Transition Metal Organometallics in Catalysis and Biology
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Module No # 03
Lecture No # 13
Types of Metathesis Reactions

Welcome to this course on transition metal organometallics in catalysis and biology over the last 2 lectures we have been discussing about olefin metathesis particularly from the perspective of their origin and their mechanism also the active species so on and hence so forth. So today we are going to look up the various kinds of metathesis reactions that are available in order to understand the scope and the breadth of this fantastic reaction. Now in the context of discussion olefin metathesis what is required is that we go back in time back by about 70 years to meet 50's to really understand this metathesis reaction.

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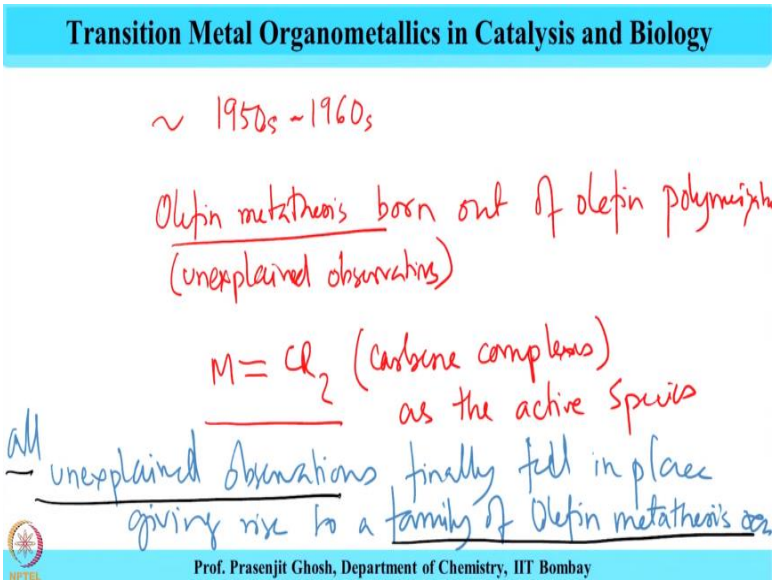

Say about this is about 70, 60 or 70 years back and olefin metathesis this is was born out of olefin polymerization and this is to say that they were some unexplained observation which eventually late to development of olefin metathesis chemistry. The olefin metathesis in that way is the very important reaction in the sense that it sort of put in place many unexplained are many different discovery small discoveries in proper perspective to give rise to this olefin metathesis reaction or the family of olefin metathesis reaction.

And the first that comes in mind is this active species which is metal carbine complexes as the active species for olefin metathesis. So these was the interesting development which was synthesized contemporary along the time by Fischer and Schrock gradually turns out that these olefin metathesis is catalyzed by these metal carbine chemistry and at that point of time unexplained observations finally fell in place all unexplained observation finally fed in place giving rise to our family or olefin metathesis reaction.

And these was possible because of elucidation of the mechanism proposed as well as demonstrated by Chauvin followed by mean other including Tomcat contribution we have discussed about in the last class. And as it turns out that this several unexplained also observation with regards to this reaction of olefin's the involving cutting and stitching of olefin's of different types all of them suddenly become explainable using these olefin metathesis mechanism and all of them then fall under the umbrella of olefin metathesis.

So what was observed that a group of about 10 to 15 reactions proceeding along this pathway of olefin metathesis which follows by 4 membered metallocyclo butane intermediate and proceeds with metal carbine active species came in being and that sort of explained the unexplained phenomenon of a variety of reactions which eventually give rise to a family of metathesis reaction. And in today's class we are going to take a look at different types of metathesis reactions which are known today and what they have called.

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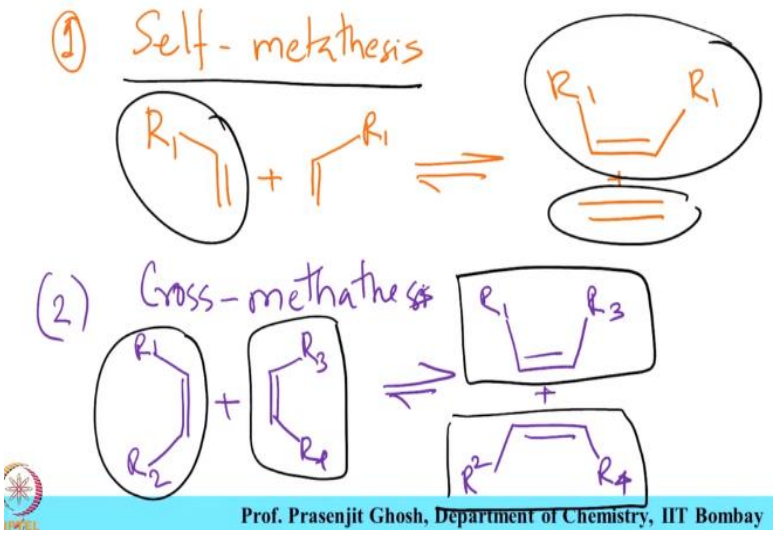

To being with the first is self-metathesis and this is about the reaction of the same olefin with itself as is shown over here. So what we have over here is same olefin one type of olefin giving rise to 2 different olefin and this is what is called self-metathesis reaction. The next in this series is cross metathesis so this is explained in this sort of example where we have a olefin R1 R2 reacting with olefin R3 R4 giving R1 R3 + R2 R4.

So what we have in cross metathesis is the fact that 2 different kind of olefin's reacting to give to other olefin's R1 R3 R2 R4 which were not in existence. So in self-metathesis we had observed one kind of olefin giving rise to 2 different kind of olefin different reacting to itself in cross metathesis what we have observe is 2 different kind of olefin's resulting into more different to other kinds of olefin so that is called cross metathesis reaction.

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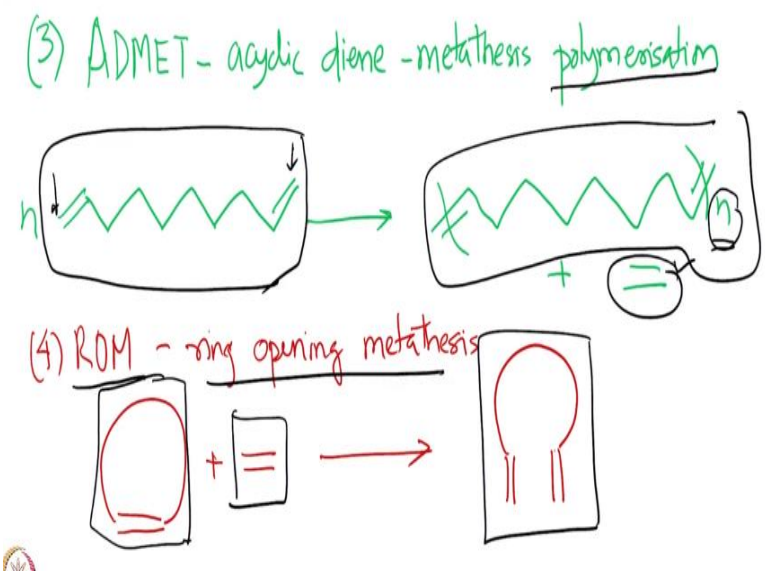

Another interesting type of metathesis reaction is called ADMET acronym ADMET and in expanded from it says acyclic diene metathesis polymerization. And what ADMET is polymerization between 2 terminal olefin's as is shown over here giving rise plus ethylene which comes from the polymerization of these terminal chain. So this end would give rise to formation of ethylene and here too what we observed in ADMET that this is polymerization reaction of where one type of alpha omega olefin's giving rise to polymer and olefin's ethylene you know this is what is called ADMET.

So all of these sort of proceeds in the by using the same mechanism and what we see that in all the cases that number of double bond is conserved and that is the beauty of these olefin polymerization process. The next in this series are ROM ring opening metathesis and this which is a cyclic olefin reacts with ethylene giving ring opening metathesis product ROM product. So what is notable over here is that 2 different olefin's this is olefin number 1 and olefin number 2 gives the metathesis product which is olefin number 3.

And that the product is a alpha omega is click olefin where the ring has been opened and hence is the name ring opening metathesis or ROM reaction this is called ring opening metathesis reaction.

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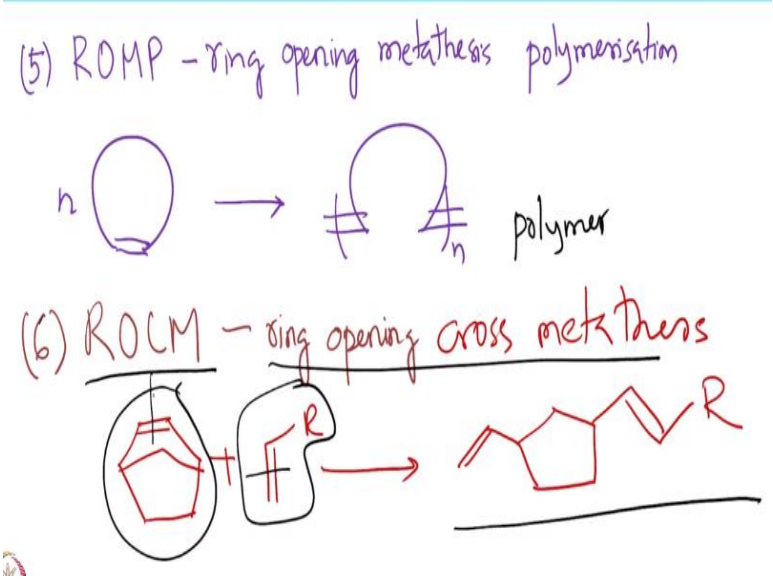

The fifth variant in this series of metathesis reaction is called ROMP so the fourth variant what we spoken about was ROM ring opening metathesis reaction and this is ring opening metathesis polymerization reaction let so this as the acronym ROMP and its stands for ring opening metathesis polymerization and these is also nicely demonstrated by this represented by this equation where when there is N mole of cyclic olefin reacting to give the corresponding polymer where the number of rings have been conserved and this is very nice reaction.

Where a polymer is obtained from cyclic olefin and the result in formation of polymer result in opening of the cyclic olefinic ring. Then proceeding further another variant of metathesis polymer is called ROCM ring opening cross metathesis this is an interesting variant as well this is called ROCM or in expanded form called ring opening and this is given by this nice equation where this by-cyclic compound reacting with another olefin where one of the double bond undergoes metathesis and one of the ring opens up to give the following compound.

So what is to be noted here is the fact that these olefin's react where these bonds undergoes metathesis reaction of each other and these rings opens up giving rise to these product with to olefinic bound. So this is called ring opening cross metathesis because in this case the metathesis happens between 2 different olefinic bond as is highlighted over here.

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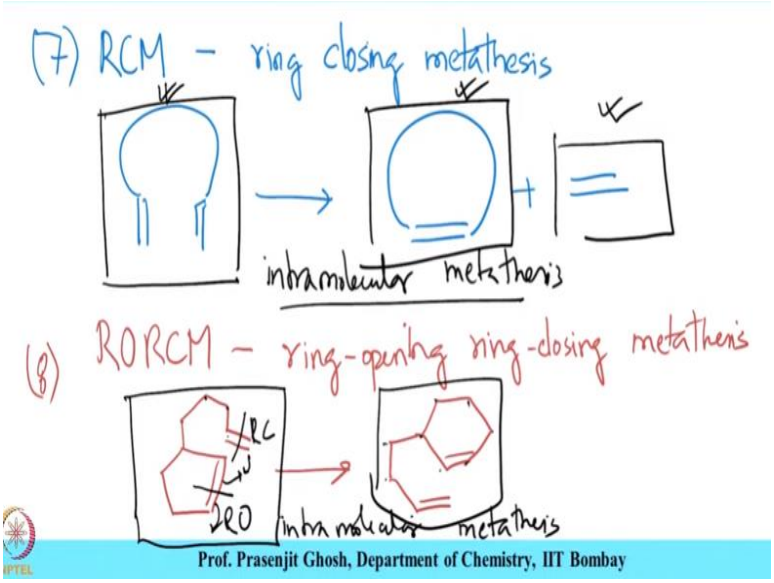

The seventh variant is exactly opposite of what we had observed for reopening of metathesis and it is rightly called ring closing metathesis is exactly opposite of ring opening metathesis and hence the name becomes ring closing metathesis and acronym is RCM. Now these is given by this reaction cluster by this reaction as is shown over here olefin becoming is a acyclic alpha omega olefin giving a cyclic olefin plus ethylene and here the point to note is just reverse of what we had observed it is intra molecular metathesis reaction.

So one type one olefin results in 2 different olefin one is cyclic olefin another is ethylene so this is exactly opposite of ring opening and metathesis were these two reacted to give this but in the RCM ring closing metathesis its opposite exactly opposite this undergoes intra molecular metathesis giving rise to this and this exactly opposite of ROM is RCM. Similarly along the same lines the next immediate variant which is number 8 in our case is called RORCM.

As the acronym suggest that this should be a very interesting reaction because it is ring opening ring closing metathesis all at the same time. So kind of very interesting both ring opening and ring closing both happening in one reaction and that is why it is called as RORC ring opening ring closing metathesis reaction RORCM ring opening ring closing metathesis. And this is beautifully illustrated by this example shown here this giving rise to.

So what is to be noted here that is RORCM is also intra molecular metathesis both one undergoing closing another undergoing ring opening so this one is undergoing RO and this one is

undergoing RC ring closing. So giving rise to the product so in RC what is happening is ahh this end and this end are stitching up and this end is opening up so this exactly what is happening and in this case too we would have observed that this one type of olefin resulting in the other type of olefin.

So here we have a fragment which is 5,6, 7, 8, 9, 10 and over we also have 1 to 10 so it is exactly the molecular remaining that is the total number of atoms remaining the same only the position of the olefinic bonds and the structure of the molecule becoming different.

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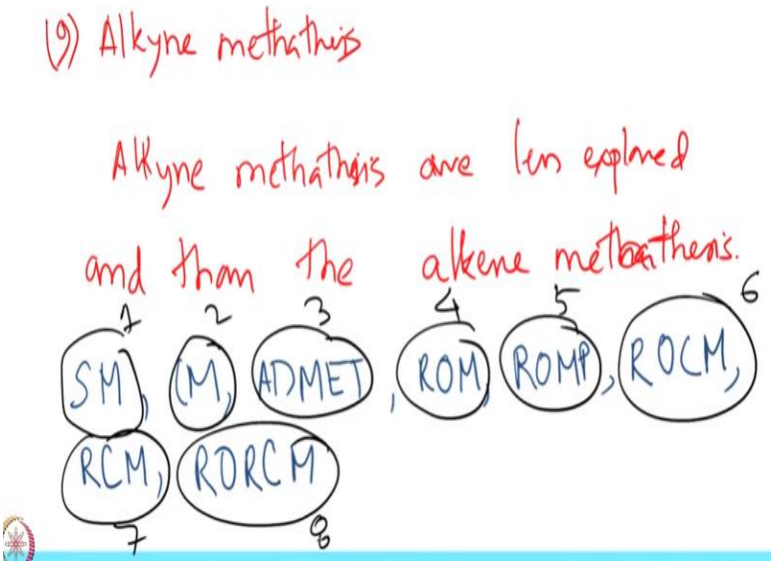

The next in this series is alkyne metathesis and they also come in various types what is interesting to note over here is the fact that alkyne metathesis are less explored ad studied than the alkyne metathesis reaction however I have been said that this alkyne metathesis also proceeds by similar pathway and they are very much studied as an extension of olefin metathesis reactions are rather they fall in the larger group of alkyne metathesis reaction.

So with these we come to conclusion of today's lecture in which we had focused on various kinds of metathesis reactions and there is kinds of olefin metathesis reaction to say the truth and the things that we have covered is starting from metathesis there are about 8 variant starting from self-metathesis where the olefin undergo metathesis with itself intra molecular metathesis is the self-metathesis and then we have cross metathesis which is CM then what we have another interesting one which is called ADMET or acyclic diene metathesis polymerization.

So this gives rise to polymer acyclic diene polymerization reactions then we had seen ROM ring opening metathesis followed by ring opening ring metathesis polymerization ROMP followed ring opening ring closing metathesis RO sorry ring opening cross metathesis followed by ring closing metathesis RCM followed by ring opening ring closing metathesis. So there are about 8 different types of metathesis reaction that we have studied this being 1, 2, 3, 4, 5, 6, 7, 8.

So the point to note over here is that now we again going back in winding back 70 or 60 years what is observed that all these 8 different types of reactions which at that point were extremely intriguing and complex to understand and all of them involved in cutting and stitching of different kind of olefin's. Now of these sort of become all of sudden explainable and answer to all of this complexity could be solved with the mechanism which has been proposed for olefin metathesis as proposed by Chauvin.

So that help brought bring all these different kind of olefin metathesis reaction all of sudden it seemed that they are not different but belong to the larger same family of larger as of different types of reaction all coming under one umbrella and that is beautifully observed in this olefin metathesis reaction. So what we study as olefin metathesis actually is classic is a summation of different types of different classes of similar type reactions 8 variants of which have just listed over here and in the next class we are going to look up alkyne metathesis which also as is from olefin metathesis and we will so many more variant of alkyne metathesis can also be explained by olefin metathesis.

And hence one can sort of understand the beauty of metathesis reaction what is also interesting to note in today's discussing is the fact that understanding mechanism is so important in understanding a reaction because a proper understanding with help explain the mechanisms are so many different types of reaction as for olefin metathesis only we could see that these active species and the cyclo butane intermediate in metathesis could explain 8 different variety of metathesis types of metathesis reaction as we have discussed today.

In this context I would also bring to our discussion in the previous course where we had seen how these cross coupling reaction held immediate cross coupling reaction as first understood from Suzuki or reaction Suzuki reaction could be also reacted to other variety are so many

different types of other cross coupling reaction like (()) (27:42) and all of these reaction would also follow the same or similar type of mechanistic cyclic involving oxidative addition trans-metallation and reductive elimination.

So these also further illustrates the importance of understanding mechanism and that is why we find so many different groups studying mechanism so seriously while understanding reaction. So with these today I am going to stop on today's discussion on different type of metathesis reaction we are going to pick up the another variant or variety of alkyne metathesis reaction in the next class and till then thank you for being with me and I look forward to being with you when we discuss alkyne metathesis in the next class thank you and good bye