Transition Metal Organometallics in Catalysis and Biology
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Module No # 02
Lecture No # 08
Mechanism approaches of Metathesis Reaction (Part -1)

Welcome to this lecture on transition metal organometallics in catalysis and biology in the course of the last few lectures. We have been discussing a very important reaction which is olefin metathesis and has been also a seminal discovery by its own right and merit with regard to the polymerization reactions and in fact this is the second noble price award winning like discovery after olefin polymerization and then subsequently the one that you are discussing which is olefin metathesis.

Now we have noted in the previous lecture that this olefin metathesis reaction has it is origin from olefin polymerization reaction in terms of its discovery because research on the area of olefin polymerization led to observation of some unexpected results which at that point of time could not be explained and later on this unexpected discovery resulted in the field of olefin metathesis. So this olefin metathesis has its birth in olefin polymerization reaction now with regard to olefin metathesis the thing which was perplexing is this cutting and stitching of olefins.

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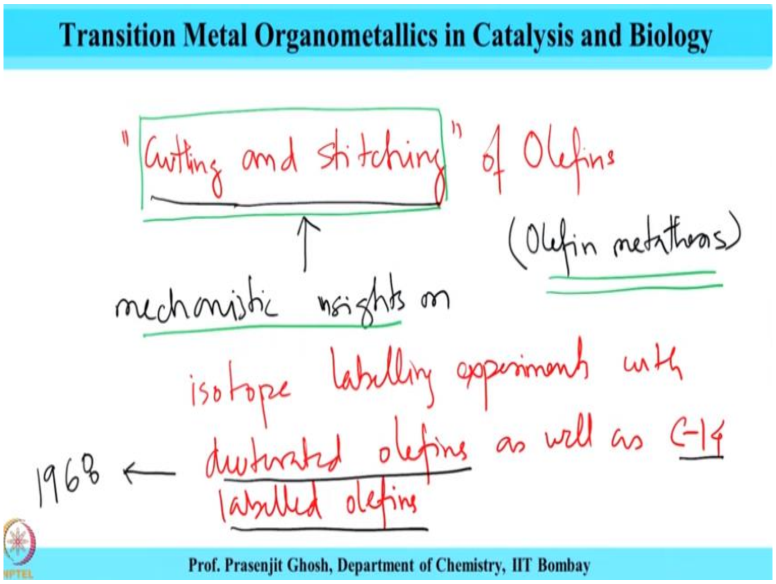

Transition Metal Organometallics in Catalysis and Biology

"Cutting and stitching" of Olefins

(Olefin metathesis)

mechanistic insights on

isotope labelling experiments with

1968 ← deuterated olefins as well as C-14

labelled olefins

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Olefins that was observed when olefin’s where studied for polymerization reaction it is seemed that this cutting and stitching olefin was a very clean and conveniently accomplished under presence of the catalyst and that was what intriguing at that point of time. Olefin metaphysis as we have also noted has its origin industry when people where studying olefin polymerization and we had also seen that the name olefin metathesis was coined by researcher at Good Year tyres and was first traced back to (()) (02:56) publication in 1967.

Subsequently we have observed that the race was on explaining or developing and understanding on the mechanism of this cutting and stitching reactions of olefin where happening on this cutting and stitching of olefins which were deemed as olefin metathesis reaction. Now these where studied intensely particularly with respect to the obtaining mechanistic inside using mass spectrometry studies as well as (()) (03:57) studies using isotope labeling experiments with deuterated olefins as well as C14 labeled olefin’s.

Now these where important developments which were simultaneously studied in US as well as in Europe and they were parallel independent publication using the results of this labeling studies deuterated olefin as well as C13 labeled olefin both appearing in 1968. Now once this cutting and stitching mechanism of these olefin metathesis has been established then the focus shifted on obtaining the mechanistic inside this reaction.

Today what we are going to do take up is on various mechanistic hypothesis which was at that time thought to be the main path way for performing this olefin metathesis reaction and which we would be discussing in more details in today’s discussion. Now the first of the mechanistic inside was out hypothesis was proposed by researcher of Good Year tyres in their 1968 JCS publication.

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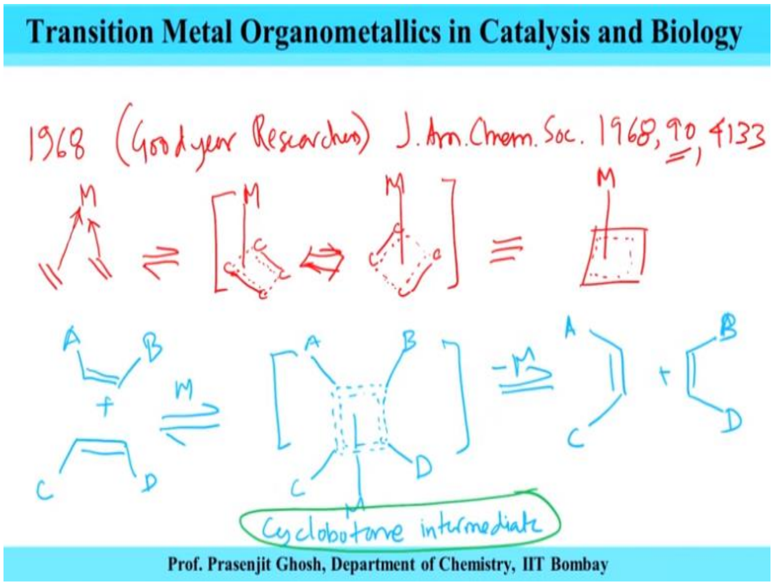

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1968 (Goodyear Researchers) J. Am. Chem. Soc. 1968, 90, 4133

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What they had proposed is the reaction of olefin resulting in cyclobutane type of intermediate I am illustrating this with the help of an example the olefin being bound to metal then forms a kind of transition state of which an exist kind of intermediate. So basically a giving rise to do different kind of olefin swapping. So these is again to similarly to what is shown over here so in short it can be written something like this or 2 kinds of olefin in presence of the metal it goes through cyclic intermediate then this cyclo butane intermediate which is which then loses metal to give the olefins with a and c and b and d a counterparts.

Now the main drawback to this theory is the fact that there were no observation of any kind of cyclo butane in intermediate. So formation of cyclo butane in the processors of metathesis as never observed which sort of led to discarding the theory. So but none the less this was very a what clever attempt in explaining this unusual phenomenon of cutting and stitching of olefins and the obvious proposed pathway was suggested that in went by the formation of cyclo butane intermediate.

And was first published researchers from Good year in 1968 JCS paper. The next attempt was in explaining the mechanism was by petit in 1971 professor Roland prett.

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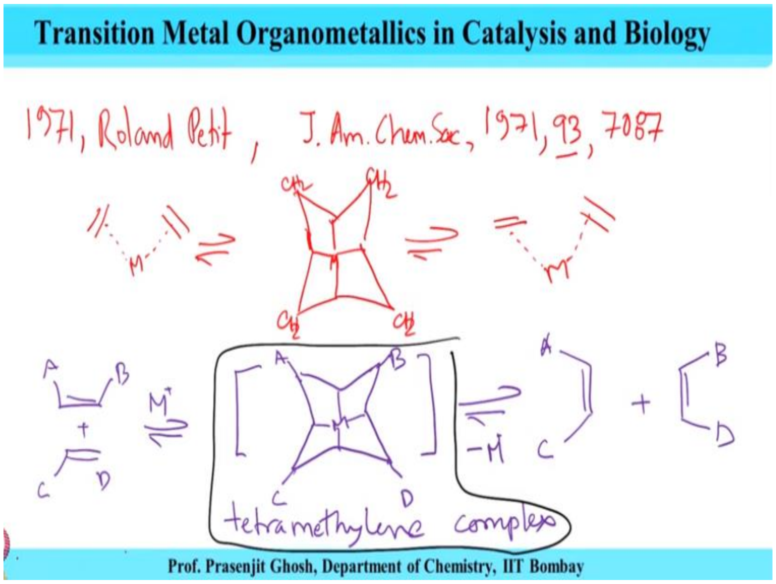

Transition Metal Organometallics in Catalysis and Biology

1971, Roland Petit, J. Am. Chem. Soc., 1971, 93, 7087

tetramethylene complex

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And this was also reported in the Journal of American chemical society in 1971 well the proposed catalytic species was proposed to be tetra methylene metal complex as is as shown over here. So this resulting in very fancy and that being in equilibrium with the other metal (()) (13:28) complex. So this is illustrated as follows for the 2 olefin's in presence of metal giving this compound the which would then lose metal to give the desired cross couple olefin's and this is called tetra methylene complex even though this looks like a very nice way of explaining the formation of 2 different kind of olefin.

However the main drawback to this is the proposed intermediate which is this tetra methylene complex and then that is what did not go through finally and some point was deducted was (()) (15:32) mechanism for the reaction. That the next proposal was also very nice effort towards its explaining this formation of cross coupled olefin's using this carton stage mechanism and this time too it was proposed none the then by this future mobile winning researcher professor Robert drops however the mechanism that he had for proposed for metathesis actually turned to be wrong.

None the less it is interesting to see another new approach as hypothesis as proposed by professor Grubbs in explaining the mechanism of this olefin metathesis.

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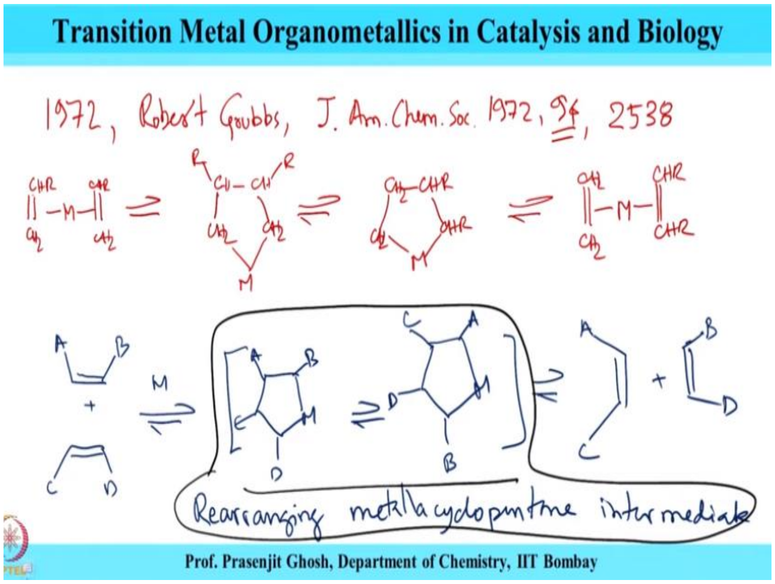

Transition Metal Organometallics in Catalysis and Biology

1972, Robert Grubbs, J. Am. Chem. Soc. 1972, 94, 2538

Rearranging metallacyclopentane intermediate

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So professor Grubbs mechanism was proposed in another JCS paper in 1972 in the JCS paper and the mechanism what it proposed is via instead of going through the earlier 4 member tetra methylene complex or via cyclo butane complex actually the one that is proposed was of metalocyclo propane complex which sort of rearranges to give the product. Let me illustrate this over here so is to olefin so is to binding to the metal.

And then this formation of the metalocyclo propane occurring resulting in these metallocyclo propane complex and that undergoing some sort of rearrangement to finally giving the olefin (()) (18:57) of the cross coupled metathesis olefin’s to the metal. These I will explain in a cartoon as A and B type of olefin reacting with C and D type in presence of the metal to give C, D, A, B that undergoing rearrangement to give B, D, C, A and then finally resulting in A, C, B, D type of (()) (20:25) product.

So the this main this was rearranging hypothesis was rearranging metalo cyclopentane intermediate. So what is interesting over here is that is that even this attempt of explaining metathesis of using this rearrange in metalocyclopentane intermediate turned out to be a wrong and that the final of the other attempt by professor Irwin was one which finally one over all these different proposed inside.

But what is by and large overwhelmingly cleared is the fact that how intricate this mechanism establishing this mechanism of metathesis had been that so many brilliant minds had worked tirelessly to come up with a mechanism unfortunately many of them could get it right. So finally a the one which really one over are the all is the mechanism by Chauvin professor Chauvin which was published much later in 1971 in a obscure relatively obscure journal of macro molecule Kimi written in French.

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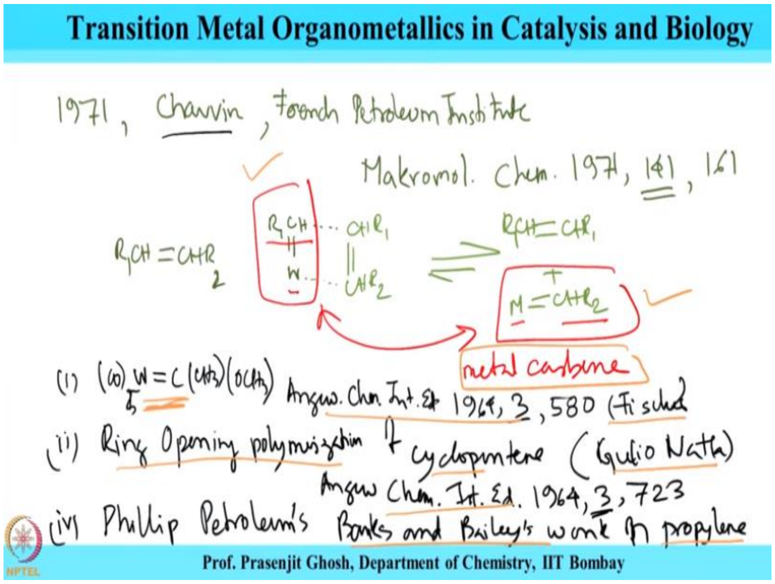

Transition Metal Organometallics in Catalysis and Biology

1971, Chauvin, French Petroleum Institute

Makromol. Chem. 1971, 141, 161

(i) $(CO)_5W=C(CH_3)(OCH_3)$ Angew. Chem. Int. Ed. 1964, 3, 580 (Fischer)

(ii) Ring Opening polymerization of cyclopentene (Gulio Natta) Angew Chem. Int. Ed. 1964, 3, 723

(iv) Phillip Petroleum's Banks and Bailey's work on propylene

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So 1971 by professor Chauvin from French petroleum institute and this published I Makromol chem 1971 141 volume 161 page number and this is based shown by the mechanism and what it says? That it goes through formation of metal (()) (23:31) bond. So these is suggested to be the main active species for the reaction so that turns out to be the correct one so that reacting with the olefin ended up giving or to so what is to be noted here is the fact that the now of the metal carbon pieces has swapped from becoming CHR1 metal to be CHR2 metal.

So this was interesting proposal whereby it is suggested that this metal carbon species is the active species responsible for performing this olefin metathesis and indeed this turn out to be extremely true later on and this is what it got the field going now what is a all the more interesting is the fact that the complexity in the problem is highlighted very much in this failed and successful attempt the number of failed and successful attempt made by eminent minds at the time in trying to get an inside on to how the metathesis reactions are progressing.

And what is to be appreciated over here is the depth and the power of organometallic chemistry to accommodate so many different kind of hypothesis and proposals that may lead to the formation of this metathesis products and however another interesting thing that emerges out of this study is the fact that this results of which were finally turned out to be incorrect where published in the premium journals whereas the correct one was published in not so very popular as the journal as the earlier ones.

And also in a different language and in that of English so the science by enlarge this highlights the importance of science and the good quality of work nonetheless if the work is good no matter where it gets published it will see the light of the day. Now as per professor Chauvin he said that 3 papers which are kind of work by Fischer in terms of the Fischer carbon complex CO5 times 10 CH3 OCH3 and there was published in Angew Chan in 1964 by professor Fischer.

And also the polymerization olefin polymerization getting opening polymerization of cyclopentane by professor Nata. Again in Angew Chan internal edition 1964 373 and the industry work by Philip petroleum (()) (28:58) Bank's and Bailey now on profiling. So inspired him to come up with this proposal so what professor Nata did is we looked at the metal carbine and complex for its synthesized by Fisher then the reopening polymerization of cyclopentane by Gulio Nata both appeared in Angew Chan 1964 journal and the Philip petroleum Bailey's research on propylene now getting converted to ethylene and butane.

So he kind of looked at all of these discovery and came up of this idea of metal carbine species and the active species for this metathesis reaction and then I have proposed these kind of coupling of olefin via a metal carbine species. So this is an interesting proposal which one can appreciate now the way the perfect solution was arrived at by looking at various other complexes and various other chemistry being reported contain around at the time and then explaining this mechanism for olefin metathesis which been a remarkable breakthrough.

So with this I would like to conclude today's lecture where we have discussed about various mechanistic approaches that had been taken in trying to explain the mechanism of olefin metathesis and this started with the formation are proposed intermediate of cyclo butane bound to metal by caldron and that did not find support has there are no evidence of formation of cyclo butane during this olefin metathesis reaction.

The second reaction mechanistic hypothesis that we are looked at that by Petit in another JCS 1971 paper in which tetra methylene metal complex was proposed to the main intermediate in olefin metathesis and that also did not find ground in the because of the fact that there were no evidence for such tetra methylene complex could be seen during a metathesis reaction. And the third another important paper by professor Bob Grubbs in JCS 1972 where he had suggested or to spoken about rearranging metalpentane cycle pentane as the main active intermediate for olefinic metathesis column polymerization.

However even this turned out to be wrong and the beauty is even though professor Grubbs had lost out in proposing the correct mechanism for the metathesis however his subsequent studies were significant enough to fetch him a Nobel prize later for the same discovery. And all of these efforts were going on in US where this was on to explain the mechanism for metathesis and around at the time same time by following in Europe in France particular by following the work of professor Fischer in synthesizing carbon.

Or that our professor Nata for carrying out link opening polymerization of cyclopentane and as well as that of banks and Bailey's observation propylene and giving disproportionate to ethylene and butane. Professor Chauvin in French petroleum came up with mechanism which involved the formation of metal carbon as the active species responsible for carrying out this olefin metathesis and this fortunately was published in a little bit of obscure journal macro molecule chemistry in 1971 and also written in French.

But however it stood the test of time and went on to become the most acceptable mechanism for this olefin metathesis the reaction. So today with this we come to an end on the discussion on various approaches that where taken in trying to explain the olefin metathesis more on olefin metathesis particularly in trying to appreciate how the reaction propagates and what are its application so on and hence so forth in a lot more detail when we meet next for this NPTEL course.

So with that I conclude today's lecture thank you once again for being with me in this lecture when I look forward to discussing with you for bit more detail on olefin metathesis when we meet next on the next lecture since then good bye and thank you.