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 9
Transition metal/Organometallic complexes Unique reactions

So, welcome again. So, if you remember in the last class, we discussed about the transition metal organometallic complexes, which are used as a catalysts. We also discussed in a brief way, what is the role of the catalyst. Today, we will discuss some of the unique reactions associated with organometallic or transition metal complexes. These are very important to understand the polymerization mechanism, because if you see any catalytic cycle, there are some elementary steps.

And these elementary steps, it is very important to understand how does it proceed, and how these elementary steps are affected by the metal center, and the other ligands which are called the ancillary ligands. So, this today's lecture will give a very brief idea or concept to understand the unique reactions associated with organometallic complexes.

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CONCEPTS COVERED

- Unique reactions in organometallic catalysis
- Role of metal centre and ligands
- Elementary steps in catalytic cycle

So, the concepts covered in this lecture will be the unique reactions in organometallic compounds or catalysis. The role of the metal centers and ligands, this is very useful, the same ligands, but the different metal centers or the same metals with different ligands might have different reactions or the driving force. Elementary step in catalytic cycles that is, that we have to understand in very depth, otherwise we cannot design a catalyst if we do not understand the elementary steps involved in the catalytic reactions. So, this concept we will try to understand in today's reactions in today's lecture.

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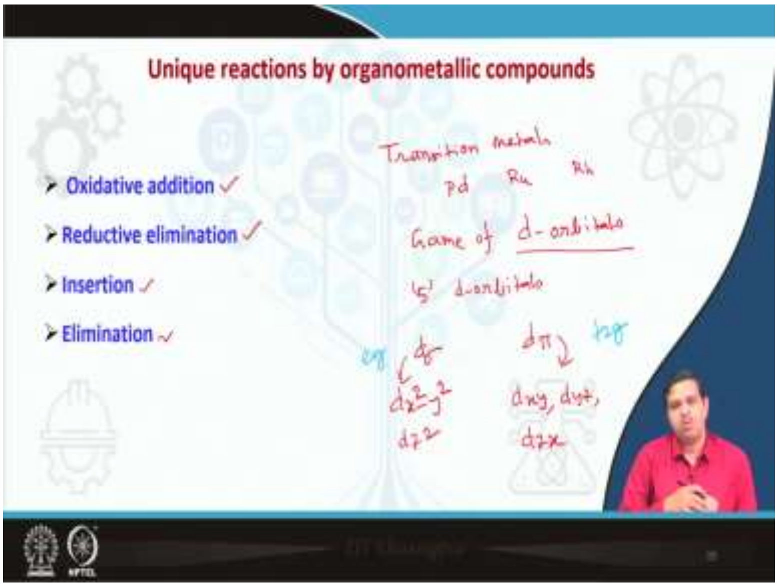

Unique reactions by organometallic compounds

- Oxidative addition ✓
- Reductive elimination ✓
- Insertion ✓
- Elimination ✓

Transition metals

Pd Ru Rh

Game of d-orbitals

5 d-orbitals

eg $d\sigma$ $d_{x^2-y^2}$ d_{z^2}

$d\pi$ t2g d_{xy}, d_{yz}, d_{zx}

So, you will see that organometallic compounds are very unique, and you know that specifically the transition metal complexes, transition metals I am sure you know what are the transition metals. So, it is basically the 3D, 4D, and 5D we routinely use for catalytic purposes. So, as example the palladium, ruthenium, rhodium, there are lots of catalysts in 4D series. Also the different organometallic compounds of the 3D transition metals are also known. So, what is the beauty in the organometallic compounds?

This is the game of d orbitals. I will show you in the later part how this d orbitals plays a role. So, you know that there are 5 d orbitals and which can be sub categorized depending on the symmetry. One is the d sigma and one is the d pi. So, d sigma is dx square minus y square and d z square and d pi is dxy d yz and d zx. If you recall the crystal field splitting of the d orbitals followed by crystal theory of the octahedral transition metal complexes, we have read these two category of the d orbitals.

In that, there we have learnt it as a eg and here we will we learnt as the t2g. So, is nothing but is a d pi and d sigma and this d sigma and d pi categories according to their symmetry. So, these are the 4 unique reactions associated with the organometallic compounds - one is the oxidative addition, what is the reductive elimination, one is insertion and one is the elimin, last one is the elimination reactions. Why we will try to understand because you will see in all the catalytic cycle, multiple steps of oxidative addition or reductive elimination or insertion or eliminations do exist.

So, all the catalytic cycles will be involving these 4 reactions, either 4 or either 2 or either 3, but you will see that any catalytic cycles you will see the elementary step involving these 4 type of reactions. So, it is very important to understand what type of reactions is it, which are actually not possible in other type of complexes or other type of reactions, these are very unique for the organometallic compounds. So, let us try to understand the type of reactions.

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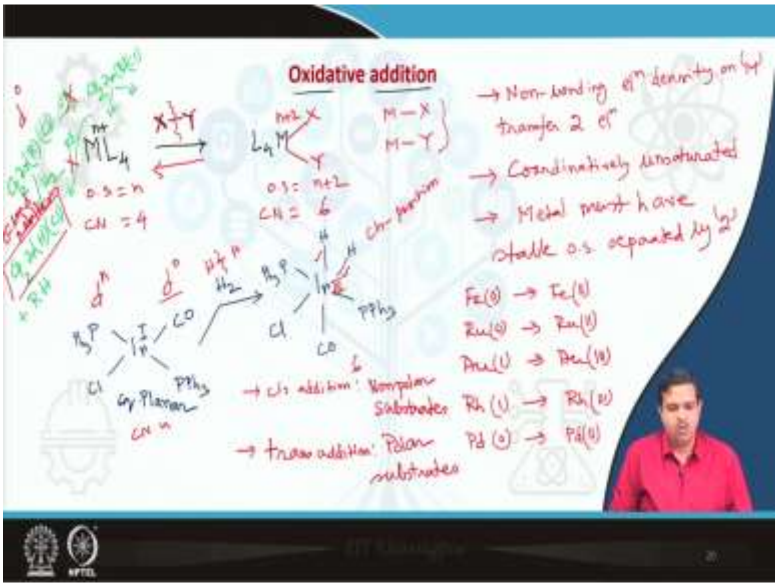

Oxidative addition

→ Non-bonding e⁻ density on 'M'
transfer 2 e⁻
→ Coordinatively unsaturated
→ Metal must have
stable o.s. separated by '2'

Fe(0) → Fe(II)
Ru(0) → Ru(II)
Au(I) → Au(III)
Rh(I) → Rh(III)
Pd(0) → Pd(II)

→ cis addition: Nonpolar substrates
→ trans addition: Polar substrates

So, first we will start with oxidative addition. So, as the name suggests that there will be oxidation and there will be addition. So, how it is possible? So, suppose I am taking a just arbitrary complex where M is my transition metal, L is any ligand and I am taking the oxidation state of this one as N plus. Now I am reacting with let us say one reagent, xy. So, this one I am just trying to first discuss with in a very general way and then I will give, I will tell you the specific examples and how does the reaction proceeds.

So, what will happen now L 4 M and then in oxidative addition you will see there is two new bond forms, that is the M X and M Y, that is the two new bonds are formed in this oxidative addition. So, what does it happen? You see carefully. So, initially the oxidation state of the metal was N plus and now it is N plus 2, these two bonds are formed and here, so, oxidation state was N, now oxidation state is N plus 2. Now use the coordination number of the metal because here 4 ligands.

So, it is 4 and here the coordination number is 6. So, you will see that oxidation state is increased by 2 unit as well as the coordination number is increased by 2 units. So, that is why it is called the oxidative addition. And you will see in the most of the catalytic cycle this has been, you can regard it as a activation step. I will give a real example, then you will understand. So, this can be regarded as a activation of the substrate. Most of the catalytic cycles you will see the first step is the oxidative addition, but not necessarily in all the catalysis reactions.

So, what happens here? Here few things to note down that nonbonding electron density on metal. So, you should have the nonbonding electrons on the metal. So, d orbital should not be empty, M transfer 2 electron, 2 L. So, here as a result this X Y bond is cleaved. So, you basically this 2 electron transferred to the anti-bonding orbital of the X Y and that is the way the X Y bond is cleaved and then coordinate to the M X and M Y. And definitely you will see that coordination number should be, is increased by 2 units.

So, your initial metal complex should be coordinatively unsaturated. What does it mean? If suppose the maximum coordination of a metal center is 6, then it cannot undergo the oxidative addition unless one ligand or multiple ligands are de coordinated. So, there should be the scope of adding the 2 new ligands. So, that is why the coordinately should be the, this initial complex should be coordinatively unsaturated. And the last part that metal must have stable oxidation state separated by 2 and this is you see that here oxidation n, n plus 2.

So, for mononuclear complexes there should be 2 oxidation state which are stable. As example like iron 0, this can undergo the oxidative addition because it can form the stable oxidation state Fe 2, we know that iron 2 is quite stable. Similarly ruthenium 0, it can undergo the oxidative addition. Similarly gold 1 can undergo the oxidative addition, rhodium 1 can undergo, palladium 0 possible. And as I told that there should be non-bonding electrons density on the d orbitals.

So, obviously, if there is no electron that is the d 0, then oxidative addition is not possible. So, one real example I am giving then we will understand although I will not discuss in depth, I just want to refresh your memory about the unique reactions of organometallic compounds. So, this is popularly known as Bosch's iridium complex. So, you will see that this is iridium is in oxidation state of 1, 2 triphenylphosphine in trans, this is a square planar complex com planar.

And you see here that another carbonyl and chloride and 2 triphenylphosphine is in the trans. Now, if you reacts with hydrogen H2 you will see. So, this is you can get this product very easily. So, here you will see here, the two new bond has been formed that is this one and this one and this bond is cleaved, H H. And if you see carefully, the iridium is now in 3 oxidation state and coordination number now 4, 2, 6. So, you will see that the iridium complex has undergone the oxidative addition in presence of dihydrogen.

Now, you will see that this H and H, that new N H bonds, that iridium hydrous bonds are in cis position. So, cis addition is for non-polar substrates and the trans addition is polar substrates. I will not go in detailed mechanism. I will suggest that to refresh your memory you please read any standard textbook, you will understand and you can recall because I am sure you know all these things. So, this you see that in oxidative addition you are basically activating the quiet, the stable bond; as example here, the H H and then it is you are forming two new bonds.

So, you can regard it is a kind of a activating step. So, not necessarily that only the oxidative addition is the activating step as if you recall one example this may be regard as a assignment, interesting assignment you can solve this problem. So, here I am writing one complex, very interesting and very funny, same as well, very interesting. So, if you react with hydrogen, you will get this one. Now, you can, so, if you react with this hydrogen you will get this one.

So, when you try to understand how does the reaction proceeds. So, I am sure first thing comes in your mind that you will do the oxidative addition with H H and then the reductive elimination of R H and you will get the zirconium, H and C L, but you have to be very careful. This is not the step we will follow to get this complex. Why? Because this is D0 system. You see the oxidation state. So, this is the D0 system. So, that means, it cannot undergo the oxidation. So, you have to be careful that first you have to, as I told that there should be nonbonding electron density on metal center, otherwise it will not go the oxidative addition.

So, this is not the step and that is why I told is very interesting and very funny. So, for this reaction it proceeds through different mechanism that is the sigma bond metathesis reaction. How does it proceed? You solve yourself, ok. Fine. Now we know that what is oxidative addition. Now what will happen if you think the reverse reaction? So, if the forward reaction is oxidative addition, now if you think the reverse reaction and just replace this oxidative, the reverse reductive and replace addition the reverse elimination.

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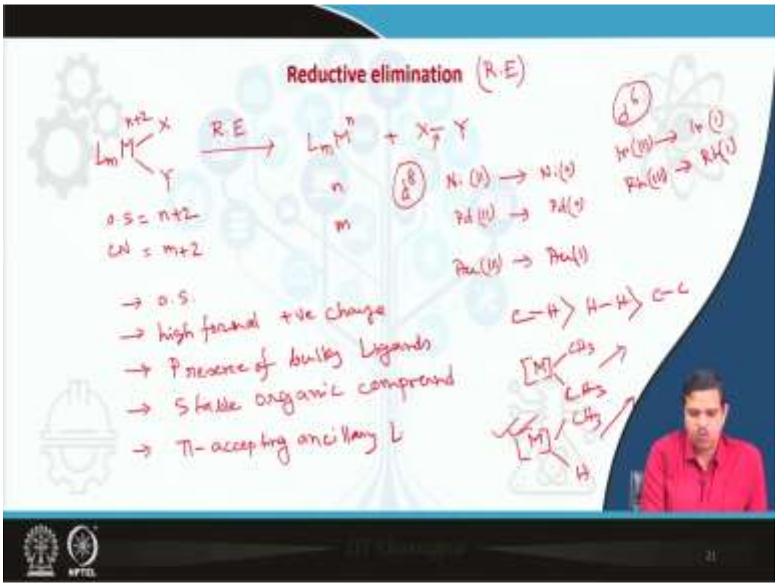

Reductive elimination (R.E)

$L_mM^{n+2}(X)(Y) \xrightarrow{R.E} L_mM^{n} + X-Y$

O.S = n+2 → n

CN = m+2 → m

d^8: Ni(II) → Ni(0); Pd(II) → Pd(0); Au(III) → Au(I)

d^6: Ir(III) → Ir(I); Rh(III) → Rh(I)

→ O.S

→ high formal +ve charge

→ Presence of bulky Ligands

→ Stable organic compound

→ π-accepting ancillary L

C–H > H–H > C–C

So, let us try to understand what is reductive elimination. Obviously, as I told, so, this is just a reverse reactions of the oxidative addition. So, suppose here if I have metal center like x y and here is my oxidation state let us say n plus 2 and if there is a reductive elimination, RE, I am writing as reductive elimination short form. So, what will happen? You are getting this with oxygen state n and you are getting your x y. So, here you will see that oxidation state is n plus 2, here it is n and the coordination number here you will see here if it is n again if I take it is a m, so, it is m plus 2 and here it is m.

So, here you will see that coordination number is decreasing, oxidation state is decreasing just opposite to the oxidative addition. So, what are the criteria we mentioned in the oxidative addition the reductive elimination will be exactly the opposite. So, you should have the two oxidation states, stable oxidation state separated by 2. So, that is why like nickel 2 to nickel 0, then palladium 2 to palladium 0. That means, all the D8 system can undergo the reductive elimination, go to the gold 3 to gold 1 and not only that iridium 3 can undergo the reductive elimination to give the iridium 1 complex.

So, these are the D6 system. So, 6 electrons in the d orbitals. Similarly, the rhodium 3. So, these are the common metal center which can undergo the reductive elimination. So, what are the criteria? As I mentioned that you will have a two oxidation state, stable oxidation state separated by 2 and apart from the high formal positive charge because if there is a high oxidation state it will be happy to come to the lower oxidation state or lower positive charge and presence of bulky, presence of bulky ligands.

So, that means, what I am telling that if there is a lot of bulky ligands as a ancillary ligands, so, reductive elimination will be more favorable because it will reduce the steric hindrance by eliminating this x and y. And another one, the stable organic compound formation what I am telling that if this is thermodynamically stable that x y, then this reaction is more favorable. As example if you form like CH bond, it is more favorable then H H or C C bond formation.

So, if you see that reductive elimination is associated to have the organic compound with the formation of the CH bond, it will be more favorable then the carbono carbono. So, as I am giving example like if this scenario comes like let us say CH3 CH3 or here, sorry CH3 or H. So, here after reductive elimination what you will get? You will get methane. That means, you are forming CH bond. And here what you will get? You will get ethane. That means, you are forming the C C bond. So, this will be more favorable.

I hope you understand this concept. And another the pi accepting ancillary ligands. Why? Because you see that you are basically transforming higher oxidation state to the lower oxidation state. And as you know in organometallic chemistry that the lower charge that is the low oxidation states are stabilized by the pi acceptor ancillary ligands. So, by through the back bonding so, that there is a charge neutrality. So, that is the one of the strategy to make the organometallic compounds with low oxidation state.

So, as example in organometallic chemistry the oxidant state 0 minus 1 formal oxidant state minus 2 are possible, but for that you have to put your ligands as good pi accepted ligands; as example PPS 3, PF 3, carbon monoxide like that. So, this information is very helpful to understand the reaction mechanism when we will come to the polymerization by transition metal or organometallic catalysts.

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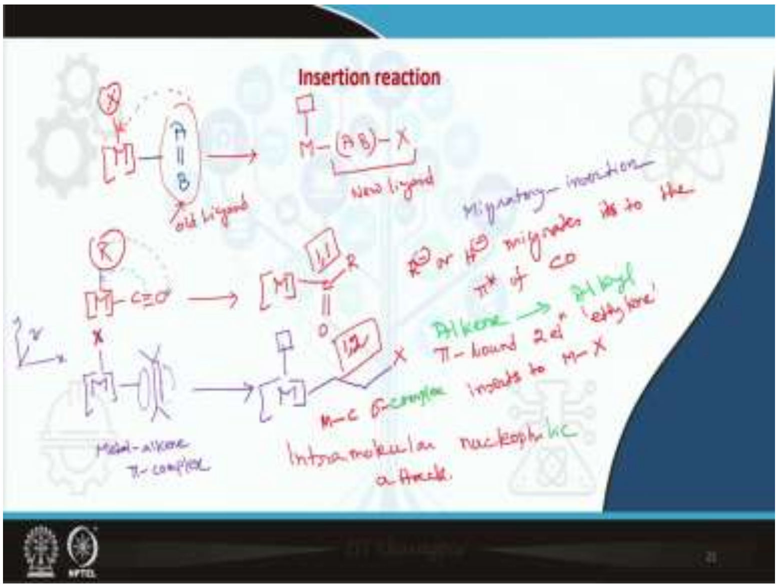

Insertion reaction

One of the very important and very beautiful reaction is the insertion reactions. I will discuss what is the insertion reactions in general way. So, what is, suppose I have this metal center and I have one bond that is the M X and I have a pi complex like that. In insertion what happens that you are, so, try to understand what is happening. So, here this one is a new ligand, sorry this one was the old ligand and now you see the new ligand is this one and obviously, this is now back in sight.

So, here what happens you see that looks like that AB, this one is inserted in this bond. So, this whole moiety is inserted in this M X bond. So, that is why this reaction is called the insertion reactions. I will give some example like if you have carbonyl compound, I am not writing the full ligands distribution on the metal, I am just writing as a metal center. In the third bracket means just a metal center and the ligands for which we are interested in a particular reaction.

So, now, you will get like this, sorry this is, this should be R. So, here you will see that this is looks like inserted, this carbon monoxide is inserted here and also you can look in a different way that this R has been migrated here. So, that is why sometimes we also call is migratory insertion. So, now, let us see the similar situation may also come for other type of ligands as example like this one. So, you see this is the alkene complex. So, this is metal alkene complex.

Please try to understand this reaction because this will be needed in our polymerization catalyst, to understand the polymerization mechanism, metal alkene or we call the pi complex because the pi electron clouds are basically donated to the metal orbitals. So, how does it donate? Because these are my pi electrons and these electron clouds are donated to the a suitable metal orbitals. As example like dx square minus y square if you consider the plane, this is my x, this is y, this is z.

So, we can consider that T x square minus y square orbital is taking the pi electron cloud. Now, what will be the outcome of the insertion reactions? So, it will be like that. So, this is my back end and here this x will come here. Now, you see for this one, this for carbonyl, this you can regard as 1 1 addition because this carbon is attached with metal and also attached with that migrated ligand, that is R. But this one, in one carbon center is attached to metal and one carbon center is attached to the that migrating ligand.

So, you can tell this thing as 1 2 migration and this one is 1 1 migration. So, here the pi bond 2 electron, that is this one, the pi bond 2 electron insert into the M X bond. So, pi bound ethylene moiety actually inserts to M X bond. So, here same way this R that is the, in most of the cases it is alkyl or hydride. So, this x that is the sigma electrons of this R actually is migrating to the CO pi bond. So, basically what is happening? The R minus or H minus migrates to the pi star of CO. So, you know that when you are putting electron density on the anti-mounting orbital of any molecules then that bond will be weak and it will cleave.

So, exactly that thing is happening here. So, here the, so, it is a basically intramolecular nucleophilic attack by, see the R or x here. So, here you will see that how beauty this reaction it is. So, you are basically do it, one group here this is x or this is R is migrating to the another ligand and you are basically forming a different ligand. Here, the ligand was carbon monoxide, now the ligand is R CO. This case also the ligand was pi complex, ethylene; now the ligand is different.

So, it is now you can so, that is why you can regard this is the pi complex and this is metal carbon sigma complex. So, you are transforming a metal complex to the sigma complex by doing the insertion reactions. So, the complex nature is totally different, in one case, pi complex and one case, sigma complex. And you are basically forming a ethylene to the alkyl in this here and why I am emphasizing this one because this one is very important to understand the polymerization mechanism by the catalyst. So, here you what you are doing? You are transforming a alkene to alkyl.

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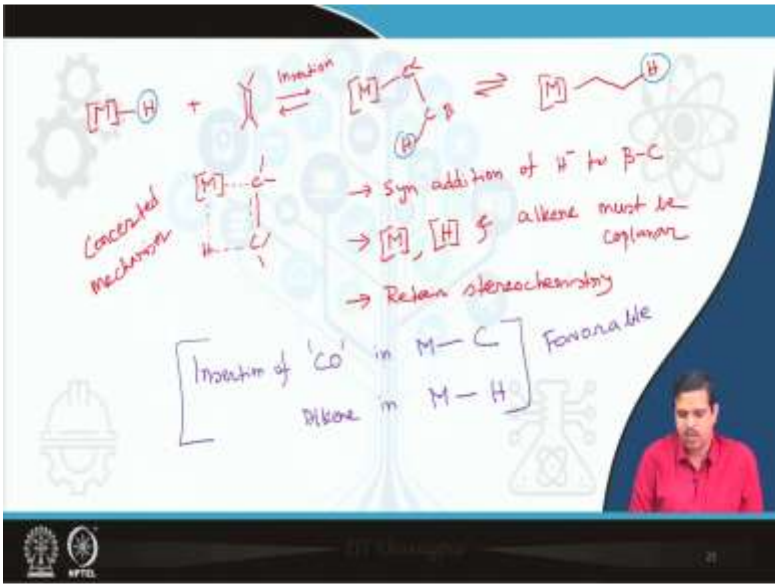

→ Syn addition of H^- to β-C

→ [M], [H] & alkene must be coplanar

→ Retain stereochemistry

Insertion of 'CO' in M—C
Alkene in M—H
Favorable

So, I will give you one specific example because this is very helpful, it will be very helpful to understand at the later stage that you will see that if you have the metal center and let us say is a hydrogen and you are reacting with alkene. Let us try to understand how the reaction proceeds because I am emphasizing again this alkene insertion particularly because this is the key step in the polymerization of alkene by transition metal catalysts. So, what happens? You have, you get this kind of complex and this is obviously the alpha and beta.

So, this is what happening? This insertion reaction is happening. So, this H is now is here; this hydride, this H is remain as a hydride in this complex. So, this hydride is now migrated to the beta carbon and you will get this kind of a intermediate. Now, after this you will get here, this complex. Now, why I am writing? I just want to emphasize few unique features of this insertion reactions. First of thing, that this insertion reactions proceeds through a planar concerted mechanism like that I am drawing.

So, you can also draw with me for practice purpose. So, here you will see and this one. So, this proceed through a concerted mechanism. Now, you will see that as it is a concerted mechanism, so, always the same addition is favorable. That means, if your alkene and the hydrogen should be cease in position, if they are in a trance then this reaction cannot proceed to beta carbon. And you will see that this metal center hydrogen, that means, hydride and the alkene must be coplanar.

And the most beautiful feature of this in reaction that is retain stereochemistry. So, in organometallic reactions you will see that very common insertion reactions are of CO ligand in metal carbon bond and the insertion of alkene in metal hydrogen bond, this one is like a take home message. So, we have to know that this is more favorable and in the later part of the classes, you will understand when we will discuss the mechanism that how this is used frequently, this will be used frequently. So, alkene insertion in M-H bond is more favorable then the alkene insertion in metal carbon bond. Now, you know that insertion reactions how does it happen; we know oxidative addition, reductive elimination; we know the relation between oxidative addition and reductive elimination. So, basically reductive is just opposite to oxidative addition.

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Elimination reaction

So, now, you think that what will be the opposite of the insertion reactions. So, suppose I have this scenario. This. So, this is a alkyl complex and this is my alpha and this is beta. So, now, I am trying to understand the opposite reaction, that is the reductive elimination reactions. Sorry, this is the elimination reactions.

Now elimination reactions are generally two types or maybe three types, one is the beta hydride elimination or alpha hydride elimination or sometimes the gamma eliminations are also possible. In many rare cases, the other hydrides can be eliminated, but the most common is the beta hydride elimination. This is the most common is the beta hydride elimination and you will see very frequently in the organometallic catalysis reactions the beta hydride elimination are taking place. Now, how this happens?

You have to understand as I told that this organometallic chemistry is nothing, but a game of d orbitals. So, we are very familiar with the ligands like pyridine, like this one, amine, like this one you are quite familiar, even anionic amine ligands, but have you thought about that this may also act as a ligand, this moiety. It is surprising, looks like surprising, no? that how this moiety can act as a ligand? Yes, it is possible. If you design your organometallic compound with a specific metal centers or ligands, this may act as a ligand. How it is possible?

So, this can act as a ligand. How it is possible? You know that this CH has this is I am writing R3, this has, this is a sigma bond, so that means, you have a sigma electron density. So, like this one, this is the sigma electron density and you have the sigma star. So, if I write this is sigma, I am just considering only CH and what will be the sigma star? So, sigma star will be like this one. So, if this is plus, this is minus. Now, coming to the metal part. Now can you imagine the matching symmetry of the metal d orbitals?

So, as I told if you think like this is my x, this is my y, this is my z. Now, you will see that this sigma electron density can donate to the dx square minus y square orbitals, this one. Now, you have a sigma star, this sigma star what d orbitals will match with the symmetry? Any idea? Yes, like that. So, let us assume it is a d xy orbital. So, now, here you see that perfectly matching. So, if you have a field d orbitals like that then what will happen? It will give electron to the sigma star.

So, d orbital to the sigma star of the CH. Is it clear? Now, if you so, what you are taking? The electron density from the bonding orbital and you are now putting electron density on the anti-bonding orbital, so that means, what is happening? You are, make the bond weak. So, if the bond is weak, sufficiently weak, then it will be cleaved. So, if this scenario comes like that, if your this hydride is close proximity on the metal center in this scenario we call agostic interaction.

I am sure you have heard this name agostic interaction. If this agostic interaction is very strong then what will happen? It will undergo the elimination reaction. So, this, this. So, now, this hydride you are forming. So, this will be again here and it will form this one. So, again you are forming sigma complex to metal pi complex and how you are doing? You have to design your metal orbital complex with suitable metal center and also ancillary ligands so that this bonding and the back bonding is favorable, is interesting, very interesting.

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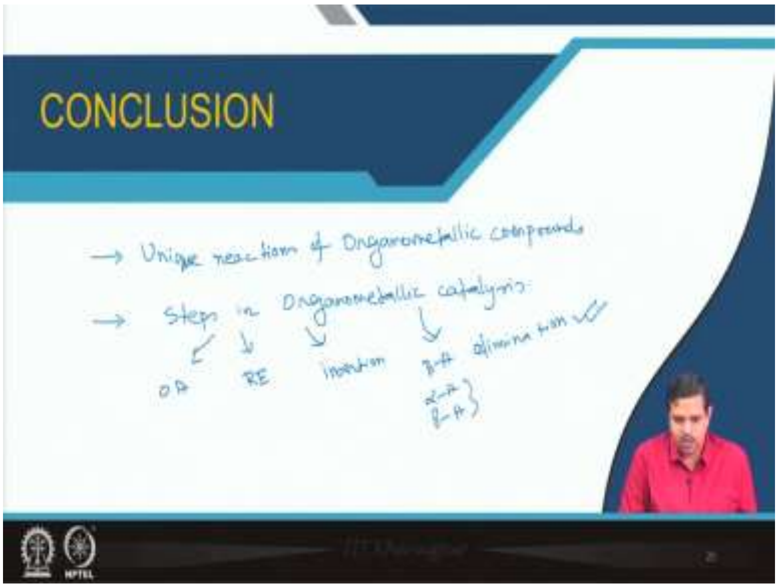

CONCLUSION

→ Unique reaction of Organometallic compounds

→ Steps in Organometallic catalysis:

OA RE insertion β-H elimination ✓✓

α-H
γ-H }

So, today's class we have tried to understood the unique reactions of organometallic compounds, namely the oxidative addition, reductive elimination, insertion and beta elimination reactions. We understood the steps in organometallic catalysis. So, these are nothing but the oxidative addition, reductive elimination, insertion reaction and again this beta H elimination reaction.

As I told there may be possible or alpha H or gamma H which is not very common, but it is also possible, but more common and frequent is the beta H elimination. These are very important and very useful concept in organometallic chemistry and the related catalysis reaction.

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REFERENCES

[1] Principle of Polymerization by George Odian, Wiley
[2] Organometallic Chemistry of the Transition Metals by Crabtree, Wiley
[3] Introduction top Polymer Chemistry by Charles E. Carraher Jr., CRC Press

So, today we have discussed the topics of the unique reactions in organometallic chemistry. You will get the information from these following books here and the polymerization, the protocols like anionic radicals you can consult the books by Odian and the Charles E. Carraher book.

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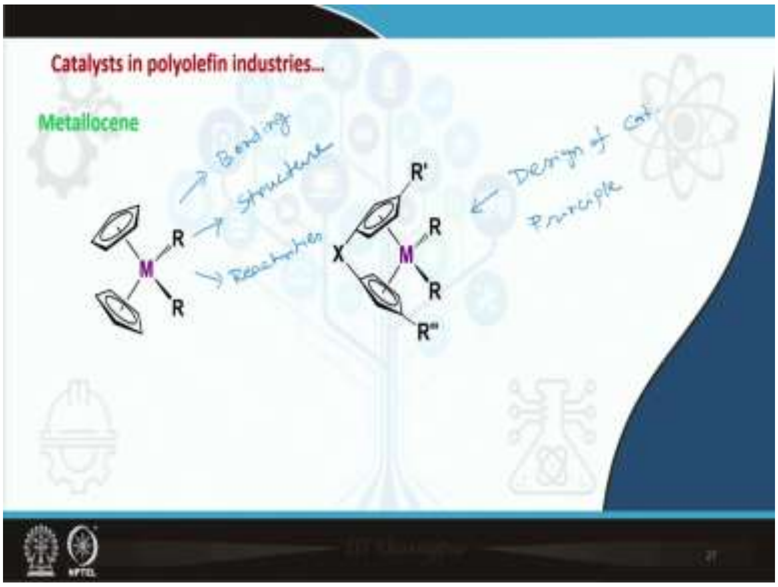

Catalysts in polyolefin industries...

Metallocene

In the next class, we will enter to the chemistry of the metallocene and we will try to understand first the bonding because this is very important; you have to before going to the catalysis, we should understand the bonding, what, which orbitals are involved, the structure because as I told that varying the structural parameters you can change the polymerization protocol; the reactivity and obviously, the design of the catalyst, the designing principle. So, bye then, thank you very much, we will see in the next class.