Metallocene and Metal-carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts
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Lecture 35
Bonding and Electronic properties in Metal-carbene complexes

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NPTEL ONLINE CERTIFICATION COURSES

Lecture 35: Bonding and Electronic properties in Metal-carbene complexes

Welcome once again to our classes, now we are discussing the metal carbene complexes and our obvious goal is to explore and to study its catalytic applications in olefin polymerizations called ring opening metathesis polymerization ROMP.

So, so far what we have done, we have now discussed what are the metal carbenes and also metal carbines, what are the basic structure, what are the metathesis and what are the alkene metathesis reaction, what are the type of alkene metathesis reactions and we have discussed quite elaborately what are the possible the reactions can be done by the (())(1:17) single metathesis catalysts.

So we discussed in the last class that this can be termed as a single lock for, single key for multiple logs, so now today we will focus our discussion on the metal center and what are the electronic, what are the electronic properties and the what are the bonding interactions between the metal and the organic carbon forming the stable metal carbene complexes.

So today's topic is bonding and electronic properties in metal carbon complexes this is very much important to understand in depth because if we want to design a metathesis catalyst for polymerization reactions or any other reactions we have to be really very clear concept about the metal centers, about the ancillary ligands and about the carbene fragment.

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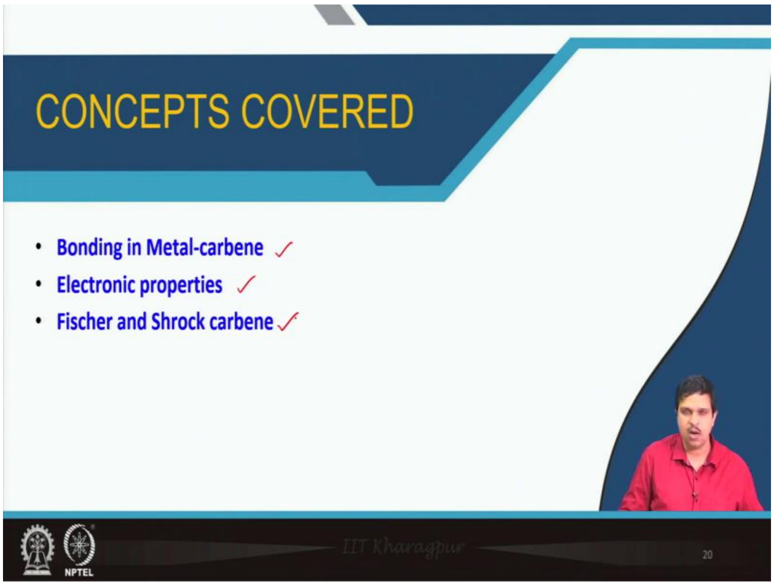
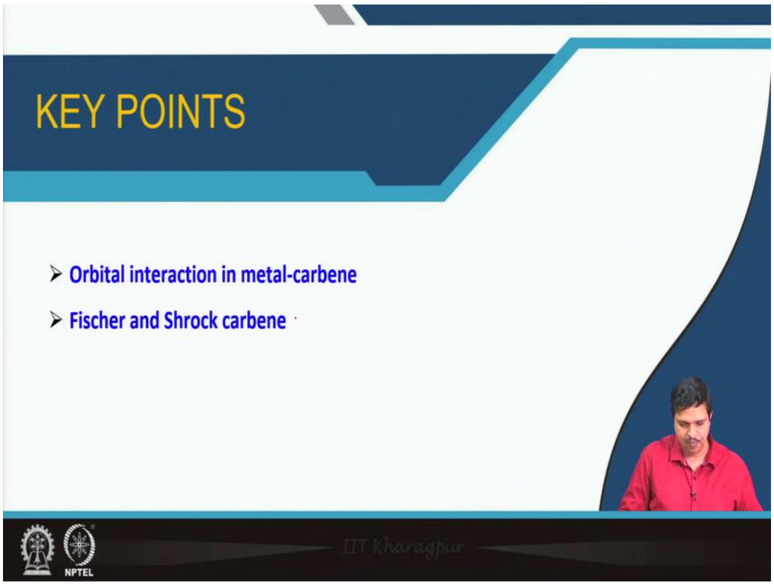


CONCEPTS COVERED

- Bonding in Metal-carbene ✓
- Electronic properties ✓
- Fischer and Shrock carbene ✓



KEY POINTS

- ➢ Orbital interaction in metal-carbene
- ➢ Fischer and Shrock carbene

So the concepts we learn here, the bonding in metal carbene, electronic properties and the different type of metal carbon complexes mainly classified into Fischer and Schrock, so what are the Fischer carbene and what are the Schrock carbene and why, what is the basic difference between the Fischer and Schrock carbene in the bonding as well as in the electronic properties.

As you know that electronic properties actually dictate the reaction, the reactivity so it is very much important to understand the difference between, difference in electronic properties in the Fischer and Schrock carbene so that is our target today.

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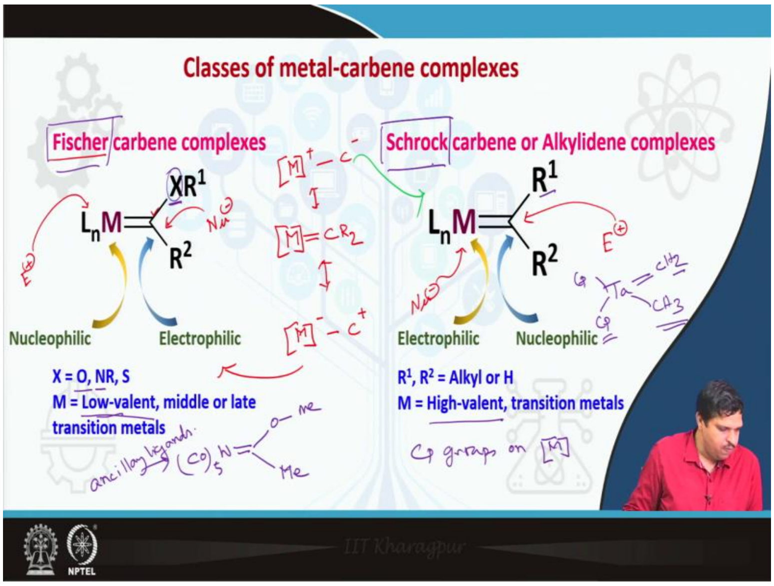

Classes of metal-carbene complexes

Fischer carbene complexes

Schrock carbene or Alkylidene complexes

$X = O, NR, S$

M = Low-valent, middle or late transition metals

R^1, R^2 = Alkyl or H

M = High-valent, transition metals

So this one, these are the two types of the metal carbon complexes, so in the last class in the beginning the first class of the metal carbene we discussed that that these are the metal carbene complexes you can regard is like this one, so here is let us say this is the just arbitrary I mean not real molecules so in obvious informally there is a metal carbon bond, the two is a double bonds, metal carbon double bonds, two bonds and you if you think about the canonical form you can consider as like M plus C minus and the other one is M minus C plus.

So we will really try to understand today that whether this is the possibility or not, whether these two canonical structure or the whether the difference in the electronic properties of the metal centers and the carbon of the carbene centers are really is really possible or not that we will try to understand today.

So if it is let us say the left hand side that the metal is nucleophilic that means it is electron rich so if it is like that so if it is nucleophilic then and obviously the other one the carbon of the carbon center is will be electrophilic that means here the nucleophile can react here and electrophilic.

So it will undergo the nucleophilic reactor attack on the carbon and the electrophilic attack on the metal center and if this scenario exists then this is the Fischer carbene complex so here in the Fischer carbene complex you will see that metal center is nucleophilic in nature that means it and the carbon center is electrophilic in nature that means this is the, this one M minus C plus.

Now the other scenario that is the opposite where that your metal center is electrophilic in nature and the carbon of the carbene is nucleophilic in nature that means this is the electrophilic attack is can happen on the carbon and the nucleophilic attack can happen on the metal center so exactly difference it is and here so in this case you will see that this is the best representative of this canonical structure that is the this one.

So yes, it is possible depending on the designing, proper designing of your carbene organic carbene and also the choice of the metal center as example like for here the Fisher carbene here you will see that this is the low valent generally 0 plus 1 plus 2 or minus 1 most maximum is generally plus 2 and here you will see this is generally middle or late transition metals form this kind of Fisher carbene complex.

And another criteria of this kind of Fisher carbene complexes that here you see that there is ox the pi donors as example oxides or amines or any other like sulfur should be attached with the carbene carbon. As example like here CO5 tungsten and here OMe and here it is the methyl so here that is why you see this is the heteroatom that the X and with that one any other alkyl groups may be there.

And we will discuss why it is like that and this is the stock carbene here the difference is that the metal center is high valent late transition metals generally and here you see that this the R groups that is the on the carbene carbon there are alkyl or hydride or CP groups on the metals as ancillary ligands CP groups on the metal center.

As example that that tantalum CP CP and this is CH2 and here is CH3 this is one example, so here either the hydride you see or any other alkyl groups and on the carbon of the carbene there should be the alkyl groups and also the CP groups on the in general CP groups on the metal centers as ancillary ligands as example here you see this one.

Now for the Fischer carbene as it is low valent so generally the good pi acceptor ligands as example carbonyls, the phosphenes are generally on the metal as the ancillary ligands so these are as ancillary ligands because these are the low valent so to stay stabilize the low valency of the metal centers we need to have a good pi acceptor ligands.

And here that I discuss after some time that why the importance of this O group O or amine this acts as a pi donor of the in on the Fischer carbenes so these are the basic structure of the Fischer and Schrock, so basic structure of the Fischer carbene and the Schrock carbene you understand how for the basic difference.

Obviously from as a simple, it looks like as a simple model it looked like where both in both the cases are the metal carbon double bond but the electronic properties are just reverse and very much different and one here is M delta plus and other cases is M delta minus, fine.

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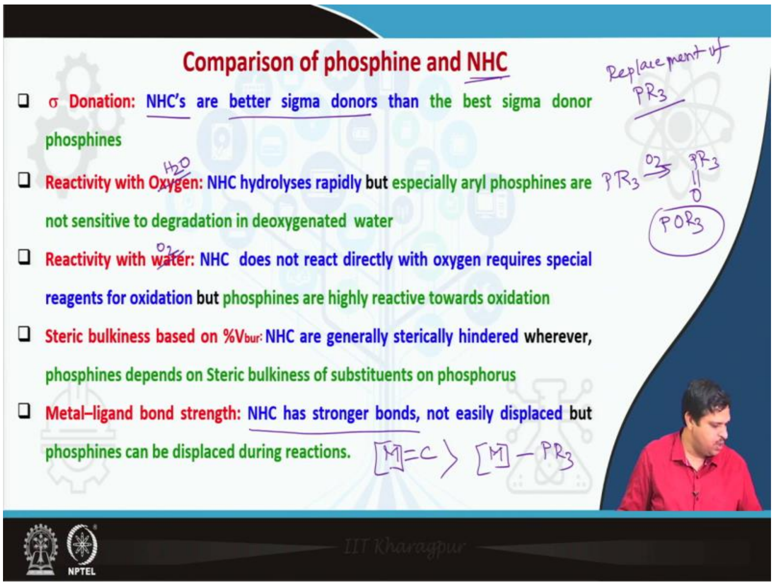

Comparison of phosphine and NHC

Replacement of PR_3

- ☐ **σ Donation:** NHC's are better sigma donors than the best sigma donor phosphines
- ☐ **Reactivity with ~~Oxygen~~** H_2O**:** NHC hydrolyses rapidly but especially aryl phosphines are not sensitive to degradation in deoxygenated water
- ☐ **Reactivity with ~~water~~** O_2**:** NHC does not react directly with oxygen requires special reagents for oxidation but phosphines are highly reactive towards oxidation
- ☐ **Steric bulkiness based on %V_{bur}:** NHC are generally sterically hindered wherever, phosphines depends on Steric bulkiness of substituents on phosphorus
- ☐ **Metal–ligand bond strength:** NHC has stronger bonds, not easily displaced but phosphines can be displaced during reactions.

$PR_3 \xrightarrow{O_2} \underset{O}{\overset{}{PR_3}}$

$\boxed{POR_3}$

$[M]=C > [M]-PR_3$

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So this is before going in more depth, so we this is a good information and important information, we call, we if you see the recent papers or the books or the reviews we call, we generally become very excited if we can replace, replacement of the phosphine ligands in any catalytic system, why you are interested, because the phosphenes are generally toxic environmentally is not good, hazard, is regarded as environmentally hazard compounds, bad smells obviously and it is not bio friendly.

So that is why if we can develop a catalyst by replacing the existing catalyst by exchanging the phosphine with any other ligands which are eco-friendly I mean environmentally friendly and not toxic as example like in heterocyclic carbene or carbene we will become really very happy and it is more acceptable and why because without sacrificing the electronic properties.

Because the electronic properties of in heterocyclic carbine and the phosphenes are very much similar and basically that stabilizing and too much compromising of its catalytic activity, why it is like in heterocyclic carbenes are (bet) or also a good sigma donors as example as compared to the phosphenes and these are actually better sigma donors than the phosphine ligands so is actually better sigma donors than the phosphene ligands.

Reactivity wise NHC hydrolyzes rapidly but the aryl phosphines are not that much sensitive in water however this, however in presence of oxygen it in presence of oxygen it undergoes the oxidation reactions the phosphines so like what it is formed, it is formed like in aryl undergoes the aryl oxidation and form like the P double bond O, P O R 3 and you see the it undergoes from the oxidation from plus 3 oxidations to plus 3 to plus 5 so the electronic property is completely changed.

So in it reacts the phosphine reacts rapidly with the oxygen but NHC does not react rapidly with oxygen, so actually there is a mistake, here it will be O2 and here it will be H2O fine and another is that if you consider about the steric bulkiness the requirement of the NHC is I will later I will discuss that the N heterocyclic carbines generally are stabilized if there is a sterically hindered groups.

So for if you consider the steric hindrance the NHC are more sterically hindered the sterically demanding compared to the phosphines because in phosphines you can change if you have if you recall the Tolman angle, cone angle, Tolman cone angle is basically the quantifies the steric bulkiness of the phosphine you can tune very nicely if you need a less steric demanding phosphines you can take a smaller R groups and if you need a bulkier you can choose accordingly.

And N heterocyclic has, for N heterocyclic in other words you have a you have a stronger metal carbon bonds that is this is much stronger than the metal fostering bonds and that is why in sometimes it is difficult to replace the carbene bond by the phosphines however the vice versa is very easy.

So the metal so in the carbene complex metal carbene bond is much stronger than the metal phosphine complexes fine, so these are information because in catalytic chemistry you will see in many cases that it is claimed that yes these catalyst is designed by replacing the phosphines by the carbon so it is good to know that what the advantage and disadvantage.

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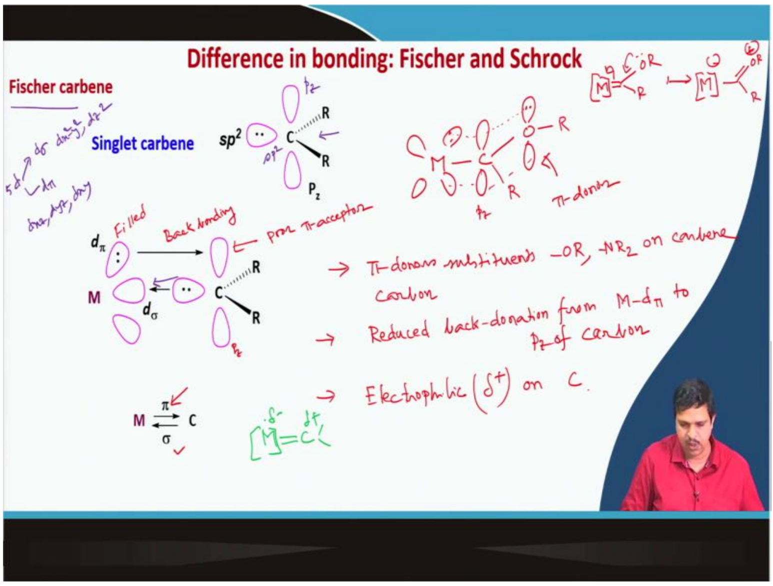
Difference in bonding: Fischer and Schrock

Fischer carbene

Singlet carbene

→ π-donors substituents –OR, –NR$_2$ on carbene carbon

→ Reduced back-donation from M-d$_\pi$ to p$_z$ of carbon

→ Electrophilic (δ^+) on C.

Now let us come to again the more detailed discussion about the Fischer carbon and we will discuss in very qualitatively by the with the help of the orbital interactions or (())(16:21) model, so in the beginning of our class we discussed that this is the singlet carbon and you would see that this is the sp2 hybridized and this is my P Z fine.

So now we have this one is at one lone pair if it is housed in the sp2 orbital and this is singlet carbene and now if we have the metal d orbital, suitable metal de orbitals so here you will see that this is if any kind of a d sigma you know that d sigma we can the 5 d orbitals we can categorize as d sigma and d pi, d sigma is d x square minus y square and d z square and d pi is d x z d y z and d x y.

So this is you see that any of the d sigma orbitals which can interact as a sigma bond fashion. So what will happen this lone pair will be donated to the empty d orbitals empty d orbitals d sigma orbitals of the metal centers like here fine here, now and you have now you have a P Z orbitals that is the empty P Z orbitals and you have a d pi orbitals filled d pi orbitals if you have then there is a possibility of back bonding like this one.

So as you in the last slides we discussed that generally in the Fischer carbene complexes you have this kind of moiety M C and you have the O R and you have any other R group here and you have this one you have the this one you have a so this is basically as a pi donor and this is empty p z orbitals of the carbon and this is the d pi orbitals like this one.

Now you have to consider that this is a poor pi acceptor, this is a poor pi acceptor and that is why what happens that to stabilize this back bonding is quite less so the pi donors substituents like O R and N R2 here on carbene carbon is essential and there is reduced back donation from metal d orbital d pi orbital to P Z of carbon orbitals, so now what happens this one there is a like this kind of extended conjugation is like that.

So if you can imagine like this one R OR so here the lone pair is there so it is like that then so OR plus and here the R so M will be more with delta minus so here what happens this carbon is electrophilic delta plus on carbon so that is why you will see that there is one sigma bond between the carbon to metal that is the donation from the SP2 orbitals electrons housed in SP2 orbitals of the carbon through the d sigma orbitals MT d sigma orbitals of the metal.

And the back bond back bonding is (quite pure) quite poor and as a result you will get the electro, the delta plus on the carbon center. So here it is in this case what happens in the Fischer carbene complexes here you will get a delta plus and you get a delta minus, so this is the bonding interaction between the in between the metal d orbitals and the carbon orbitals in the Fischer carbene complexes.

We already, I already discussed that the role of the other substituents and also the ancillary ligands because here you will see that low oxidation state metals are generally formed the Fischer carbene complexes.

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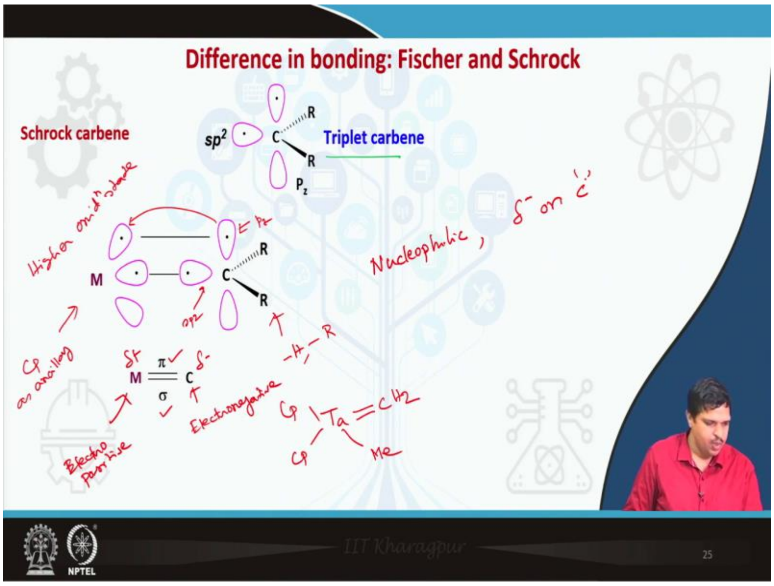

Difference in bonding: Fischer and Schrock

Schrock carbene

Triplet carbene

Now what is in will happen in the Schrock carbene, so in the Schrock carbene the carbenes are actually triplet carbenes and what is happening here the bonding interaction is quite different and that is also reflected in its electronic properties so what is happening here you will see that in this case as we already discussed that this is a generally higher oxidation state metal, transition metals and in this case R groups are generally H or any other alkyl groups and here the CP as ancillary ligands.

Now here what is happening here you see that this is the SP 2 orbitals of one electron and one electron in the p z orbitals so now similarly that if you this electron is donated to the d sigma orbitals of the P, of the metals and form a like a real covalent bond because you have also one electrons in the d sigma orbitals, now in the p z you see the d pi orbitals one electron if there is a one electron two unpaired electrons on the metal center.

One is on the d sigma and one is in the d pi then the best fit for the Schrock carbene complexes if you have a triplet carbene, so this is p z and p z so here you will also you will see that there is a bond between the metal and carbon 2 formal covalent bonds. So here the scenery you will see that this is the one sigma bond and one pi bond because one is forming like a sigma fashion d sigma and SP2 and one is the d pi and the p z orbitals.

Now here you will see that one of the real example I already discussed that this is like this one so if you have the CH2 and this is basically the methyl the tantalum you will see that oxidation state is tantalum is here plus 3 and in this case as the metal carbon carbon is more electronegative, electro negative and metal is electro positive.

So that means this is delta minus and this is delta plus, so here you will see the nucleophilic delta minus on so carbon is nucleophilic and as delta minus on the carbon so that is the basic difference in the electronic properties between the Fischer and Schrock and accordingly the reactivity difference are observed for the fissure and stock carbene complexes fine.

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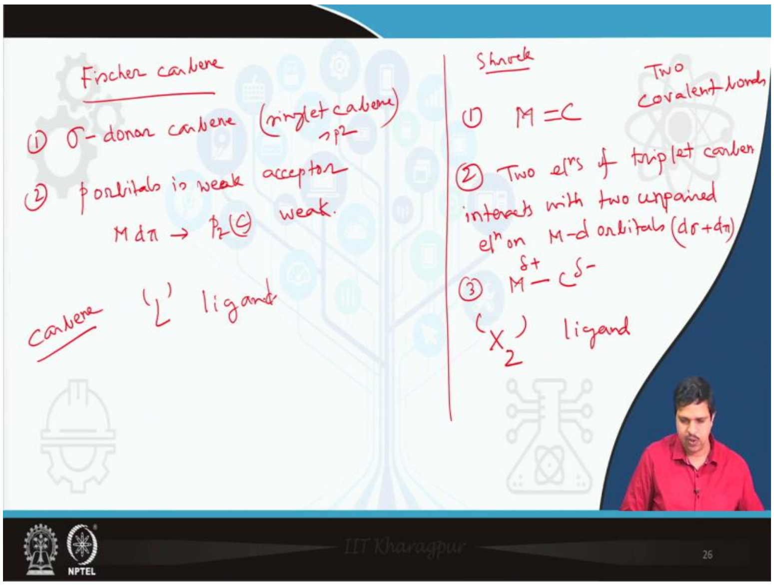


Fischer carbene

① σ- donor carbene (singlet carbene) sp2

② p orbitals is weak acceptor

M dπ → p_z(C) weak.

carbene 'L' ligand

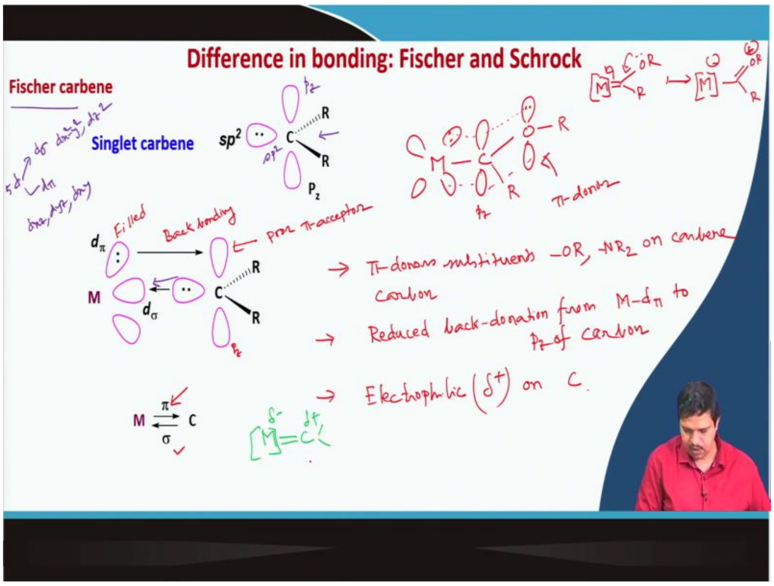
Shrock

① M = C Two covalent bonds

② Two el's of triplet carben interacts with two unpaired el^n on M-d orbitals (dσ + dπ)

③ $M^{\delta+} - C^{\delta-}$

'X_2' ligand



Difference in bonding: Fischer and Schrock

Fischer carbene

Singlet carbene

→ π-donors substituents –OR, –NR$_2$ on carbene carbon

→ Reduced back-donation from M-d_π to p_z of carbon

→ Electrophilic (δ+) on C.

So in here you will see that for Fischer carbene, I am, the qualitative orbital interactions from the qualitative orbital interactions so what are realized and or postulates we can do for the Fischer carbene and I am writing here Schrock carbene so here you will see that the carbenes are sigma donor because this is singlet and singlet carbene because these are, these lone pairs are on the sp 2 orbitals and the p orbitals is weak acceptor.

This is very important to understand so that means the M d pi to p z of carbon is not very, this is interaction is very weak interaction so that is why you will see that nucleophilic and that is the reason why you get that this is the C is with delta plus and metal is with delta minus so this is now very much understandable and here the Fischer carbene it acts as a like an L ligand L so it is the carbene here is like L so neutral ligand, just a neutral ligand.

Now in the stock carbene you see that is basically M double bond C is like a covalent 2 covalent bonds in the stock carbenes fine and here so two electrons of triplet carbene interacts with two unpaired electron of on metal d orbitals, one is d sigma and one is in the d pi, fine and as you see that there is a carbon is more electronegative so this is C minus and the is this is plus so entirely different and here as it is formed two covalent bonds.

So this actually acts as a X2 ligand so we have as a X2 ligand the triplet carbene in the Schrock complexes Schrock carbene complexes and here it is as a L ligand. So you will see that totally different in the bonding as well as in the electronic structure.

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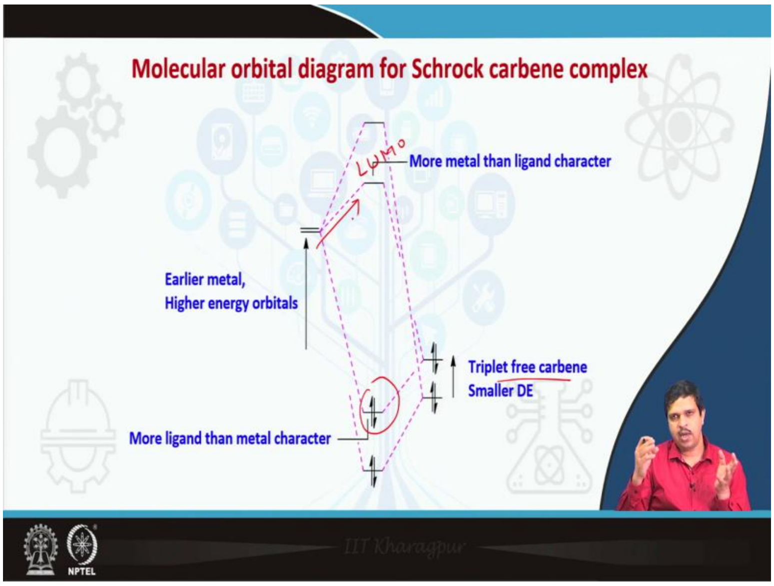
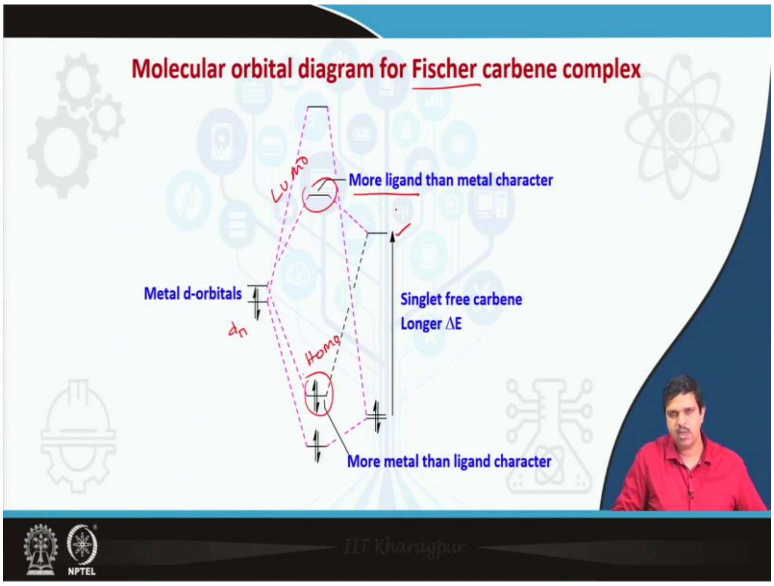

Molecular orbital diagram for Schrock carbene complex

More metal than ligand character

Earlier metal,
Higher energy orbitals

Triplet free carbene
Smaller DE

More ligand than metal character


Molecular orbital diagram for Fischer carbene complex

More ligand than metal character

Metal d-orbitals

Singlet free carbene
Longer ΔE

More metal than ligand character

So if you see the very simplified molecular orbital diagram of the Fischer carbene complexes so here the metal d orbitals that is you will consider as a d pi here and this homo you will see that this one is the more metal like character than the ligand because you see here that this is a like a more close to the metal the orbitals and the lumo here this is close to the lumo of the free singlet carbene and that is why the lumo is more ligand character than the metal character.

So here this is the lumo and this is the homo, so in a homo the character of the homo is more like a metal like so that means the it is has more contribution from the metal d orbitals and lumo would be like more like a ligand character, so this is for the Fischer type of carbene and entirely different in the your Schrock carbene here you see that homo will be in the homo.

It will be like a more ligand character like you will see that this is the more very close in energy to the triplet free carbene orbitals the homo of the triplet free carbene orbitals and the lumo that is the this one you will see that is a more like a metal like because you will see that this is very close to the metal d orbitals.

So the that is why the reactivity is much more different in the Fischer and Shrock carbene you see the lumo in one case lumo is more metal like character like in the Shrock carbene and in the earlier case you will see that it is mode like ligand type character that is for the Fischer carbene complexes.

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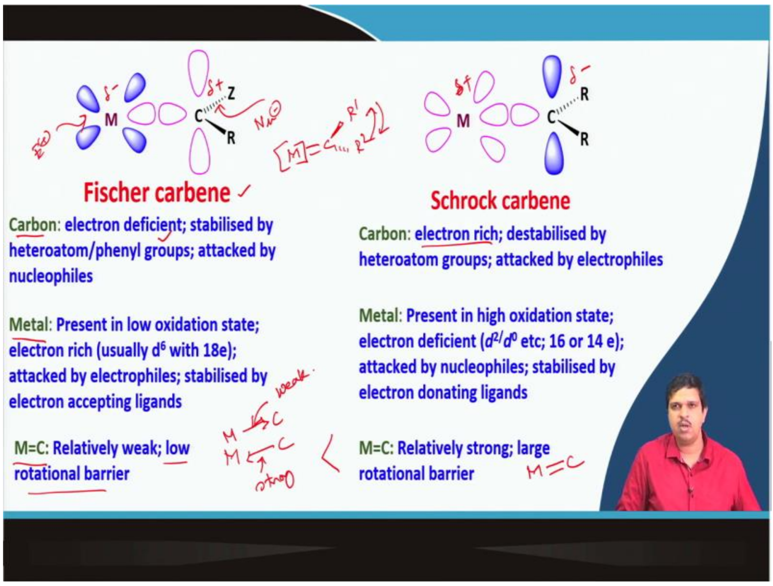

Fischer carbene ✓

Carbon: electron deficient; stabilised by heteroatom/phenyl groups; attacked by nucleophiles

Metal: Present in low oxidation state; electron rich (usually d^6 with 18e); attacked by electrophiles; stabilised by electron accepting ligands

M=C: Relatively weak; low rotational barrier

Schrock carbene

Carbon: electron rich; destabilised by heteroatom groups; attacked by electrophiles

Metal: Present in high oxidation state; electron deficient (d^2/d^0 etc; 16 or 14 e); attacked by nucleophiles; stabilised by electron donating ligands

M=C: Relatively strong; large rotational barrier

So from our discussion about the orbital interaction the electronic properties now it is very much clear that what are the electronic properties on the carbene centers and the metal centers and what are the basic properties of the metal carbon bond now this is the Fischer carbene complexes we already discussed that carbon is electron deficient that means it is act as a C delta plus d delta minus and why it is deficient, we have already discussed this stabilized by heteroatom that is the oxide, amide like that and is attacked by the nucleophiles.

So here this is it will attack very easily here and here the electrophiles like that and metals here it will act as a electrophiles and it is as it is a low oxidation state so it generally stabilized by electron accepted ligands as example carbene monoxide or phosphenes and in the Fischer carbene you will see that it is basically a in between single and double bond because you will see this sigma donation is strong and but the back bonding that is this one is weak.

So that means you will compare to the Schrock carbene where you see that you have a two covalent almost covalent bonds so here the reactivity the metal carbon bond in Schrock carbene is quite strong then the Fischer carbenes so and as a consequence you will see that the low rotation barrier is observed for metal carbon but in the case of Schrock carbene it is the large rotational variant that means so if you have like this one R1 and R2 it can exchange because the metal carbon bond is very low but for Schrock carbene it is not possible.

So here the exactly reverse of the Schrock carbene so this is electron rich that means this is delta minus and delta plus and here you see that we already discussed about the why the difference it is in on one case delta minus and in one case delta plus on the carbon and exactly reverse on the metal centers, fine.

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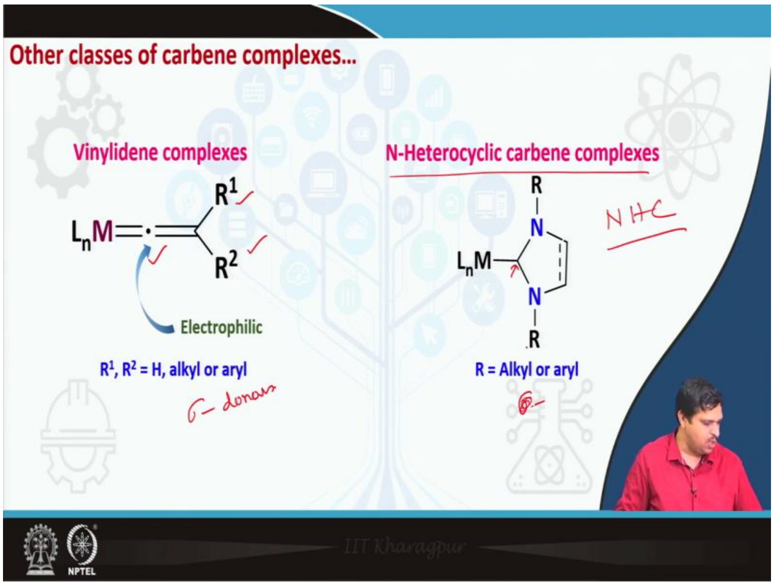
Other classes of carbene complexes...

Vinylidene complexes

Electrophilic

R^1, R^2 = H, alkyl or aryl

σ– donors

N-Heterocyclic carbene complexes

NHC

R = Alkyl or aryl

σ–

So these are the other classes of carbene complexes where you will see we will discuss later that is the vinylidene complexes this is another carbene complexes and this is again the carbon center is electrophilic and here R1 and R2 are more like alkyl aryl so the highly sigma donor type of ligands so those are all sigma donors ligands so here also alkyl and aryls here and here you will see this is a very special type of carbenes this we call NHC N heterocyclic carbene we will discuss in the later classes this is a very special category of carbene ligands.

So here you see that this carbene this is the carbene carbon this is and this kind of design is very much important to stabilize the carbene why it is so, we will discuss later, you just now try to understand what the versatility in the metal carbene complexes.

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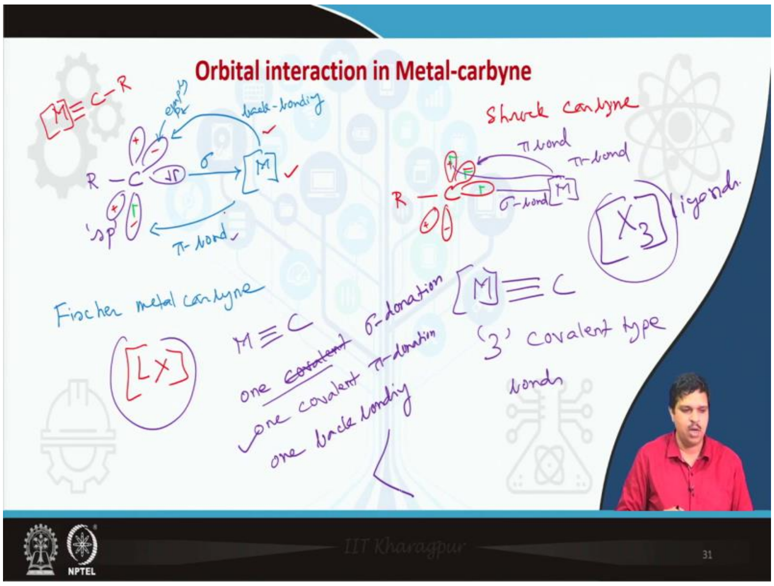

Orbital interaction in Metal-carbyne

So similarly the about the metal carbene we have also the metal carbine complexes, fine so this is the metal carbine complex so if you understand the metal carbene complexes the orbiting interaction you will be able to draw the qualitative orbital interaction for metal carbine also what are they let us draw with me then you will understand.

So this is the metal carbine fragment so let us set at this one so this is this you understand this is the sp hybridized carbene center, so you have the this one and you have, now and so this is the two P orbitals, one is so I can let us say plus and plus minus minus and you have another electron that is let us say here.

Now consider the metal orbitals like here so this can donate to the d sigma of the metal so this is basically the sigma bond formation and this one again is a pi bond formation and this is back bonding possible because you will see that this is my empty PZ so there is a from the field d orbitals d pi orbitals to the empty PZ orbitals so back bonding possible.

So this is the called the Fischer metal carbyne complexes. So if you consider that up to this, this one and this one so it is a basically L type of ligand, the neutral ligand like just like a Fisher carbene and if you consider the pi bond so this is basically L x so that is why here the carbine where it is regarded as a L x type ligand in Fischer metal carbine complexes.

Now you consider the Schrock type of carbene ligands, carbine complexes, what are the basic difference again you draw the carbine so here, so plus minus plus minus now what are the electronic arrangement so three electrons total I have to arrange so this is one electron here, one electron here and one electron here, fine.

Now if I have a metal center now the what are the possibilities, the possibility that this if there is a three unpaired electrons then it can form one sigma bond here through the d sigma of the metal centers, now here another pi bond and the another pi bond here so you see that three bonds are possible.

So here metal carbon, here you see that three covalent type bonds and here you see that one covalent and other two here this is the covalent sigma donation one pi donation, one back bonding and that is why this is regarded as X3 ligand, so I hope you have understood the difference between the X 3 and x, L x.

So here I am see that one covalent bond and this is actually this we should not know this is one covalent, this is the one covalent real, this is we can, we should not tell this is we can simply tell the sigma donation to avoid the confusion, so here you will see one covalent that is why this L x is there so L so here it is L x type and here it is X 3 type in the Schrock carbine complexes.

So obviously the bond string is much higher for the metal carbyne in the stock type of complexes compared to the Fischer which is very similar to the metal carbene complexes also so bonding introduction is very much similar as metal carbene complexes so I will not discuss in more depth, however the if you understood the concept of the metal carbene you can apply to the metal carbyne complexes also.

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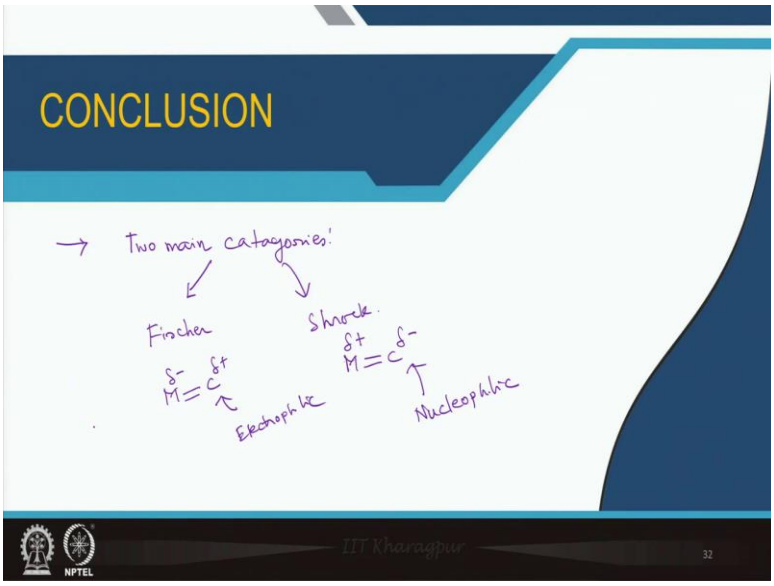

CONCLUSION

→ Two main catagories:

Fischer

$\overset{\delta-}{M}=\overset{\delta+}{C}$ ↖ Electrophilic

Shrock.

$\overset{\delta+}{M}=\overset{\delta-}{C}$ ↑ Nucleophilic

So in conclusion we have, we can list out that what we are the conclusion from the today's lectures, the first one is that the two main categories of the carbene complexes, one is the Fischer and one is the Schrock and the Fischer carbene complexes you will see that this is carbene is electropositive and here it is electronegative sorry, the carbene is delta plus and in the metal it is delta minus and in the Schrock exactly it is opposite.

So here it is delta minus and it is delta plus and that is why the carbon center is electrophilic and here it is nucleophilic in nature. So you understand that how difference it is and also we have understood the qualitative molecular orbital diagram of the Fischer and the Schrock and you see that lumo character of the lumo and homo orientally different as actually the just reverse in the Schrock carbenes complex to the compared to the Fischer complexes.

So in this class we have understood that what is the basic difference between in the bonding and the orbital interaction in the Fischer and Schrock type of carbene complexes and we have understood that why the carbene center is totally different in view of the electronic properties in for the Fischer and Schrock type of complexes.

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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
- Organometallic chemistry and catalysis by Astruc, Springer, 2007.
- Basic Organometallic Chemistry by Gupta and Elias, University Press, 2010.

So these are the references you can consult, the all very popular textbooks and in the next class we will be discussing about the basic synthetic protocols of the metal carbene both Fischer and the Schrock type of carbene complexes also the metal alkylidene type of complexes and then we will discuss about the reactivities.

We will also try to introduce the one of the very popular carbene complexes that is the metal in heterocyclic carbene complexes as you see the basic structure of the graphs catalyst, generation graph you will see that one of the phosphenes has been substituted by the N heterocyclic carbene complexes.

So it is important to understand about the N heterocyclic carbene complexes, this is becoming very popular in various domains. So thank you very much and then we will again see you in the next class with the continuing our discussion on the metal carbene, thank you until then bye bye.