Transition Metal Organometallics in Catalysis and Biology
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Module No # 03
Lecture No # 14
Alkyne Metathesis

Welcome to this course on transition metal organometallics in catalysis and biology we have been discussing olefin metathesis in the past 2 lectures. And in the immediate past lecture we have looked into types of olefin metathesis reaction that are known and what we had observed that this olefin metathesis reactions are of 8 variants that we had discussed in the previous class.

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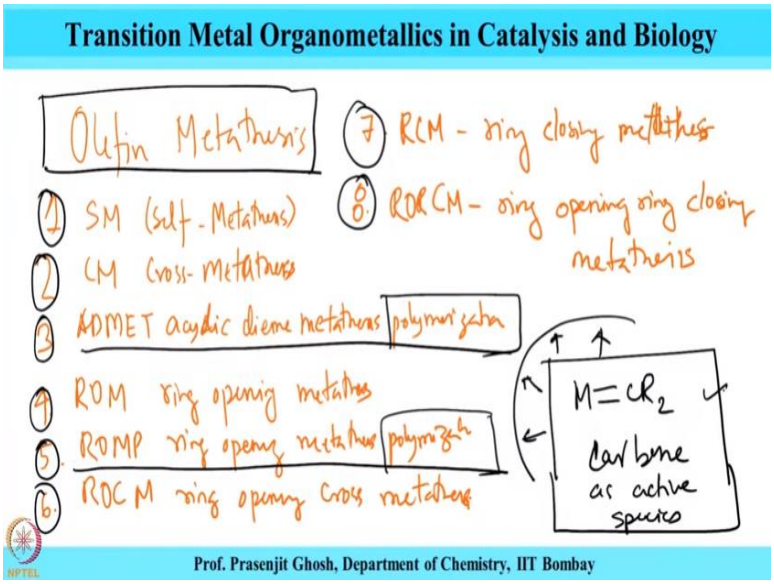

So to recapitulate the type of olefin metathesis reaction that are known today are about 8 types by enlarge and they start with being self-metathesis SM or self-metathesis then comes CM or cross metathesis then comes ADMET a cyclic dieme metathesis polymerization this is 1, 2, 3, 4 this is 1, 2, 3 the fourth being ROM ring opening metathesis fifth one is ROMP ring opening metathesis polymerization sixth one is ROCM ring opening cross metathesis then comes seventh one RCM ring closing metathesis and finally the eight one is RORCM ring opening ring closing metathesis reaction.

So what we had discussed in the previous class is various types of metathesis reactions which are known and quite a lot of them about 8 different kinds of metathesis reaction that are reported

today it also all of these 8 reaction could be explained by the active species which is a metal carbine is the active species as the active species for the metathesis polymerization and what is important over here is the fact that these active species could help explain so many different kind of reactions.

And all of them which initially where so difficult were brought together under the umbrella of olefin metathesis. So olefin metathesis then eventually can be said that in consisted of about 8 different types of subclass reactions. Few other things which come into prominent when we compare our discussions on various types of metathesis reaction and what is observed here is that of this 8 2 of them ADMET acyclic metathesis polymerization as well as ring opening metathesis polymerization.

These 2 reactions are involves making polymers so these 2 reaction yield polymers going from olefinic monomers. Whereas the remaining 6 varieties just converts olefin to olefin one type of olefin to another type of olefin so on and hence so forth. We had also observed in a previous discussion that these metathesis reaction can be intermolecular as well as intra-molecular depending on the type of reactions that we are looking at.

The last but not the least and important factor to note is that all of these proceeds by this metal carbine intermediate and that in the course of the reaction many types of metal carbine active species are formed in a chain process in a different olefin reacts with the particular carbine and the carbonic fragment gets transferred on to the new product olefin and carbonic fragment comes from the substrate olefin and creates to the metal and makes a new metal carbonic species.

So the active species keeps on changing its identity even though it remains the metal carbine persist through a chain reaction process as the reaction proceeds. So this is important thing to note and this also help understand how the olefin metathesis consists of so many different kind of variety of reaction. Today in our discussion we are going to look into the alkyne metathesis as been noted in our previous class that alkyne metathesis is relatively less explode and less studied as compared to olefinic metathesis.

Nonetheless olefin metathesis is also is a part of metathesis part of reaction proceeds by similar mechanism and we are going to see how many different types of these alkyne metathesis reactions are there as we go proceed further along to this class.

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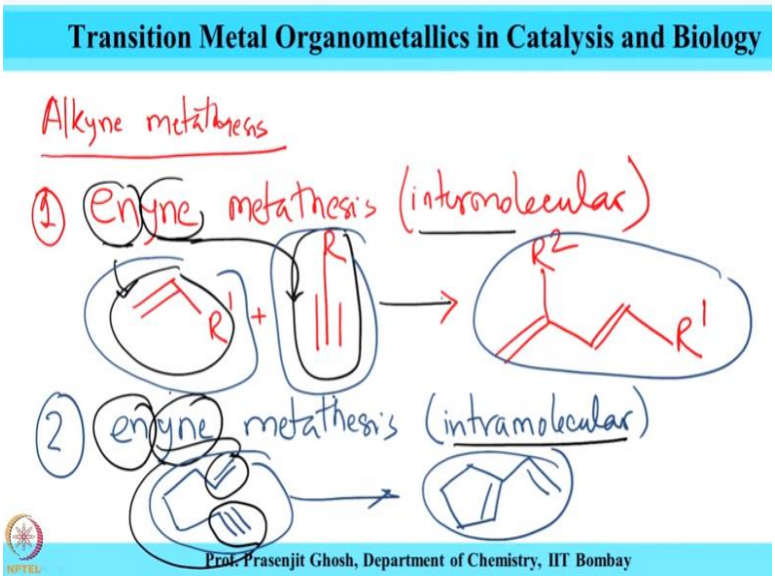

Now Alkyne metathesis also comes in many variety as the olefin metathesis and can be seen as we initiate the discussion further. The first of its among its class is called enyne metathesis reaction which is intermolecular reaction first variant is called enyne which is intermolecular. And this is explained by this variant so as the name suggest that this is a enyne en stands for olefin and yne stands for alkyne.

So it is a reaction between an olefin and then alkyne so this is the olefin and this is the alkyne resulting in the corresponding product. So this is a interesting reaction this reaction of metathesis happens in a intermolecular fashion as is noted over here intermolecular between 2 molecular one is an alkyne the other is an alkene. So this is called enyne metathesis we also there is also example of enyne metathesis being intra-molecular.

The second variation again is a enyne metathesis and this one is intra molecular and this is beautifully explained by these enyne as the name suggest here also there is in which is an olefin and the enyne which is over here and all of these are belong to the same molecule and hence it is called intra molecular enyne metathesis reaction. So this undergoes metathesis to give this product which is cyclo pentane to the vinyl group attached to it as.

So here also what we see that in enyne metathesis intra molecular we see 1 molecule giving 1 molecule whereas in the enyne metathesis inter molecular giving 2 molecules giving 1 molecule. So this is exactly what we see how the distinguish among themselves.

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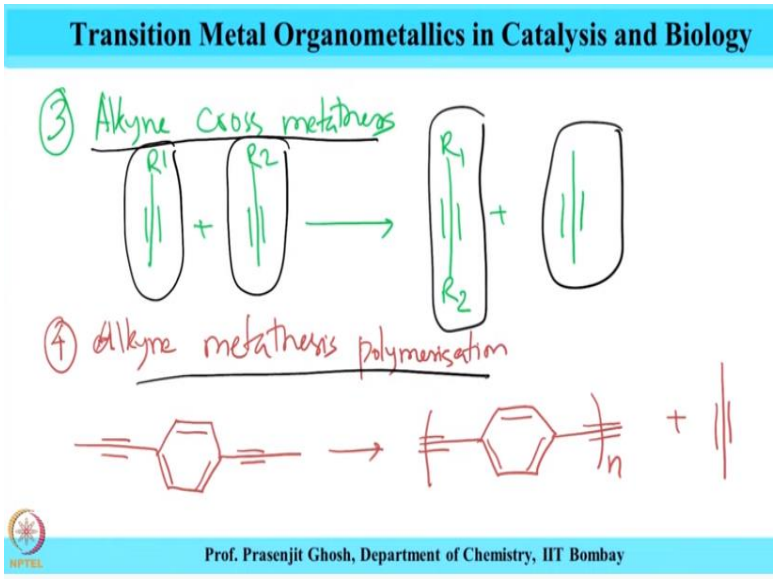

The third variant is called alkyne cross metathesis and this similar to what we had observed in case of olefin cross metathesis where metathesis happened between 2 olefin's in this particular case alkyne cross metathesis it would be metathesis reactions between 2 alkynes and this is illustrated nicely in this series of examples. R1 reaction with R2 giving R1R2 + so here the point to note is that 2 different olefin's giving rise to 2 different products.

So these also is similar to what we had seen for olefin metathesis cross metathesis exactly same thing except the substrates are reacting substrates of alkynes as the name suggest as opposed to olefin's as which we were discussed earlier. The next one is called next variant is called alkyne metathesis polymerization and this is also beautifully illustrated by this example giving rise to the polymer plus another alkyne.

So the point to note is that again this is similar to olefin counterpart where there was polymerization resulting information of ethylene and in this case what we get is formation of alkyne. So what we see is that there is a parallel in terms of the reaction that is happening for

alkyne metathesis once similar to what had been observed in case of olefin metathesis once is called ring closing alkyne metathesis.

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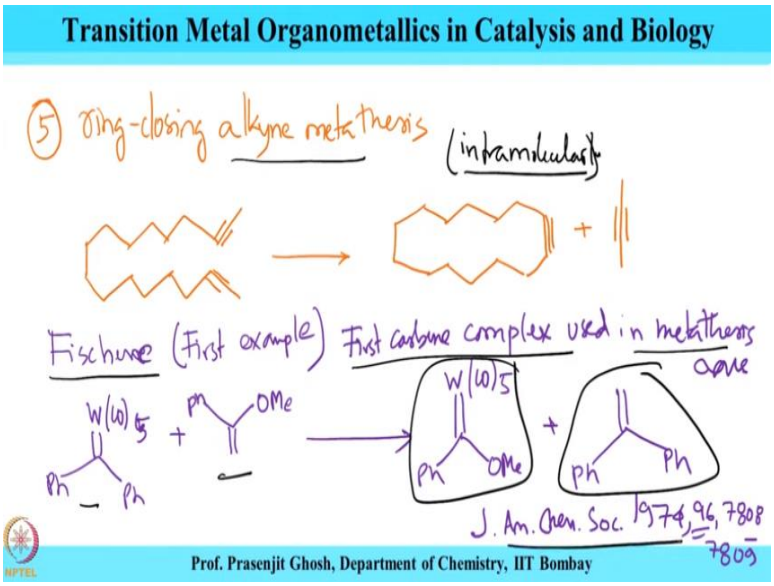

And this is illustrated by example shown over here giving rise to the cyclic alkyne plus another alkyne. So this is called ring closing alkyne and in this case what we see alkyne metathesis which (()) (17:55) intra molecular fashion there is a intra molecular ring closing metathesis reaction. This reaction is also parallel to link closing olefin metathesis ROMP so this is this also is similar to what is observed for alkyne has been translated in case of alkyne.

So what we see is that these metathesis alkyne metathesis reactions they also come in large variety and largely they are similar to what similar to what has been observed for olefin metathesis counterpart and they in terms of variety they are not as many as been observed for olefin were about 8 sub classes of different types of metathesis reaction have been observed. Whereas in the case of alkyne metathesis about 5 of them which are similar 5 of them have been noted and so that is sort of consistent with the fact that alkyne metathesis is less explored less compared to the olefin metathesis as a field.

So with these we are going to look at some of the synthesis methods that have been utilized from making these alkyne metathesis reaction. And to start with we are going to look at the first example of alkyne metathesis was reported by Fischer. First example and then the Fischer synthesized these carbine from this reaction of Tungsten pentacarbonyl and treated that with

another olefin resulting in Tungsten pentacarbonyl OMe plus this is a first carbine complex using metathesis reaction.

So this is sort of the first carbine complex used in metathesis reaction and this study was reported in JACS 1974 96 7808 to 7809. So what is important about this experiment is that this was the first time the carbine complex was used in a metathesis reaction was that mean the carbine complex was reacted with olefin to generate another carbine complex and another olefin. So these sort of validates the evaluates the metathesis reaction and was successfully demonstrated by Fischer in this JCS 1974 article.

So we are also observed similar demonstration or validation of the reaction coming from the reactivity of different olefin as done by professor Thomas Katz and here also we see the first example where carbine was treated with olefin to generate another carbine complex and the corresponding different olefin was firs also successfully demonstrated for carbine complex by Fischer way back in 1974.

And another interesting fall out of this metathesis reaction is development of very important intermediate which is very useful intermediate in organic synthesis which is known as tebbe's reagent

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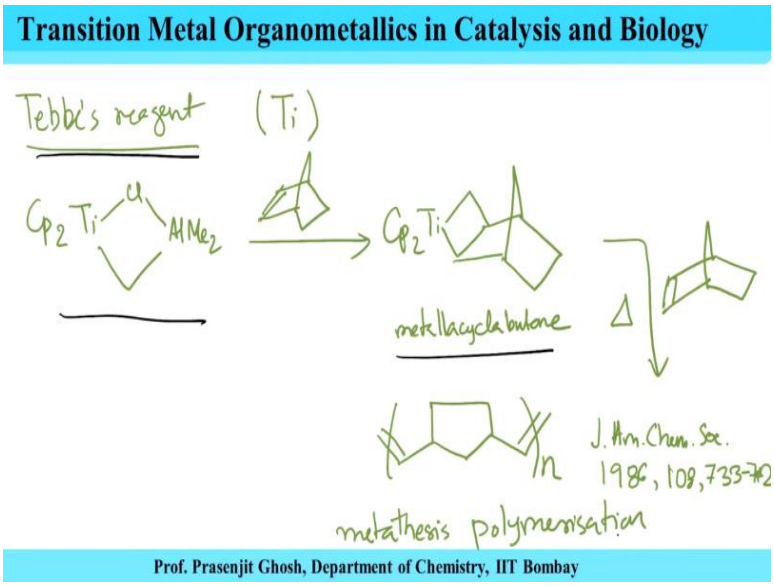

And these tebbe's reagent is of titanium compound and has the formulation of the type so these is similar to that of titanium carbine complex or sort of precursor to carbine complex. And for example when reacts and this can be elucidated by reaction with norbornene to give the following compound which is a metalocyclo butane compound and that when heated with norbornene gives the metathesis polymerization giving product of the type and these is interesting work was published in journal of American chemical society 1986 108733 742.

So these is a interesting development where the application of these olefin metathesis reagents can be observed in terms of development of this interesting reagents called tebbe's reagent which has the formula of these and this is nothing but a titanium carbine active species which reacts with in olefin to give this cyclo metallocyclo butane intermediate and then subsequently reactions with more norbornene would give the corresponding metathesis polymerization and this beautiful work and extension of application of olefin metathesis was published in JACS 1986 108 with 733 742 paper.

So with these we come to the conclusion of today's lecture where we had looked into various types of alkyne metathesis reaction that are known. And then also looked into application of olefin metathesis reaction. Now with regard to different types of alkyne metathesis reactions that we have covered today what we are observed that quite fair amount of alkyne metathesis variants about 5 of them are known and all of these 5 of them their corresponding parallels in the olefin metathesis reactions.

So in that one can say that alkyne metathesis reactions are almost are similar or draws its route from alkyne metathesis reaction and we have also looked into the first reaction utility of these metal carbine complexes in metathesis reaction as reported by Fischer when reacted in his carbine Tungsten carbine complex with another olefin generating another Tungsten carbine mighty and subsequently a different olefin and second application of metathesis alkyne metathesis we have seen in form of tebbe's reagent which is titanium carbine complex which undergoes an metathesis polymerization reaction with norbornene as observed from JCS paper.

So with these we come to end of today's class and we are going to be discussing more on these metathesis reaction particularly on catalyst front. So far we have spoken about mechanism active

species the pathways different types and we are going to focus bit more on catalyst development on this aspect of metathesis reaction in the next class. So again thank you again for being with me in the particular class and I look forward to being with you in taking up this discussion in bit more detail when we meet next till then goodbye and thank you.