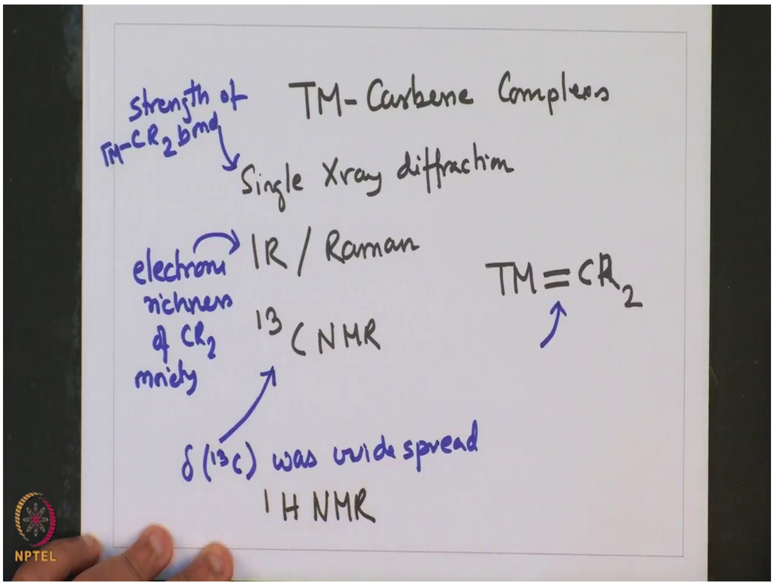
Transition Metal Organometallic Chemistry: Principles to Applications

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

Week - 07
Lecture - 35
Transition Metal Carbene Complexes: Reactivities

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. In our last lecture we were discussing about various characterization techniques that are employed for characterizing transition metal carbene complexes and in that regard what we had seen that various methods including that of x-ray diffraction as well as IR Raman and carbon 13 NMR were extensively used in characterizing transition metal carbene complexes.

(Refer Slide Time: 00:53)



TM-Carbene Complexes

strength of TM-CR_2 bond → Single Xray diffraction

electronic richness of CR_2 moiety → IR / Raman

$TM=CR_2$

^{13}C NMR

$\delta(^{13}C)$ was wide spread

^1H NMR

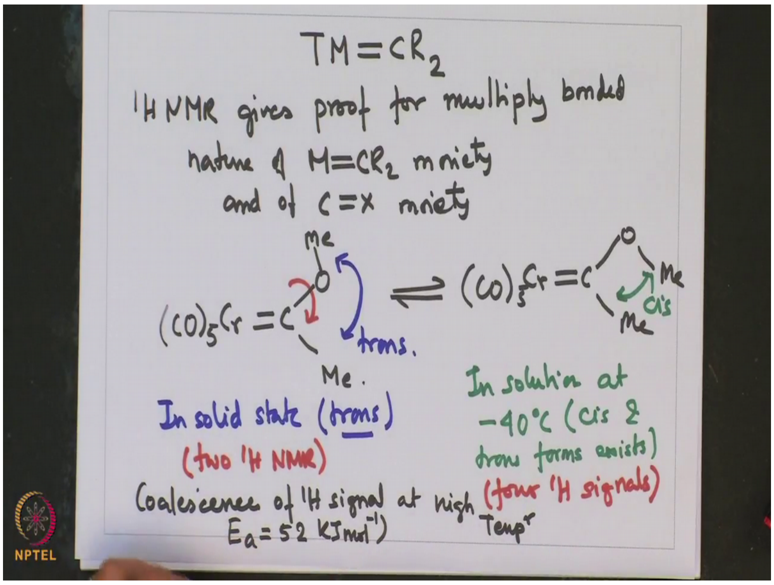
The techniques that we discussed in our last lecture was single crystal, x-ray diffraction, then IR Raman spectroscopy as well as 13 CNMR spectroscopy. And what we had seen that these techniques are extremely good at characterizing various transition metal carbene complexes of both types that is the Fischer and the rock types x-ray gives a clear idea as to the transition metal carbon bond length which would be a sort of multiply bonded and should have a very short distance we had seen that reflected in the transition car carbene bond lengths both in the Fischer type as well as the Schrock type

Similarly, the infrared Raman spectroscopy was used in quantifying the electron richness of the carbene centre by monitoring the stretching frequencies of the transient metal carbon which were trans to NHC ligands. So, these threw light on the electron richness electron richness of Cl 2 moiety bound to a transition metal the bond length and the x-ray similarly through gave ideas on the bond length on the strength of the Cl 2 bond like threw light on of CR 2 transition metal CR 2 bond that we had seen in terms of that being multiplied bonded and shorter bond length.

Similarly, we had also looked at the chemical shift in the carbon NMR which was widespread chemical shift of carbon NMR was widespread and that did not provide any indication as to the reactivity of the type of the carbines that are studied. So, of these 3 even though the carbon 13 could characterize these moieties, but they were they did not provide any insight onto what kind of reactivity these carbon moiety would exhibit depending on the chemical shift whereas, IR or Raman studies clearly he gave a method for quantification of the electron richness of the carbonic centre as well as x-ray diffraction study by looking at the metal carbon bond length we are also able to give insight as to the strength of this metal carbon bond as to with the multiple bonding nature of this metal carbon bond leading to it is greater strength.

Now, we are going to continue this discussion in bore bit more detail and we are going to look at another most powerful technique for characterization of this metal carbon moiety and that is from the perspective of proton NMR. Now, proton NMR is a very common ubiquitous tool that is used for characterization of all compounds and this is no different in case of organometallic compounds too. So, they provide a very useful and effective method for terrorizing these organometallic compounds and we are going to be discussing this the effective use of proton NMR are in providing insight onto the metal carbene moiety.

(Refer Slide Time: 05:36)



$TM=CR_2$

^1H NMR gives proof for multiply bonded nature of $M=CR_2$ moiety and of $C=X$ moiety

In solid state (trans)
(two ^1H NMR)

In solution at −40°C (cis & trans forms exists)
(four ^1H signals)

(Coalescence of ^1H signal at high Temp^r $E_a = 52\ kJmol^{-1}$)

So, this is from the perspective of how does proton NMR can be effectively used for characterizing metal carbene complexes. For example, proton NMR give the proof of multiple multiply bounded nature of middle carbon moiety as well as multiply model nature of C x double bond character. And the same can be seen from the proton NMR of official carbene complex particularly for pentacarbonyl chromium CO methyl, methyl.

Now, this geometry a is called a trans geometry, trans with respect to the two methyl and in the solid state is exclusively exist in the transform, transform prevail and as a result if one were to record proton NMR of these compounds. There are two methyl resonances, two types of methyl resonances, one is methyl, another is O Me and for O Me there is only a single resonance in the transform where as in solution this compound exists in the both sees and the transform and that equilibrium can be given as this. Now this is the cis form. So, in solution at minus 40 degree centigrade both cis and trans forms exist and as a result there are 4 proton NMR signals you know. So, resulting in 4 proton NMR signals to from the cis from and the two from the transform whereas, in the solid state where only transform exists that would exist exhibit only 2 proton NMR signals, if one were to record NMR of fate, but in solution the sort of inter interchange between cis and trans.

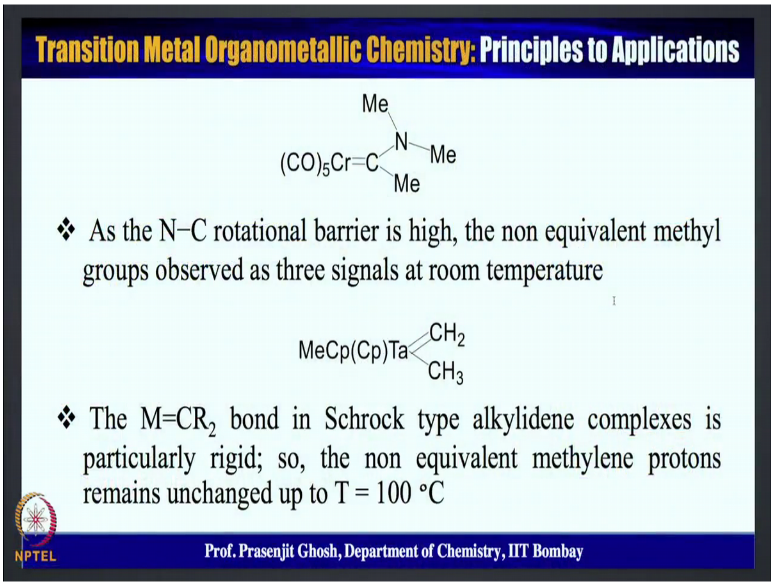
Now, this is a very important observation that in solid state you have only transformed exclusively whereas, in solution you have both the forms assistant trans. What does that imply is that implies that there is a rotation along the CO bond. Now, this rotation of the

CO bond would allow the inter conversion between cis trans and this rotation is supposedly quite fast because at minus 40 only you can see the inter conversion happening. So, this rotation happens at very fast a time scale and that is why you have to really go down a temperature of minus 40 to be able to slow the rate of conversion between the cis on the transform.

And higher temperature going to very rapid exchange coalescence is observed, coalescence of is observed at high temperature and one can sort of estimate the activation barrier for this exchange which is about 52 kilo Joule per mole for the rotation along the CO bond that for the rotation along CO bond. So, what it proton NMR, provides a useful insight in terms of the ability of the CO bond to rotate by looking at the spectroscopic signature and this is something which is unique to proton NMR spectroscopy and cannot be observed by other spectroscopic method that we had discussed in the last lecture.

So, let us sort of study this rotation in a bit more detail.

(Refer Slide Time: 12:14)



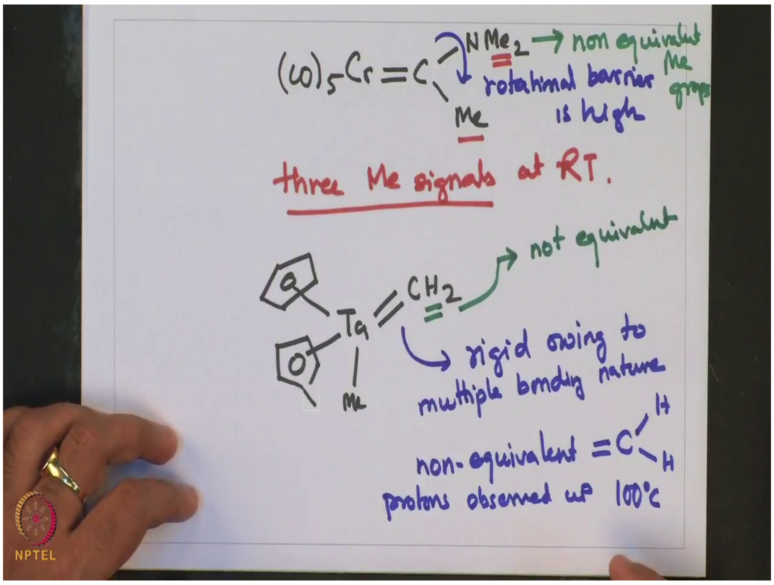
Transition Metal Organometallic Chemistry: Principles to Applications

- As the N–C rotational barrier is high, the non equivalent methyl groups observed as three signals at room temperature

- The M=CR$_2$ bond in Schrock type alkylidene complexes is particularly rigid; so, the non equivalent methylene protons remains unchanged up to T = 100 °C

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

(Refer Slide Time: 12:24)

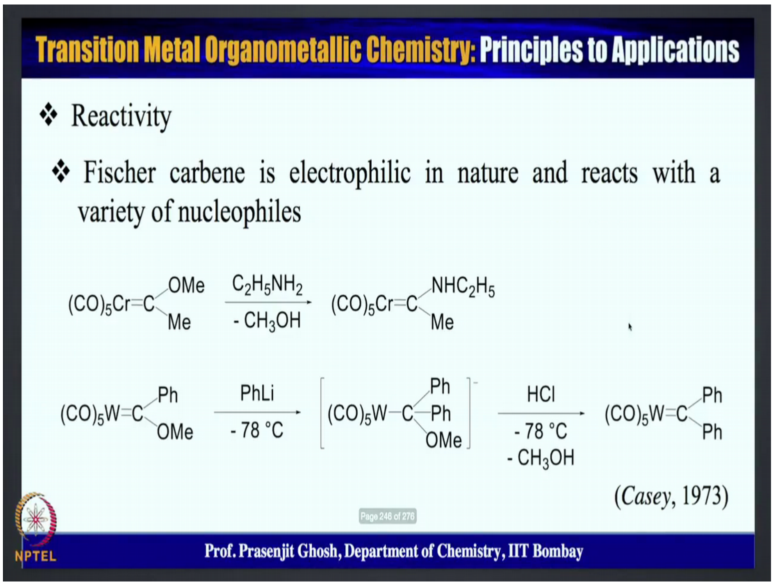


For example in the, my nitrogen an log variant of these feature carbine complex particularly where the rotation is not very fast for example, in this compound where pentacarbonyl chromium methyl with N Me 2 this rotational barrier is high and the rotation is that means, very slow, the rotational barrier. As a result these methyl groups are non equivalent and which gives rise to three a methyl signals at room temperature. So, these three comes from one of these and two of they and methyl all 3 are in equivalent because this rotational barrier is high and that leads to observation of 3 different signals at room temperature.

Now, what one sees is the fact that if the C heteroatom rotation barrier is increased then the non equivalent methyl groups or the protons show up and that results in equivalent spectrum that we observe. Now, in case of Schrock carbene for example, C p, tantalum, methyl, complex, now this C M CR 2 you is very rigid, this is rigid going to multiple bonding nature as a result non equivalent, non equivalence CH 2 protons observed up to 100 degree centigrade.

So, it shows that where there is multiple bonded carbene to tantalum the rotation is not really possible as a result these two hydrogens are in equivalent not equivalent and this can be observed from proton NMR and this non equivalency exist up to a very high temperature of 100 degree centigrade. So, what we are seeing, that proton NMR is providing some extremely useful insight about the dynamics of these carbene compounds in solution particularly with respect to the metal heteroatom rotation or with respect to the metal carbonic carbon rotation by looking at the equivalence or non equivalent nature of the substituent on the carbonic carbon or of that on the hetero atom.

(Refer Slide Time: 17:07)



Transition Metal Organometallic Chemistry: Principles to Applications

❖ Reactivity

❖ Fischer carbene is electrophilic in nature and reacts with a variety of nucleophiles

$$(CO)_5Cr{=}C(OMe)(Me) \xrightarrow[-\,CH_3OH]{C_2H_5NH_2} (CO)_5Cr{=}C(NHC_2H_5)(Me)$$

$$(CO)_5W{=}C(Ph)(OMe) \xrightarrow[-\,78\ ^\circ C]{PhLi} \left[(CO)_5W{-}C(Ph)(Ph)(OMe)\right]^- \xrightarrow[-\,78\ ^\circ C,\ -\,CH_3OH]{HCl} (CO)_5W{=}C(Ph)(Ph)$$

(*Casey*, 1973)

Page 248 of 276

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

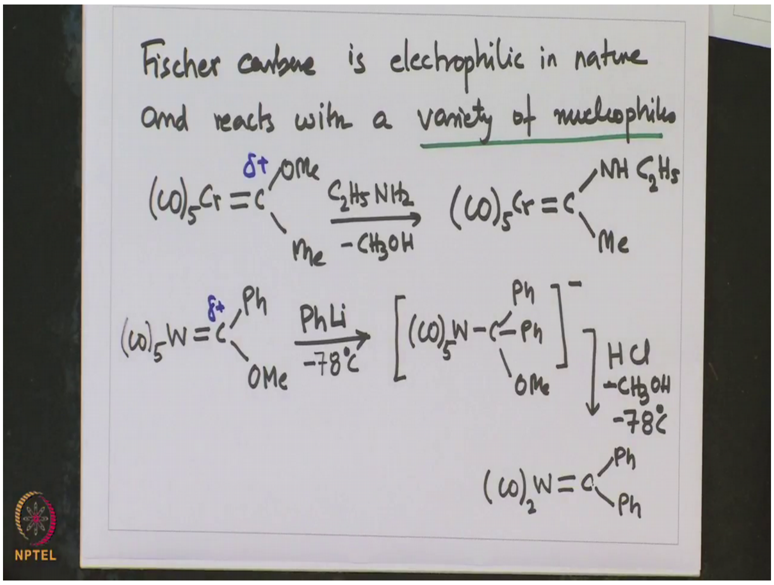
So, these he provides a very useful a method for getting an insight on the dynamics of these metal transition metal organometallic complexes using proton NMR spectroscopy. Now, with that we are going to move on to another important aspect of transition metal organometallic carbene chemistry and this is with regard to reactivity of transition metal carbene complexes.

Now, as mentioned in our previous discussion that transition metal carbene complexes can be classified into two types Fischer carbene as well as the Shrock carbenes, and both of these carbons have metal carbene multiple bonding character and however, their interaction with the metal is different. For example, for Fischer carbene it is a singlet carbenes species which interact with the transient metal whereas, for the Schrock carbene our triplet carbene explicit interact with the transient metal using the same or similar metal to ligand and ligand to metal kind of bonding.

Now, our analysis of transition metal carbene interaction we had seen that going to this type of metal ligand ligand metal type of bonding that occurs for singlet Fischer carbene as well as for triplet Shrock carbene, there is a significant amount of the difference in reactivity observed for these complexes and the kind of behave in a very different fashion because of the different reactivity that arise because of their different way of interacting with the transition metal.

Now in this few minutes now, we are going to look at some of the examples of differential reactivity that this Fischer and Shrock carbene exhibited.

(Refer Slide Time: 19:05)



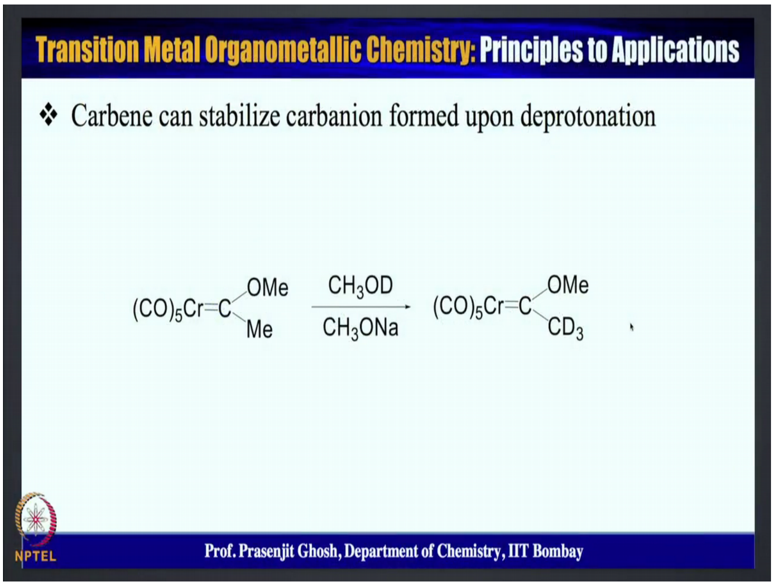
Fischer carbene is electrophilic in nature and reacts with a variety of nucleophiles

For example, Fischer carbine is electrophilic in nature and reacts with a variety of nucleophiles. For example, for this chromium CO Me methyl reacting with C 2 H 5 NH 2, gives methanol particularly from the amine protonating the omethoxy and then give this corresponding C NHC 2 H 5 a carbene complex. So, what we see over here that you omethoxy has been protonated by this amine to release methanol and these complex of the Fischer carbene is observed.

Similarly other nucleophile like phenyl lithium also works reaction analogue is for example, for this pentacarbonyl tungsten C Ph O Me complex reacting with phenyl lithium at minus 78 degree centigrade undergoes the attack of the final moiety onto the positive carbon side to give the transition state. Something like pentacarbonyl tungsten C Ph Ph Ph minus which in presence of acid eliminates methanol at very low temperature of minus 78 degree centigrade to give the following tungsten C Ph Ph carbene complex.

Now, what is important to remember over here is that the Fischer carbine reacts with a variety of nucleophile and that this attack arises from the carbonic centre being partially a positively charged and that is because of the carbene to metal sigma rotation cannot be matched by metal to carbene pi back donation. As a result there is always a positive charge on the carbene which is the reason for the nucleophile attacking the carbonic centre. So, this is a very important feature of Fischer carbene that because of the bonding and the way it shows that the carbon is slightly positively charged and that allows it to reacts with variety of nucleophiles the way it is shown over here.

(Refer Slide Time: 23:36)



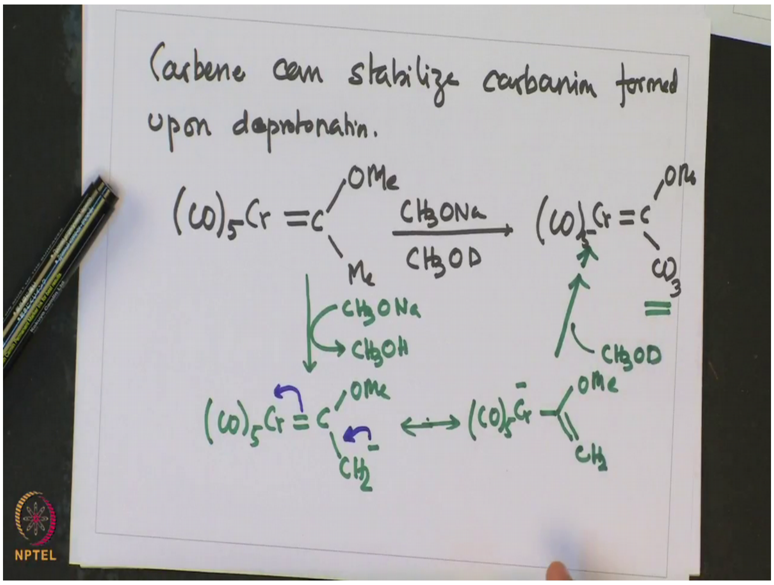
Transition Metal Organometallic Chemistry: Principles to Applications

- ❖ Carbene can stabilize carbanion formed upon deprotonation

$$(CO)_5Cr{=}C(OMe)(Me) \xrightarrow[CH_3ONa]{CH_3OD} (CO)_5Cr{=}C(OMe)(CD_3)$$

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

(Refer Slide Time: 23:42)



Carbene can stabilize carbanion formed upon deprotonation.

Similarly, carbenes can stabilize carbanions carbonion formed upon deprotonation. Now, this is illustrated by very nice example over here CO 5 chromium CO Me methyl, in presence of base CH 3 O Na and deuterated methanol CH 3 O D.

What is observed that formation of CO 5 chromium CO Me C D 3 is formed which indicates that there is accumulation of deuterium at this methyl moiety and that happens because this methyl gets deprotonated to make a carbonion which is stabilized by the carbene moiety. For example, in presence of a base this methyl gets deprotonated to give ethanol and the corresponding carbonion. This carbonion is there stabilized by resonance to in this canonical form and these when treated with CH 3 O D, protonates the are puts deuterium on this methyl moiety a an after several such species it gives C D O 3. So, what we have done is that the carbon ion which is formed by the protonation of the methyl moiety is stabilized by the carbene and that is because of the electron deficient nature of the carbonic carbon.

Now, let me summarize what has been taught in this lecture. We have looked at proton NMR as a useful characterization technique to gain insight in the carbon metal complexes, particularly that provides insight into carbon metal bond rotation as well as CO carbon atom bond rotation, and leading to different kind of resonances equivalency and non equivalency of resonances, leading to different kind of see saw transforms of the carbonic structure. We have will also looked at differential reactivity arising from the nature of charge accumulated on the carbonic carbon for Fischer and the carbene Schrock carbene complexes. And for the Fischer one we had looked at the nucleophilic addition at the carbonic centre with various nucleophile and also we have seen that Fischer carbene can stabilize carbon ions forms upon deprotonation and this was proved using isotopic experiment where C is the accumulation protonix proton little in exchange in form of the example a given over here.

So, with this I conclude this lecture on characterizations of transition metal carbene complexes and we are going to discuss more about the reactivity of transition metal carbene complexes in the forthcoming lecture which will deal about differential reactivity of both Fischer and Shrock carbene complexes. So, till that time goodbye and I look forward to seeing you in the next lecture.

Thank you.