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

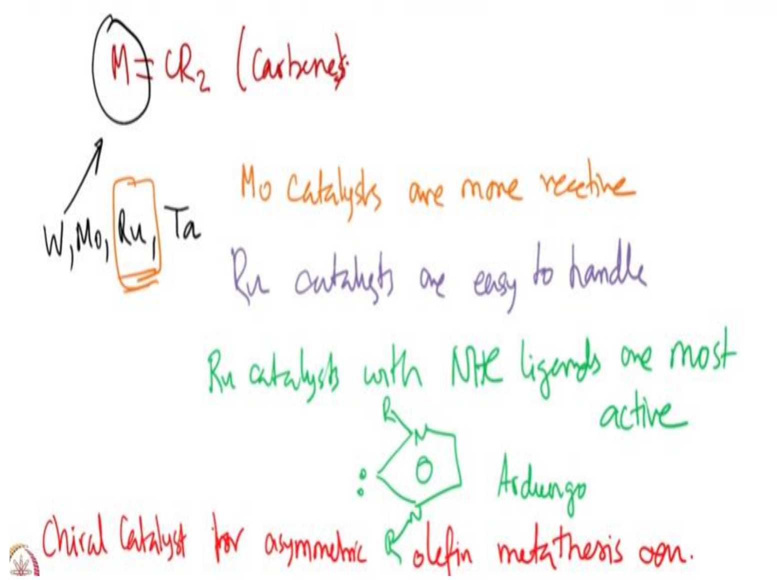
Module No # 03
Lecture No # 15
Catalysis Development Aspect of Olefin Metathesis (Part – 1)

Welcome to this course transition metal organometallics in catalysis and biology we have been discussing various aspects of olefin metathesis in the past few lectures starting with its origin then we have looked into the developmental aspect of the metathesis reaction of time like how the reaction involved. We have also looked at the mechanism that was developed in order to understand that these metathesis reaction.

We have also noted and observed in previous lecture that how understanding this mechanism was a important breakthrough because as that led to unification of several group of reactions which fell in the umbrella of larger group of metathesis reaction and about 15 variant of alkyne about 8 variant of olefin metathesis reactions all came into being and all came under the umbrella of olefin metathesis even on the alkyne metathesis front we saw that alkyne method matrices also drew with parallel from olefin metathesis and about 5 variant of alkyne metathesis were also reported subsequently.

We had seen this development from various angles from various perspectives in order to get a holistic understanding of this phenomenon of olefin metathesis which indeed is a very important development and has rightfully being recognized with the award of Noble prize in 2005. So today we are going to add a different perspective to our discussion on olefin metathesis and these more or less is about the catalyst development aspects.

(Refer Slide Time: 02:39)



Now so far we had noted that metal carbine are important active catalyst for olefin metathesis so these are called carbine species as important catalyst for this olefin metathesis reaction and there as been subsequent studies on synthesis a various kinds of carbines and as a organometallics chemist these metal has been studied for studied as a function of metal with several metal coming into play for example Tungsten molybdenum ruthenium so on and hence so forth.

So as a result many carbine complexes were subsequently synthesized starting with the Fischer carbine as well as Schrock carbine tantalum like early transition metal so on and hence so forth. And these also led to formation of various types of metal carbine species Fischer type carbine and Schrock type carbine and were we have also discussed in great details and where we had observed that even though these all are metal carbine might moieties however there the reactivity as well as electronic mature of bonding between metal and carbonic fragments are different and hence they behave differently.

In this context today we are going to focus our discussion bit more on metal and trying to understand the function of the reactivity of the metal carbine species as a function of metal. Now what emerges from the various synthesis studies that have been undertaken is the fact that molybdenum catalyst are very reactive are usually more reactive (()) (04:54) reaction. On other hand ruthenium catalyst are easy to handle.

So these sort of implies that rational complexes are catalyst are more moderate in reactivity and hence they do not decompose or sometimes they are more stable aerobic conditions and because of which the ruthenium catalyst becomes easy to handle. The subsequent observation are the ruthenium catalyst with NHC ligands are most active. Now these is important observation and also a important breakthrough because that gave lot of importance to the developmental aspects of NHC as a ligand.

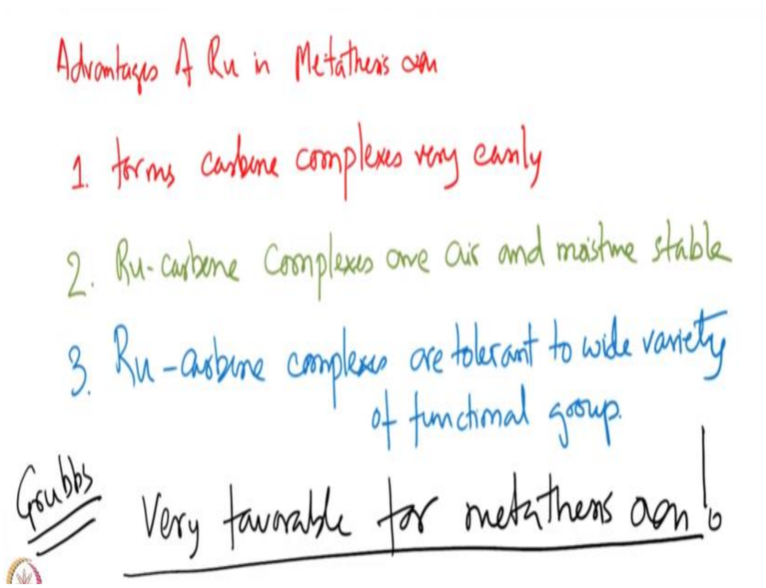
Now in our last class we also spoken about how these simulate carbine in the form of in heterocyclic carbines which are of the formulation of this type have been synthesized and stabilized by Ardengo and that what we see later that becomes very good ligand for developing this metathesis catalysis. So this is a interesting development which sort of came out different carbonyl complexes that people have one on to make in order to study the civilization of metal carbine moiety.

And also the implication of carbine complexes in olefin metathesis reaction finally important development is in synthesis chiral catalyst in for asymmetric olefin metathesis reaction. So these also is a next level of development where one can carry out or one strives to undertake these metathesis reaction in the next level in terms of being able to doing it in a asymmetric fashion using chiral catalyst.

So all of these lead to development of the that catalyst from different aspects in terms of the reactivity in terms of the their ability to being ability to handled in air or as well as in their ability to carry out the reaction in asymmetric fashion and also for the rate of the reaction. So among the various metals that have been used for studying for making this carbine complexes for studying metathesis reaction the one that emerges out successfully is this ruthenium catalyst because this is what made the carbine complexes carry out metathesis reaction under aerobic conditions high yield.

So ruthenium emerge out to be victorious in this race for developing catalyst for carrying out olefin metathesis reaction. So it is ruthenium wining in the end because it sort of brought the whole carbine chemistry which is extremely air moisture sensitivity out of glove box to be able to carry out this reaction in open bench under a aerobic condition which added a great amount of practical utility to the reaction and hence making the reaction so popular in the world of organic synthesis.

(Refer Slide Time: 10:19)



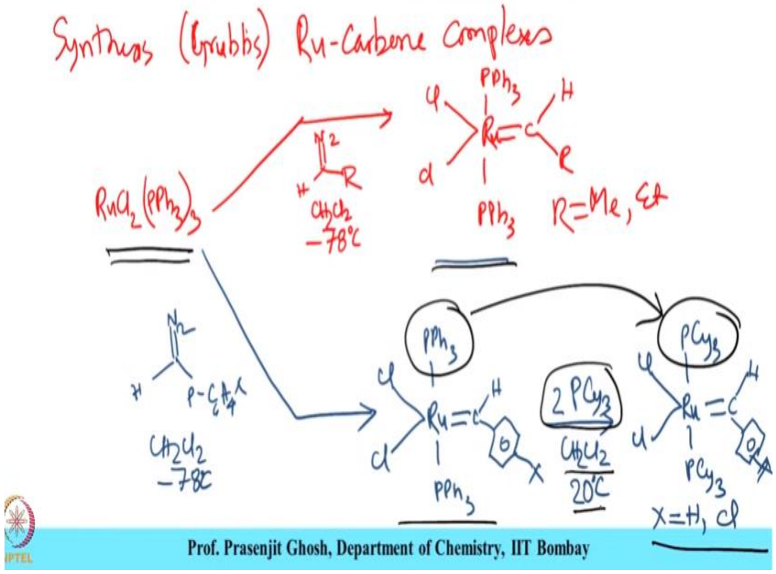
So we are going to talk bit more about the advantages of ruthenium catalyst in olefin metathesis and what we see that this ruthenium forms easily stable carbine complexes the ruthenium carbine complexes are also air and moisture stable. Third the another important attribute of ruthenium catalysts is this ruthenium carbine complexes are tolerant to a wide variety of functional group that they do not react and get poisoned by the functional group and what is the outcome of this is that you know it does not participate does not sort of participate in other kinds of secondary reactions or decomposition reactions.

And hence overall this ruthenium carbine complexes for metathesis reaction so this is the overall verdict in favor of ruthenium winning over and these probably is what made Grubbs famous because Grubbs is the one who made ruthenium carbine catalyst from metathesis reaction and it is to be noted at this juncture is that Grubbs initial proposal hypothesis for the mechanism of metathesis reaction did not turn out to be true however that is made up by these development of ruthenium catalyst which sort of brought these very sensitive metal carbine complexes out of the glove box for in open air for bench top chemistry which is added great applicability to this reaction eventually Grubbs went on to win the Noble prize because of this contribution.

So it is Grubbs who is noted for the development of ruthenium catalyst from metathesis reaction and the reason they have become so successful is illustrate over here by the fact that they are very easily synthesizable they are also very easy to handle stable in air and moisture and also they are tolerant to wide variety of functional group. So a large types of different reactions can be taken up using ruthenium.

So this these we are going to now focus bit more on Grubbs chemistry about the development of ruthenium carbine complexes particularly we are going to start off from it synthesis of how these complexes were synthesized.

(Refer Slide Time: 15:22)

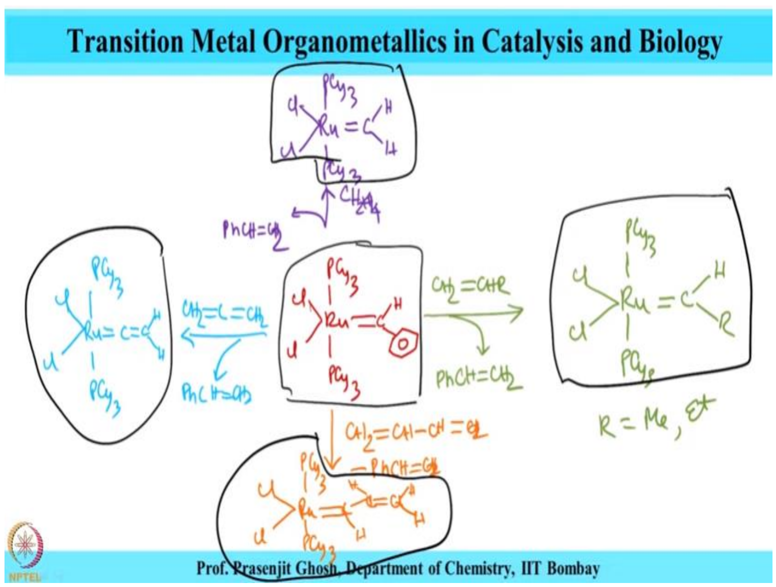


Ruthenium carbine catalyst and its starts with RuCl2 pph3 whole thrice that been react with this does the compound in dichloromethane at -78 degree centigrade gave this ruthenium dychlorocarbine complex R equals methyl ethyl. Also this when treat with another para C6H4X again in dichoro methane at -78 degree centigrade give this ruthenium dichloro carbine complex with further reacting with 2 cyclo hexyl phosphine 2 equivalents in dichloro methane at 20 degree centigrade giving Pcy3 X equal hydrogen chloride.

So the point to note here that these are kind of very facile reactions which are synthesized from this ruthenium dichloride triphenyl phosphine trace compound by reaction with these the (()) (18:39) compound and that it gives rise to1 carbonic complexes as is shown over here as well as here and then here also shown a reactivity of this carbine complexes in terms of removing this or replacing this triphenyl phosphine with more bulky tricyclohexane phosphine and this is just done by reacting with tricyclic 2 equivalent of tricyclics hexane phosphine in dichloro methane at 20 degree centigrade.

So these shows that how is easy it is to synthesize this ruthenium carbine complexes by the method which has been reported by Grubbs. The Grubbs also did the analogous experiment similar to what we had discussed about Fischer in the previous class that he took the ruthenium carbine complexes and reacted with various olefin to generate the subsequent new type of ruthenium carbine complexes of the olefinic fragment and different olefin. Similar to what we had observed the Fischer did in earlier discussion so we are going to discuss that in bit more detail.

(Refer Slide Time: 20:14)



So this is best illustrated by this ruthenium dichloro carbine complex so that when treated with ethylene C2H4 then an olefin which is fragment of C2H4 and these is eliminated along with new ruthenium dichloro carbine species. Similarly the reaction with another olefin get the corresponding different olefinic fragment along with generation of different kind of ruthenium R equals methyl ethyl the reaction with an allene eliminated the corresponding olefin with the generation of following interesting carbine complex.

And lastly the reaction with another diene eliminated and get this interesting ruthenium carbine complex. So this is very beautiful study in which one could Grubbs had shown that how this ruthenium carbine moiety could be converted to 4 different types of ruthenium carbine compound depending on the reactions. So this indeed is a very interesting result which had come out of this Grubbs study.

Now these compounds further more highlights importance of ruthenium in metathesis reaction because what it shows is the versatility of formation of various kind of ruthenium carbine complexes under reaction with different olefin and this further reinstates the fact that these ruthenium carbine complexes can generate many other active species carbine species by reacting with different olefin during the course of the reaction and this is what had been highlighted as the chain aspect chain reactivity aspect of olefin metathesis reaction.

So with these we come to the end of today's lecture we had discussed about the important of ruthenium in developing olefin metathesis catalyst. What it turns out that ruthenium by far is the best choice for developing olefin metathesis catalyst is particularly from the fact that these complexes are easy to synthesize their air and moisture stable their functional group tolerance and they are the once which can be used under aerobic conditions.

So it is ruthenium which has brought the whole of metathesis chemistry from the confines of rigorous handling dry box to the more amenable and easy to use bench top chemistry. And this had been seminal contribution of Grubbs which indeed had made otherwise so difficult organometallics chemistry being converting being so easy to be carried out in open air. So we had looked into the reason as why ruthenium succeeded over other kind of carbines like Schrock and Fischer carbines in developing olefin metathesis reaction.

We have also looked the versatility of the ruthenium carbine and complexes in terms of the one type of ruthenium carbine complexes getting converted to other type of ruthenium carbine complexes as a course by the treatment with different olefins. So with these we again conclude come to the conclusion of today's class and we are going to be looking into the development catalyst development aspect of olefin metathesis reaction in much more detail when we convene for the next class till then goodbye and thank you.