Transition Metal Organometallics in Catalysis and Biology

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Module No # 03
Lecture No # 12
Types of Carbenes

Welcome to this course on transition metal organometallics in catalysis and biology. We have been talking about the olefin metathesis in the last few lectures and in that regard, we have looked into various kinds of mechanisms which have been proposed for olefin metathesis and come across names like Cauldron Petite Grubbs Chauvin. And also we had seen the mechanism gaining consensus with regard to the correct one.

And in that process, we had seen how Chauvin's mechanisms of having a metal carbene intermediate being accepted as the main active species for carrying out olefin metathesis reaction. In that regard we had also discussed in the previous lecture about the Seminal work by Professor Tom Katz who had correctly predicted the olefin products for by using different olefin explaining their formation through metal carbene intermediates.

Now in that time in that point of time we have also looked into the active species much more details and what we had observed is that this metal carbene intermediate or metal carbene moiety is at that time can be of 2 types is better known as Schrock carbene and Fischer carbene. And in our previous class we had also looked into the type of bonding present in in Schrock carbene as well as Fischer carbene.

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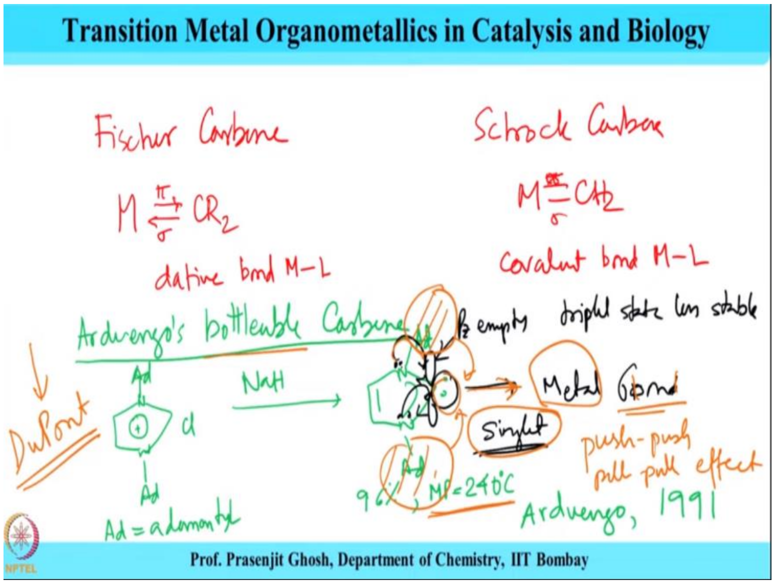

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And what we had seen that in Fischer carbene both are carbonic moiety but the way they differ is in the type of bonds they make whereas in the Fischer carbene it is ligand to metal sigma donation followed by metal to ligand Pi donation. Whereas in Schrock carbene both are in a covalent bond both the sigma as well as the Pi bonds are in simple covalent bonds. So one can say that this is dative bond between metal ligand and this is covalent bond between metal ligand.

So in these context another important discovery it was made by Arduengo or dango and this called this Arduengo is a bottleable carbene. Now usually a carbene can exist in the singlet and triplet state with the triplet state being more stable. Whereas Arduengo successfully isolated singlet bottleable carbene and that is why you know which is supposedly the excited carbene. And there were Arduengo could stabilize them and the interesting thing about it is that they were so stable that they could be isolated and even crystalized and that led to the discovery of huge field of n heterocyclic carbenes which were found to be excelled ligand for and have great catalytic properties.

So these Arduengo bottleable carbene became a big hit in the area of homogeneous catalysis. And we will just take a brief moment to discuss this carbenes in bit more details. Arduengo synthesized these from their imidazolium chloride salt in presence of sodium hydride as a base which resulted in formation of this singlet stable carbene in 96 % yield. And it is kind of highest stable very stable with melting point about 240 degree centigrade.

This Ad is a bulky adamontyl group and Arduengo discover this in another JCS paper in 1991. Now what is key thing over here is the strategy which Arduengo used in stabilizing these carbenes which are singlet carbene means that these carbene can donate this lone pair to metals and make a good sigma bond. Also the way adding our stabilized the singlet carbene is because of the presence of 2 nitrogen hetero atoms which would sort of pull the carbene lone pair towards inside.

And then it would have its empty Pz orbital partially populated by lone pair on nitrogen giving onto the carbon so that is how these carbene were prevented from going back to their triplet state less stable or not accessible. So as a result singlet carbenes were formed. So these is a furthermore what Arduengo did is that Arduengo took help of bulky adamantyl substituents which would protect this lone pair from dimerization.

So this mechanism is a of protecting using sterics by the adamantyl group as well as electron donation from the nitrogen lone pair as well as presence of hetero atom is called push-push pull-pull mechanism effect of which is sort of led to the stabilization of the singlet carbene. And to the extent that this singlet carbene is so stable that it has a very high boiling point of about 240 degree centigrade it can be bottled you can even buy it this singlet carbene and then use it you know for complexation with the metal.

And they are extremely a good binder to metals and they form sigma bonds with metal. So this is a how another extremely good ligand for catalysis that is singlet in heterocyclic carbene came into being and this is also is a development which had happened in the industry particularly at DuPont we had we had also spoken about referred to a DuPont in the context of the fact that the first observation of metathesis of observing ethylene propylene copolymer from a feed of ethylene for olefin polymerization over a molybdenum catalyst was also indeed first observed at DuPont.

So here we see that another interesting contribution coming out of industrial lab this is these bottle level singlet carbene from Arduengo. Now we going to spend some more time on explaining the singlet and the triplet nature of the carbene as we go along so as to help understand and appreciate the different types of metal carbene moieties that are possible.

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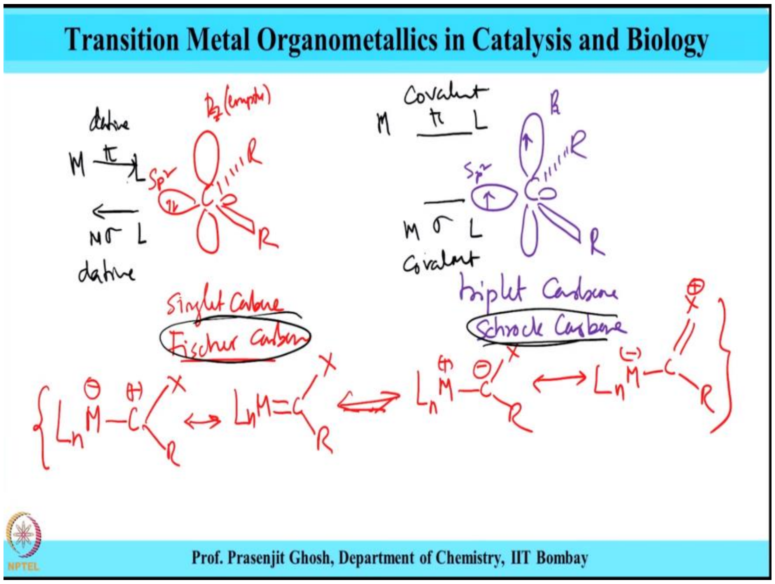

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In a Singlet carbene moiety bound to metal the carbene lone pair is an SP2 orbital and then there is a empty Pz orbital and there is why this is called singlet carbene is more common in Fischer and then the Fischer carbene it is said that the carbene moiety has a heteroatom and that has the following kind of resonance structure which is regulated over here.

The metal is an anechoic nature particularly because of electron donation for the singlet carbene which makes the carbene positive and the metal negative that can so this is the ionic structure and then there is a canonical form which is neutral with another canonical following existing as n + C-X R and that existing with LM - C X + R. So what we see that this has several chemical forms primarily all of them are ionic in nature except for one neutral form which is carbonic in nature.

Similarly one can draw structure for the triplet carbene bound to metal and here also one set of C’s now here also it is a SP2 orbital. Now the Pz orbital is not vacant and also has a single electron and hence it is called triplet carbene as a so what one can see that when and this is called Schrock carbene and the singlet carbene is in Fischer carbene. So what one can see that similar carbene Fischer carbene can engage into two kind of bond one is ligand to metal sigma dative bond because of this lone pair being donated as well as metal to ligand Pi dative bond as this one over here. Whereas for the Schrock carbene it can only make a ligand metal sigma bond which is covalent.

And similarly it can make metal ligand Pi bond also covalent. So in terms of Fischer carbene both to dative bonds are made in terms of Schrock carbene to covalent bands are made. And there is a Schrock distinction in the reactivity of these 2 types of carbene as we have seen. Now we will sort of take a look at Fischer carbene interaction with the metal in with more detail.

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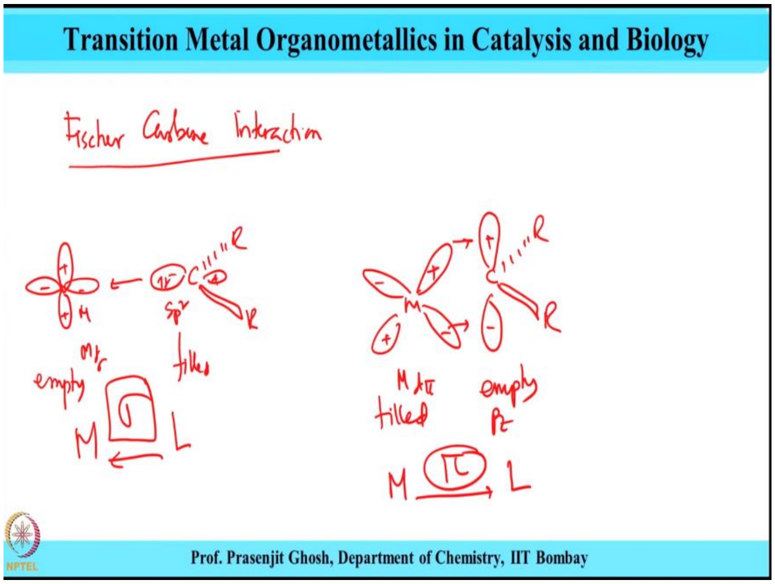

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Fischer Carbene Interaction

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So in Fischer carbene thus the interaction that occur this is filled to metal d sigma orbital which is empty. Whereas this is the sigma interaction and the corresponding Pi interaction is depicted over here. Now this one is empty this is SP2 filled and this is Pz empty interacting with metal d Pi orbital and which is filled and this is a Pi type interaction. This is a metal to ligand Pi and this is ligand Pi to metal sigma interaction.

And these is a typical Fischer carbene type of interaction near the way of carbon moiety interacts with the metal center. Similarly we are going to look at the interaction of Schrock carbene with the metal center.

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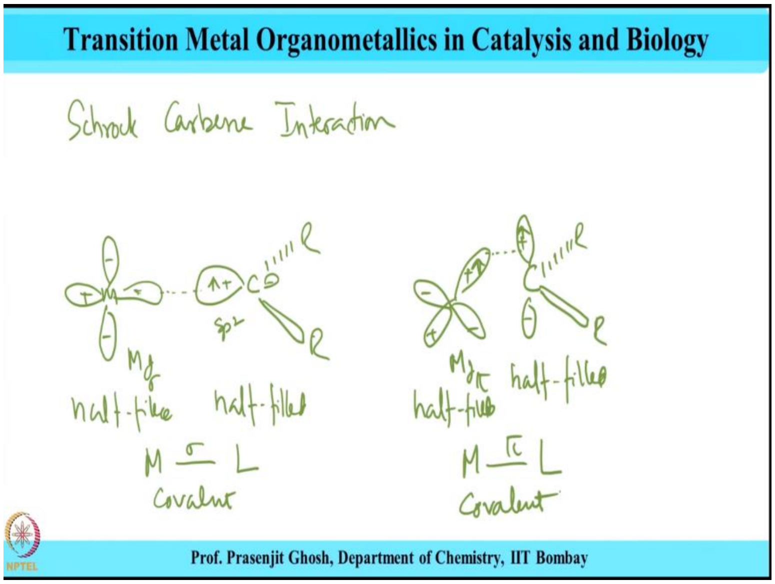

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Now in that case both this SP2 orbital as well as the Pz orbital will have a single unpaired electron. So this is called half-filled and the metal d sigma orbital this is also half filled and they make a bond which is metal ligand sigma kind of bond covalent. Similarly the corresponding Pz orbital having 1 unpaired electron is also half filled interacting metal sigma d Pi orbital which is also half filled and this is metal ligand Pi interaction and which is also covalent interaction.

So what is interesting over here is that both the metal carbene moiety would look like to have a metal carbene double bond a sigma bond and the Pi bond. However the nature of bonding in Schrock carbene and Fischer carbene are completely different and which sort of results in different kind of reactivity between these carbonic complexes. So we are going to sort of take a look at some of the interesting methods what have been used in synthesizing these carbene complexes starting with the Fischer carbene complex by from (()) (19:50) hexacarbonyl.

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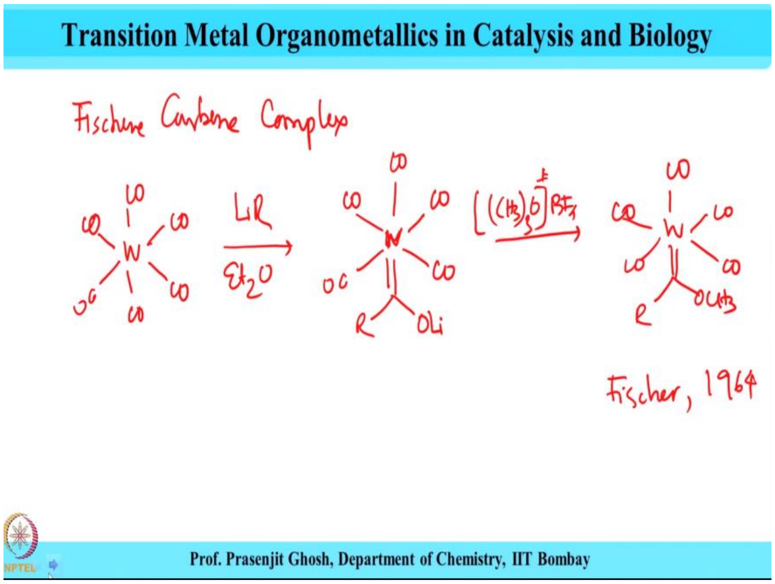

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Fischure Carbene Complex

Fischer, 1964

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(())(20:14) extra carboning in reaction with lithium alkyl in diethyl ether give a the Fischer carbene complex as shown over here. And that when reacted with CH3 whole 3O + BF4 minus give the Fischer carbene complex in 1964. Fischer carbene complex can also be synthesized by other method by the way is shown over here

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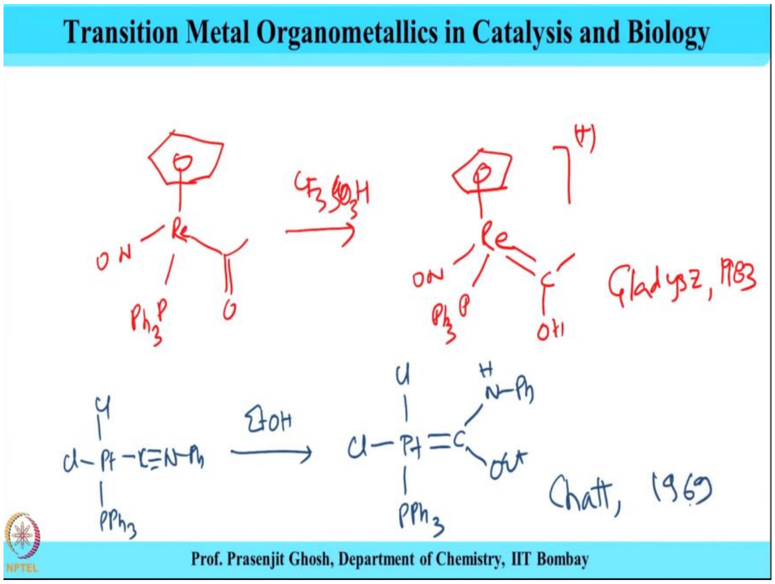

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CO+CF3 SO3H resulting in the cationic complex of rhenium and this was made by John Gladys in 1983. Another synthesis method involves reacting platinum dichloride PPh3 isocyanide c and Ph in ethanol giving Cl Pt PPh3 double bond C N H Ph O Et and this was reported by Chatt in 1969.

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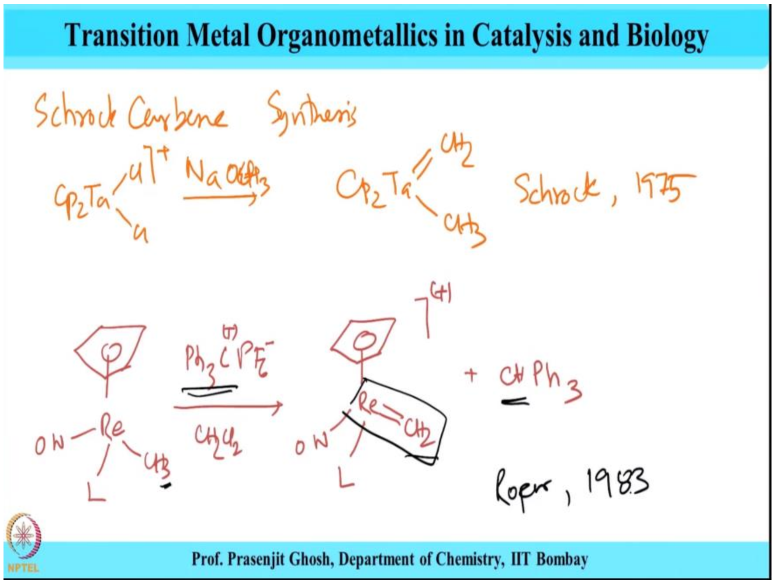

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Similarly there have been a few extremely nice examples of method have been reported for Schrock carbene complex starting with tantanium dichloride as it is shown here Cp2 tantanium dichloride plus sodium ethoxide sodium ethoxide giving CP2 tantanium CH2 CH3 this is was reported by Schrock himself in 1975. And another example was reported by Gladys in the reaction of rhenium CP NOL CH3 in presence of Ph3C+ PF6- endichloromethane giving Cp rhenium CH2 LNO + CH Ph3.

So this is a important reagent this is called (()) (25:21) CH3 C+ and this (()) (25:24) sort of abstracts are protons. So these is a hydrogen abstraction reagent which sort of abstracts this hydrogen from methyl and converts into rhenium carbene bond and resolves in formation of CH PH3. So this was reported by Roper in 1983. A another interesting approach for making these Schrock carbene is shown over here.

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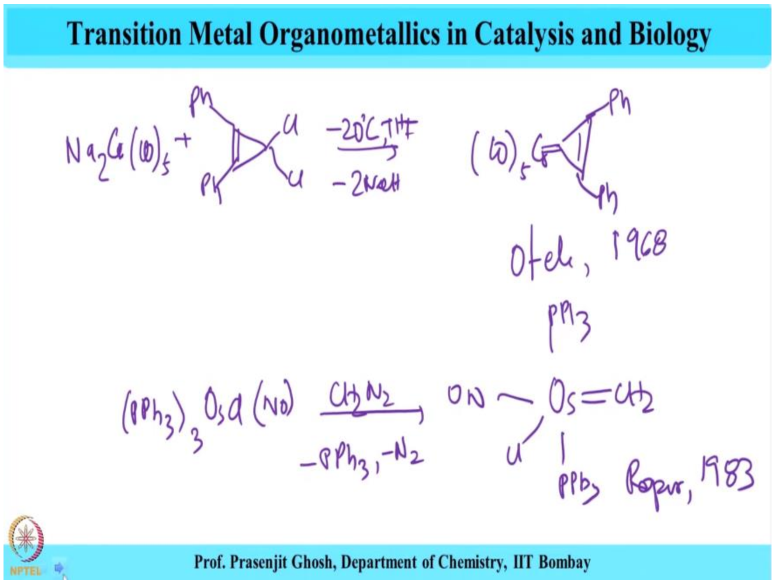

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So another started with Na2 it is a metallate lathe Cr O CO5+ these cyclopropane dichloride at minus 20 degree is centigrade to NaCl in THF gave the corresponding CO5 Cr carbene complex as is shown over here. And this is reported by a Ofeli in 1968.Another interesting example are method for synthesizing is this ppH3 whole thrice osmium chloride NO reacting with diazomethane CH2 N2 giving PPh3 and -N2 into giving this osmium carbene complex with p ph3 PPh3 Cl NO by Roper in 1983. So what we see is indeed interesting examples in which these carbene complexes were made.

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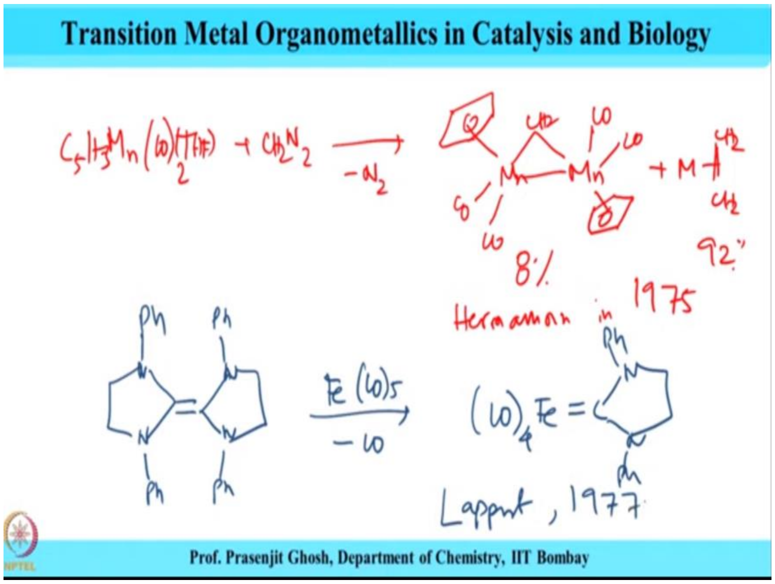

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Some another interesting one is a discussed here in which reaction of C5H5Mn Co whole 2 THF in presence of diazomethane eliminates a molecule of nitrogen to give this dimer Mn Co Co Mn

Mn with CH2 Co Co in 8% yield +M bound to olefin CH2 CH2 92% this was reported by Herman in 1975.

And not but not the least another interesting reaction that involves cleavage of an olefin for accessing this carbene has been reported by Lappert which took this olefin and inserted that onto a iron pentacarbonyl which loses a Co to give this tetra methylene carbene complex which is accessed from the olefin. So this is synthesized reported by Lappert in 1977. So with this we come to an end at of today's lecture.

Whereby we looked at these important intermediate of olefin metathesis which is metal carbene moiety and then what we have done is we have looked into the various kinds of metal ligand interaction present with metal carbene moiety. We have also looked at Arduengo bottleable singlet carbene the strategy and in synthesizing it behind stabilizing it and the strategy that were successfully observed while synthesizing this bottleable carbenes.

We have also looked at various synthetic methods which are available for synthesizing the original Fischer and Schrock carbene. And what comes out of all this discussion is the beauty of organometallic chemistry in general because we saw that work by Lappert, Herman, Ofeli, Schrock and so many others Gladius relate to different beautiful synthetic roots to each of these carbene complexes.

So that sort of explains the aesthetics and beauty that organometallics chemistry presents as such. So with these I come to the conclusion of today's lecture which looked into the catalytic species of olefin metathesis which is metal carbene species in general we have looked into classification of metal carbene species the synthesis behind each of them. We have also looked into various kind of carbenes including these otherwise so famous in heterocyclic carbenes and the strategy used for synthesizing that.

So this has been extremely fruitful discussion where we looked at the chemistry and the way reactivity of the metal carbene species and carbene species in general and their relevance to olefin metathesis. So more of this discussion on olefin metathesis can would continue in the next class where look at the development of olefin metathesis in bit more details. And also lastly I would like to note that industry as we had been saying over and over again that industry had been a key player in development of organometallic chemistry and this context I would like to mention also here that the bottleable carbene by Arduengo was indeed industrial contribution Ardueng who had reported it from DuPont.

And we had observed the same thing that olefin metathesis the integrity of olefin metathesis was first observed indeed at DuPont in 1956 when they were trying to explain the observation of ethylene propylene copolymer when they were trying to carry out polymerization with only propylene. So with this I conclude today’s lecture we are going to be discussing more on the development aspect of olefin metathesis in the next class. Till then goodbye and thank you.