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

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

Lecture 11

Metallocene Compounds: Structure and Bonding (Contd.)

Hello welcome again. So, will be continuing in this class the discussion about the structure and bonding of Metallocene compounds. So, in the last class we, if you remember we discussed about the different type of ligands with PI system. And we discussed that the different modes of the cyclopentadienyl ligands.

And today will mainly discuss about the different type of the metal cyclopentadienyl complexes can exist and then will try to understand the bonding very simple way with the help of molecule or vital diagram we try to understand the HOMO and LUMO and the electronic properties which will be helpful for our further discussion.

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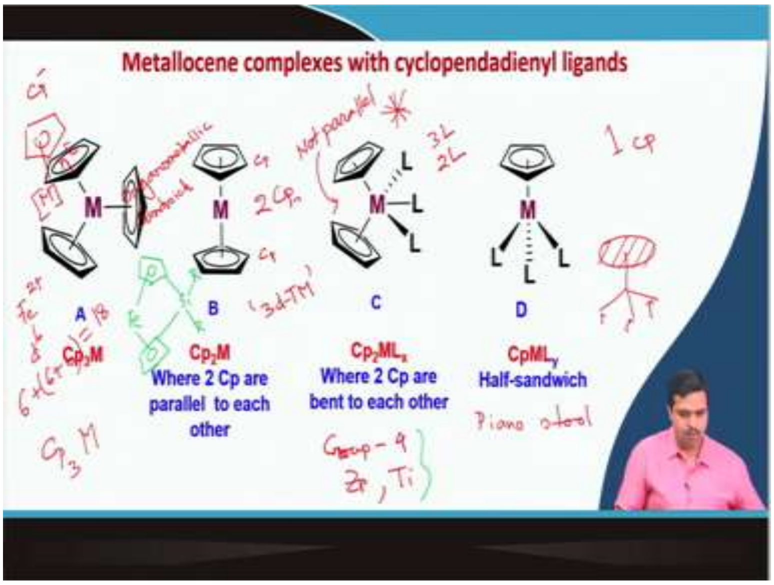


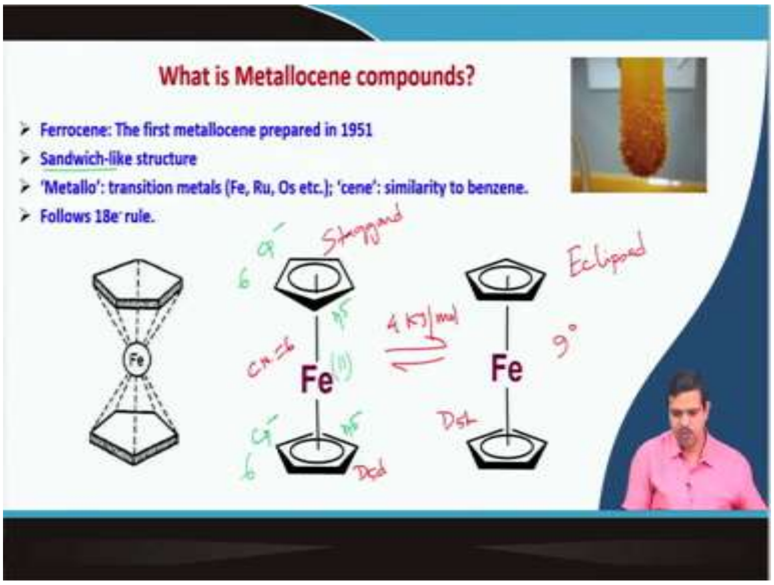
Metallocene complexes with cyclopendadienyl ligands

A
Cp_2M

B
Cp_2M
Where 2 Cp are parallel to each other

C
Cp_2ML_x
Where 2 Cp are bent to each other

D
$CpML_y$
Half-sandwich



What is Metallocene compounds?

- Ferrocene: The first metallocene prepared in 1951
- Sandwich-like structure
- 'Metallo': transition metals (Fe, Ru, Os etc.); 'cene': similarity to benzene.
- Follows 18e⁻ rule.

So, as you know that that ETA 5 CP mode we discussed extensively in the last class that if you have we will discuss the synthesis later after understanding the bonding and then will discuss how to synthesize the ligands as well as the metal complex the common synthetic protocols. So, if we take the CP minus because it is synthesized from the CP h and if you put a base then you get the CP minus with 6 electron donor.

And you will see that it makes a bond like this and this is called the ETA 5 bond. And most common metallocene complexes are actually with this type where you will see that we have a CP bond here and here we have CP bond so 2 CP ligands which are parallel to each other just a parallel to each other, fine CP and CP and if you just imagine a sandwich how the sandwich to bread slice and inside what do we put we put stuffing and if you remember if you can just imagine that these are my breads. And these are just stuffing or just put a tomato then what will how do it look like it will look like a sandwich compound.

So, this kind of compounds is called sandwich organometallic sandwich compound very interesting category of complexes and you will see the beauty of the structure metal center and the CP ligands which are bonded through the pi to the pi system of the 2 CP ligands and a very common example is the ferocene I will discuss in the next slides or so, about the ferocene the bonding and molecule orbitals.

So, very common examples where the 2 CP are parallel to each other and generally most of the 3d transition metals. 3d transition metals are generally formed this kind of M CP 2 M complexes. Like iron 2 plus, nickel 2 plus, manganese 2 plus, cobalt 2 plus, (())(4:31) 2 plus generally form these kinds of cyclopendadienyl complexes by 2 CPD ligands are parallel to each other.

This is also quite common where you see that here 2 CP and here one CP ligands just one CP ligands. So, this is called the called half sandwich complex. That means you will see somebody is if you just imagine that that upper bread slice has been eaten away by somebody in a sandwich then what will have left over you will be a sandwich where the upper sliced bread is missing.

So, this kind of scenario it is called the half sandwich complexes, this is also called as a piano stool why it is it is just try to imagine. So, look this is like your if you just this one and you make. So, this is your leg of the piano stool. So, this will be the like a leg so it is sometimes (())(5:54) pianos stool metallocene complexes. So, there see the structure and very different structural variation here actually if you see that how it can form.

So, suppose say for iron so iron 2 plus iron 2 plus is a D 6 system. So, if we check it validate by 18 electrons. So, this is 6 electrons from the metal and the CP minus these are the anionic CP, so CP minus is six electrons again. So, 6 plus 6 12 so it is 18 electron. So, this is 18 electron complex now if I replace 1 CP by 3 ligands with 2 electron donor then again it will be electron system. So, you can make so compounds should be stable if with the same oxidation state.

So, if you are satisfying the 18 electron by replacing the CP ligands and with the proper oxidation state of the metal center not only that there are other type of ligands here you will see that is this is the CP 3 M type this is the CP 2 M L x that means again you will see that here all the 3 CP ligands there is no other monolith or bidentate ligands here you will see that in this case one CP ligands has been replaced by the three ligand.

So, this is a generic structure I am giving we will discuss the specific example later. So, here 3 CP ligands here 2 CP ligands here 2 CP ligands but other non CP ligands are there this may be 3 this may be 2. So, depending on the oxidation state of the metal centers these ligands will vary, 3 L or 2 L. And here you will see that one CP ligands and other ligands monodentate may be monodentate it may be cleating, it may be bidentate.

So, this is a very code structure I am trying to show to give you a flavor that what kind of structural variations is possible in the metal cyclopentadienyl ligands. Another possibility for the bent. So, this is you see that this one is parallel. But here the beauty is that this stool is not parallel here these 2 CP ligands are not parallel. So, this is basically in this ferrocene like the B category, it is like that one and in the C category so this will is like this one so it is bent not parallel.

And actually, we are in this course we are more interested about this bent cyclopentadienyl complex but to understand the bonding we should first start with the parallel CP2M complex that is ferrocene type of complex then will try to understand the bonding reactivity's with the bents metallocene compounds. So, that is the catalyst so we are interested and to learn and to understand the reactivity and the mechanism is basically based on the bent metallocene compounds.

And group 4 the group 4 metals, as example jarconium and titanium this coin, metals are formed this bent kind of structures. So, not only that 3d transitional metals also can form the bent metallocene compounds with some if you do some engineering on the metallocene as example, I will show one engineering of the metallocene where you can see that this is bent.

So, in this category I will show here. So, this is CP and you will see these are bent and when it will be bent if you put some bridging here as example like this one. So, here you will see this is called a phen type of metallocene, metalloceniphen. This is called metallocenophen and you see that this what we are doing we are putting we are basically threading the 2 CP rings by a one bridging atom this may be silicon carbon or multiple atoms.

So, we have to design in such a way that these two CP rings are threaded and then you will see that these CP rings will be bent and obvious, the bent is obvious because this has been threaded now so there is a strain in this molecules. So, this would be strain molecules and this is very useful monomer for making a different type of polymers that is ergonometric ferrartion containing polymer.

So, what I am trying to tell that there is a lot of structural variation in the metal cyclopentadienyl complexes whether you see that the 2 CP positions are in a different position and 2 CP ligands are in a different position whether it is a parallel whether it is a bent, whether it is the 2 CP rings are threaded to induce the bent point or to induce the strain and some cases you will see for this category, these 2 CP cyclopentadienyl rings it not necessarily you have to thread it to induce the bending.

So, that is it is inherent structural properties. So, this is I am sure you are very interested and excited that how this kind of structural variation happens. So, before that let us start from a simple and well known metallocene compounds to understand the bonding between the metal and CP.

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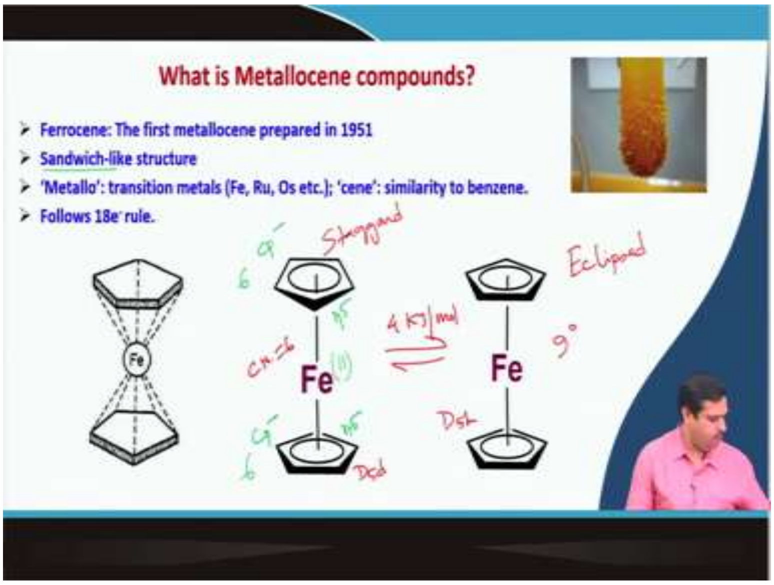

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So, this is a ferrocene as I told that this is the category of the B in the in this category. So, where CP rings are parallel to each other. So, here you will see that again is it like as I explained just it is a like a sandwich type of structure. So, if you see this is 2 flat bread slice and iron is imagining as a stuffing, so you will get the sandwich that is why it is called sandwich type of complexes sandwich like structure and why the name is metallocene is basically these are aromatic in nature, the CP minus.

So, that is why that it just if you take the like a benzene from the benzene the cene has come and metallo come from the metals, transition metals. That is where the name is. The category of the name is metallocene like a benzene like similarity benzene like structure similarity in benzene. Actually, yes, there is a lot of similarities with benzene particularly in view of the electrophilic substitution reactions.

So, whatever the benzene can show that the reactivities electrophilics, particularly electrophilic substitution reactions, the ferrocene also undergoes similar reactions and many cases that reactivities is more than the then the benzene so there are a lot of similarities between benzene and the ferrocene. I will discuss when I will discuss some general reactivity and properties of the ferrocene. And obviously, as I saw this is the it can follow the 18 electoral rules.

So, if you dig six electrons, this is six electrons and this is oxidation state is 2. So, iron 2 plus because this is cp minus this is cp minus anionic ligands and the hapticity is 5. So, this is ETA 5, this is ETA 5. So, the hapticity is 5. Can you tell the, what is the coordination number of iron here in the ferrocene, any idea, coordination number. So, coordination number is what will be the coordination number, coordination number will be 6 because 6 electron pairs are donated to the iron formally.

So, that is why coordination number 6 ironing oxidation state plus 2 oxidant state CP minus ligands so mono anionic, cyclic ligands. And you see, now, if you see very carefully in this in this ferrocene, that ferrocene can also exist in two form. Here try to understand what is the difference here that these 2 CP rings are in a staggered conformation.

So, this is staggered conformation and here you see these CP rings are is in Eclipse conformation and this is the difference between the staggered and Eclipse is around four kilojoules per mole in solid state actually, the 2 CP rings are exist as in just 9 degree away from each other just 9 degree away generally. So, that means these 2 CP rings have slightly slipped from the Eclipse position 9 degrees width. So, and you know the point group.

So, if it for the Eclipse, this is D 5 h and for the staggered D 5 D. So, this can be taken as a homework, find out the point group and assign the point group and show the symmetry how you wish to the d5h and d5d, point group with by drawing the planes and the axis. And the ferrocene is very interesting.

You will see that you can this is commercially available but you can synthesize very easily in your lab will show the later that how what are the synthetic positives, it looks like very nice orange crystals you can crystallize, you can sublime routinely used for many purposes many even the ferrocene based chiral ligands there is a lot of chiral ligands based on ferrocene (())(18:53) there are lots.

So, these are very interesting and famous metallocene compounds which has been discovered first in 1950 1951. And then later it was characterized and you will remember that the Nobel prizes was awarded in 1973 to Wilkinson, for the discovery of the structure or proposing the structure of these kinds of metlocene compounds.

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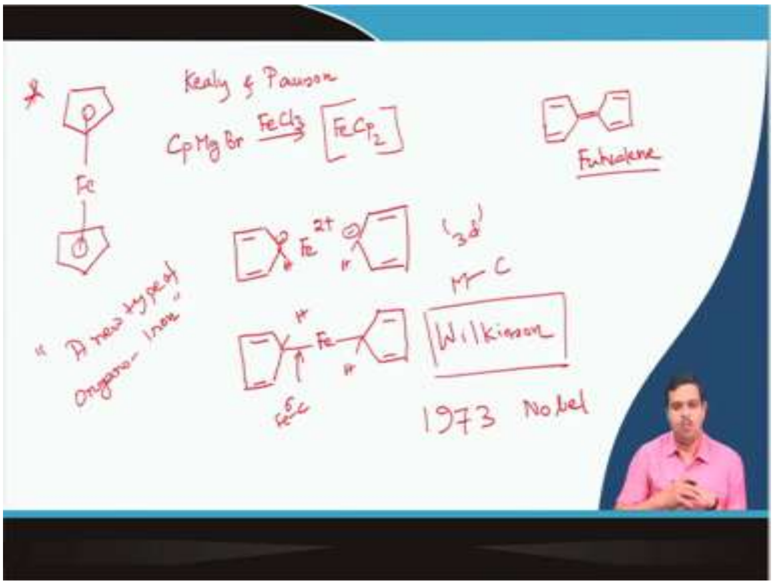

So, will go in little bit more detail about the bonding if you see that the ferrocene is like that. So, you may draw on pen and paper with me, so that you understand much better. So, very interesting this actually compound was discovered accidentally not the it was not targeted that this will be synthesized and in back in 18, back in 1951 the 2 scientists call Kealy and Pauson they actually tried to synthesized the Fulvalene compounds with the reagent Cp Mg Br through the oxidative coupling in the presence of Lewis acid FeCl3 so what was their target their target was to make the.

So, their initial target was to make the Fulvalene through the oxidative coupling of the CP Mg Br, and they did not get, they get, they got a compound where the composition was matching with iron and CP 2 and it was very difficult that time to understand because the model to explain the pie complex metal pie complex was not that time it was very well known. So, they thought that with this composition.

So, there may be possibilities of this type of complex where they proposed that probably. So, here this is hydrogen and this is minus. So, CP minus and, so, they propose the ionic. So, it was proposed that probably this kind of ionic model with the help of ionic model that this kind of complex has been formed or this kind of with the covalent same composition, but the covalent bond model.

So, because that time iron carbon bond. sigma type of bond was easy to understand. So, if it is there is a sigma donor alkyl or aryl based, it can form the sigma bond. So, this is the traditional way, but however, it was kind of a puzzle because you know that 3d transition metal carbon bond with 3d transition metals was not kinetic is not kinetically inert.

It is very labile and that is why it is very difficult to make compounds with metal carbon bond where metals is the 3d transition metals 3d transition metals means like nickel, iron, manganese like that, although they are a report but you have to do some special design you have to design your metal complex with specific geometry, the specific (())(24:35) ligands with particular oxidation state.

So, this is not easy to stabilize the 3d metal carbon bond. So, this is a new type of propose as a new type of organo-iron compound was proposed and it was in around 1963, after almost 10 years the Wilkinson proposed, the Wilkinson propose the real structure, Wilkinson Fisher proposed the real structure that it is a sandwich type of model. So, this is the model sandwich complex and in 1973 he got the Nobel Prize in discovery of the metallocene structure.

So, 1973, so, you see that there is a kind of a (())(25:49) in organometallic chemistry a new era developed where a different type of ligands that is the pi electrons ligands was came into picture and it was a great interest to the scientists to discover with the discovery of these kinds of a very unusual organometallic compounds.

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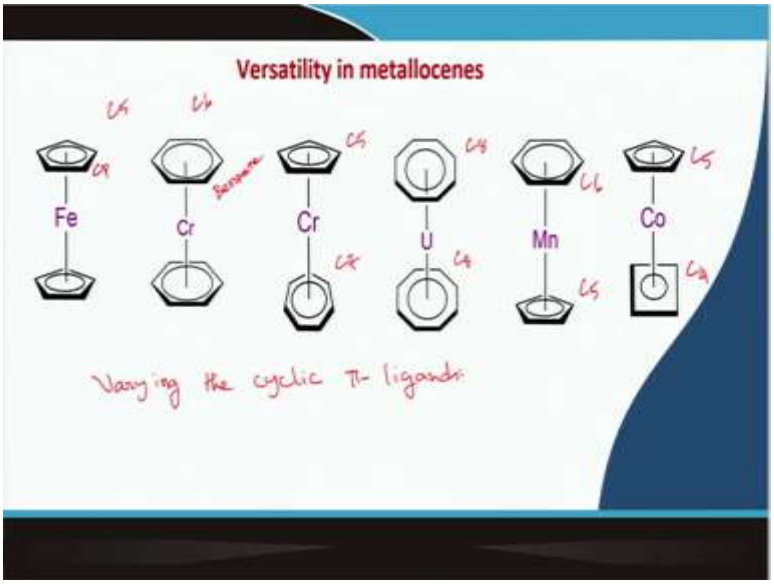
Versatility in metallocenes

So, you see that there is a, after that there is lot of these kinds of cyclopentenyl and the allied cyclic pi complexes, the complexes with cyclic pi ligands were developed. As example here I showed this you can see here this is a very common that is the ferrocene. Here the CP rings, here you will see this is the chromocene, here you will see that these are the benzene here. So, these are the benzene.

So, this is the C 5 cyclic ligands, this is the C 6 cyclic ligands here you will see that this is the C 5 and here 1 2 3 4 5 6 7, here you will see C 7 cyclic ligands. So, here you will see 1 2 3 4 5 6 7 8. So, this is the C 8 cyclic ligands and here you will see not only the homolytic there are other mixed kind of cyclic pi bonded systems were also reported here it is C5, here it is C 6 here you see very interesting C 4, there it is C 5 (())(27:50).

So, varying the you can tell that versatility in metallocene varying the cyclic pi ligands. And obviously, if you once you vary the cyclic pi ligands you have to also vary the metals centers, the oxidation state, etc to stabilize it a particular metallocene compound. So, you see that there is a versatile complexes and versatile kind of metal centers, the CP ligands. And also there is some representative example there are lots. Because these kinds of complexes are really very interesting not only for (())(28:40) purpose also for various practical use.

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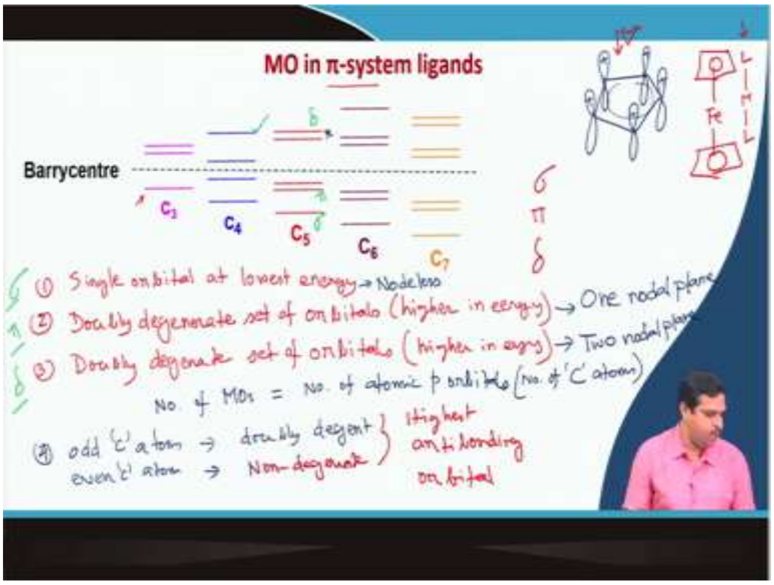

MO in π-system ligands

① Single orbital at lowest energy → Nodeless

② Doubly degenerate set of orbitals (higher in energy) → One nodal plane

③ Doubly degenerate set of orbitals (higher in energy) → Two nodal plane

No. of MOs = No. of atomic p orbitals (No. of 'C' atom)

④ odd 'C' atom → doubly degent } Highest antibonding orbital
even 'C' atom → Non-degenerate

So, now, will discuss about the molecule orbitals in PI System. This will help us to understand the bonding of between the metal center and the CP ligands. So, let us start from a small, and then will apply to the bigger system. So, let us assume that there is a, there the pi orbitals of the ligands, where already the C 3, 3-carbon atoms are there, or 4 carbon atoms are there.

Now, then, will try to understand the molecular orbitals, the pi orbitals of the PI ligand system, and then will then try to find out the matching orbitals of the transition metals and then will try to understand the bonding between the metal orbitals and the pi orbitals of the ligands. So, let us understand the molecular orbitals of the PI system. So, here you will see that the pi orbitals here one always in always when will you construct the molecular orbitals of involving only the PI System, the at the lowest what you will get, you will get the single orbitals at lowest energy.

So, that is this one. So single orbitals at lowest energy, fine. Now, next what will be there, you would be doubly degenerate set of orbitals slightly higher in energy, higher in energy, fine and then next will be again the again one set of doubly degenerate set of orbitals, here orbital means all pi orbitals I am telling.

So, again higher in energy compared to this one. Now, there is another property. So, here you will see that this one will be nodeless and for the next set of degenerate orbitals which slightly higher in energy that will have a one nodal plane, one nodal plane and that is the with the containing the along the principal axis and this one that is the next degenerate orbitals you will get the two nodal plane.

So, in higher, in net, in the second set of degenerate orbitals you will have a one nodal plane and then next degenerate set of orbitals with more higher energy you will get two nodal plane. Now, in this way you will construct the further pi orbitals molecular orbitals and up to the and you have to continue till the number of molecular orbitals are equal to the number of p orbitals involving in the pi system.

So, you need to continue like that number of molecular orbitals should be equal to the number of atomic p orbitals involving in the, involving in the pi system of the ligand. As example here you see for C 5. You have one single orbitals at lowest energy. Now then you will see the two that is the one set of doubly degenate, one set of doubly degenate, now total you see that 1 2 3 4 5 because the five p orbitals if you see so here this you draw the five p orbitals and these are conjugated, so, you see plus, plus, plus, plus.

So, that means here you will see the number of atoms orbitals is five. So, number of molecular orbitals of the PI system will also be total five. So, that means number of atomic orbitals or number of carbon atoms involved in the pi bonding. So, here you see and another one so, there may be the odd or even a carbon atom in the cyclic system, poly in system.

So, in this case you have to consider one more point that for odd carbon atoms, for odd carbon atoms the highest antibonding orbitals that is the width in this case like for CP the highest antibonding orbitals will be doubly degenerate, doubly degenerate and when it is even, even cyclic poly, (())(36:17) polyene system then what will happen you will see that we will have a singlet highest molecular orbital is non-degenerate like in this case you will see that is the degenerate the highest one here and for even carbon atoms this is non-degenerate here you will see.

So, non-degenerate and this is for the, this I am telling for the highest energy, highest antibonding orbital I am telling. This is very simple approach but very effective, fine. Now, you have to understand here that if you view from here. So, you are viewing from here. So, your eye is from here. So, you are viewing from the, viewing from the, suppose you have a ferrocene. So, I am just drawing the ferrocene structure they need to be more clear. So like this one.

So, if you view from the ligand metal ligands. So, from here we are viewing. So, we will try to understand the symmetry of the associated orbitals by viewing from the top towards the top down view. So, here you will see we can assign the or we can categorize the different orbitals of this molecule orbitals of the PI system as cylindrical as if the symmetry is cylindrical then we assign as sigma, we assign as pi, one nodal plane and we can assign as delta where you have a two nodal plane.

So, what I am telling that this will be the symmetry will be sigma, this will be pi and this will be delta as viewed from the top down. So, this is important sigma, this is pi and this is delta. So, you will have a like for CP, will, our discussion will be mainly on the CP ligands. So, you see here so one sigma symmetry with single of the low the lowest energy and then doubly degenerate will have a PI symmetry and the highest energy that is this one will have a delta symmetry. So, this is the sigma, this is the pi and this is the delta.

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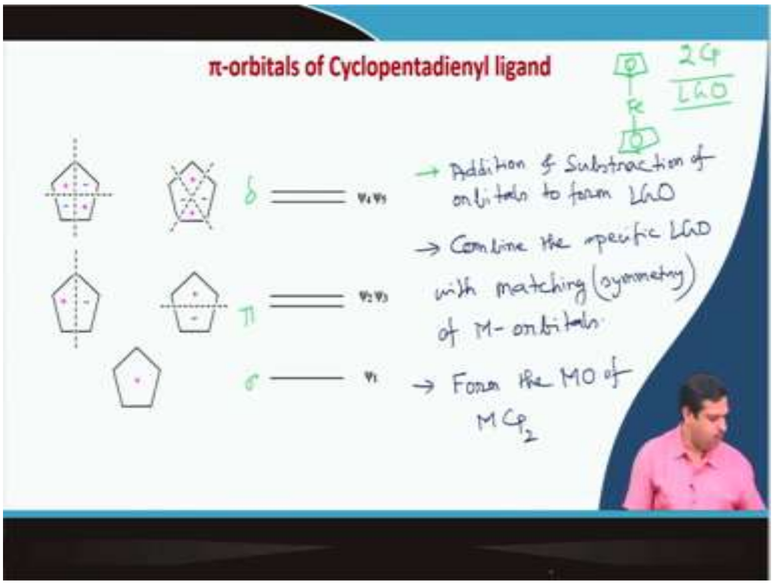
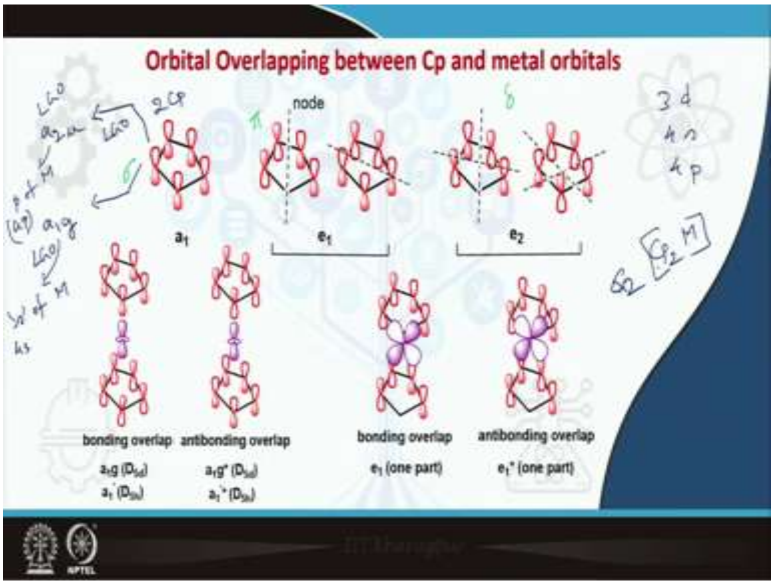


π-orbitals of Cyclopentadienyl ligand

→ Addition & Substraction of orbitals to form LGO

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

→ Form the MO of MCp_2



Orbital Overlapping between Cp and metal orbitals

And this will be interested. This will be useful to understand the ligand group orbitals when we will consider two CP orbitals, so you know that for ferrocene again I am drawing here. So, here we have one metal center and two CP ligands and you know the concept of the, you know concept of the LGO, that is the ligand group orbitals.

So, once we know the molecular orbitals the cyclic pi system like CP now you have to consider the ligand group orbitals, when there is a multiple CP ligand in the specific organometallic compounds, this LGO can form by sub, addition and subtraction of the particular symmetry of the pi orbitals. So, what we will see here, so, here again I am showing that these are the sigma, these are the PI and these are the delta you will see there is no node if you see from the top and here you will see there are two nodes here.

So, if you see this one like this one. So, there is 2 node, no node. So, this is the sigma and here you see in this scenario you will have a node nodal plane here or here. So, two possibilities. So, this is the pi and another case that is the highest doubly degenerate you have a delta symmetry, sigma, Pi and delta. So, you have a no node, single node and two nodes.

So, similarly, here, this is a simple way to present that that is, that is the three set of the pi orbitals associated present in the cyclopentadienyl ligand. Now, what we will do we will have to do the LGO, and to construct the orbitals which can interact with the specific d orbitals of the metal centers. So, what will do the addition and subtraction of orbitals, fine, to form LGO, fine. Now, then what will do to construct the molecular orbitals in present in metal CP bond.

So, what we will do we will try to combine the LGO, the specific LGO with matching here basically matching in view of the symmetry of metal orbitals. To construct the molecular orbitals of the ferrocene or metallocene in general. So, that is the way. We will form the molecular orbitals of metal CP 2 complex, that is our target. So, as example like here you will see that I will give one example like this one.

So, if I do addition and if I do the subtraction, so what you will get you will get a 1 g set of orbitals. And if you do the subtraction, you will get the a 2 u set of LGO. So, this is the LGO, this is also a LGO, with two CP rings. Under when the ligand group orbital you will get two LGOs one is the a 1 g symmetry and one is the a 2 u symmetry and you will see from the a 1 g is perfectly matching with the S orbitals of transition metals, for 3d transition metals that S orbitals will be the 4S, and this one will perfectly match with the p orbitals of the metal centers and for 3d transition metals, this will be the 4 p.

So, perfectly matching the addition, the LGO by resulting from the addition of this set of pi orbitals of the CP by addition, we will get the perfect matching with the S orbital of the metal and if you do subtraction you will get the perfect matching with the p orbitals of the metal center. In this way you can, we can get the you will see that here this is a 1 g, this is the e 1, this is e 1 star from here.

So, you will get the LGO orbitals, which now we have to match with the D orbitals the metal orbitals D or S 3d, 4s 4p. So, you know that if you take the 3d transition metals, the 3d 4s and 4p, can these orbitals can interact with the LGOs resulted from the two CP rings. And this is the way you can now form the molecular orbitals.

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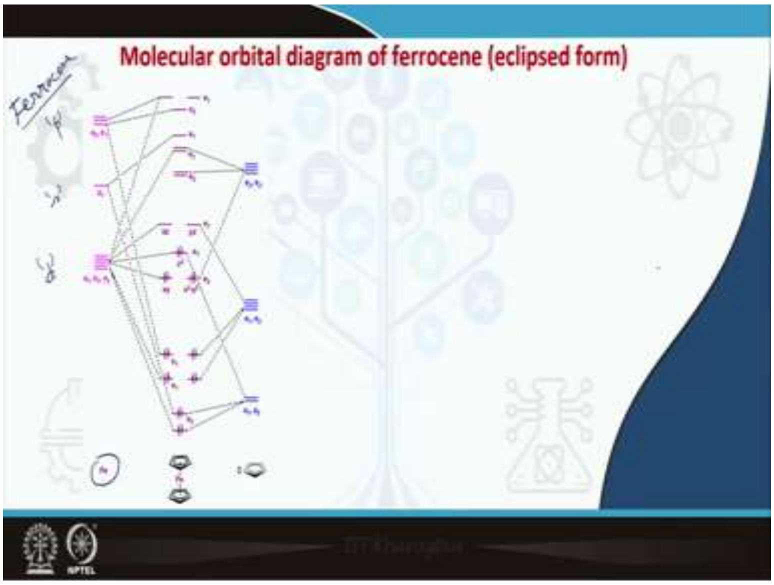
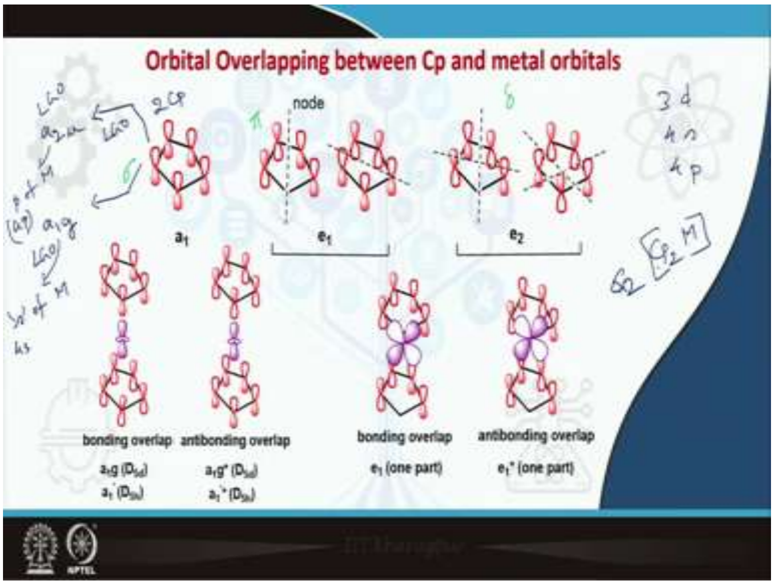


Molecular orbital diagram of ferrocene (eclipsed form)



Orbital Overlapping between Cp and metal orbitals

Here you see that these are the iron, if you consider the ferrocene and so, these are the iron orbitals. So, these are the d orbitals, these are the s orbitals and these are the p orbitals. So, in the next class, we will discuss some of the unique electronic properties of the molecular orbitals of the metallocene compounds in for the CP 2 M category, CP 2 M category, C P 2 M category with the specific example of the ferrocene and then will try to understand what is the unique electronic factors in the molecular orbitals of the metallocene or ferrocene like compounds and this will be very helpful try, to try to understand the reactivities of the metallocene compounds.

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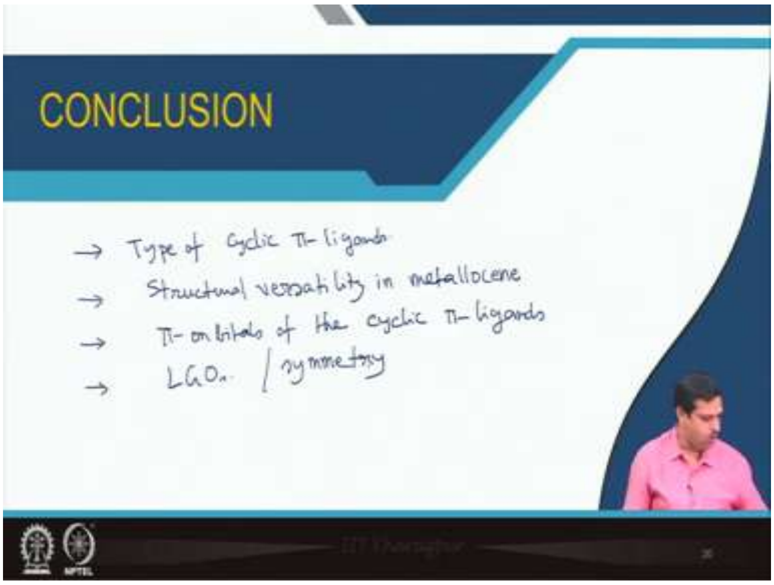

CONCLUSION

→ Type of cyclic π-ligands

→ Structural versatility in metallocene

→ π-orbitals of the cyclic π-ligands

→ LGOs / symmetry

So, in conclusion, we have understood now the type of cyclic pi ligands. Now, it is understood that structural versatility in metallocene compounds and we understood the pi orbitals of the cyclic pi ligands and then we constructed the LGO and we understood that how this can interact with the perfect symmetry, with the metal orbitals of the perfect symmetry. So, in the next class, we try to understand the molecular orbitals of these metallocene kind of compounds.

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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

And these are the books you can read whatever we have discussed in the last two classes. So, thank you and we will discuss again, will continue the discussion again in the next class. Thank you very much. See you in the next class.