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

Professor Sanjib K. Patra
Department of Chemistry
Indian Institute of Technology Kharagpur

Lecture 13

Bonding and Electronic Nature in Bent Metallocene

(Refer Slide Time: 0:31)

NPTEL ONLINE CERTIFICATION COURSES

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

SANJIB KUMAR PATRA
DEPARTMENT OF CHEMISTRY, IIT KHARAGPUR

NPTEL ONLINE CERTIFICATION COURSES

Lecture 13: Bonding and Electronic nature in Bent Metallocene

Hello students welcome once again to our course metallocene and metal carbene based organometallic compounds for industrially important advanced polyolefin catalysts. So, far what we have discussed we have discussed how the Cp ligands that the cyclopentadienyl ligands can interact with metal d orbitals, how the pi orbitals of the Cp ligands undergoes the linear combinations and forms a set of ligand group orbitals.

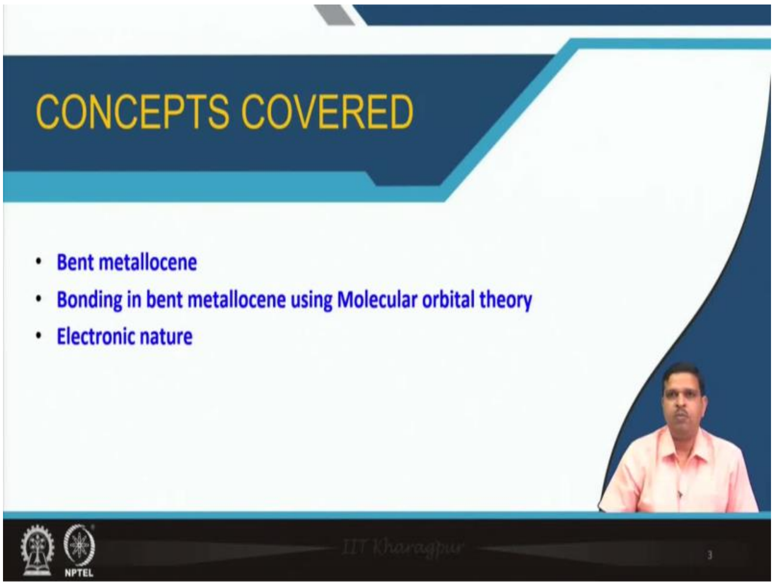
And then we have taken the approach of forming the molecular orbitals through symmetry edited linear combination of molecular orbitals to construct the molecular orbitals and why we constructed because to understand the orbitals and understand the homo nature of the homo and to understand the electronic properties of the orbitals in the metallocene, this is very important to understand the reactivity and the structural parameters associated with metallocene.

So, far we have discussed the parallel metallocene where Cp ligands 2 Cp ligands are parallel like ferocene that is the classical example. Although Cp ligands can exist in two forms, one is the eclipsed and one is the staggered so, that we discussed. The molecule orbitals are similar for the eclipsed and staggered eclipsed symmetry group is D 5h staggered is D 5d only the symmetry level of the resulting molecule orbitals will be slightly different, that we discussed in the last class.

Now, I have very briefly shown that the catalysts metallocene based catalysts for olefin polymerization, which we will be discussing and that is our main interest in the course or falls in the bent metallocene. So, it is not like a ferocene, but it is like a bent.

Now, we have to understand that what does it happen if the Cp rings are tilted like bent? What will be the difference in molecular orbitals? This is very crucial to understand because without this understanding, we will not be able to understand the reactivity and the mechanism of these catalysts. So, let us discuss the bonding and electronic nature in bent metallocene in today’s class.

(Refer Slide Time: 03:22)

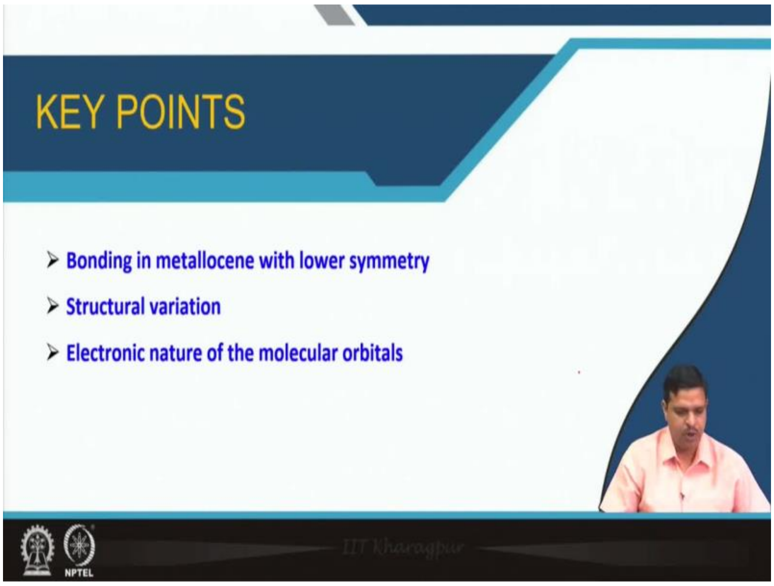


CONCEPTS COVERED

- Bent metallocene
- Bonding in bent metallocene using Molecular orbital theory
- Electronic nature

So, just in a brief points which concepts will be covered, we will cover what are the bent metallocene? How the paint can be created, in the metallocene? Then bonding in the main metallocene bent metallocene using molecular orbital theory, and then definitely the purpose is to understand the electronic structure.

(Refer Slide Time: 03:47)

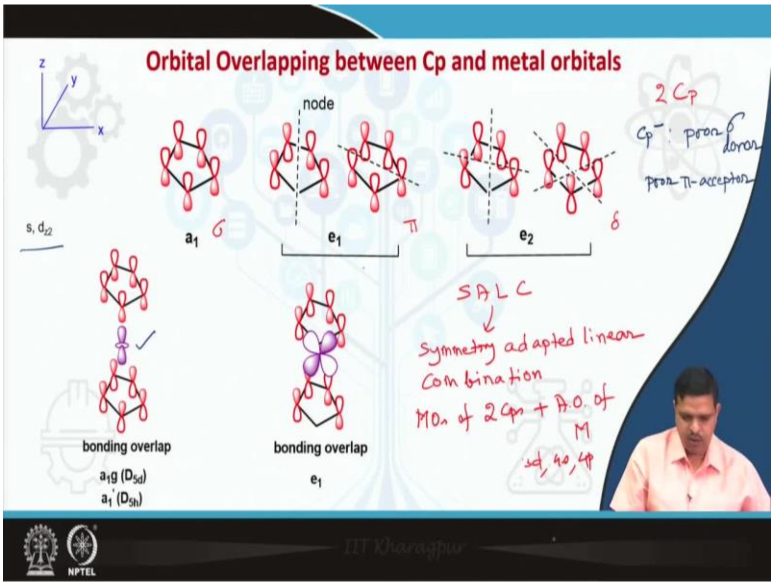


KEY POINTS

- Bonding in metallocene with lower symmetry
- Structural variation
- Electronic nature of the molecular orbitals

So, these are the key points like electronic nature structural variation and bonding in metallocene, which will be discussed in today's class.

(Refer Slide Time: 03:56)



Orbital Overlapping between Cp and metal orbitals

2 Cp

Cp⁻ : poor σ donor

poor π-acceptor

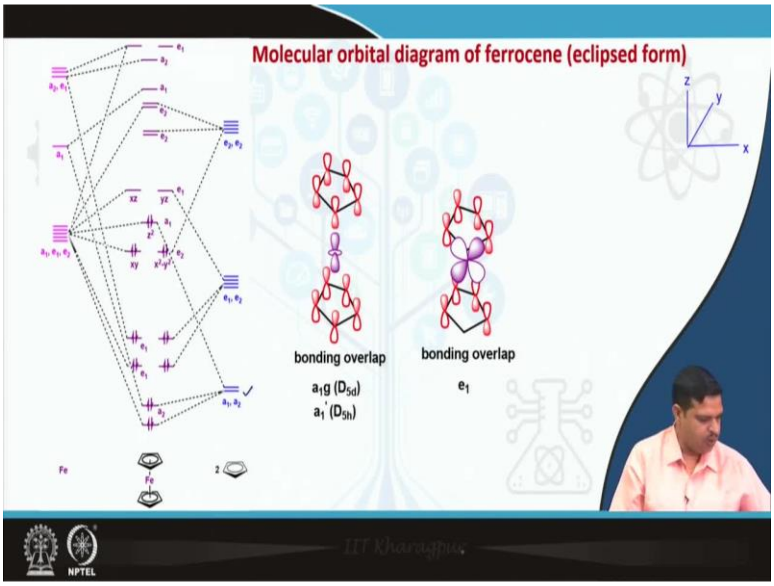
SALC

↓

Symmetry adapted linear combination

MOs of 2 Cp + A.O. of M

3d, 4s, 4p



Molecular orbital diagram of ferrocene (eclipsed form)

So, in the last classes, if we remember that we have understood very systematically that what are the pi orbitals of the Cp ligands that is that this one that is you know the sigma symmetry that is the pi symmetry and that is the delta symmetry what we did? We then checked the symmetry of these pi orbitals and that is the LG orbitals of the 2 Cp ligands, the 2 Cp ligands and then we tried to match with the atomic orbitals of the metal and then we constructed molecule orbital to orbital theory and this process is called the SALC, S A L C means, symmetry adapted linear combination.

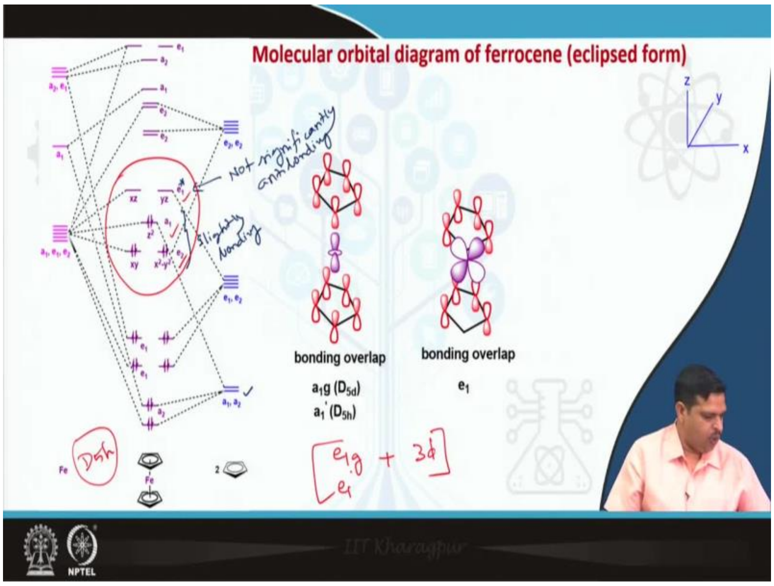
So, what we did here basically, we did the combination of the molecular orbitals of 2 Cps plus the atomic orbitals of metal for let support 3d transition metals which atomic orbitals into 3d 4s and 4p, so that we discussed and just to refresh here you see that this one as I told that the molecule orbitals will be very similar for the eclipsed and staggered confirmation of the ferocene, but only the labeling will be slightly different.

So, here you will see that this is the a 1g that is the this one so, this is the LGO after addition of this to Cp a 1. So, now, this is perfectly matching with the d z square. So, this is perfectly matching with the d z square you see and also it will be fine for s and then we found we then checked and did the SALC method to construct the molecule orbitals.

Similarly, for e 1 you see that also we checked the specific symmetry of the d orbitals and then we constructed the molecule orbitals of the iron Cp of parallel metallocene as example iron Cp to moleculer orbitals. Few things we noted this is very important because, we have to understand the difference between the parallel and the bent metallocenes.

So, in the last class we discussed that Cp minus is a poor sigma donor Cp minus is poor sigma donor because if you see the molecule orbitals. If you remember so, this you see this is the Cp minus is the highly stable. So, it is very slightly contribute in the bonding and similar way the Cp minus is also a poor pi acceptor due to the energy mismatch. So, not good pi acceptor and also not good sigma donor.

(Refer Slide Time: 07:59)



Molecular orbital diagram of ferrocene (eclipsed form)

And also we this discussed that these are the main interest e 2 e 1 and e 1 this is actually the antibonding slightly antibonding nature although we discussed in the last class that e 1 although it is antibonding but the antibonding character is not really pure. It is slightly antibonding in nature.

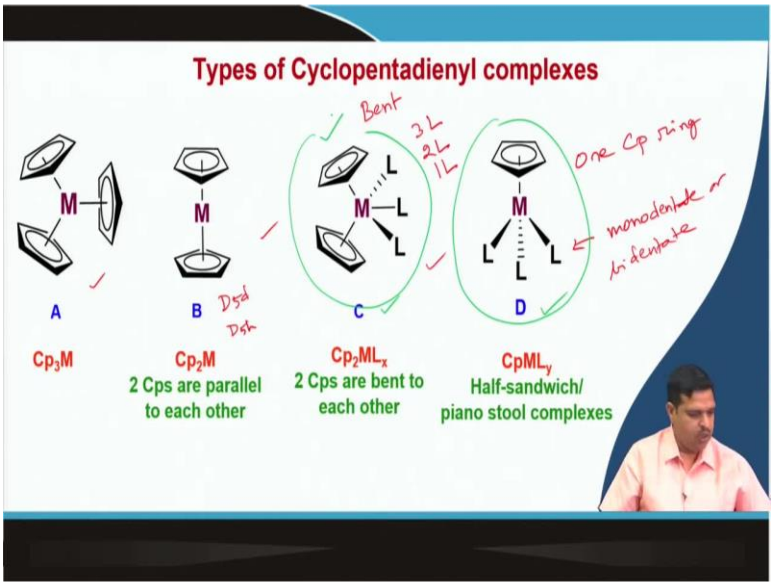
And similarly, for e 2 and a 1 these are the bonding character is not pure that means it is e 2 g and a 1g are slightly bonding and slightly bonding and this one is not significantly sorry so, this is not significantly antibonding. So, for the metallocene compounds e have to be we are actually interested of the orbitals you see.

So, this region, this region, so, the feeling of this three set of orbitals, that is the e 2 a 1 and in e 1 star actually will dictate the properties and the stability of the metallocene compounds. So we will try to understand the difference between the parallel to the bent metallocene. So, the molecule orbitals for the parallel metallocene is important otherwise we will not be able to understand for the bent metallocene.

So, also you have to be you have to understand that this is we are considering that D 5h symmetry and you have to understand that what will happen if it is bent which symmetry because the symmetry will basically dictate the orbitals energy and the symmetry which will be important to construct the molecule orbitals or molecular orbitals, we will see in the next slide.

So, you want you see that and also in the last class we discussed that the major contribution for the stability is actually the e 1g or e 1 plus the 3d so, these are the major interaction for the stability of the metallocene parallel metallocene compounds.

(Refer Slide Time: 11:23)



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

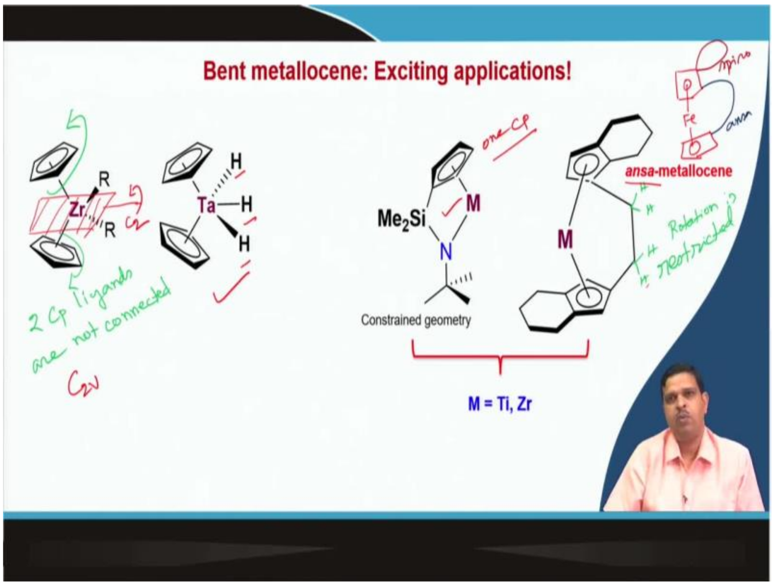
Now, we will see that what are the bent metallocene compounds and what will be difference in from the parallel metallocene compounds. So, here you will see that this is the ferocene this is the staggered so, that is the D 5d. And if it is eclipsed then it will be of course the D 5h this is the bent metallocene you will see bent and the L maybe number of L maybe 1 2 or 3. So, this L here I have shown with 3L, but here there may be 3L may or there may be 1L well they had maybe 1L depending on the metal centers and oxidation state.

And this is the half sandwich complex that is also equivalent to we call the piano stool complexes here only 1 Cp rings and 1 Cp rings and here the more than 1 Cp ring in other cases here, here, here more than one Cp rings and in this one this case half sandwich complexes the other ligands will be mono dented these were mono dented or bidentate or tridentate, but not Cp ligands.

So, these are the categories mainly are found in metallocene chemistry. As I told that we will be interested for this category of the bent metallocene and this category of the bent metallocene, because later we will see that most of the metallocene based catalysts are have the structure either the C category or the D category.

So, it is important to understand first that what is the electronic nature and the orbitals of this category that is the bent metallocene where you have a 2 Cp rings which are not in parallel bent and the other also have ligands that ligands may be alkyl or allele, halides or number will vary from 1 to 3 let us try to understand the electronic nature of this bent metallocene. So, before going to the molecular orbitals and to understand that what orbitals are involved in the interaction.

(Refer Slide Time: 14:23)



Bent metallocene: Exciting applications!

Constrained geometry

ansa-metallocene

M = Ti, Zr

So, I just first try to give a some highlight that what how the additional parameters can be imposed in metallocene to for its variation in structure, these are important, because you see here that what we have done that these are the Cp ligands where these are free Cp ligands 2 Cp ligands are not connected.

Now, if these 2 Cp ligands are not connected then what will happen? Because this one will rotate okay because these are free. So, this will rotate as example it happens for ferocene you will get the eclipsed and staggered and the barrier energy is very small 4 to 5 kilojoules per mole. Similar this will also rotate like this because these are free.

Now, if I do something if I how we can restrict? You have to if we can bind together thread it these 2 Cp ligands then the movement or the rotation will be restricted. So, here if it is like this, so, what we have done these 2 Cp ligands this is actually called indenyl ligands, few Cp ligands these ligands have been threaded by some linkers here this is basically the ethane linker.

So, what we have done here now, now it cannot rotate, so, rotation is restricted rotation is restricted. So, now your symmetry will be different. Now, here you will see this, what are the symmetry here. So, this is you have this if you consider this is C 2 this line is C 2. Now, this will this plane is the sigma V so, symmetry will be C 2V. Now, here the symmetry will be now different and also there will be no restriction, now, and also there is restriction in the moment.

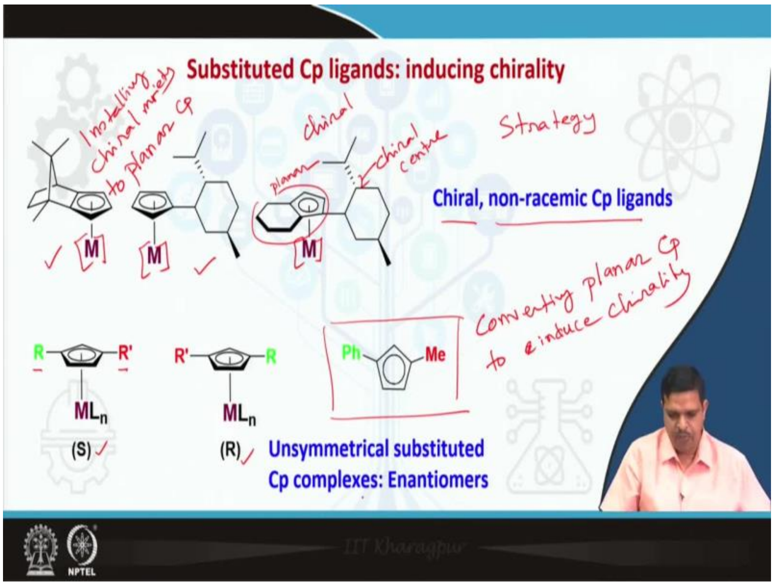
So, there if we make a chiral ligands with this threaded then the chirality will be permanent. So, there will be no possibility of have getting the respect mixture by the rotation of the Cp ligands. So, this kind of bent metallocene is called ansa metallocene, ansa is that you see that this ring is closed in different atoms if it is, if this is closed, so, I am just telling like if you have like this scenario suppose you are if performing a ring here so, this is called ansa. So, ring closing in to other atom of different Cp.

And if you close the ring like here, this will be spiral. So, you understand what is the difference between spiral and ansa. So, this will be our interest in the following classes. And here you will see this is a basically the example of half sandwich complexes, metallocene complexes because here there is one Cp ligands here you see.

And these are as I told that they are maybe chelating ligands okay. So, here maybe a mono dented maybe chelating okay to satisfy the coordination of the metal center. So, this kind of complexes is called the half sandwich metallocene complex or the constant geometric because this is in high constant, this ring.

So, as I told that, in this category, this has also bent but here the 2 Cp are not connected here and you will see that this it can vary. There may be 1 ligand 2 ligand and 3 ligands. But now we will try to understand in the Bimolecular orbital theory that how this bent happen and that bending will influence which parameters, and which how it will dictate its reactivity.

(Refer Slide Time: 19:45)


Substituted Cp ligands: inducing chirality

Chiral, non-racemic Cp ligands

Unsymmetrical substituted Cp complexes: Enantiomers

So, not only the simple Cp you will see that different types of Cp ligands are reported and possible in this metallocene chemistry. Here you will see that this is the examples of chiral and non-racemic Cp ligands. So, here is a planner you will see so, this is a planner. So, these are you will see that but this is the, this CP is planner but here you will see there is a chiral center so, what happened this moiety has been installed in the planner indenyl group.

So, now this ligand is become chiral so, as a whole this ligand is become the chiral. So this also the chiral, this also chiral, so you will see you can make so this is I am showing the design I am not showing the real catalyst I am just showing the design or strategy, to make the chiral Cp complexes, so you can see here I am not showing the simple Cp ligands, it is maybe Cp just maybe few Cp like indenyl we will also see that other kinds of Cp few Cp ligands like for phenyl also possible and in this case, you will see the Cp ligands are further functionalized to make the chiral ligands.

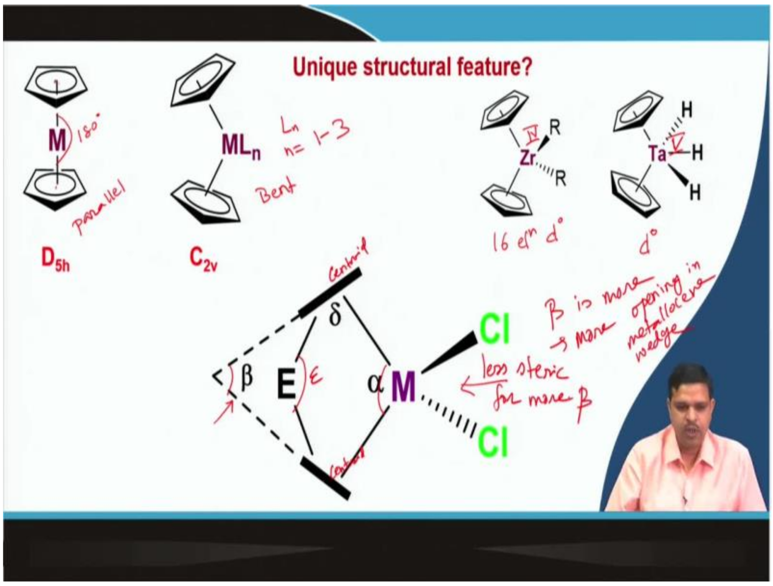
So, here you will see all the chiral and non-racemic Cp ligands which will be important in future classes to understand that how we can make this metallocenes chiral and to get a specific tactility of the from the pro chiral monuments. So, here you will see that you can make the unsymmetrical. So, if you these are you will see that here we are putting the chiral moiety here.

So here we are putting we are installing the chiral moiety to planner Cp and here what we are doing we are trying to make converting planner Cp converting planner Cp to induce chirality, so, how is it possible if you put the 2 unsymmetric are groups then you are now you have now destroying the plane of symmetry and that is why you are now inducing the chirality you can make here 2 possible in a two Enantiomers possible.

Let us see if I name is S it will be R so, one very simple Cp base ligands is this one, the unsymmetrical substituted phenyl and methyl. So, from there you can make two enantiomeric metal metallocene compounds. So, unsymmetrically substituted Cp complexes you will give an enantiomers of the metallocene.

So, these are very important in our future classes, how we can make the chiral catalyst and how the enantiomers, enantiomeric pure catalyst will give a different tacticity when compared to the racemic mixture of the catalyst that will we will discuss in the future classes.

(Refer Slide Time: 23:53)



Unique structural feature?

Now, so, let us come to the our main discussion today’s that is the what are the unique structural feature from a parallel metallocene to a bent metallocene. So I am going slowly because it is very important to understand this feature. So, this is you see this is the parallel and this is the bent so, as I told that L maybe here in this n, n maybe 1 to 3. So, some examples of the bent metallocene is this category here zirconium is in 4 oxidation state, tantalum is in 5 oxidation state. And this is the d 0 this is 16 electron system. So this is also d 0.

We understand this, this one very systematically. Let us so here you will see that this here that if you draw a centroid so, this angle is how much angle will be centroid? Middle and centroid is almost 180 degree but this one is the centroid. So, this is not 180 degree. So, there is some structural parameters associated with bent metallocene which will be interesting and we use to quantify how much it is bent.

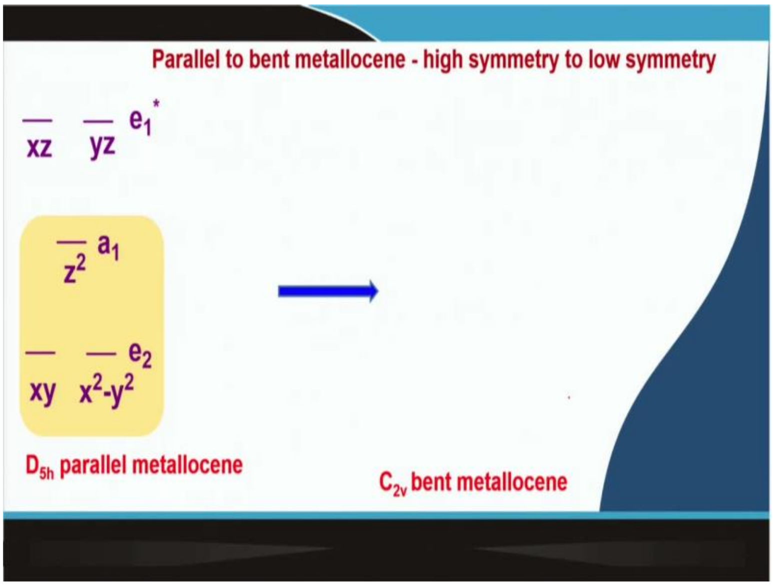
So, one is the main angle of interest is this beta. So, beta is basically the, this is the centroid okay this is the centroid and this is the centroid and sorry this is the plane of this is the Cp plane and this is the Cp plane and you extend and the angle this angle is called the beta angle. So, this is a important structural parameters to quantify that how much bent it is.

This one is the centroid, this is you just assume that this is the centroid so the centroid of the Cp ligands metal and centroid this is the alpha this also clearly quantifies the how much bent it is, and this one also one important structural parameters that is the bridging atom. So, it is easier if it is there just single atom sometimes the bridging made is consisting of the multiple atoms. So, here centroid, the bridging atom and the centroid, that is also important structural parameters.

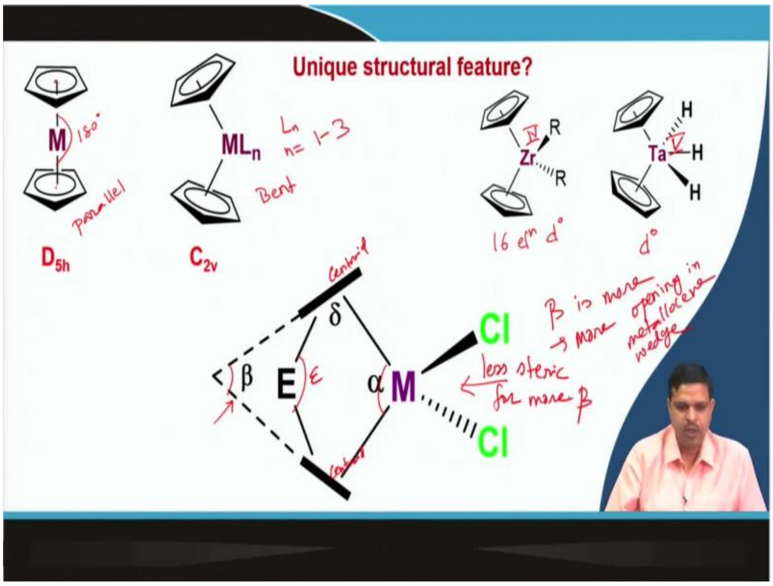
Now, from here you will see that if beta is so, it is like a crocodile’s mouth. So, if you see beta is small it will be like this if beta is big it is like this. So, what is the consequence if beta is small then there is more openness. So, if beta is more, beta is more means the more opening in metallocene wedge. So, and what is the consequence?

The consequence is that, it will that substrate can approach very easily here. So, if beta is small, then there is less opening, so, it is like you can assume like a crocodile mouth. So if small, and if it is big, so it is a more space here for the substrate to approach. So, there will be less steric hindrance in this side, this side. So, less steric that is more opining ness for more beta.

(Refer Slide Time: 28:42)



Parallel to bent metallocene - high symmetry to low symmetry



Unique structural feature?

So, that will try to understand in the, by using the molecular orbitals, and we will try to constitute from the parallel metallocene, so that we can understand very easily, we will just try to compare what will happen if it is bent metallocene from the parallel metallocene.

So, in the next class, we will try to understand that if we decrease the symmetry of the metallocene, then what would be the impact in the metallocene compounds. As I told that, this is the D 5h, this is the C 2V here. So, what we are doing? We are basically decreasing the symmetry, lowering the symmetry. So, what will happen if we do it, and what is the impact in the molecular orbitals diagram?

So, in the next class, we will continue these molecule orbitals and the understanding of the electronic nature for the bent metallocene, which will be very important to understand the reactivities and the properties of the bent metallocene because our metallocene based catalysts for olefin polymerization, actually falls in the under the bent metallocene categories. So thank you very much we will see in the next class again.