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

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Lecture 38

Alkene metathesis by metal-carbene catalysts and its mechanism

Welcome to our course Metallocene and Metal-carbene based organometallic compounds for alkene polymeration. So, we now have started, started the metal carbene complexes for using the catalysts for a very efficient polymerations reactions, alkene polymerian reactions. So, far we have studied and in a very quiet depth about the metal carbene complexes, and their electronic structure, their chemical structure, their the synthesis, and the type of the ligands, and also ancillary, and what are the ancillary ligands, and how it influences its reactivities geometries and obviously the electronic properties.

We also discussed the types of metal alkene complexes as example fissure carbon, stock carbon, what are the basic difference in structure and the geometry and the metal centers as well as the the ligands. And also we have discussed about the various type of alkene metathesis reactions. Today we will concentrate about its versatility and the and its mechanism of the alkene metathesis reactions.

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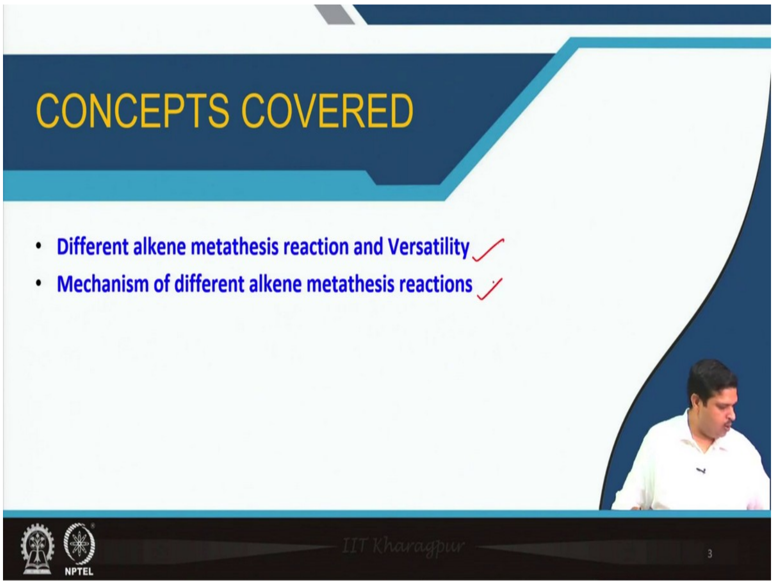
CONCEPTS COVERED

- Different alkene metathesis reaction and Versatility
- Mechanism of different alkene metathesis reactions

So the concepts we will cover today is the versatility in the alkene metathesis reactions and the very well accepted and the mechanism for this kind of alkene metathesis reactions.

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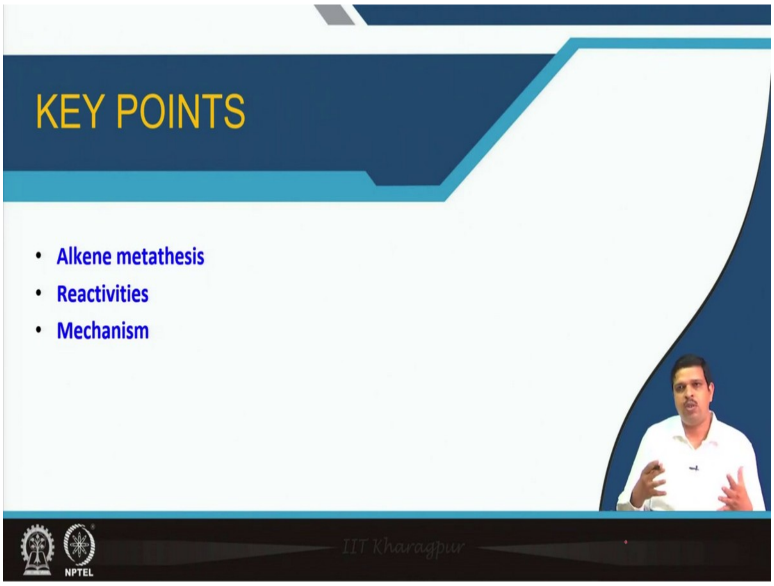

KEY POINTS

- Alkene metathesis
- Reactivities
- Mechanism

So with the, with this will the key points of our today's lecture will be obviously the reactivities, mechanism will more concentrate on the mechanism and the versatility in the alkene metathesis reactions.

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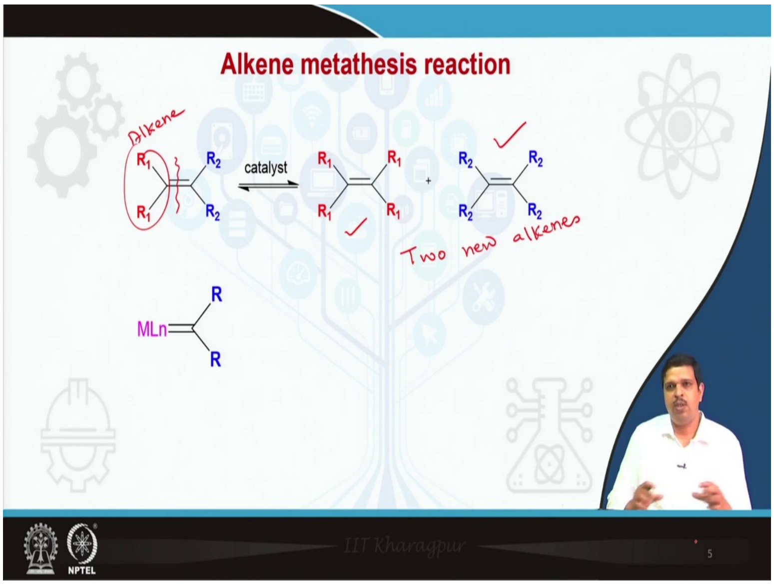

Alkene metathesis reaction

So, this one now we all know that what is alkene metathesis reactions. So, this is one example of the metathesis reactions where you see that this is a alkene. So, here in one alkene and here you will see by using the metal carbene catalyst you are actually making the 2 new, 2 new alkenes.

So, here from you will see that it looks like that somebody has broken this part and then again it is threaded. So, like this red part like you will see is this one, this one, and another half of this red part if you thread it, you will get this alkene. And the blue part similarly if you thread the 2 blue parts you will get this this alkene. So, this kind of reaction is called a metathesis reaction.

And we are now well aware that what is metathesis reaction and what are the catalysts. Now today we will discuss that what are the versatility in this kind of metathesis reactions? As if you recall I told in the last classes that this is a single key for multiple logs that means a single catalyst can do a various type of metathesis reactions.

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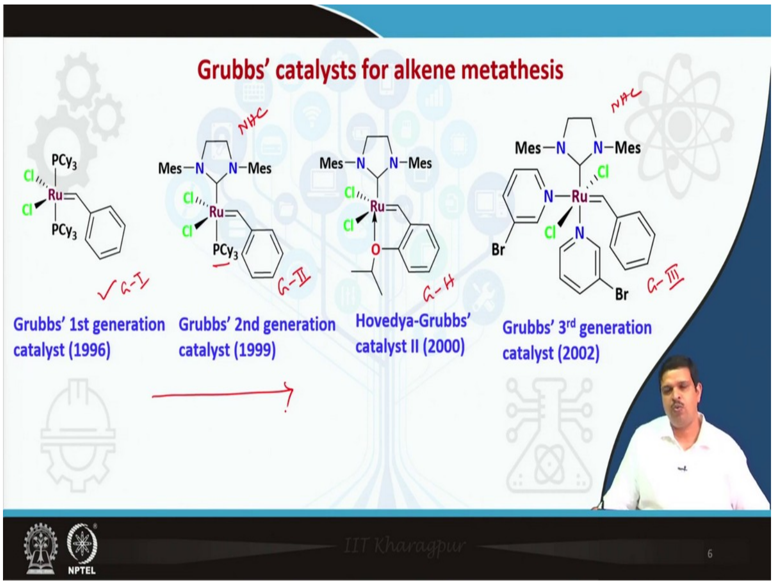

Grubbs' catalysts for alkene metathesis

Grubbs' 1st generation catalyst (1996)

Grubbs' 2nd generation catalyst (1999)

Hovedya-Grubbs' catalyst II (2000)

Grubbs' 3rd generation catalyst (2002)

So, that will today discuss and this is just to recall because we all have I have discussed in very depth about it what are about this its geometries, the electronic properties, and also the synthesis. So, just to recall that this is actually the first graphs catalyst that is called the first generation. Sometime it is called just simple G1, this is the graph. Second generation catalyst this sometimes called just simple G2. And here you will see that this is actually the N heterocyclic carbon NHC and this is the graphs third generation catalysts.

Here this is also NHC but here you will see that one cyclohexal phosphine has been substituted by 1 by 3 bromo pyridine. And this one the Hovedya Grubbs catalysts sometimes will we call just a GH Catalyst and there are a different type of others like a Pritchard and others kind of metal carbene complexes. And here you will see all the ruthenium based plus 2 oxidation state and you will see the reactivity is generally increases from left to right. And these were needed because all the substrates are not equally reactive that will discuss in the following classes.

And you know that these kind of catalysts are very famous for different type of alkene metathesis reaction that actually you are going to study today and that is why it is so popular.

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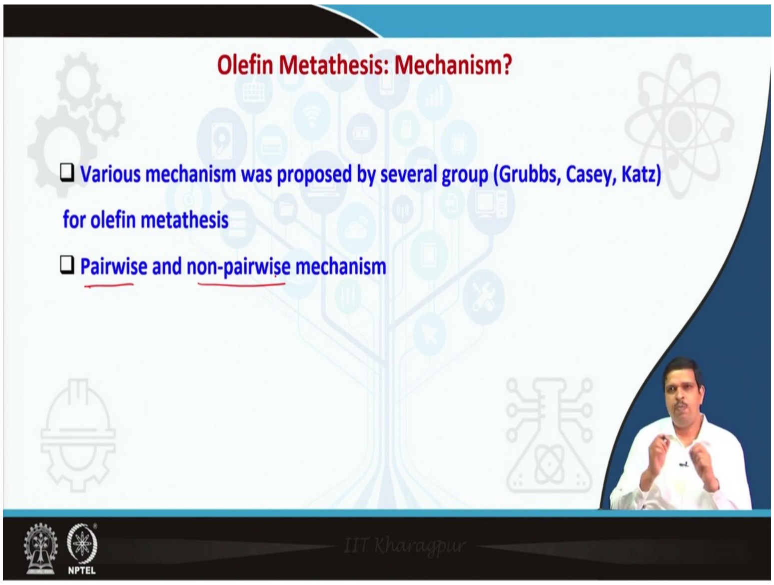

Olefin Metathesis: Mechanism?

☐ Various mechanism was proposed by several group (Grubbs, Casey, Katz) for olefin metathesis

☐ Pairwise and non-pairwise mechanism

This is another very interesting point is that this kind of catalysts are also tolerable to compatible to different functional groups. So, metathesis reactions actually the mechanism is initially it was proposed it was seen to be very complicated and that is why different groups propose different mechanism and among them 2 mechanism that is the pairwise and non-pairwise mechanism was reported. And it was proposed that it may happen through the 2 main ways that is the pairwise and non-pairwise. Non-pairwise in the last plus I very briefly mentioned in one class that what is the pairwise and non-pairwise.

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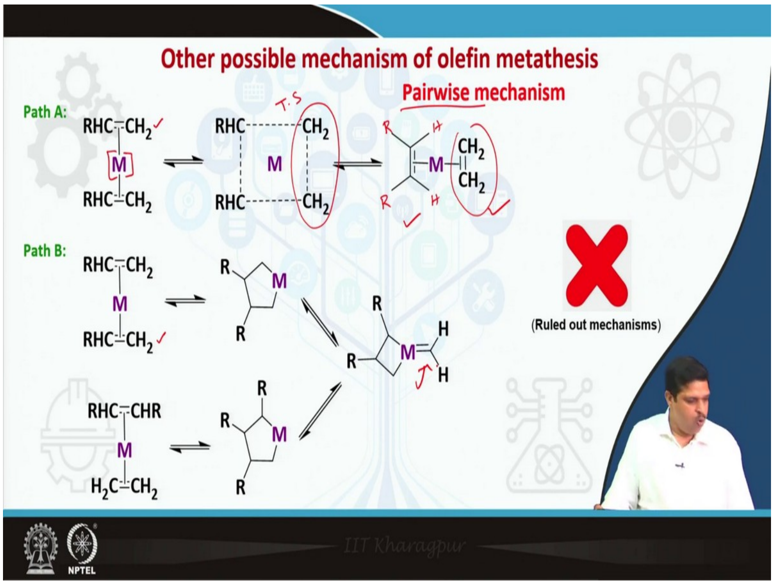

Other possible mechanism of olefin metathesis

Pairwise mechanism

(Ruled out mechanisms)

Today we will discuss in more depth that what is the pairwise and non-pairwise. So, this is let us see first discuss the pairwise. So, pairwise is what? So, like this is my metal centers and if I have alkene let us say this RCH double bond CH2. So, this can coordinate in pairwise that is the one alkene pair one alkene pair is coordinated to the metal at the same time and it forms a this kind of to a transition state that is the 4 member but metals, metal is coordinated with 2 alkenes.

And what happens you see here that you are we will be getting the alkenes that is here this the alkenes CH2 CH2. So, this is the ethylene. So, this is my ethylene moiety, and this is my R, and this is H, and H. So, here you will see that in this pathway that from 1 alkene we are getting 2 alkene that is this one and this one. So, trans to some extent trans isomers can also be formed and the path B that is also pairwise mechanism and very similar. So, here you see that this one can form the metallo cyclopentene and through this one, then it forms a metal carbene complex. So, both the cases are actually it is a pairwise, because the 2 alkene are coordinated to the metal centers and form a intermediate.

However the modern, however the recent spectroscopic methods have proved that this both the mechanisms are ruled out. That means the pairwise mechanism actually does not, do not, does not work I will give one example that how it can be proved.

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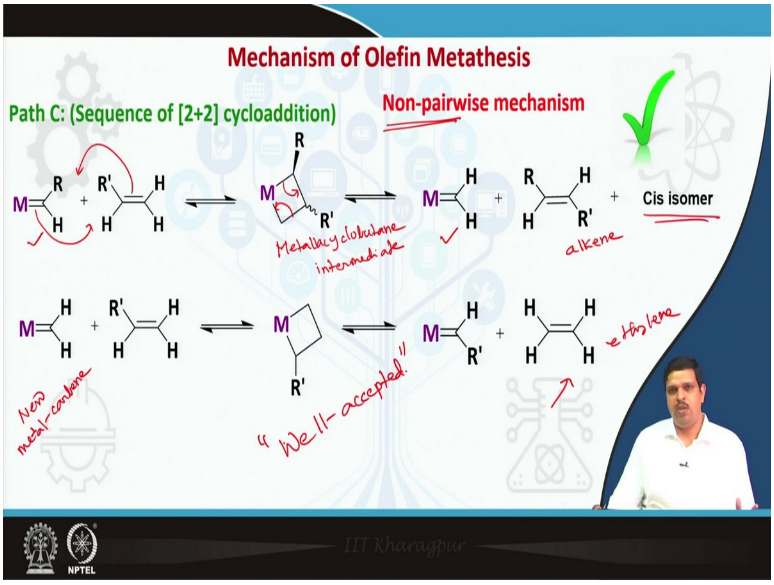
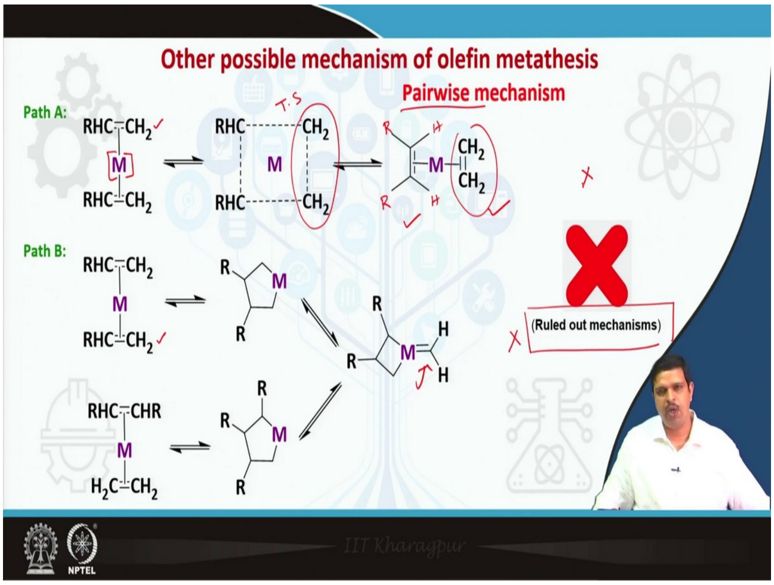


Mechanism of Olefin Metathesis

Path C: (Sequence of [2+2] cycloaddition)

Non-pairwise mechanism



Other possible mechanism of olefin metathesis

Pairwise mechanism

So, what is the more well accepted mechanism, that is this one that is called the non-pairwise mechanism. What is the non-pairwise mechanism. So, here you see this is my metal carbene, this is the, this we have just taken as a general form nothing more specific metal carbene. So, this is assume as a metal carbene and it forms a cyclobuta metallocycllobutane.

So, this is basically the reactions is we already discussed in the previous classes like that. So, it forms a metallocyclobutane, this is called the metallo cyclo butane, this is a intermediate and so, and then it the bond breaks just the reverse as it was formed. So, how does it work? So, it is basically what happens the bond formation was in this direction. So, now it will be just opposite in direction like this, the bond breaking will be just opposite direction. And you will get that this new metal carbene and this is your new alkene.

And similarly Cis isomers can also be formed. So, again this new metal carbene again that this is the new metal carbene that actually can again react with the another alkene and form the another new alkene that is the ethylene in this case. So, this is the ethylene. So, this mechanism that is the non-paired mechanism is the most well accepted mechanism and it is believed that, that metal alkene metathesis reactions are proceeds through the non-pear wise mechanism that is through a metallo cyclo butane intermediate, I hope it is clear.

So, again these reaction, these mechanisms are ruled out that is the pairwise mechanism and so no need to think about it this, the that is the non-pairwise mechanism that is through the metallo cyclo butane is the well accepted mechanism for the alkene metathesis reactions anyway. But what is the proof?

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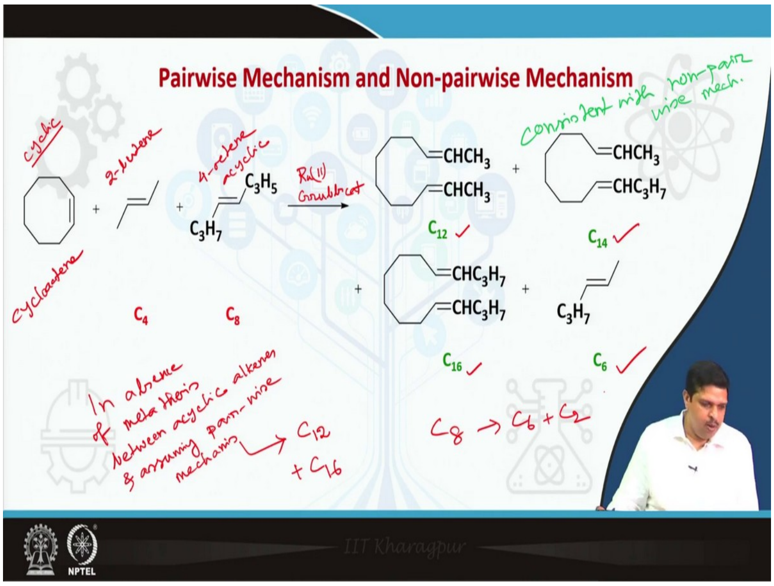
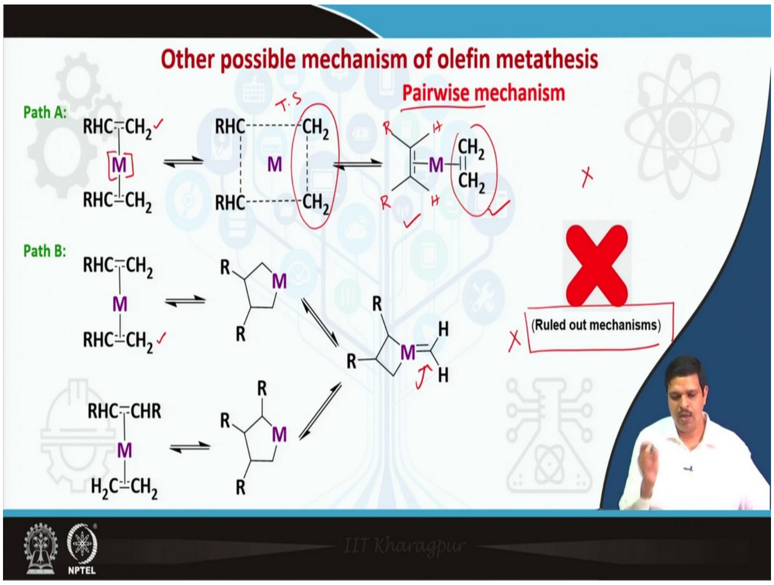

Pairwise Mechanism and Non-pairwise Mechanism


Other possible mechanism of olefin metathesis

Pairwise mechanism

(Ruled out mechanisms)

This can be proved in by a very easy experimental methods and by is designing a suitable experiments, this is one of them is a very well and famous experiment to prove that, that this proceeds through a cyclo butane metallo cyclo butane that is the non-pairwise mechanism. So, here what is, what you have seen here you will see that this is a cyclo octene and this is the 2 butane and this is 4 octene. So, this is cyclic and this is as acyclic with the same number of carbon atoms CH cyclic alkene and CH acyclic alkenes.

Now if you do the metathesis reaction let us take, let us assume that you take a ruthenium to any graphs catalyst. Then what happened, if you consider the pairwise mechanism then and cyclo octene should undergo the reaction and what you will get, you will get only the 12 member at 12 C12 and C16 at the initial step of the reactions. So, in absence of metathesis between acyclic alkene and assuming pairwise mechanism. Then at the initial stage you should get all the C12 and 1C6 because if you recall this mechanism this one. So, this is you will see that, at the initial this is alkene will form. So, C 12 and C12 that is the 2 alkene you can get it.

But we, what we observe experimentally, we observe the C14 and C6 also. And how it is possible, if you consider the non-pairwise then only this C14 and C6 can be can be formed. So, because see from C8 you will get C6 because you will get from C8 you will get C6 plus C2. So, this observation is consist consistent with the non-pairwise mechanism. So, the observation the statistical distribution of different alkenes at the initials phase of the reaction is consistent with non-pairwise mechanism that is through (cycl) metallo cyclo butane.

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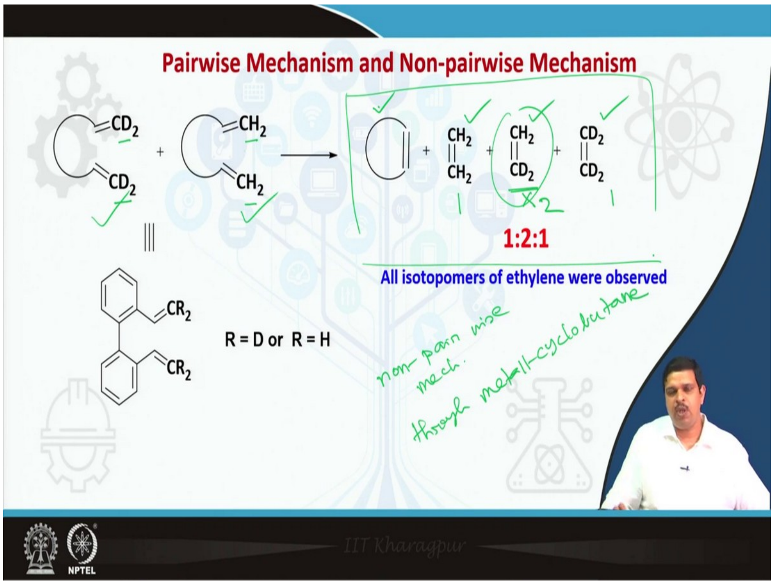

Pairwise Mechanism and Non-pairwise Mechanism

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All isotopomers of ethylene were observed

R = D or R = H

non-pair wise mech.

through metall-cyclobutane

So, another very very famous proof of whether it is pairwise or non-pairwise that is this one. So, here you will see that 2 alkenes has been taken one is with deuterated and one with H2 CH2 CH2. Now if all here you will see that if in object in reality in experiment what you get you will see that all the isotopomers that is the, this one, this one, this one and obviously this one. If it is pairwise mechanism then you should not have got this part but as it is a pairwise mechanism you will get the statins statistical distribution as 1 2 1.

So, this actually clearly proves that the alkene metathesis reactions proceeds through the non-pairwise mechanism, that is through metallo cyclobutane, metallo cyclone butane. So, I think it is very clear. So, again you will see that if it is pairwise then this one or this one will coordinate this one or this one will coordinate to the metal centers and you will get either CH2 ethylene the non deuterated or the deuterated CD2 CD2 fully deuterated ethylene. If it is non-pairwise, then only you can we can get the partially deuterated ethylene that is the CH2 CD2 that is 1 is to 2 is to 1 statistical distribution.

So, as experimentally all the ethylenes, all the ethylenes were observed and so it directly proves that, that the mechanism proceeds through the non-pairwise mechanism.

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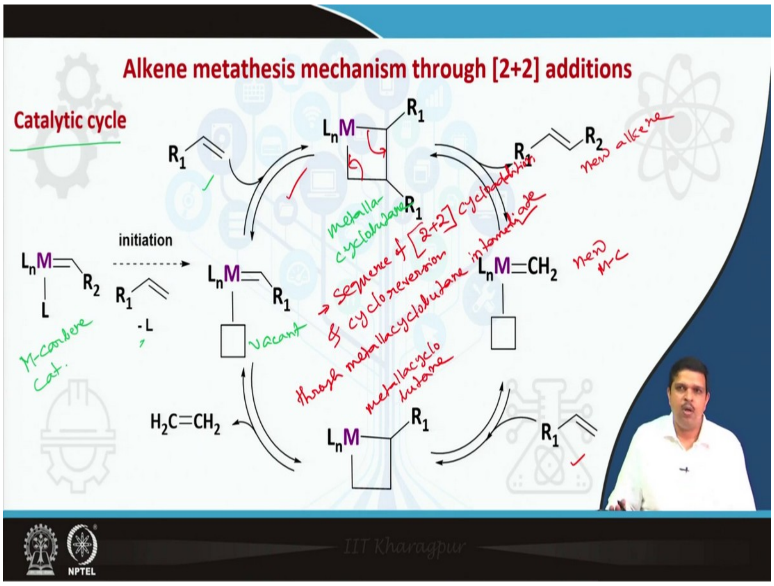

Alkene metathesis mechanism through [2+2] additions

Catalytic cycle

So, now with the knowledge of this experiment and the concept the following mechanism can be constructed, you know that this is called the catalytic cycles. We in organometallic chemistry or catalysis we try to construct the catalytic cycle to show that catalyst can be again back to the initial state, so that it can be reused.

So, here you will see that, if we start with let us say this is my the the pre-catalyst or the metal carbene catalyst, catalyst and you will have to have some make the coordinate to unsaturated. So, that the alkene that is the new alkene coordinates. So, this is called the initiation step. So, that the one M comes out and you get the vacant site.

And then you will see that this alkene coordinates and it forms a metallo cycllo butane. And then you get your, this intermediate. And then again this metallo cyclo butane breaks at and this way. So, you will form a new metal carbene and this new alkene also will be formed. And then you see again thus alkene will coordinate and form the again the metallo cyclo butane. And again it will break like that and this breaking will be just the reverse of the bond breaking, bond making.

So, bond breaking and bond making the, it will be just the reverse direction. So, that is why you will see that, this alkene metathesis the catalytic cycle is basically the sequence of 2 plus

2 cycloaddition and cycloreversion. You see that this is addition and this is the cycloreversion breaking and forming the cyclo butane and then making the cyclo butane and it is repetitive pathway through the metallo cyclo butane intermediate. So, I hope this is very clear.

So, alkene metathesis mechanism proceed through a 2 plus 2 cyclo addition reactions through a non-pairwise mechanism through metalo cyclo butane formation.

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Versatility in alkene metathesis

Now mechanism is understood, how, what, how the reaction proceeds. Now I will discuss about the versatility in alkene metathesis reaction and after that I will come to the alkene polymeration reactions, how it is possible by the this kind of catalyst. Before that, it is it is very important to understand that how the other and the other alkene metathesis reactions are possible, then we will discuss that how it can be applied to polymeration synthesis, polymeration and for polymer synthesis reaction.

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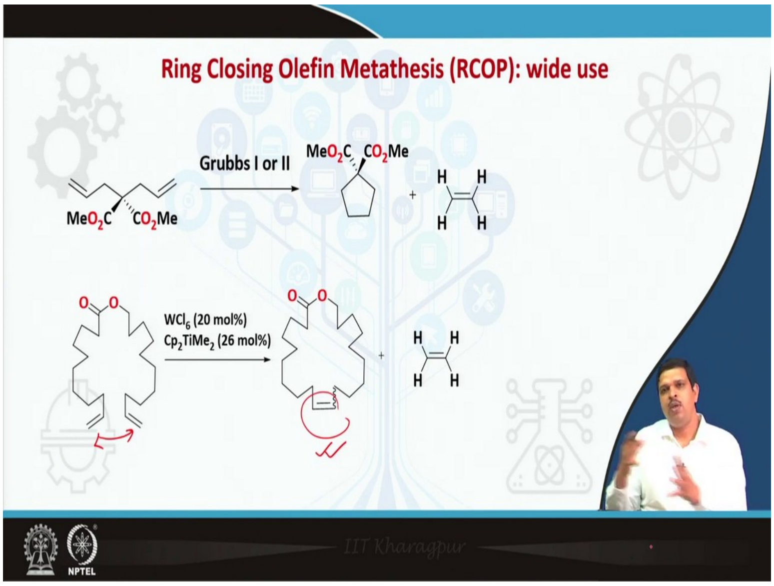

Ring Closing Olefin Metathesis (RCOP): wide use

So, first we will see that ring closing olefin metathesis in the beginning of our metal carbene complexes I mentioned that different type of alkene metathesis reactions are possible like ring closing metathesis, ring opening metathesis, cross metathesis, and very related to the ring opening is ring opening polymerization ROM, ring opening metathesis polymeration. So, this is the ring closing polythene metathesis reaction.

So, here you will see that, this alkene is basically threaded by using a using the catalyst. So, this kind of reaction is called the ring closing metathesis. That means you are, suppose I have alkene this here and what we are doing we are basically the or closing the ring and forming the another this alkene if it CH2 to CH2 and then. So, here you will see that this is called the ring closing metathesis reactions.

So, in from obviously from this reaction you will see the different type of valuated organic compounds may be synthesized as example if x is heterocyclic, then different type of heterocycles may be synthesized and these are very popular in organic chemistry to make different functionalized organic compounds and very quite popular in also in the medicinal industries.

So, here you will see that different type of examples like here you here see here that how different interesting functional the cyclic rings can be formed by the different type of catalyst or like graphs catalyst or different modified the metal alkyne catalyst. So, here example here you will see, it is basically here we are threaded, this alkene. And here you will see, it is a just threaded this one and you getting a from acyclic to a cyclic organic compounds.

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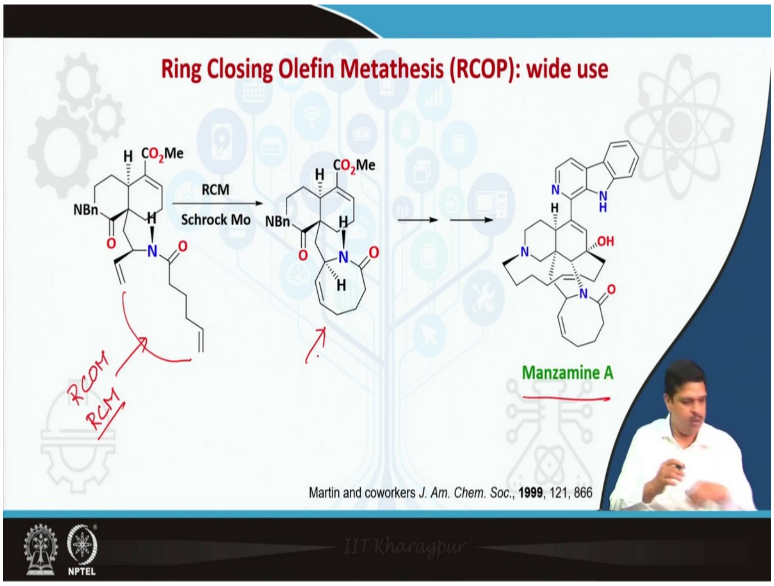

Ring Closing Olefin Metathesis (RCOP): wide use

Martin and coworkers *J. Am. Chem. Soc.*, **1999**, 121, 866

So, not only that this ring closing metathesis reactions are very popular and widely used in multiple steps in synthesis of natural products like one example is the manzamine A, here you will see, this step you see that this is actually the ring closing metathesis reaction. So, this is ring closing metathesis reaction call or sometimes called RCM green closing metathesis reaction. So, here you will see that this step is, this is just a one example there are numerous examples, where multiple, where different for synthesis of different type of natural products in one or more or more than one steps the graphs catalysts have been used very widely crops or stock type of metal carbene catalysts.

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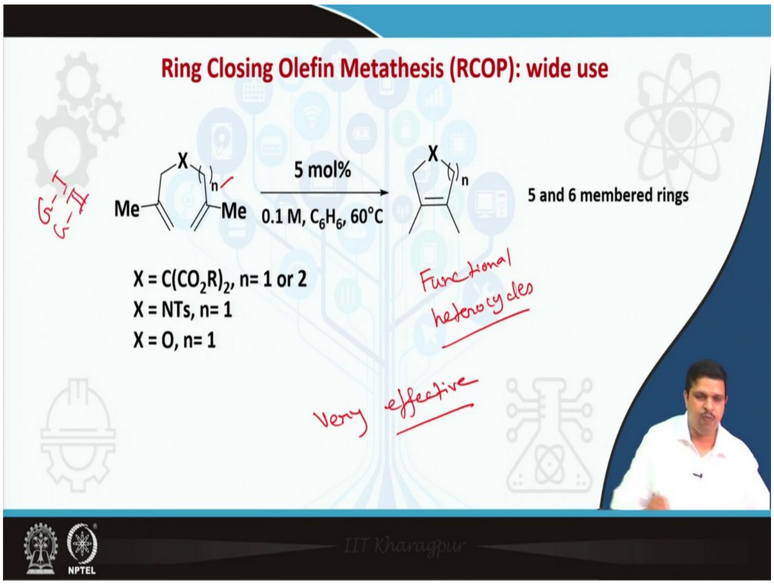

Ring Closing Olefin Metathesis (RCOP): wide use

X = C(CO$_2$R)$_2$, n= 1 or 2
X = NTs, n= 1
X = O, n= 1

So, you will see this very popular nowadays and here you will see the very similar the different type of heterocyclic organic heterocycles can also be synthesized you will see that depending of your n. So, you can make 5 members, 6 members, 7 member heterocyclic compounds different functionalized, functional heterocycles and is a very effective very effective method and that is why it is so popular in organic synthesis and also in medicinal chemistry. So, all the graphs catalysts, graphs catalyst G1 G2 are very effective for this kind of a reactions.

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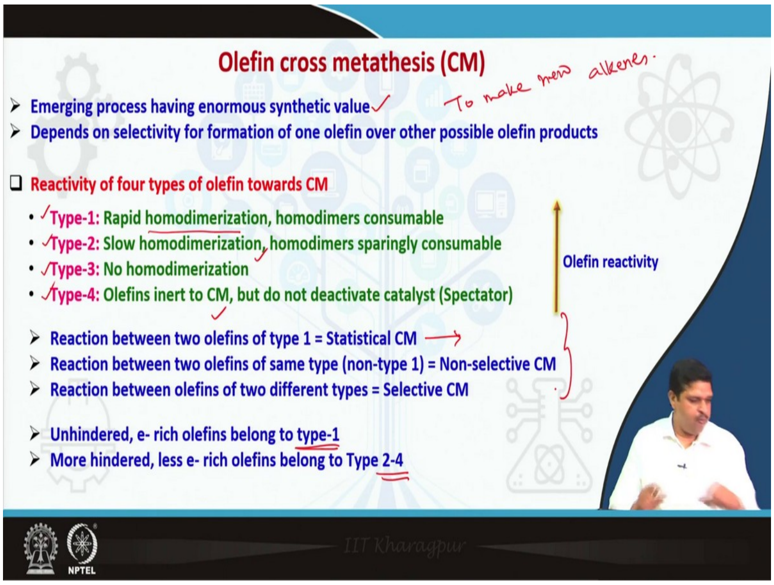

Olefin cross metathesis (CM)

To make new alkenes.

- Emerging process having enormous synthetic value ✓
- Depends on selectivity for formation of one olefin over other possible olefin products

☐ Reactivity of four types of olefin towards CM

- ✓Type-1: Rapid homodimerization, homodimers consumable
- ✓Type-2: Slow homodimerization, homodimers sparingly consumable
- ✓Type-3: No homodimerization
- ✓Type-4: Olefins inert to CM, but do not deactivate catalyst (Spectator)

Olefin reactivity

- Reaction between two olefins of type 1 = Statistical CM
- Reaction between two olefins of same type (non-type 1) = Non-selective CM
- Reaction between olefins of two different types = Selective CM

- Unhindered, e- rich olefins belong to type-1
- More hindered, less e- rich olefins belong to Type 2-4

So, not only the just a ring closing metathesis the cross metathesis reaction is also very popular in organic chemistry and also different industrial domains to make the new alkenes or modified alkenes. So, these are lots of synthetic values and also the lots of opportunities to make, to make new alkenes. And here you see this is just a guidelines I have shown here that how we choose or how you, how will justify that what alkene will be more reactive, what which one will be not reactive or less reactive. You can you can categorize by the different type like type 1, type 2, type 3, type 4, the type 1 are generally the unhindered and electron rich. So, these are the type 1 and more hindered that is the less electrons, these are belongs to the type 2 and 4.

And why these are important, these are important to judge that which alkene will be more reactive for alkene metathesis reaction as example for type 1 its undergoes the rapid homodimerization and this homodimers communal that means it can react again, type 2 slow homodimerization, type 3 no homodimerization, and type 4 olefins inert to see a cross metathesis reaction but do not deactivate catalysts. So, it just acts as a ligand.

So, reaction between 2 olefins this is the guideline. So, if you react with 2 olefins you will get a statistical cross metathesis reactions, reaction between 2 olefin of same type. You will get the non-selective cross metathesis reactions and reaction between olefins of 2 different type then you will get the selective cross-metathesis reaction. That means if there is a enough difference between the alkene metathesis the reactivate of the 2 alkenes then I will tell that, yes I will get this product in a major amount. So, this is good to know very useful guidelines to choose the or to judge that what product I will get or what ligands or what alkenes I will take it. So, this is a very useful general guidelines.

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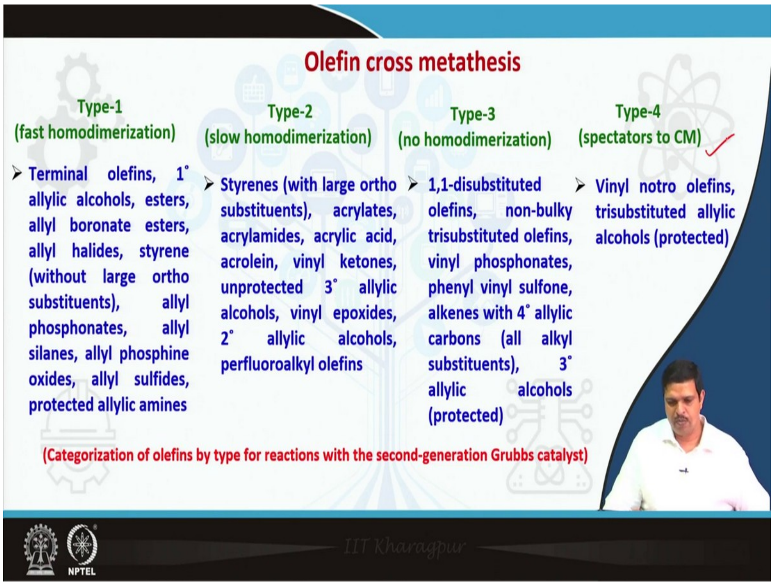
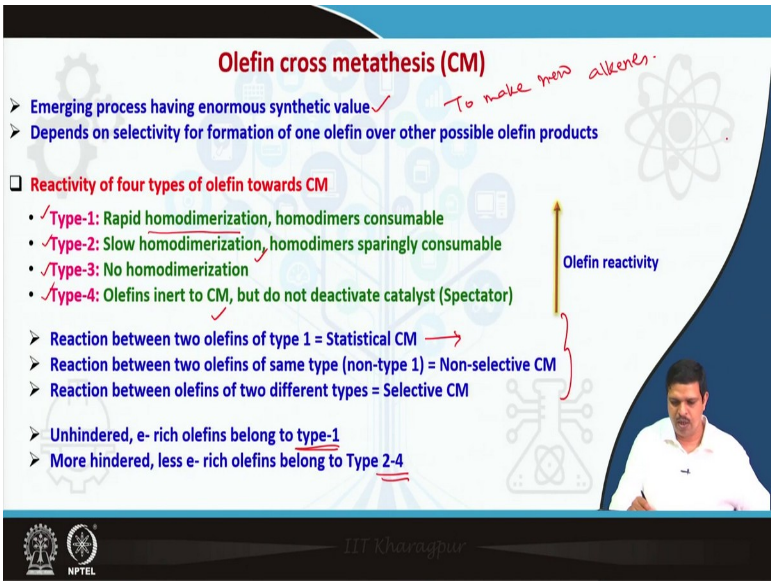


Olefin cross metathesis

Type-1 (fast homodimerization)	Type-2 (slow homodimerization)	Type-3 (no homodimerization)	Type-4 (spectators to CM) ✓
➢ Terminal olefins, 1° allylic alcohols, esters, allyl boronate esters, allyl halides, styrene (without large ortho substituents), allyl phosphonates, allyl silanes, allyl phosphine oxides, allyl sulfides, protected allylic amines	➢ Styrenes (with large ortho substituents), acrylates, acrylamides, acrylic acid, acrolein, vinyl ketones, unprotected 3° allylic alcohols, vinyl epoxides, 2° allylic alcohols, perfluoroalkyl olefins	➢ 1,1-disubstituted olefins, non-bulky trisubstituted olefins, vinyl phosphonates, phenyl vinyl sulfone, alkenes with 4° allylic carbons (all alkyl substituents), 3° allylic alcohols (protected)	➢ Vinyl notro olefins, trisubstituted allylic alcohols (protected)

(Categorization of olefins by type for reactions with the second-generation Grubbs catalyst)



Olefin cross metathesis (CM)

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❑ Reactivity of four types of olefin towards CM

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- ➢ Reaction between olefins of two different types = Selective CM

- ➢ Unhindered, e- rich olefins belong to type-1
- ➢ More hindered, less e- rich olefins belong to Type 2-4

This is just for the extra knowledge I have tabulated this one. So, this is basically nothing but continuation of this one.

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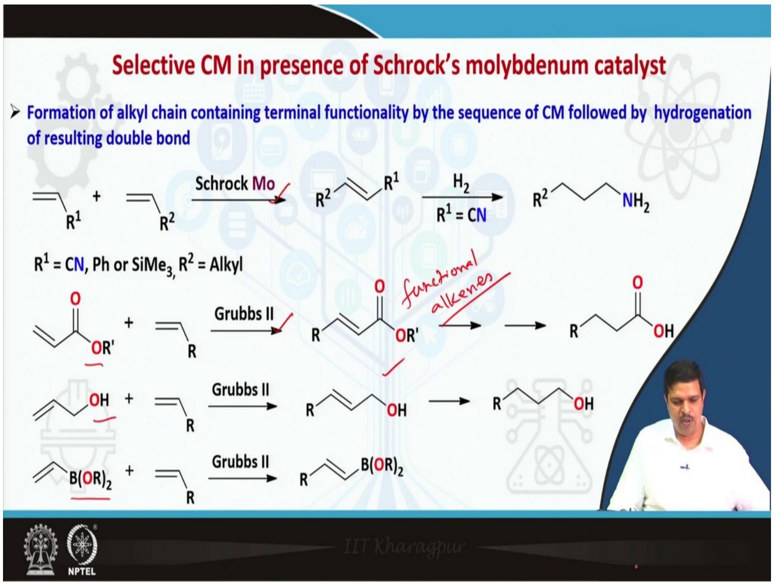

Selective CM in presence of Schrock's molybdenum catalyst

- Formation of alkyl chain containing terminal functionality by the sequence of CM followed by hydrogenation of resulting double bond

R^1 = CN, Ph or $SiMe_3$, R^2 = Alkyl

functional alkenes

So, here you will see the different type or some examples of the cross metathesis reactions and here you will see that stock molidum catalysts or Grubbs 2 catalyst or Grubbs can undergo, can undergo very efficient cross metathesis reactions and here you will see as I told that this kind of catalyst are very compatible with different functional moieties. Here you will see ester, alcohol, even the borate, even the amines, so that is why it is so useful to make the functionalized new alkenes. So, here you will see functional alkenes.

So these are and then after that you can again modify the alkenes, 2 different acids, alcohol, ester whatever you need.

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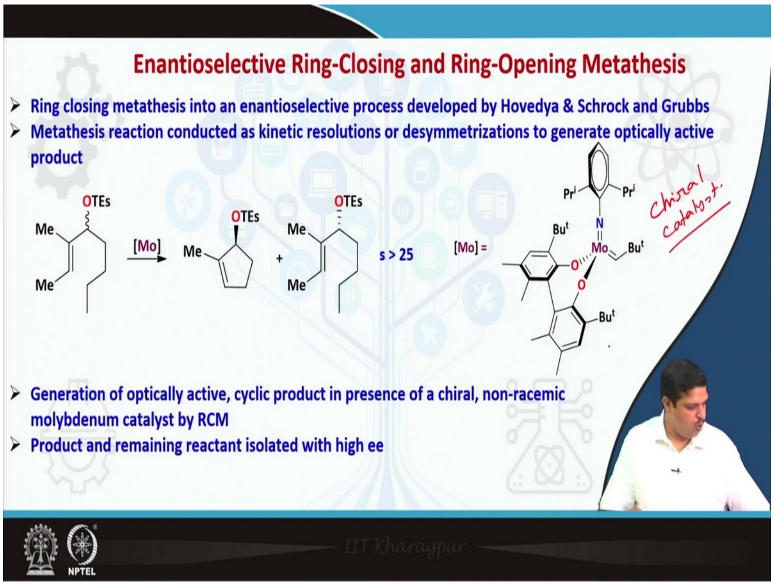

Enantioselective Ring-Closing and Ring-Opening Metathesis

- Ring closing metathesis into an enantioselective process developed by Hovedya & Schrock and Grubbs
- Metathesis reaction conducted as kinetic resolutions or desymmetrizations to generate optically active product

Chiral catalyst

- Generation of optically active, cyclic product in presence of a chiral, non-racemic molybdenum catalyst by RCM
- Product and remaining reactant isolated with high ee

If you, so this is really very useful method and very effective method for to make a new valuated, valuated alkanes not only that one, you can also make a stereoselective, make this reaction stereoselective by choosing the chiral catalyst in, we have already discussed about how you can make a particular reactions asymmetric by choosing the chiral catalyst which proceeds through the CSC, that is the catalyst site control mechanism.

So, here you will see that if you use the chiral catalyst you can control the stereoselectivity and you can get a particular stereo isomer.

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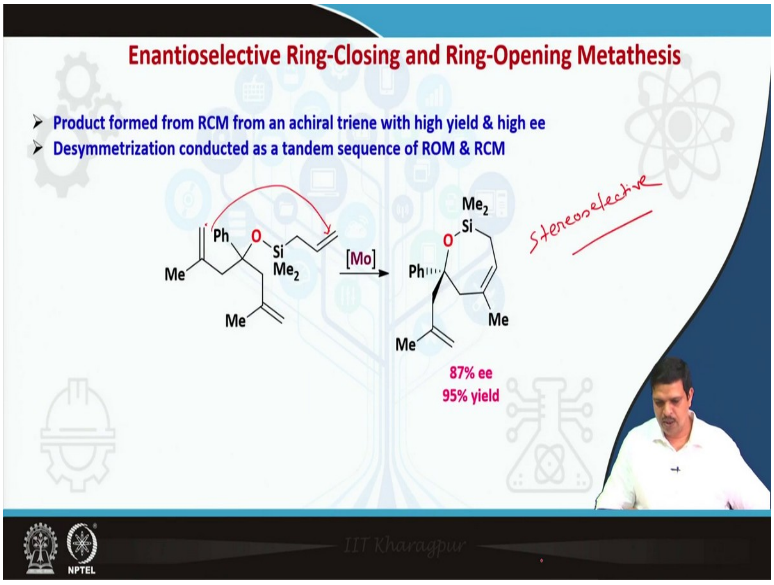

Enantioselective Ring-Closing and Ring-Opening Metathesis

- Product formed from RCM from an achiral triene with high yield & high ee
- Desymmetrization conducted as a tandem sequence of ROM & RCM

87% ee
95% yield

Stereoselective

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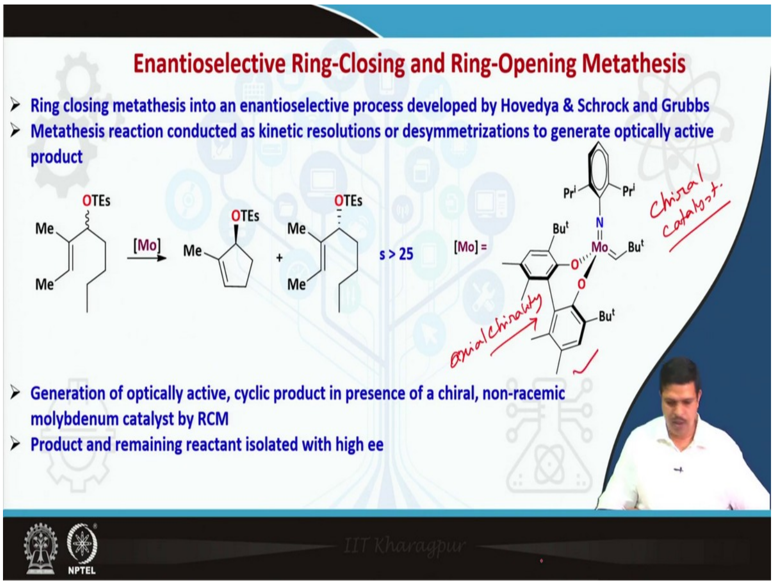

Enantioselective Ring-Closing and Ring-Opening Metathesis

- Ring closing metathesis into an enantioselective process developed by Hovedya & Schrock and Grubbs
- Metathesis reaction conducted as kinetic resolutions or desymmetrizations to generate optically active product

chiral catalyst.

axial chirality

- Generation of optically active, cyclic product in presence of a chiral, non-racemic molybdenum catalyst by RCM
- Product and remaining reactant isolated with high ee

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And here you will see one example. So, what you will see that you are basically you are closing. Here you see that you are you are making this reaction stereoselective by the chiral modified, modified the stocks catalyst, here you will see that the chirality is coming from the, this axial chirality, axial chirality of substituted by phenyl. So, that you know that, how this axial chirality is a plays a role to make optically active.

So, here these are some basically this is just for your knowledge and showing the examples to prove that how versatile these reactions are. Not only that that is, not only this.

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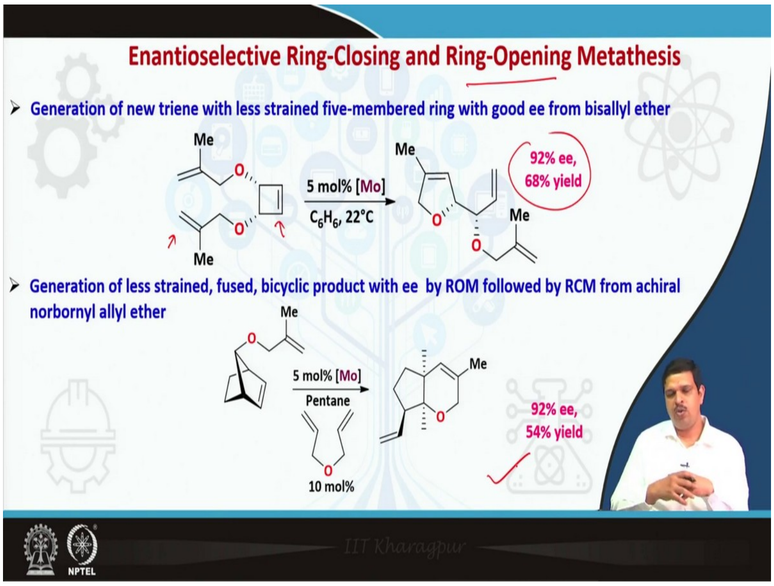

Enantioselective Ring-Closing and Ring-Opening Metathesis

- Generation of new triene with less strained five-membered ring with good ee from bisallyl ether

- Generation of less strained, fused, bicyclic product with ee by ROM followed by RCM from achiral norbornyl allyl ether

But there are various examples here you will see again that, you are how you can make the ring opening metathesis reactions by ring opening and ring closing both here actually. So, here basically what you are doing? You are closing the metathesis, closing the ring here, and here the opening, so simultaneous simultaneously ring closing and reopening reaction and here you will see that how you can make the stereoselective. So, here also same thing.

So, using the chiral metal carbene catalysts. So, these are some kind of a some kind of example that how you can design your catalysts to make the chiral and to make the reactions to setereoselective.

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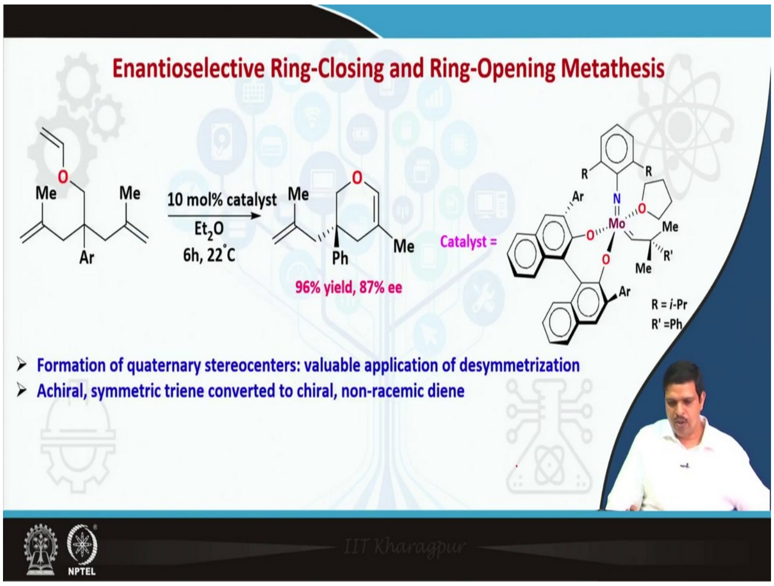
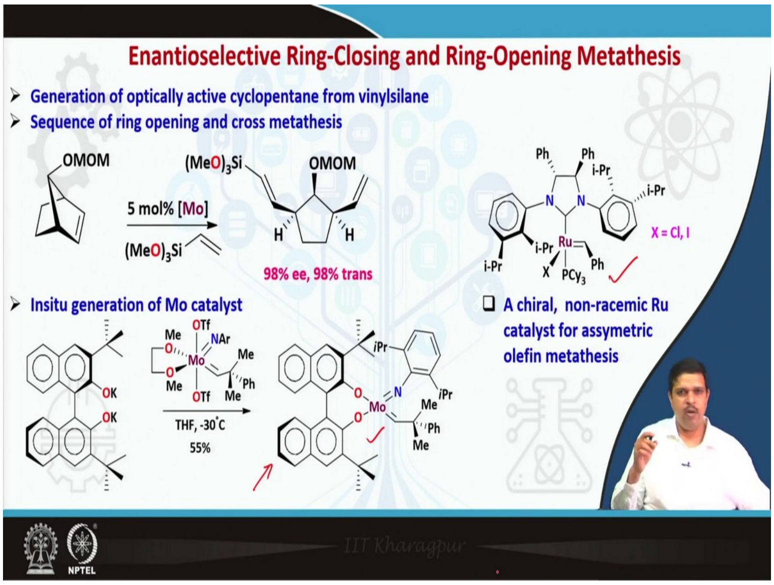


Enantioselective Ring-Closing and Ring-Opening Metathesis

96% yield, 87% ee

- Formation of quaternary stereocenters: valuable application of desymmetrization
- Achiral, symmetric triene converted to chiral, non-racemic diene



Enantioselective Ring-Closing and Ring-Opening Metathesis

- Generation of optically active cyclopentane from vinylsilane
- Sequence of ring opening and cross metathesis

98% ee, 98% trans

- Insitu generation of Mo catalyst

☐ A chiral, non-racemic Ru catalyst for assymetric olefin metathesis

So, these are again another examples. So, you will see that here not only the stocks there are different catalysts like ruthenium catalyst, the graph modified, graphs catalyst also you can make the chiral and you will see that like for molybdenum if you this is like a binap. So, again it is a axial chirality and this is the chiral ruthenium graphs type of catalyst. This also chiral catalyst and this chiral catalyst actually control the stereoselectivity of different type of metathesis reactions.

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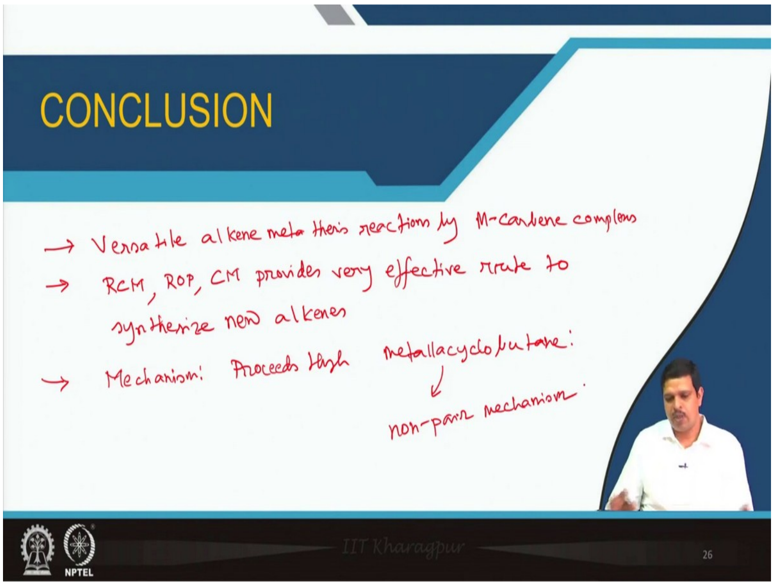

CONCLUSION

→ Versatile alkene metathesis reactions by M-carbene complexes

→ RCM, ROP, CM provides very effective route to synthesize new alkenes

→ Mechanism: Proceeds through metallacyclobutane:

↓

non-pair mechanism.

So, in conclusion you will see that versatile, versatile alkene metathesis reaction. Reaction by metal carbene catalyst complexes, you will see that ring closing metathesis or ring opening metathesis or the cross metathesis provides very effective root to synthesize new alkenes. And mechanism we have learned that proceeds through, through metallo cyclo butane. That means you will see that, it is proceeds through a sequence of cyclo butane metallo cyclo butane formation, and then metallo cyclo butane breaking. So, and this through a through actually the non-pairwise mechanism. That means at a time only one alkene is coordinates and forms the metallo cyclo butane.

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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, the today's lecture, you can, for the today's lecture you can read the books mainly the Hartwig and the Crabtree’s book, most of the contents are available in these 2 books. So, thank you very much for today's lecture. And in the next class we will discuss about the another versatile, that is the main topic of our metal carbene classes, that is the polymeration alkene polymeration by metal carbene catalyst.

We will discuss how this polymeration proceeds. And the again the versatility of the monomers. And what are the scope of, and the future prospect of the alkene polymeration by metal carbene catalysts. Thank you and see you in the next class.