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

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Lecture 34

Metal-carbene complexes as versatile catalysts for multiple useful reactions: A short introduction (Contd.)

Welcome, so in the last class, we started about the metal carbon complexes and we discussed and we started the discussion about each applications as versatile catalysts for multiple and useful reactions. So, in the last class, if you remember, we started to know about the metal carbon, what are the metal carbon complexes and also metal carbon complexes?

And what are the basic chemical structure and today, we will be continuing to our discussion about the metal carbene.

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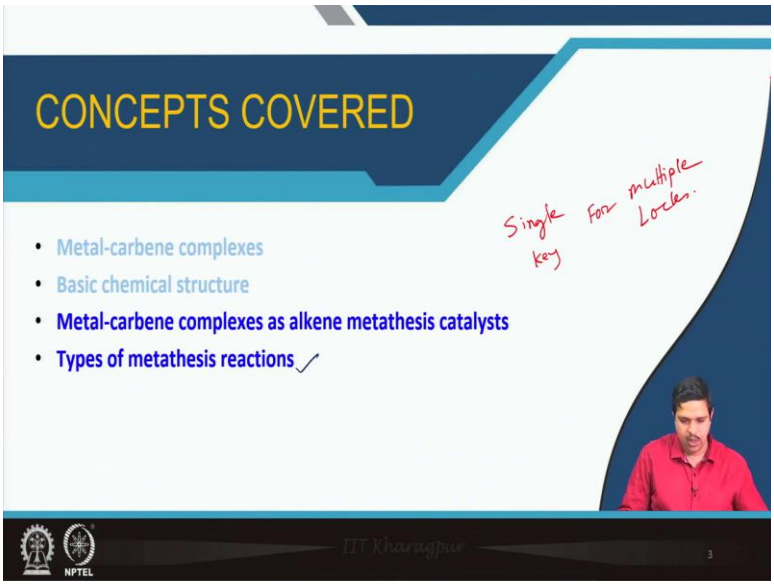
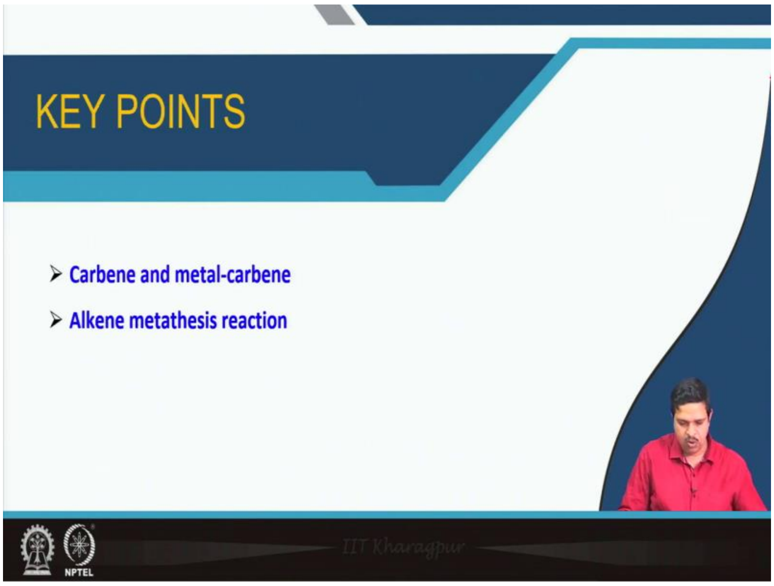


CONCEPTS COVERED

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

Single key For multiple Locks.



KEY POINTS

- Carbene and metal-carbene
- Alkene metathesis reaction

And today we special focus on the types of alkyne metathesis reactions. And it is catalysts. And today mainly we will learn that how many types of reactions can be performed by the same type of molecules. So, it is basically you will learn here and you will see that it is a kind of a single lock single key, for multiple locks.

So, this is really interesting. See, one catalyst can perform many various types of alkene metathesis reactions. So, this is that is why it is so popular and useful in various domains of applications starting from the ground industries to the polymer industries, so we will be discussing.

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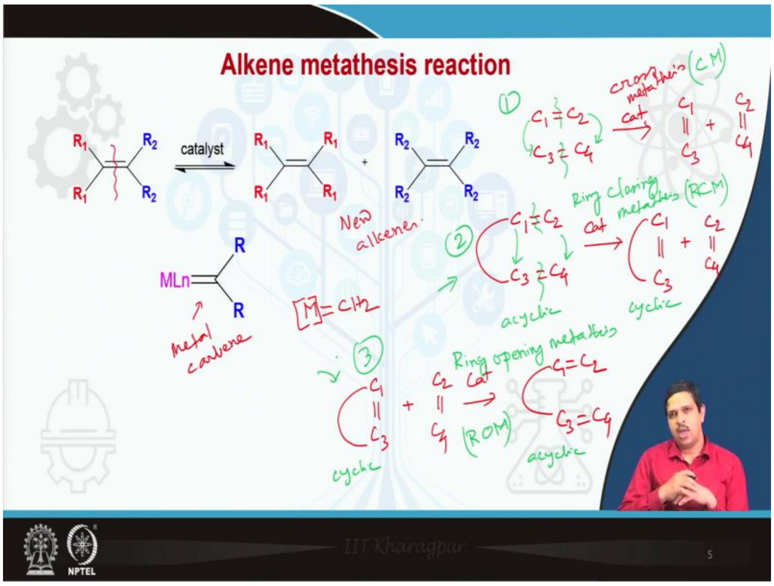

Alkene metathesis reaction

So, this one, now you are familiar, so this is called the alkene metathesis reactions. So, here you will see that this one if you can break it, and then you can again join the hub, the hub of the alkene to the another hub the alkenes and you will get the new alkenes, so the these are the new alkenes. And the basic structure of these kinds of catalysts is the this one, so that is actually the metal carbene.

And you will see that formerly you have double one. So, you can write like this one, there are other ancillary ligands are there. So, these are the basic structure of the metal carbene and various type of reactions we can perform. As example, like if you see here, C1, I am just writing all the alkene moiety. I am not writing a real molecules here. So, C3, C4. So, using this kind of catalyst, you can get the C1, C3 plus C2, C4.

So, you will see that two type of new alkenes you are getting. And this is obvious to them. So, what yeah, basically you see the exchanging of the carbon fragments. So, here that is why it is called the cross-metathesis reaction, what you are getting basically you are here showing in a different colour, so that it is easily so here basically.

So, it is breaking here and joining with this one and joining with this one so you are getting two new alkenes from other two alkenes. Now, very similar you can if this is, suppose this is a terminal alkene of one longer carbon molecules, or acyclic molecules. So, you will see there is some spatial here, that I am not writing in a real molecule. I am just showing the strategic way how, what are the…

So, this is now if you add, if you react with any catalyst the alkene… here I am catalyst means I am mentioning about the alkyne metathesis catalyst. Now, what you will be getting? You will be getting again the same like cross metathesis reaction you would be getting like this one and C2 C4. So, basically the reaction is same.

So, as you see the cross metathesis so here breaking here breaking here and then adding this one and adding this one. So, this is called the ring closing metathesis reaction. So, basically, you are getting a cyclic organic compound from a acyclic organic compound. So, this is the cyclic and this is the acyclic and this reaction called ring closing metathesis reaction.

So, this is the Cross Metathesis we call CM, this is called RCM Ring Closing Metathesis. And various types of similar reactions can be performed one another, which is very common. You will see that C again, I am showing as just as a unit as I told I am not showing any real molecule. So, now I am doing the reverse one, I am taking a cyclic alkene and then what will happen you see, this one and I am taking another alkene and taking and treating with this kind of alkene metathesis catalysts.

So, now what will happen, you can imagine what will happen. So, it is basically the reverse reaction and reverse reaction. So, this is C1, C2 and C3, C4. So, that means you will see here that I am making a cyclic to acyclic. So, basically, here I am closing the ring, and here I am opening the ring. So, that is why the name is Ring Opening Metathesis reaction, in short, we call our ROM.

So, these are the three very important we can call the reaction protocols or by the alkyne metathesis catalysts and using these three types of reactions, you can also do the various type of advanced alkene metathesis reactions, but as I told the basically the reactions pathways are exactly will fall in these three categories. So, what are they, and you will after learning all the possible metathesis reactions you will understand how versatile applications are possible okay including the polymerization catalyst. And that is why it is so popular.

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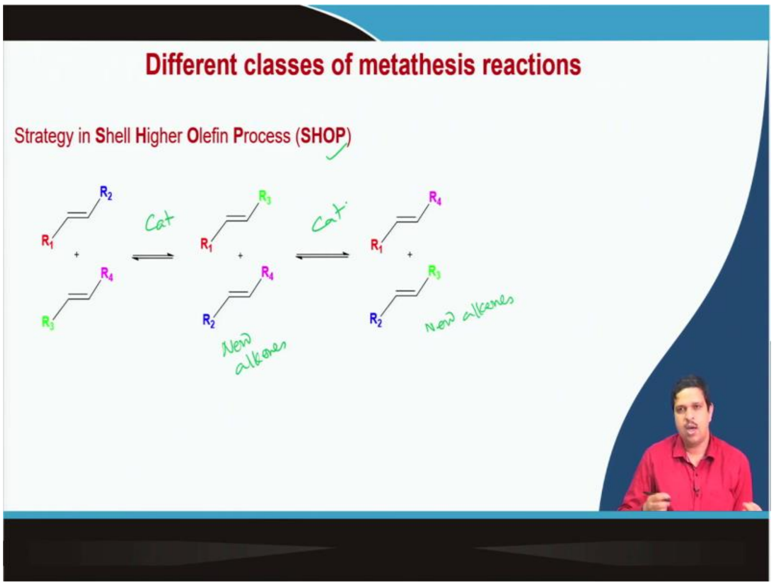

Different classes of metathesis reactions

Strategy in Shell Higher Olefin Process (SHOP)

So, let us try to understand in more depth. And here you see this is we already discussed that what are the strategy in the SHOP, SHOP means Shell Higher Olefin Process, in the last class also I just mentioned briefly and you will be realizing here what we are doing, so we are doing basically using a catalyst and we are making new alkenes and here again the new alkenes and within the same catalyst.

So, what you are see basically the changing of the R groups the substituents all the alkyne, and it is suppose if with this one if you make a want to make a higher alkenes you can start from the lower alkenes then to react with a medium… with a medium number of carbon atoms, then it will be higher and then again, that higher number of carbon atoms continue alkenes will react with another alkene and slowly it would increase the number of carbon atoms in the alkyne and that is the strategy will make alpha olefins from the simple Ethelene.

So, that is really very interesting that you see that how the metathesis catalysts are used in and this are quite old process, it is not that it is an… it is very much kind of very advanced. So, this is a old process, the SHOP process but very useful and using the concept of the alkene metathesis reaction, so that we already discussed, so I not go in again to repeat.

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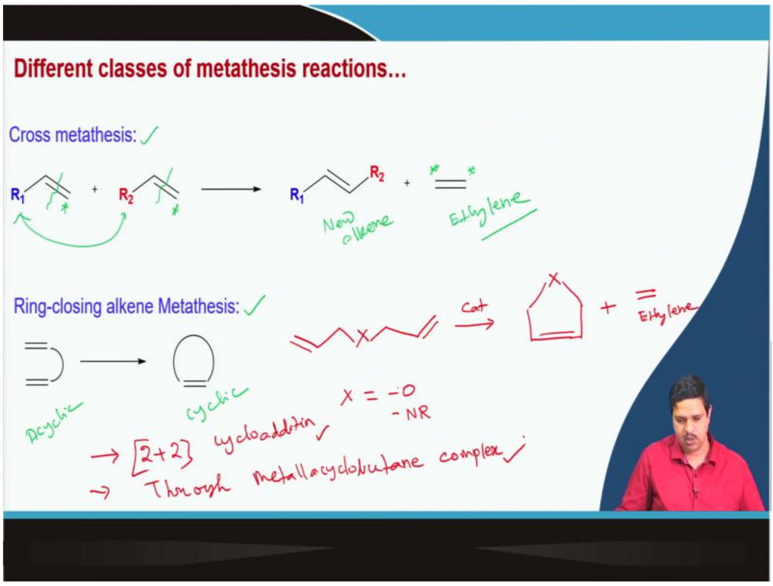

Different classes of metathesis reactions...

Cross metathesis: ✓

Ring-closing alkene Metathesis: ✓

→ [2+2] cycloaddition ✓

→ Through metallacyclobutane complex ✓

So, very similar as I told that cross metathesis reactions now, you understand, so I already discussed that, what is the cross metathesis here, so it is basically you will see you are breaking the bond here. And here and you are making and you are basically threading this R1 and R2 and you are making a new alkene. And you are getting the Ethelene that is that this part, this part and this part, so you are making Ethelene. So, this is called the cross-metathesis reaction. So, basically the exchanging of the substituents of one alkene, fine.

And this type of reactions as is called the ring closing metathesis So, it is basically as discussed just now that you can make a acyclic to cyclic. And here you will see that this is very common, using the catalyst I will come in more detail… later in detail about the catalyst structure, I just want to now discuss or give the highlight about the various types of the alkene metathesis reactions.

So, here one of the one very real example I am giving like if you have a X and like this one. And if you use the catalyst that is the alkene metathesis here I am catalyst spins alkene metathesis catalyst and X is equal to maybe oxide or maybe amide kind of things. And sorry, this is NMe will be… it may be NR fine, and then what will happen if you do the ring closing then what will happen?

So, this you will get a five-member alkene like that. And as a biproduct, you get the Ethelene. So, this is routinely used in as discussed in to make the valuable organic compounds in drug industries or as in other applications, so this is one of the very popular strategy of making a big cyclic molecules from a linear molecules using the metathesis reaction strategy, fine.

So, here you would see that in the ring closing alkene metathesis reactions there are if you see… this kind of alkene metathesis reactions goes through a 2 plus 2 cycloaddition through metallacyclobutane complex, so I am sure how it is possible. So, if you now see, if you consider these two steps, for forming for the metathesis reactions, that is two possibilities. And that way we will be discussing now.

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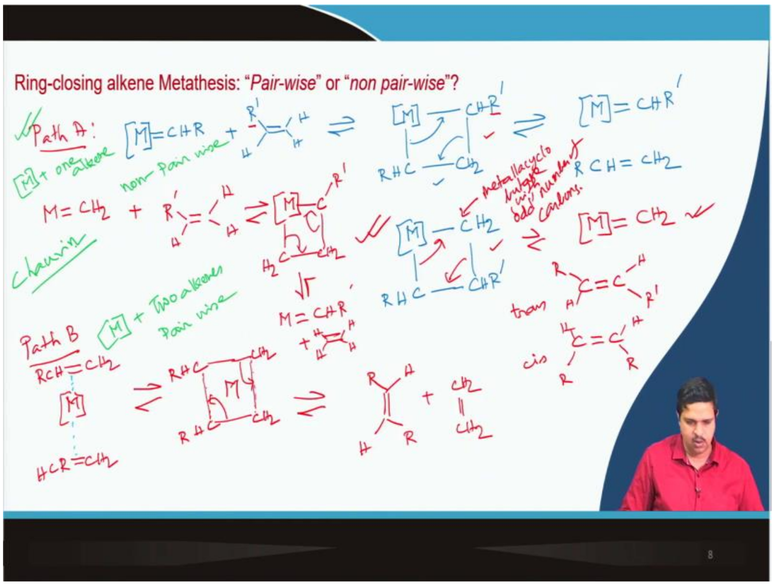
Ring-closing alkene Metathesis: "*Pair-wise*" or "*non pair-wise*"?

That ring closing metathesis what are the different pathways are possible one is the pairwise and one is the non-pairwise and what are they? It is easy to understand if I hear you see that I you can practice with me, so that it will be more clear to you. Now, I am considering as path A the possibility number 1 I am taking a arbitrary molecule and the catalysts

So, let us say this is the M CHR and this is obviously arbitrary. So, just keep it like third bracket I am not mentioning the real metal centre or any of the ancillary ligands. Now, I am reacting with one alkene. So, this is my R prime and this are just simple hydrogen. Now, as I told that this goes through a metallacyclobutane intermediate.

So, what are these? So, this is basically like C HR and… now, then what will happen? You will see here so this is my R prime this is the R prime group that the group on the alkene and then what will happen? You will see that now, we can further it can now, it will be the breaking of the metallacyclobutane.

So, what alkyne will be now form? The new alkene will be like this one. And that one. Now, so you will get CHR prime and you will get the CHR, so that is this one CHR and CH2. And another possibility maybe there, that is the this one and CH2 that is two metallacyclobutane will be may form that is the this one.

Now, so is basically this alkene how it is arranged, either this way or either this way. So, this is will be favoured and if you get this one then what new metal alkene you will get? You will get this one and you will get so this is like this way. So, you will get a new alkene and also the cis and here obviously the hydrogen and hydrogen, hydrogen will be there. So, this is could be the trans and this will be the cis.

Now, again the MW CH now this is formed this one and now this one can react with M CH2 plus my the original alkene that is the this one. H, H, H and again it will form the metallacyclobutane that is the C CH2 and… So, this is the R prime and this is again the CH2. And now, this will now again it will break to this one and that one. So, you will get again M double bond CHR prime and you will get the Ethelene.

So, this is the one possibility. So, here what is happening you will see, that this is called the metallacyclobutane with odd number of carbon so here or means 1, 2, 3 three number of carbons and what are the other possibilities, the path B? So, Part B is basically two alkenes will interact simultaneously. So, suppose this is my metal fragment and I am this is my CH and similarly CH2 RCH now, there will be pi interaction.

So, there will be pi interaction here and then it will form like this one, so here CH2 CHR CH2 CHR. So, this kind of intermediate and then eventually you will get the new alkenes. So, that is the RH and CH2 double bond CH2. So, it is basically you are what you are getting we are getting here this kind of so here and here like that. So, in this case what so now try to understand what are the basic difference here.

So, here metal in this path A, metal carbene plus one alkene and here the metal carbene plus 2 alkene. So, that is why this is called pairwise and this is non-pairwise. So, two type of mechanism are possible and experimentally it is followed, it has been observed that path A is the best possible mechanism. This is also proposed by the scientist Chauvin.

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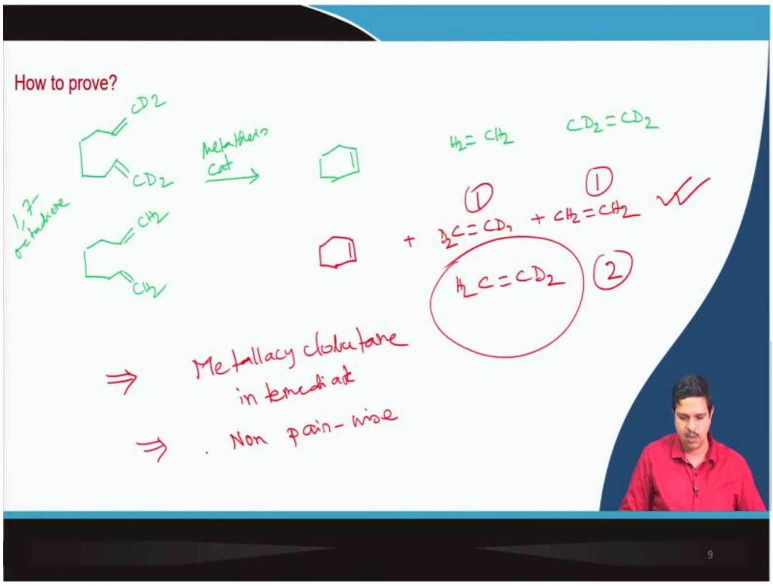
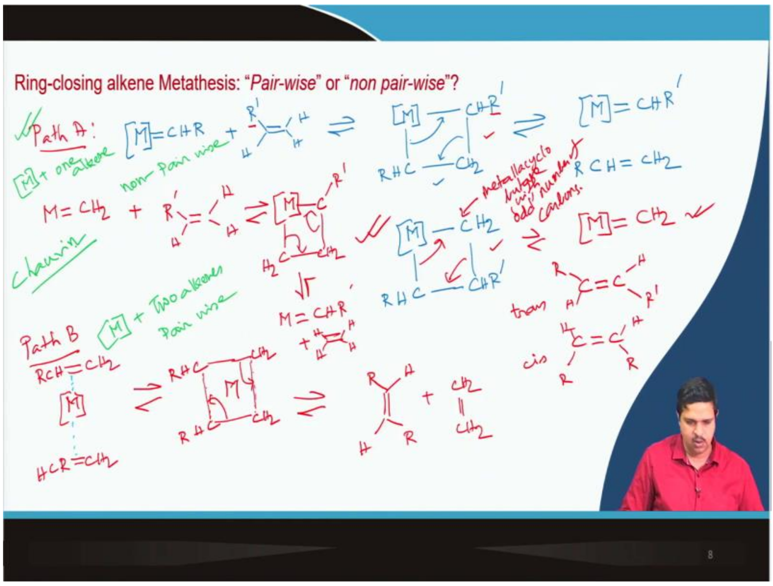


How to prove?



Ring-closing alkene Metathesis: "*Pair-wise*" or "*non pair-wise*"?

Now, you will now ask that how to prove it, that how it is happening non-pairwise, pairwise two possibilities are there one is the pair and one is the non-pairwise now how to prove it? You can sit a very simple reactions. Suppose I am making… take two substrates. And another one you take, non-diaurated version.

So, that means you can take CH2 and the CH2 one is the rotated diaurated version one is the non-diaurated version of 17 octadiene. So, now if you do the alkene metathesis reactions, you take the you charge these two organic compounds with metathesis catalysts. If you see this one the first as path B that is the pairwise then what are the possibilities?

The possibilities are this one and this one now, because these two alkenes will interact as a pairwise and these are the two possibilities, so if it is pairwise mechanism then you will get the hexi fine and you will get the other pair that is the CH2. Now, if you take it as non-pairwise mechanism that is the path A non-pairwise that is through the metallacyclobutane, then what may be the products total?

So, in obviously you will get the cyclohexene that is this one then you will get the CD2, CD2 that is and then you will get the CH2, CH2 and in additionally you will get the CH2 double bond CD2. So, here you will see you will get additional this one that is the Ethelene one side CD2 and one side CH2 the diaurated the mixture of the Ethelene.

And if it is non-pairwise mechanism that is a Chauvin mechanism through metallacyclobutane, then the statistical distribution of these products will be, this will be 1, this will be 1 and this will be the 2 and experimentally it has been observed that experimentally these statistical distributions are isolated.

So, that means, the alkene metathesis reactions are happens through the metallacyclobutane intermediate, that is through the non-pairwise wise mechanism. So, basically the intermediate with the odd number of carbon atoms. So, if you recall so you will see this odd number of carbon 3 three number of carbon atoms and in a pairwise there will be four number of carbon atoms. So, this is the direct proof that this metathesis reactions happens through the non-pairwise mechanism fine, it is really interesting.

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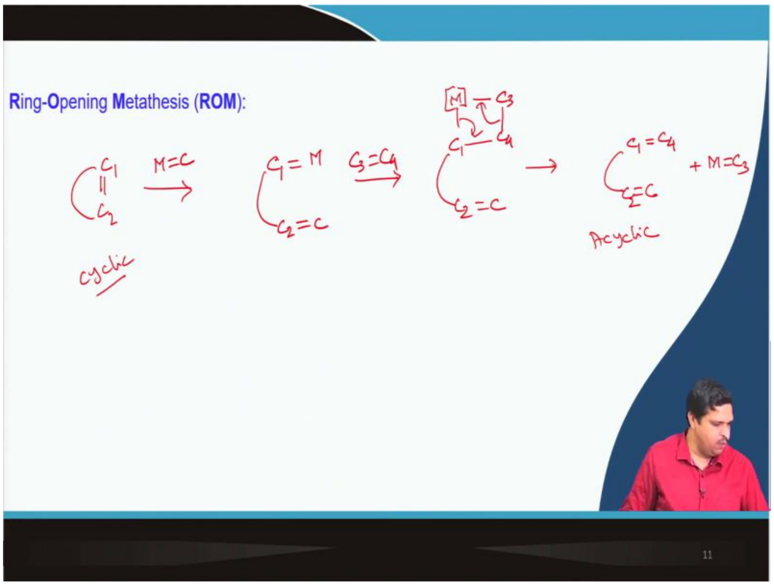

Ring-Opening Metathesis (ROM):

So, now, I will discuss about the Ring-Opening Metathesis reactions, what are the Ring-Opening Metathesis reactions? So, this is the ring opening metathesis reactions one example C1 C2. So, let us say like this one and then basically it will happens through the C1. So, if you take on catalyst that is the metal carbon, then what will happen? That this one will be C2 double bond C and then it will happen. The C1 level double bond one and C2 double bond C.

Now, here if you react with C3 double bond C4 now C here and then there will be another metallacyclobutane ring formation here C3 C4 and here the M metal. So, now here you will see now again it will break and then what will form? It will C2 double bond C as it is and then here you will see C1 double bond C4 and M double bond C3. So, like that one. So, here you will see that this is the cyclic and this is the acyclic, this is one of the example of the ring opening metathesis reactions.

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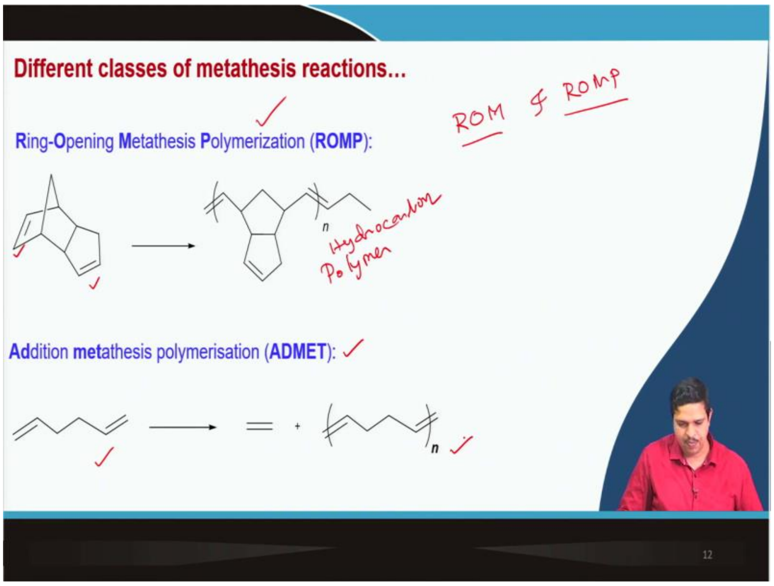

Different classes of metathesis reactions...

Ring-Opening Metathesis Polymerization (ROMP):

ROM & ROMP

Hydrocarbon Polymer

Addition metathesis polymerisation (ADMET):

And if we explored this one to a special category of the alkenes like this one, there were two alkenes group, you can do also polymerization that is a Ring Opening Metathesis Polymerization. So, basically the ROM and ROMP is similar, but here if you have a special monomer like this one two alkyne groups, you can do the ring opening polymer metathesis polymerization and you can get the hydrocarbon polymers.

So, we will discuss in more detail later about the ring opening metathesis polymerization, but this is the basically strategy to make the polymers by the alkyne metathesis catalyst we will discuss later this is another possible reactions. So, what we have learned? We have learned the ring cross metathesis reaction, ring closing metathesis reaction, we have learned the ring opening metathesis reaction, we also now know ring opening metathesis polymerization reactions.

Now, next one you will see this is called addition metathesis polymerization. So, this is also another polymerization reactions using the Grubbs… using the metathesis catalyst. So, here you will see if you pick it 2 L one compound with 2 terminal alkenes you will get the corresponding polymers which is through a addition metathesis polymerization that we will discuss later about the mechanism. But as you see that there is so many versatile reaction can be done using the single type of catalysts.

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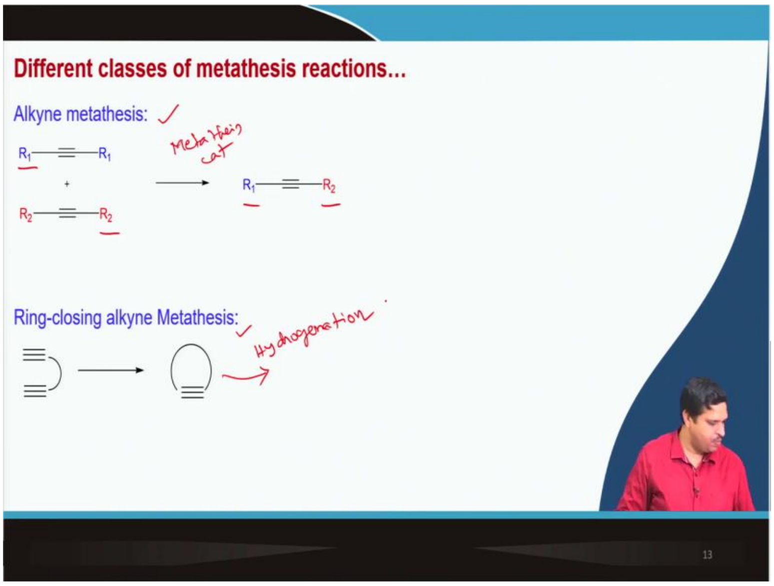

Different classes of metathesis reactions...

Alkyne metathesis:

Ring-closing alkyne Metathesis:

And not only that one it can be extended to the other pi complexes pi compounds like alkyne. So, here you will see is very much similar. So, this is alkyne metathesis reactions, so you can just correlate with the cross metathesis of alkenes. So, here is basically the cross-alkyne metathesis reactions. So, you see the exchanging the R1 group here. So, same metathesis catalysts.

Also you can also do the similar ring closing alkyne metathesis reactions, you can close it the ring closing alkyne metathesis reactions like that one and also you can then do the hydrogenation if you want the alkyne and if you need the sp3 carbon centre you can do the further hydrogenation. So, you can make your desired cyclic organic molecules.

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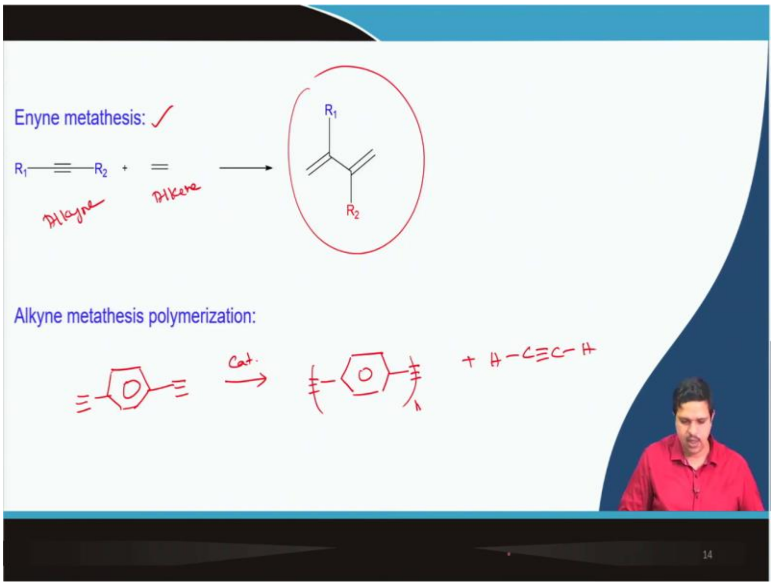

Enyne metathesis: ✓

Alkyne metathesis polymerization:

Not only that, you can also explore or extend to the other alkene metathesis reactions like you will see the Enyne metathesis reaction so one is the alkene, and one is the alkyne, so it is basically you will see the reacts alkene metathesis reactions with one alkyne and one alkene and you will get this kind of, compounds from the alkyne.

And not only that, so you can also do the alkyne metathesis polymerization, as you have already learned that this the addition metathesis polymerization does seem very good very much similar. So, here you see if you take I am just giving you a very simple example. So, if you take the, this para this alkyne benzene and if you do the metathesis reactions like suitable catalysts, so what you will get? You will get, and you in return you will get the acetylene. So, you will see that so many reaction can be done in using the alkyne metathesis catalyst.

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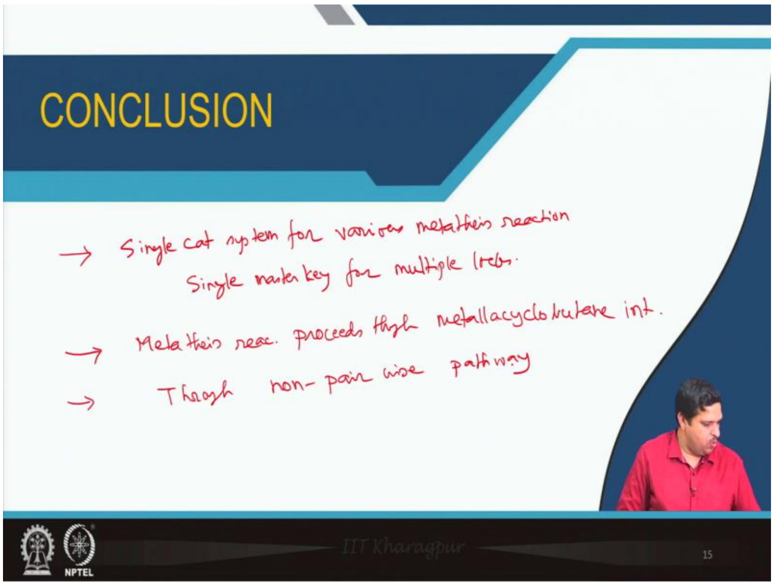

CONCLUSION

→ Single cat system for various metathesis reaction
Single master key for multiple locks.

→ Metathesis reac. proceeds thgh metallacyclobutane int.

→ Through non-pair wise pathway

So, what we have learned? That single catalytic system, system for various metathesis reactions. So, you can assume as a single master key for multiple lock, and we learn that the metathesis reactions proceeds through metallacyclobutane intermediate through non-pairwise pathway with the odd number of carbon atoms so that is a metallacyclobutane will be the odd number of carbon atoms here like a in a four member it is 3 carbon atoms.

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

So, we this we now very familiar about the different types of metathesis reactions and this is very important to understand because when we will go to these are the references you can read it all the very basic whatever you have discussed we have discussed the very basic metathesis reactions and all are available in this textbooks.

So, why you will have read or discussed? Because these reactions the versatility of the reaction the type of reactions are very important to understand, otherwise we cannot really explore this carbon metathesis catalyst for the polymerization and you see that the polymerization is nothing but the extension of the ring opening metathesis reactions and also you see that how this reaction proceeds.

So, it is very important to understand the mechanism so that we can choose the right monomer for and the right catalyst for the polymerizations if we select the pathway using the metathesis catalysts. So, in the next class, we will be discussing about the mainly, about the metal centres, what are the carbons? What are the electronic properties of the carbon? What are the bonding and orbital interaction between the carbon and the metal centres. So, see you in the next class. And till then bye bye.