsed form)

$[e_{1g} + 3d]$ Best match

e_{1g} antibonding

a_{1g}

e_{2g}

→ a_{1g} orbital of Cp is very stable

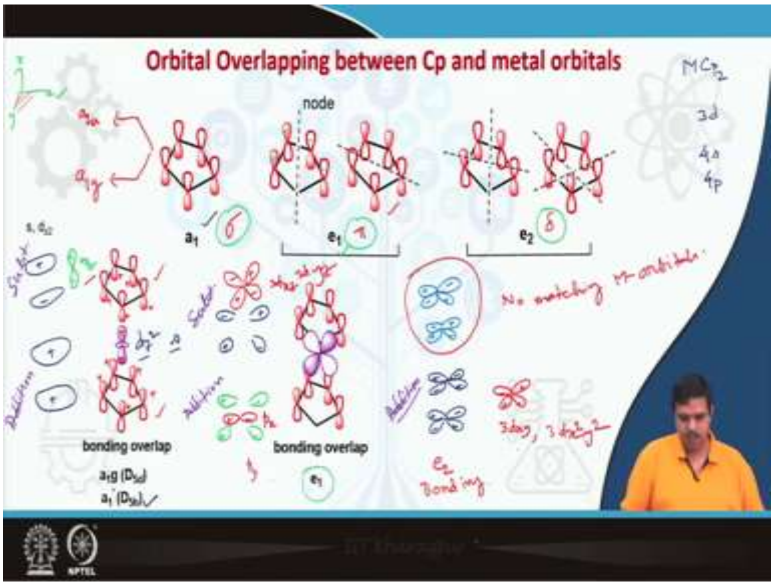
→ Cp^- is a very poor σ-donor

→ e_{2g} (δ) is high in energy (interaction is little)

→ Not good π-acceptor

→ e_{2g} & a_{1g} are slightly bonding in nature

→ e_{1g} is not significantly antibonding



Orbital Overlapping between Cp and metal orbitals

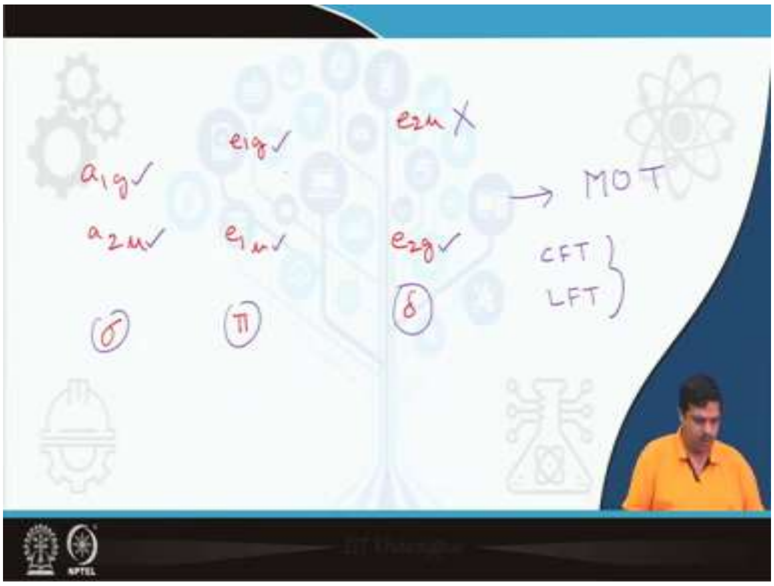
No matching π-orbitals.

bonding overlap

a_1g (D_{5d})

a_1' (D_{5h}) ✓

bonding overlap



a_{1g} ✓ e_{1g} ✓ e_{2u} ✗

a_{2u} ✓ e_{1u} ✓ e_{2g} ✓

σ π δ

→ MOT

CFT }
LFT }

Let us try to consider, try to construct the molecular orbitals of ferrocene. Let us now we now all we have the set of the LGO orbitals which can interact with the metals. So, you see here in this case, so this is the relative this one is the 2 c p ligands this is basically the all the these are the LGO what we learned from the last 2 slides and this is the f e and as I told this is the 3d this is the s orbitals that is the 4 s and that is the 4 p orbitals.

Now it is very interesting now we have this set of orbitals now we know that this symmetry and this symmetry now what does this symmetry we know you consider the symmetry and the notation here that is very important and we also see that relative energy. So, here you will see that this one this one that is the a 1, a 2, a 2 symmetry LGO orbitals are much lower in energy compared to the a 1, a 2 atomic orbitals of the metals.

So, these are basically the atomic orbitals this side, the left side is a basically atomic orbitals of the metal and the right side is the LGOs of the 2 c p ligands. Now, if you match with respect to the symmetry of the LGOs you will get this kind of molecular orbitals so here main important is the is here what you are getting from here so this is the e 2 that is and then you are getting the a 1 and then you are getting the e 1, in several books they also write e 2 g I am just writing in general.

So, you can also write e 2 g, a 1 g and e 1 g, this is basically anti bonding. So, this is actually anti bonding this is actually not bonding and these are the bonding we no need to consider this area because these are quite in high energy, the electrons will not be occupied in these orbitals for the 3d transition metals or 3d and 4d transition metals.

So, few points you have to consider here some of the points very important points. So, here very important point, this will be very helpful later so here you will see that you will see that in this case here you will see that a 1, a 2 is much lower in energy this one much lower in energy compared to the atomic orbitals. So, that is why the a 1, a 1 g orbital of c p here c p means c p minus.

So, generally call it just a c p but actually it is cyclopentadienyl that means c p minus of c p is very stable due to the mismatch in energy and for that reason the interaction between the metal center metal orbital and the ligand LGO of the a 1 g LGO is very less and that is why is c p minus this you have to understand that c p minus is a very poor sigma donor c p minus is a very poor sigma donor and what is the reason because the a 1 g LGO is very much stable and you will see that energy difference between the a 1 g symmetry LGO and a 1 g symmetry of the metal orbitals is quite different.

Now, another interesting point is that that e 2 g that e 2 g is high in energy so here also interaction is little and for that reason this c p minus ligand is not good pi acceptor so c p minus is neither a good sigma donor or not a good pi acceptor and the reason is very clear from the molecular orbitals.

So, another few features that e 2 g and a 1 g, e 2 g and a 1 g that is this one and this one are slightly bonding in nature and also e 1 g that is this one because you see that if electron I have to take from the metallocene the electron will take come from the a 1 g and if I put want to put one electron in the on the metallocene that will I want to reduce the one metallocene that electron will come here e 1, now e 1 g is also not good not significantly anti bonding and this is due to the mismatch in energy.

Now, what will be the impact of this one. So, the impact will be that as this e 2 g and a 1 g are not really is a very in true sense is not really a bonding orbitals. So, what will happen if I take electron that is if I oxidize the electron oxidize the metallocene if I take one electron then the if you consider the stability that stability difference will be not really dramatically change.

So, that means you can oxidize the metallocene and also the reduce the metallocene why because the e 1 g is not significantly antibonding that means if you put one electron in the antibonding orbitals then also the stability will not be like a very different but yes obvious if you are all the bonding orbitals are filled and there is no electron and antibonding orbitals that like ferrocene which satisfies the 18 electron rules that will definitely the most stable.

And that is why ferrocene is the most stable here you see that 1 2 3 4 5 6 7 8 9 the 9 orbitals that means 9 into 2 18 orbitals and there is no electrons in the antibonding orbitals. So, here the ferrocene that is why very stable in nature. So, you will see from the molecular orbital diagram, molecular orbital theory you can get lot of information about the electronic nature of the metallocene.

So, if you now consider like the all the interaction so the best interaction is and why I am telling the best because this actually dictates most of the properties of the metal centers that is the e 1 g plus the 3 d and you if you see the last slide that the e 1 g that is that this one. So, this the orbitals from the pi symmetry. That is this one e 1 g this actually mostly dictates the electronic properties and the stability because this is the best match e 1 g 3d interaction is the best match for the ferrocene like metallocene compounds.

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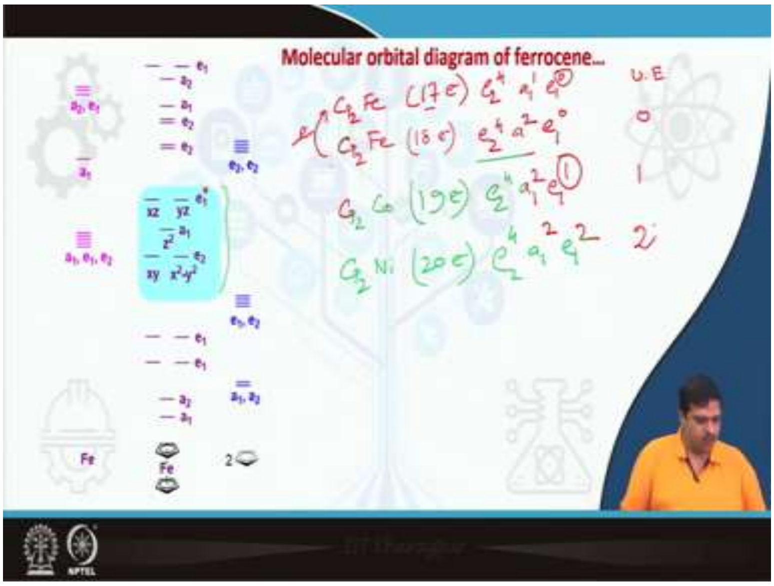

Molecular orbital diagram of ferrocene...

Cp_2Fe (17e) $e_2^4\ a_1^1\ e_1^0$

Cp_2Fe (18e) $e_2^4\ a_1^2\ e_1^0$

Cp_2Co (19e) $e_2^4\ a_1^2\ e_1^1$

Cp_2Ni (20e) $e_2^4\ a_1^2\ e_1^2$

U.E

0

1

2

So, in summary in the molecular orbital diagram of ferrocene like metallocene you will see that this is the most important these orbitals and the most important because it actually dictates the electronic nature of the metallocene. Now as example like if you see that c p 2 ferrocene I just told that this actually 18 electron system.

And you see that how if you fill up the electrons how you can fill up so you will fill up like e 2 4 because all bonding orbitals will be filled up this is the (())(36:05) anti-bonding in nature. So, e 2 4, a 1 2 and here e 1 0. Now, here you will see. So, here these are all the non-antibonding orbitals are filled up. Now, if I oxidize it what will happen now 17 electron system and you will get e 2 4, a 11, e 1 0.

So, what I am trying to say that although this is 17 electron system so it should be definitely less stable but what I am telling that you can prepare by oxidation chemically or electro chemically to C p 2 F e plus and this you can synthesize it or you can get it because you are, we are taking all electron from the orbitals which have are not really 100 percent bonding in character and that is why actually we can we can synthesize this 17 electron system.

Now, similarly if you consider the cobalt to cin, this is 19 electron system. So, definitely this is less stable than the ferrocene because it has a 19 electron system but what I am trying to tell that you can prepare it the cobalt to cin. Because, if what we are doing compared if we compare with the ferrocene molecular orbitals, then we are basically putting one electron here as I told that this is not really kind of a true antibonding orbital.

So, that means you there is not much sacrifice in the stability. So, this is the main features in the metallocene molecular orbitals. Similarly, you can also prepare the (())(38:28) it is 20 electron system and what will be the electron arrangement. So, like this one so very easy.

So, if you also you can get lot of information from here one as example like, here you see unpaired electron I am writing you unpaired electron. So, here you are getting unpaired electron is 0, here you are getting unpaired electrons 1, here you are getting unpaired 2. So, these are interesting you can get lots of information electronic nature, the stability, the orbitals which are important to understand the reactivity and the structure property relationship.

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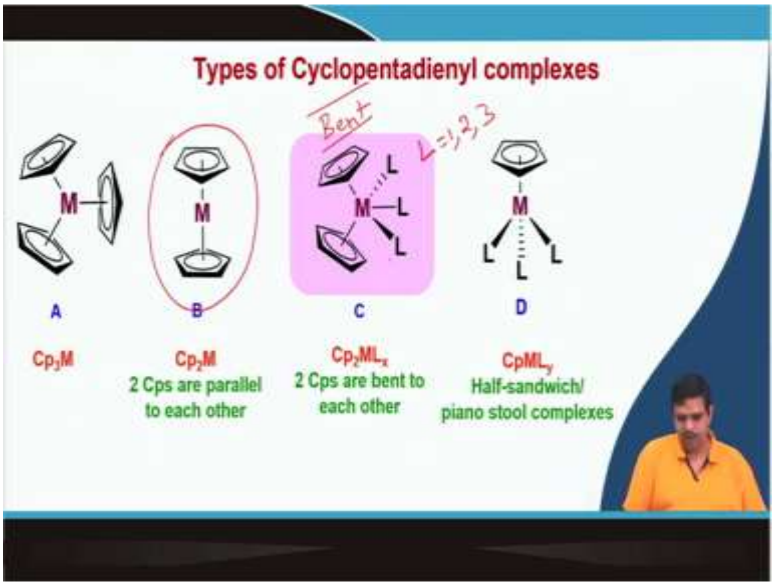


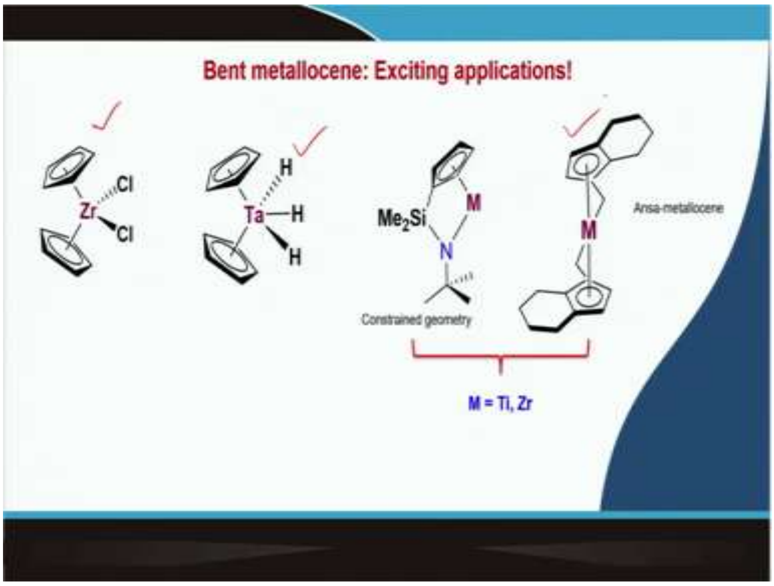
Types of Cyclopentadienyl complexes

Cp_3M

Cp_2M
2 Cps are parallel to each other

Cp_2ML_x
2 Cps are bent to each other

$CpML_y$
Half-sandwich/ piano stool complexes



Bent metallocene: Exciting applications!

So, as I told that, whatever we have discussed so far in the molecular orbitals diagram, we have discussed for the metal, this kind of category B metallocene where the 2 c p ligands are parallel and we will be mainly interested for bent kind of metallocene, the bent metallocene that will be our interest because this is also another unique features compared to the metallocene compounds where your c p ligands are in parallel and here you will see these are bent and these L can be 1 2 3 like that.

So, the number of L I am telling this maybe 1 2 or 3 depending on the valancy electrons of on the metal. So, this is very unique and there are lot of applications in various organic synthesis mostly catalysis there are a lot of applications on this bent metallocenes. So, that will be discussing in the next classes.

So, you will see that how this bent metallocene due to some unique features are plays a vital role in not only in academics, but also in, in industry, where we routinely use the bent metallocenes like this kind, this kind or this kind of things in catalysis in organic synthesis, to synthesize value added products, commercial products. So, that will be really interesting, will try to combine the electronic nature, the orbitals and try to understand the its reactivities and mechanism to have a very clear concept. So, we will discuss, continue discuss in the next class.

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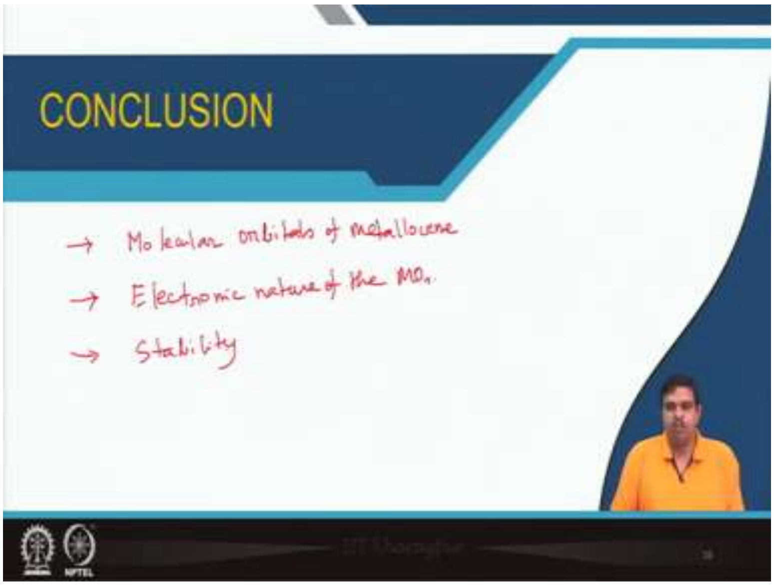

CONCLUSION

→ Molecular orbitals of metallocene

→ Electronic nature of the MO.

→ Stability

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So, as a summary what we have dis, what we have learned in this today’s class so we now understood the molecular orbitals of metallocene with one simple example of ferrocene where 2 c p ligands are parallel we try to understand the electronic nature of the MO and the stability of the metallocenes.

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REFERENCES

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So, the majority of our discussion from this class has been you can read from the Crabtree or the Hartwig books. So, thank you and we will again see in the next class and in next class, we will try discuss more extensively about the bent metallocene, the unique feature, electronic nature and the reactivity studies and then we will enter to the catalytic polymerization. Thank you very much.