Transition Metal Organometallics in Catalysis and Biology

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Module No # 02
Lecture No # 09
Mechanistic approaches of Metathesis Reaction (Part – 2)

Welcome to this course on transition metal organometallics in catalysis and biology. We have been discussing metathesis reaction in details over the last few lectures. As we had observed in a previous lecture that olefin method metathesis is a very important polymerization reaction which involves cutting and stitching of olefins. Now this reaction has wide applicability which we are going to cover subsequent lectures.

But what is more intriguing about this reaction is its complexity its difficulty in comprehending the mechanistic pathway how the reaction was proceeding or how the polymerization was proceeding and in its earlier stages of development. Olefin metathesis actually has its origin from olefin polymerization this also we had discussed in at length in earlier lecture. And what we had also observed that there were about 4 different mechanisms which have been proposed for explaining olefin metathesis and 3 of them proved to be not true.

However that does not take away any (()) (01:38) from the mechanism which have been proposed because those are the ones that gives the glimpses of a various path way that are feasible for explaining such complex mechanism. So let me just recapitulate what we had discussed in the earlier class.

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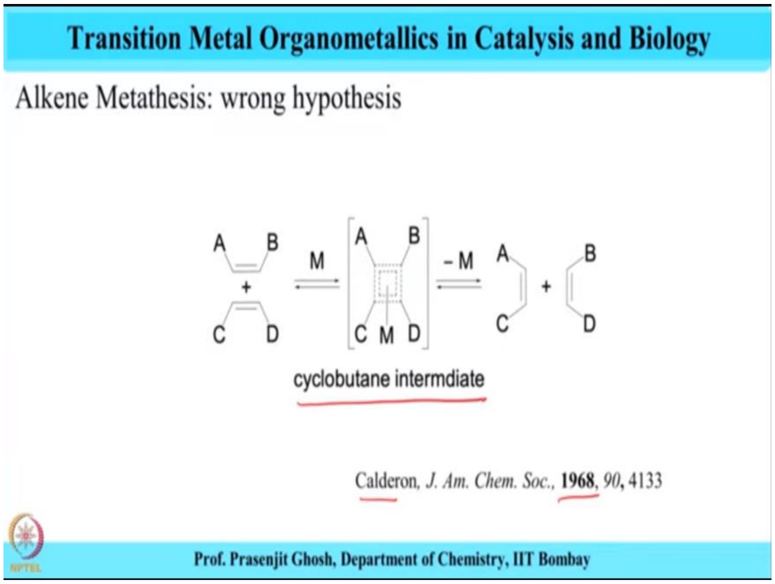

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Alkene Metathesis: wrong hypothesis

cyclobutane intermdiate

Calderon, *J. Am. Chem. Soc.*, **1968**, *90*, 4133

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In particular we had spoken about mechanism by Calderon in that was published in JC 1968 that speaks about the presence of cyclobutane intermediate. However the reaction or this pathway was deemed not true because there were no evidence of formation of any kind of cyclobutane during the olefin metathesis reaction that has been suggested in the mechanism.

So what it says that two different olefins A and B a for example reacts in presence of M to give this metalo cyclobutane coordinated to M and then the metathesis reaction happens finally the M is released to give the cross metathesis product. However we had also observed in our previous class that this mechanism was not found to be true.

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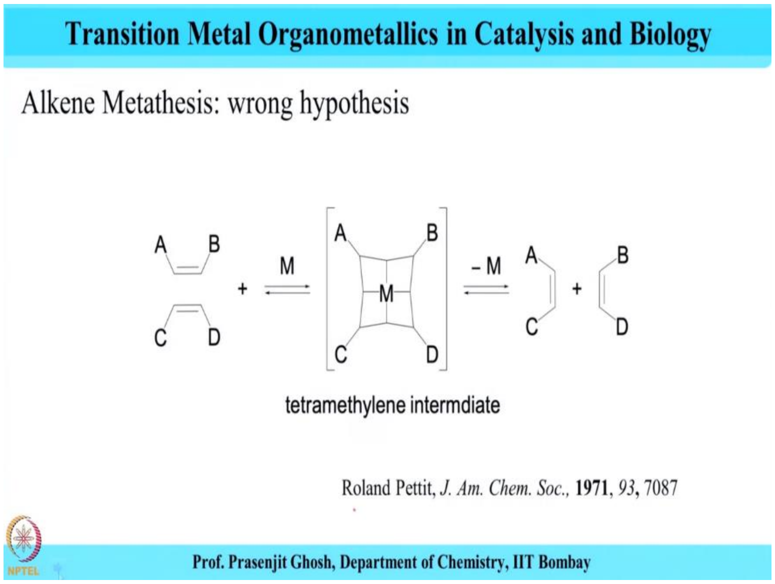

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Alkene Metathesis: wrong hypothesis

tetramethylene intermdiate

Roland Pettit, *J. Am. Chem. Soc.*, **1971**, *93*, 7087

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Next mechanism was proposed by Roland Pettit in JCS 1971 which spoke about the presence of tetra methylene intermediate bound to the metal which is the 4 methylene groups at this 4 corners formation of a tetra methyl in metal bound intermediate resulting in the desired metathesis product. However this later on in this stage of the game these evidence also this mechanism also lost support because of lack of evidence and hence proven to be not true.

And then there was another evidence which was proposed by Grubbs that was this metal cyclopentane intermediate and which was also proven to be not correct and we had discussed this in details.

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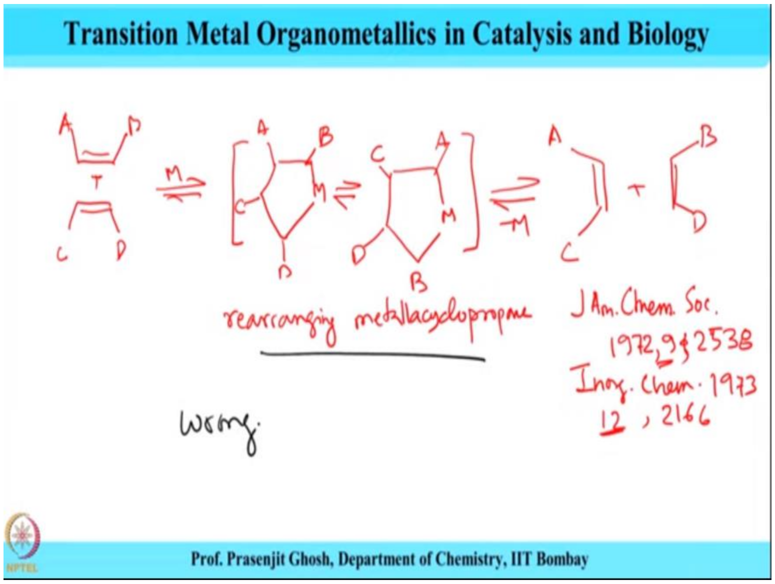

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rearranging metallacyclopropane

J Am. Chem. Soc. 1972, 94 2538

Inorg. Chem. 1973 12, 2166

Wrong.

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In our earlier class where we have 2 olefins A B react reacting with the other one C and D in presence of metal gives metal o cyclopentane intermediate and which sort of undergoes spontaneous rearrangement and that would eventually result in formation of intermediate. And these are called rearranging metallacylopropane intermediate and this was proposed by Bob Grubbs himself in 1972 2538 followed by inorg chem paper in 1973 2166.

However this particular rearrangement also did not find support and was proven to be wrong subsequently.

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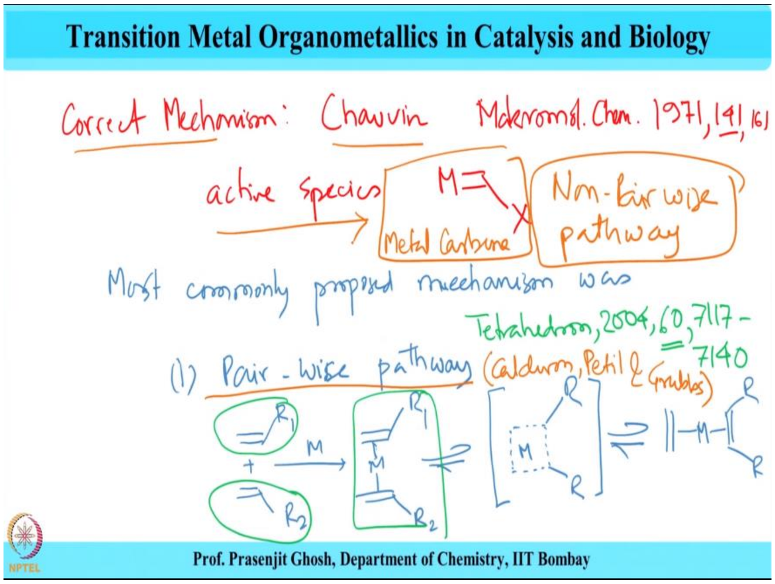

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Correct Mechanism: Chauvin Makromol. Chem. 1971, 141, 161

active species → M= Metal Carbene ✗ Non-Pair wise pathway

Most commonly proposed mechanism was

Tetrahedron, 2004, 60, 7117-7140

(1) Pair-wise pathway (Calderon, Petil & Grubbs)

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And the correct mechanism as we had observed was proposed by Professor Chauvin in correct mechanism has been proposed by Professor Chauvin in macromolecule chemistry1971 141 161.Now these was completely different mechanism and he has proposed this mechanism on the basis of three evidences or three observation as we had also mentioned earlier. First is the formation of Fischer carbene complex that was published that time (()) (08:09) and then by Professor Fischer and the second paper that he sort of used or at least taken notice of before proposing this mechanism was this ring opening polymerization of cyclopentane.

And third was this observation from Philip petroleum about this preparation of propylene. So all of these led him to propose that the active species is indeed a metal carbene species of the type of this which sort to helps in propagating these olefin metathesis reaction. Now these at the time was a radical belief because that instance of time they are two popular belief in the sense that these olefin cross metathesis reactions are olefin metathesis reaction proceeds by two pathways or two proposed pathways.

One was iron pair pathways and the other one was the pairwise pathways and non-pairwise pathways. So let me look elaborate that in bit more details the most commonly proposed mechanism was first of pairwise pathway. Now pairwise pathway it seems very simple from the name in the sense that two olefins form a pair undergo metathesis polymerization has brought about by a metal.

So pairwise pathway a an example of it is shown over here for example if there is 2 types of olefin they react to each other in presence of a metal to make a pair and that sort of proceeds by formation of some kind of cyclobutane templated with the aid of the metal resulting in the formation of the olefinic product. So these conventionally is called the pairwise pathway where the two olefins they come and a form a pair.

So this two olefins this two olefins they make a pair as shown over here and then cyclobutane intermediate of the metal to give the corresponding product. This has been very nicely covered by a review by Professor Bob Grubbs in tetrahedron 2004, 60, 7117 to 7140. Our requests are interested student of this course to look up this review which will explain and the contemporary a arguments that were put forth of that time in elaborating the mechanism.

Now in this context it is also worth mentioning that at that point of time even though the pairwise pathway later on proved on to be wrong but much of the mechanism were on the basis of pairwise pathway the three mechanism which I had discussed earlier as proposed by Calderon Pettit and Grubbs they were based on the different version of a pairwise mechanism. Whereas Chauvin proposed the correct mechanism and this turned out to be non-pairwise mechanism.

And this non pairwise it was an outcome of a metal carbene complex species being the active species of this reactions. So these sort of source that how radical had been Chauvin proposal of a non-pairwise pathway. And this mechanism was later known as the carbene mechanism in which this is illustrated as shown below.

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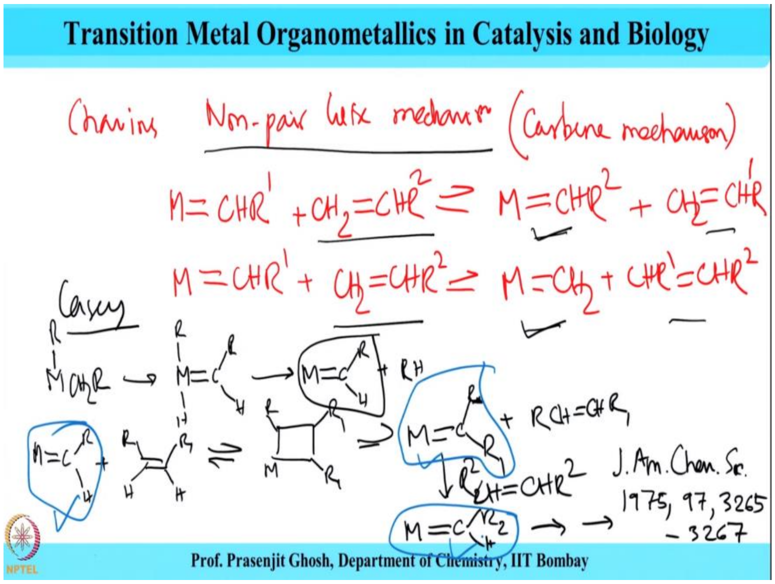

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Chauvins Non-pair wise mechanism (Carbene mechanism)

$M{=}CHR^1 + CH_2{=}CHR^2 \rightleftharpoons M{=}CHR^2 + CH_2{=}CHR^1$

$M{=}CHR^1 + CH_2{=}CHR^2 \rightleftharpoons M{=}CH_2 + CHR^1{=}CHR^2$

J. Am. Chem. Soc. 1975, 97, 3265 – 3267

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So Chauvin’s non pairwise mechanism are also popularly called as carbene mechanism and this is illustrated by the creation CHR and the corresponding products is M CHR2 + CH2 CHR1 and the reaction also could go the other way CHR1 + CH2 CHR2 giving M CH2 + CHR1 CHR2. So basically this carbene non pairwise mechanism what it gave is it gave a range of different kind of olefinic products obtained by the combination of these 2 olefins which is this and this.

So basically these 2 kinds of olefins led to 2 different active species which is over here and they participated in it and gave a wide range of product. Now these sorts of led to raise trying to understand how mechanism really is preceding and to understand this lot of substituted isotropic metaphysis reactions were performed based on which support in favor of this non-iron pair mechanism.

Now along Chauvin’s pathway Schrock like Schrock has also made the Schrock carbene and Casey has demonstrated a similar pathway similar to that of Chauvin and that mechanism is also highlighted over here CH2R giving MRH this is nothing but Schrock carbene giving MCRH + R H. Now this MCRH reacting with olefin R1 HH would give this metalo cyclobutane R R1 R1 and that would give another carbene species CR R1 + olefin RCH double bond CH R1 and this can react with another olefin R2 CH double bond CH R2 to give another species which can be CR2 H and so on and so forth.

So this was proposed by Casey and it is nicely elaborated in a JCS paper by Professor Bob Grubbs 1975 97 3265 to 3267. So now what is observed over here that the reaction seems to generate several kind of carbene species in for example RH then that participates to give CR R1 then that CR2 H and so on and so forth. So basically what is interesting about it is that there is not a single active species there are single type metal carbene.

But during the process of metathesis several metal carbene species are simultaneously formed that participates in propagating in this reaction. So what is very interesting over here is that the one type of metal carbene species here is coming more effective in carrying out these catalysis. And these was explained by isotopic experiment carried out by Professor Bob Grubbs in that JCS paper 1975 97 3265 to 3267.

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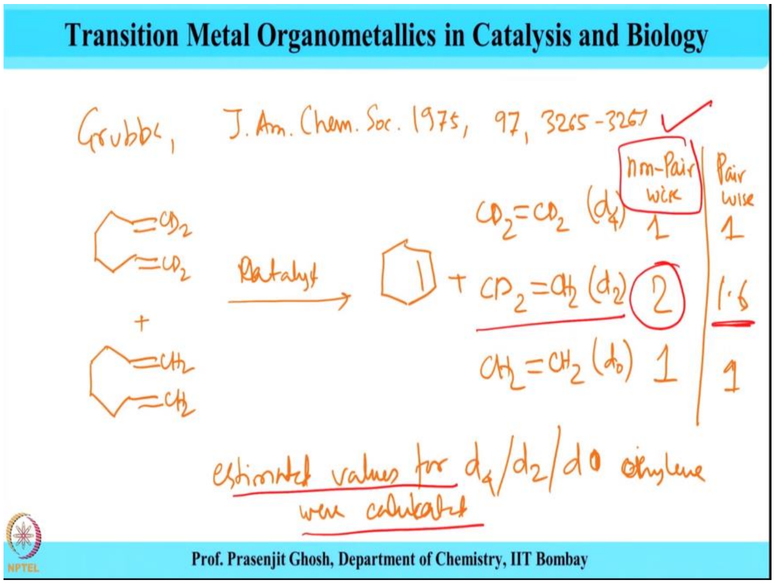

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Grubbs, J. Am. Chem. Soc. 1975, 97, 3265-3267

		non-Pairwise	Pair wise
$CD_2=CD_2$	(d_4)	1	1
$CD_2=CH_2$	(d_2)	2	1.6
$CH_2=CH_2$	(d_0)	1	1

estimated values for $d_4/d_2/d_0$ ethylene were calculated

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In that paper what they did was they synthesized this special olefin with non deuterated CD2 and then the corresponding the non deuterated counterpart CH2 CH2 and then had a metathesis catalyst and what they were looking at is the formation of this would result in cyclohexane and plus formation of three kinds of as a ethylene for example CD2 CD2 which they call d4 species or CD2 CH2 which they said d2 species and then CH2 CH2 which said d0 species.

And then they looked at the distribution of these 3 species d4, d2, and d0 for non-pairwise wise mechanism as well as pairwise mechanism. Now the values for pairwise and this value of this distribution were estimated values for d4, d2 and d0 olefins ethylene’s where calculated and what they came up with is that for pairwise mechanism if they were just simple pair this value should be 1 to 1.6 to 1 and for non-pairwise mechanism the value should be 1 to 2 to 1.

Now these values were calculated using various equations fed into the computer and their estimated was for a pairwise mechanism that this mixed d2 should be in the ratio of 1 is to 1.6 into 2 but what really was observed is that the d2 ethylene was about 2 and they closely match the pairwise mechanism and these provided support for Chauvins non pairwise mechanism for olefin metathesis.

Now the other interesting thing notable over here is the fact that even though Grubbs whose own proposal was for rearranging cyclopentane a type of intermediate his own proposal did not turn out to be true. But he did this a very good isotope famous isotope experiment from looking at the distribution of which he could establish Chauvin's mechanism of non-pairwise olefin metathesis. So with this I come to an end of today's lecture where we looked into we looked into how the Chauvin's mechanism of non-pairwise a pathway for olefin metathesis got established because of isotope level based studies performed by Grubbs.

So and another important hallmark of Chauvin's mechanism we had observed this that the active species though are of one type metal carbene type. But during the course of metathesis reactions several active species or several metal carbene species are simultaneously formed which individually a propagate this metathesis reaction. So that is an interesting observation which has come out of Chauvin's non-pairwise proposed mechanism.

Another observation we have noted is that the Chauvin's mechanism was later supported by Casey for Schrock type complexes and part of it which we have also discussed today. So with this we come to end of today's lecture we are going to be looking a bit more details of Chauvin's mechanism as we take up in the next class particularly with regard to the various kind of active species our metal carbene species that are formed during the course of this reactions. So with these we come to an end of today's lecture.

Thank you for being with me in this lecture we are going to be taking up this role of olefin mechanism in particular a bit more or details looking into various aspects of Chauvins non pairwise mechanism in the next class I look forward to being with you that time till then good bye thank you.