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

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Lecture 36

General Synthetic Protocol of Metal-Carbene Complexes

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Lecture 36: General synthetic protocol of Metal-carbene complexes

Hi. Welcome to our classes. So, in the last class we discussed about the general structure of the metal carbene complexes, the category of the different metal carbene complexes like Fischer, Shrock, Coral (())(00:43) venailidine complexes, mixed Fischer, Shrock type carbene complexes.

And then we have discussed quite elaborately about the different type of metathesis reactions where the metal carbene complexes act as an efficient catalysts and we have realized that the application is versatile and you will see that it acts as a single key for multiple locks. That means acts a single catalyst can do various type of alkene metathesis reactions.

Today we will discuss about the general synthetic protocols for the metal carbene complexes, mainly, Fischer, Shrocks carbene complexes. And then we will study the reactivities following classes and then we will come to the the special reactions which is actually the polymeration reactions to get the different hydrocarbon polymers, where metal carbene acts as catalysts. So, let us discuss first the metal carbene complexes, the general synthetic protocols. Why it is important?

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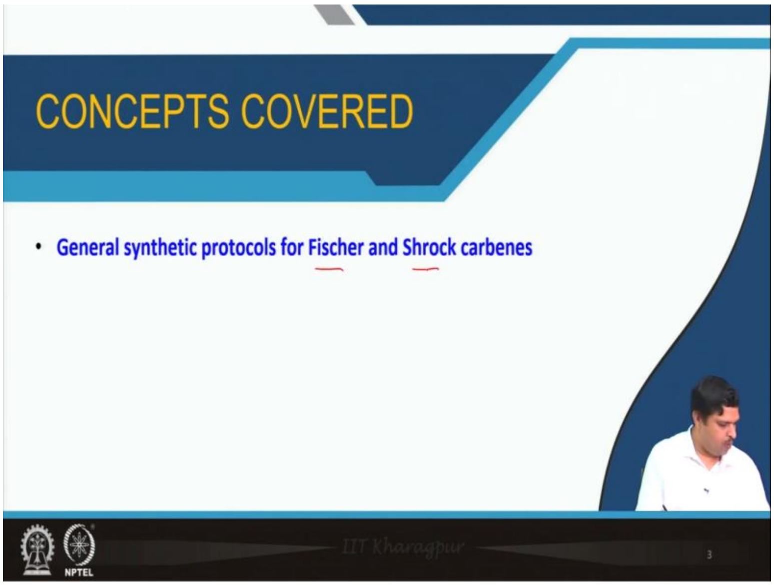

CONCEPTS COVERED

- General synthetic protocols for Fischer and Shrock carbenes

Because you know that before doing the any applications, we have to synthesize, we should know what are the synthetic protocols. If I need to design a new catalyst, how we will synthesize, how we will choose the precursors of the different carbene, what will be the reaction conditions.

So, those fundamental aspects we have to realize first, so, it will give a kind of a guideline to make the or to follow the strategy of different metal carbene synthesis. So, in this class, today's class, we will offered the concept of general synthetic protocol for both the Fischer and the Shrock carbene complexes.

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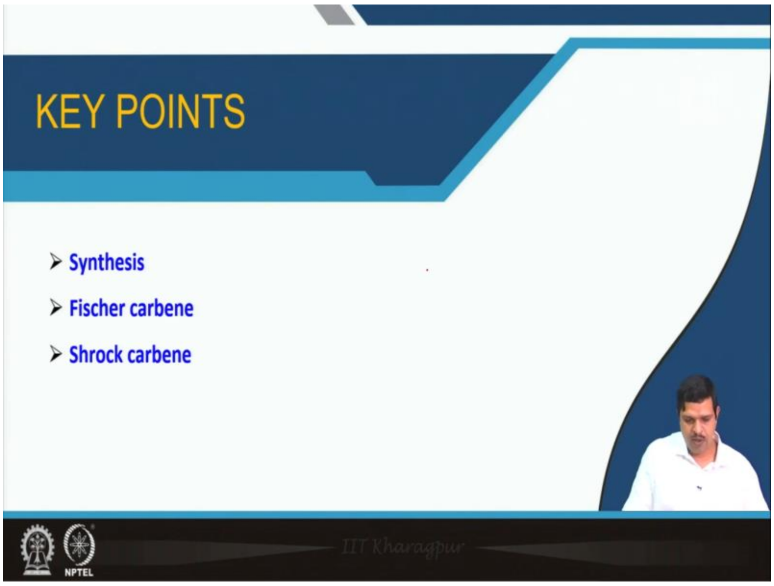

KEY POINTS

- Synthesis
- Fischer carbene
- Shrock carbene

So, the key points will be Fischer, Shrock, synthesis, general strategic synthesis.

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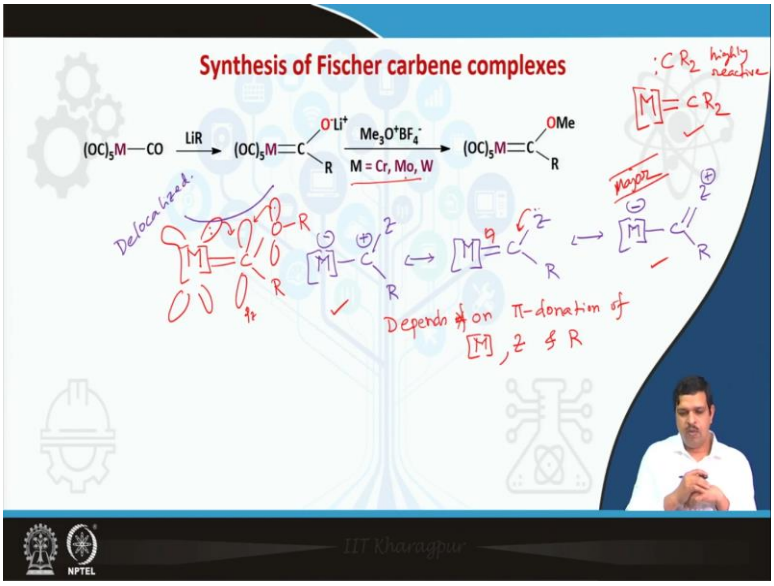

Synthesis of Fischer carbene complexes

So, we know that generally, the two type of carbene complexes, one is the Fischer and one is the Shrock carbene. And we have realized that it is the general structure is like that. So, is formally there is a two the bonds between metal and carbon and you know that CR2 it is a free carbene. This is highly reactive.

We have already discussed very elaborately and you show that this free carbene CR2 can exist as singlet and triplet and this carbene complex, these three carbons are highly reactive and it gets stabilized by forming the complex with metal fragments, definitely with suitable metal species, precursor and form this kind of metal carbene complexes.

And we know that now difference between the Fischer and Shrock carbons. So, Fischer carbons you see that it form generally from the low oxidation state, as example like middle transition metals with low oxidation state and middle or late transition metals and the Shrock carbons are generally early transition metals with high oxidation state.

And the formally two covalent bonds in Shrock carbons and Fischer carbons is basically one is the covalent bond and one is the pi back donation and you see the metal carbene bond for Shrock carbene is quite strong and whether the Fischer is not that much stable that much strong.

And accordingly, the polarity of the metal carbon in Fischer Shrock is exactly opposite, like for Fischer we know now that it in the Fischer carbene complexes the C plus is actually the delta plus and in the Fischer carbene in the Shrock carbene it is delta minus. So, the reactivity of the carbene is metal carbene is very much different, actually the reverse in the Fischer and Shrock.

Now, how to synthesize it? So, this is generally synthesized by a metal carbene complexes. Actually, that this is the first synthetic protocol followed by the EO Fischer and I will give the specific example of the first Fischer carbene complex is synthesized by EO Fischer in 1964.

So, you see that, here, the Fischer carbene complexes, the general structure is like this one. O R and this R, we know that we already discussed that this is the loan pair like oxygen nitrogen synthesis loan pair, that is a hetero atom and it is a fit P orbitals and this is the P Z orbitals, (())(06:55) P Z orbitals and it has a D orbital, so, perfect matching.

And that is why it can this PZ orbitals, it can accept electrons from here to here and it is basically behave as a delocalized between M C O. So, fully delocalized system and make it thermodynamically stable system. So, that is why if you make consider the Fischer complex like say Z R like that one, so, it can.

So, I should not put the equilibrium sign, actually, I should put the this is I want to see the two different canonical structure. So, one is possible is this one M minus C Z and this is R. So, this is the plus and another one is. So, this has a loan pair and so, what is a heteroatom like oxygen and nitrogen.

So, this will be plus and this will be minus. Now, so, you see here this say this is. So, it is basically formed like this one and that one. The contribution of this one is the major, however, the contribution of the two canonical forms, this one and this one depends on the pi donation of, what? Any idea? The pi donation of M B orbitals M Z and obviously the R. So, depends on the nature of the metal Z and the heteroatom and the also the R.

So, however the major contribution is this one, where you will see that Z from delta plus and M is delta minus. And generally, the Fischer carbene complexes are more common with chromium, molybdenum, tungsten. However, it is not limited, it is ruthenium, iron, others, but this is the first synthetic protocols. So, how you will go in more detail about the synthesis.

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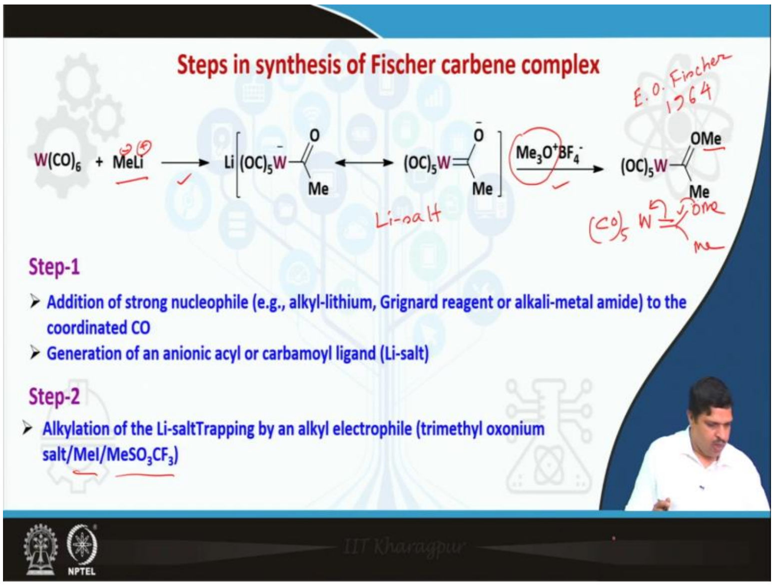


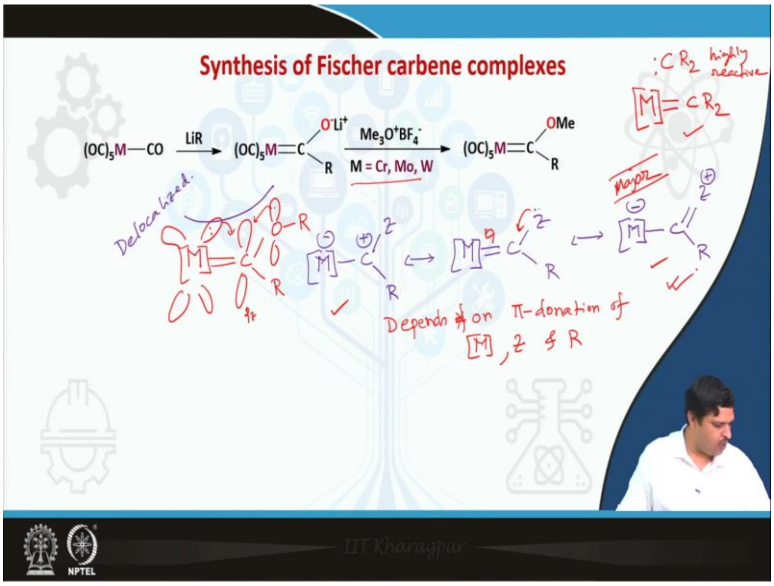
Steps in synthesis of Fischer carbene complex

Step-1

- Addition of strong nucleophile (e.g., alkyl-lithium, Grignard reagent or alkali-metal amide) to the coordinated CO
- Generation of an anionic acyl or carbamoyl ligand (Li-salt)

Step-2

- Alkylation of the Li-saltTrapping by an alkyl electrophile (trimethyl oxonium salt/MeI/MeSO$_3$CF$_3$)



Synthesis of Fischer carbene complexes

So, here you will see that this is the actually the first Fischer carbene complexes, synthesized by E O Fischer back in 1964. And see the strategy, strategy. So, you need a metal carbamoyl here, like a tungsten carbamoyl and then you need an alkyl lithium. So, M minus Li plus. So, addition strong nucleophile alkyl lithium or even Grignard reagent or any alkali metal amide.

And it attack on the carbonoyl carbon and form the lithium salt of the anionic acyl or carbonoyl ligand. And the second step. That is the first step and this the second step is that the methylation of the lithium salt by the alkyl electrophile. So, here, you will see this O Me3 plus is a very good alkaline agent. In many cases in laboratory, we use this reagent to alkyl it.

However, it is not limited, you can also use the other alkylating agent, methylating agent. As example, methyl iodide or methyl triplet you can use, no problem. And then what you would see? You will get the methylated the Fischer carbene complex. So, it will convert to the anionic to the neutral complex, neutral metal carbene complex. And this is the synthesis of the Fischer carbene complex. It is the first report of the Fischer carbene complexes.

So, it is basically the CO5 W OMe and Me we saw. So, this has been written in other form actually. So, this is basically the O plus, sorry, O plus O minus. So, as we discussed it here, same thing. So, you see that when generally two steps one step is involving the a strong nucleophile, generally alkyl lithium and then using a alkylating agent, to alkylate the lithium salt.

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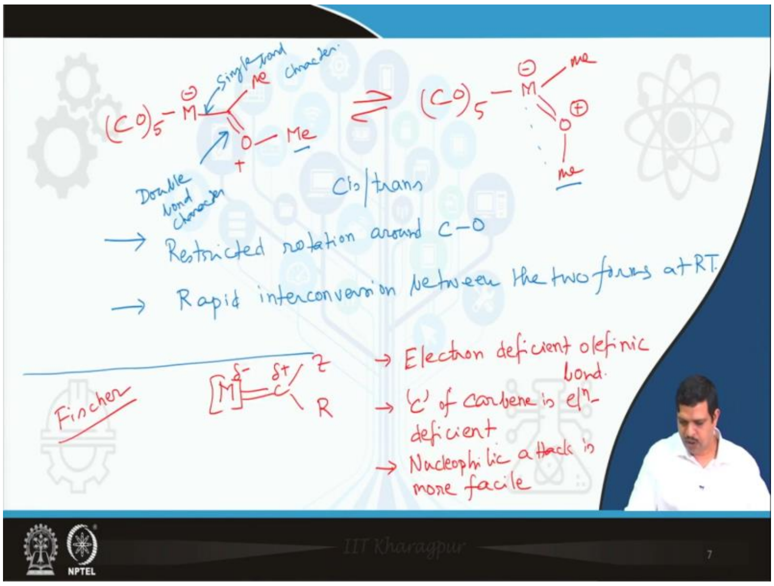


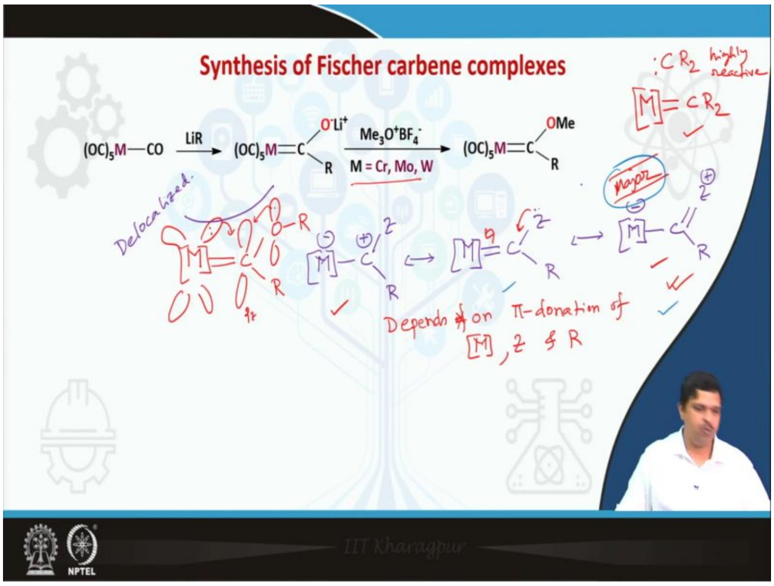
→ Restricted rotation around C–O

→ Rapid interconversion between the two forms at RT.

→ Electron deficient olefinic bond.

→ 'C' of carbene is el^n- deficient

→ Nucleophilic attack is more facile



Synthesis of Fischer carbene complexes

$$(OC)_5M{-}CO \xrightarrow{LiR} (OC)_5M{=}C(O^-Li^+)R \xrightarrow[M\,=\,Cr,\,Mo,\,W]{Me_3O^+BF_4^-} (OC)_5M{=}C(OMe)R$$

So, here one thing to note that in the Fischer carbene complexes is good to know, although it is not the synthesis slide but it is good information and good to understand that this one. So, as I already told that this is the major contribution of the canonical form between the two possible, between the three possible canonical forms, due to the pi donation of the oxygen, pi electrons.

So, here you see carefully that two type of geometrical isomers are possible. This is one and any idea, which one is the other one? You can guess it. You see the double bond character between, while it is between the carbene and oxygen. So, then you will realize that which one will be the other geometrical isomers. So, here you will see that like this one. So, now it is very clear that here C trans type of isomers are possible around the carbon oxygen double bonding.

And due to the double bond character, here you will see this is double bond character. However, this one is the single bond character. The single crystal extra x-ray crystallography nicely proves about this single and double bond character looking at the corresponding bond density. So, here thait is why you will see that restricted rotation around CO because as it is a double bond character, so, it cannot rotate freely. And you can very nicely monitor by the proton NMR spectra. However, there is a rapid inter conversion between the two forms at room temperature.

But if you cool down, let us say you record the NMR at minus 40 degree Centigrade, you may get two type of signals of this methyl groups. One will be this side, near the metal and another one is the way of from the metal center. So, you will get a two type of signals for the methyl groups, if you note down the temperature.

So, here, you will see that this also proves that the contribution of this canonical structure, if you compare this one, this one and this one, that this one is actually the major contributor. This is good to know while designing any metal carbene complexes. So, now we understood that how we make a simple Fischer carbene complexes by from starting from a metal carbonyl complex.

Now, as we already discussed that and we already know that the metal carbene complexes like this one that is Z R R, so, this is delta plus and this is delta minus for the Fischer type of metal carbene complexes. So, this is basically a electron deficient polyphenic bond. So, obviously, it is not carbon carbon olefin but it is an oliphenic type of bond. Why no?

Where one carbon is replaced by one metal fragment. So, thait is why this carbon is electron deficient, the carbon of the carbene is electron deficient in nature. That means it reacts with nucleophile. So, nucleophic attack is more fascile. I think it is very clear now for the Fischer carbene complexes. So, it is now very clear that what I am what I am telling you.

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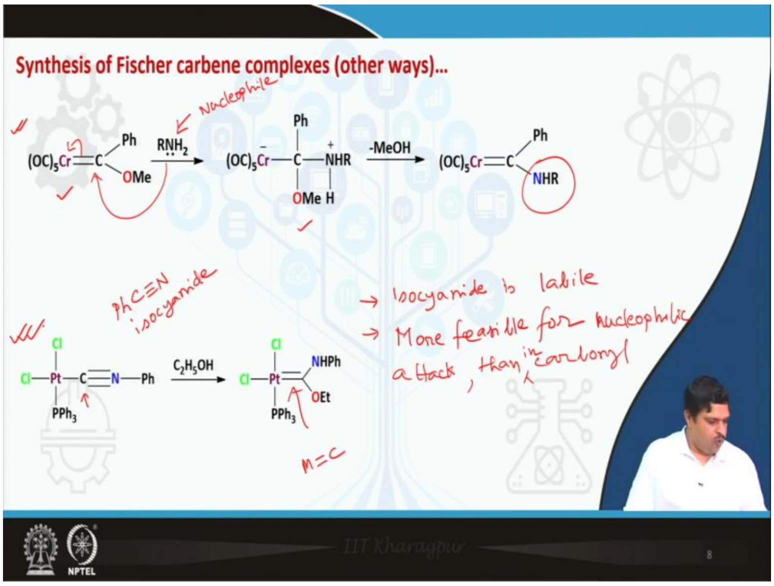
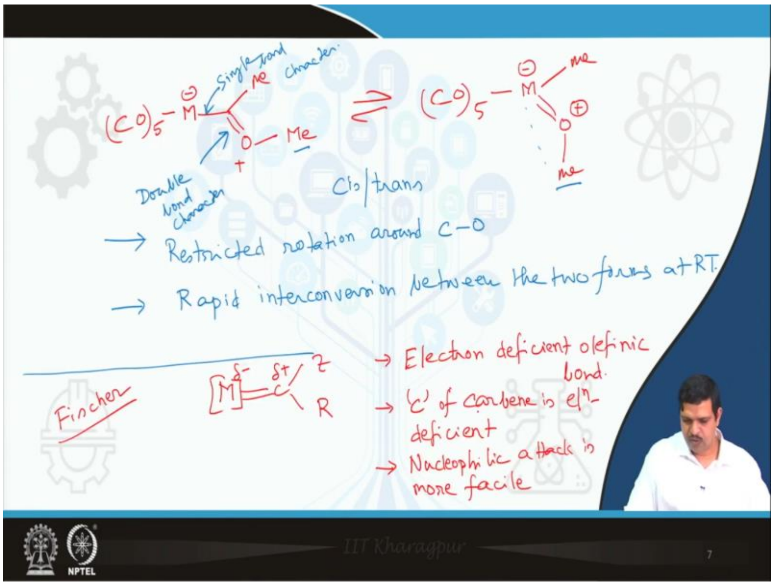

Synthesis of Fischer carbene complexes (other ways)...

→ Isocyanide is labile

→ More feasible for nucleophilic attack, than in carbonyl



→ Restricted rotation around C–O

→ Rapid interconversion between the two forms at RT.

→ Electron deficient olefinic bond.

→ 'C' of carbene is el^n-deficient

→ Nucleophilic attack is more facile

So, now you see that what may be the, what strategy we can follow to make other type of Fischer carbene complexes where the hetero atom is not the oxygen. Like here you will see following this concept, here you will see what it has been done, you tick this Fischer carbene complexes as a starting material and then you react with amine and amine has a loan pair.

So, it is basically acts as a nucleophile, is very common know that amines can act as a mucophile and so, its reacts with this amine reacts with nucleophile and so, is basically reacts with here and then it is become delta plus and it becomes minus. So, this is the, see this is the species.

And then the elimination of methanol. And you form the, this is new Fischer carbene where the heteroatom is amine. So, here you will see that this is a very nice synthetic strategy with the help of the carbene, electron deficient nature of the carbene of metal carbine. And not only that we can also use this kind of precursor where the, here, it is basically that this is also fantastic ligand and this is called the phenyl isocyanide and the category of this kind of ligand is isocyanide. It is routinely used to make the precursors of different metal complexes.

And this one is very is a labile and also it is more feasible, the these ligands, isocyanide is labile, very labile, very weak bond and more feasible for nucleophelic attack than in carbonyl. So, very easily the necrophile can attack on the carbon here and you can get the corresponding metal carbene bond, very simple one simple strategy. So, here, you will see that this one you can see the first one is the strategy one, this is the strategy two, this is the strategy three. So, different type of precursor you can take it and to make the other Fischer carbene complexes. It is quite easy and that is why it is so popular.

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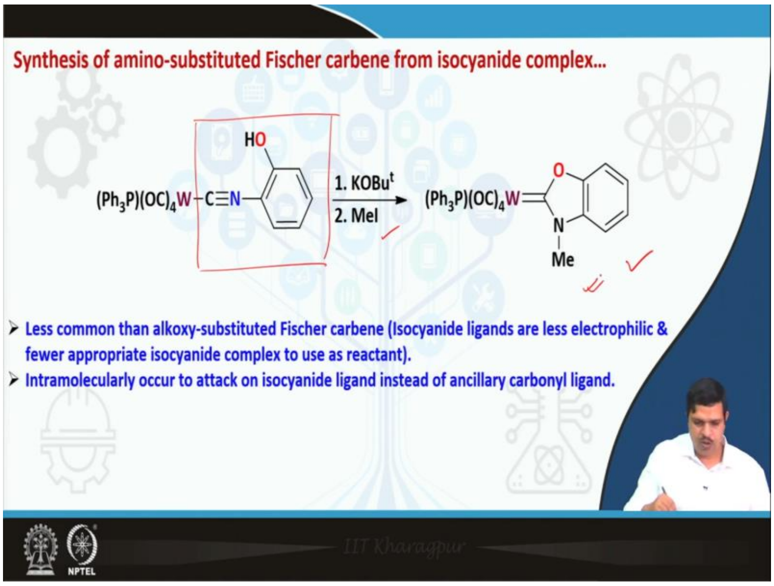
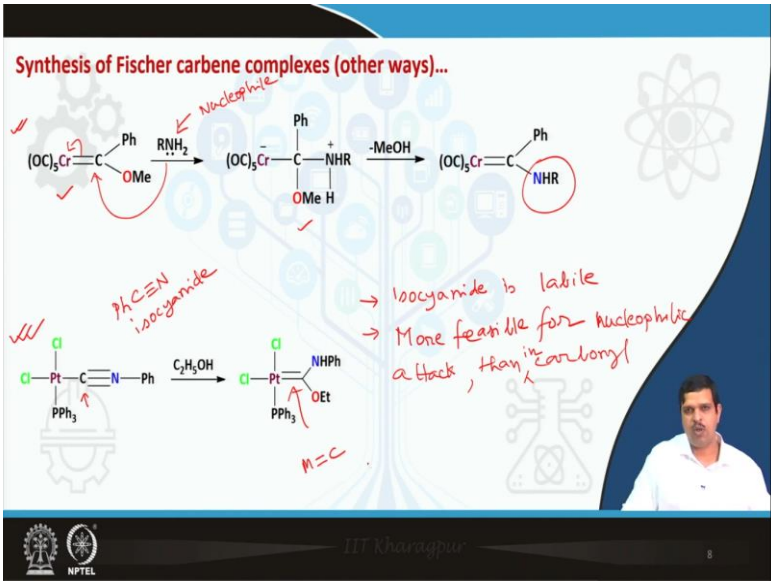


Synthesis of amino-substituted Fischer carbene from isocyanide complex...

- Less common than alkoxy-substituted Fischer carbene (Isocyanide ligands are less electrophilic & fewer appropriate isocyanide complex to use as reactant).
- Intramolecularly occur to attack on isocyanide ligand instead of ancillary carbonyl ligand.



Synthesis of Fischer carbene complexes (other ways)...

→ Isocyanide is labile
→ More feasible for nucleophilic attack, than in carbonyl

So, these are another type of metal carbene complexes where you will see that here is basically the this is nothing but isocyanide complex, no? But it is a functionalized isocyanide ligand and you are using a strong base and you make this kind of a metal carbene complexes. It is basically extension of this one, is nothing new, the second one.

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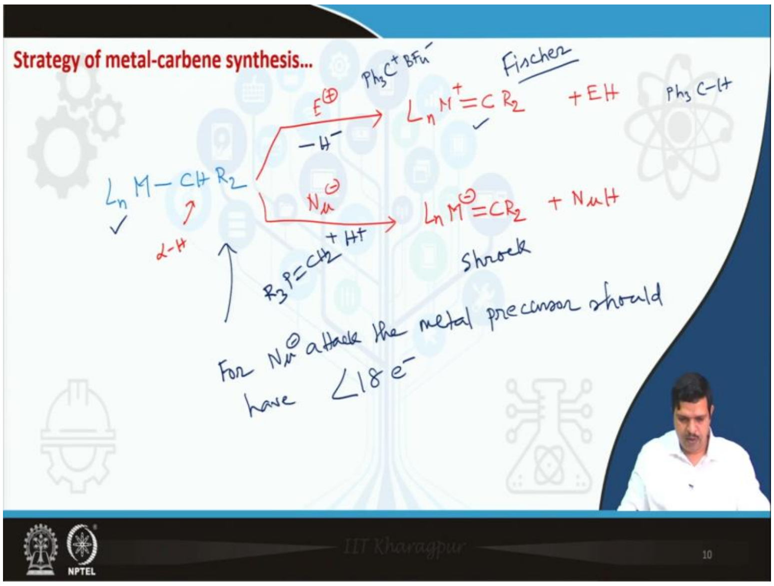
Strategy of metal-carbene synthesis...

So, here you will see the strategy of the metal carbene complexes, I will just write down here in a very strategic way. So, no need to remember. So, you just see the strategic way to make the metal carbene complexes from a another category of the precursors. What we are doing? I am doing here. So, here you will see I am taking the metal alkyl complex where the alkyl has a alpha proton. So, this is the alpha proton. This is alpha proton. Now, what I am doing?

Now, if I attack with a electrophile, e plus then what will be the reaction and the product? So, you will get this kind of a. So, I am writing in a very general way. And you will get the E H. Now, if you do with nucleophile then what will happen? Ln M minus double bond C R 2 and Nu.

So, as example of electrophile is maybe the ph3 C plus. You know that take this one. So, c t s 3, the triphenyl carbene cation is a very good hydride or alkyl abstructor. So, if you use then what you will get? Thus, H will be deprotonated, the alpha H will be eliminated it will be taken by c p s 3 plus and form actually this one and you will get this carbene complexes.

So, you see this is generally you will get the Fischer type carbene complexes. Now, if you in the in last, the second case that where you are adding the nucleophile, what will happen here you see. As example like nucleophile you can take is as a base like R3P double bond C H 2. So, this is like a base it act which will act as a nucleophile then you will get this kind of carbene.

And generally, this strategy is followed to make the Shrock carbene complexes. So, it is here you will see, you are adding nucleophile that is the more electrons that is why for this one the precursor for the Fischer complexes, the for second one, the precursor should be that is for nucleophile attack, the metal precursor that means this one should have less than 18 electrons, that is the total valency electrons. Or if it is 8 electron then some ligand has to come out to make the coordinately unsaturated and also to make the system less than 18 electrons.

So, that the nucleophile can attack on the metal center. So, I am sure it is very clear now. So, these are the strategies to make the Fischer and the Shrock carbene from any the alkyl metal alkyl complexes, either electrophile or nucleophile. Here, what we are doing? Here, it is as a H minus it is coming and here it is you see as a H plus it is coming. Hydride or the proton, hydride abstract or the proton abstractor.

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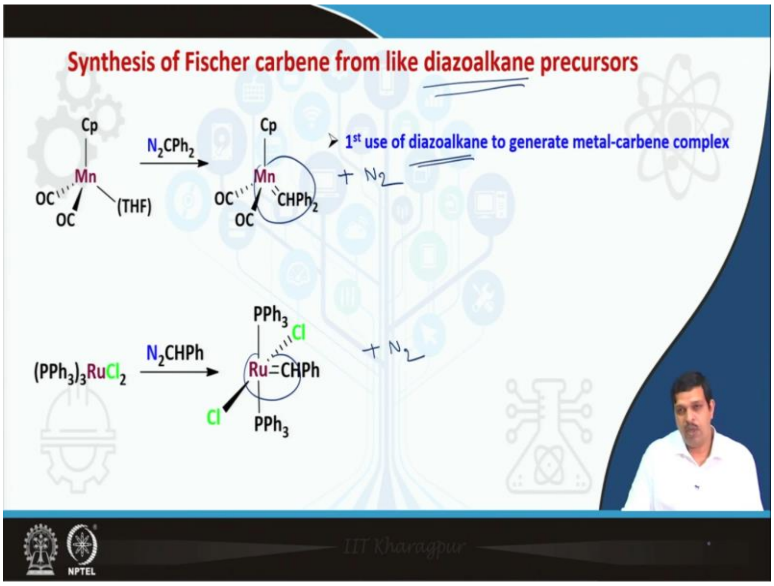

Synthesis of Fischer carbene from like diazoalkane precursors

- 1st use of diazoalkane to generate metal-carbene complex

So, another strategy of the Fischer carbene complexes is, it is a very popular and very clean reaction that is the with the diazoalkane compound, the driving force is the formation of the nitrogen. So, if varieties of precursors you can take. Very simple precursor and very clean reaction, very easy reaction.

You make the corresponding alkyl, diazoalkane and you will get the metal carbene bond here. So, this is one of the very clean synthetic strategy. So, we have discussed now total four synthetic strategy to make the Fischer type carbene complexes. And you can make in your own without much complexity. So, it is so easy and thait is why it is so popular.

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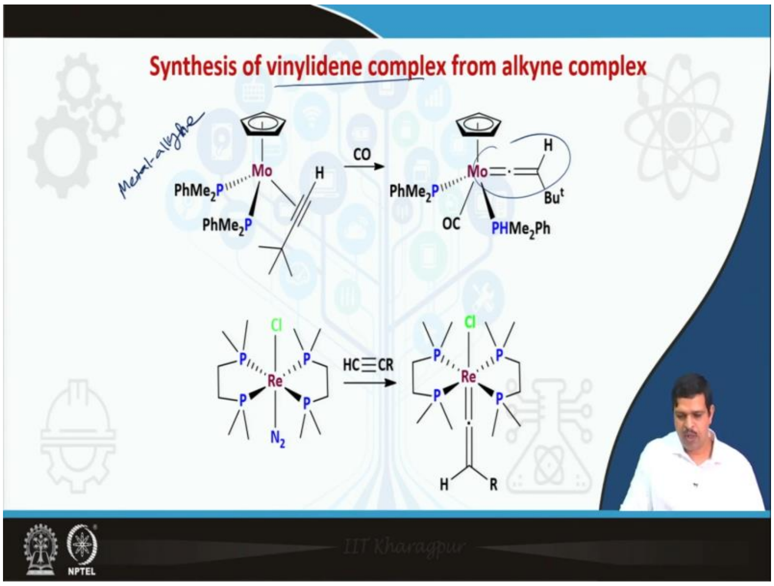

Synthesis of vinylidene complex from alkyne complex

So, very similarly, you can also make the vinylidene complex, we already discussed in the in the earlier classes, the classification of the Fischer, Shrock and vinylidene. And the vinylidene complex are generally synthesized from the alkyne complexes, alkyne pi complexes. And here you will see that in presence of carbene monoxide, it forms the vinylidene fragment. So, this is a root to make the vinylidene complexes from the alkyne complexes.

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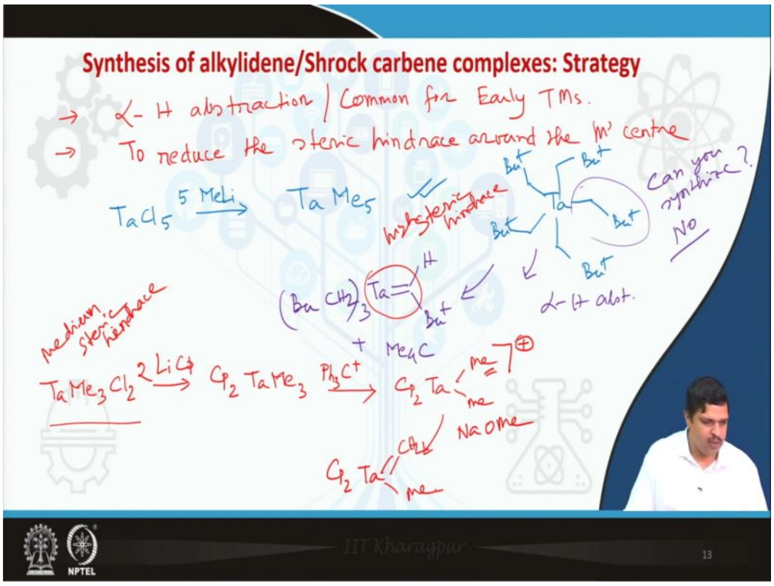

Synthesis of alkylidene/Shrock carbene complexes: Strategy

→ α- H abstraction | Common for Early TMs.

→ To reduce the steric hindrace around the 'M' centre

So, now I will come to the Shrock carbene. Shrock carbene is also regarded as a alkaline complex and we already discussed about what is the basic properties of the Shrock carbene.

So, Shrock carbene is generally formed by early transition metals and with high oxidation states. So, what will be the synthetic strategy to make the metal carbene complexes?

So, we already discussed just 2 3 slides back about the alpha H abstraction. And this alpha H abstraction for early it is common for early transition metals unlike the late transition metals of transition metals. And it is actually done for to reduce the steric hindrance around the metal center.

So, let us see. I will give one comparative, a very interesting example. So, like here, if you take the tantalum, pentaclhoro tantalum and you react with methyl lithium five equivalent and you can nicely prepare tantalum, this one. No problem, you can synthesize it. But if you increase the steric crowding around the tantalum, let us say you form butyl group, tertiory-butyl group, can you synthesize it? Any idea? Can you synthesize this one? Any idea?

Now suppose, the way we have synthesized with five equivalent of methyl lithium and if I can use here that this group is called new pentile group, new pentile group, if five equivalent of lithium salt of new pentile then can use synthesize it? The answer is no, cannot. It undergoes the different and interesting and beautiful reactions. This is alpha H abstraction, alpha H elimination. So, that and what the outcome?

So, you will get the butyl 3 CH2, sorry, butyl CH2, butyle CH2 3 tantalum and here H butyl and you will get the Me 4 C. So, here you will see that it will undergo the spontaneous, it is not stable, you can undergo spontaneous alpha H abstraction, elimination and then you will form this metal carbene complexes. Similarly, if you start from tantalum Me 3 that trimethyl and dichloro and reacts with Li Cp, two equivalent of Li Cp, you will get this one and then you can synthesize it.

Now, if you use any alkyl abstructor Cp 2 alkyl abstructor like the C Ph 3 plus like this one then what we will get? Cp 2 Ta Me Me. That means you will get this one. So, it is basically in we are increasing the acidity of this methyl proton. So, thier steric hindrance is not much. So, here is a it happen due to the steric hindrance. Now, what I am doing?

We hear steric hindrance is medium. So, medium, high steric hindrance. And here we have medium steric hindrance. So, what we are doing? We are increasing the acidity of this that CH, the methyl hydrogen by putting cationic charge on the methyl on the tantalum center. Then what will happen?

It will in presence of strong base, as example sodium methoxide, so, it will form this one Cp 2 Ta, tantalum CH2 and the methyl. So, you will see these are the general synthetic strategy to make the Shrock carbene complexes. You have to put the steric hindrance around the metal center. If there is not much steric hindrance, you have to also can induce, forming the carbene complex by putting cationic charge to make that proton, the alkyl protein is acidic, the alpha H proton and then it can undergo the carbene formation reactions in presence of a strong base.

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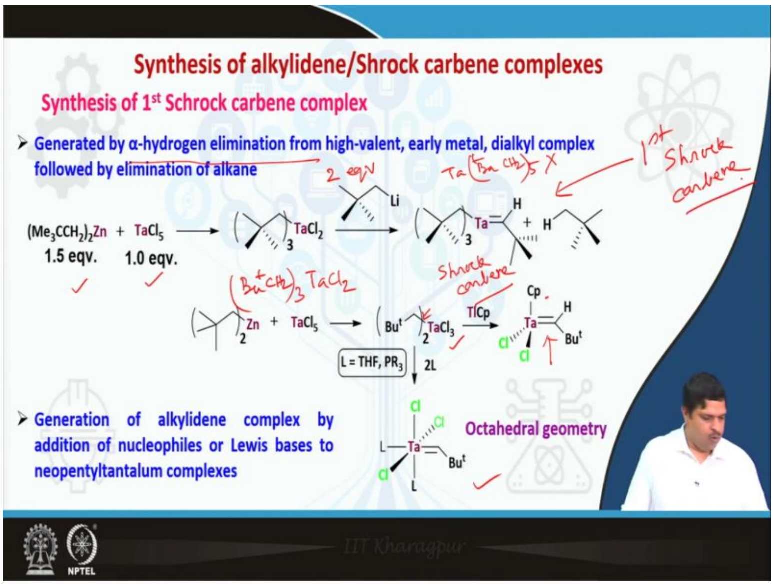

Synthesis of alkylidene/Shrock carbene complexes

Synthesis of 1st Schrock carbene complex

- Generated by α-hydrogen elimination from high-valent, early metal, dialkyl complex followed by elimination of alkane
- Generation of alkylidene complex by addition of nucleophiles or Lewis bases to neopentyltantalum complexes

So, now I am sure you have realized that how you can make the Shrock carbene complexes. So, let us say with one specific examples, we already discussed the strategy. So, if you take that 1.5 equivalent of the new pentile, this new pentile zinc reagent and 1 equivalent of tantalum, penta chloro tantalum then you will get 3.

So, this is basically butyl CH2 3 tantalum chloride and then you with two equivalent of new pentile lithium salt and you will get the, as I told that you cannot prepare this one, the butyl, tertiory butyl CH2 5, you cannot prepare. It is not stable; it will undergo the spontaneous carbene formation that is the Shrock carbene. We already discussed in detail in the last slide.

So, similarly here you will see that this tarcibutyl as already discussed in the last slide, you can also get the tantalum, this new pentyl titanium, trichloro tantalum and react with thallium CP and you will get then this one and then it will undergo the carbene formation that is alpha H elimination and get the corresponding metal carbene that is the Shrock type of carbene complexes.

And if you use a good ligand like phosphine then also you can replace the labile metal alkyl bond and you can get the corresponding metal carbene complexes. So, here, the alpha hydrogen elimination reaction is from the high valent, high valent is required to make it much acidic that that alpha H proton, to make the reaction more feasible. So, that is the strategy to make the Shrock carbene complexes. This is basically that this complex, this is the first Shrock carbene complexes.

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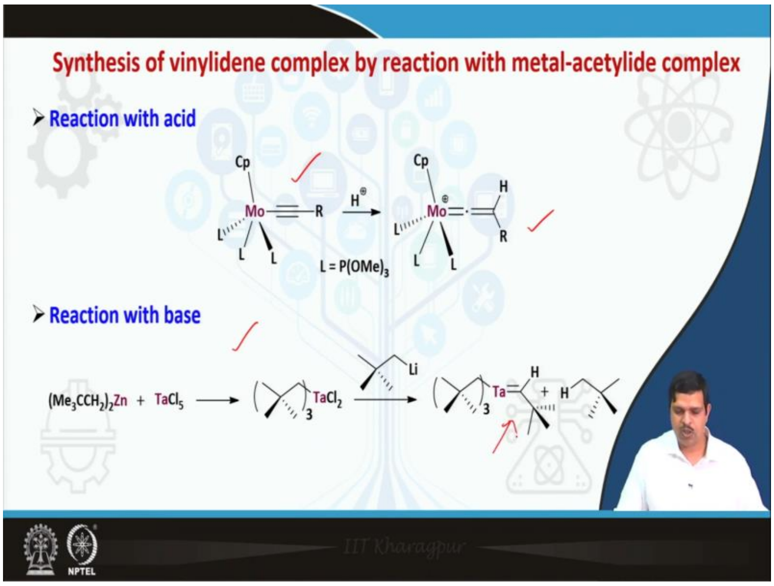

Synthesis of vinylidene complex by reaction with metal-acetylide complex

- Reaction with acid

- Reaction with base

So, similarly, with different type of strategies like from a alkyne complex, if you put, if you react in presence of Bronsted acid you can get the vinylidene complexes and if you use the similar strategy with base you will see here, you can get the metal carbene that is the Shrock carbene type complex is already discussed.

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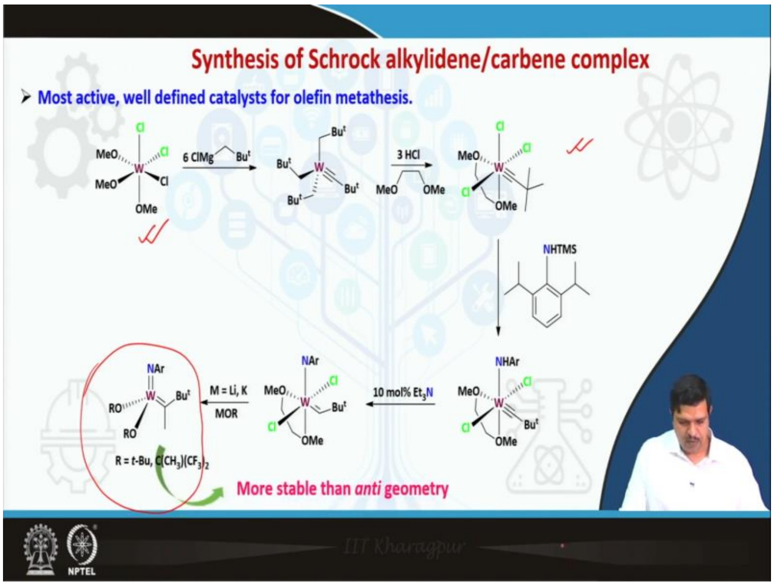

Synthesis of Schrock alkylidene/carbene complex

- Most active, well defined catalysts for olefin metathesis.

So, these are some of the efficient metathesis catalyst. We will discuss later about the reactivity. So, this is the general, this is the synthetic protocol to make the tungsten metal carbene complexes, the Shrock carbene complexes. These are the synthetic strategy starting from this precursor. So, similar here you will see it is have been it has been used as a Grignard reagent it has been used as a nucleophile.

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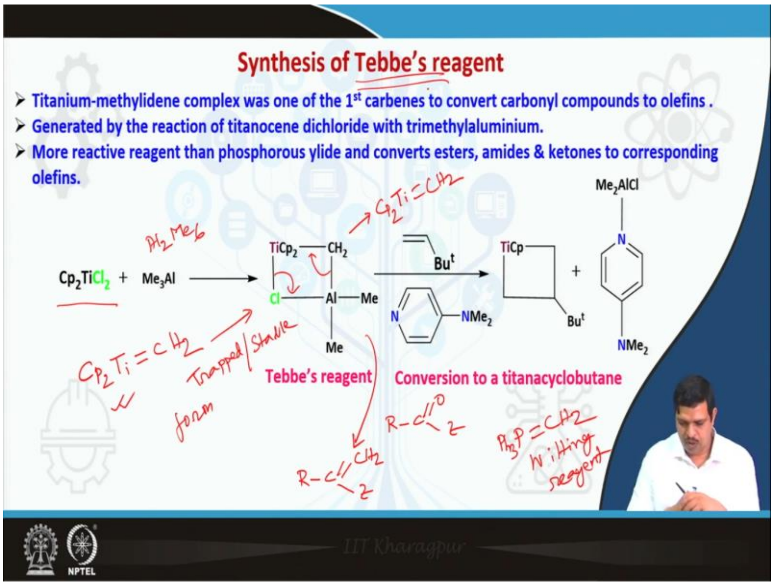

Synthesis of Tebbe's reagent

- Titanium-methylidene complex was one of the 1st carbenes to convert carbonyl compounds to olefins .
- Generated by the reaction of titanocene dichloride with trimethylaluminium.
- More reactive reagent than phosphorous ylide and converts esters, amides & ketones to corresponding olefins.

So, this discussion will not be completed without mentioning the Tebbe's reagent because Tebbe's reagent we already discussed in a beginning of the classes in a very brief way that this was the you see if this Tebbe's reagent is basically the stable form of the highly reactive carbene complexes, this one.

So, it can it is very, it is kind of trapped form. So, this is the trapped form, for trapped or you can tell the stable form of the reactive carbene complex. This is the actually Tebbe's reagent. So, if you react with Cp 2 Ti Cl 2 in presence of Me 3 Al or actually this is Me2 that it exists as a dimer and it is actually forms this kind of metalacyclobutane type of complex type with titanium aluminum and it undergoes the carbene, that is the this way.

And it forms the titanium Cp 2 and this Tebbe's reagent. And this is, this acts as a Wittig reagent that what is the Wittig reagent. So, if you react with this one, any carbonyl compound like this one. So, you will get the this one. So, that Wittig reagent is, if you remember, this is the Wittig reagent.

So, its acts, it is a actually better reagent, in some cases, the Wittig reagent is unsuccessful but this one the, Tabbe's reagent is very successful and works in some complicated scenario. So, that is why it is very famous and one of the very highly used reagent to make the alkene compounds from the carbonyl compounds.

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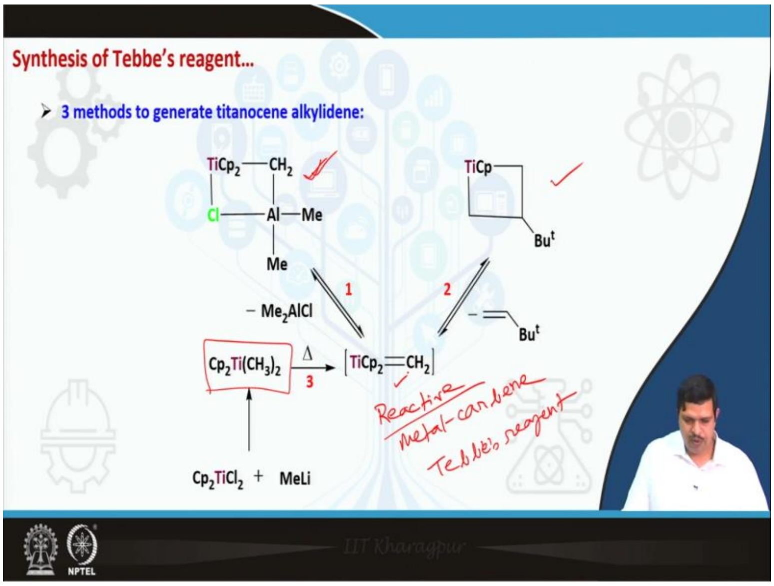
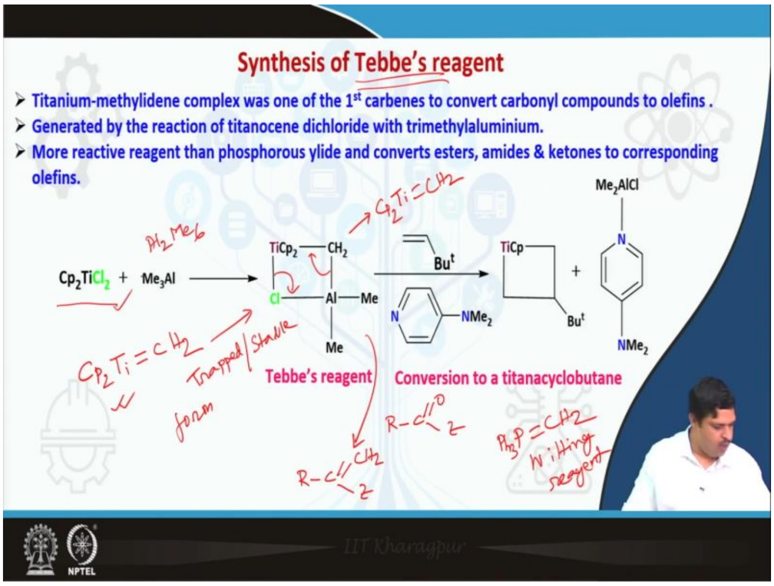


Synthesis of Tebbe's reagent...

- 3 methods to generate titanocene alkylidene:



Synthesis of Tebbe's reagent

- Titanium-methylidene complex was one of the 1st carbenes to convert carbonyl compounds to olefins .
- Generated by the reaction of titanocene dichloride with trimethylaluminium.
- More reactive reagent than phosphorous ylide and converts esters, amides & ketones to corresponding olefins.

So, these are the some strategies to make the metal carbene complexes. This is good to know. You can start from here that we already discussed in the last slide that is that this strategy and this one you can make from the this metallacyclobutane and also from the this one just by heating. So, these are the different type of strategies to make the reactive metal carbene complexes and you see this is actually the Shrock type of metal carbene complexes, very stable, very reactive, sorry, the reactive metal carbene complexes which form the Tebbe's reagent. We in situ, as it is very reactive, so, we cannot store it, but we prepare in situ, we prepare this one and then we react and in the reaction mixture by slight heating it forms this carbene and then react with carbonyl complexes.

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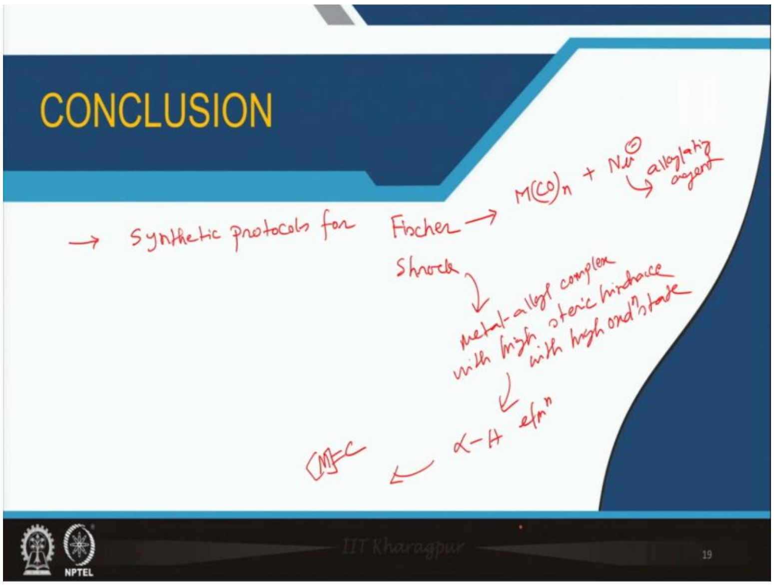

CONCLUSION

So, in conclusion, what we have learned? We have learned the synthetic protocols for Fischer and Shrock carbene complexes. And you see that for the Fischer complexes, we start generally from the metal carbonyl complexes and then we use the strong nucleophile and then we use the alkylating agent that is to make the Fischer carbene complex.

In general way, in general, general and Shrock carbene complex if you see that you make a metal alkyl complexes with high steric hindrance so that it can undergo alpha H elimination and also with high oxidation state so that alpha H elimination is more favorable and then you get the corresponding metal carbene complexes. So, I am sure that from today's lecture you are now will be able to set up your synthetic strategy to make the different type of complex carbene complexes, the Fischer and Shrock carbene complexes and you will be able to choose your reagents and the metal recursors.

In the next class, we will be discussing the another category of metal carbene complexes that generally falls in the category of the Fischer that is the metal in heterocyclic carbene NHC that is actually very useful, very famous and you will see that later when will come after that the Grubbs catalyst, the Grubbs catalyst also involves the carbene in heterocyclic carbene complexes. You can tune the properties.

We have already discussed what is the NHC, NHC that is n heterocyclic carbene. So, then after that after realizing that what is the main synthetic strategy, we will discuss the general reactivities of the metal carbene complexes and then will come to the mechanism and then the our application in polymerations chemistry.

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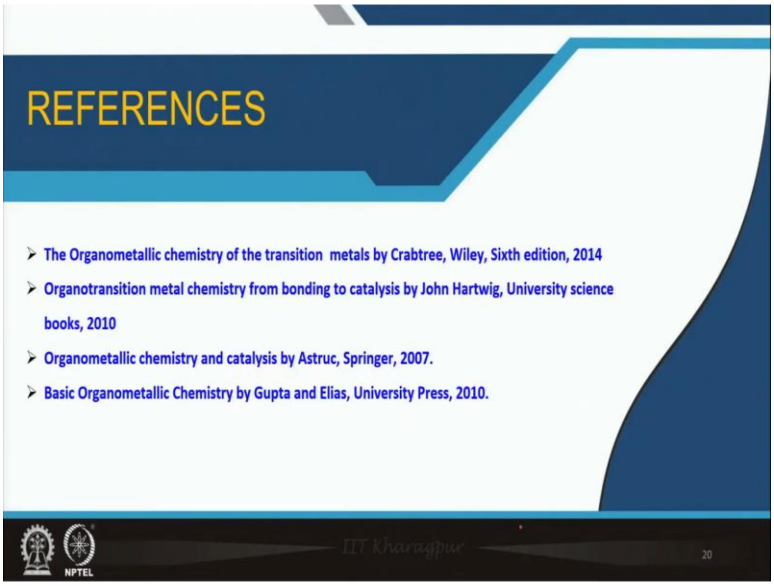

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- Basic Organometallic Chemistry by Gupta and Elias, University Press, 2010.

So, these are the references you can consult. These are all the very well-known textbooks. And thank you very much and see you again in the next class. Till then bye bye.