Transition Metal Organometallic Chemistry: Principles to Applications
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Week - 08
Lecture – 39

Transition Metal Carbynes: Properties

Welcome to this lecture on transition metal organometallic chemistry, from principles to applications. We have been discussing a very important class of compounds called transition metal carbyne complexes, and we have been looking at their preparation properties and reactivity the studies.

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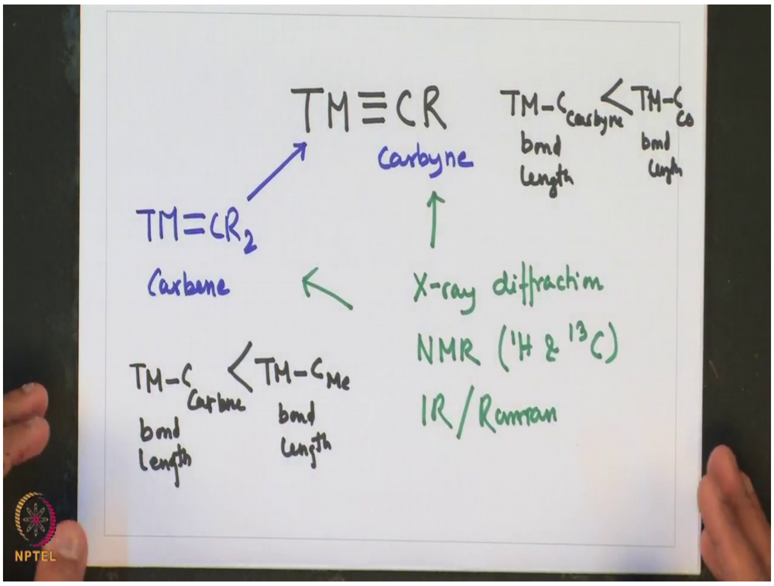

So, these transition metal carbynes are markedly bonded metal carbonyl species, where you have a sigma and 2 pi bonds attached to transition metals.

Now, most of the synthetic strategy that we have discussed about preparing this transition metal carbyne complexes, involved construction of this carbenic triple bond from the corresponding transition metal carbene complexes.

So, most of the strategies involved conversions of transition metal carbene complexes to the corresponding transition metal carbyne complexes, these are carbene complexes and these are car byne complexes. And what we have seen that the methods which were available for preparing these transition metal carbene complexes are also effective, for preparing the transition metal carbyne complexes.

And hence, whether a large number of methods which are available for synthesizing these complexes, we have also seen the spectroscopic techniques or characterization techniques that are of often in place for characterizing these complexes that involved in x ray. And diffraction and studies as well as NMR, both proton and 13 C, IR Raman IR spectroscopy, and most of these are equally available for characterizing both of these carbene and carbyne about this bond to transition metals.

Now, with that in the backdrop we were discussing about various characterization of cabyne molecule including that of x ray diffraction studies. X ray diffraction is a very a powerful method which gives direct measure of the bond lengths and bond distances, and what has been found that transition metal carbene a bonds and as well as transition metal carbyne bonds shorter than that of the transition metal co bond.

So, that will illustrate that like TM C carbyne, this bond length is shorter than transition metal C co bond length. So, that little indicates that this is a more strongly bonded to that of transition metal carbyne. And similarly transition metal carbene bond length is shorter than transition metal carbyne lets say methyl bond length.

So, what really 1 can see that this is partially double bond character and this is partially even triple bond character. So, with this backdrop we are going to take up few more examples of transition carbyne complexes particularly with respect to their characterization using x ray diffraction, with regard to the existing examples of structural characterize metal carbyne complexes, 1 interesting examples that are come to the fore is that of a transition carbyne complex of the formula given below.

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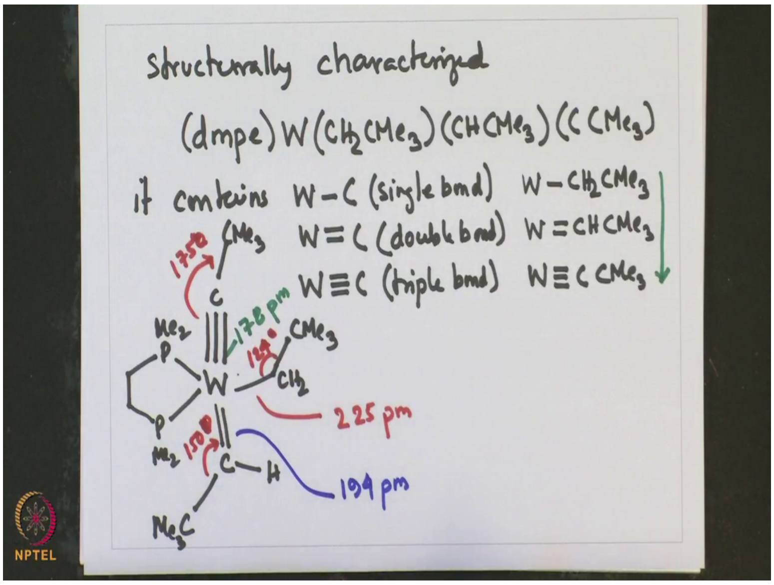

Structurally characterized

$(dmpe)W(CH_2CMe_3)(CHCMe_3)(CCMe_3)$

it contains $W-C$ (single bond) $W-CH_2CMe_3$

$W=C$ (double bond) $W=CHCMe_3$

$W\equiv C$ (triple bond) $W\equiv CCMe_3$

So, structurally characterized example of a tungsten carbyne complex having the formula dmpe tungsten CH 2 CMe 3 CH CMe C CMe 3, now what is interesting about this compound is that it contains, tungsten carbon single bond, it contains tungsten that is with respect to tungsten CH 2 CMe 3 bond, it contains a tungsten carbon double bond which is given by tungsten double bond CH CMe 3.

And it also contains a tungsten carbon triple bond and it's given by tungsten C CMe 3. So, what we see that this is a very interesting example where in the same molecule three different bond lengths exist, and the molecule is given by CMe 3 CH 2 CMe 3 CH CMe 3 P.

So, this is this dmpe ligand and as for the bond lengths are concerned this tungsten carbon single bond is about, 225 picometer tungsten carbon double bond is about 194 picometer, and tungsten carbon triple bond is 178 picometer. So, we see that how the tungsten carbon bond decreases as bond goes to single bond the double bond the triple bond starting from 225 to 194 to 178 picometer.

And this angle is also not linear it is slightly deviated from this 180 degrees is supposed to be the linear angle and it comes at around 175 degrees. These triple which is supposed to be 120 this is about 150 degrees, and the sp 3 bonds which is a single bond that is about 124 degrees. So, we see that 3 a different bond lengths and the bond angle for this structurally characterized constrained complex which contain all the single bond, double bond, triple bond moieties it is a very interesting example from that perspective.

Now, we are going to sort of look at the carbonyl transition metal interaction we are going to look this perspective upon little carbene, transition metal interactions and see how the interaction of carbyne molecule, with transition metal vary with that of carbene moiety with transition metals. So, we are going to sort of look at transition metal carbyne interaction with from the perspectives of the carbyne electrons now as let us start with carbenes.

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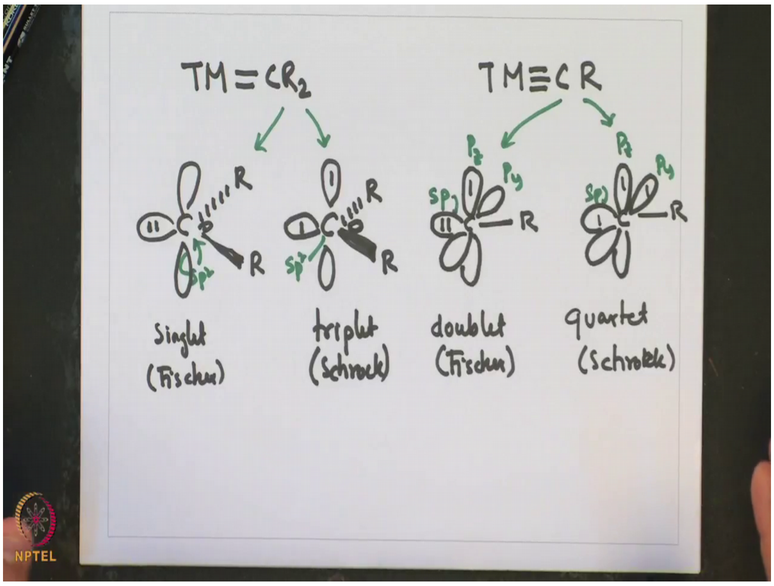

Now, as in the carbenes we saw the carbenes that generally sp 2, hybridized and they had two systems. So, let us look at transition metal carbyne interactions particularly we are going to look at or try to understand transition metal carbyne interaction with respect to transition metal carbene interaction.

So, to start with there is sort of look at transition metal carbene or frontier orbitals that are involved in interaction with their carbene complexes. So, as for the transition metal carbenes what we saw that, there was a sp 2 carbon center. Which had a sp 2 lobe and a empty pz orbital, and this sp 2 lobe had loan pair that is for Fischer carving this was a singlet carbene whereas, for the schrock ones it was a triplet carbene. So, this was in a triplet spin state, and these were for carbenes.

The carbenic moiety sort of a looked like this, in case of the schrock and the Fischer carbenes and as for the carbyne, where the metal is in where the carbon is in sp hybridized state. Where this is Py and this is Pz orbital, and this is sp orbital unlike the sp 2 over here, sp 2 over here in carbyne it is a sp orbital over here.

Now, carbyne also are of two types 1 is a doublet carbyne, which is a Fischer carbyne where the sp orbital has 2 electrons, and the Pz orbital has 1 electron, and proc crabyne which is. So, this is the Pz orbital, this is the Py orbital and this is the sp orbital, in the schrock carbyne all of this is contains 1 unpaired electron. So, this is in quartet spin state and these are called schrock carbyne.

So, here too what we see that CR carbonic moiety, exist in spin state which is doublet and quartet. Now if one were to compare the reactivity or the fragment orbital of the carbene and the carbyne, then one sees that all the 4 spin states are covered starting from singlet, which is a Fischer carbene then are doublet becomes Fischer carbyne then a triplet, which is a schrock carbine then a quartet, which is schrock carbyne also what is important over here to realize is the fact that in Fischer carbene where the sp 2 orbital was occupied and the Pz was vacant.

Similarly in the Fischer carbyne case, sp 2 is occupied Pz is half filled and Py is completely empty, and similarly a for the triplet state in the schrock carbene from can see that both the sp 2, and the Pz orbitals are half filled as well as in the quartet schrock carbyne case both sp Pz and Py each of them are singly filled.

So, this provides overall perspective of the carbenic as well as carbynic moieties and their electronic structure and how they form the basis for interaction with the transition metal, and how that their reactivity would vary as to their interaction with the transition metal. So, with that we are going to sort of take a bit more, we are going to look a bit more in details about how this kind of metal carbyne interaction happens.

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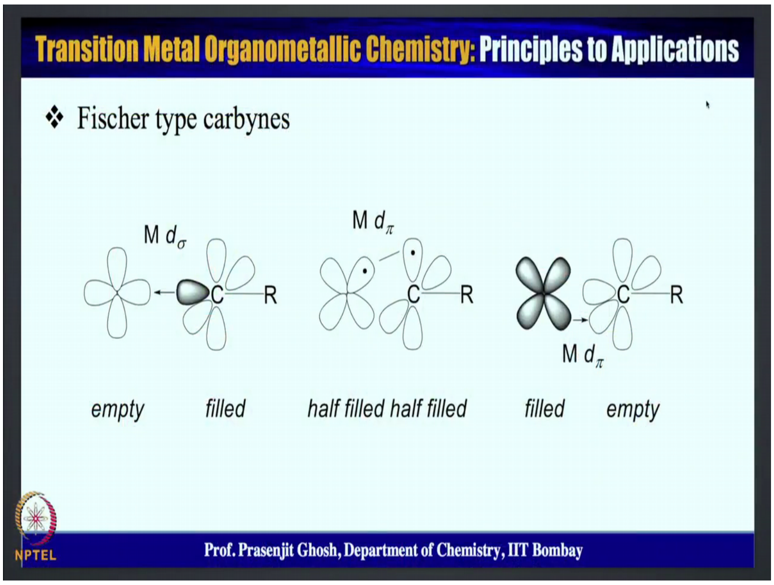

Transition Metal Organometallic Chemistry: Principles to Applications

❖ Fischer type carbynes

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To begin with we are going to restrict ourselves to this Fischer carbyne moiety a and then we are going to take a look at the schrock carbyne moiety. Now as we had seen a metal carbine organ metal compounds that there are two kinds of interaction called ligand to metal or metal to ligand, and similarly for carbyne 2 these metal ligand and ligand to metal interactions predominant and they play their own assigned role.

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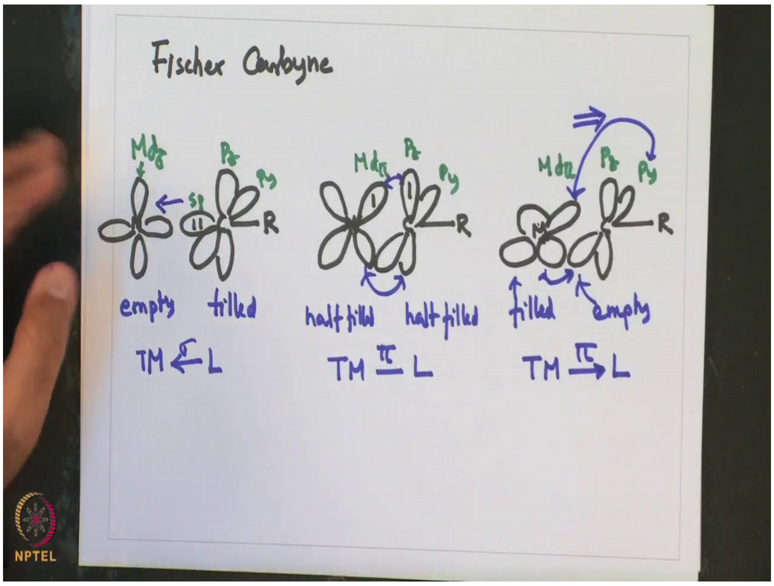

So, let us start with Fischer carbyne a complexes for example, Fischer carbyne has carbon sp hybridized interacting with a metal. So, this is the Sp Pz Py orbital, and that interacting with a metal orbital of metal d sigma symmetry metal d sigma. And this being filled there is a net electron donation, which happens from sp to the empty metal orbital. So, this is filled and this is empty and this began through metal sigma interaction, the next set of interaction is between, a half-filled metal interacting with half-filled carbon Pz orbital.

So, in this case the metal so this is a Pz orbital for clarity purpose the sp orbital has is not being shown over here interacting with a metal t type, d pi type orbital and in this case the single filled orbital interacting with single filled. So, this is the interaction which is sharing that happens between this t orbital and this p orbital. So, this is half-filled, and half-filled interaction.

So, this can be represented as transition metal to ligand pi interaction. So, this is a Py orbital, Pz orbital, and the metal with having filled orbital. So, this is metal orbital having the pi symmetry and here the interaction is between the filled with empty Py metal. So, here this d orbital, d pi orbital is filled and this Py orbital is empty and that the interaction takes place, between this and this Py, Py and this interaction is from metal to the ligand filled to empty.

So, this can be designated as transition metal to ligand pi interaction. So, this is half-filled, half-filled there is no arrow in the bond this is filled to empty there is a arrow designating, how the coordinate that bond this happening and this is empty to filled and here. So, the first one is sigma, second one is pi, and third one is a dative pi type interaction.

So, what is seen over here that in Fischer carbyne species that the carbon is sp hybridized and then there are 2 p type orbital 1 is Pz and Py, Py remains vacant and Pz is half-filled that when interacts with the metal d sigma orbital of sigma symmetry. Then there is ligand metal as seen over here as well as the there is d pi orbital of a metal interactive partially filled, half-filled d pi orbital of a metal interacting with the partially filled Pz orbital, of the carbynic moiety and this is.

So, called a half filled half-filled interaction, and then we have these the metal filled orbital interacting with an empty Py orbital and this is filled to empty transition metal to ligand pi bag donation. So, with that what we have learned today is the fact that transition metal carbynes are a very interesting pair of compounds; we started off with a structurally characterized example of a tungsten complex.

Where all the three forms of metal carbon bond whereas, metal carbon a single bond, as well as metal carbene double bond, as well as metal carbyne triple bond all have been stabilized on this tungsten structurally characterized complex and what we saw that these bond lengths shortened with the increase in multiple bonding character. And that the single bond as expected is was the longest whereas, the triple bond b was the shortest and the double bond being the intermediate 1.

And also we have seen that the depending on the change in hybridization of the carbon from sp 3 in a single bond to sp 2 in a double bond to spn as a triple bond, the angle at the carbon moiety is changed from being linear to being bent depending on their hybridization which was sort of expected.

We have also looked at the spin states of these carbyne moieties, and what we had seen that carbynes 2 can be classified as Fischer and schrock type with the Fischer type carbynes being doublet as well as the schrock 1 being quadrate. So, what this brings us is the fact that overall all the spin species are covered if we compare the spin states of the carbenic as well as carbyne moiety a. So, from Fischer carbene being singlet whereas, Fischer carbyne being doublet and schrock carbene being triplet and schrock carbyne being quartet.

So, we have looked at the distribution of the electrons in the frontier a valence orbital of this carbyne fragment, further on we have also looked at how the interaction we have occurs between the carbyne fragments in the doublet spin state along with the metal orbitals.

And what we saw that these Fischer carbyne interactions are of three types the first one is a filled carbon sp orbital donating electron to the empty d sigma orbital of appropriate symmetry on the metal. So, this is ligand to metal sigma dative coordinate donation.

The next one of the interaction that we see is a filled covalent interaction involving half-filled d pi orbital of metal interacting with half-filled Pz orbital of the sp hybridized carbynic fragment. And the last of the interaction we saw was this filled metal d pi orbital interacting with empty Py orbital of the carbynic fragment.

So, Fischer carbyne type interaction consists of one carbine to transition metal sigma donation, another pi interaction between covalent pi interaction between transition metal and the carbynic fragment. And the last one, transition metal to carbonic pi back donation in the carbynic fragment.

So, with this I would like to conclude todays lecture which was looked into various facets of a carbyne chemistry, and we are going to be looking at such a similar orbital interaction for the schrock type carbyne complex in the subsequent lecture. And compare its reactivity with that of the Fischer type once we have discussed in this particular lecture, along with that we are going to look at various reactions of carbynes that are unique to these a moiety and several other aspects of carbon chemistry will be the topic of next lecture.

So, with that I thank you for being with me in this lecture, and I look forward to being with you in the next lecture.

Thank you.