Transition Metal Organometallics in Catalysis and Biology
Prof. Prasenjit Ghosh
Department of Chemistry
Indian Institute of Technology-Bombay

Lecture - 29
Alkene Alkyne Metathesis (Part-1)

Welcome to this course on Transition Metal Organometallics in Catalysis and Biology. In this course so far we have been talking about various kinds of olefin metathesis reaction apart from other industrial processes reactions, which has come out of organometallic chemistry discoveries. In the context of olefin metathesis, we have covered alkene metathesis and alkyne metathesis.

And we had seen how there exists a similarity or parallel of reactions for both these kind of metathesis reaction alkene as well as alkyne metathesis. And today, we are going to discuss another interesting topic in more detail which is called alkene alkyne metathesis reaction.

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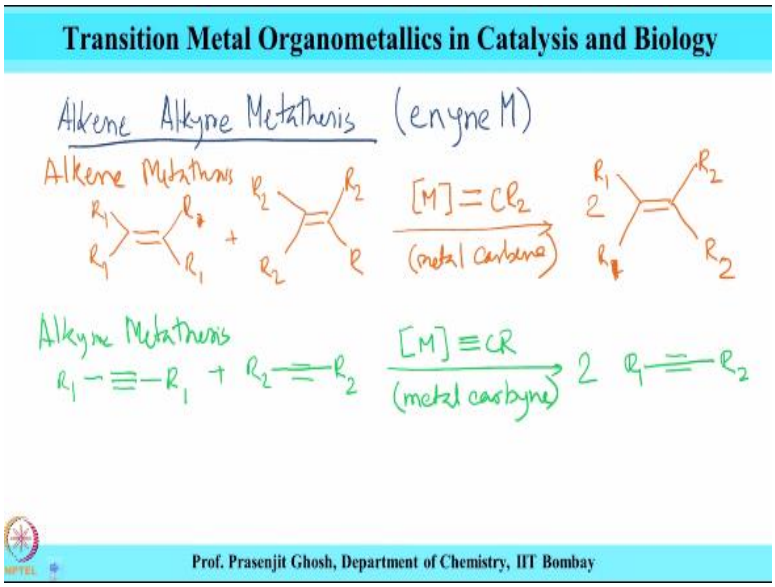

Alkene or which is called enyne metathesis reactions. Now in order to understand this reaction, this reaction is kind of a bit different than its predecessors which is alkene metathesis or alkyne metathesis. And in order to understand this, we need to reflect on the initial characteristics of these two alkene metathesis and alkyne metathesis individually.

So let me just start with alkene metathesis you know, which is the reaction between these two olefins giving this and the catalyst present is a metal carbene species. So this is a metal carbene catalyst. Now the alkyne metathesis is also a similar kind of reaction and it involves two types of alkynes giving two of the mixed alkyne and the catalyst is a metal carbine catalyst. So this is alkyne metathesis.

And the earlier one that we had discussed was alkene metathesis. So now the question comes what about the reaction that we are discussing now, which is alkene alkyne metathesis. So now, this has both the substrates which we will take a look.

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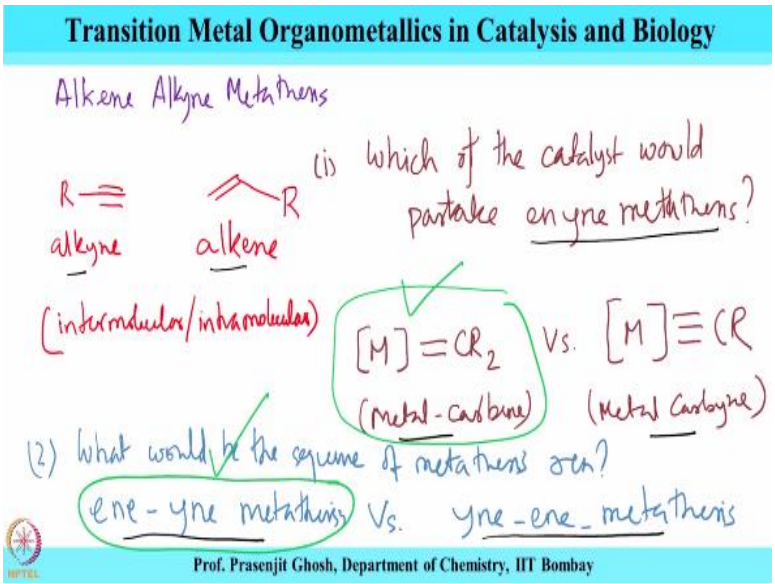

This has both the substrates for example, so it has both the substrates and alkyne and as well as an alkene and the question which comes to mind is which of the catalyst would be a more would be able to carry out such metathesis. So as far as the catalyst is concerned which of the catalyst would partake in enyne metathesis. So this is a intrinsic question.

This means that there are possibility of metal carbene versus metal carbine. So the interesting thing to note over here is that the first question is this which, which of these two catalyst the carbene or the carbine would be effective for this enyne metathesis reaction that involves reaction of alkene and alkyne. Now the next question which comes to the fore with regard to this chemistry is the question number two.

It says okay even if one of the two one of the two is or both of them is effective for carrying out this enyne mechanism, enyne metathesis then the question is what will be the sequence of metathesis ? What would be the sequence of metathesis reaction. By this whether it will be ene and then yne metathesis versus yne ene metathesis.

So this also is a very relevant and interesting question is that even if either of the two is effective in carrying out this metathesis of alkene and alkyne then the question is which one would be the first to undergo metathesis whether this is ene yne metathesis, where the alkene would undergo metathesis first followed by the alkyne or it is yne ene metathesis which would be starting with alkyne first and then alkene in the order of the metathesis reactions it would go.

So **so** these are important questions like what kind of catalyst, what would be the sequence of reactions? As now, the substrates contain both unsaturated alkyne as well as alkene. And then another interesting attribute is that they can be a present in the same molecule which can be intermolecular or intramolecular. So both possibility exists for alkene alkyne metathesis reaction.

Now these are the issues that had challenged the people who had been working in the area and several studies has been done in order to illucidate the exact mechanism or exact active species responsible for this ene yne metathesis reaction and to sum up the finding what is said that it is the metal carbene complexes, you know, they are effective for alkene alkyne metathesis reactions.

So the catalyst are indeed this metal carbene species. The evidences point that the active species are indeed the metal carbene species, which is responsible for alkene alkyne metathesis reaction. Now with respect to the second question that what would be the sequence of metathesis whether it will be a olefin first and then alkyne second metathesis or alkyne first olefin second metathesis?

The answer to that which the evidences point is that this ene yne metathesis which is supposedly the one which is followed in most of the cases and most popular. So the take home point is that alkene alkyne metathesis or ene yne metathesis is a complex metathesis maneuver, which has come out of this individual step classes of alkene

metathesis and alkyne metathesis and given the complexity that arise regarding the pathway the metal carbene species are supposed to be the active species for this ene yne metathesis.

And second thing that the mechanism proceeds by ene first or ene yne metathesis that olefin gets attacked first and then alkyne undergoes metathesis second. So I am going to now go deep into this the mechanistic aspect of this enyne mechanism and talk about this in bit more detail.

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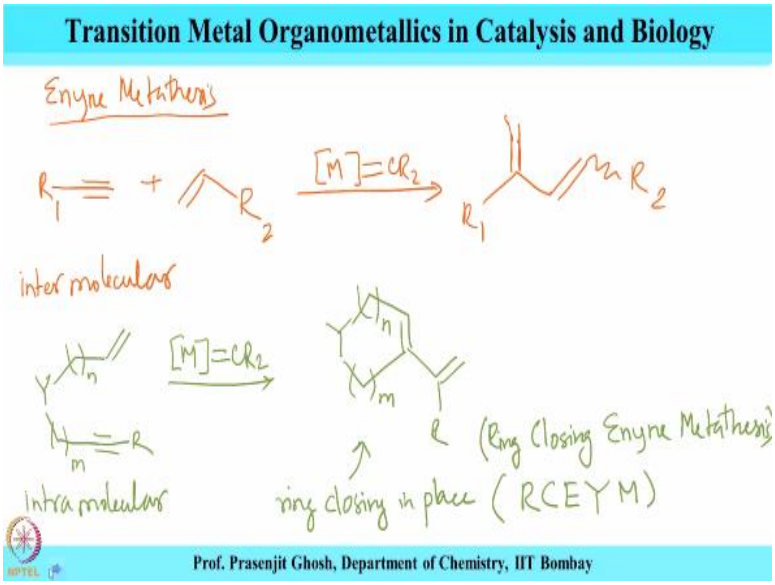

So now of these there can be a two variants as I said that this can undergo intermolecular as well as intramolecular. And I am showing it by examples to catalyst giving R 1. So this is a example of intermolecular enyne metathesis. Similarly, the intramolecular metathesis are also reported, which involves a bridging group or substrate containing a linker in which the substrate contains both, the alkene and the alkyne moiety are present.

And then the catalyst as I mentioned is that in the present case also this is a carbene type of the catalyst which gives a product of the type of the type this. This is a five membered. So this is a example of intramolecular enyne metathesis. But in this case as there is a ring closing occurring in place ring closing in place. So this mechanism is also popularly called as ring closing enyne metathesis or RCEYM.

This is called ring closing enyne metathesis. So both the possibilities, as I mentioned earlier exists for the enyne mechanism and we are going to take a look at it in bit more detail as we look at individual example.

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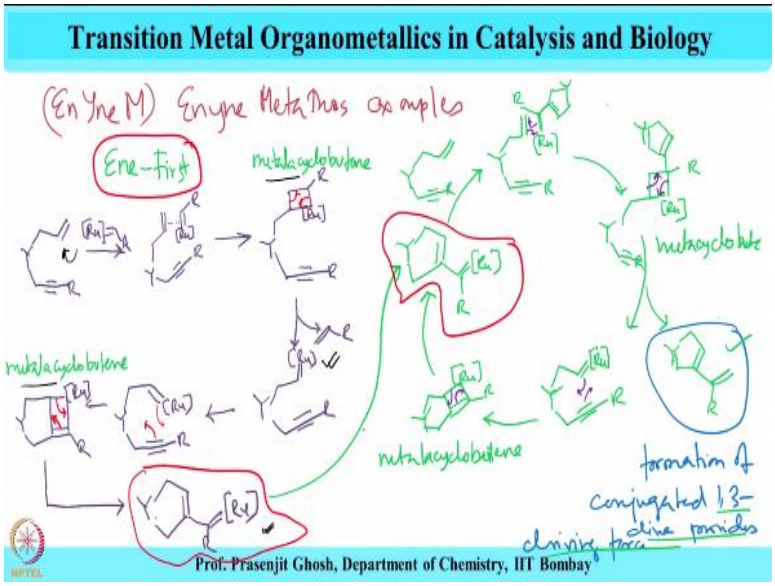

En Yne enyne metathesis examples. Now I am going to illustrate this with respect to the intramolecular substrate as is shown over here. Now this reacts with the ruthenium carbene complex. This will give this metallocyclopropane intermediate and that will further rearrange to give this olefin and the substrate activated ruthenium carbene species.

Now this then could go through this intermediate as is shown over here to give cyclobutene intermediate of the type this which will then rearrange as is shown over here to give the desired active species on the R. Now these there are two intermediates being formed metallacyclobutane intermediates. This is called metallacyclobutane and this one is called metallacyclobutene intermediate.

So a transition state, these are the transition state. Now once this is formed which I will draw it over here, the first path is about ene first. So metathesis what we are observing happens on the olefin. That is the first pathway is the ene first. And then the second pathway where the metathesis of the yne would happen. And for that these species goes and enters into a second cycle as is shown over here.

Now in this the first substrate further adds to give where similar kind of transition state, metallacyclobutane transition state is further formed as is shown over here. And then this transition state undergoes rearrangement to give the product and one active species of the ruthenium species of the type this. That then undergoes again metathesis with the yne to give this metallacyclobutene as it is shown over here.

And that further undergoes rearrangement to give the species which is this. So and the driving force of this reaction is the formation of conjugated 1, 3 diene. Formation of conjugated 1, 3 diene provides driving force for the reaction. So the formation of this conjugated diene provides the driving force for this reaction.

Now what we had seen that this enyne mechanism is quite complex and actually it involves a number of steps, number of steps in which the first is that the metal carbene complex proceeds with ene first mechanism where it does not attack the alkyne but attacks the olefin first and then it undergoes metallacyclobutane intermediate.

Once it has formed the metallacyclobutane intermediate with the ruthenium carbene on the substrate then it attacks the alkyne to give a metallacyclobutene intermediate which undergoes rearrangement to again giving the ring closing metathesis. So it closes the ring and the active site now resides on the vinyl carbene which is stable.

Now that reacts with the second substrate again to give metallacyclobutane intermediate butane, which undergo metathesis to give this 1, 3 conjugated diene product which is this which is the provides the driving force and for the reaction and then it undergoes the reaction with the second alkyne moiety to give a metallacyclobutene species.

Then and subsequently it goes back to the starting product. So one thing which is important is to note is that this species this vinyl carbene species of the substrate, these two species are exactly the same species and they get translated from one cycle to the another cycle and carry out this enyne metathesis. We are going to talk more on the mechanistic aspect of this ene first pathway of enyne mechanism as we move in the next lecture.

However, we have come to the end of this lecture in which we have just looked into various mechanistic pathway that are possible for enyne mechanism. We have also looked into the rational that behind this enyne mechanism starting with questions like what is the active species, whether it is a metal carbene species or a metal carbine species, which would be effective for this enyne metathesis, because enyne contains both alkene and alkyne.

And what we have found is that it is the carbene species metal carbene species which carries out this enyne metathesis. We have also looked into other aspects like whether it is going to be the alkene first pathway or alkyne first pathway. And in this class we have summarized the effectiveness of alkene first pathway, which involves two cycles two different types of pathways combined as is shown by the pink and the green cycles.

And then we have also looked into the conditions which will which provides the driving force for this enyne ene first pathway which is nothing but the formation of this conjugated 1, 3 dienes. So with this I conclude today's discussion on enyne metathesis mechanism. And we are going to dwell a bit more on the other possibility which is the yne first and the effectiveness of enyne mechanism as we meet in the next class.

Till then thank you for being with me in this class and I look forward to being with you in more details when we take up this enyne mechanism next in the next lecture. Till then goodbye and thank you.