Transition Metal Organometallic Chemistry: Principles to Applications
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Week - 07
Lecture - 31
Transition Metal Carbene Complexes: Preparations

Welcome to this lecture on transition metal organometallic chemistry from principles to applications. In the last few lecture, we have been discussing a very important topic called transition metal carbene complexes now these carbene complexes are designated by the formulation of this type m double bond.

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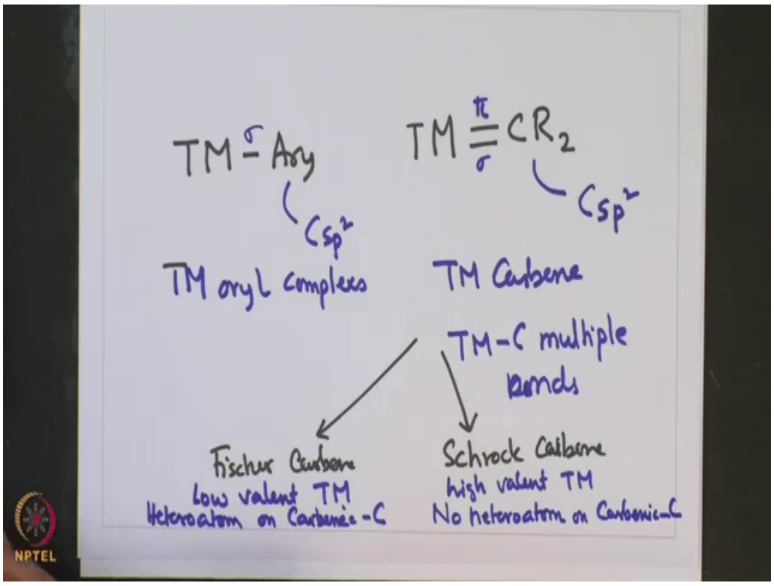

CR 2 and contain a carbon which is a SP 2 type hybridization. Now with regard to these transition metal carbene complexes, we have also discussed another kind of transition metal complexes that has C SP 2 centre mainly transition metal aryl type of complexes which to had carbon with a SP 2 centre.

Now difference between these 2 type of compounds are that in this there is only a transition metal sigma bond whereas, over here there are 2 kinds of bond one is sigma the other is pi. So, they contain transition metal carbon multiple bonds and this is how this transition metal carbene complexes are different from transition metal aryl complexes which to had C SP 2 type carbon centre, we have also looked into various kinds of transition metal carbene complexes that are known and they basically are of 2 types called Fischer carbene and Schrock carbine.

In our last class, we have also discussed about the requirements of the properties of the metal centre with respect to the formation of these are these 2 times of carbene and what was discussed was that the Fischer carbene is usually formed for low valent transition metals whereas, Schrock ones are formed for high valent transition metals also for Fischer carbene there is a hetero atoms of substituents carbonic carbon whereas, for the Schrock carbene there are no hetero atom substituents on carbonic carbon.

In our last class, we have also looked at the preparation used for synthesis of a Fischer carbene complex which was by the reaction of lithium alkyl reagent or nox tungsten hexacarbonyl compound followed by alkylation with a alkylating reagent resulting in Fischer carbene complex which was first used for making this kind of transition metal multiply bonded carbene compounds we have also noted that these carbene compounds are of extreme importance catalytically as they play they are important species in olefin metathesis reactions and which was recognized by the award of noble prize as late as 2010. So, this is indeed is a hot area of research in contemporary a chemistry.

Now in this lecture, we are going to look at some of the important applications preparatory methods for transition metal carbene complexes apart from the one that we are discussed in our previous lecture. So, the next method involves protonation or alkylation of neutral acyl complexes.

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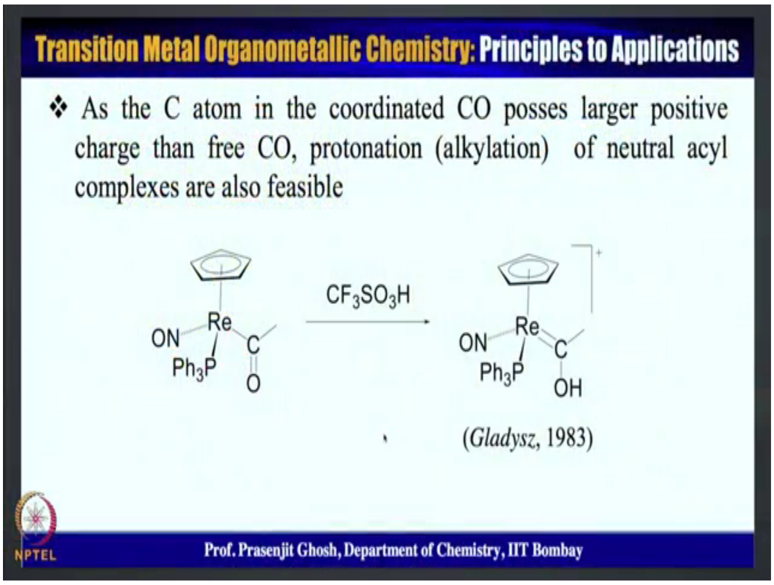

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- As the C atom in the coordinated CO posses larger positive charge than free CO, protonation (alkylation) of neutral acyl complexes are also feasible

(*Gladysz*, 1983)

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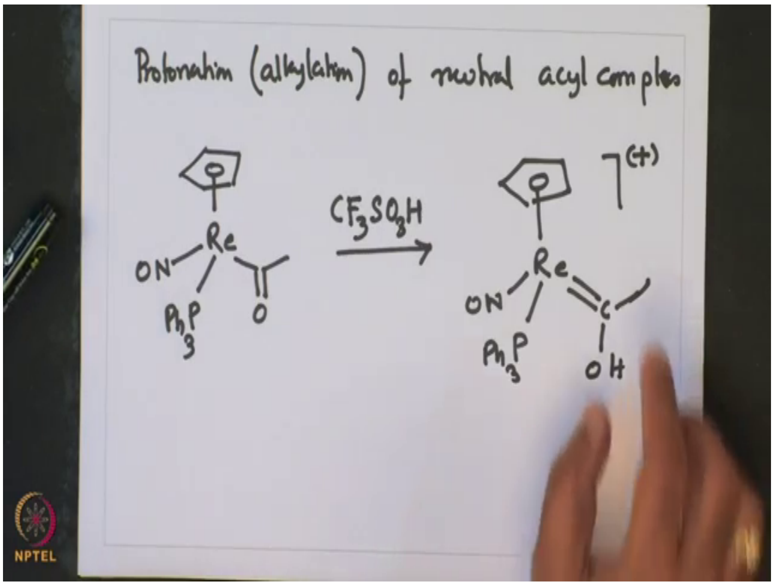

Protonation (alkylation) of neutral acyl complex

Leading to the formation of the Fischer type carbene a very good example starts with this rhenium c p complex having you know P; Ph 3 and C S u moiety which when protonated with 3 flick acid gives the following Fischer type rhenium compound and here we see the rhenium is bound to N O P, Ph 3 CP and the carbene contain a heteroatom which is hydroxide as shown over here the next method involves addition of alcohol to metal coordinated isocyanides complexes; this also is a very useful method for preparing Fischer type carbene complexes.

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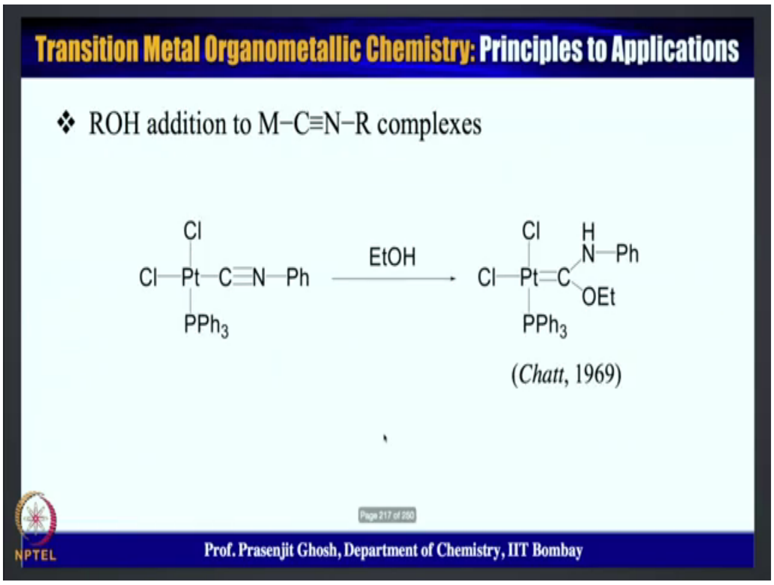

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- ROH addition to M–C≡N–R complexes

(*Chatt*, 1969)

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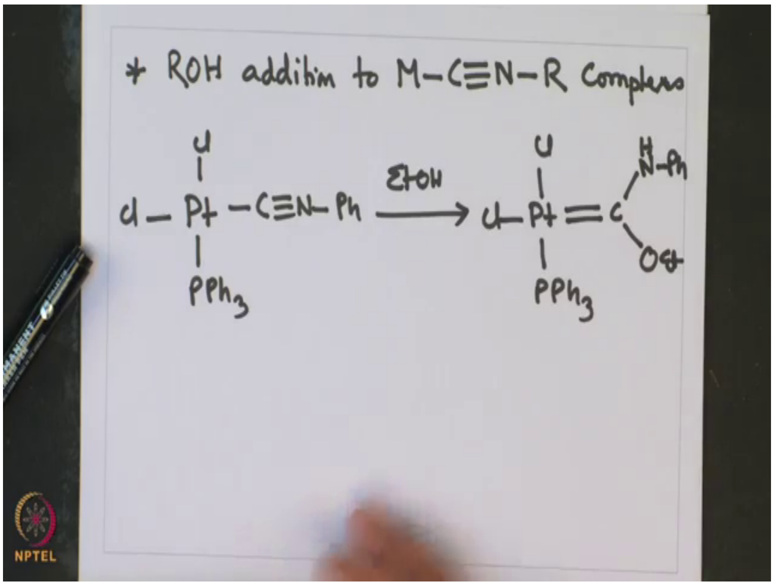

* ROH addition to M–C≡N–R Complexes

So, a very good example of this is seen in this C is chloro platinum P Ph 3 C N Ph in treated with ethanol produces this C is; this chloro P Ph 3 carbene complex as shown over here.

So, this is also a very useful method of adding this alcohol on this C triple bond N with the OEt moiety binding to carbon and the hydrogen protonating the nitrogen to form this Nh Ph resulting in this carbene bound to the platinum another.

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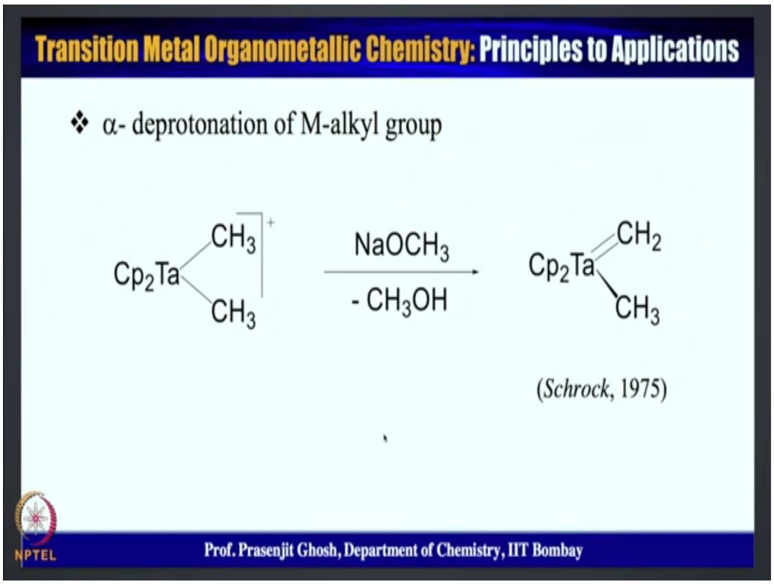

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- α- deprotonation of M-alkyl group

(Schrock, 1975)

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Method is the alpha deprotonation method by Schrock which was used for preparing Schrock carbine complexes here.

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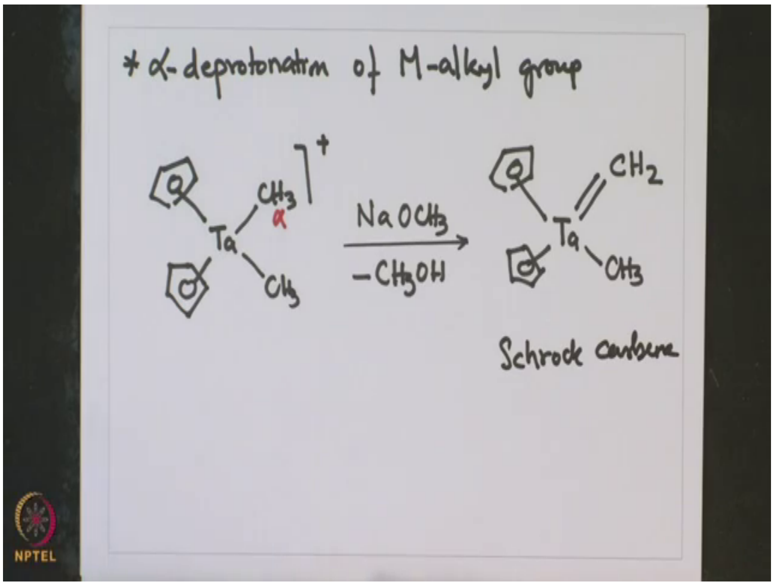

* α- deprotonation of M-alkyl group

Schrock carbene

B Cp tantalum dimethyl cationic plus when one of these alpha hydrogen which is over here this alpha hydrogen is deprotonated by base sodium ethoxide yielding methanol gives this carbene complex P cyclo pentadienyl CH 3 double bond CH 2. So, this is an example of Schrock carbene and was first prepared by Schrock by this method way back in 1975. So, what we are observing is that there are few versatile methods for preparing.

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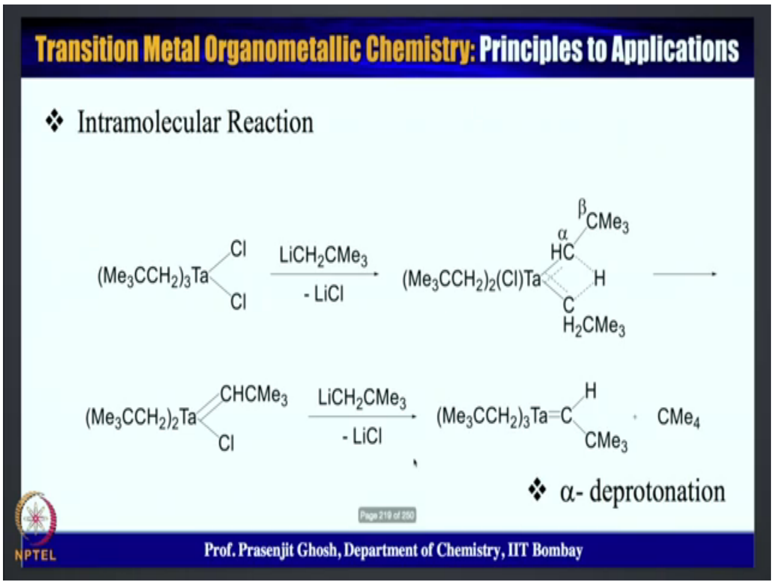

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❖ Intramolecular Reaction

❖ α- deprotonation

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These carbene complexes that can vary from Fischer to the Schrock ones here is an interesting example for preparing Schrock carbene through intramolecular reaction as is shown below Me 3 CCH 2 tantalum 3 of this and i chloride reacting with i CH 2 CMe 3 eliminates lithium chloride giving mono alkylated compound. So, here of the 3 nupentyl group and 2 chloride one more has added.

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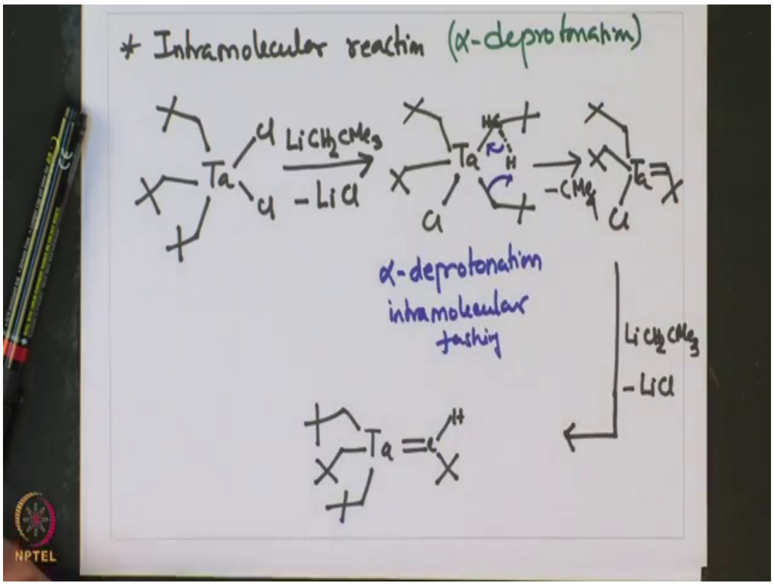

Now, there are four nuclearpentyl group 1, 2, 3, 4 and one chloride still remains now that interacts with the CH 2 CCM 3 species such that this alpha deprotonation happens in a intramolecular alpha deprotonation which is the hallmark of Schrock synthesis occurs over here in a intramolecular fashion resulting in this carbene complex along with generation of CMe 4 to give tantalum this neopentyl chloride with this carbene that further reacts with another molecule of lithium CH 2 CM 3 resulting in loss of lithium chloride and gives this Schrock carbene complex.

So, this is an extension of Schrock strategy, but in an intramolecular fashion giving rise to similar Schrock type carbene complexes of the type which are shown over here. So, the versatility of the Schrock method of alpha deprotonation is observed not only in intramolecular fashion which is shown over here, but also in intermolecular fashion which was originally used for making Schrock carbene complexes hydra de abstraction is another Very good method for preparing carbene complexes.

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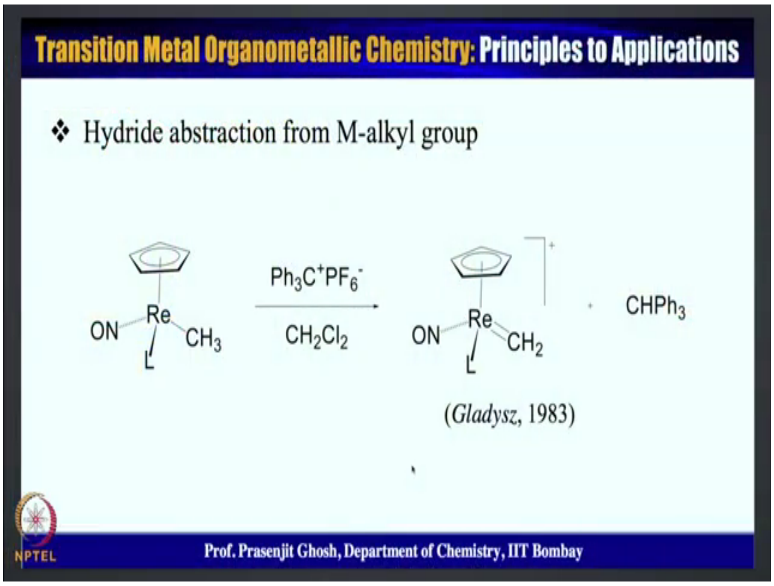

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- Hydride abstraction from M-alkyl group

(*Gladysz*, 1983)

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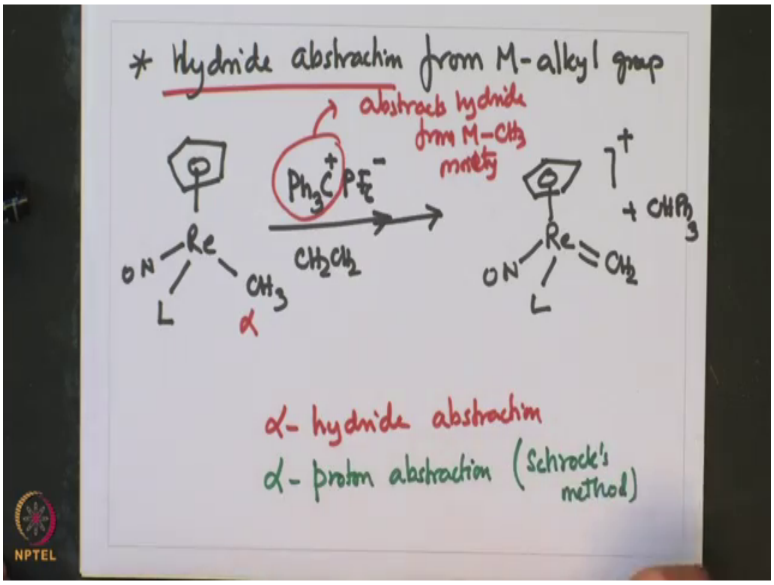

* Hydride abstraction from M-alkyl group

α- hydride abstraction

α- proton abstraction (Schrock's method)

And this hydride abstraction is usually done from the metal alkyl group is a good preparation and that can be seen for this rhenium complex which when reacting with Ph 3 trityl cation in dichloromethane this trityl cation abstracts hydride from m CH 3 moiety to give the corresponding rhenium complex having rhenium bound the CH 2 moiety or carbonic moiety this plus CH Ph 3.

So, this is a complementary strategy to the one that Schrock used where it was alpha proton abstraction and in this case this is alpha hydride abstraction. So, this is an example of alpha hydride abstraction to give a carbene complex where as a Schrock had reported alpha proton abstraction to give a carbene complex and that is known as Schrocks method.

So, what we are saying is that the versatility of formation of this carbene not only by an hydride, but also by an proton from the alpha position of the metal alkyl bond that results in this carbene formation another method of making carbene strains from the reaction of carbonyl metallates and geminal dichloroalkenes.

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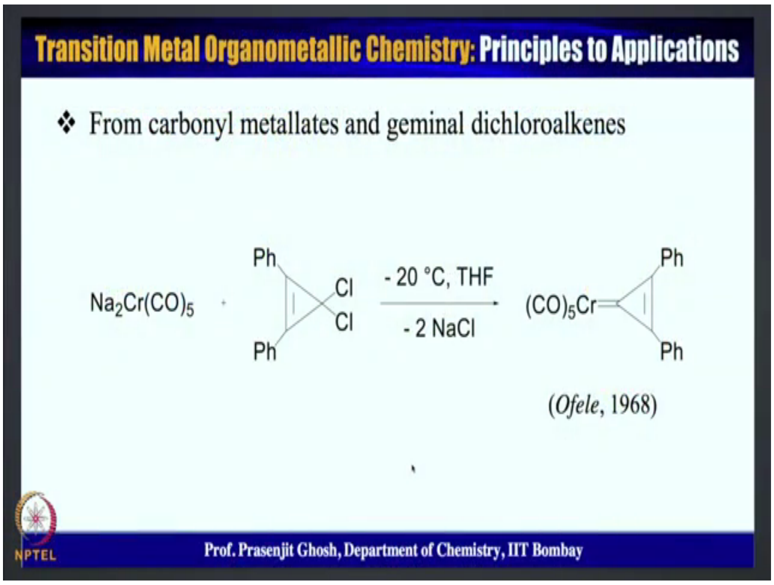

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- From carbonyl metallates and geminal dichloroalkenes

(*Ofele*, 1968)

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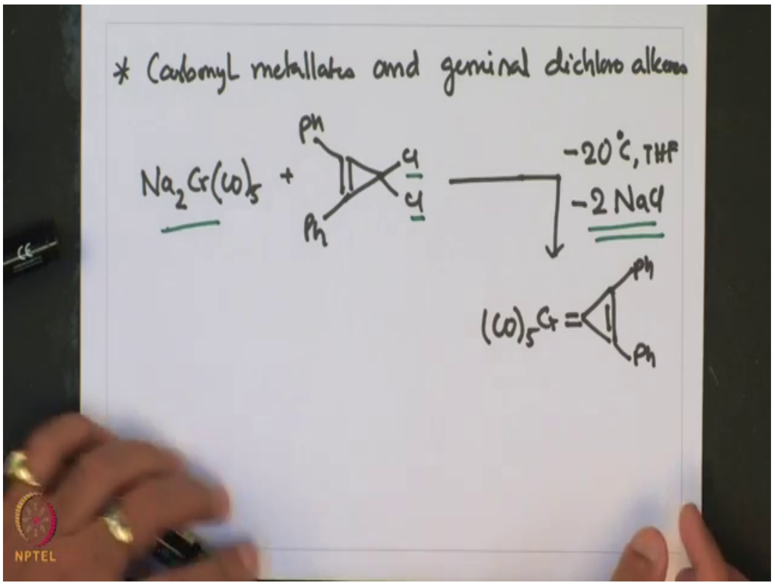

* Carbonyl metallates and geminal dichloro alkenes

And this is shown by reaction of any 2 Cr CO 5 plus Ph Cl; c l, Ph at minus 20 degree centigrade in THF that results in elimination of 2 Na Cl giving the corresponding carbene complex of the one that is shown here in this case that these carbonyl metallate, then anion was reacted with this geminal dichlocarbene where this Na Cl is evolved from reaction of this metallate with the chloride leading to the elimination of 2 Na Cl and resulting information of this carbene complex.

So, this also is a very interesting way of making carbines.

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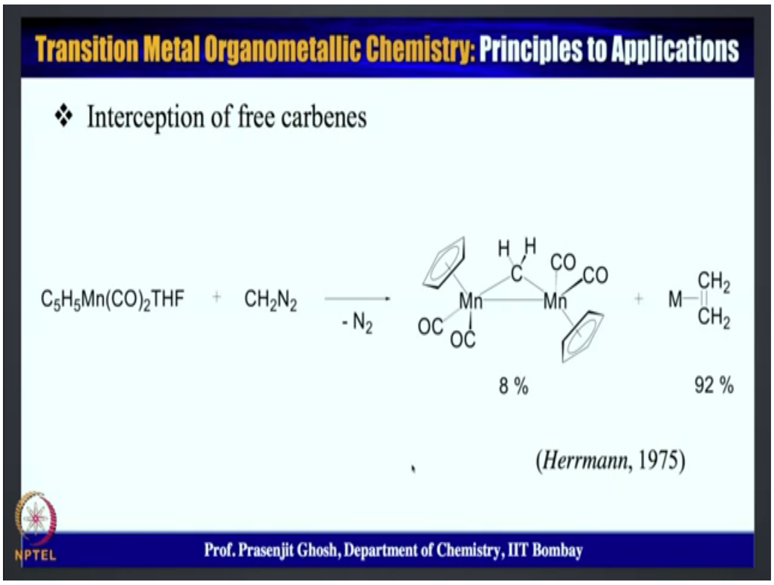

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❖ Interception of free carbenes

(*Herrmann*, 1975)

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Another; obviously, is a very simple way of trapping free carbenes using an a metal metal bond and this is a very clever way of intercepting free carbene reagents which it is themselves are extremely reactive and very difficult to characterize or isolate, but this is a very nice way of intercepting them thereby proving their existence.

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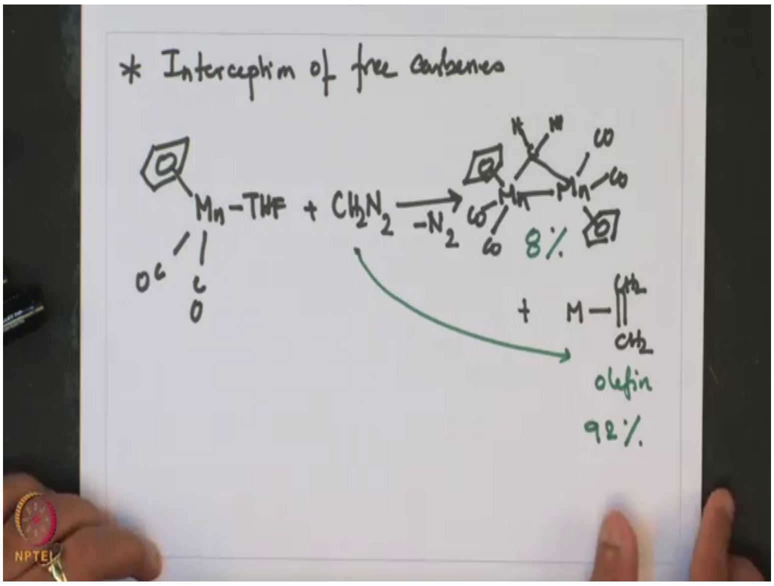

So, this method involves C 6 H 5 Mn CO 2 THF reacting with CH 2 N 2 which elements di nitrogen to give this by nuclear bridging dicarbonyl cyclopentadiene manganese complex plus the dynamic complex bound to the metal; obviously, this olefin complex is formed by combination recombination 2 of the carbenes to form the olefin which is then found coordinated to the middle. So, that is the maximum product about 92 percent of yield whereas, the intercepted carbene is only eight percent of the yield and this was reported first by Herman as a method for making metal carbene complexes another important attribute of this method is that it provides a bridging mode of this carbene between 2 metals enter.

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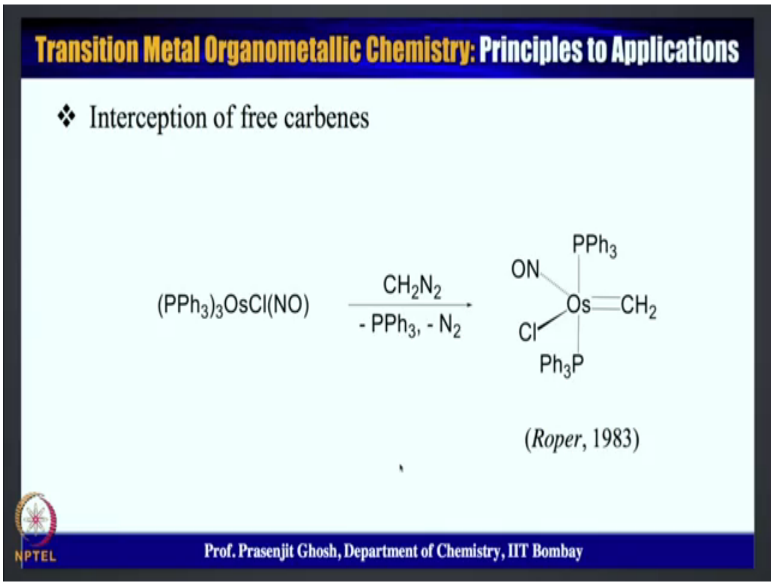

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- Interception of free carbenes

$$(PPh_3)_3OsCl(NO) \xrightarrow[- PPh_3,\ - N_2]{CH_2N_2}$$

(*Roper*, 1983)

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Another example of interception of free carbine has been reported for osmium complex as shown here.

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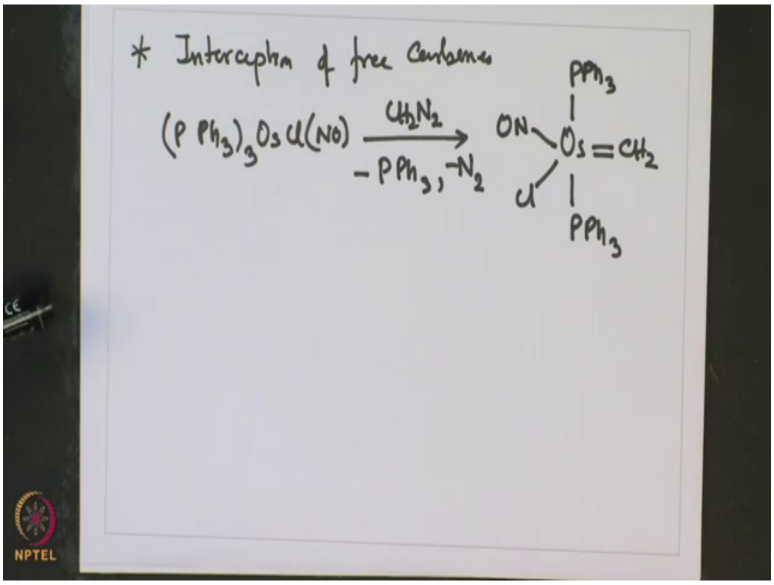

* Interception of free Carbenes

And they spend it with CH 2 N 2 yields P Ph 3 1 into giving this osmium carbene complex, here the carbine has been interest intercepted by osmium to give these osmium carbene complex of the type shown over here.

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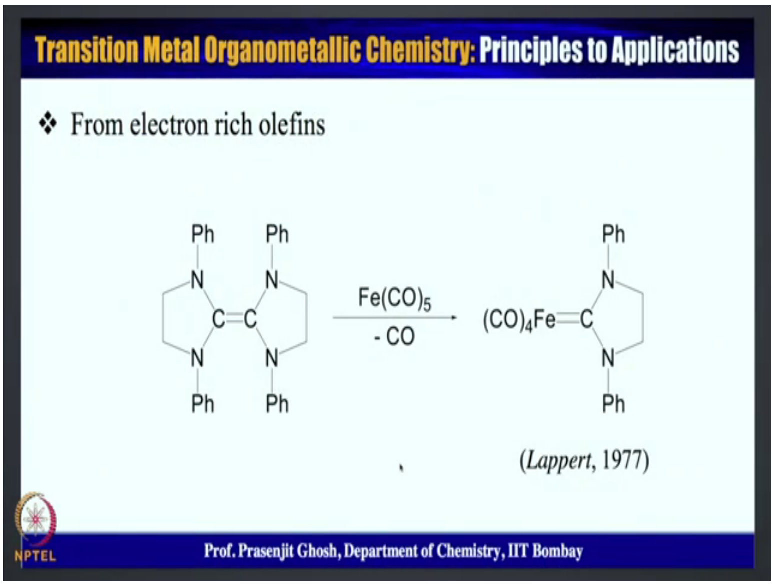

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- From electron rich olefins

(*Lappert*, 1977)

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Carbenes can also be prepared from electron rich olefins these are one of the; this was one of the earlier methods of obtaining these compounds and these methods involves electron reach olefins.

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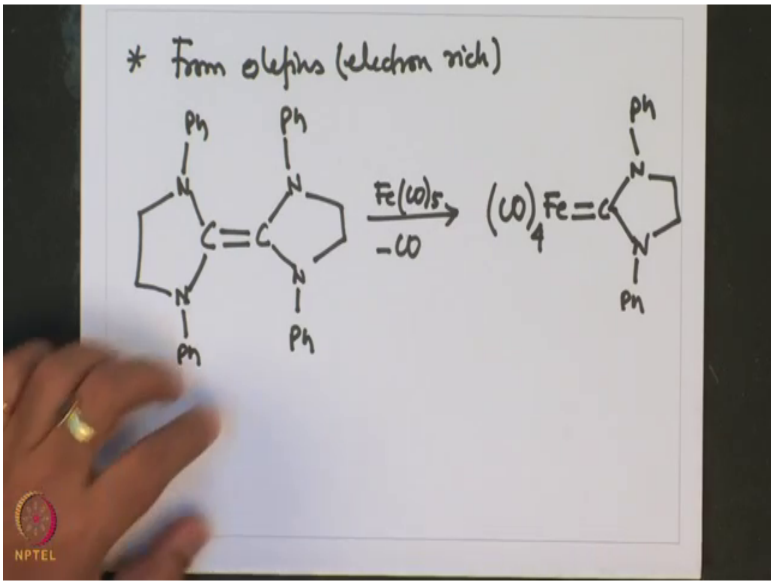

The particular reaction involves C double bond CNN Ph Ph N Ph that reacts with Fe CO 5 minus CO gives CO 4 Fe CN Ph Ph.

So, in this case, what is observed that the FeCO fragment binds to the carbene which is obtained by the splitting of this di olefin resulting in formation of the carbene as shown over here?

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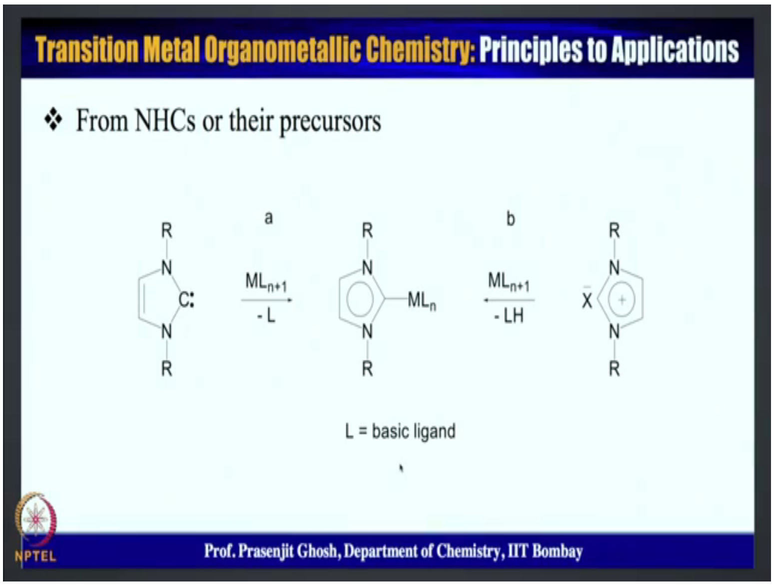
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❖ From NHCs or their precursors

L = basic ligand

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Another interesting method involves preparing carbene from in heterocyclic carbenes or their precursor complexes. So, this is a very a new method of preparing stable carbenes and they are obtained from emitters are based in heterocyclic carbines or NHC is From NHC is or their precursors N hetero cyclic carbenes or NHC is, are called N hetero cyclic carbenes.

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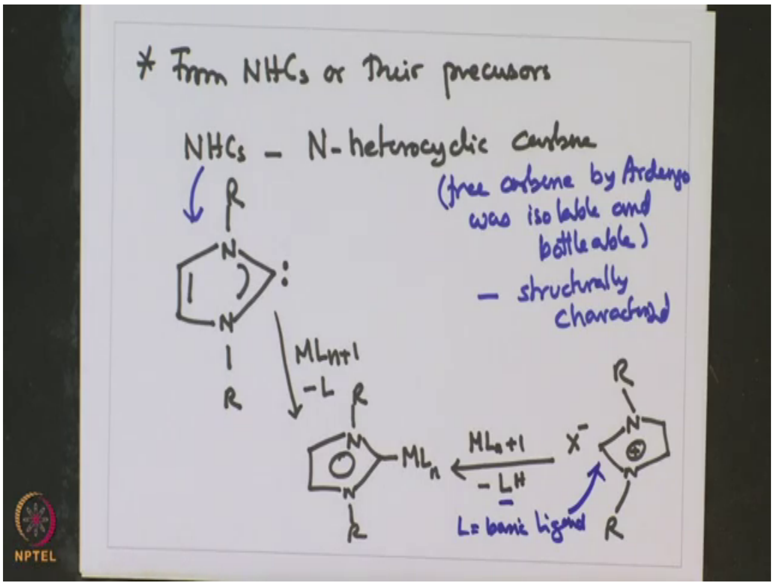

And they are designated as this where there is a heterocycle containing nitrogen atom nitrogen is substituted by 2 substituents and then there is this carbonic centres these are called n heterocyclic carbenes these are first reported by arduengo who by putting proper sterics could stabilize free carbene and which was isolable and bottle label free carbine by arduengo was isolable and bottle able and even structurally characterized.

So, these carbene complexes when treated with metal precursors lose is the L to give carbene metal complexes and the same can be obtained from the imidazolium halide precursor by treatment with M L n plus one and L H where this L deprotonates is hasidic proton and gives the base NHC metal complexes and L is a basically ligand that deprotonates this acidic CH.

So, with this let me summarize the highlights of today is lecture in this we have looked into various kinds of repetitive methods that are available for preparing this highly unstable transition metal carbene complexes that in co involved the reaction of nucleophile to carbonyl complexes as was done by Fischer and other kind of method which involved alpha proton deprotonation alpha proton alpha hydride abstractions then from die olefins from electron literally olefins from inertial carbenes and several other methods that were successfully used in preparing these transition metal carbene complexes. We have also looked at the strategies of Schrock which involved alpha proton deprotonation not only in a intermolecular fashion, but also in intramolecular fashion that was used for preparing these carbene complexes.

They were various other of kinds of addition reactions to our n c moiety that also produced carbene with the desired carbene complexes now these gives and us a brief overview on various synthetic methods available for preparing this very important catalytic relevant transition metal carbene compounds and then with this, I conclude today is lecture and in the next lecture, we are going to look up at the reactivity property and the bonding scenario that persists in the transition metal carbene complexes till then goodbye and I look forward to seeing you in the next lecture.

Thank you.