Transition Metal Organometallics in Catalysis and Biology
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Lecture - 30
Alkene Alkyne Metathesis (Part-2)

Welcome to this course on Transition Metal Organometallics in Catalysis and Biology. We have been discussing alkene alkyne metathesis in the last lecture and we have been talking about it in the context of the individual metathesis reactions that is the alkene metathesis and alkyne metathesis.

What we have also learned is the fact that these alkene alkyne metathesis indeed is metathesis reaction in which the alkene is undergoes metathesis first followed by the alkane alkyne and in principle these are in short they are called Ene Yne metathesis.

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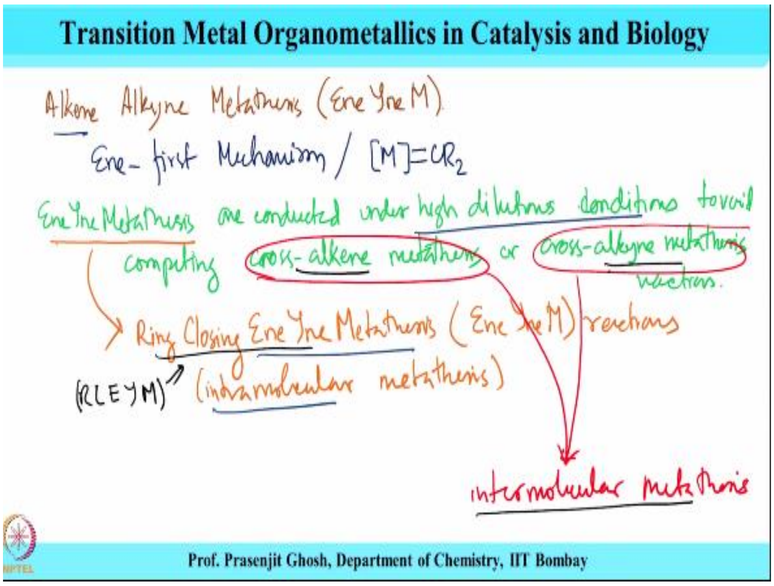

Transition Metal Organometallics in Catalysis and Biology

Alkene Alkyne Metathesis (Ene Yne M)

Ene- first Mechanism / $[M]=CR_2$

Ene Yne Metathesis are conducted under high dilutions donditions toavoid computing cross-alkene metathesis or cross-alkyne metathesis reactions.

Ring Closing Ene Yne Metathesis (Ene Yne M) reactions

(RLEYM) (intramolecular metathesis)

intermolecular metathesis

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In this context, in our previous lecture we had looked into the mechanism which is relevant for Ene-first pathway or which simply means that the alkenes undergo metathesis first, followed by the metathesis of the alkyne and what is the implication of this mechanism is that a metal carbine species is the active species for performing this metathesis reaction.

So in the previous class we have also looked into the full catalytic pathway for this Ene-first mechanism, and in today's class we are going to look at different factors which are put in place to carry out this Ene Yne metathesis in a Ene-first pathway and in the process also to avoid cross metathesis or other side metathesis reactions, which might as well also be carried out under similar conditions.

So one of the safeguard in place to carry out this Ene Yne metathesis reaction is that these reactions Ene Yne metathesis these reactions are conducted under high dilution conditions to avoid competing cross alkene metathesis or cross alkyne metathesis reactions. And these Ene Yne metathesis in particular is more applicable for ring closing Ene Yne metathesis reactions.

And these reactions are nothing but intramolecular metathesis reactions. So you know it seems very intuitive to think that these intramolecular Ene Yne metathesis are carried out under high dilution conditions in order to suppress all other kind of cross metathesis which are intramolecular in nature. So other cross metathesis which have been suppressed by these methods are for example cross alkene metathesis and cross alkyne metathesis and both of these intermolecular metathesis reactions.

So it is no surprise that these in order to suppress intermolecular metathesis reactions like cross metathesis and cross alkene metathesis and cross alkyne metathesis this ring closing Ene Yne metathesis are RCEYM in short what is called, which is a intramolecular reaction that is carried out under high dilute conditions.

So now a lot of investigation has been performed with respect to establishing the mechanism of this Ene Yne metathesis reaction as we are overseeing and in one of our seminal example by Mori et al who had showed that by taking suitable substrates presence of ethylene as a gas provides better opportunity for catalyst regeneration.

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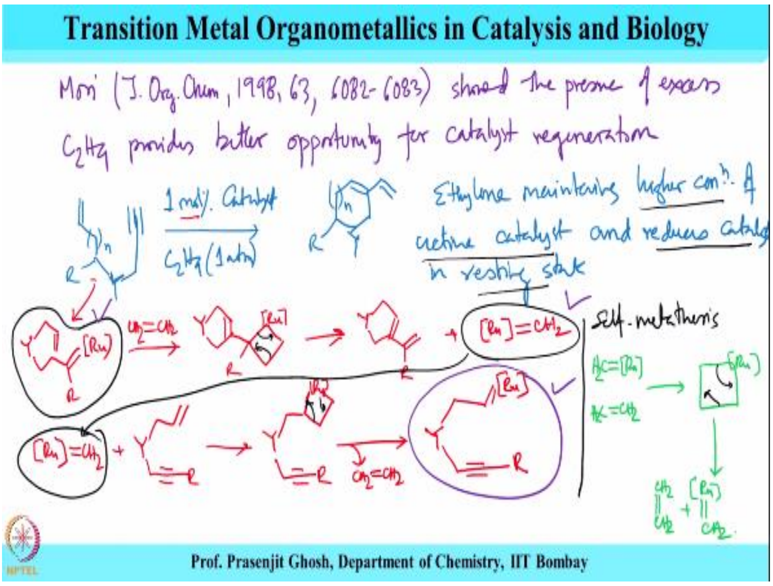

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Mori (J. Org. Chem, 1998, 63, 6082-6083) showed the presence of excess C_2H_4 provides better opportunity for catalyst regeneration

Ethylene maintains higher conc^n. of active catalyst and reduces catalyst in resting state

Self-metathesis

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So example by Mori in J. Org General of Organic Chemistry, 1998, 63, 6082-6083 showed presence of showed the presence of excess ethylene provides better opportunity for catalyst regeneration. So this provides better opportunity for catalyst regeneration and this is has been developed for the system shown over here. One mole percent and ethylene 1 atmosphere gave the cyclic compound.

Now the advantage of ethylene was ethylene maintains a higher concentration of the active catalyst maintains higher concentration of active catalyst, active catalyst and reduces catalyst in resting state. Now this is shown by the equations for example, the substrate and the catalyst they would react and in the process which was discussed earlier would generate this active species, which is the ruthenium carbene moiety attached to this cyclopentene ring giving a precursor which is conjugated or this is properly called as the vinyl carbine.

So that in presence of ethylene would give one atmosphere of ethylene would give this metalacyclobutane species and that would undergo rearrangement as is shown over here to give the product plus the active species. Now this is a different active species, different active species compared to the active species which is shown over here.

And again reacts with the substrate as is shown here to again give a metallacyclobutane ruthenium compound. So this active species comes again and then reacts with the substrate to give this metallacyclobutane compound which eliminates ethylene to give the active species, so which is another active species as is formed over here.

So in terms of active species what we see is that there are about three active species. The first one being this, second one being this, third one being this that are being formed. So if we look at the earlier statement that what has been achieved by ethylene that ethylene maintains higher concentration of the active catalyst. So all of these can now come into the cycle and carry out this metathesis.

And the second point it says that reduces catalyst resting state, because all of these active species can further participate in the reaction so they reduces the active state. Now another take home message is that the catalyst species can also undergo self-metathesis as is shown over here to give metallacyclobutane ruthenium compound. And that can undergo rearrangement as is shown to give these two species.

Now **now** this is a interesting improvement on Ene Yne metathesis and what it does is that by carrying the reaction under high dilute condition also in presence of gases like ethylene, the catalyst resting state time is reduced and the effectivity of the reaction is increased. Now this leads this is building up more on this Ene-first mechanism where the alkene is formed first, undergoes metathesis first.

Now there is also another line of investigation which was on the Ene-first mechanism in which the alkyne would undergo metathesis first. But this from the experimental evidence experiment studies it has shown that an alkaline first pathway would lead to various regioisomers the selectivity would not be as good as for the Ene Yne Ene-first pathway.

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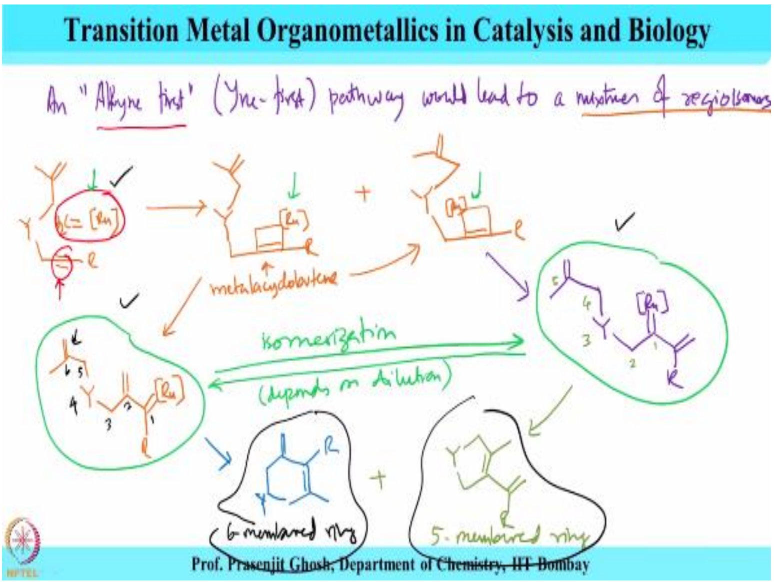

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An "Alkyne first" (Yne-first) pathway would lead to a mixture of regioisomers

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So an alkyne first or Yne-first pathway would lead to a mixture of regioisomers and this is illustrated by this beautiful example. For example for the substrate that reacting with the active species. So what we have over here is this alkene reacting with the active species carbene in this Yne-first pathway, resulting in this metallacyclobutene compound.

Now the mixture of regioisomers the selective issue comes from the fact that there are two kinds of metalacyclobutene can be formed the other being so the catalyst can bind in both ways, one is this, the other is this and this would give a product as is shown over here. Whereas the other mode of binding would give a product which is shown over here.

And the interesting thing is that these two products a different kind of active species and they can undergo exchange or interchange from one form to other depending on isomerization rate and which depends on dilution. So these two species which are formed by the differential binding of this ruthenium carbene species to the alkyne would result in two different active species which can also interchange depending on the dilution.

And as a result the products that emerge from there are also a mixture of products as is shown here. Now this is formed from the cyclization of this carbonic species with this olefin which gives a six membered ring. Whereas the cyclization of this carbene species with this would give a five membered ring as is shown here.

And what we see is that the mixture of two different this is a five membered ring that two different mixture is formed if this was going to be Ene-first mechanism and that arises because of formation of two different active species and that of because of the binding of this active species in two different pathway.

So even because of the complexity in the number of different products obtained in terms of the loss of regioisomers formed as the reaction were to proceed by alkyne first pathway the evidence is based on NMR and other mechanistic study, it does favor this Ene-first pathway where such problem of regioisomorphism does not appear.

So with this, we come to the end of today's discussion on the various mechanistic aspects of alkyne or Yne-first pathway which has been discarded given the fact that this mechanism if at all would happen would show the formation of various kinds of regioisomers because of differential binding of the active species to the alkene.

However, such a possibility does not is observed in the real Ene Yne metathesis reaction, which supports the earlier proposed mechanism that this is an Ene-first pathway, which is prevalent in the Ene Yne metathesis pathway. Now with this, let me just sum up what we had been discussing in today's class. In today's lecture we have looked at the method involved in improving this catalyst of Ene Yne metathesis and this has been done by performing this Ene Yne metathesis in presence of one atmosphere ethylene.

What ethylene does actually is that it provides a better opportunity for catalyst regeneration by maintaining a higher concentration of the active catalyst and also decreases the resting states of the catalyst. So basically a presence of ethylene helps in carrying out these Ene Yne metathesis reactions better. And also these reactions we have noticed is that they are carried out under high dilution conditions in order to avoid cross alkene metathesis and cross alkyne metathesis reactions occurring under concentrated conditions.

This is quite intuitive given the fact that cross alkene metathesis and cross alkyne metathesis are both intermolecular phenomenon. Whereas this ring closing Ene Yne metathesis is a intramolecular phenomenon and the better done under dilute conditions. We have also looked in the possible pathway of Yne-first mechanism and what is the main drawback of Yne-first mechanism is that it produces a large number of regioisomers and there is a lack of product selectivity.

However, given the fact that these Ene Yne metathesis reactions are highly selective and exclusively gives one product that also provides a circumstantial evidence in favor of Ene-first mechanism. So with this, I come to the conclusion of today's lecture. We are going to take a look at some more examples of Ene Yne metathesis or alkene alkyne metathesis when we meet next in the course. Till then goodbye and thank you.