Transition Metal Organometallics in Catalysis and Biology
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Module No # 02
Lecture No # 10
Mechanistic approaches of Metathesis Reaction (Part – 3)

Welcome to this lecture on transition metal organometallics in catalysis and biology. We have been talking about olefin metathesis reactions in the last few lectures. And in particular we have been discussing the various mechanistic pathways that have been proposed with regards to explaining olefin metathesis reaction. And also we have noted in the previous lecture that how even though different mechanisms have been proposed for olefin metathesis. How the one which is the correct one gained credence know gradually over the period of time.

Now what we had discussed in the last lecture is that there are 2 schools of thoughts which were initially proposed for olefin metathesis reaction. The first one was this pairwise mechanism which was indicating that both the olefinic form a pair and then reaction proceeds. However and there were 3 pathways or 3 hypothesis that were put forward based on pairwise mechanism by Calderon Pettit and Grubbs. However in the end by more details isotope leveling studies confirmed the reaction proceeding by non-pairwise mechanism and the one which has been proposed by Chauvin.

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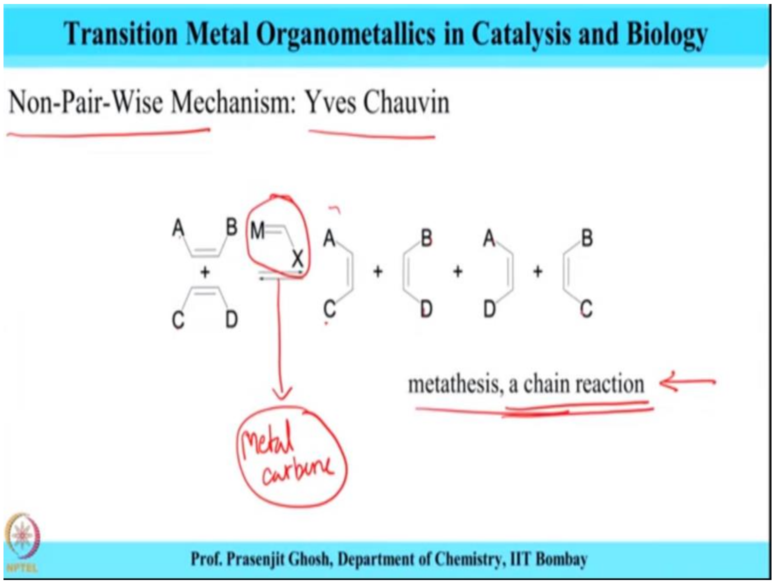

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Non-Pair-Wise Mechanism: Yves Chauvin

metathesis, a chain reaction

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And here the important criteria is that the active species is metal carbene species has shown over here is the active species that carry out these metathesis reaction. Another important fallout of the Chauvin mechanism is that it is a chain reaction in the sense that there are several types of metal carbene species which are generated and they carry out these metathesis reaction in a chain fashion.

We are going to looking at it with bit more details particularly this chain reaction aspect of metathesis when we in today’s lecture we take up this topic in much more detail. So what this slide says is that 2 olefin with different substitutes A and B, C and D come together to give olefins which are now A and C, B and D as well as A and D, B and C. So this is that famous cutting and stitching definition as if somebody had cut these olefins in fragment and then stitch them up needlessly to give all the combinations possible through this chain reaction.

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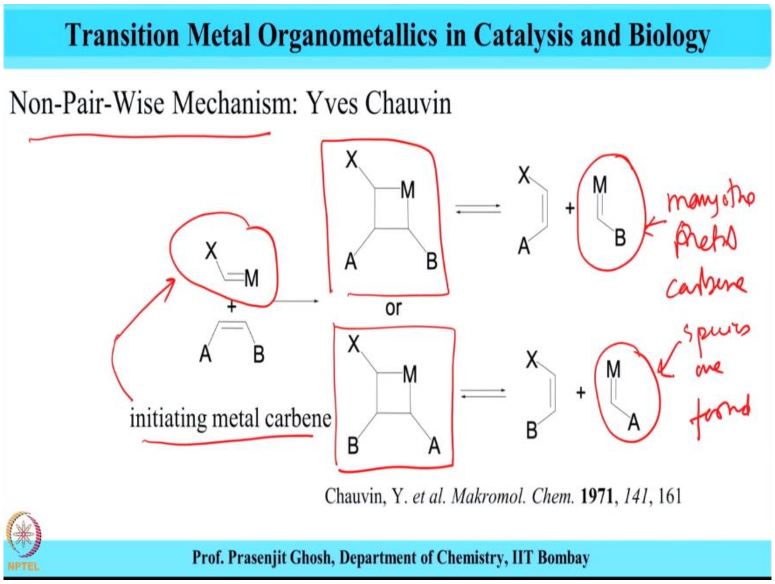

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Non-Pair-Wise Mechanism: Yves Chauvin

initiating metal carbene

Chauvin, Y. *et al.* *Makromol. Chem.* **1971**, *141*, 161

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Proceeding further we have also discussed this non-pairwise mechanism and what we had observed that how it goes via formation of these metallacyclobutane intermediate and then results in the different kind of olefins as well as different kind of metal carbene active species. So what is interesting to see is that there is one the starting initiating process metal carbene active species but however during the course of the metathesis is many other metal carbene species are formed.

And these two which is shown over here and they are also equally capable of carrying out these olefin metathesis reaction and this is why this is called a chain process. So that asset of chain reactions take place this by this formation of many species. The main support of this non pairwise mechanism was provided by Grubbs in this JCS paper where he had synthesized time this deuterated and the terminal deuterated octane and which according to him would give this cyclohexane which is unreactive, and this should give d4 ethylene.

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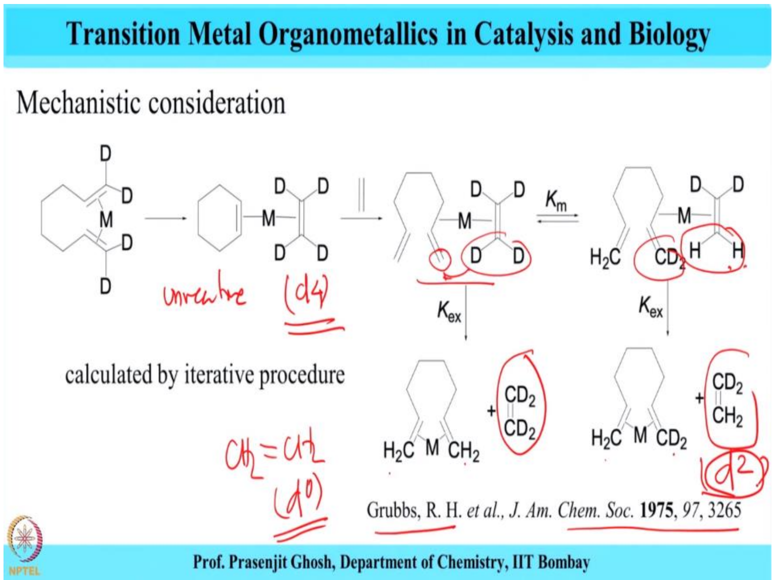

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Mechanistic consideration

calculated by iterative procedure

Grubbs, R. H. *et al., J. Am. Chem. Soc.* **1975**, *97*, 3265

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Whereas that when this cyclic hexene that can be knocked off by this protonated octane to give these complex. Now that can undergo fast metathesis exchanging these groups CD2 to CH2. So what we have here is CH2 and this side is CD2 that can fast exchange to give the product which is CD2 and then CH2 CH2 whereas these can first exchange to give CD2 CH2 which is this and then CD2 CH2.

So what Grubbs did is Grubb proposed these various product that may be obtained particularly with we get to the formation for d4 and this is CD2 CH2 is d2 and CH2 CH2 is d0 which would also be formed this should be d0 and what he tried to do in this paper is that he estimated the statistical distribution of these two types of ethylene d4, d2 and d0 and then observed how closely the statistical distribution was matched in terms of pairwise or non -pairwise product.

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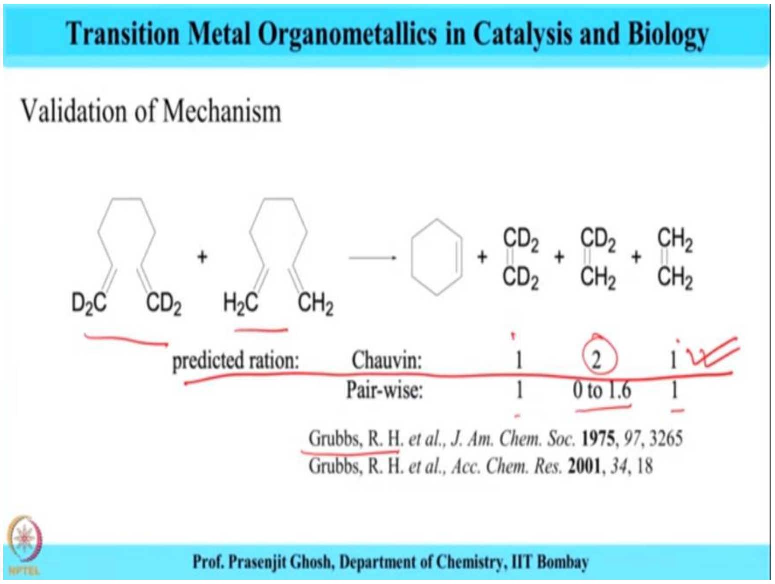

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Validation of Mechanism

predicted ration:				
	Chauvin:	1	2	1
	Pair-wise:	1	0 to 1.6	1

Grubbs, R. H. *et al.*, *J. Am. Chem. Soc.* **1975**, *97*, 3265
Grubbs, R. H. *et al.*, *Acc. Chem. Res.* **2001**, *34*, 18

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So let me illustrate this in bit more detail. So for these 2 type of olefin which is deuterated verses protonated the graph estimated that according to pairwise mechanism the ration would be 1 to 0 to1.6 to 1 for these two these three products. Whereas of Chauvin it will be 1 to 2 to 1 and this is what was experimentally observed giving a prediction in favor of the pairwise mechanism.

So this was fantastic set of experiments performed by Grubbs that sort of finally settled the issue put all the confusion to rest and give a verdict infirm in favor of Chauvins pairwise mechanism. Now what to give a perspective of how the reaction proceeds I am going to sort of just show the chain wise propagation of my olefin metathesis in the following few steps over here.

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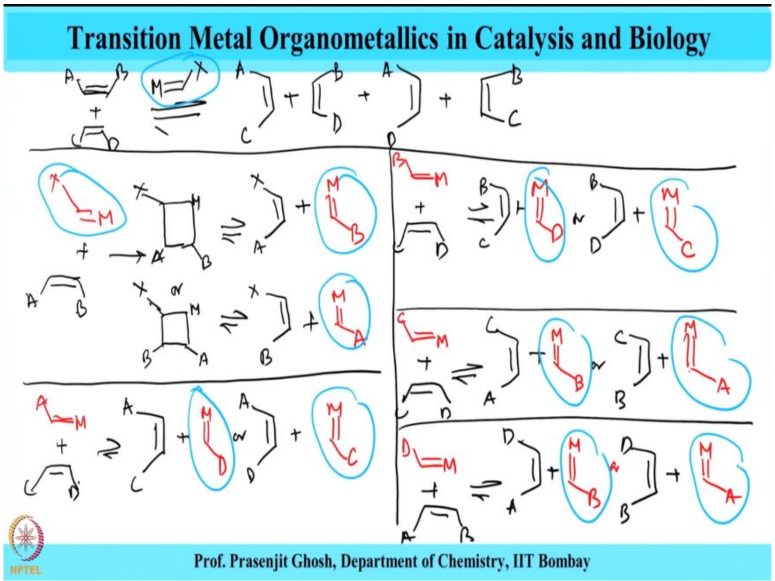

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For example these 2 olefin in presence of a metal carbene species give olefin with A C B D + A D + B C. Now the reaction proceeded as follows so the initiating species is a metal carbene species and that reacting with a olefin A and B giving X A B or B A and that would give X A + M B whereas this would give X B + M A. Then the another possibility would be this species which is M A then + C D the other olefin giving A C + M D A C + M D + A D + M C.

Now again M B which is formed over here can react with C D giving B C + M D + M D + B D, B D + M C. Again this M C can react with C D to give A C + M B, M B + C B + M A and lastly again M D + A B and can give D A + M B D B + ok. So now what is interesting about here is the fact that from 1 carbene initiating species so many different carbene species. So from M X which was the starting species all of the species M B, M A, M C, M D a and so on and so forth M D, M C, M B, M A, M B, M A.

So many different species are being generated as the course of the reaction. So that is why these sort of acts as a chain reaction and that is why these mass isotopic experiments were performed in order to know all the statistical distribution of these various products which sort of finally helped to explain these Chauvin's non-pairwise mechanism in explaining the metathesis reaction. So we have seen how complex these metathesis reaction in and one can see that by just looking at a different active species that are being produced by these initiating metal carbene species and how that helped in propagating the reaction in the chain fashion all giving and stitching in different forms of olefin.

Now we will sort of explain this olefin metathesis in bit more details and these olefin metatheses is not only can be expected for alkenes but can also be observed for alkynes.

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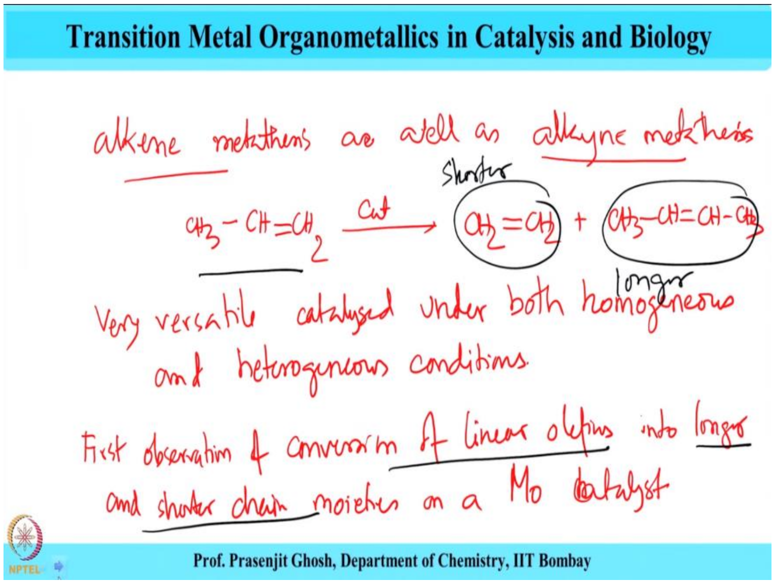

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alkene metathesis as well as alkyne metathesis

$$CH_3-CH=CH_2 \xrightarrow{Cat} \overset{\text{shorter}}{CH_2=CH_2} + \underset{\text{longer}}{CH_3-CH=CH-CH_3}$$

Very versatile catalysed under both homogeneous and heterogeneous conditions.

First observation of conversion of linear olefins into longer and shorter chain moieties on a Mo catalyst

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So alkene metathesis as well as alkyne metathesis we are able to see that this reaction is not only limited to alkenes but also known for alkynes a very nice example of this is what we have just discussed earlier is that of propane in presents of catalyst giving ethylene plus butane. So these another interesting thing is that the first ability of the metathesis reaction very versatile and can be catalyzed by homogenous and heterogenous catalyzed under both homogenous and heterogeneous conditions.

And the first observation of conversion of linear olefin is not longer and shorter chain moieties at molybdenum catalyst. So this was the first observation of conversion of linear olefins in to longer and shorter chain moieties at a molybdenum catalyst. And this was sort of seen with the first observation of conversion of a linear olefin into longer and shorter chain moieties on molybdenum catalyst.

So and this is very much illustrated by the above example where propylene got converted in to a shorter ethylene and longer butene. So this was first sort of observed by conversion of olefin to the longer and the shorter moieties. Now olefin metathesis was intriguing phenomenon and failed to begin with and then once the mechanism was once sort of understood the next biggest challenge was trying to earmark the boundary of the reaction or the capability of the reaction.

And what came into being that there are a wide range of different types of reaction all of which belong to the family of olefin metathesis. So in that context a large number of olefin metathesis reaction came into being. And all of them those slightly different in type but they all fell in this subclass of olefin metathesis reactions. And we are going to sort of mmm take a look at some of the classification or different types of olefin metathesis reactions that are being.

Now as mentioned earlier that as we had said that the olefin metathesis is very versatile and is not only restricted to olefin but also is equally observed for alkyne which also undergo similar kind of metathesis reaction. Now one thing to note here is the fact that alkyne metathesis is less explored then alkene metathesis.

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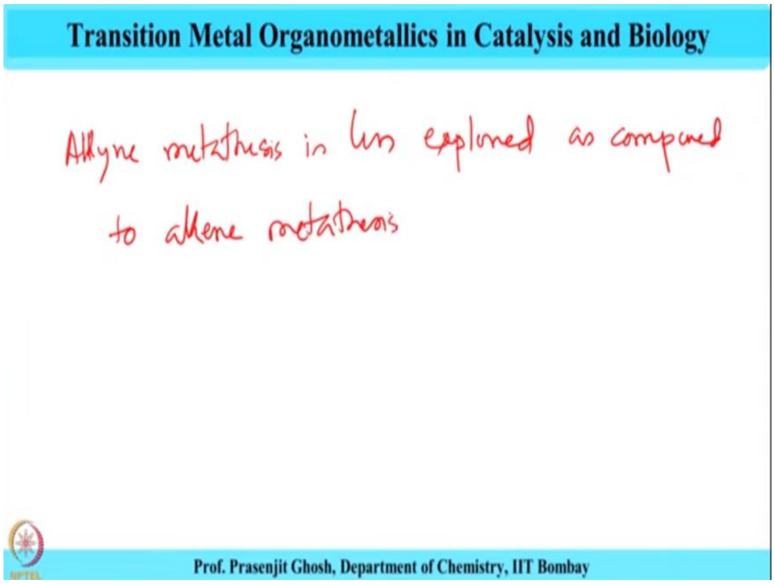

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Alkyne metathesis in less explored as compared to alkene metathesis

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Alkyne is alkyne metathesis is less explored as compared to alkene metathesis. Now with these we come to the conclusion of today's lecture where we have looked into the different mechanistic aspects of these non-pairwise mechanism proposed by Chauvin where no one can see that this non pairwise mechanism was establishes through isotope labeling experiments in terms of the ratios of different (()) (25:13) isotopic labeled olefins were produced in a particular experiment.

What it was what came to the fore by during this course of experiment is that the active species or the initiating species is the metal carbene species which is different from that of the two olefins involved. And this metal carbene species during the course of metathesis reaction transforms or changes to many other types of metal carbene species. So singular active species gives rise to several types of many more metal carbene species all of which are equally active in olefin metathesis reaction.

As a result a chain reaction set in place leading to formation of different combinations of olefins which can possible be formed. Another interesting point that we had observed is that the transition state for these metathesis reaction is a metal cyclobutane kind of intermediate which leads to the formation of the olefin as well as active species which is metal carbene species. So these isotopic experiments were reported by Grubbs which favored Chauvin's proposal of non-pairwise mechanism towards a formation of olefin metathesis products.

So with these we come to the end of the our discussion of various kinds of mechanism which have been proposed in explaining the metathesis reaction and we going to look at taking up different varieties of metathesis reactions or different types of metathesis reactions that have been reported so far and also the subsequent application of metathesis reactions in the coming lectures.

So once again I thank you for being with me in this lecture and we are going to be looking at different types of metathesis reactions in more details when we cover the topic in the next lecture. Till then goodbye and thank you.