Transition Metal Organometallics in Catalysis and Biology
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Module No # 04
Lecture No # 16
Catalysis Development Aspect of Olefin Metathesis (Part – 2)

Welcome to this course on transition metal organometallics in catalysis and biology. We have been talking about a various aspect of olefin metathesis over a series of lecture. And in the past lecture we have focused on a new aspect which is the aspect of catalyst development. Now in this what we have observed is that this is a key area of which sort of led to the explosion of the field of olefin metathesis.

This is an area of which showcased the capability of olefin metathesis as a reaction in terms of transformations that it can undertake in terms of the amounts to the product that it can turn out in term so basically the depth and the breath of this olefin metathesis reaction was built on the back of catalyst development aspect. So in this regard have spoken about the various types of metal carbene complexes which were synthesized.

One this for sure to note is that carbene is a kind of very a react sensitive moiety to be stabilized on metal and they are extremely reactive not only to the various substrates but also to the presence of air and moisture in the reaction vessel. So to make a catalyst out of this extremely active species is of a challenge just for stabilizing them is itself a challenge and in this process of catalyst development among the various metals lead transition metal early transition metal that have been used. What we have observed is Grubbs contribution in making ruthenium emerging out as victorious for developing olefin metathesis catalyst.

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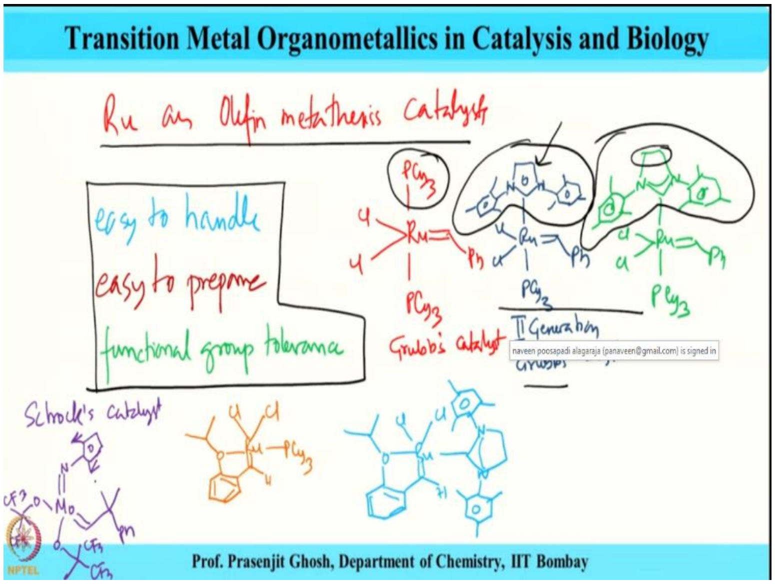

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Ru as Olefin metathesis Catalyst

easy to handle

easy to prepare

functional group tolerance

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Ruthenium as and this is because is easy to handle also easy to prepare and functional group tolerance. So this is what makes ruthenium carbene complexes as extremely a good catalyst for among other metal carbene catalyst for olefin metathesis reaction. Now in this race for developing good ruthenium carbene complexes for olefin metathesis several ruthenium carbene complexes were synthesized.

And in these regard prominent are those which have been which are made by Grubbs and actually several versions of improved versions of Grubb catalyst were subsequently turned out by Grubbs himself. So these are known as Grubb catalyst then second generation Grubbs catalyst third generation Grubb catalyst so on and so forth. So we are going to take a look at some of the existing catalyst which have been developed for olefin metathesis centered around ruthenium.

So this is what is prominently called as Grubbs catalyst. The next comes Grubbs second generation catalyst which is with a heterocyclic carbene with material substituents. So this is second generation Grubbs catalyst. Actually there are 2 versions so this one is a saturated version and also there is a unsaturated version of the same type it is just the backbones unsaturated version.

And then there are several other so what is to be noted over here is that this cyclohexyl one of the piece cyclohexyl phosphine has been replaced with a heterocyclic carbene. This is a imidazole based where it is a there is a unsaturated backbone and then this is five membered where this is a completely saturated program of CH2 CH2.

So these when a cyclohexane phosphines are replaced with in a heterocyclic carbenes they become even better in terms of olefin metathesis activity. And hence these 2 are called second generation Grubbs catalyst where one of the phosphines has been replaced by NHCs. Now there are other variants of carbenes as well. One such prominent variant is Schrock's catalyst which we will see and this is the molybdenum based 2 6 isopropyl substituents phenyl CF3 CF3 CF3 CF3 CH3. So this is the Schrock's molybdenum catalyst.

And then comes a tethered alkoxy compound of ruthenium which this another variant of the stated alkoxy complex with carbene is also reported and so this slide sort of provide a glimpse of the glimpse of the kind of imagination that goes into developing this so many different variants of the catalyst based centered around the ruthenium and molybdenum. So not only the richness of the side in terms of the catalyst development where so many different catalyst of similar types have been synthesized.

And the other thing which also talks about is the ability to stabilize so many different variety of carbon complexes this also highlights the synthetic capability of organometallic chemistry as such in which the successful synthetic route to so many variants could be established. Now the next what we would be talking about is in trying to understand the developmental aspect of catalyst with regard to the mechanism of this reaction.

So what is important to note over here is all of these catalyst actually are pre catalyst because the real catalyst is slightly different from these pre catalyst in the sense that it undergoes phosphine dissociation to give a vacant coordination site. And that sort of then reacts with olefin to give the product. So this is illustrated in more detail in the subsequent slide.

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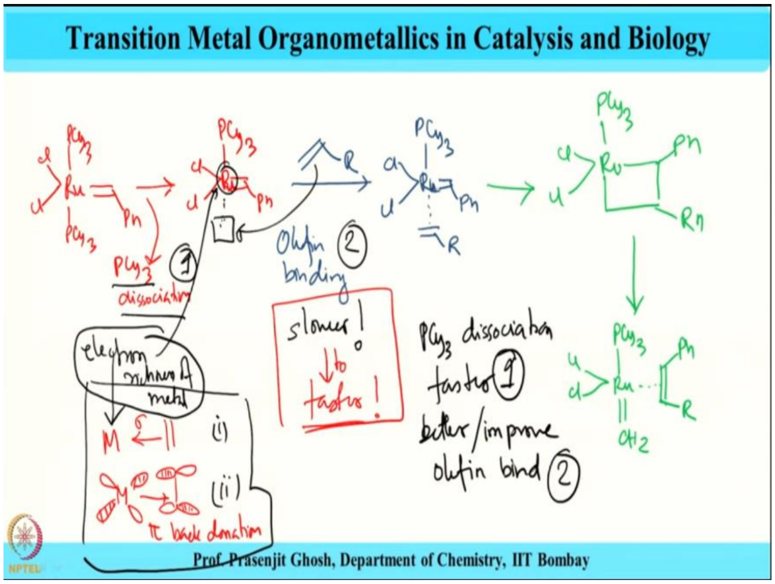

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For example so now the first step what happens is these phosphine dissociation resulting in these active species of ruthenium having a vacant site and the next step does involves reacting these species with ruthenium to give this alkene bound ruthenium species as shown over here. Now what is to note is that once these species is formed then the reaction sort of can move towards metathesis in the sense that it can provide the required metallacyclobutane intermediate.

And that can then finally give the corresponding product. So if one were to follow these metathesis using the ruthenium carbene in 4 simple step of reaction. What is important in catalyst development is the first 2 reaction which is step 1 involves phosphine dissociation and then step 2 involves olefin binding and that is determined represented by step 2. Usually olefin binding is a slower and also that is why what sort of is needed to enhance the metathesis reaction.

So now the effort is more in trying to convert this olefin make this olefin binding from slower to faster. And this can be achieved by following strategies. The reason olefin binding is slower because the ruthenium binds to olefin in 2 way fashion. First is the metal to olefin Sigma donation and then is metal by back donation. So this is important in understanding this metal olefin by binding. This forward Sigma donation as well as PI back donation.

And this is dependent on electron richness of the metal. So what is important is that to design catalyst which will not only make phosphine dissociation faster PCy3 dissociation faster as a result that will promote a better or improve olefin binding which is so this is step 1 then step 1 becomes faster then step 2 improves. Now if the step 2 improves then subsequently the metathesis also would improve.

Now for binding of olefin the 2 factors are required which is metal to ligand to metal Sigma donation and metal to ligand Pi back donation. And for which the metal has to be electron rich. So in the strategy for developing the catalyst what is required is to make step 1 faster that is phosphine dissociation faster. And how is that done we are going to take a look that is done by putting more sterically demanding ligands on the ruthenium.

So that it becomes crowded at the first dissociation becomes faster secondly to if the first dissociation become faster then the first dissociates and there is vacant site there is a vacant site where the olefin would come and bind. So that would indirectly help binding of olefin. Now binding of olefin is also facilitated further by making the metal center more electron reach in terms of putting ligands which are more a better Sigma donor.

So there are like both sterics and as well as electronics both are modified such that these 2 reaction 1 for phosphine dissociation and reaction 2 of olefin binding are optimized so as to get a better olefin polymerization catalyst. And this is achieved by the following strategy for these ruthenium complex as is discussed here.

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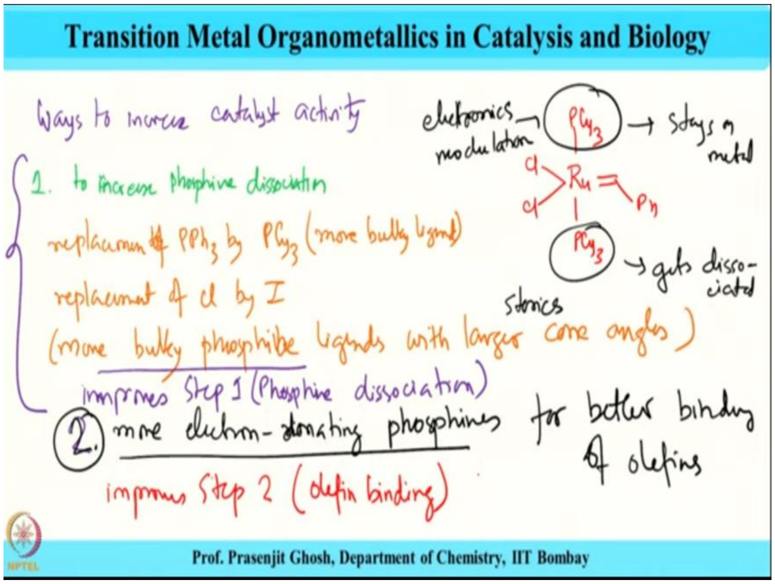

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Ways to increase catalyst activity

1. to increase phosphine dissociation

replacement of PPh_3 by PCy_3 (more bulky ligand)

replacement of Cl by I

(more bulky phosphibe ligands with larger cone angles)

improves Step 1 (Phosphine dissociation)

② more electron-donating phosphines for better binding of olefins

improves Step 2 (olefin binding)

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And we are going to now talk about how to improve this increase the catalyst activity and the first is in this regard the first strategy is to increase phosphine dissociation and this can be brought about by replacement of PPh3 by PCy3 more bulky ligand. So by putting more bulky ligand it facilitates phosphine dissociation as well as by replacement of chlorine by iodine on the catalyst.

So the idea is more bulky phosphine ligands with larger core dangles will more bulky phosphine ligands with larger cone angle would be a better for the dissociation of the phosphines. Similarly, what is to be noted over here is the fact that the only one of the phosphine gets dissociated and the other gets dissociated whereas the other states stays on the metal. Now this dissociation is facilitated by sterics and the electronics are modulated by this phosphine which stays relation by this the second first beam that stays on to the metal.

And for these what is required is more electron rich phosphines donating phosphines this is actually applicable for the phosphine one that particular one which stays on the metal for better binding of olefins. So what one sees that the first the strategies of going for bulkier phosphines that improves step 1 which is phosphine dissociation. And the second strategy of more electron rich phosphines this one improves step 2 that is olefin binding.

So and this is electronics. So what we see this is electronics modulation. So steric modulation is more appropriate for step one that which was phosphine dissociation and electronic modification is more appropriate for the step 2 which is electronic olefin binding. So in this class what we have done is we have looked into various kind of phosphines ruthenium catalyst which have been synthesized for olefin metathesis.

We have looked at how various improvements have been done in terms of replacing one of the phosphines with more electron donating and bulkier inheterocyclic carbene variants ligands. We have also seen how tethering of alkoxy group in the ruthenium carbene carbon complexes have been undertaken. We have also seen molybdenum catalyst has developed by Schrock. Then in the course of further discussion in this lecture what we have also done is we have looked at this elementary step in which the catalyst ruthenium carbene complexes undertake olefin metathesis.

And then looked upon the strategies which are put in place in order to improve other the activity of the ruthenium catalyst. What we have observed is that the most many all of the ruthenium complexes which are used for metathesis are actually pre catalyst that means that they go on to the form different species by more unsaturated electronics as well as a coordinated by unsaturated species by dissociation of phosphine in the first step to form the active species to which the olefin then binds to give the olefin coordinate at that and then that subsequently undergoes metathesis reaction.

So what the general affinity shows that olefin binding is very slow which happens in the step 2. What we have seen that proper modulation of the interplay of the steric as well as the electronics can help facilitate the metathesis reaction by improving or increasing phosphine dissociation this has been achieved by putting more bulkier ligands around the metal center. For example on moving from the triphenylphosphine to tricyclics hexyl phosphine or ongoing form chlorine to iodine the more bulkier the ligands around ruthenium is the first step is facilitated in terms of phosphine dissociation is affected.

And the second things is about increasing the binding of the olefin which by inherent nature is a slow binder to the ruthenium and this has been achieved by improving the through electronics by improving the electron density of the metal center. And this has been done by putting more electron rich phosphine or in heterocyclic carbenes on the metal. Now it is to be noted that Grubbs first generation catalyst are the Grubbs original catalyst has 2 cyclohexyl phosphine of which one dissociates to give the active species.

Whereas the second phosphine stays on to the metal and that phosphine then modulates the electron density around metal for it to effectively bind to olefin. So that the metathesis reaction becomes faster. So what we see is the successful implementation of sterics implementation of strategies based on sterics and electronics in enhancing or jacking up the activity of the olefin metathesis catalyst.

So with these we come to conclusion of today’s lecture where we have looked at different types of ruthenium metathesis catalyst that have been synthesized all the variants of faith and also we have looked at the different strategies that have been put in place in order to improve on the activity of the ruthenium catalyst. What we have noted is that there are 2 key steps which are in the beginning of this metathesis reaction.

First is the formation of the catalyst through phosphine dissociation. This has been improved upon by putting more bulkier ligand around the metal. And the second step is of course the olefin binding and this has been improved upon by putting using electronics as the tool by putting more electron rich or Sigma donating ligands on the metal so that olefin binding is isolated and as a result the metathesis goes up.

So with these we come to conclusion of today’s lecture we are going to look at the strategy of catalyst development in much more detail as we take up this topic of olefin metathesis in the next class. Till then goodbye and thank you.