Transition Metal Organometallic Chemistry: Principles to Applications
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Week - 07
Lecture - 32
Transition Metal Carbene Complexes: Properties

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. In the last lecture we have been discussing a very important topic on transition metal carbene complexes. In this particular topic we have looked into various synthetic protocols that are available for making these transition metal carbene complexes. We have also spoken about the importance of transition metal carbene complexes particularly with regard to their catalytic applications, we have also looked into various kinds of transition metal carbene complexes that are known or the classification of transition metal carbene complexes and these mainly are of two types Fischer carbene, as well as Schrock carbene and their reactivity and properties as well as methods is available for preparing them are also different.

With that overview what we are going to discuss today is some more synthetic protocols that are used for preparing these transition metal carbene complexes particularly the Fischer and the Schrock types.

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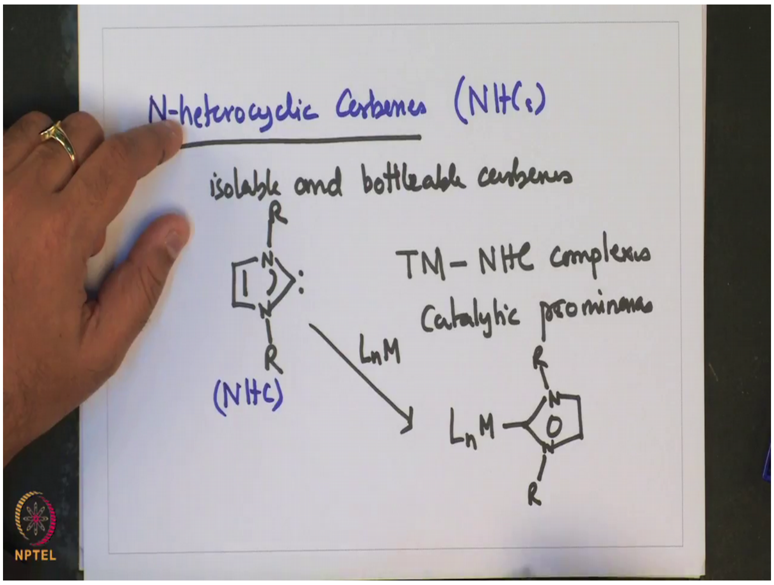
N-heterocyclic Carbenes (NHCs)

isolable and bottleable carbenes

TM – NHC complexes

Catalytic prominence

Now, with regard to transition metal carbene complexes we had come across the free carbenes which are called N-heterocyclic carbenes or refer to as NHCs. Now, usually a carbenes are extremely a reactive molecule and different very difficult to isolate and characterize and from that perspective these NHCs are important because they are isolable and bottleable carbenes. And these are first prepared by our dingo which contain an imidazole on an immediate basis sole base ring that contain imidazole with substitutes on the nitrogen atom and the free carbene lone pair.

Now, what it turns out that these carbene complexes these carbenes where complex to metal shows remarkable catalytic property and that is why NHC, a bond transition metal bonded NHC complexes have gained catalytic prominence. And in the last lecture we have discussed that how these transition metal NHC complexes are formed and one approach had been the reaction of free carbene with transition metal and for example, treatment of this free carbene with M would give type of transition metal carbene complexes. We have also seen that transition metal carbene complexes can be obtained from the imidazolium precursors, which gives free carbene upon reaction with a base to give the transition metal carbene complexes.

Now, of the types of imidazolium precursor usually a one of their type is the CCl 3 H bonds as shown over here.

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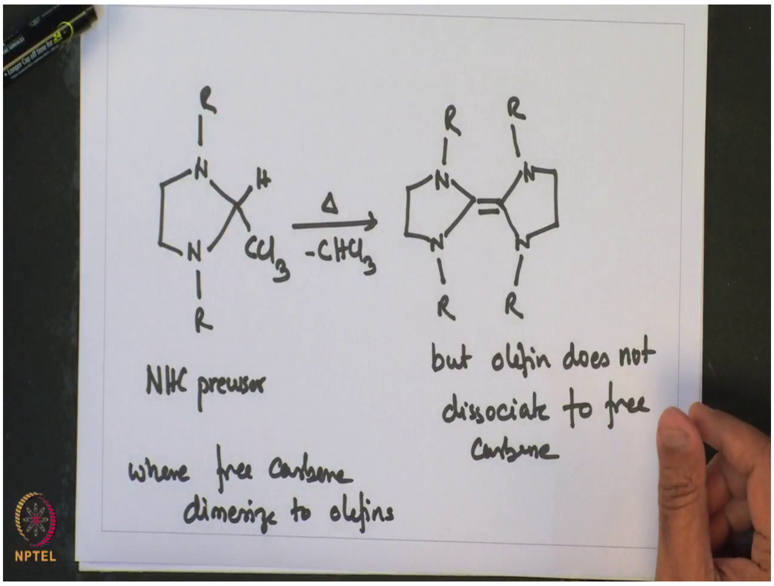

And it has a hydrogen and CCl 3 moiety and these are called NHC precursor of which upon heating gabe is of chloroform CHCl 3 leading to free carbenes that dimerizes to give an olefin of the type shown over here. But this olefin does not dissociate two free carbene whereas, free carbene dimerize to olefins. So, carbene transition metal carbene can and complexes can be synthesized from the carbene precursor as well as carbene by treating it with metal precursor in presence of a base.

Another very interesting method for preparing carbene from its milling proposal is shown over here.

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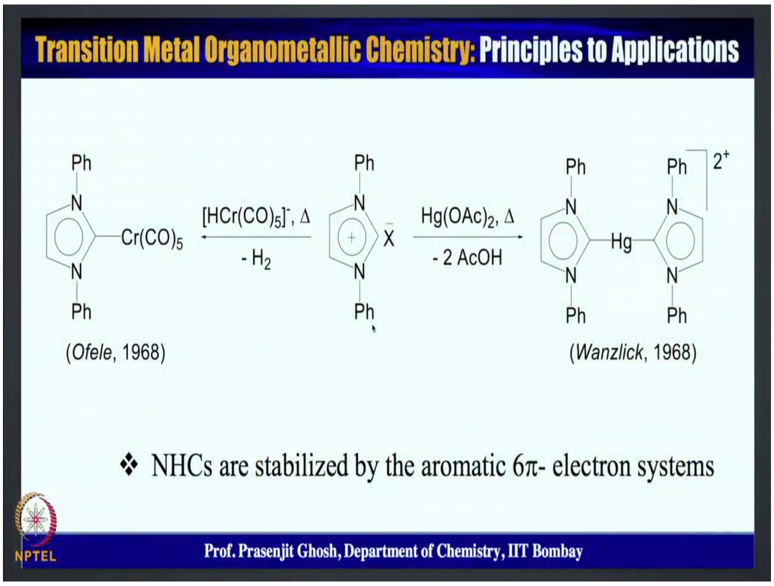

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(*Ofele*, 1968)

(*Wanzlick*, 1968)

- ❖ NHCs are stabilized by the aromatic 6π- electron systems

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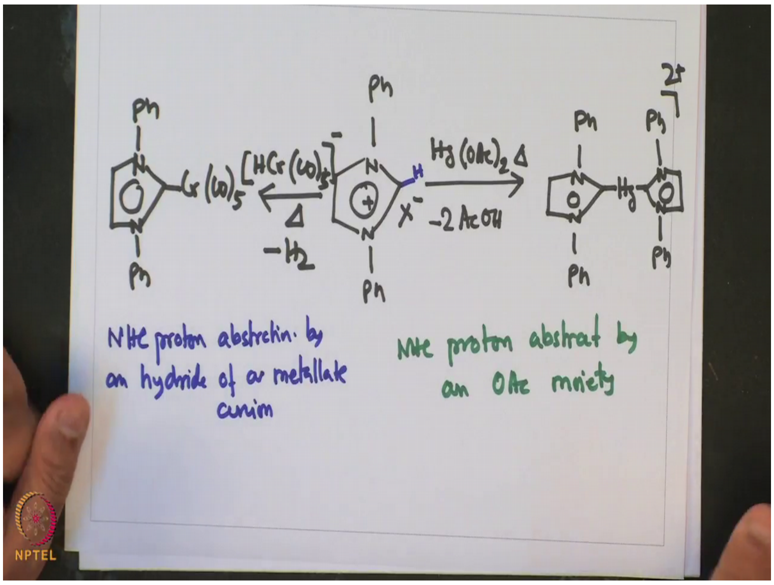

NHC proton abstraction by an hydride of a metallate anion

NHC proton abstract by an OAc moiety

For example, when this imidazolium solved he is treated with or heated with mercury acidic it that releases two acetic acid molecule the proton of this C H bond that gets obstructed by the acetate anion, giving to, giving rise to NHC carbene complex of the type shown over here. And the same obstruction instead of the acetate can also be achieved by a metallate. For example, H C R C O 5 minus which when heated eliminates the hydrogen the hydride and this proton gives die hydrogen giving this [noise]-heterocyclic carbene chromium complex.

Now, the beauty about this experiment is that this is NHC proton abstraction by an acetate moiety and on this side the same NHC proton abstraction by an hydride of methylate anion and both yielding transition metal NHC complexes from this precursor. And in both case this acidic proton of the NHC precursor is abstracted in this case it is by the anionic acid moiety and in this case the hydride of this a metal ate abstracts this proton leading to evolution of hydride the hydrogen and along with the formation of the chromium carbene complex. So, this is a really elegant route whereby both, whereby the NHC precursor is converted to transition metal NHC complexes.

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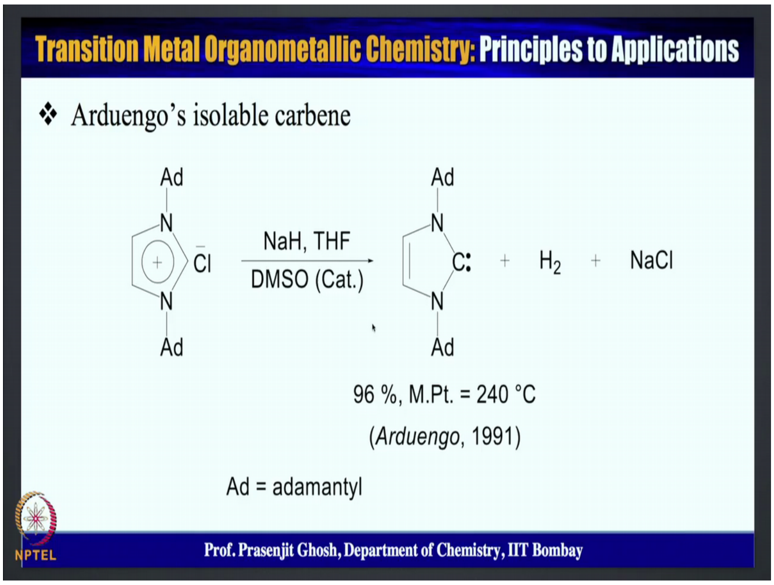

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- Arduengo’s isolable carbene

96 %, M.Pt. = 240 °C

(*Arduengo*, 1991)

Ad = adamantyl

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Now, as mentioned in our earlier discussion Arduengo’s was succeed successes and it was exceeded in preparing free NHCs and he did that by putting a steric bulk on the nitrogen substituent which would prevent this carbene free carbene to dimerize.

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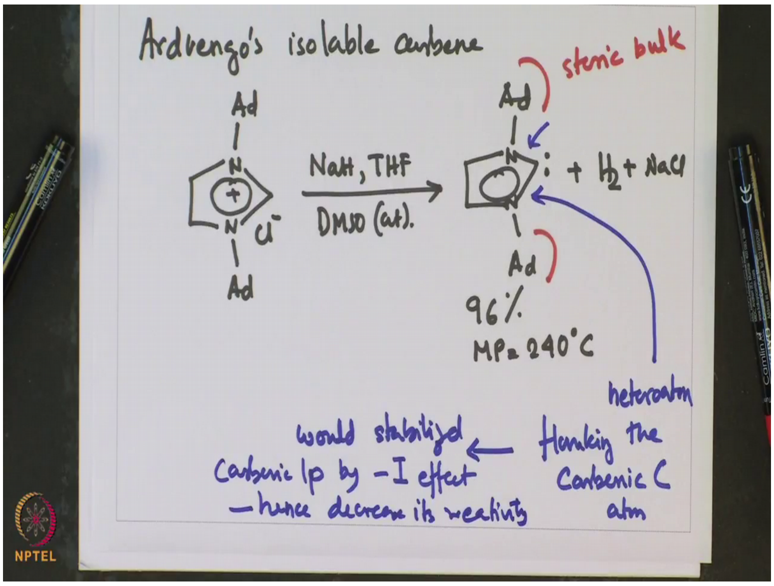

Ardvengo's isolable carbene

96%

MP = 240°C

heteroatom flanking the Carbenic C atom ← would stabilized Carbenic lp by −I effect − hence decrease its reactivity

And this was successfully done by putting adamantyl as the N substituents which led to isolation of free carbene. So, Arduengo’s isolable carbene was obtained when this adamantyl substituted imidazolium halide was treated with sodium hydride as a base in THF and DMSO as a catalyst to give the free carbene plus hydrogen plus NaC l. This free carbene was obtained in high yield about 96 percent yield and was characterized with all techniques including x ray and hydra melting point of 240 degrees centigrade which showed how stable this carbene was.

So, this was important breakthrough in being able to isolate transient species which otherwise are extremely difficult to isolate and had only been observed insert buys some very sophisticated spectroscopic techniques. Arduengo succeeded in this Arduengo's by adopting two approaches. First by putting bulky groups like adamantyl groups around the carbene moiety which prevented this free carbene in reacting with another moiety to give a olefin complex. So, this steric bulk was an important milestone in isolating free carbine. The other apart from the steric the electronic strategy which Arduengo put in place for isolating the carbene was to have a heteroatom flank heteroatom flanking the the carbene carbenic carbine.

So, they were to heteroatom flanking the carbenic carbon and the that would stabilize that would stabilize the carbonic centre by the electron with by its minus I effect, would stabilize carbenic lone pair by minus I effect and hence decrease its reactivity. With; the successful implementation of this strategy which have both electron steric as well as electronic components towards isolating this free a carbene a lot of catalytic reaction using transition metal carbene complexes came into being and their rule as catalysts in these transformation where looked at very seriously.

This NHC is as mentioned was found to not only make bonds to transition metals, they form bonds to various electron deficient entities like protons are electron poor species as well as electrophiles. So, various carbene attacks that have been reported with free carbene shown below.

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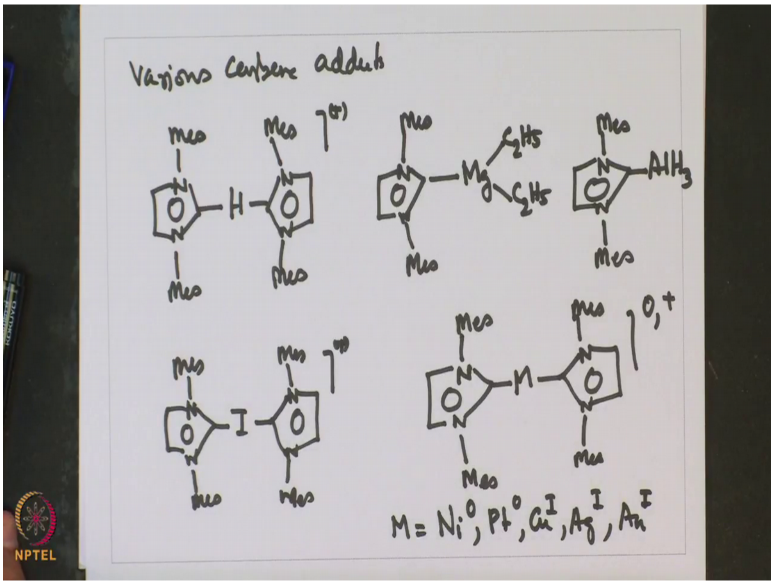

For example the proton adapt with to mesityl substituents. Similarly, a I plus stabilized by 2 carbene mesityl magnesium die then mesityl aluminium H 3. It even symbolizes various metal in their mobile and oxidation state like piece NH 3 the carbene which is a 0 or plus 1 oxidation state and that is true for m equals nickel, platinum, then copper, silver, gold.

So, what it brings to the fore that carbenes not only can bind to transition metal, but it also can binds to various electrophiles or cationic sources and stabilize them. Furthermore because of the presence of bulky substituent some the nitrogen atom the group which is flanked by the carbene is well protected and stabilized and in this way reactive metals in their low oxygen state have been stabilized using carbene ligands.

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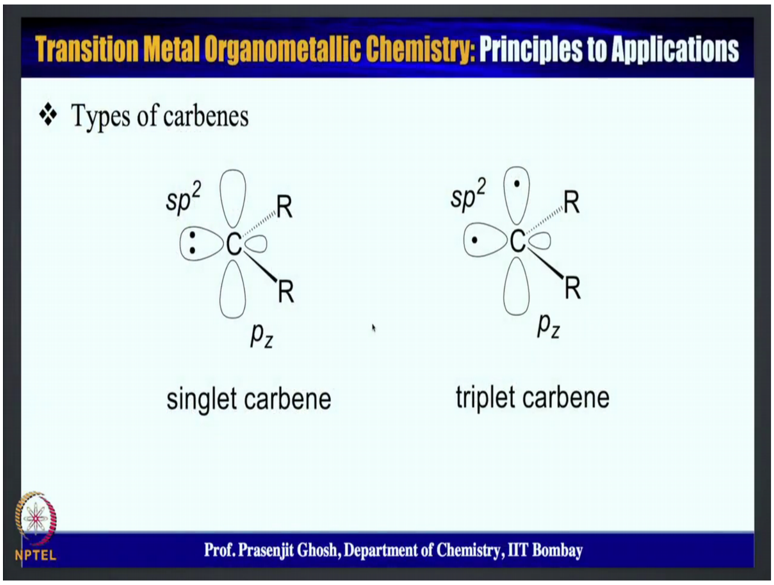

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❖ Types of carbenes

singlet carbene

triplet carbene

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Now, regarding the classification of carbenes we had discussed and we have found that there are two classes of carbene Fischer carbene as well as Schrock carbene, Fischer type and Schrock type.

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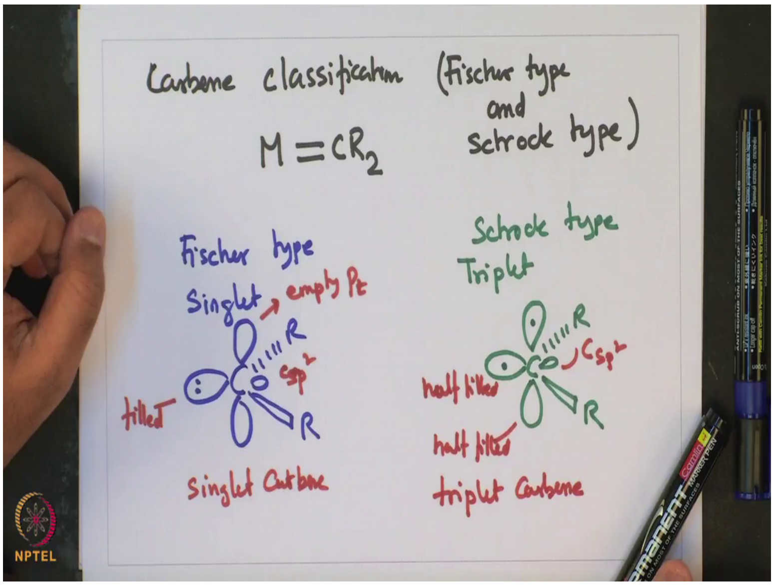

Carbene classification (Fischer type and Schrock type)

$M = CR_2$

Fischer type

Singlet, empty Pz

Singlet Carbene

Schrock type

Triplet

triplet Carbene

So, even though a carbene is represented by CR 2 the electronic nature of bonding differ the type of bonding differ between an Fischer type as well as Schrock type carbenes. And what has been found that Fischer type carbene is mainly in the singlet state is mainly in the singlet state where carbene for this CR 2 moiety has two orbitals one in plane which contains the electron and which is full and the other which is outer plane which is empty. So, this is filled S p 2 orbital and this is empty P z orbital.

So, we have two orbitals of which one is filled another is empty and hence this is called a singlet carbene. Schrock type carbene or however, different they are generally called triplet carbene and electronically though the carbonic centre is still S p 2, but both orbitals has one electron each. So, this is C S p 2 similar to what it is, but this is half filled as well as the empty P z is also half filled. So, this type of carbene represents triplet carbene. So, as the orbital of this carbene are different their inter and the electronic structure of these carbenes are different their engagement with the metal centre is also different and they define two kind different kinds of reactivity.

So, let us now look in details about the type of reactions which are present type of interactions which are present in Fischer and Schrock type carbene complexes.

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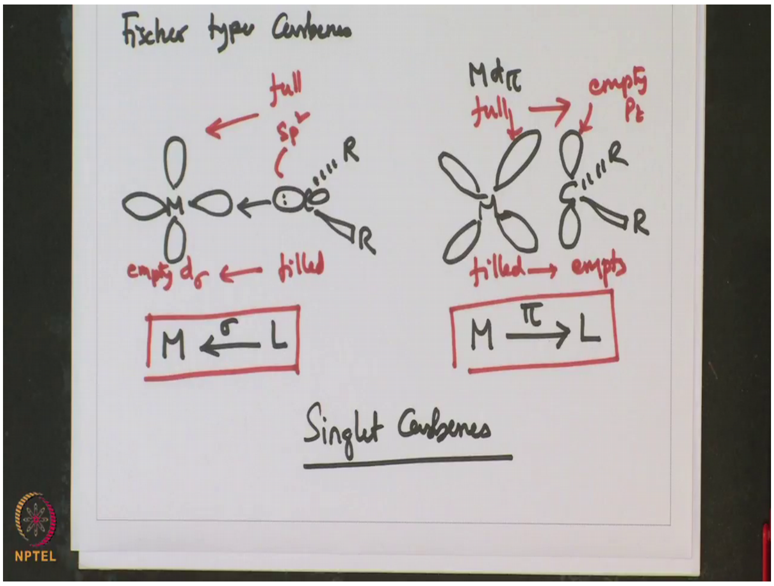

In Fischer type carbene there are two types of interactions one is metal to ligand sigma donation and that is given by, this is a S p 2 orbital and this is full containing 2 electrons and this is a empty d z orbital, empty orbital. So, this is a donation from full to empty and this is appropriately said designated by metal ligand sigma inter interacting orbital.

The next type of interaction is the metal to ligand pi back donation, pi type interaction where a metal full orbital this is metal d pi type orbital donates its electron to the empty P z type orbital. So, in this case this one is full and this is empty P z orbital and then the donation is happening from fill to empty this is from filled to empty and this is from filled to empty. So, this is metal to ligand pi interaction.

Now, despite the fact that both of these interactions are happening both are of sigma type in the sense that dative interaction of the sigma type happening in the forward direction and similarly a data from filled to empty pi type interaction is happening on the reverse direction.

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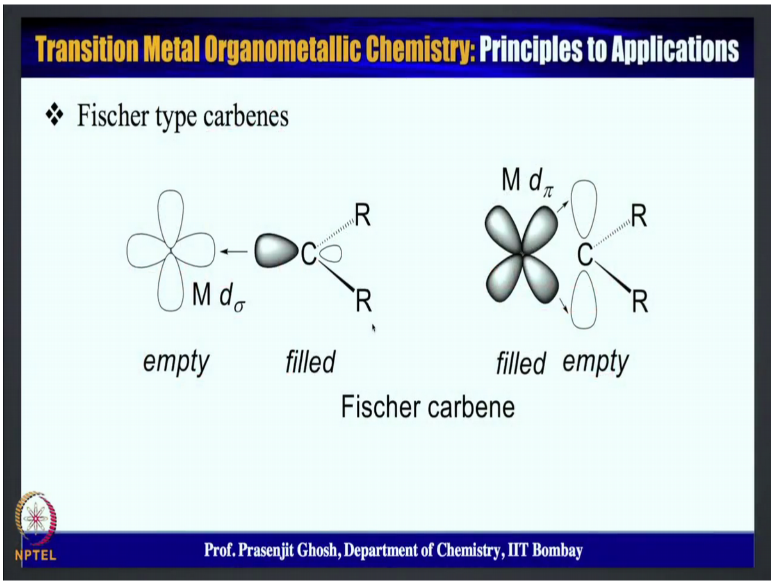

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- Fischer type carbenes

Fischer carbene

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And this is the interaction which is prevalent in Fischer type of carbene complexes those represents singlet carbenes.

So, with this I summarize the topic that have been covered in today's lecture which involved various synthetic protocols that are available for preparing the Fischer and Schrock type carbene complexes.

We have also looked at the stability of these two type of complexes, looked at the electronic nature of these two type of complexes particularly the Fischer type ones being the singlet type carbene which are highly reactive as compared to the Schrock type ones which are of triplet type. In the Fischer type one there is a filled S p 2 orbital and empty P z orbital which participate in interaction with the metal centre; as for the Schrock type once both the S p 2 carbene orbital as well as the P z orbital both contain one electron each and each of them is half filled and this is how they are in the triplet state and that they interact with transition metal with these two type of orbitals.

We have looked into the vilius protocols which are responsible for that and with that let me conclude today's lecture and we will take up the carbene a bit more detail in looking into various properties and reactivities of metal carbine complexes. The ramification of these two type of interactions in terms of the properties that they exhibit we have in the following class. In this particular class we have also looked at these very famous in heterocyclic carbenes, their stability, how they are stabilized to get a free a carbene where dimerization or the olefin information has been suppressed and this was first done by Arduengo and the strategy which was successfully used was not only to proton bulky statics to prevent dimerization around the carbeneic centre. But also to put with electron withdrawing heteroatom that there to civilize the free carbenic lone pair and prevent them from reacting.

So, with this thank you for being with me in this lecture and I look forward to being with you in the next lecture where we will take up a few more reactivity of metal carbene complexes.

Till them goodbye and thank you.