Metallocene and Metal-carbene based Organometallic Compounds as Industrially Important Advanced Polyolefin Catalysts

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Lecture 33

Metal-carbene complexes as versatile catalysts for multiple useful reactions: A short introduction

So, welcome once again to our course. So far, we have discussed about the metal machine-based catalysts and very extensive discussion we have done, how it has been developed, how it is it has been so popular in industries for polyolefin synthesis, and not only for it is reactivity activity.

And also, for its stereo selectivity for the polymers where we will be using the Pokharel monomers, you can tune the fine properties you can use as a tool box, you can also convert it to a heterogeneous catalyst so that it is becomes less cost effective and industrially accepted. And today, we will start a new topic, which is metal carbon-based organometallic compounds for similar collaborations.

Although compared to the metal machine-based catalysts, this is relatively less developed, but the prospect is use, many monomers are polymerized by metal carbon based organometallic compounds where the polymerization is not possible or some difficulties with other catalysts. So, we will discuss we will start today the metal carbon based organometallic catalysts, we will start first what is this system?

What is the uniqueness of this metal carbon system? And then slowly we will go to the basic structure electronic properties, then react synthesis then reactivities and its application in polymerization reactions.

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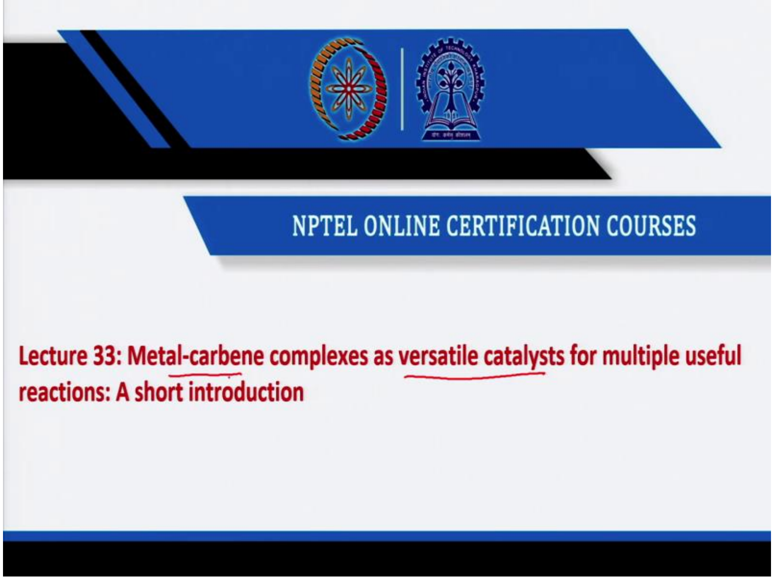

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Lecture 33: Metal-carbene complexes as versatile catalysts for multiple useful reactions: A short introduction

So, let us start. So, today as I told I discuss the metal carbene complexes as a versatile catalyst for multiple useful reactions, this is very important first before going to the polymerization reactions. So, let us start today.

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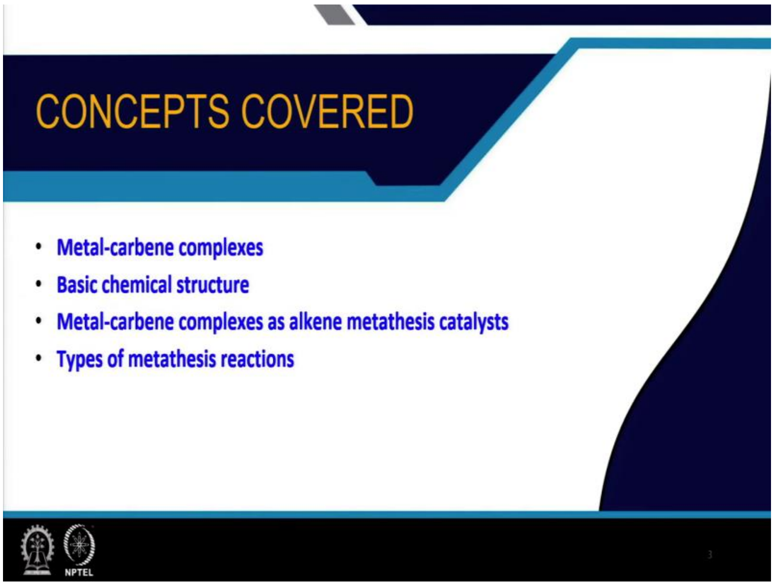
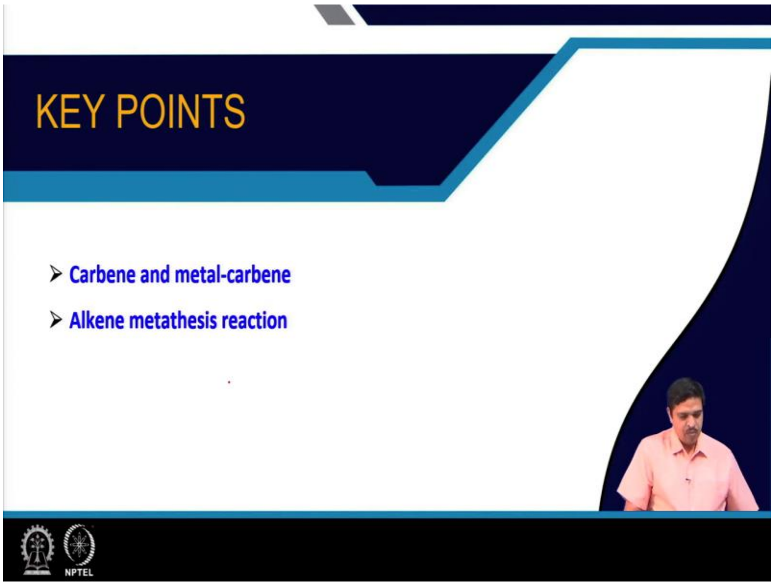


CONCEPTS COVERED

- Metal-carbene complexes
- Basic chemical structure
- Metal-carbene complexes as alkene metathesis catalysts
- Types of metathesis reactions



KEY POINTS

- Carbene and metal-carbene
- Alkene metathesis reaction

So, the we will learn the concept of metal carbene complexes, metal carbene complexes as alkyne metathesis catalysts and also, we will learn today the types of metathesis reactions, here metathesis not sigma metathesis, here will alkyne metathesis or alkaline metathesis reactions.

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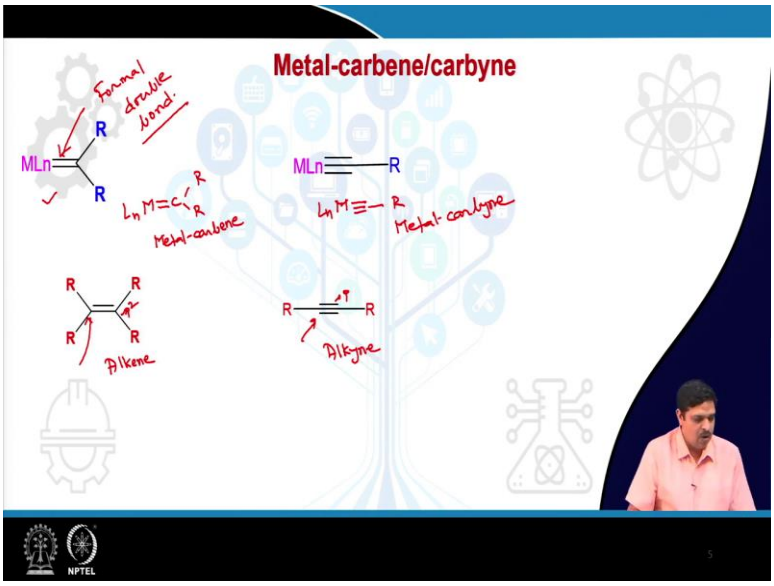

Metal-carbene/carbyne

So, this you know that this is alkene all we know and this is the alkyne, everybody knows and we are very familiar with this one the alkene this carbon is sp2 hybridized and this 2cp 2 carbon carbon are sp hybridized. And this is we know that this is a planner the alkene and alkyne is a linear structure, if suppose we have the similar compounds instead of one carbon if you have like metal carbon bonds this one, and it obviously they are the ancillary ligands that is this one.

So, it is basically analog, the metal analog of the alkene if this formal structure is possible, then we call it is metal alkene, metal carbene. So, this kind of complex complex is called metal carbene. So, what we are doing basically, if you replace one this carbon by metal centre then it is metal carbene, not metal alkene (())(04:29). Similarly, here if we replace this one with one metal then you will get this kind of structure this is similar as metal alkyne this is would be metal carbyne.

So, this is and here obviously the ancillary ligands so, this would be your metal carbyne. So, here you will see there is a formal double bond between carbon and metal here. So, there you will see that the formal double bond between the metal and carbon, in this kind of complexes we call metal carbene complexes if you have a triple bond, formal triple bond then it is metal carbine complexes.

And you will see that how these kind of complexes are interesting not only for its structure academic perspective, but also its versatile applications in different sectors like to make the valuable organic synthesis, valuable for the synthesis of valuable organic compounds, for specially in medicinal drug industries and also for the polymer synthesis. And you will be surprised that this this type of single complexes can do several type of meta thesis reactions.

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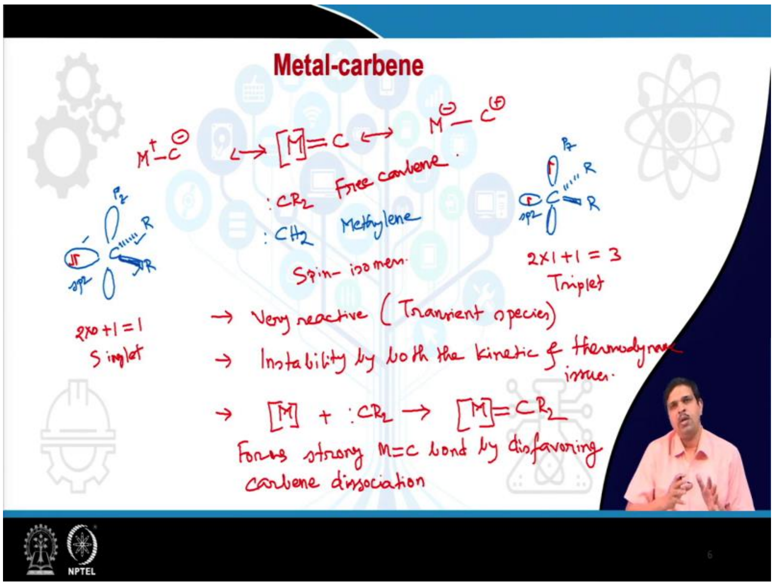

Metal-carbene

$M^{+}-C^{\ominus} \longleftrightarrow [M]=C \longleftrightarrow M^{\ominus}-C^{\oplus}$

$:CR_2$ Free carbene.

$:CH_2$ Methylene

Spin- isomers.

$2\times0+1=1$ Singlet

$2\times1+1=3$ Triplet

→ Very reactive (Transient species)

→ Instability by both the kinetic & thermodynamic issues.

→ $[M] + :CR_2 \rightarrow [M]=CR_2$

Forms strong M=C bond by disfavoring carbene dissociation

Now, what is metal carbene? We will just try to discuss in a little bit depth before going to the what to understand what is the metathesis reactions. So, as I told already that this is in a metal carbon complexes, you have a formal double bond metal carbon. So, you can I am just writing as a third bracket that means, there is other ancillary ligands are there, you just in a simplified form and if you see the chemical form you might have this one minus minus C plus or you might have this form.

So, here you will see one metal in one case the left side case the metal centre is electrophilic and the right-side side it is nucleophilic. So, here depending upon the canonical form… it can do the… it can behave in different way either it as a electrophilic or as a nucleophilic I am telling about the properties, electronic properties of the metal centres and oppositely that just reverse scenario will be all the corresponding attached carbon centres.

Now, all we know that this is the which group? This is methylene group and this is highly reactive methylene group. If you recall our 10 plus 2 chemistry or basic first year chemistry we have read about the metal carbon organic carbon, carbon-based carbon chemistry, like Reimer-Tiemann reactions like that. So, you know that this methylene can exist in to spin isomers and these are very, very reactive. And what are the isomers?

So, this we can draw it. So, this is let us say I am writing in a general form. So, like R will be hydrogen or RR alkyne group? And, so you know that this is the sp2, so this one, this one and this one is basically sp2 hybrid orbitals. And this is actually pz orbitals. And now, if there is a possibility of two (())(09:49) isomers, one is, let us say the two unpaired electrons. You know that valency of the carbons is 4 so, two unpaired electrons may be paired of act as a known pair housed in sp2 hybrid or hybridized orbitals.

In other case what may happen? In other case, so this is similarly and this is your sp2 and again this is pz and this is your sp2. So, what will happen now here? Another possibility that one electron is here and one electron is here. So, you would see that this is if you see if you calculate the multiplicity it will be 2 into 0 plus 1 that means 1.

So, it is singlet and this one half and half so, 2 into 1 plus 1 so, it is 3 that means it is triplet. So, that is why these are basically the spin isomers and you know that these are very reactive like methylene or CR2 dot very reactive, it is actually behave as a transient species in various reaction that means it is very difficult to isolate, but it can it may behave as an intermediate or transition state.

And instability by both the kinetic and thermodynamic issues and that is why it actually forms a strong metal carbon bond. So, when there is a possibility like a metal species, condition metal species and you have this carbon so, it forms like that. And this is basically so, you can tell that forms strong metal carbon bond by disfavouring carbon dissociation.

So, it is basically the free this is called free carbon, this free carbon is very unstable. So, this free carbon is now after reacting with metal suitable metal species, it may be neutral ketonic, maybe transition metal, maybe non-ferrous metal, it can react to form the metal carbon bond and stabilized. So, you understand that in later we will understand that how, what type of bond exists between the metal and the carbon and what are the orbitals involved. So, that we will discuss in detail.

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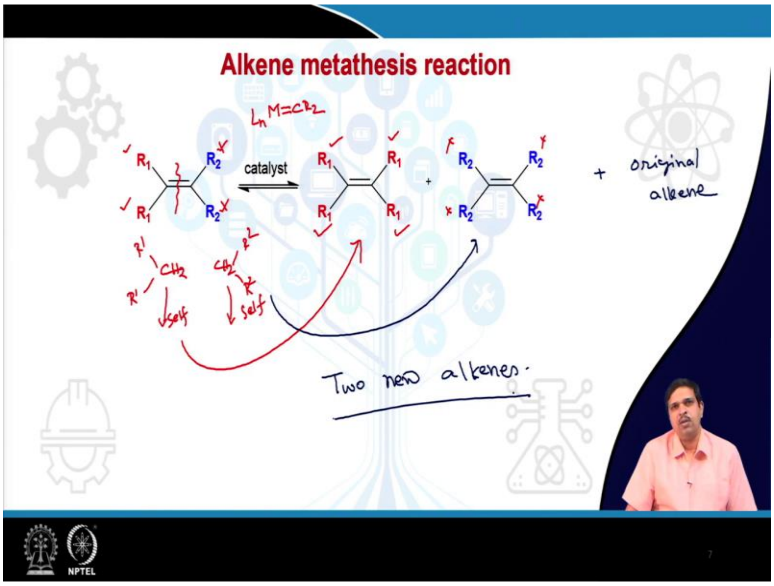

Alkene metathesis reaction

Today, we just try to understand that what are the reactions and what are the applications of these metal carbon catalysts? It is basically to show that we excited and inspired to study. So, this is you see, in this screen you see this is a alkyne metathesis reaction is simple example of alkyne metathesis reactions, you if you see very carefully what is happening here? Here you will see that this one and this one, it same group in one alkene R1 R1 and here is another group, let us say R2.

Now, if we put the catalysts, like any carbon catalysts, what will happen? You will see that the reactions here R1 both the cases in both the alkenes R1 R1 R1 Here you see I am just crossing R2 and here you will see all are R2 R2 R2 that means if you see, very roughly what is happening here? Is basically here it is clipped. So, you are forming formally, then we will discuss the mechanism later do not worry. So, this one like this form like this one.

And now, it is again so cleaving the carbon-carbon double bond and then again threading, so cleaving and then threading. So, this thread now may happen like 2 ways one is the self, and these two molecules two species of this. So, this self-coupling, the self coupling will form this one and the other self-coupling will form this one, although there is a chance of forming the again the starting material also. So, there is also other possibility of the reaction of the original alkene.

So, this is already in equilibrium. So, you understand this catalyst so, it is basically breaking a very stable alkyne bond and then again threading and what we are getting? We are bit getting basically two new alkenes and this is the applications. So, you can make new alkenes from one alkene by a metal carbon catalyst using the alkene metathesis reactions looks very simple, what do we do, from the new alkene this can be done in other ways, but there is a lot of applications. I will this discuss, so that you will be you will be understanding.

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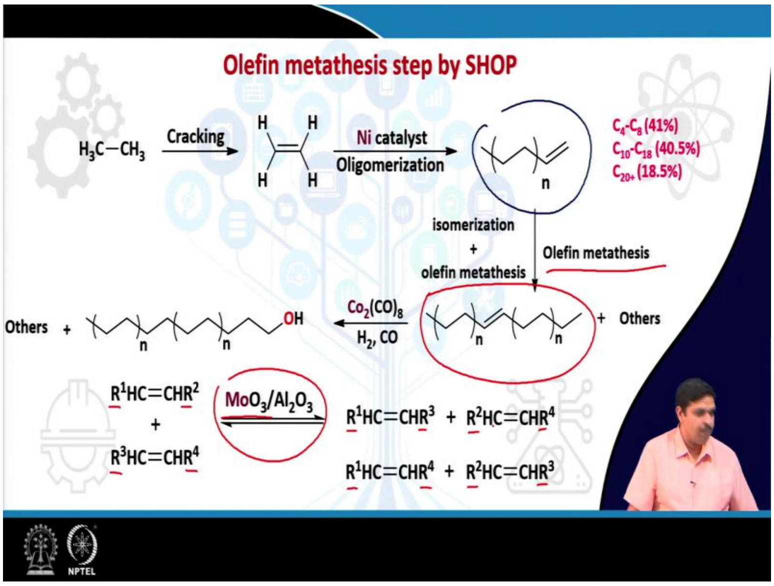

Olefin metathesis step by SHOP

This one is we already discussed in the last classes it just to recall that how important it is the olefin metathesis reactions and developing the catalysts. So, this is a sub process, sub means we already discussed is a SIL higher olefin process SHOP this in for many purposes, the SHOP reactions have become famous not only for too valuable to make evaluable organic compounds from a smaller alkene but also to make it a new or higher alpha olefin for copolymerization alkene cooperation to make LLDP.

So, we have discussed how important it is. So, if you recall this tape from here to this one, we if we recall we used a olefin metathesis catalysts. So, this is basically the olefin metathesis reactions and what catalysts to use if you remember, we use the one oxide that is the molybdenum oxide that is the second step of the SHOP process SHOP process.

So, here what you will see that in this case you can make a different type of higher alkenes, higher alkenes by the olefin metathesis reaction, the mechanism will come in detail, but I just try to give some highlight about the its use applications. So, here we already you see that used the alkene metathesis reactions. In the following lectures we will discuss in in more depth about the catalyst design and the mechanism.

So, here are you see same thing happened here. So, if you have a like different type of alkene we will understand what kind of reaction it is called the cross-metathesis reaction. So, it is basically you see this R1 R2 R3 R4 groups, these are basically scrambling, scrambling around the around the alkyne bond double bond fine.

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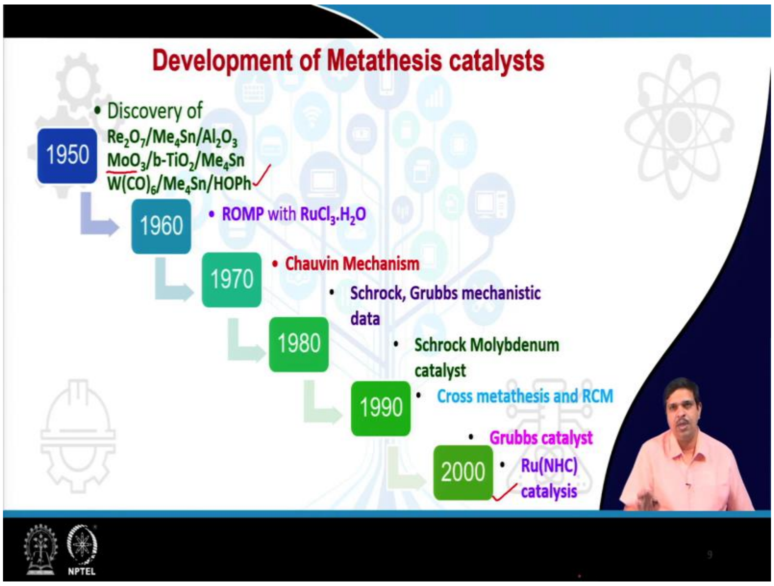

Development of Metathesis catalysts

1950
- Discovery of
  $Re_2O_7/Me_4Sn/Al_2O_3$
  $MoO_3/b\text{-}TiO_2/Me_4Sn$
  $W(CO)_6/Me_4Sn/HOPh$

1960
- ROMP with $RuCl_3.H_2O$

1970
- Chauvin Mechanism
- Schrock, Grubbs mechanistic data

1980
- Schrock Molybdenum catalyst

1990
- Cross metathesis and RCM
- Grubbs catalyst

2000
- Ru(NHC) catalysis

So, these are the milestone of the metathesis… developing metathesis catalyst, you will see that around 1950 different oxides type or carbon type firstly oxides type catalysts are developed for different purposes as example, we see already you know, that molybdenum oxide was used for SHOP process, then different carbonyl compounds are developed or discovered for metathesis catalysts.

And then slowly Schrock, Grubbs came in the picture and now in around 2000 you know that this metathesis catalyst has been enriched by the use contribution of Grubbs and today, you know that in a multi-step reactions like 20 or 15 steps in (())(21:34) or medicinal or drugs industry, you cannot really think any scheme without the alkene metathesis using the Grubbs catalyst reaction it is so useful.

And although the there other catalysts like schrock based catalysts or (())(21:53) based catalysts, there are a lot of metal carbon catalysts have been developed time to time we will discuss in more detail about what are the metal centres? What are the ligands? How does it work?

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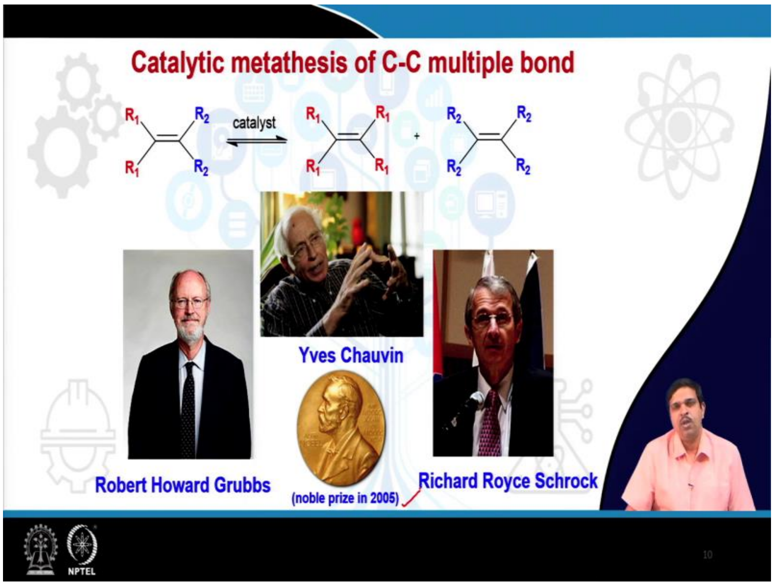

Catalytic metathesis of C-C multiple bond

Robert Howard Grubbs

Yves Chauvin

(noble prize in 2005)

Richard Royce Schrock

So, this is again that we let us see, try to understand that what is the metathesis reactions? So, this is basically the reactions around the carbon-carbon double bond, you will see that there will be change of the substituents, change of the carbon atoms. And change of the structures around the metal centre, you will more understand when I will discuss the types of different alkene metathesis reactions.

So, for as told that we should not we cannot really discuss any metathesis reactions without remembering this trios that is the Robert Grubbs, Richard Schrock, and Chauvin because they are the pioneers, they are the discoverer. And due to them, due to discovery of this type of catalysts, many problems in organic synthesis mainly have been sorted out and have and the process has become more easier.

And also, definitely this opens up a new catalyst for a different type of polymerization alkene polymerization of different types of complicated monomers. So, and that is why, for their great contribution they were awarded Nobel Prize in 2005. So, you will see that this chemistry is not really very old, it is relatively new.

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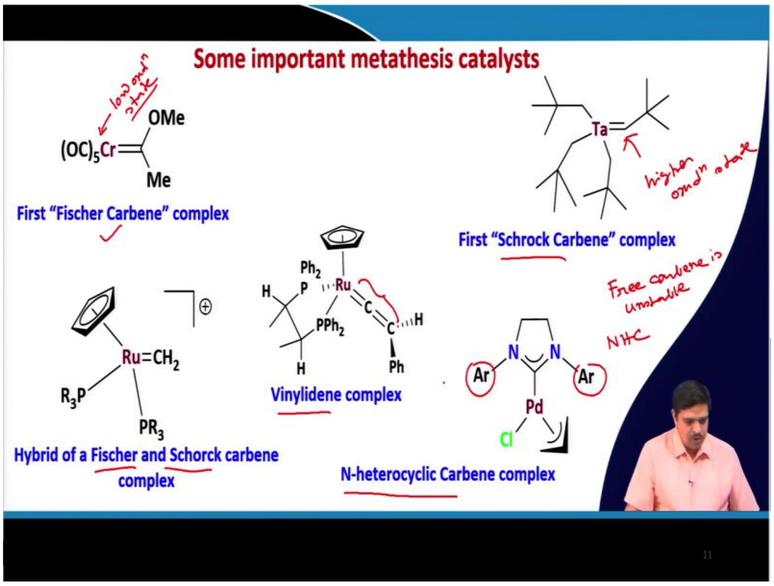

Some important metathesis catalysts

First "Fischer Carbene" complex

First "Schrock Carbene" complex

Vinylidene complex

Hybrid of a Fischer and Schorck carbene complex

N-heterocyclic Carbene complex

So, these are the some important metathesis catalysts. So, this you see that this is Fischer carbene catalyst Fischer carbene complexes, these mainly you will see that metal centre is low oxidation state, low oxidation state, we will discuss in more detail what is Fischer carbene what is top carbon complexes, this I just want to give a highlight about different or to introduce the structure of the metal carbon complexes.

So, this is you see, this is one example of Schrock carbene complexes here the metal centre would be relatively higher oxidations, higher oxidation state. Now, this is you will see, this is also another metal carbene. This is Vinylidene complexes. Here you see because this the structure due to this one, this called the Vinylidene complex, and this is a hybrid of Fischer and Schrock complex.

So, you will see the how there are many possibilities of versatility in the metal carbon complexes and more opportunity or more versatile means more easy way to tune the electronic properties and to tune their reactivities, this is in heterocyclic carbene complexes as we told that free carbene, free carbene are very unstable is unstable.

The N-heterocyclic carbene, specially developed by (())(25:40), they showed that some of the organic carbenes can also be stabilized if you, if we design the carbene judiciously. So, here you will see that, in this is called NHC N-heterocyclic carbene, and here there will be historically demanding groups on a nitrogen so that the carbene is stable, some of the carbons, three carbons can also be isolated.

So, that is really amazing that was one of the problem in this carbon ligand synthesis, because you have to be really very careful and you need a expert hands to make the carbon ligands.

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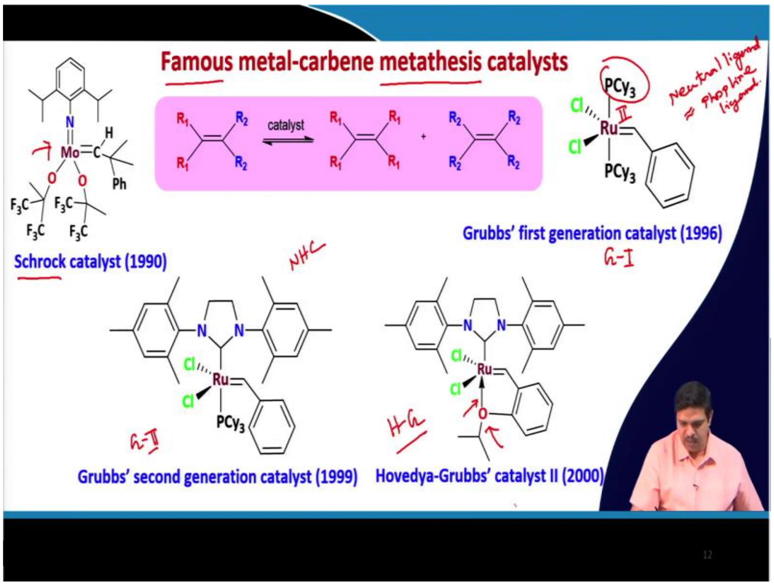

Famous metal-carbene metathesis catalysts

Neutral ligand ≈ Phosphine ligand.

Schrock catalyst (1990)

Grubbs' first generation catalyst (1996)

G-I

NHC

G-II

Grubbs' second generation catalyst (1999)

HG

Hovedya-Grubbs' catalyst II (2000)

So, here are some of the real metathesis catalysts. In the earlier slide, we discussed the structure of the metal carbon complexes, and here are some of the very famous metal carbene metathesis catalyst. I am sure you have heard the Grubbs catalyst. I am very much sure. And you know that what metal is in there? Metal centre in the Grubbs catalyst? Any idea?

Yes, it is ruthenium. And what is the oxidation state? This is plus 2. So, we will discuss in the next class about the nature of the ligands of carbon, how does it, it is actually regarded as phosphines. And we will discuss why, and it is neutral. So, metal carbene, carbene ligands is a neutral ligand.

So, when you will calculate the total valence electrons to shake that whether this molecule is satisfying 8 electron rule or not, you have to count 0 for the carbene and it is regarded as phosphine ligand, so, that is why the metal carbene, so, the carbon ligands is very good substitute of the phosphine ligands because some of the phosphines are toxic not very healthy.

So, here you will see this is called the Grubbs first generation catalyst in some book, it is a simply written as G1. Then, second one is you will see this is the Grubbs second generation catalyst here, this here you will see this is the cyclohexyl phosphine, tri-cyclohexyl phosphine, this is the PCy3, this PCy3 has been replaced by NHC, one of the PCy3 has been replaced by NHC and other moieties are same. So, this is Grubbs second generation catalyst.

And this one is called Hoveyda Grubbs catalyst, HG catalyst. So, this you also here you see that one the second PCy3 has been replaced and this phenyl group has been functionalized by isopropyl oxide and that oxygen actually quickly donates to the ruthenium centre and this is very reactive quite reactive. On the other hand, Schrock is mainly for molybdenum catalyst.

Here you see this is high oxygen state as I told… this molybdenum and this also used for different reactions and heavily used in alkene polymerization. So, stock catalysts the main difference is the high oxidation state metal centre and the Grubbs catalyst is a kind of Fischer type of catalyst these are low oxidation state metal centres.

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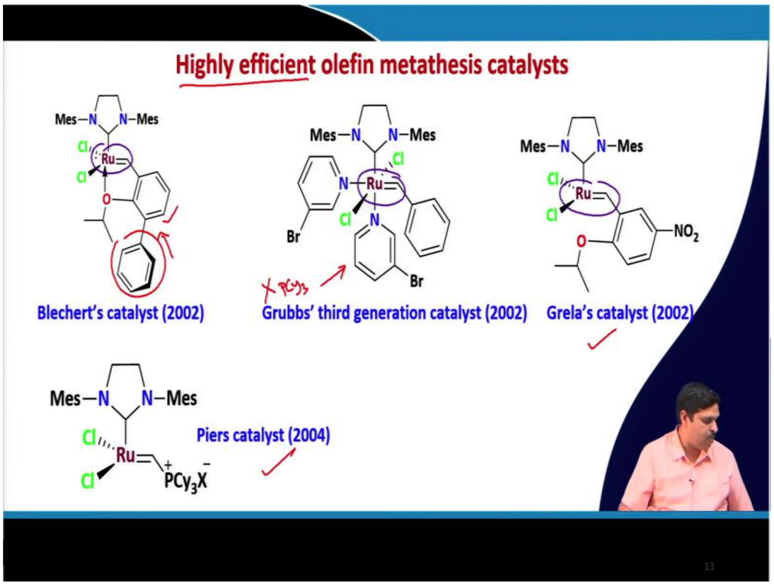


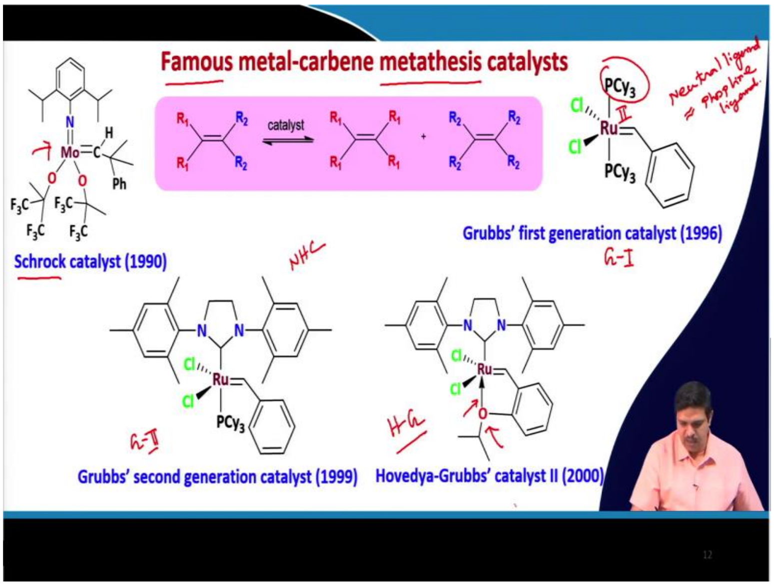
Highly efficient olefin metathesis catalysts

Blechert's catalyst (2002)

Grubbs' third generation catalyst (2002)

Grela's catalyst (2002)

Piers catalyst (2004)



Famous metal-carbene metathesis catalysts

Neutral ligand ≈ Phosphine ligand.

Schrock catalyst (1990)

Grubbs' first generation catalyst (1996)

G-I

NHC

G-II

Grubbs' second generation catalyst (1999)

H-G

Hoveyda-Grubbs' catalyst II (2000)

So, these are the very recent I mean we can sell comparably much newer chemistry and these are highly efficient olefin metathesis catalysts you see that most of this chemistry was developed in around 90 after 90. So, from 1990 to 2005 was the actually golden era for developing metathesis catalysts, all of the catalyst actually have been developed in that era.

So, these are also very similar. So, these you would see that this has been used as a axial stereo the chirality has been induced by using the concept of axial chirality and other thing is very much similar you see this one and this one is very much similar, the Grubbs third generation catalyst here you will see that instead of one here does instead of cyclo hexyl phosphine.

So, initially if you remember this one was there, this has been replaced by one pieridine 3 bromo pieridine, then the Grela's catalyst that is also very much similar as the Hoveyda Grubbs catalyst and the Piers catalyst you will see that this is also in hetero cyclic carbon type catalyst.

So, all are very much similar just ancillary ligands or the ligand surroundings have been changed and you would see that main structure okay the main unit is actually this one, this is the metal carbon part. And you see that how with tiny change of the ligand environment can enhance the reactivity by influencing the electronic properties.

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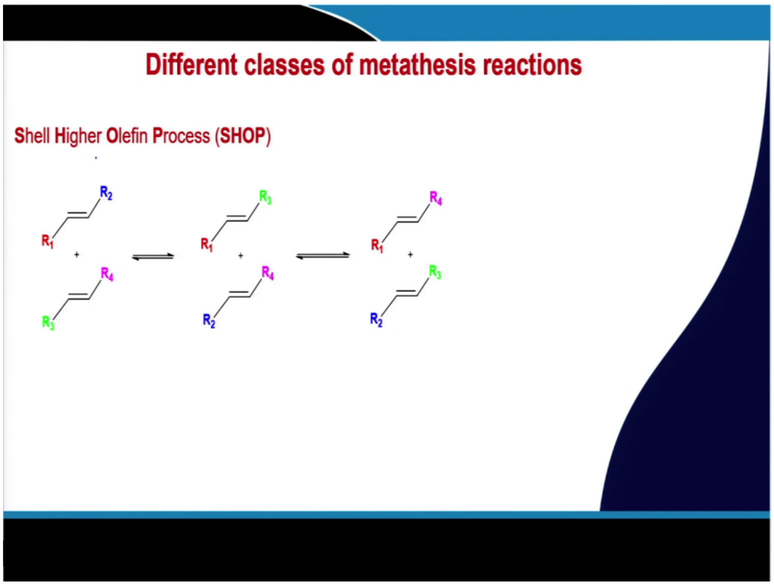

Different classes of metathesis reactions

Shell Higher Olefin Process (SHOP)

So, that is really amazing. So, in the next class, we will be continuing about the different classes of metathesis reactions. You would see that using the same catalysts, metal carbon catalysts, you will be… we can do various type of metathesis reactions, we can increase the number of the carbon atoms of alkene.

We can make the cyclic alkenes or alkyne if I use the alkyne because substrates we can make the polymers by using the appropriate alkene monomer, we can also do the ring closing metathesis reactions that means to make a very big cyclic alkene, big very big cyclic carbon derivatives.

And also, we can do the cross-metathesis reaction that means, we can make a new alkenes by from a particular alkenes by using this kind of metal carbon catalyst and these reactions are very efficient not only for to make the valuable organic compounds, but also for the polymer industry. So, next classes will discuss about the electronic properties and the orbital overlap between the metals and the carbon species.

And also, we will try to see that what the nature of these carbon ligands, so thank you and see you in the next class.