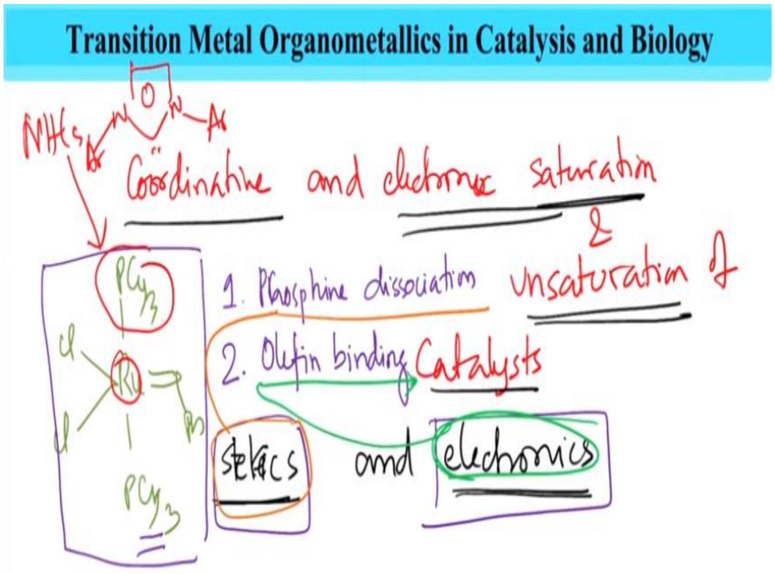
Transition Metal Organometallics in Catalysis and Biology
Prof. Prasenjit Ghosh
Department of Chemistry
Indian Institute of Technology – Bombay

Module No # 04
Lecture No # 17
Catalysis Development Aspect of Olefin Metathesis (Part -3)

Welcome to this course on transition metal organometallics in catalysis and biology we have been discussing olefin metathesis in the context of catalysis development perspective and in that regard what we had discussed is the fact that strategies which were put in place in making the catalyst effective one with that effectivity I mean that the catalyst should be highly active in terms of being able to convert substrate to product and towards this goal several designing changes have been adopted in the course of making catalyst for olefin metathesis.

We had seen the strategies which have been employed by Grubbs, Schrock (()) (01:06) and others for designing gladis for designing catalyst for olefin metathesis reaction. Now in this discussion I would like to draw the attention towards the discussion about coordinative and electronic saturation and unsaturation aspects that plays a crucial role in a design of catalyst.

(Refer Slide Time: 01:43)



Transition Metal Organometallics in Catalysis and Biology

Coordinative and electronic saturation and unsaturation of catalyst now by these one refers to the statics as well as electronics statics and electronics. So one place with the statics and electronics of the catalyst complex by changing the coordination and making the metal center more crowded when it is saturated as well as when if something is co-ordinatively unsaturated that means that they are week inside accessible to the metal centers.

Same means the in case of electronics saturation or unsaturation now these follows from the fact that there are ligands which either donate electrons to the metal center or ligands which pull away or suck electrons density from the metal center making the metal more electron richer or more electron deficient as is the case and thereby modulating the reactivity of the catalyst with refer to particular substrates.

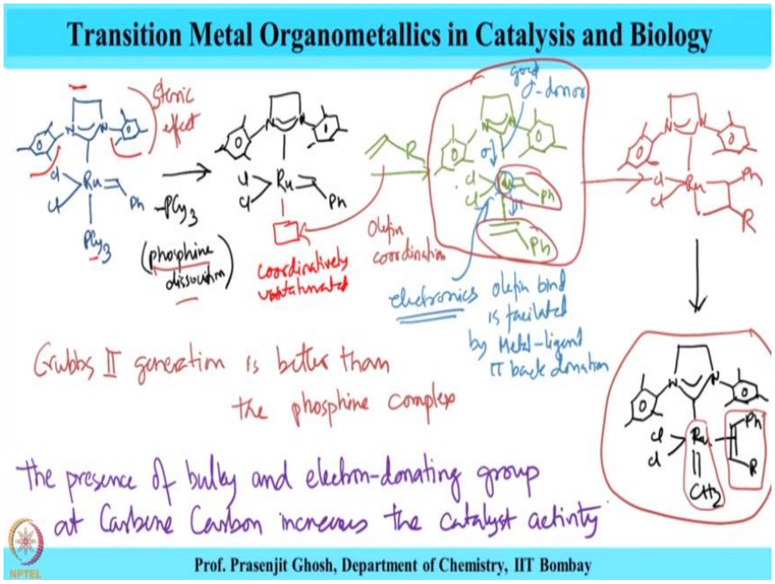
So here is the discussion about the modulation of statics as well as electronics in designing the catalyst aspect. Now in these discussion in our previous class we have spoken about how these static and electronic factors were put in place for designing Grubbs catalyst and what we had observed is that for the ruthenium carbine Grubbs catalyst the measures were taken to make a these metal center more favorable for the metathesis reaction.

And this case what we are observed that the people have played with the statics in terms of putting bulky triphenyl phosphine substitution and then also played with electronics in terms of making more sigma donating ligand and so that the metal center is more electron rich and hence can help perform metathesis reaction in a better way. So we are also seen that these catalyst the Grubbs catalyst you know carries out metathesis but initiation takes place by 2 important step one is phosphine dissociation.

And the second one is olefin binding so what to be discussed over here is the point that the statics have been employed the steric factors have been used for taking care of phosphine dissociation where as these olefin binding is successfully taken care of by modulating the electronics of the metal center. So I am going to illustrate this in another set of example particularly with Grubbs in second generation catalyst in which the cyclohexyl phosphine is replaced with NHC or in heterocyclic carbines and these are ligands of the type shown over here and they are very (()) (06:37).

So when the cyclohexyl phosphine one of the phosphine is replaced by a heterocyclic carbine or NHC then the Grubbs second generation catalyst which is supposedly more active than the first generation catalyst in metathesis reaction can be synthesized and that have been successfully employed by controlling enhancing the stake and electronics at this ruthenium metal center.

(Refer Slide Time: 07:12)


Transition Metal Organometallics in Catalysis and Biology

Grubbs II generation is better than the phosphine complex

The presence of bulky and electron-donating group at Carbene Carbon increases the catalyst activity

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

Let me illustrate this with this example so this is Grubbs second generation catalyst which has cyclohexyl phosphine bound to ruthenium as well as a carbine with bulky misudual substituent's bound to the metal center. So these the steric allows the first step which is phosphine dissociation to give this complex which is to give this complex which is co-ordinatively unsaturated because this is co-ordinatively unsaturated because there is a vacant site which is generated.

So this is the active species which is co-ordinatively now to this the olefin comes and binds to give the this olefin comes and binds the vacant site and this is called olefin coordination step or olefin binding step this is facilitated because of the first step which is dissociation of the phosphine and that is promoted by the steric factor promotes this phosphine dissociation which helped in term allows the olefin binding.

Now once the olefin binds then that results in the complex now this a olefin bound ruthenium complex now what we had observed that both steric and the electronics are important in modulating the metathesis reaction and this is the instance where the electronics comes into play as NH sees boot sigma donors. So they make the meta center more electron range and as a result olefin binding is facilitated by metal to ligand by back donation.

So this is a important contribution what we see that electronics kicks in or helps the second step where the good sigma donating ability of the NH cyclic ligand makes the metal ruthenium metal very electron rich and as a result the metal to olefin by back donation is favored and which results in binding good binding of this olefin otherwise olefins are not very good binding ligands to the metal.

Now once that successful binding of olefin happens the next is the metathesis reaction which gives this 4 member ruthenium metal at cyclo butane intermediate and that eventually gets converted to product with the formation of different kind of carbon species and different kind of olefin bound to the metal. So what is to be seen over here is that different olefin bound species is formed where instead of ruthenium benzoyl species carbon species over here.

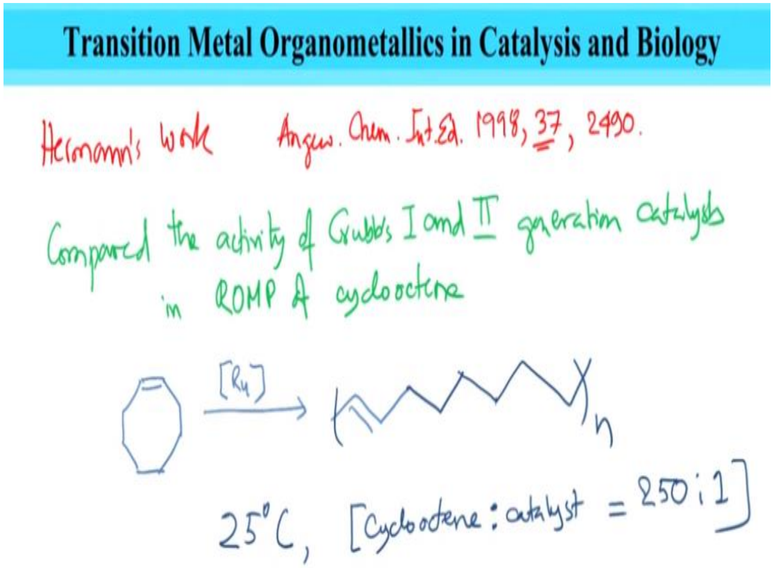
Here is an new kind of ruthenium carbon species and instead of the olefin over here a new kind of olefin metathesis product olefin is formed. So here what is observed is proper choice of Steris and electronic help facilitate the first steps first is the phosphine dissociation and the next is the olefin binding resulting in favoring the metathesis reaction. So this is a very important demonstration of the catalyst development strategies which often involved modulation of sterics and electronics.

And what has been observed that this strategy has been put in place in a very efficient manner while designing Grubbs second generation catalyst in which one of the phosphine has been replaced by bulky heterocyclic carbene ligand which because of its bulky (()) (16:01) in substituents help facilitate phosphine dissociation giving rise to coordinatively unsaturated species and now that also allows olefin binding and then simultaneously with the presence of very good sigma donating ligand further reinforces the olefin binding to ruthenium because of metal to olefin by back donation.

And then this stabilization of the ruthenium olefinic complex because of the streics and electronics leads to the formation of the ruthenium metallo cyclo butane intermediate resulting in formation of another ruthenium carbons species with the metal thesis catalyst. So overall Grubbs second generation is better than the phosphine complex and presence of bulky and electron donating group at carbane carbon increases the catalyst activity.

So this was very nice demonstration of modulation of statics and electronics in enhancing the activity of the metathesis catalyst. Now in this context it is important to mention a beautiful work done by Hermann in which he had indeed shown superior activity of the second generation catalyst over the first generation catalyst.

(Refer Slide Time: 19:18)



Transition Metal Organometallics in Catalysis and Biology

Hermann's work Angew. Chem. Int. Ed. 1998, 37, 2490.

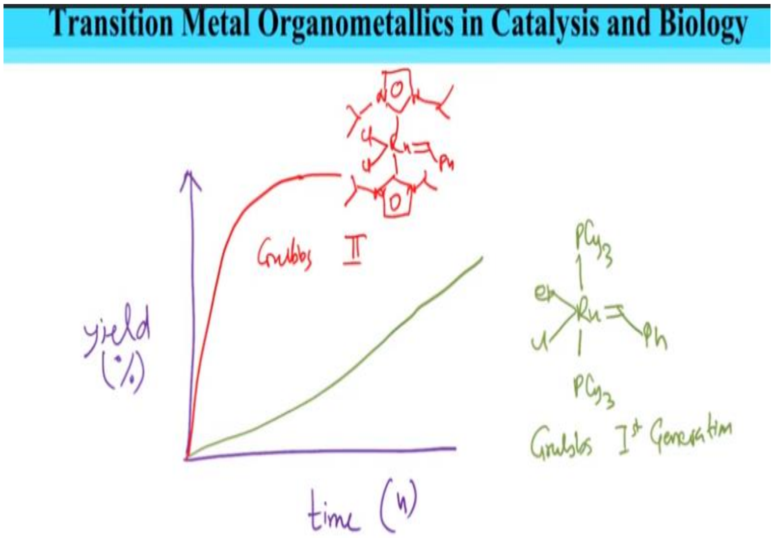
Compared the activity of Grubb's I and II generation catalysts in ROMP of cyclooctene

25°C, [Cyclooctene : catalyst = 250 : 1]

Hermann's work demonstration that second generation of catalyst is better than the first generation and this as beautiful work is published in Angew Chem 1998 37 2490. Now what Hermann did? Hermann actually heard the activity of Grubbs first generation, second generation catalyst in ring opening polymerization of cyclo-octane compared activity of Grubbs first and second generation catalyst in ring opening metathesis polymerization of cyclo octane this is best illustrated by the equation.

And this was carried out at 25 degree centigrade in cyclo octane to catalyst ratio of 250 is to 1 and the startling result of superior activity of the second generation catalyst could be seen very prominently in Hermann's experiment and which sort of once for all establish the superiority of the second generation catalyst over the first generation wants.

(Refer Slide Time: 23:27)

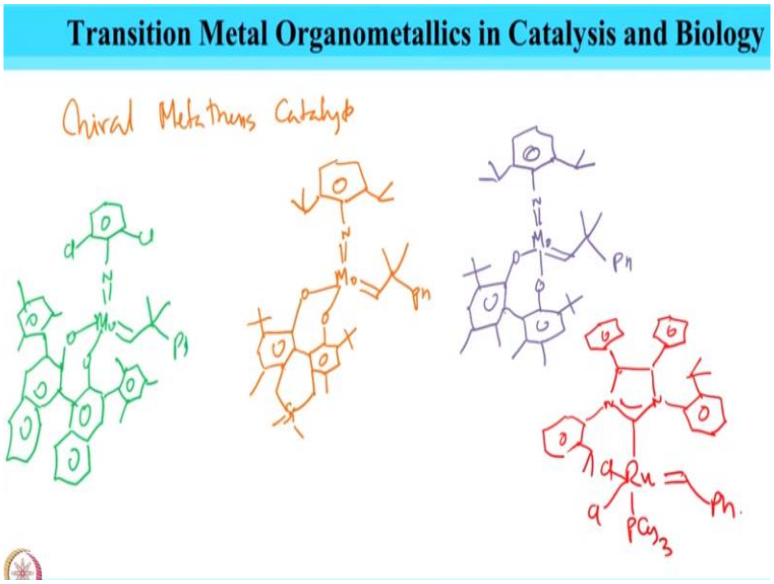


Transition Metal Organometallics in Catalysis and Biology

So what Hermann observed is the superiority of the second generation over the first and when and he observed that by plotting yield of with time that the conversion and for the catalyst which is first generation for the catalyst shown over here Grubbs first generation he observed sort of steady growth in the product. Whereas when he took the second generation catalyst which was in isopropyl he observed a drastic increase in the reaction yield and then plotting.

So this is generation 2 so the result distinctly showed that the second generation catalyst is a better then the first generation catalyst. Now these late to the development of the Grubbs second generation catalyst in much more detail and then the next ongoing thing over here was in development of chiral catalyst.

(Refer Slide Time: 26:26)



Transition Metal Organometallics in Catalysis and Biology

Chiral Metathesis Catalysts

And in this regard significant development in chiral metathesis reaction was also observed with the following complexes metathesis catalyst is been synthesized of molybdenum seems to SIMET this is the answer which kind of complex another is the derivative of similar type with (()) (28:20) the third one is another type with the dichloro amido kind of setup and the last but not the least is the carbine (()) (29:39) Carbene with one side (()) (30:22) group.

So these shows this sort of shows the extent of creativity in terms of people coming up with so many different modification of chiral metathesis catalyst that not only were synthesized but also their applicability in the asymmetric metathesis reaction performed and some of representative is examples of such range of complexes are also shown over here. So with these that the molybdenum ones are amido carbine complexes there is a metal ligand multiple bounding 2 types one is metal carbine and metal nitrogen these are all amido carbine complexes and the last fourth one is the ruthenium complex where it is bound to NHC's as well as cyclo XL phosphine.

So with these I come to conclusion to today's lecture where we have looked into the catalyst development aspect particularly from the use of sterics and electronics in facilitating the binding of olefin and subsequently favoring the metathesis reaction and we have also in that process looked into Hermann's experiment which sort of distinguished Grubbs generation 2 catalyst from generation 1 and successfully stored that these second complex is better than the first one.

So with that we comet to end of today's lecture and we are going to be talking about this catalyst development particularly from the application point of view in more details when we meet next in this course as series of course lectures. So with that once again l would like to thank you for being with me and I look forward to being with you in your next lecture where we take up this topic in more details thank you.