Transition Metal Organometallics in Catalysis and Biology
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Module No # 03
Lecture No # 11
Mechanistic approaches of Metathesis Reaction (Part – 4)

Welcome to this lecture on transition metal organometallics in catalysis and biology. We have been discussing about metathesis reaction in the past 2 lectures and in this context, we have been looking at mechanism of this metathesis reaction. What we had observed is that several probable candidates were proposed to explain the metathesis reaction and then and several of them was proposed unsuccessfully till the final mechanism as proposed by Chauvin emerged to be the accurate one.

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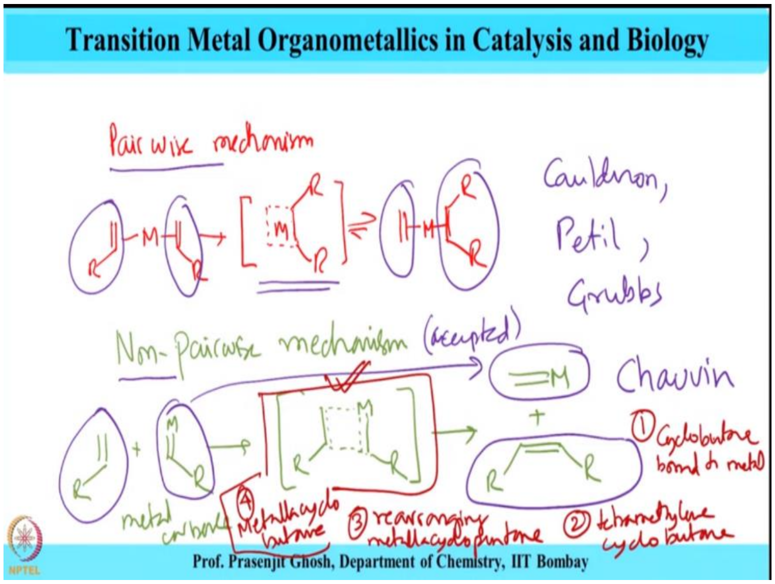

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Now in this regard in the last class we have spoken about pairwise mechanism. In pairwise mechanism what is said that 2 olefins gets paired up in presence of metal to give some kind of paired intermediate with the metal in it and that sort of results in obtaining the metathesis with different olefins. So for example the one that is shown over here what we saw that the olefin of this type they get paired up in this pairwise mechanism through some metal template intermediate and then finally the metathesis happens and then results in 2 different kind of olefin and this is sort of what was called pairwise mechanism.

And the other mechanism which was came out turned out to be correct is this non pairwise mechanism in which 1 olefin reacts with a metal carbon species this is the active species metal carbon species to give an intermediate metallacyclobutane intermediate and that sort of results into the corresponding carbene plus the olefin which is the metathesis product. So what we saw over here in the pairwise mechanism is that there is 1 active species generating or converting to another active species as a course of metathesis reaction and simultaneously 1 kind of olefin giving to another kind of olefinic species.

So this is the accepted mechanism and in this context we have discussed the way various famous name starting from called cauldron, petit as well as Grubbs who had proposed pairwise mechanisms. And which unfortunately did not turn out to be correct followed by Chauvin the French scientist who had actually proposed the correct mechanism the one non pairwise mechanism that we have just discussed right now.

Now in these cases we have also seen that various kind of intermediate being proposed to be intermediate through which metathesis reaction occurs. And they start from being cyclobutane butane bound to metal to tetra methylene cyclobutane to rearranging metallacyclopentene to finally this metallacyclobutane which is the one which is shown over here and the one which is the correct one.

So these sorts of provide a glimpse of the intensity of research which was undertaken in order to explain this metathesis reaction particularly to understand how this complex reaction proceeded. Another thing which is important in the mechanism non pairwise mechanism proposed by Chauvin is the fact that the active metal carbene species many of its kind are generated in the course of metathesis reaction. And as a result this is more of a chain reaction where several metal carbene type species react with olefin to give the corresponding metathesis products.

So the reaction is also characterized by a chain type reaction that take place during the proceedings of this metathesis reaction. Now while discussing the mechanism it is a kind of incomplete if we do not talk about the contribution of another great scientist professor Tom Thomas (()) (07:32) and professor Thomas J Katz of Columbia university. Who actually a first give the proposition of metal carbene being the active species in the metathesis reaction?

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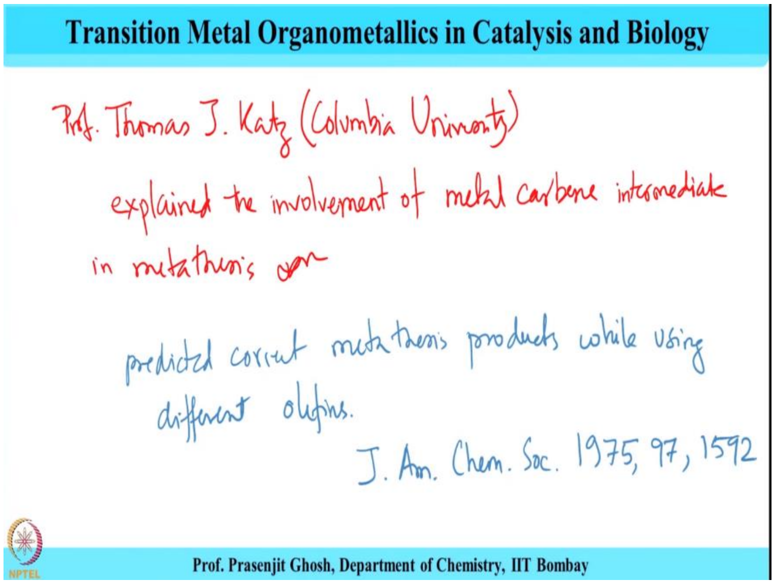

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Prof. Thomas J. Katz (Columbia University)

explained the involvement of metal carbene intermediate in metathesis

predicted correct metathesis products while using different olefins.

J. Am. Chem. Soc. 1975, 97, 1592

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So professor Thomas J Katz Columbia university and I am happy to say that I have been fortunate enough to undertake a course offered by professor Thomas Katz when I was a student PhD student at Columbia university and a good friend of mine he is renowned professor now was a direct graduate student of professor Katz when of my class when we were doing our PhD work.

So what Katz did is? Katz for the first time explained the involvement of metal carbene interacts intermediate in metathesis reactions carbene intermediate and the Katz through this he confirmed this by proposing a correct formation of product predicted correct metathesis products while using different olefins. And you know this is very nicely explained in this journal of American chemical society paper 1972.

So what is recognized to be of Katz system contribution is the fact that Katz further substantiated and validated with experimental evidence the mechanism which had been proposed by Chauvin with that proceeded via the formation for metallacyclobutane intermediate.

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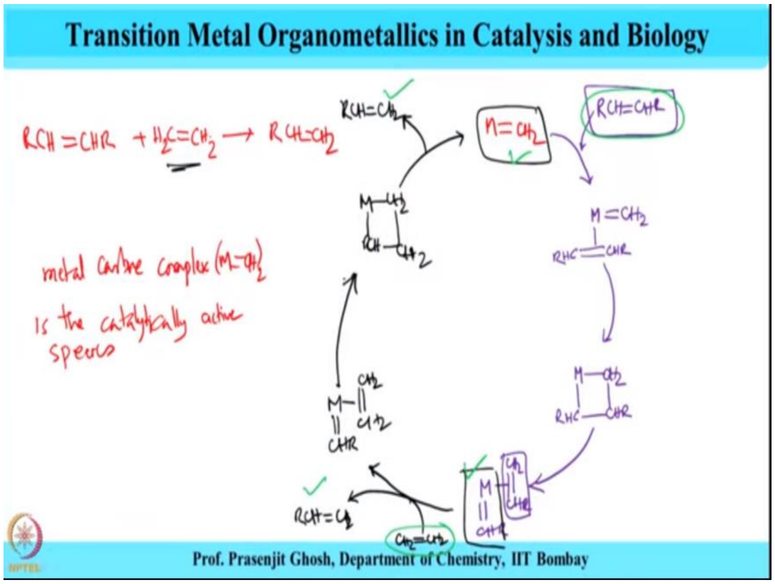

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$RCH=CHR + H_2C=CH_2 \rightarrow RCH=CH_2$

metal carbene complex ($M=CH_2$) is the catalytically active species

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And the product is and what Katz had proposed is the fact that metal carbene complex is the catalytically active species. This is best described by the mechanism as is shown over there this is the active species reacting with the olefin just by simple coordination to give the olefin coordinated carbene species a M CH2 bound to CHR that then undergoes this (())(13:30) insertion or formation of metallacyclobutane ring as is shown over here and that leads to the formation of the metathesis product coordinated to metal with a different carbene moiety.

So with that I mean that as the formation of another olefin is produced from this are different metal carbene active species is also formed as a result of that. Now in presence of the second olefin coming and replacing the metal coordinated olefin giving out RCH double bond CH2 and metal carbene species bound to CH2 CH2 that then undergoes this metathesis reaction to form the metallacyclobutane species as is shown over here which finally gives the metal carbene with the formation of the metathesis olefin.

So what we see is that the different kind of carbenes are formed as is shown over here and similarly different olefins are formed as is seen over here. And they start from 2 reacting olefins which is this one as well as this one. So this is what Katz had proposed as supposed to be the intermediate for metathesis reactions with metal carbene being the active species called metathesis reaction.

So the name of Katz discussion on Katz is done in the same breath with that of Chauvin, Grubbs, Petit and Cauldron because it is he who validated the first mechanism through more experiments of Chauvin and that is why Katz name is also taking in the same breath as all of the previous researchers. Now in this context it is important to mention a bit about carbene complexes mainly with regard to Fischer carbene and Schrock carbine.

Because those complexes containing metal carbene double multiple bonds double bonds in general where synthesized at that point of time and was an important breakthrough in term of stabilizing metal began double bond or multiple bond. Have some discussion on these metal carbene complexes to see how that the development or discovery of this at that point?

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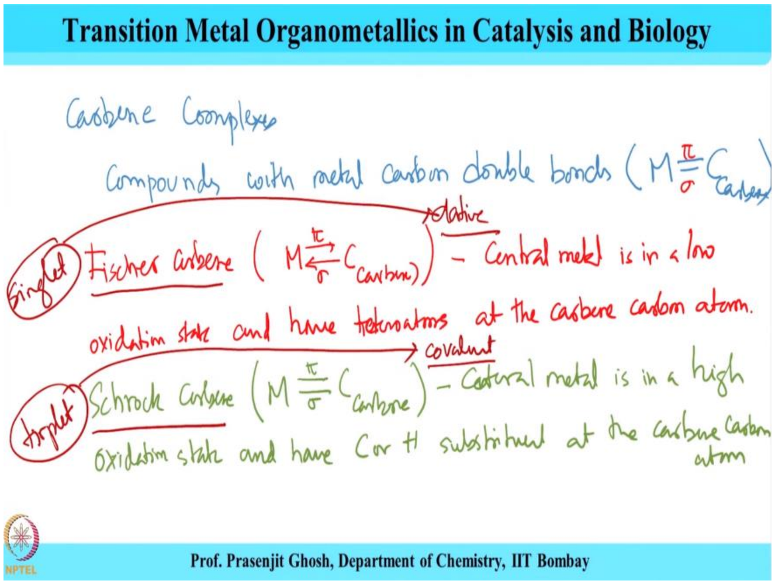

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Carbene Complexes

Compounds with metal carbon double bonds ($M \overset{\pi}{\underset{\sigma}{=}} C_{carbene}$)

dative

Singlet

Fischer carbene ($M \overset{\pi}{\underset{\sigma}{\rightleftarrows}} C_{carbene}$) – Central metal is in a low oxidation state and have heteroatoms at the carbene carbon atom.

covalent

Triplet

Schrock Carbene ($M \overset{\pi}{\underset{\sigma}{=}} C_{carbene}$) – Central metal is in a high oxidation state and have C or H substituted at the carbene carbon atom

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How it helped elucidate metathesis reaction has done rightfully by Chauvin. So these carbene complexes is are compounds with metal carbon double bonds and usually it is donated by a MC carbene with the first bond being a sigma bond and the second one being a Pi. And usually that is a possibility where one is a sigma bond another is a Pi bond and now there is a discussion and debate as to what extent the is the Pi bond occurring in order to stabilize this metal carbene moiety.

Now this is a open debate and also the other important thing is that how where what kind of bonds are these Sigma and Pi bonds are and in terms in the types in terms of discussion on the types of bonds that Sigma and Pi are the discussion is around whether they are dative bond or they are covalent bond. And what we will see that both types of carbene, carbenes were metal and carbon are bound by a dative bonds one dative Sigma bond another dative Pi bond is also possible.

This is a covalent bond involving (()) (20:31) electron between 1 Sigma covalent bond and once sigma pi bond between metal and carbene moiety that is also possible. So what is interesting to note is that 2 types of carbene mainly Fischer carbene and this is sort of the carbene which consists of 2 types of dative bonds which is ligand to carbene to metal Sigma bond and metal to carbene Pi dative bond.

So they are both dative bonds they are characteristic of Fischer carbene and in such case the central metal is in a low oxidation state and have another characteristic Fischer carbene to attain that state is that they have hetero atoms at the carbine carbon atom. And as a just mentioned earlier that there are also metal carbene moiety were both the bond between metal and carbene both the Sigma and the Pi bonding existing between metal and carbene can be covalent bond x type covalent bond and these are more common Schrock carbines.

And these are more x type covalent bond and not a dative bond and involves a sharing of electron of a metal from the carbine sides. And these are more common for complexes where central metal is in a high oxidation state and have carbon or hydrogen substituents the carbene carbon atom. And another thing to note here is that the if there is no hetero atom (()) (23:56) carbene it is also called alkylidene complex.

So these are 2 types of carbine which are synthesized in which the first one is Fischer carbene that involves dative bond existing between metal carbon Sigma bond as well as date metal carbon Pi bond. And then comes Schrock carbene which is involves covalent metal carbon Sigma bond and metal carbon Pi bond. Furthermore, these 2 carbenes are characters characteristic by the state of the carbene itself so future carbene the carbene moieties in a singlet state whereas the 4 carbene the carbene moiety is in a triplet state.

And that explain the formation for covalent bond in Schrock carbene. Whereas in singlet state explain the formation of the dative bond in the Fischer carbene. So with these what we saw is a nice convergence of a several discoveries particularly a the isolation of the metal carbene moieties containing metal carbene bonds and they being put in the picture as a active species for the metathesis reaction as a initially proposed by Chauvin and later on unsubstantiated by beautiful work of Katz through which who really showed and predicted character product formation using the metal carbene intermediate in explaining the olefin metathesis reaction.

So with these we come to conclusion of today's lecture where we sort of looked into the postulates made by Professor Tom Katz in help carbonating and validating the original mechanism proposed by Chauvin. And this Katz did that by correctly predicted the metathesis product in by judiciously using different carbenes. And these all were done using metal carbene intermediate.

And also supported the fact that during the course of metathesis reaction many active species carbene type active species are formed which also take up another olefin and proceed to carry on metathesis in a chain fashion. In the course of this todays lecture we have also looked at this active species metal carbene bonds. And what we saw that there are 2 types of carbene that have been stabilized particularly the Fischer carbene which has carbon to metal Sigma dative bond as well as metal to carbene Sigma Pi dative bond.

Whereas Schrock carbene which contains both metal carbon Sigma and Pi covalent bonds in Fischer carbene what we saw the central metal is in a lower oxidation state as a result of binding of singlet carbene and have a heteroatom stabilization of the carbonyl carbon. Whereas Schrock carbene has a central metal atom in a higher oxidation state and there is no hetero atom on the carbonyl carbon it is usually carbon and hydrogen.

So with these I conclude today's discussion on the role of Katz in explaining the olefin metathesis reaction. We are going to be taking up our olefin metathesis in bit more detail when we take up this course apart from mechanism in trying to look at different types of reactions that are possible when we meet for the next lecture. Till then goodbye and thank you.