Metallocene and Metal-carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts
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Lecture 10
Metallocene compounds: Structure and Bonding

Hello, welcome once again. So, in this course metallocene and metal carbene based organometallics for polyolefin catalyst. So, today we shall discuss metallocene compounds structure and bonding, I will basically introduce that what are the metallocene compounds. So far what we have learned, we have learned in the last classes, we have learned the basic and unique organometallic reactions which will be useful to understand the reactivity and the mechanism of the metallocene compounds. Now, today we will try to understand what are the metallocene compounds, the basic structure, basic bonding.

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CONCEPTS COVERED

Metallocene
- Classification of metallocene compounds
- Cyclic polyenyl ligands
- Structure
- Bonding

So, the concepts we will cover here, the classification of metallocene compounds, the ligands associated with that one, that is the cyclic polyenyl ligands, the structure and the bonding. Because you know that if we do not understand the bonding of a specific compound, we cannot understand fully the reactivities and how it is properties, how it will undergo the in the bond breaking and bond making process. So, it is very essential to understand the bonding. So, we will try to understand in a very simple and qualitative way which will be very useful.

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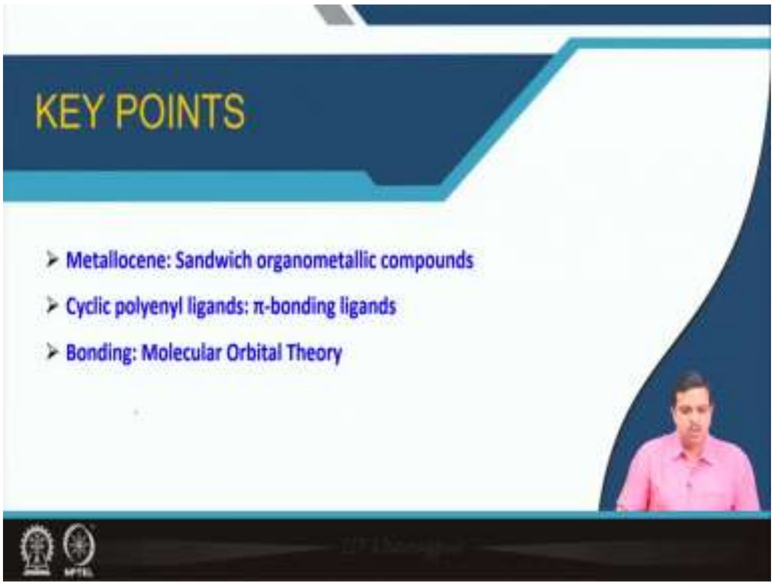

KEY POINTS

- Metallocene: Sandwich organometallic compounds
- Cyclic polyenyl ligands: π-bonding ligands
- Bonding: Molecular Orbital Theory

So, the key points will be the metallocene, cyclic polyenyl ligands, that is the pi bonding ligands and we will try to understand its bonding with the help of molecular orbital theory. So, before that we should first understand about the pi bonded ligands.

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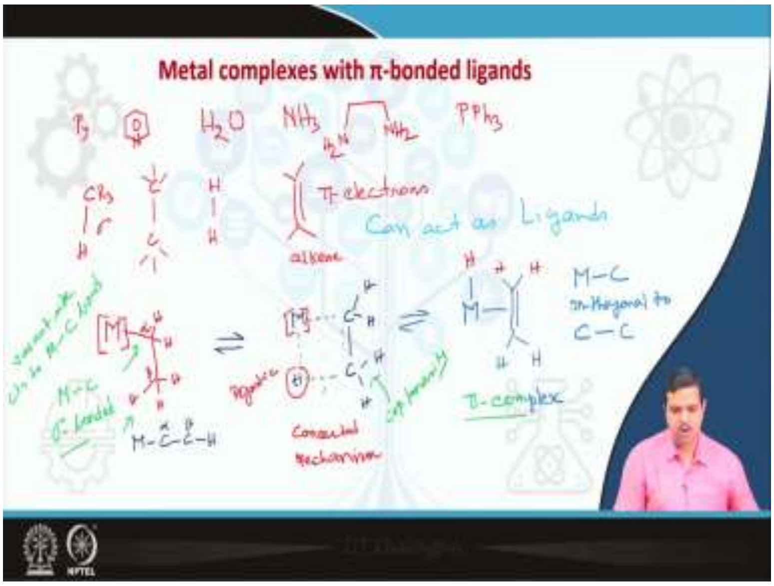

Metal complexes with π-bonded ligands

As we know I already, many times I told that we are very familiar with the ligands and I am sure you have in your previous studies, you have very familiar with like this kind of ligands like pyridine, okay, pyridine ligands. And you know that even the water is a very good ligand, even the ammonia is very good ligands. You also know the many chelating ligands like that phosphine type of ligands all are you are familiar, but in organobolic chemistry there is more interesting.

Many ligands which are not is a traditional act as a traditional donor, you will see in organobolic compounds that they can interact, they can coordinate with the metal centre. As example I told in the last classes that this kind of bond CH, this also can act as a ligand. And not only that, the carbon carbon single bond also can act as a ligand. So, even the hydrogen hydrogen can also act as a ligand and coordinate to the metal centre definitely in the special condition. So, that is the beauty of the organic chemistry and that is why it is a more interesting than the traditional transition metal complexes.

So, as I told that metallocene involves the pi bonded ligands. So, we will discuss little bit about the pi complexes. So, these are all you see the sigma bond. So, this one this kind of compounds that is the alkene. So, this also can act as a very good ligands for transition metal centre. So, here you will see what is there? There the pi bonded ligands here, these are the pi bonded ligands and the pi electrons are there. And these pi electrons can be donated to the to the specific metal centre if the orbitals of the alkene and the orbitals of the transition metals matches in terms of symmetry and they are kind of close in energy.

So, the main point is the symmetry matching, we will try to discuss with a specific example. So, you see this is a really very interesting, how this kind of compounds can act as a ligands. So, these as I told that these are very good ligands, can act as ligands. So, in the last class if you remember we discussed about one reaction that is the beta elimination reaction. And you will see that what is the beta elimination reaction? So, where if is the metal centre as I told that in the third bracket means I am just conventionally it is represented as a metal centre, I am not mentioning the ancillary ligands or which metal centre, general form of writing.

And if you like that and suppose I have, so this is my and this may be… Now, you see this is the alpha position and this is the beta position. So, this is a metal alkyl complex, the metal carbon bond. So, this is a, if you see this one this is a metal carbon bond. So, metal carbon and you can see, you can tell that this is the sigma bonded complex. Now, interesting is that that as I told that if you see that this M C C and H, that is this one, metal, C and C and H, if they can come, if they exist in a coplanar situation and if you have a beta proton, that is the beta H. So, this is alpha, this is beta and this is beta H.

If they can exist in a coplanar situation and if this beta hydrogen that means, this alkyl group and if there is any vacant position at the cis position of the metal centre, they can go through a intermediate. So, they can go through a intermediate like this one. So, is a concerted intermediate, it is called that because, so, this is H hydrogen hydrogen will be there, this may be R group may be different alkyl group also may be there, but essential point is that there should be beta hydrogen.

Now, you see that what will happen. So, this is a through a concerted, proceed through a concerted mechanism and now as this one is now interact with the this metal centre, this is called the acoustic type interactions if you recall we discussed in the last class. So, what happens? This CH is donated to the metal centre and in return through back bonding the metal electron density, the electron density housed on the d orbital metal is now donating back to the CH sigma star, as a result it breaks this CH is breaks.

And then what you get it basically you get the, so, this hydrogen and you will get this one. So, you will see now can you see the difference between the two complex? You see this is a sigma bonded complex and yes right. So, this is the pi bonded complex because now pi electrons are coordinate to the metal centre and your metal centre is here, now it is you see that metal carbon bond, the axis of the metal carbon bond is now orthogonal to the carbon-carbon bond.

So, you see what I am telling, this metal carbon bond direction is now orthogonal to two C-C bond and so, here see this kind of situation we call pi complex because pi electrons are donated to the metal centre. So, why I am discussing? You see that I am now, as I told that metallocene is a class of the organometallic complexes where you will see the pi bonded ligand. So, this is one of the example how this pi complex can be formed from a sigma complex.

So, you see this is a sigma complex and this is a pi complex and here the scenario is that you have to have beta hydrogen proton which is kinetically feasible for the beta hydrate elimination you know this reaction is called beta hydrate elimination and from there you are getting a metal carbon sigma bonded complex to the metal alkene pi complex. So, here as I told that this kind of reactions are very common in organometallic chemistry where your criteria are matched.

As example here, you have to have the beta hydrogen in the metal alkyne and this M C C H that should give a coplanarity in the transition state; if there is no coplanarity, you cannot form a coplanar transition state, then the beta hydrate elimination will not be favoured and above all there should be one vacant position at the cis position of this metal carbon bond. So, these are the criteria. So, here all should be coplanarity, here vacant site cis to metal carbon bond. So, these are very common in organometallic complexes where the ligands are not the traditional like pyridine, water, ammonia, amine or phosphine.

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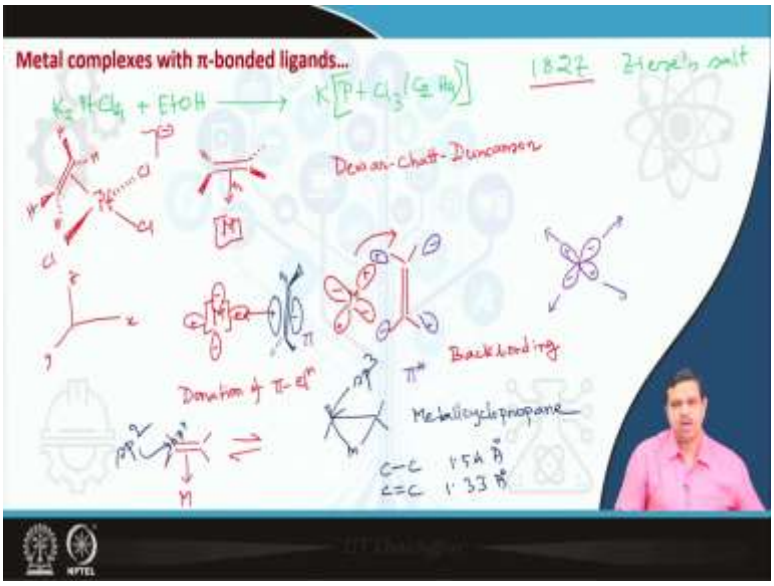

Metal complexes with π-bonded ligands...

So, you have heard the gysalt. What is the gysalt? This is the believed to be a one of the first organometallic compound, well characterized, synthesized organometallic compounds compound. This is the gysalt. I am sure you know what is this. This is basically if you boil tetrachloro platinate in ethanol, you will get a very interesting compound with this composition. And you know this was synthesized in 1827 and it is called the gysalt.

Now, it was very difficult to understand the structure of this kind, exact structure of this kind of complex. The composition was confirmed by various techniques like CHN analysis in that. You remember, you see that this was the 1827 and that time there is no much sophisticated characterization tool as example like single crystal exerting instrument. So, this structure was in puzzle for more than 100 years; after 100 years the exact structure was revealed and what is that?

I am sure many of you know, still I am drawing because this is one of the famous and the first organometallic complex with pi bonded ligands. So, I am just trying to draw in a 3 dimensional. So, that you can feel the exact structure of this complex. So, here now the 3 chloride and so is a K plus P T, this anionic complex and platinum is in so, obviously, plus 2 oxidation state. Now here you have… So, this is the ethylene, now here you will see that again this the what kind of structure it is. So, this is like your like this is and it is bonded to metal center like this one.

So, that means, as I told that so, C-C bond axis is orthogonal to the metal carbon and after discovery of the real structure almost after 100 years this became a highly interesting field in the organometallic chemistry that how this alkene is bonded to the metal center in a orthogonal manner. Because we all know that the very familiar where the transition metal complexes where the ligands are basically bonded like a sigma fashion. So, there are several models were proposed, one of the model is the Dewar-Chatt-Duncanson model.

So, what was proposed here? So, this proposed that if you have so, let us say this is my z axis and this is my x and y Cartesian coordinates, then let us this is my alkene, you can draw with me so that it will be easy to understand. Now, you know that in ethylene, you just imagine the only the pi bond how it is happened. So, due to the lateral overlap of the pi orbital, that is a p orbital. So, you have the pi electron density like this.

So, if I (())(19:05) plus minus… now, I have the metal center and if I see, this is the z axis, this is the x and this is the y. Now, if you imagine that this orbitals… Now, what will happen? So, this is now, this electrons loosely bound electrons, pi electrons can be donated to the 3D orbitals where the symmetry is matching. So, this is so donation of pi electron. Now, you also have to think another interaction, this is my again ethylene and we have the pi star orbitals and you see the pi star orbitals, I am putting in a different color.

So, pi star orbitals will be like this one. So, this is this, this is this. Now, you see that how this pi orbital looks like. It is you know that 3D orbitals are like that, okay, minus minus plus plus let us say that d x z orbitals. Now, if you just pull it, these lobes just lobes, how does it look like? It will look like exactly the pi star of the… So, the pi orbital, this is the pi star orbitals. So, now, you can imagine there is 3D orbitals where the symmetry is matching perfectly with the pi star orbitals.

So, you can now draw like this one. So, here minus. So, what will happen? Once the pi electrons are donated to the metal center it will have a sufficient electron density. So, it will be now donated to the pi star orbital of the ethylene. So, this is called the back bonding. So, by that way what we will have you are basically strengthening the metal, new metal carbon bond, that is the this one and you are taking out the electron density from the pi orbital, bonding orbital and putting electron density on the pi star orbital.

So, as a result the bond length will decrease of the CC bond. So, if there is a enough back bonding then this kind of scenario may happen like this one. So, this is metallocyclopropane and this is the simple metal pi complex and obviously, as I told if you put, if you can make a scenario where the back bonding is more operating then you can basically get the single bond character of this.

So, here it is SP 2 character. So, here is basically the metal centers are SP 2 and here the metal center are SP 3 and this is reflected in the bond length because you know that the bond length of the saturated carbon carbon bond is around 1.34 angstrom and 1.54, 1.54 angstrom for the single carbon carbon bond that is the SP 3, SP 3 is around 1.54 angstrom.

And whether the free alkene it is 1.33 angstrom, that is for and always you will get in the metal pi complex always you will get the CC bond distance more than 1.33 and in some specific case you can get the bond length very nearby to the SCC SPC CC bond length that is very close to 1.4745 angstrom. This is due to this kind of … so, this is again it is a kind of a metal carbon sigma complex, this one is the metal carbon pi complex. So, this kind of are very quite known in organometallic chemistry. So, these are acyclic pi ligands. That means, these are not cyclic.

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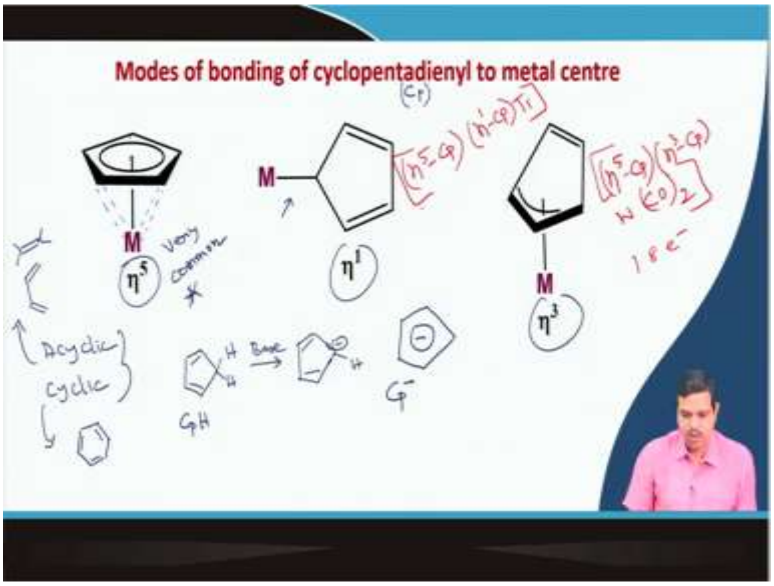

Modes of bonding of cyclopentadienyl to metal centre

So, there are a lot of similar ligands - both acyclic and cyclic, the pi bonded ligands are used in organometallic chemistry. So, as I told that acyclic is one of the example the acyclic is ethylene kind of ligands, maybe butadiene kind of ligands, those are acyclic. And cyclic, one of the examples is the CP psychopentadienyl and also, so, these are the acyclic and these are the cyclic, like this one, this is the one example of cyclic pi ligands and not only that one, this also is very good, act as a very good pi ligands, that is the benzene or benzene derivative other derivatives.

So, there are lot of example of the pi systems which can act as a ligands, both acyclic and cyclic. So, in this course we will be more interested on the cyclic kind of ligands because you will see that metallocene are basically are the category of the organometallic compounds where we use the ligands of the cyclic pi system. So, here you see that this is a very common the CP complexe structure that is called psychopentadienyl, we call the CP, we will later we will discuss the common synthetic strategies how we can make the CP.

So, this is actually is this. So, you have a two hydrogen here and we call this is CpH; although there is two hydrogen we write as CpH, there is a reason. Now, if we put base, okay this is quite acidic and what you will get? You will get like this one and this one. And this one is aromatic in nature because it is a 6 pi electrons like benzene. So, what will happen? This we represent as like this one and this we call the Cp minus, psychopentadienyl. So, most of the complexes you will see that psychopentadienyl complexes exist as like this one.

So, here you will see this one is coordinated to the all carbon centers. So that if you have a real single crystal XRD structure of any CP complexes like this one you will see that bond distance, this metal carbon bond distance are equal for all the 5 metal carbons. So, that means, these are, all the distance are equal and this kind of scenario we call it as a eta 5 coordination mode, eta is the hepticity. So, this is the eta 5 mode. This is very common in the metal psychopentadienyl organobolic compounds.

Sometimes we also, you see that this kind of coordination mode between the metal center and the Cp this is called the eta 1 mode where you see only one carbon center is donated. So, this is eta 1 mode and some uncommon, but exist in some special scenario this is eta 3 where 1 2 3, 3 carbons are donated to the metal center. So, here eta 5 eta 1 and eta 3, 3 possible coordination mode or hepticity are possible. However, eta 5 is the most common, this is also possible this is quite rare.

This one we will discuss extensively in the future classes, but as I told, this is very uncommon. Some of the example you may find in the test book like this kind of. As I told it is a uncommon I should give one example. So, this is, so here you will see two Cp ligands - one is eta 5 mode and one is eta 3 mode. That is the tungsten complex like carbonic. And also this kind of coordination mode exist in various catalytic cycles or reactivity studies where there is a rearrangement or in the mechanism pathway, it is possible and you will find in a quite common that during the reaction pathway if you see carefully, that mechanism proceeds through a eta 5 to eta 3 and to the eta 5 coordination mode.

So, this is as I told this is quite common, but you cannot isolate and in many cases, but it is quite common in the reaction mechanism. So, this is good to know how these bonding happens. So, again this is a 18 electron system and this one you will see that eta 1, this is also quite common for some special scenario. As example you see that one complex, I am sure you have if you have taken the organometallic course in your previous degree you have seen this kind of complex in textbook that is the titanium.

So, this is you see that both the Cp - eta 5 and eta…two Cp ligands are there, but one is eta 5 and one is eta 1. And you see that if this kind of compound sometimes acts as a fluxional behavior. Since there is a equilibrium it change this C p, it change to eta 1; this Cp change to eta 5. So, like that. So, many fluxional behavior we can sometimes see for this kind of complexes. So, now I think it is clear that what kind of coordination modes are possible for the Cp type of ligands.

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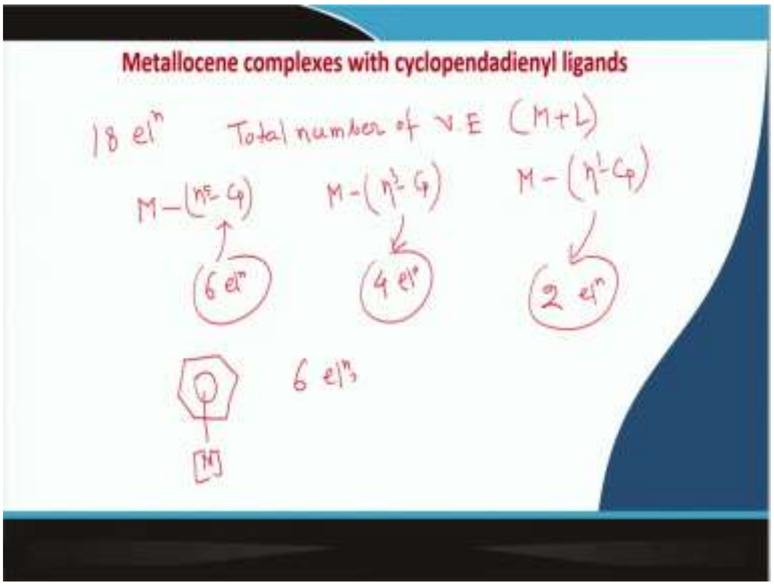

Metallocene complexes with cyclopendadienyl ligands

18 el^n Total number of V.E (M+L)

$M-(\eta^5-Cp)$ $M-(\eta^3-Cp)$ $M-(\eta^1-Cp)$

6 el^n 4 el^n 2 el^n

6 el^n

Now, I am sure you are familiar with the 18-electro rules in the organometallic chemistry. Actually discussion will not be completed if I do not tell about the 18-electro rules. You know the 18-electrons means the total number of valence electrons, total number of, I will not go in detail because I am sure you will know all this, total number of valence electrons either metal from metal and ligand. And you should know that how I mean in which case how many electrons are donated.

Like for metal when it is eta 5 Cp complex that this, for this case if you consider the oxidation state method then this eta 5 will the eta 5 Cp ligands will donate 6 electrons. When it is eta 3 Cp then how many electrons will be donated if you consider the oxidation state method? Any idea? 4 electrons yes. So, this is 4 electrons. And if it is eta 1 Cp then how many electrons? Yes, correct, 2 electrons. So, this one you should know because when you will discuss the mechanism to have a idea about the stability or whether the feasibility of forming complex by checking that whether it is satisfying the 18-lectrons rules or not, this information will be useful.

Similarly like benzene if it forms the metal alkene complex then if this is the scenario then how many electrons will be donated from the benzene? Obviously, yes 6 electrons. So, this information are important for understand the mechanism and it will be very useful in the future class when we will discuss the mechanism.

So, we will continue the structure and bonding of the metallocene compounds in the next class because as I told we have to be very clear concept of the bonding and structure of the metallocene so that we can understand very clearly the orbitals involved in the reactivities and the mechanism when we will discuss the polymerization and how does react to ethylene, what reactions happens, why the reaction, this reaction is feasible.

So, to understand that, this bonding concept will be very much useful. So, thank you and we will see in the next class for continue our discussion on the structure and bonding of the metallocene compounds.