Transition Metal Organometallic Chemistry: Principles to Applications

Prof. Prasenjit Ghosh
Department of Chemistry
Indian Institute of Technology, Bombay

Week - 08
Lecture – 40
Transition Metal Carbynes: Properties

Welcome to this lecture on transition metal organometallic chemistry from principles to applications. We have been discussing about transition metal carbyne complexes in the last few lectures and we have looked into the various methods available with regard to synthesis of these transition metal carbyne complexes as well as with regard to the properties of this is of these transition metal carbyne complexes these transition metal carbyne complexes are designated as something like this where there is a multiple bonded carbyne moiety with the transition metal.

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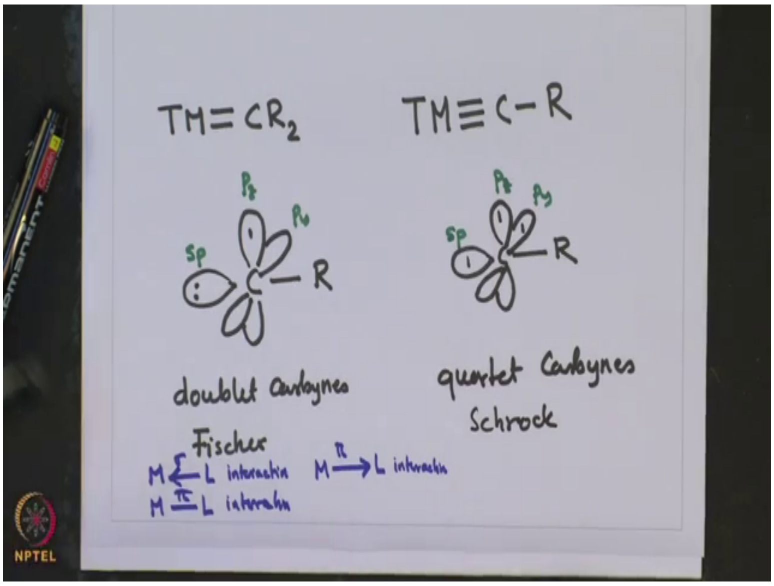

Now, these transition metal carbyne complexes were discussed in the pretext of transition metal carbene complexes which has this double bond character between the transition metal and transition carbonic moiety.

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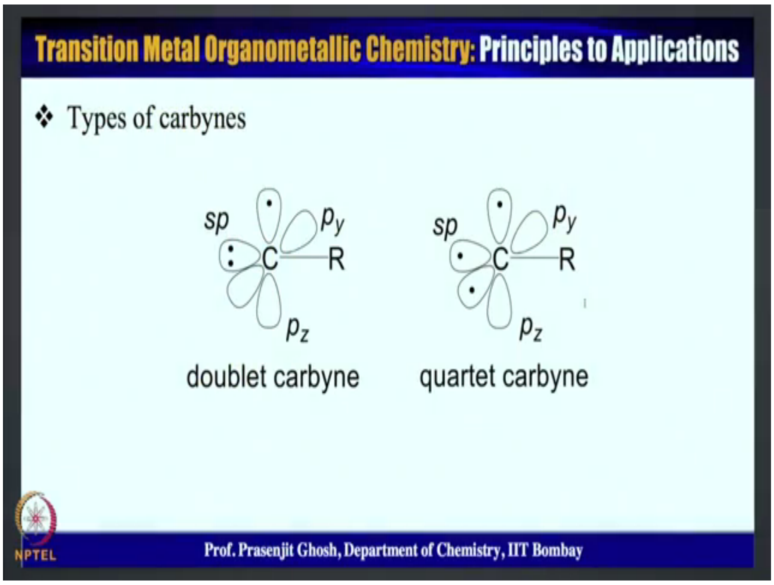

Transition Metal Organometallic Chemistry: Principles to Applications

- Types of carbynes

doublet carbyne quartet carbyne

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Now, with regard to transition metal carbyne complexes what we have seen that they come in 2 classes one is doublet carbyne as well as the other one is a quartet carbyne now in the last lecture we had looked into the bonding or interaction of the of frontier atomic orbital of these carbine moiety with the transition metal for these doublet carbyne species.

So, let us sort of take a look that at how this frontier molecular orbitals are placed for these carbyne complexes what it has it has a 1 sp a orbital which had 2 electron one pc orbital which has which has one electron and 1 p y orbital which is a vacant. So, these are called doublet carbynes and these are mainly a classified as Fischer carbyne complexes.

Now, we had discussed in details about the interaction with the these carbenic carbynic species with transition metal for this kind of Fischer carbyne complexes and what we found that these contains 3 kind of interaction one began 2 metal sigma interaction the next one is metal ligand pi interaction and the last one is metal to ligand pi interaction.

So, what we saw is that there are 2 dative kind of interaction one is ligand sigma orbital donating to empty metal orbital that is a dative interaction and another kind of pi interaction which is also dative where a filled metal orbital donating electron to the empty py orbital of the carbynic moiety and then we saw that one simple covalent half filled have half filled interaction between the metal d orbital as well as between the a ligand pz orbital which is partially occupied now this is what we had discussed in our previous lecture about Fischer carbyne complexes which has doublet carbynic species bound to the transition metal.

Now, in today's lecture, we are going to be talking about the Schrock carbyne species which are quadrate carbenes. So, let us take a look at how these Schrock carbyne species is particularly with respect to its fragment molecular orbital. So, this also has sp a hybridized orbital and sp orbital and pz orbital and py orbital similar to that of the Fischer carbyne species, but what is different over here is the number of electrons in each of these orbital as one in sp one in pz and one in py.

So, since this has a 3 unpaired spin these are called quartet carbynes or Schrock carbyne. So, we are going to look in more details about how these Schrock carbyne interacts with the molecular orbital of the transition metal having proper symmetry and what kind of interaction this Schrock carbynes need to.

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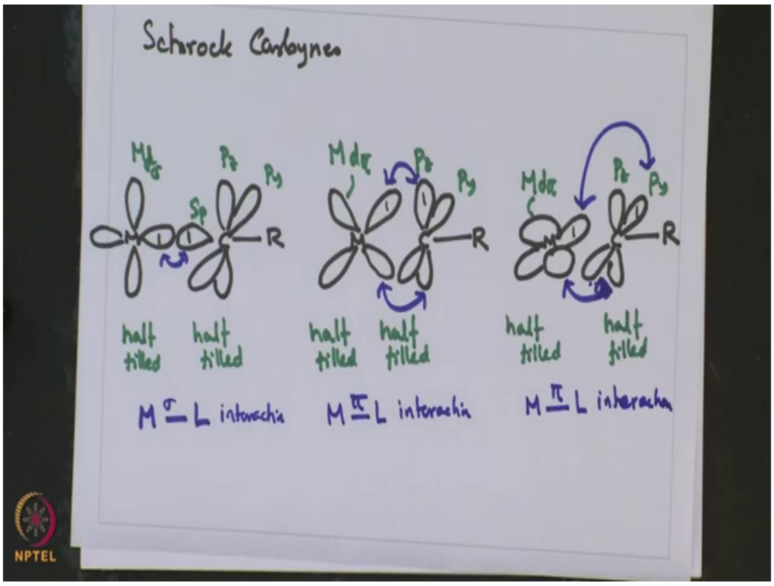

So, the first one is; so, this is a metal d sigma orbital this is sp p z py and the first one is just half filled half filled interaction interaction between metal and the ligand and this is denoted by metal ligand sigma interaction.

The next interaction is between the metal d orbital with the pz orbital of of the carbenic moiety which has one electron and pz also has one electron. So, this interaction is primarily between this metal d pi orbital and pz orbital which is this and this also is a half filled half filled half filled orbital and the the last one is between the p y and and the metal d pi orbital and this is py pz and this also has 1 electron, 1 electron and hence this is the interaction between p p y and the metal d pi,

So, this also is a half filled half filled interaction and both of these interactions are metal ligand pi type interaction and this one also is a metal ligand pi type interaction. So, what we see is the fact that these 3 half filled carbonic orbital which is a pz, py and 1 sp each of them interact with the metal orbital having appropriate symmetry and also half occupied to give 3 multiple bonds between the carbonic and the metal fragment and these 3 are pure covalent bond that involves sharing of electron from the metal fragment and that they form metal ligand sigma bond metal ligand pi bond and metal ligand pi bond in the process of such interaction.

So, carbonic species because of 3 unpaired electron these are called quartet carbene as well. So, with these we have gotten full insight as to how this carbon carbyne orbital be it Fischer type or be it Schrock type interact with the metal orbital of appropriate symmetry and also electron occupancy to give these carbyne complexes and now we are going to look at some of the reactivity of transition metal carbyne complexes as to how these interaction lead to the differential reactivity that these carbyne complexes display.

Now, one thing which is coming out from this discussion and also has been referred to as a in our earlier lecture is that carbynes are very strong pi acidic ligand even stronger than that of the carbon monoxide which usually is among the few benchmark strong pi acidic ligands that one actually refer to and because of this carbyne exhibits extremely strong trans effects in suchtute substitution reaction.

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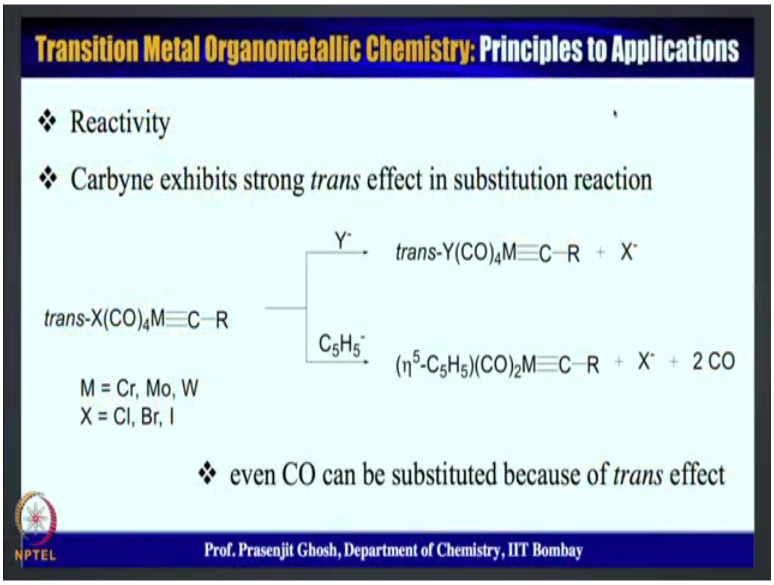

Transition Metal Organometallic Chemistry: Principles to Applications

- Reactivity
- Carbyne exhibits strong *trans* effect in substitution reaction

trans-$X(CO)_4M\equiv C-R$ $\xrightarrow{Y^-}$ *trans*-$Y(CO)_4M\equiv C-R$ + X^-

trans-$X(CO)_4M\equiv C-R$ $\xrightarrow{C_5H_5^-}$ $(\eta^5\text{-}C_5H_5)(CO)_2M\equiv C-R$ + X^- + 2 CO

M = Cr, Mo, W
X = Cl, Br, I

- even CO can be substituted because of *trans* effect

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Trans effect means if a ligand which is attached trans to the carbyne gets substituted during a substitution reaction as carbine himself is strongly bound to the transition metal because of its 3 multiple bonds.

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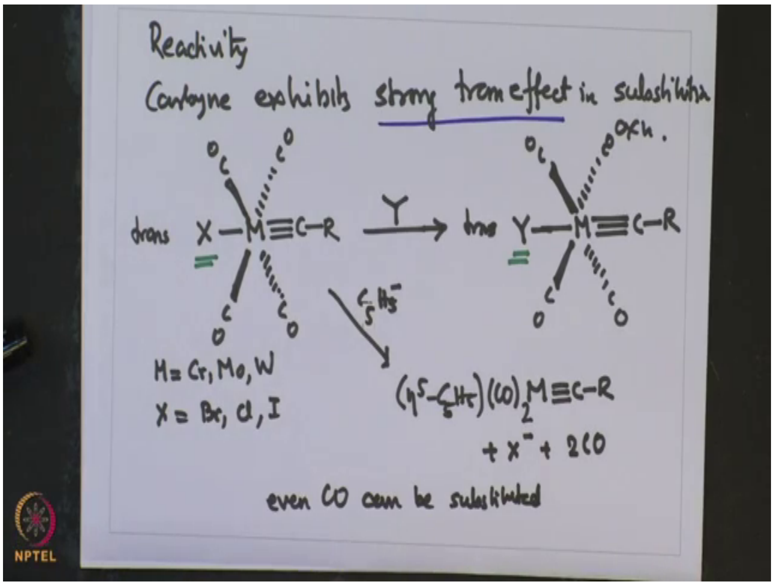

Reactivity

Carbyne exhibits strong trans effect in substitution rxn.

M = Cr, Mo, W
X = Br, Cl, I

$(\eta^5\text{-}C_5H_5)(CO)_2M\equiv C-R$
$+ X^- + 2CO$

even CO can be substituted

So, reactivity wise carbine exhibits strong trans effect in substitution reaction strong trans effect is a ligand found disposed trans to the carbyne moiety a would get displaced for example, for these complex when treated with a nucleophile like Y minus gives.

So, what we see over here is the fact that these strands X gets replaced by this nucleophile Y and this is because of the strong trans effect that this carbonic moiety is put here M equals chromium molybdenum tungsten X equals bromide chloride as well as iodide the same can be seen that if this reaction is treated by C 5 H 5 or cyclopentadienyl anion, then the product formed is eta 5 C 5 H 5 CO 2 MCR plus X minus plus 2 CO and what it says that even CO can be substituted in these carbine complexes usually CO is supposedly a very strongly bound to the transition metal because of the forward as well as the backward sigma relation.

But here is the instances where the carbonic moiety is bound even more strongly to the than the CO to the metal and as a result in this carbyne complexes even the Co; O gets substituted as shown in the reaction, Now carbyne complexes also undergoes nucleophilic attack this is similar to what we had encountered for carbenic complexes and here is an example of the same.

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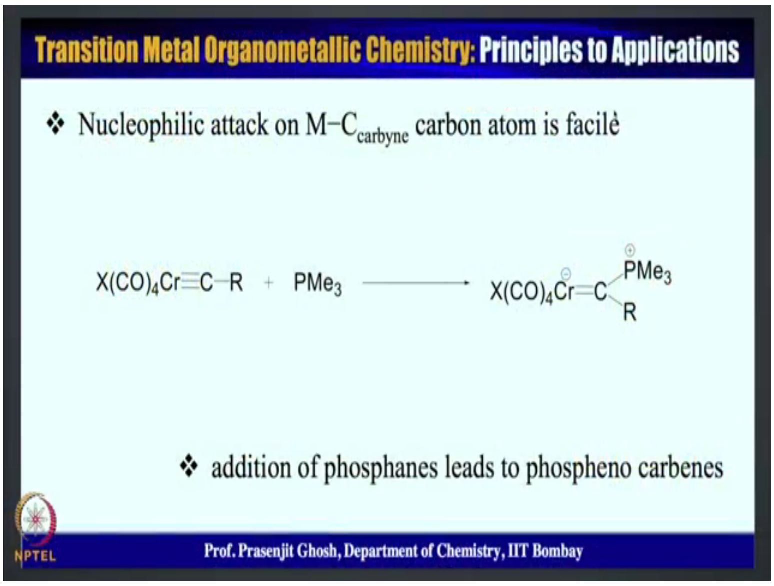

Transition Metal Organometallic Chemistry: Principles to Applications

- ❖ Nucleophilic attack on M–$C_{carbyne}$ carbon atom is facile

$$X(CO)_4Cr{\equiv}C{-}R + PMe_3 \longrightarrow X(CO)_4\overset{\ominus}{Cr}{=}C(\overset{\oplus}{P}Me_3)(R)$$

- ❖ addition of phosphanes leads to phospheno carbenes

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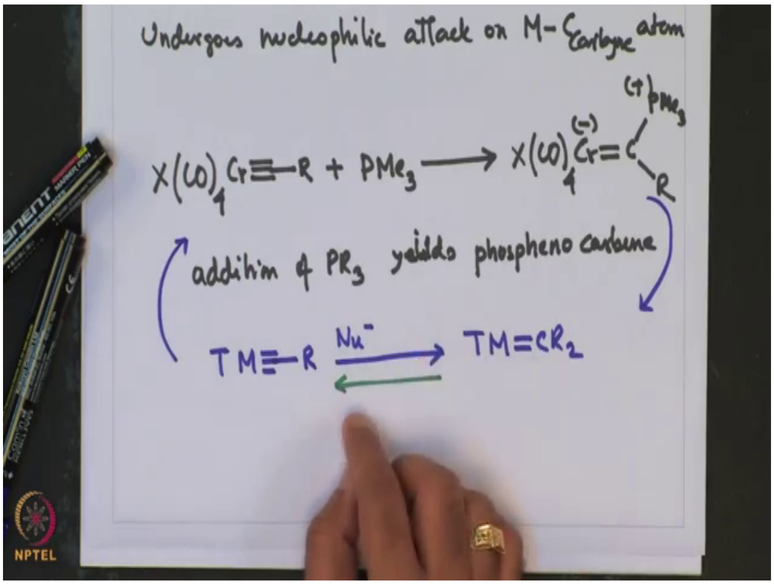

Undergoes nucleophilic attack on M-C carbyne atom

$X(CO)_4Cr\equiv R + PMe_3 \longrightarrow X(CO)_4\overset{(-)}{Cr}=C(\overset{(+)}{P}Me_3)R$

(addition of PR_3 yields phospheno carbene)

$TM\equiv R \underset{}{\overset{Nu^-}{\rightleftarrows}} TM=CR_2$

So, it undergoes nucleophilic attack at metal carbyne atom and this is represented by this equation plus PMe 3; the PMe 3 attacks the carbonic carbon to give XCO 4 chromium minus C PMe 3 plus R and this reaction is thus addition of phosphine yields phospheno carbene phospheno carbine.

Now, one thing what most we mentioned over here is that because of this nucleophilic attack the carbyne moiety is getting changed to a carbene moiety it. So, the complex which is a transition metal carbyne complex over here becomes transition metal carbene complex on going from here through nucleophilic attack and what is to be remembered over here that the reverse process of going from car carbene to carbyne was effectively used in synthesizing this transition metal carbyne complexes.

So, if we when we discussed the strategy for the synthesis of transition metal carbyne complexes, what we have seen that the most of the transition metal carbyne complexes were formed from the corresponding transition metal carbene complexes. Now, here we see that the cycle sort of repeating itself in terms of going back in the reverse direction where this transition metal carbyne complex is once formed when treated with nucleophile or undergoes a nucleophilic attack to give back to the transition metal carbene complexes.

So, what we see is a good amount of interchangeability between transition metal carbene and transition metal carbyne complexes and they have been favorably exploited not only for their synthesis, but also for their sub the reactivity studies as is shown in the slide below electrophilic reactivity of carbene is higher and I can be a seen in the example discussed below.

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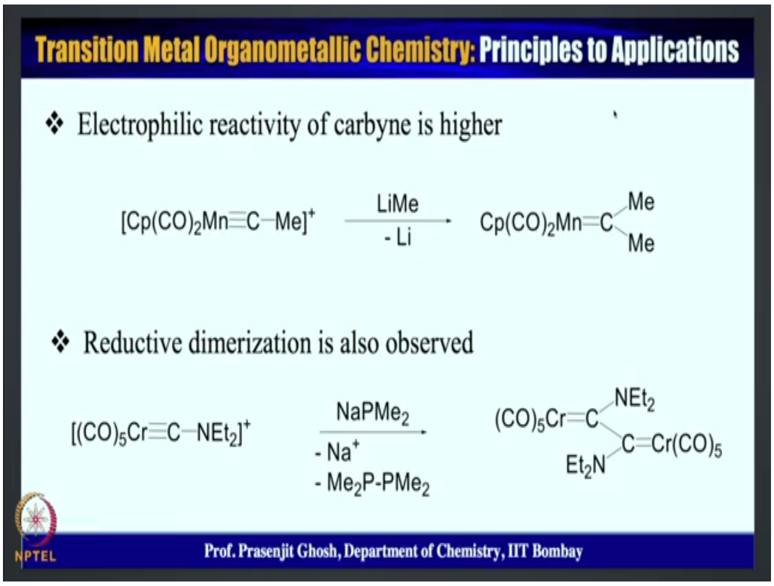

Transition Metal Organometallic Chemistry: Principles to Applications

- Electrophilic reactivity of carbyne is higher

$[Cp(CO)_2Mn{\equiv}C{-}Me]^+ \xrightarrow[-\,Li]{LiMe} Cp(CO)_2Mn{=}C(Me)_2$

- Reductive dimerization is also observed

$[(CO)_5Cr{\equiv}C{-}NEt_2]^+ \xrightarrow[-\,Na^+,\ -\,Me_2P\text{-}PMe_2]{NaPMe_2} (CO)_5Cr{=}C(NEt_2){-}C(NEt_2){=}Cr(CO)_5$

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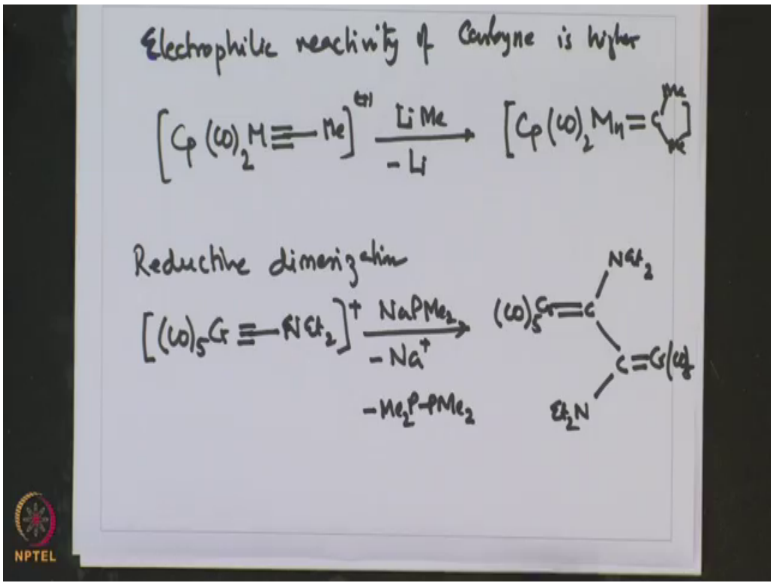

Electrophilic reactivity of Carbyne is higher

$[Cp(CO)_2M{\equiv}{-}Me]^{(+)} \xrightarrow[-\,Li]{LiMe} [Cp(CO)_2Mn{=}C(Me)_2]$

Reductive dimerization

$[(CO)_5Cr{\equiv}{-}NEt_2]^+ \xrightarrow[-\,Na^+,\ -\,Me_2P\text{-}PMe_2]{NaPMe_2} (CO)_5Cr{=}C(NEt_2){-}C(Et_2N){=}Cr(CO)_5$

For example, for this CP CO 2 Mnc methyl complex when treated with methyl lithium it gives lithium and reduces carbyne to a carbene complex.

So, what we see is that carbyne complexes upon reacting with the methyl lithium gives rise to these carbene complexes. So, here also we see such a carbynic moiety going back to carbonic moiety after the reactivity in the reactivity studies.

Similarly, another example is known of reductive dimerization and this can be seen for this chromium complex which in presence of Na P Me 2 eliminates sodium R plus eliminates Me 2 P Me 2 to give this carbene complex N Et 2. So, here what we see is that under these conditions the carbyne moiety sort of becomes carbonic moiety and then there is this dimerization happening to give this carbene a complex and hence this overall reaction is thus named as reductive dimerization reaction.

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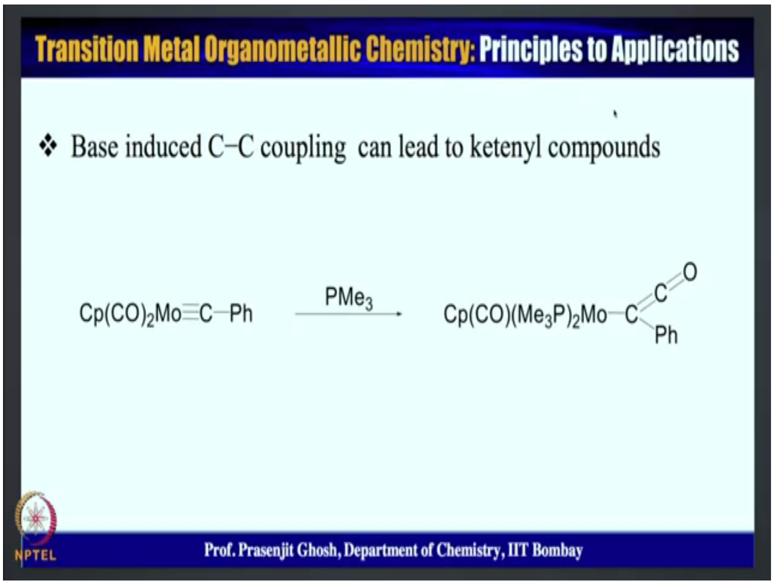

Transition Metal Organometallic Chemistry: Principles to Applications

- Base induced C–C coupling can lead to ketenyl compounds

$$Cp(CO)_2Mo\equiv C-Ph \xrightarrow{PMe_3} Cp(CO)(Me_3P)_2Mo-C(=C=O)Ph$$

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Here is another interesting example of induced C-C coupling observed for carbyne complexes.

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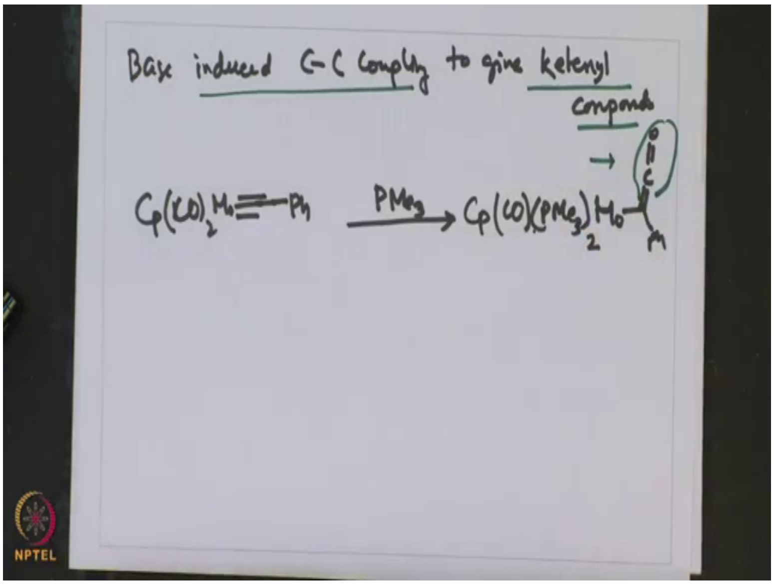

Base induced C–C Coupling to give ketenyl compounds

Coupling to give ketenyl compounds and this is explained through this example. So, molybdenum carbyne moiety when treated with PMe 3 have one of this CO migrated onto this carbyne moiety to give this to give this CO inserted into the carbyne fragment to give a ketenyl moiety. So, what we see that there is this induced base in this cc coupling resulting to give ketenyl compounds. So, which is these kind of species.

Now, with that let me conclude; what we have discussed in today's lecture particularly on carbine, we have looked into the metal ligand interaction using frontier molecular orbital diagram at the Schrock kind of carbene which is which has a quartered spin state we have also seen how these carbynic moiety interacts with that of the transition metal resulting in formation of 3 bonds a one metal ligand sigma bond one another metal ligand pi bond and another metal ligand pi bond.

With that we also discussed about the reactivity of transition metal carbyne complexes and what we have seen that the reactivity sort of mirrors the synth a synthesis of carbyne complexes, but in the opposite direction which is seen from the fact that much of the reactivity of transition metal carbyne complexes lead to the formation of transition metal carbene complexes and these transition metal carbene complexes were employed to synthesize synthes synthesize transition metal carbyne complexes.

So, what we see is that much of the reactivity of trans metal carbyne complexes lead to these transition metal carbene complexes we have seen these with respect to the nucleophilic addition of the anions to the transition metal carbyne complexes we have also seen trans effect of the ligand situated trans to this carbyne moiety getting substituted in the substitution reaction also we have seen the electrophilic reactivity towards of carbyne moiety towards regions like methyl lithium and finally, we have also seen dimerization of this transition metal carbyne complexes leading to the formation of these transition metal carbene complexes in this lecture.

So, with that I would like to conclude today's lecture and I will discuss some more of carbyne chemistry in the subsequent lecture until than the time goodbye and I hope to join with you in the next lecture.

Thank you.