Transition Metal Organometallics in Catalysis and Biology
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Module No # 04
Lecture No # 18
Catalysis Development Aspect of Olefin Metathesis (Part – 4)

Welcome to this lecture on transition metal organometallic in catalysis and biology. We have been talking about olefin metathesis particularly catalyst is development aspects in the last few lectures. And we had focused on alkyne metathesis to begin with and what we had seen in the last few lecture is that both sterics and electronics they play a powerful role in modulating in the catalyst activity. Particularly in making catalyst more efficient in their catalytic processes.

So in that regard we had seen how putting more bulky ligands on the metal help facilitated better activity for Grubbs catalyst by allowing phosphine dissociation and further incorporation of very good sigma donating ligands on the metal facilitated olefin binding which both together help facilitated these metathesis reaction.

So this quite a bit of which organometallic chemistry a particularly with regard to metal ligand binding as well as metal ligand by back donation all of those interaction played a crucial role in the evolution of olefin metathesis catalyst which went on to become better with discovery of second generation catalyst as opposed to the Grubbs first generation catalyst. We had also discussed about Hermann’s work on the comparison of Grubbs first generation and second generation catalyst in the ring opening metathesis polymerization of cyclooctane.

And that definitely proved that indeed the second generation catalyst bearing in exocyclic carbenes were more superior in terms of fastness to produce the product then the corresponding Grubbs first generation catalyst. So with these behind us today we are going to sort of look at the key points of these metathesis catalyst. As we proceed in today’s lecture and these are particularly with respect to alkene metathesis that we are talking about.

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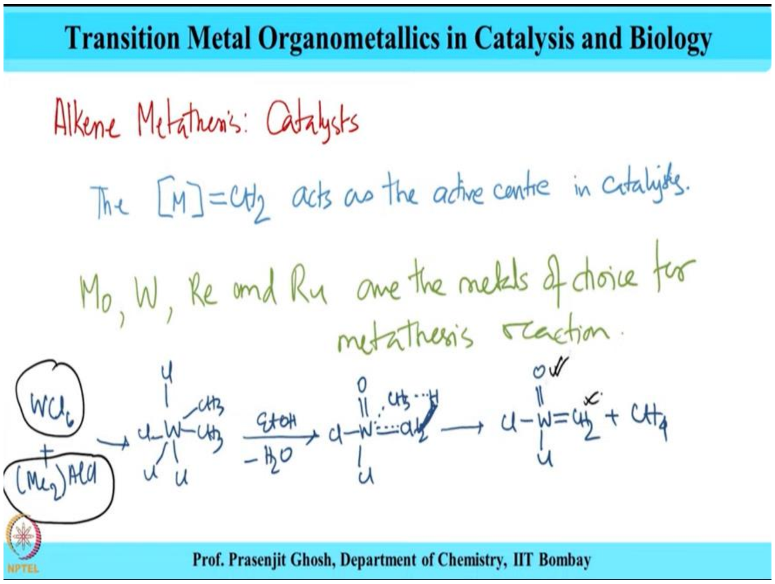

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Alkene Metathesis: Catalysts

The $[M]=CH_2$ acts as the active centre in catalysts.

Mo, W, Re and Ru are the metals of choice for metathesis reaction.

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So this metal carbon moiety acts as the active center in catalyst. Second thing that of the various metal which could stabilize a metal carbene moiety the metals of choice for metathesis reactions where molybdenum, tungsten, rhenium and ruthenium. And ruthenium are the metal of choice for metathesis reaction. And you know the earlier times the catalyst were derived from transition metal halide as is shown over here and carbon ion donors.

Tungsten hexachloride plus dimethyl aluminum chloride would give tungsten tetrachloro dimethyl that in presence of ethanol would eliminate water to give tungsten oxo dichloride with this intermediate transition state giving Cl W Cl oxo carbene plus methane. So this is another way of generating that tungsten oxo carbene complexes. And in this regard we should mention that some of the earlier molybdenum version that we had seen where of molybdenum amide o carbene of similar are relative of related formulation.

So the way this particular complex which was prepared from the halide and this dimethyl aluminum chloride resulting in the tungsten oxo carbonyl complex.

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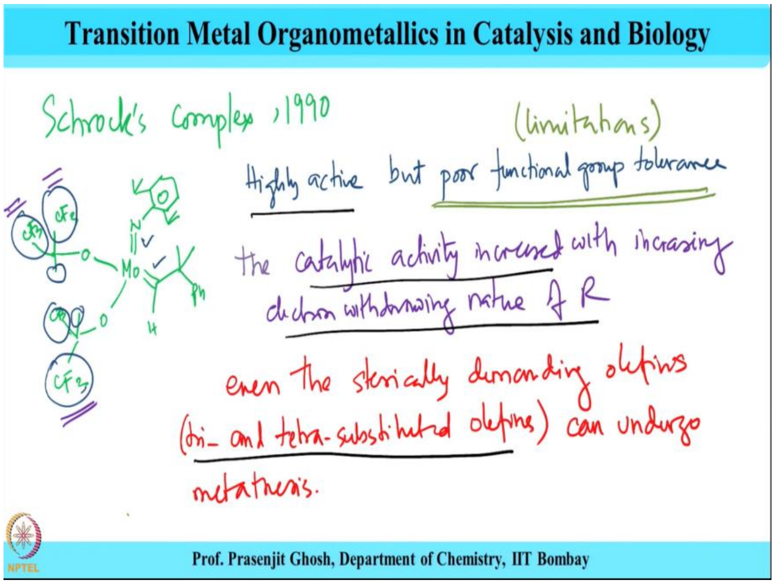

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Schrock's complex, 1990

(limitations)

Highly active but poor functional group tolerance

the catalytic activity increased with increasing electron withdrawing nature of R

even the sterically demanding olefins (tri- and tetra-substituted olefins) can undergo metathesis.

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So along the same line the Schrock had synthesized the corresponding amido carbon complex as is shown over here. So Schrock complex was synthesized much later in 1990 and when this is amido molybdenum complex C methyl CF3 so these is a very complicated complex which has both amido and the carbon complex and also has this CF3 methyl moieties CF3 methyl moieties around the alkoxides. So this is kind of a complex however this was found to be highly active catalyst but poor function group tolerant but poor.

Then the next important thing is while increasing the electron withdrawing nature of our the catalyst a catalytic activity increases the catalytic activity increased with increasing electron withdrawing nature of R. And this can be seen why this CF3 groups were put in place another important feature of the complex is the sterically demanding olefins even the sterically demanding olefin to tri and tetra substituted olefins can undergo metathesis.

So these is a very interesting development where this molybdenum amido carbene is prepared by Schrock went on to become an extremely active catalyst then the catalytic activity could be increased by putting electron withdrawing groups and also can be because of higher activity it can be used for slow reacting tri and tetra substituted olefins. The only drawback to this highly active molybdenum catalyst is that they are not very a functional group tolerant or that the catalyst could easily be poisoned by different functional groups in the olefin.

So these are supposed to be the limitation of these catalyst molybdenum catalyst. Now we had seen these tungsten oxo carbene complex which were synthesized from tungsten hexalyne then we have seen Schrock's molybdenum amido carbene complex.

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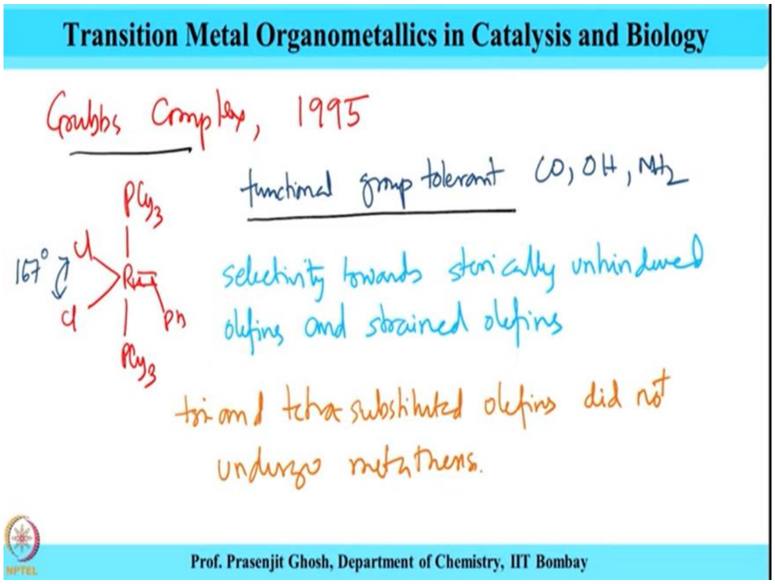

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Grubbs Complex, 1995

functional group tolerant CO, OH, NH_2

selectivity towards sterically unhindered olefins and strained olefins

tri and tetra substituted olefins did not undergo metathesis.

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And now we are going to go and look at Grubbs phosphine a carbene complex Grubbs complex and this was synthesized much later in 1995 about 5 years later than that of this Schrock which was synthesized in 1990 and these angle between these 2 halide 167 degrees. Now the main feature of this ruthenium compound is that these are functional group tolerant like and it could tolerant groups like Co OH NH2 amido.

And that the catalyst would not get poisoned by the presence of this group in the olefin. And hence this was supposedly very big attribute for this ruthenium carbene complex. Then the other important features included selectivity towards sterically unhindered olefins and strained olefin and the third thing is the tri and tetra substituted olefins cannot undergo metathesis tri and tetra substituted olefins did not undergo metathesis.

So the point to note is the following. Now when one compares Grubbs complex with that of the Schrock's complex as discussed earlier one major difference is that this is exactly opposite to that of the Grubbs complex in the in terms of being functional group tolerant. Where Grubbs compound which was molybdenum was highly reactive towards functional group and intolerant and hence the catalyst would get poisoned in presence of various functional group like CO OH NH2.

Whereas the Grubbs ruthenium complex is exactly the opposite and that it does not get affected by the presence of other functional group and hence the catalyst would survive the presence of other functionality and would effectively carry out the catalysis. Other important difference is that the Schrock’s catalyst being highly reactive if that could carry out metathesis of tri and tetra substituted olefins.

Whereas the Grubbs one is exactly the opposite and it did not facilitate or did not allow the metathesis reactions with tri and tetra substituted olefins. So and third thing the third difference is obviously the ruthenium carbene is more air stable whereas the Schrock’s molybdenum carbene is a more sensitive to air and moisture. Lastly the fourth difference is that the ruthenium carbene is has only one kind of multiple bond between ruthenium and carbonic moiety.

Whereas the Schrock’s complex had 2 kind of multiple bonding one between molybdenum and carbene and the other between molybdenum and amido moiety. Another interesting thing is that even though they are completely a complementary to each other the together they made a very good set of catalyst combination where every type of metathesis reaction could be a facilitated. Now one important thing as I was talking about this coordinative and electronic saturation and unsaturation is a very important factor in guiding catalyst activity.

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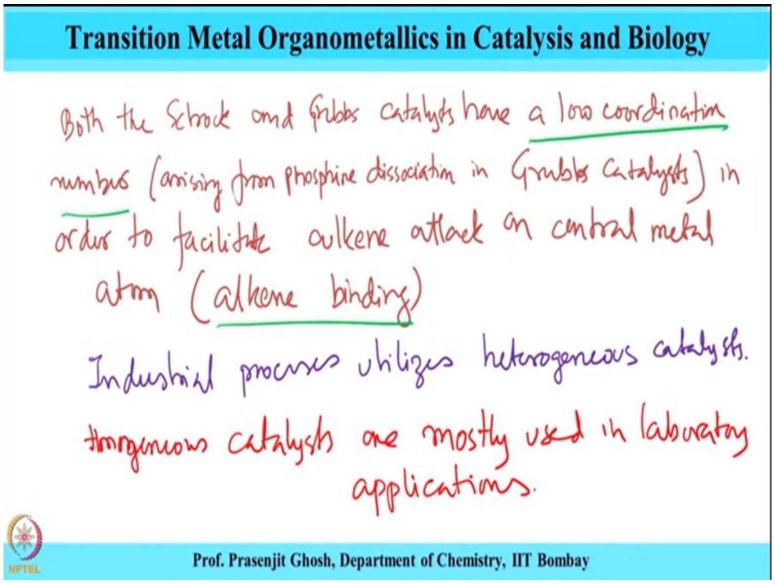

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Both the Schrock and Grubbs catalysts have a low coordination numbers (arising from phosphine dissociation in Grubbs Catalysts) in order to facilitate alkene attack on central metal atom (alkene binding)

Industrial processes utilizes heterogeneous catalysts.

Homogeneous catalysts are mostly used in laboratory applications.

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And in this regard both the Schrock and Grubbs catalyst have a low coordination number and then these primarily we had discussed by arising from phosphine dissociation in Grubbs catalyst low coordination number this is very important in order to facilitate alkene attack on central metal atom or this is called alkene binding. So the point to note is this low coordination number is very important for alkene binding and that has been achieved by phosphine dissociation in presence of Grubbs catalyst.

And another advantage of olefin metathesis reaction is the fact that olefin metathesis can be carried out both under homogenous condition as well as heterogenous catalysis condition. And as preferred by industry most of the industrial processes utilizes heterogenous catalyst till date industrial processes utilizes heterogenous catalysts. So whereas the laboratory applications of an however implies.

Homogenous catalyst are mostly used in laboratory applications and towards these development lot of different kinds of catalyst using ruthenium molybdenum and other metals were synthesized and as we had seen that in the activity of Grubbs catalyst was improved by replacing phosphines with NHC’s and so on and so forth. And several types of a several variants of Grubbs catalyst were developed and they were later characterized as first generation and second generation catalyst. And in this regard the notable few catalyst which are by far the best in terms of the activity are shown over here. The variants of Grubbs catalyst there are that show great activity.

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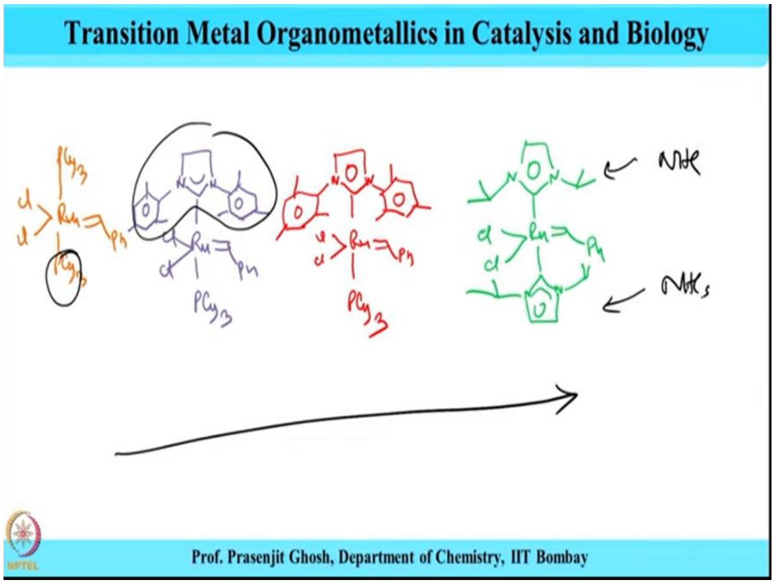

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To start with is the this is the first Grubbs catalyst then can the carbene substituted Grubbs catalyst followed by the (()) (23:40) based Grubbs catalyst followed by the carbene based Grubbs catalyst. So what we see over here is that significant improvement of Grubbs catalyst happens as phosphenes get replaced by NHC's to becoming that with two NHCs were both phosphenes have been replaced with NHC and the activity keeps getting better.

So with this we come to the conclusion of today's lecture in which we are looked into various types of catalyst that have been developed starting with tungsten based carbene complexes to that of molybdenum to that of ruthenium. And what we saw that between Schrock's molybdenum and Grubbs ruthenium catalyst that is a the presence complement complementarity a in terms of Schrock's molybdenum catalyst being extremely sensitive to air and moisture.

Whereas Grubbs ruthenium catalyst is a stable to air and moisture Schrock's molybdenum catalyst is highly reactive and hence functional group intolerant whereas Grubbs ruthenium catalyst each functional group tolerant Schrock's molybdenum catalyst is good for the reaction of tri and tetra substituent bulky olefinic substrates. Whereas the Grubbs ruthenium catalyst extremely actually does not undergo any reaction with the sterically demanding tri and tetra substituted olefins.

So there exist a huge complimentary between these 2 catalysts but the end the appreciation for metathesis reaction is more possible because of the synthesis of Grubbs catalyst which is sort of a virtually took out this meta air sensitive metathesis chemistry out of the Grubbs box to the able to successfully practiced in open air. Now one thing which is important over here that for this metathesis reaction olefin binding is a crucial step.

And that is facilitated by a low coordination number of the catalyst and this is achieved by fostering dissociation giving raise to low coordinated metal species for both Schrock and Grubbs catalyst which can then finally a bind olefin giving metathesis reaction. So apart from these industrial processes prefer heterogeneous catalyst whereas homogeneous catalysis are still preferred under laboratory applications reactions.

With this we will conclude this our discussion on olefin metathesis reaction and we are going to alkyne metathesis reaction and we are going to take up a cross metathesis another variant of olefin metathesis reaction in more detail. When we meet in the next class till then goodbye and thank you.