Transition Metal Organometallics in Catalysis and Biology
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Module No # 07
Lecture No # 34
Ring Closing Eneyne Metathesis (RCEYM) & Alkenes & Alkynes oligomerizaton reactions

Welcome to this course on transition metal organometallics and catalysis and biology we have been discussing various types of eneyne metathesis as well as eneyne metathesis reactions the condition and examples and also we had been exploring the scope of this ring closing eneyne metathesis as well as eneyne metathesis in terms of applications in this context we had discuss about cyclo addition reaction eneyne metathesis reaction in the earlier lecture.

And today we are going to take a look at some more examples of these eneyne metathesis reactions then try to finish of our discussion on eneyne metathesis reaction and then take up very interesting topic which is alkene and alkyne oligomerization reactions. Now in keeping with the main scope of this course were we had highlighted the important organometallics catalytic reactions which has make it big in terms of going beyond the confines of the laboratory and reaching the source of the industry in terms of large scale utility.

This alkyne and alkene metathesis oligomerization reaction is another such topic which had been recognized with noble prize and its utility to the mankind as well recognized and well established by now. So with these let us comeback to our initial topic of eneyne metathesis examples which we are going to be talking up now.

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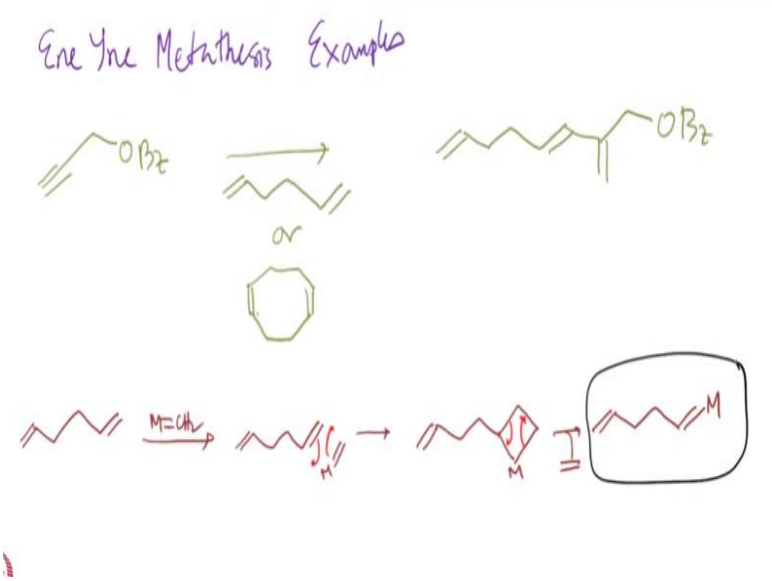

And the reaction is between these and 2 kinds of substrates one is these or the other is this substrate. Now the products formed are now to work out the product one needs to start with the substrate and the catalyst which would come along as it shown here to give the metallocyclo butane intermediate that would further generate this alkyne along with this active species which is the metal. And then these active species as it shown over here would subsequently go on to react with substrate shown in the next slide.

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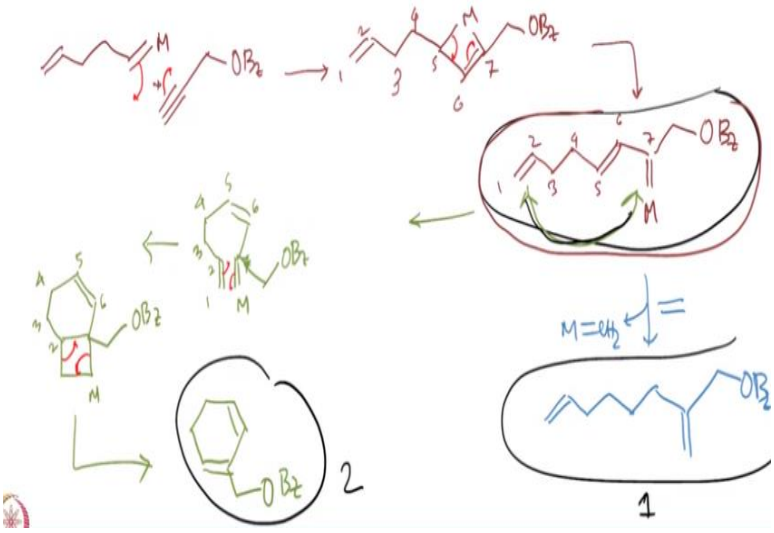

Would react with the alkene substrate OBz to give the first the metallocyclo butane transient state OBz as it shown over here and that would rearrange to give so there is a double bond between 5 and 6 and 7. Now these is a very interesting intermediate and it has to possibilities that

it can arise one is these one is this reacting with the olefin giving the corresponding alkene and regenerating back the olefin that is possibility number 1.

The other possibility is this undergoing metathesis between these 2 olefin in something which is shown over here this is 1, 2, 3, 4, 5, 6 this is 7. So this 7 also OBz so this is in this configuration if it comes around then possibility is this and that this structure is not drawn properly 2, 3, 4, 5, 6 this is 7. So that would give a structure this would undergo metathesis and structure like this 2, 3, 4, 5, 6, 7 as it shown here. And then subsequently this should undergo rearrangement to give the product OBz.

So this as a mentioned earlier that this was a important intermediate that resulted in 2 different product number 1 and the second product number 2 and that arises because of intermolecular metathesis reaction between 2 ene which occurs between these or it can give these product. Now these are very interesting reactions where depending on the orientation of the reactant intra molecular as well as inter molecular reaction may proceed and that can give rise to 2 different products.

So this is eneyne plus cyclo addition and this is just eneyne the reaction that is happening so with that we have we come to the end of our discussion eneyne metathesis reactions. We have looked into all variants of it to start with we have looked intermolecular eneyne metathesis followed by intra molecular eneyne metathesis and different product that have been obtained using this metathesis reaction.

We have also looked at various complex structures that can be obtained by eneyne metathesis reactions some can be cyclo additions tandem and with that very complex motives have been synthesized. So with this we conclude our discussion on olefin metathesis and we are going to move onto another interesting topic of alkene and oligomerization and polymerization reactions. Now to move back move on to this new reactions of olefin oligomerization polymerization I must mention that these are also important reactions particularly in terms of large synthesis and utility in industry for producing various value added chemicals using this methods.

And these also are also part of the noble prize award willing discovery of olefin polymerization so in and further more highlights utility of organometallic chemistry for large scale applications.

So with these let us move on to the next topic of oligomerization and polymerization of alkenes and alkynes.

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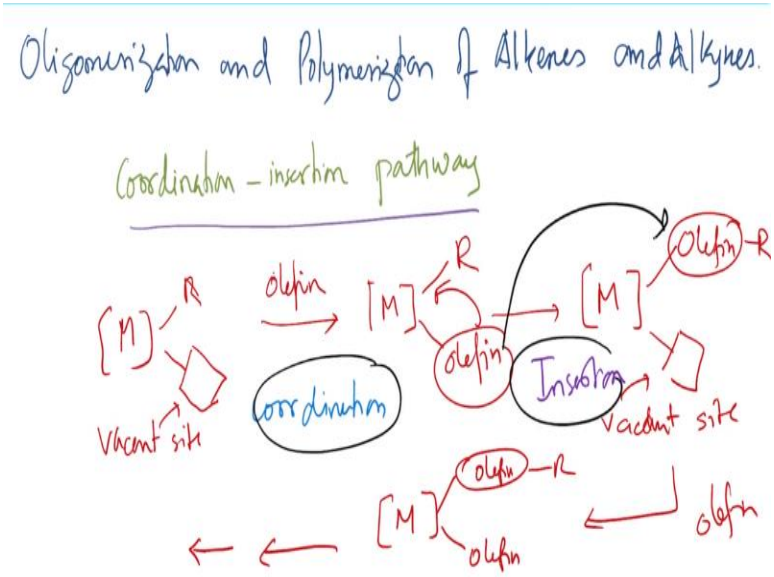

One must mention that these reactions oligomerizations of alkenes and alkynes as unpolymerizations of alkenes and alkynes they were initially discussed almost at the same time of olefin metathesis reactions. So the action was the first observation happened in around 1950's late 50's or 60's which had been the case of olefin metathesis as well as for olefin oligomerization and polymerization reactions.

But even though this metathesis reaction as well as this polymerization reactions of olefin they were initially observed in and around same time it is the olefin oligomerization and polymerization reactions were established much earlier with the noble prize coming in 1960's mid 60's 63 64 for the discovery whereas for the olefin metathesis the reaction took longer time to incubate and develop and the finally recognition came in 2005 so about 30 or 40 more years later.

So the olefin oligomerization polymerization of reactions had seen the light of the day much earlier then the olefin metathesis reaction that we had discussed in our earlier topic. Now one reason for this late recognition of olefin metathesis as a in comparison to olefin oligomerization and polymerization is because of the fact that olefin metathesis is much more complex reaction in terms of mechanism and the pathway it takes in terms of applications.

So it is much more complex much more bigger and hence it took a long time to elucidate and understand then the olefin polymerization reaction. But this does not take away any credit from the oligomerization and polymerization reaction because they themselves represent the huge field as such and due credit is given to them as well in presence or absence of any other discovers.

So with these let us start our discussion on oligomerization and polymerization of alkenes and alkynes one of the thing which is common to this oligomerization reaction is that the mechanism in which the oligomerization happens and these usually happens by a pathway called coordination insertion pathway. What is means is that the metal what it means that the metal must have a vacant site metal with all these ligand must have a vacant site to which the olefin first binds.

So this is called coordination step and the next step is this after binding the olefin that inserts into these metal alkene bond and this vacant site is regenerated to which again an olefin comes into minds and then the process proceeds on. So this in short the mechanism in which aptly followed and this is commonly referred to as coordination insertion. So the coordination step is shown over here and the insertion step is shown over here so the first step involved coordination and the step involves insertion well the olefin into the metal alkene bond.

So what is important to note is that this is sort of a common mechanism or common pathway accepted for olefin oligomerization and the polymerization reactions.

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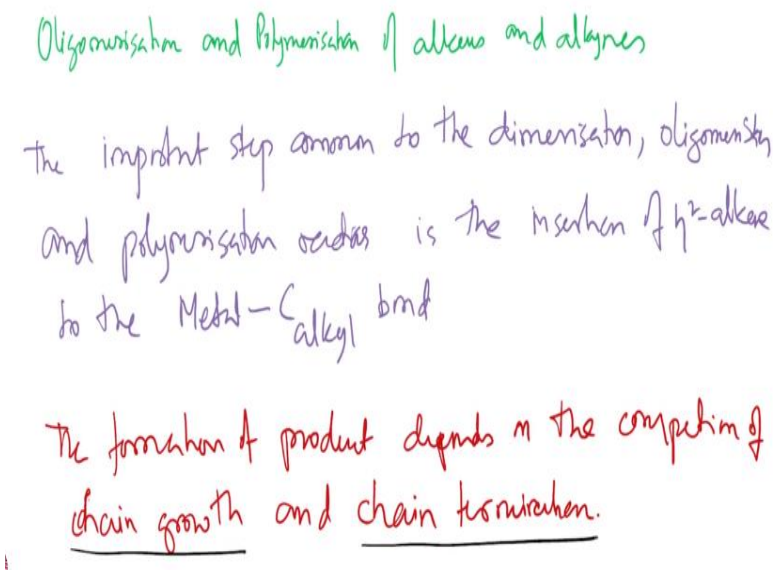

And what is the important step common to the dimerization, oligomerization, polymerization reactions is the insertion of (()) (23:36) alkene to the metal C alkene bond and this is exactly what we had referred to as coordination insertion mechanism. So important step for any oliigomerization dimerization, trimerization not in polymerization is the insertion of course the coordination of the olefin to the vacant site and then subsequent insertion of the coordinate olefin to the metal alkyne bond.

And the second important thing is the formation of product depends on the completion of chain growth on chain termination. So this is an interesting observation it says that the extent to which the polymer will grow depends on the rate of composition rate of comparative rate of chain role which is propagation step as well as the chain termination if the chain propagations step faster than the propagation step then longer polymerization will form and if the chain termination overtakes chain propagation then for the oligomers are shorter polymers or oligomers was formed.

So this is an interesting observation and in this context in this slide we are going to look at various examples of alkene oligomerization and polymerization processes as been moved on with the discussion on this topic in the subsequent lectures. So with these we come to the conclusion of today's lecture in today's lecture we have looked into another example of tandem ene yne metathesis and cyclo addition reaction resulting information of 2 products depending on the orientation of the active species and the olefin and the subsequent reaction with alkynes.

We have looked into various pros and cons or various important features of these eneyne metathesis reaction both inter molecular as well as intra molecular fashion and then in this lecture we have finished our discussion on eneyne metathesis and then imitated our discussion in another important topic of olefin oligomerization and polymerization reactions.

We have noted that these oligomerization and polymerization reaction proceed by a coordination insertion pathway where there is a vacant site to which the olefin binds and subsequent insertion of the bound olefin or coordinated olefin to metal alkyne bond is crucial to the formation of the this oligomerization or polymerization reaction. Another thing that we have noted is that the extent to which the polymer length will grow depends on the rate in which the propagation and the termination step occur.

And depending on the inter play of 2 factors would decide on the length of the oligomer. So with these we are coming to the end of today's discussion we are going to be discussing the new topic of olefin oligomerization and polymerization in more detail as we take up the topic in the subsequent lecture once again thank you for being with me in this discussion and I look forward to taking up this discussion on olefin oligomerizatioin polymerization in much detail when we meet next till then good bye and thank you.