Transition Metal Organometallic Chemistry: Principles to Applications
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Lecture - 34
Transition Metal Carbene Complexes: Reactivities

Welcome to this lecture on transition metal organometallic chemistry from principles to applications, in the last few lectures we have been discussing an important topic particularly that of transition metal carbene complexes their properties, their synthesis and their structural characterization. In this context, we have learned that there are two classes of this type of transition metal carbene complexes, they are mainly called the Fischer Carbene as well as Schrock Carbene.

We have also looked into various synthetic strategies that have been employed in preparing these two carbene complexes, mainly the Fischer Carbene as well as the Schrock Carbenes.

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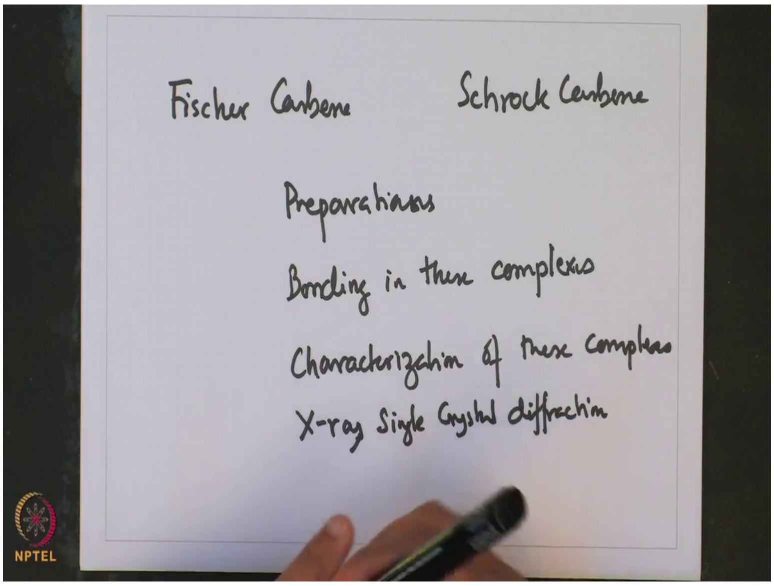

Fischer Carbene Schrock Carbene

Preparations

Bonding in these complexes

Characterization of these complexes

X-ray Single Crystal diffraction

We have looked into their preparations, we have also looked into the metal carbene reaction, the bonding in these complexes with regard to bonding, we mean the interaction of the carbonic moiety with that of the transition metal, and how these leads to different kind of reactivity for these two types of carbene complexes, we have also looked into structural characterization or characterization of these complexes, and this we had discussed particularly with respect to X-ray single crystal diffraction studies of these kind of complexes.

So, this has been the sort of the topic that we had discussed in our previous lecture. And in this today's lecture we are going to elaborate these characterization methods as well as reactivity of transition metal carbene complexes, in continuation with our previous discussion on structural characterization of an Fischer Carbene complex, whose structural parameters were discussed in the previous lecture. We are going to now take up one example of structurally characterized example of a Schrock Carbene complexes, and see how they compare with that of the earlier discussed Fischer Carbene complex, says in terms of their structural integrity and other parameters.

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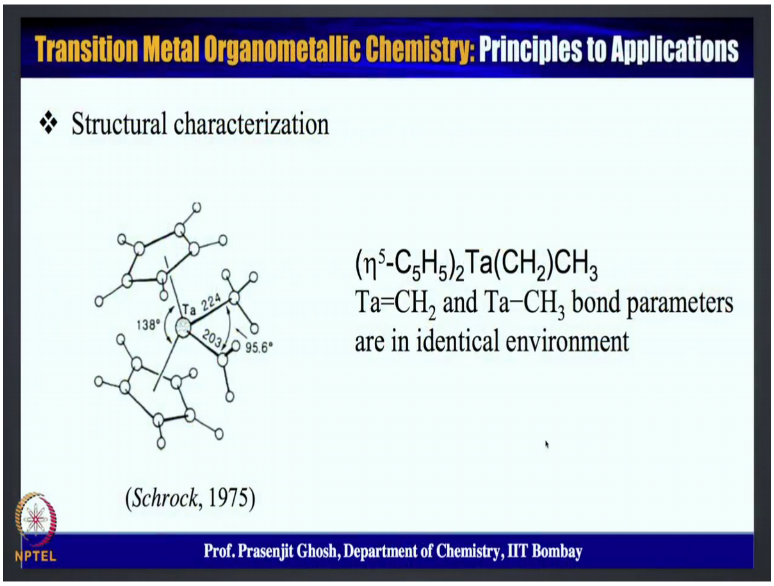

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- Structural characterization

$(\eta^5\text{-}C_5H_5)_2Ta(CH_2)CH_3$

$Ta{=}CH_2$ and $Ta{-}CH_3$ bond parameters are in identical environment

(*Schrock*, 1975)

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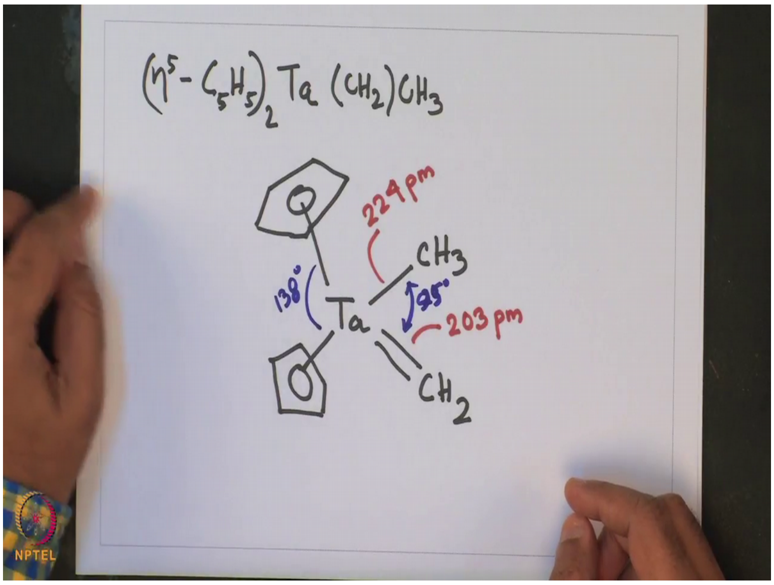

So, with this let us take a look at a structurally characterized Schrock Carbene complex. Particularly that of transition metal TCP CH2 CH3 and the structure of this molecule is tantalum bound to two cyclopentadienyl ligand with methyl moiety and carbonic moiety.

So, these compound contains a titanium carbon single bond as well as titanium carbon double bond, and as a result that is obvious from the bond distances distantly a methyl bond is much longer at 224 pico meter whereas, because of its multiple bonding nature this titanium carbene bond is way shorter at 203 pico meter, and the angle over here is, the angle between the two CPM and the retina tantalum is 138 degrees whereas, between the two titanium carbon bonds this is about 95 degrees.

So obviously, it can be same that X ray is extremely good technique for differentiating the bond that exists between tantalum and the carbon of a methyl moiety, as well as that over titanium carbene of a carbonic moiety and it shows that, because of the multiple bond in nature tantalum carbene bond is infinitely shorter, than that of the tantalum methyl single bond and that can be easily distinguished by using X ray diffraction technique.

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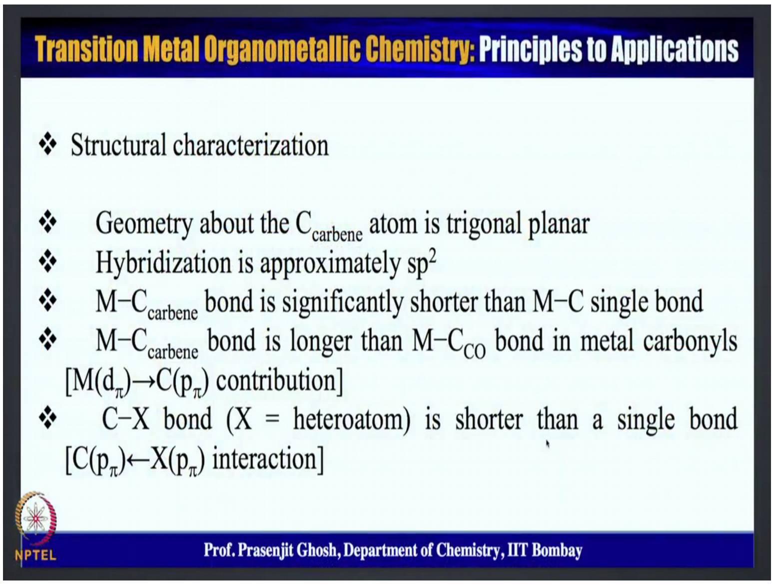

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- Structural characterization
- Geometry about the $C_{carbene}$ atom is trigonal planar
- Hybridization is approximately sp^2
- $M-C_{carbene}$ bond is significantly shorter than M–C single bond
- $M-C_{carbene}$ bond is longer than $M-C_{CO}$ bond in metal carbonyls $[M(d_\pi)\rightarrow C(p_\pi)$ contribution$]$
- C–X bond (X = heteroatom) is shorter than a single bond $[C(p_\pi)\leftarrow X(p_\pi)$ interaction$]$

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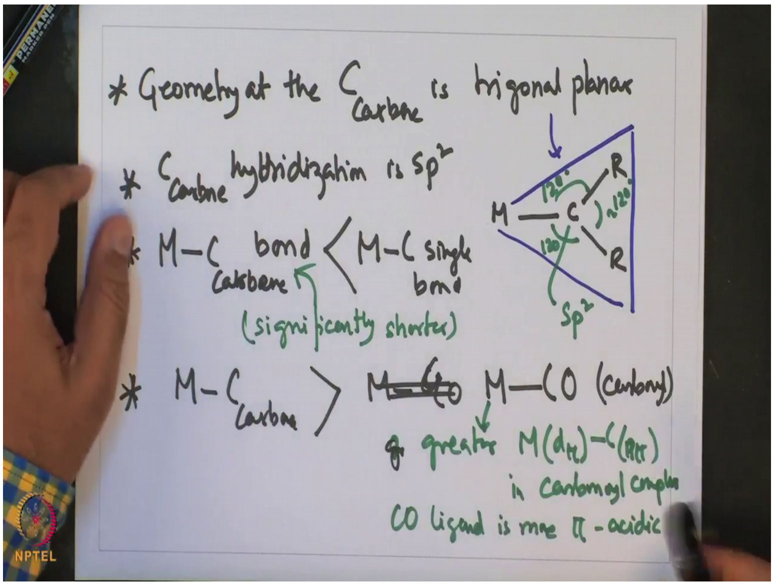

* Geometry at the $C_{carbene}$ is trigonal planar

* $C_{carbene}$ hybridization is sp^2

* $M-C_{carbene}$ bond $<$ M–C single bond

(significantly shorter)

* $M-C_{carbene}$ $>$ ~~M–CO~~ M–CO (carbonyl)

∵ greater $M(d_\pi)-C(p_\pi)$ in carbonyl complex

CO ligand is more π-acidic

Now, we are going to look at like the some of the general characterizations, think that can be obtained through structural characterization and what one sees is that this geometry about the carbon centre is trigonal planar at the C carbene is trigonal planar, which means that the metal and the carbene and the two sub streams on the carbon, they all lie in a same plane in a displaying a trigonal planar geometry, also from the metrical data what one establishes is that the hybridization of carbon is approximately sp2 carbene hybridization is sp2 type so; that means, that this carbonic center is sp2 and these bond angles are somewhat about 120 degrees.

Now, in our earlier example of a Fischer Carbene complex what we saw, that these metal carbene alkyl substituent, these bonds have expanded from 120 degrees to somewhat 128 or 130 degrees and as a result this, alkyl carbene alkyl bond has contracted from the ideal value of 120 to about 110 degrees. So, what we see that, these being sp2 centre ideally should be 120 degrees, but in specific examples, they may open up from the more ideal value of 120 a to about 130 degrees.

Whereas, the alkyl CR angle in turn may sort of become smaller the middle as observed in our earlier example. Schrock Carbene example, where there was simultaneous presence of a metal carbene single bond, as well as metal carbene bond multiple bond and what we saw that, metal carbine M C carbene bond is significantly shorter than metal carbene single bond and that is significantly shorter.

So, that is something that, we had seen and that arises because of metal carbene bond, being multiple bonded in nature as going to the presence of carbon to metals sigma bond, as well as metal to carbon back bonding in nature. Also, in our last example, we had seen that with respect to carbon monoxide metal C carbene bond is longer then metal CO bond carbonyl bond, as a result of greater metal d pi to C pi interaction in carbonyl complex.

So, what we saw that, going to greater pi acidic nature of the CO ligand is, more pi acidic. What we saw that, going to greater pi acidic nature of the CO ligand, that the metal back donates more to the empty pi star orbital of CO, as a result this metal carbon bond carbonyl metal carbon bond of metal carbonyl compounds are very shorter than, that of the metal carbon bond because, here the back donation is not as acute as that in metal carbonyl complex.

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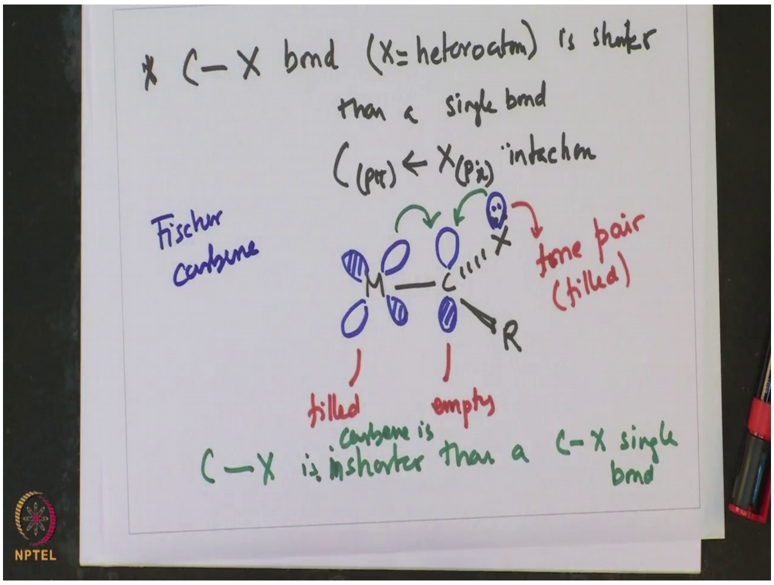

* C – X bond (X = heteroatom) is shorter than a single bond

$C_{(p\pi)} \leftarrow X_{(p\pi)}$ interaction

C – X is carbene is shorter than a C – X single bond

Also, for a Fischer Carbene, what was seen from the structural characterization data is that, the C-X bond where, X is an heteroatom is shorter than single bond, and this was because of C pi to X pi to C pi interaction. And what we see that the carbene centre is stabilized by the metal orbital, and this can be explained by in this diagram. Where we have let us say heteroatom attached to a carbene and the heteroatom is in has a the lone pair, and then there is this empty orbital on the carbine and that can interact this is empty and this is the lone pair they are so filled and this is filled.

So, these empty orbital can be stabilized by electron donation from the metal, as well as from the heteroatom lone pair as a result this C-X bond as a result the C-X bond, because of this interaction is shorter than C-X single bond in carbene is shorter, because of this stabilization our conjugation of it is lone pair onto the we can p c orbital of the carbene centre resulting in multiple bonding character between the C-X bond, as a result it becomes shorter than there are forcing X single bond distance and this is mainly observed in case of Fischer Carbene complexes.

So, overall what comes out that a lot of information can be obtained from structural data using single crystal X diffraction studies, particularly looking at various bond lengths and bond distances of the metal with the carbon or the heteroatom with that of the carbon and that gives one and the extent of relative interaction that is prevalent in each of these moieties. So, these X ray this is a very good parameter for obtaining an understanding of the interaction prevalent in these classes of compounds.

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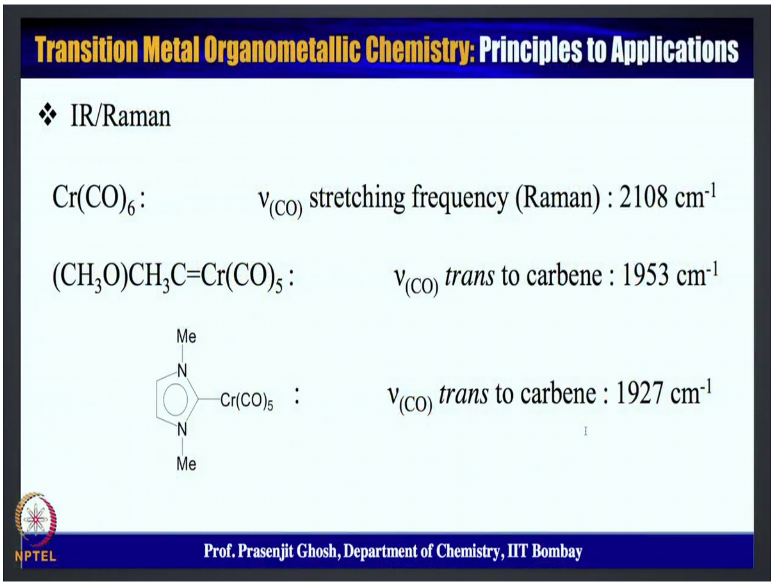

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- IR/Raman

$Cr(CO)_6$: $\nu_{(CO)}$ stretching frequency (Raman) : 2108 cm^{-1}

$(CH_3O)CH_3C{=}Cr(CO)_5$: $\nu_{(CO)}$ *trans* to carbene : 1953 cm^{-1}

: $\nu_{(CO)}$ *trans* to carbene : 1927 cm^{-1}

NPTEL

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So, now we will see that, other then X ray for example, other spectroscopic techniques like IR or Raman is also useful in understanding these metal carbene interaction and particularly this is prominent in carbonyl complexes, which shows a lot of variation in metal carbonyl stretching frequency of switching frequencies, as a result of back donation from the metal and I am going to illustrate this with an example showing the change in CO stretching frequencies, as a result of back donation from the metal centre to the CO and how that can provide input on to the electronic nature of these carbene complexes.

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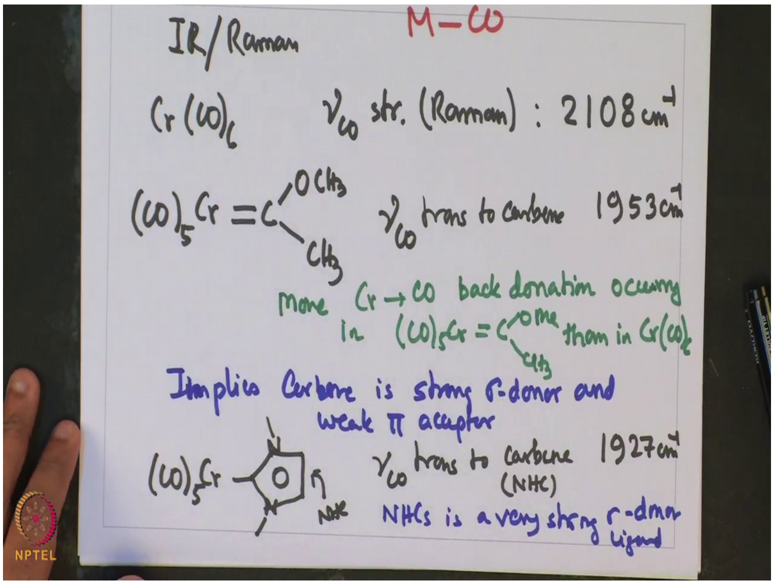

IR/Raman

M–CO

$Cr(CO)_6$ ν_{CO} str. (Raman) : 2108 cm^{-1}

$(CO)_5Cr=C(OCH_3)(CH_3)$ ν_{CO} trans to carbene 1953 cm^{-1}

more $Cr \rightarrow CO$ back donation occuring in $(CO)_5Cr=C(OMe)(CH_3)$ than in $Cr(CO)_6$

Implies Carbene is strong σ-donor and weak π acceptor

$(CO)_5Cr$ ν_{CO} trans to carbene (NHC) 1927 cm^{-1}

NHC

NHCs is a very strong σ-donor ligand

So, for example, very useful data can be obtained using IR or Raman spectroscopy for example, for chromium hexacarbonyl nu CO stretching frequency, this being a symmetrical molecule one is one can only observe in Raman, which is 2108 centimetre inverse whereas, for the nu CO trans to carbene appear at 1953 centimetre inverse suggesting, that there is more electron donation from chromium to carbonyl in this compound, then in this suggesting more chromium to carbonyl back donation occurring in Cr CO me CH3 then in Cr CO6.

So, that shows that carbine is a very weakly pi acidic and strongly a sigma donating ligand, implies carbene is strong sigma donor and weak pi acceptor. And when one moves from Fischer Carbene to n heterocyclic carbene complexes of the structure CO5Cr having 2 nitrogen and methyl then nu CO trans to carbine, these carbenes are called NHC this is called NHC.

So, nu trans to carbene he appears even down at war energy at 27 centimeter inverse, this implies that NHC is a very strong sigma donor ligand and more with extremely poor by accepting nature. So, what it shows, that how the metal carbonyl frequencies shift as a result of this metal to carbonyl back donation that appear in complexes, where their carbene is a ligand along colicataral and along with metal carbonyls for example, in this chromium Fischer Carbene carbonyl complex the carbonyl trans to chromium show a stretching frequency at a much lower energy, as a result of strong chromium to carbonyl interaction which arises because, of electron donating nature of the carbene moiety.

Now, as one goes from future carbon onto n heterocyclic carbine, which is even more electron donating as compared to the Fischer carbine, as a result the metal carbonyl interaction gets even more stronger resulting in much lower nu CO stretching frequency at around 1927 centimeter inverse. So, this mixed carbonyl carbon complexes provide a good handle at looking at the extent of electron donation, that occur between carbon and the metal centre, and as well as the CO ligand carbon monoxide and provides a useful tool for quantification of electron richness of this carbine, by looking at a series of this kind of complexes a good illustration of such electron donation occur in metal carbonyl complexes having CO ligands as carbenes is shown in the example discussed here.

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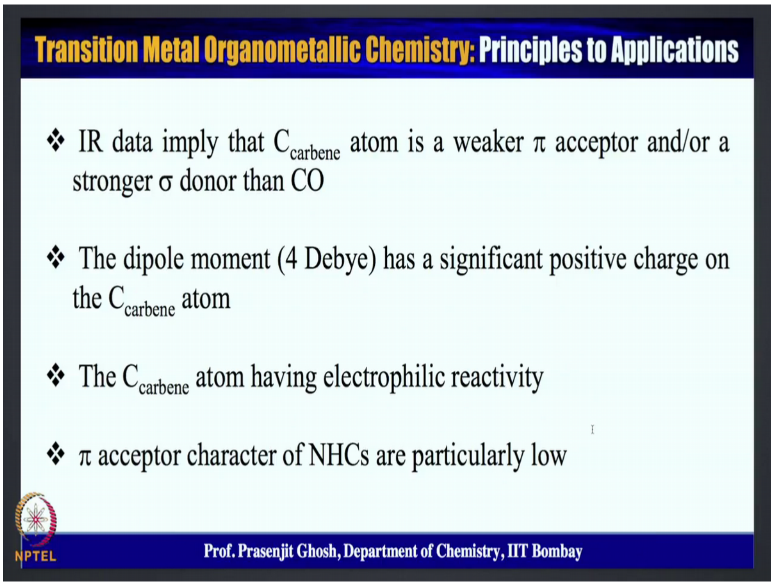

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- IR data imply that $C_{carbene}$ atom is a weaker π acceptor and/or a stronger σ donor than CO
- The dipole moment (4 Debye) has a significant positive charge on the $C_{carbene}$ atom
- The $C_{carbene}$ atom having electrophilic reactivity
- π acceptor character of NHCs are particularly low

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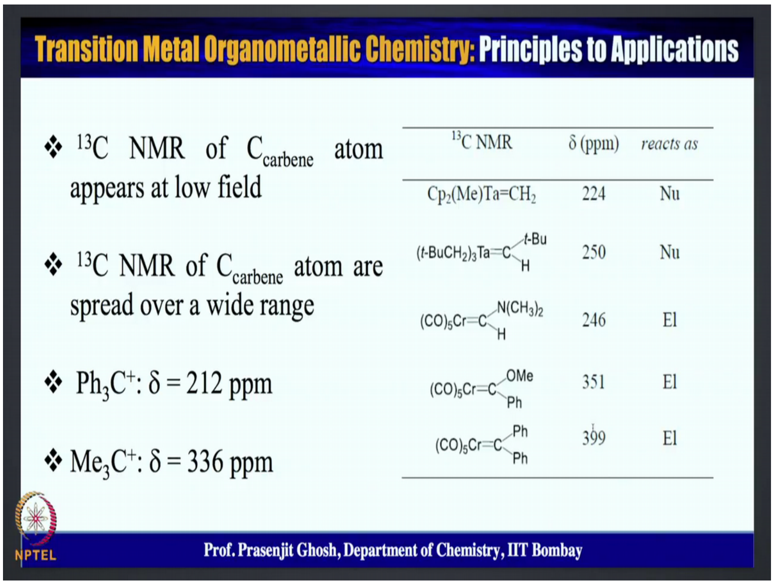

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- ❖ ^{13}C NMR of $C_{carbene}$ atom appears at low field
- ❖ ^{13}C NMR of $C_{carbene}$ atom are spread over a wide range
- ❖ Ph_3C^+: $\delta = 212$ ppm
- ❖ Me_3C^+: $\delta = 336$ ppm

^{13}C NMR	δ (ppm)	*reacts as*
$Cp_2(Me)Ta{=}CH_2$	224	Nu
$(t\text{-}BuCH_2)_3Ta{=}C(t\text{-}Bu)(H)$	250	Nu
$(CO)_5Cr{=}C(N(CH_3)_2)(H)$	246	El
$(CO)_5Cr{=}C(OMe)(Ph)$	351	El
$(CO)_5Cr{=}C(Ph)(Ph)$	399	El

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Now, thus IR provides a very good example of how these can be used to gain insight into the pi acceptor and simulating in nature of these ligands. The apart from IR carbon NMR is also a very useful method, where one can look at the chemical shift and then try to guess at the type of reactivity, that they can show and what is obvious from here, that these metal carbine resonance spread over huge range and that one cannot; obviously, a sort of distinguish their reactivity by just by looking at the chemical shift.

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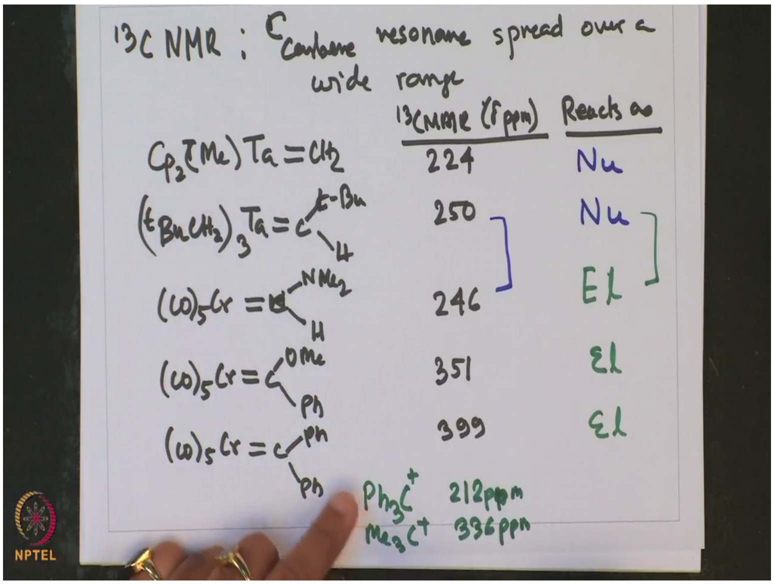

^{13}C NMR : $C_{carbene}$ resonance spread over a wide range

	^{13}C NMR (δ ppm)	Reacts as
$Cp_2(Me)Ta{=}CH_2$	224	Nu
$(tBuCH_2)_3Ta{=}C(t\text{-}Bu)(H)$	250	Nu
$(CO)_5Cr{=}C(NMe_2)(H)$	246	El
$(CO)_5Cr{=}C(OMe)(Ph)$	351	El
$(CO)_5Cr{=}C(Ph)(Ph)$	399	El

Ph_3C^+ 212ppm

Me_3C^+ 336ppm

So, in 13CNMR the C carbene resonance spread over a wide range and for example, one can sort of see that for Cp2 methyl tantalum CH2 13CNMR del ppm this is arise that 224 whereas, for another Schrock type of compound t butyl CH2 whole three tantalum C t butyl hydrogen this comes at 250, and then CO5 chromium carbene hydrogen NME2 is the Fischer Carbene this as 246 ppm, chromium five CO5 chromium C ph OMe this comes at 351 ppm, CO five chromium C p h 399 ppm and one when one looks at the reactivity reacts as the there is no correlation as two kind of reactivity that is disclosed for example, display for example, this Schrock carbine having a chemical shift of 224 ppm in carbon reacts as a nucleophile whereas, the tantalum one which also has some are very close chemical shift of about 250 reacts as a nucleophile whereas, this Fischer carbene which is also exactly a similar chemical shift behaves completely different and reacts as an electrophile, and this another Fischer type carbene showing at appearing at very high carbonic resonance of 351 also behaves like an electrophile, to that of chromium carbonyl appearing 399 also if there is a electrophile.

So, what we see what kind of one can conclude that the carbonic moiety appear in a wide range from 220 to about 400 ppm, and they can appear and any of this range and it is very difficult to predict the reactivity just based on the chemical shift carbon resonance, because we can have Fischer Carbene or Schrock Carbene showing almost near equal chemical shift, but showing extremely opposite reactivity.

So, this is consistent with the fact that the carbon resonance are indeed vary a lot for example, for the tridel cation CH3 plus, that this del is 212 ppm and for a methyl m e three plus this is 336 ppm. So, even for this cation going from the methyl to phenol substituents, there is a huge the difference in chemical shift.

So, from the carbon characterization one can say that, even though the carbene moiety has been characterized, but any attempt to draw correlation based on the on their chemical shifts on the reactivity of these complexes may not be useful because, there may be carbene complexes which has comparable chemical shift, but probably a equally opposite kind of reactivity as can be seen from this Schrock and the Fischer carbene complexes, which behave totally different and leave to each other.

So, with this let me conclude today’s discussion, we have looked at various characterization or methods that are often used for characterizing metal carbon complexes, in this regard we studied the lecture by looking at structural characterization of Schrock carbene complex, and looked at how the metrical data can indicate towards the kind of interaction that is prevalent between the carbonic moiety and the metal centre having looked into that, we have also looked at other forms of characterization which provides insights into the metal carbene interaction and that included IR or Raman spectroscopy where, we saw that how (Refer Time: 30:03) complexes of transition metal carbonic moiety and carbonyls can be used to quantify the extent of electron donation the carbine offer onto the metal centre by looking at the metal carbonyl stretching frequencies and how that can be made a useful tool for analyzing at the electron richness of the in the carbene ligands, that are bound to the metal centre from the examples that, we have discussed we have also seen that carbenes are predominantly sigma donor with very little pi acceptance ability, and that when a carbene moiety is attached to a metal carbonyl complexes, the metal becomes more electron rich and as a result of the metal carbonyl bond trans to the carbene moiety shows CO stretching at a much lower energy arising, because of the more metal to metal carbonyl back donation interaction.

We have also discussed about carbon characterizing thirteen characterization of carbonic moiety, and what we have seen that and these carbonic resonance can appear in a wide spread range of chemical shift, and that it is not useful for characterizing their reactivity directly with their carbon thirteen n m r resonance.

So, with that let me conclude today’s lecture, we are going to be discussing carbene a bit more details, as these are very important molecules having a lot of applications in chemical catalysis, and I also has been recognized by the nobel award in 2010 for olefin metathesis. So, a lot more of carbene and more insightful discussion in the next lecture in in terms of their propertivity, and reactivity that we will look up that is going to come up in the next lecture.

With that I thank you for being with me, and I look forward to being with you in next lecture, good bye.