Transition Metal Organometallic Chemistry: Principles to Applications
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Week - 08
Lecture – 38
Transition Metal Carbenes: Preparation

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. We have been covering an a very important topic in this lecture, the last two lectures that is about transition metal carbene complexes.

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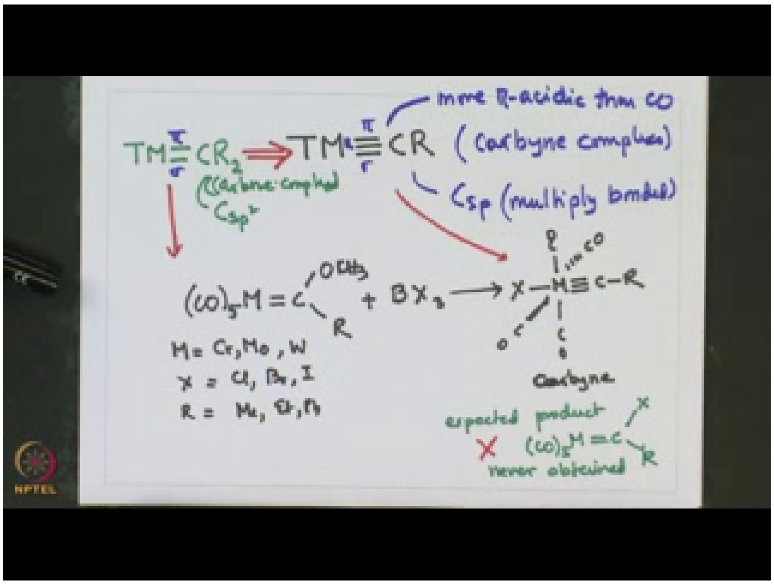

These transition metal carbene complexes or transition metal bonded to CR moiety where the carbon is sp hybridized and multiply bonded. So, as a result there exist 2 type, 3 types of bond between the transition metal and the carbene moiety which is sigma pi and pi type interactions these are called carbene complexes.

Now, carbene complexes are sort of an extension of transition metal carbene complexes which we had discussed in our earlier lecture where transition metal is bonded to a carbene moiety and where the carbene carbon is C sp 2 hybridized and these are called carbene complexes and here too there is a multiple bond that exists between the carbene and the transition metal which is a sigma and as well as pi a bond.

So, we see that transition metal carbene complexes are somewhat an extension of transition metal carbene complexes and however, their properties are strikingly different and that we are going to sort of take a look and study them in more details. For example, transition metal carbene complexes more pi acidic, more pi acidic then for usually a very pi acidic called co, these are more pi acidic than carbene complexes whereas, carbene complexes are not as a pie acidic as carbon monoxides. So, we see that even though they there is these are sort of related to that of carbene complexes; however, their properties are supposedly very different.

Now, in regard to this we have looked into various preparative methods that are prevalent for transition metal carbene complexes. And the first and the foremost method was a serendipity is discovery for the synthesis of carbene complexes that sort of started off from transition metal from a Fischer carbene complex which is over here, reactation with BX 3 reagent, where M equals chromium molybdenum tungsten, X equals chlorine bromine iodine, R equals methyl ethyl and phenyl, which can treated with that yielded the carbene complex which is X this is the carbene complex instead of complex which was initially thought that it would give and that expected product was R which was never obtained.

Now, if we sort of analyze this development of the synthesis of the carbene complexes what comes into for this carbene complex was in indeed obtained from a carbene complex. So, the first method which is a serendipitous discovery for making the carbene complex was indeed initiated from the carbene complex which got transformed to the carbene complex. So, that is a important observation because what it says that you already have a multiple bonded carbon transition metal framework in place and then if you find another mechanism of forming an additional multiple bond then you will end up in making metal carbene complex. So, this is sort of something which emerges out of this serendipitous discovery of making carbene from Fischer carbene complex.

So, with this background we are going to take a look at some other synthetic roots which have been explored and figured out for synthesis of transition metal carbene complexes and look at those preparative details with respect to what we had already covered for transition metal carbene complexes and draw a parallel between these two class of complexes in terms of the synthesis strategies that are in place for making them.

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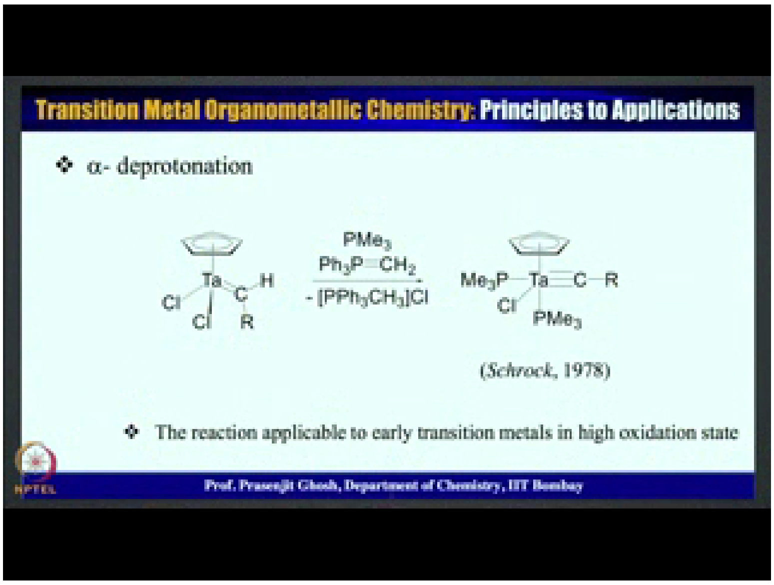

Transition Metal Organometallic Chemistry: Principles to Applications

- α- deprotonation

(*Schrock*, 1978)

- The reaction applicable to early transition metals in high oxidation state

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Similar to what we had seen for in making transition metal carbene complexes that alpha deprotonation provides an efficient method for synthesizing transition metal carbene complexes.

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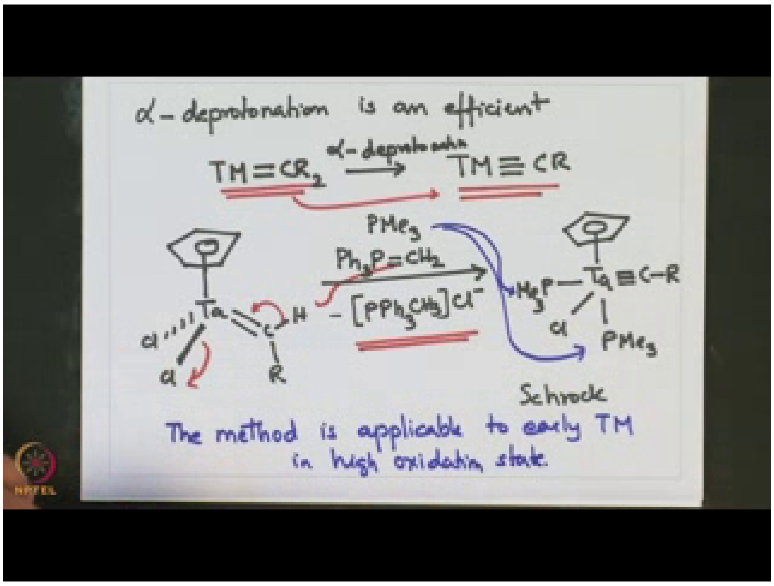

α- deprotonation is an efficient

$TM=CR_2 \xrightarrow{\alpha\text{-deprotonation}} TM\equiv CR$

Schrock

The method is applicable to early TM in high oxidation state.

So, alpha deprotonation is an efficient synthesis efficient method for synthesizing transition metal carbene complexes and here too we see that the transition metal carbene complexes have been synthesized from the corresponding transition metal, carbene complexes by alpha deprotonation.

So, let me provide an example of the same. So, here is this carbene complex of tantalum. So, this when reacts with PMe 3 with triphenyl phosphene CH 2, so what happens is that these proton gets deprotonated and then it produces this PPh 3 CH 3 cation and chlorine anion which is eliminated this chlorine anion is eliminated from here. So, basically these PPh 3 CH 2 abstracts this proton with the elimination of the chloride to give this PPh 3 CH 3 chloride salt and along with that carbene complex is a carbene complex as a form as shown over here. And the role of PMe 3 relies in the filling of the coordination sphere which remains vacant because of elimination of the chloride and formation of the carbene complexes.

So, it sort of forms dative bond in whatever vacant site that is produced. This was again a method which was originally reported by Schrock way back in 1978. So, like the Fischer who himself had reported synthesis for Fischer carbene to as well as Fischer carbene similarly Schrock to had his own synthesis available for making Schrock carbene as well as Schrock carbene complexes. And here also we see the parallel existence of similar strategy that we find that the carbene mighty is formed from the carbene moiety. So, like the Fischer synthesis of treating Fischer carbene with Lewis acids like BX 3 resulted in carbine.

Similarly, a the Schrock strategy of taking Schrock carbene and treating that with PPh 3 a double bond CH 2 in presence of PMe 3 yielded the Schrock carbene. So, this method is applicable to early transition metal in high oxidation state. So, it is also to be noted that alpha deprotonation technique was also available for preparing carbine transition metal carbene complexes and the way it is also available to make transition metal carbene complexes.

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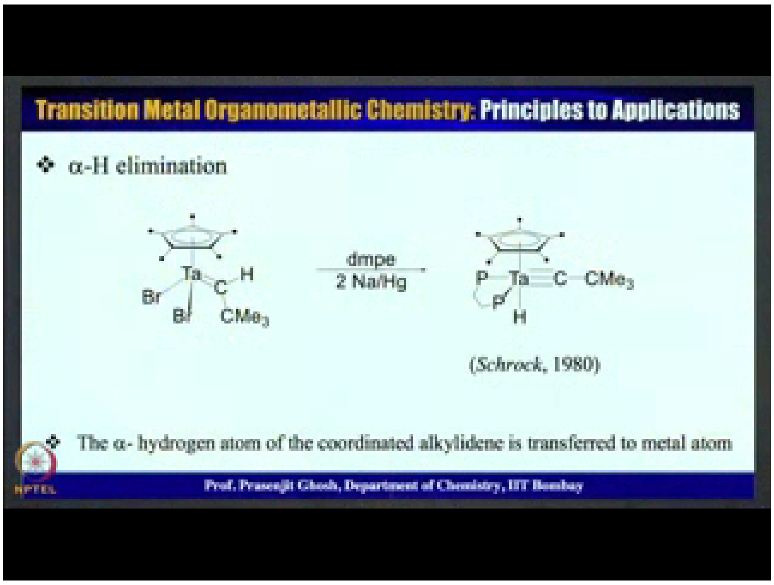

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❖ α-H elimination

(*Schrock*, 1980)

❖ The α- hydrogen atom of the coordinated alkylidene is transferred to metal atom

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Similar to or on the foot of alpha deprotonation alpha elimination, also is an effective method for producing carbene complexes an effective method, for producing alpha carbene complexes.

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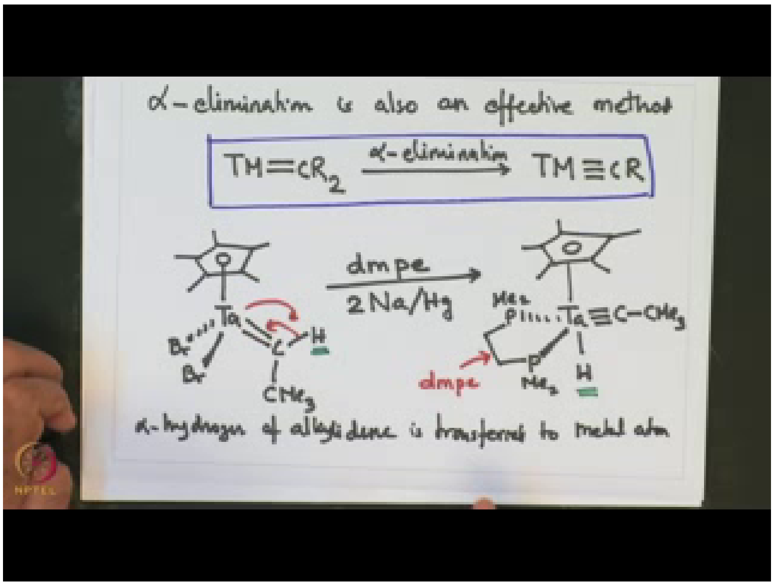

α-elimination is also an effective method

$\mathrm{TM{=}CR_2} \xrightarrow{\alpha\text{-elimination}} \mathrm{TM{\equiv}CR}$

α-hydrogen of alkylidene is transferred to metal atom

And here too we see that this method is applied to carbene complexes elimination applied to carbene complexes to get what is called transition metal carbene complexes.

So, here is an example of the same when cp star tantalum C CMe 3 reacted with dmpe in presence of sodium amalgam which is reducing agent alpha elimination of this hydride, the alpha elimination of this hydride happens to a give this dimethyl phosphine ethan carbene complexes of the cp star began which is tantalum hydride. So, what happens is that these hydrogen sort of alpha eliminates to give this triple bond and tantalum hydride complex and dmpe, e is replaces the two bromide atom to kiltie and use the suitable vacant spaces which have been created by this. So, this is a very interesting method for obtaining carbene complexes. Here also what we see that alpha elimination has been achieved on a carbene complex to result in the formation of the carbene complex.

So, in this process the alpha hydrogen of alkylidene which is alpha hydrogen of alkylidene is transferred to metal atom which is tantalum. So, for this alpha elimination is also an effective method for synthesis carbene complexes and what we see that the same can be used for synthesizing a carbene complex and this can has been achieved on a transition metal carbene complex. So, of the 3 strategies so far that we have seen for preparing the carbene complexes all use a transition metal carbene as a precursor and depending on the various methods it app they apply a transition metal carbene complexes have been formed.

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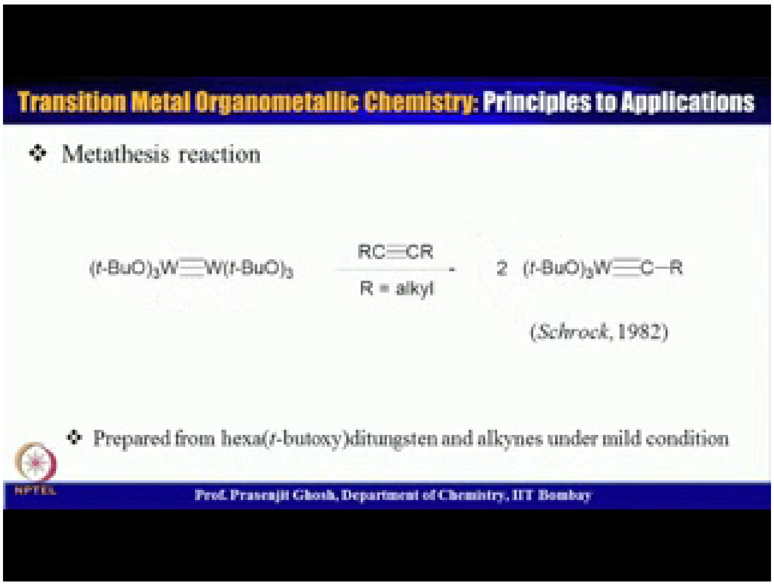

Transition Metal Organometallic Chemistry: Principles to Applications

- Metathesis reaction

$$(t\text{-BuO})_3W\equiv W(t\text{-BuO})_3 \xrightarrow[R\ =\ \text{alkyl}]{RC\equiv CR} 2\ (t\text{-BuO})_3W\equiv C-R$$

(*Schrock*, 1982)

- Prepared from hexa(*t*-butoxy)ditungsten and alkynes under mild condition

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So, let us take a look at some other examples that are prevalent for making these carbene complexes and one interesting reaction which we are going to talk about right now is this metathesis reaction.

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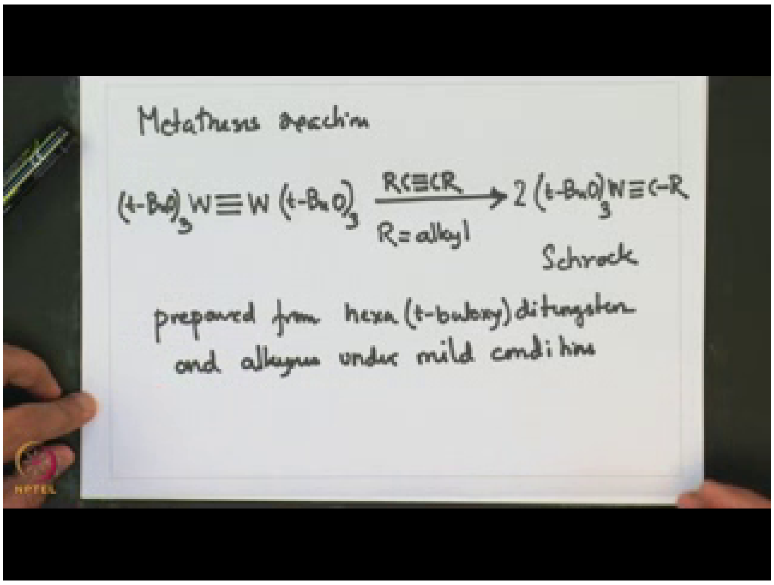

Metathesis reaction

$$(t\text{-BuO})_3W\equiv W(t\text{-BuO})_3 \xrightarrow[R=\text{alkyl}]{RC\equiv CR} 2\,(t\text{-BuO})_3W\equiv C\text{-}R$$

Schrock

prepared from hexa (t-butoxy) ditungsten
and alkynes under mild conditions

Now, this metathesis reaction is strikingly different it is strikingly different from other 3 strategies that we have discussed by the fact that it does not start from a transition metal carbene mighty to construct the transition metal carbene mighty. So, the starting precursor for this metathesis reaction is completely different and it starts with these metal metal triple bond and converts them to metal carbon triple bond in transition metal alkyne moiety.

So, the example of this reaction involves tungsten t butoxide whole 3, whole 3 that reacts with an alkynes, where R is an alkyl to give 2 of whole 3 C R and this reaction was also discovered by Schrock and that speaks volumes of about Schrock's ability to synthesize these carbene complexes by more than one method. And the first one was by alpha deprotonation and the next one is by metathesis reactions. So, in that way Schrock was kind of ingenious in creating metal ligand multiple bonded compounds particularly transition metal carbene complexes. And this reaction was prepared at under very mild condition from hexa t butoxide ditungsten and alkynes under mild conditions.

So, this reflects on the genius of that Schrock walls you know he could find to more than one methods, at least two methods that we have seen for preparing this transition metal carbene complexes which are extremely difficult to prepare.

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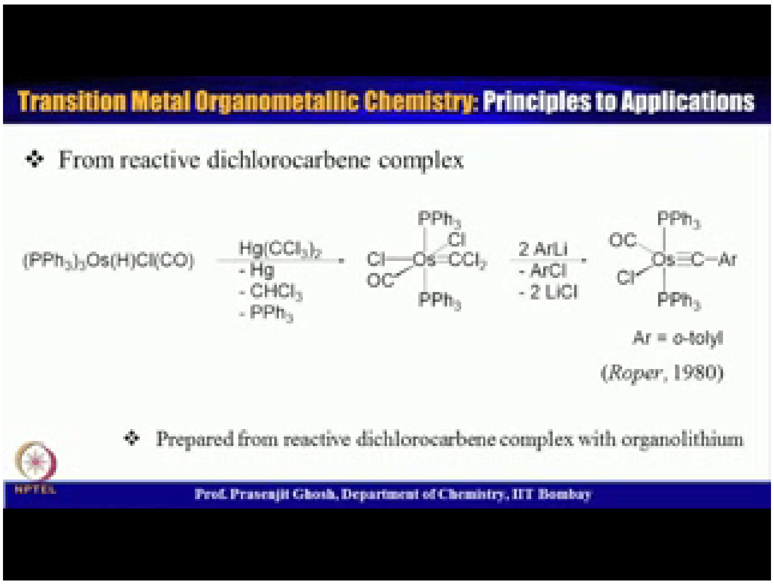

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- From reactive dichlorocarbene complex

Ar = o-tolyl

(*Roper*, 1980)

- Prepared from reactive dichlorocarbene complex with organolithium

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So, there are other methods which also produces carbene and this one is from reactive dichlorocarbene complex.

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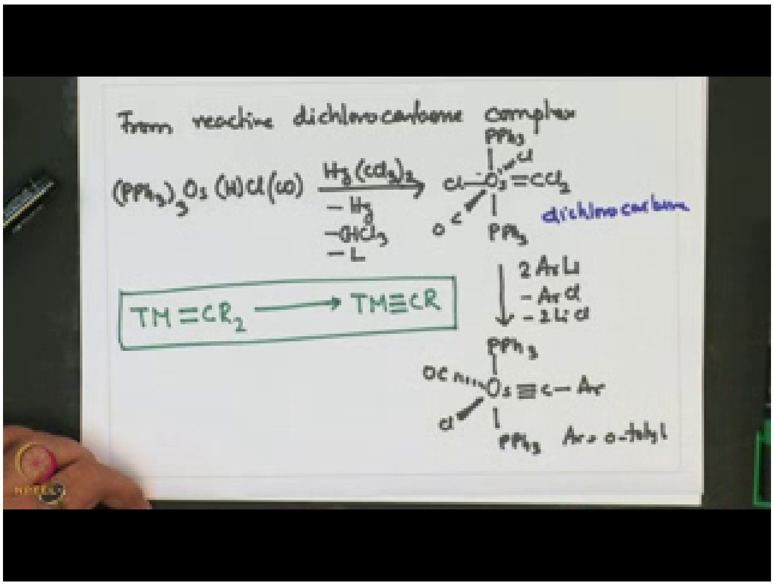

From reactive dichlorocarbene complex

So, reaction of PPh 3 osmium hydride chloride and CO with hg CCl 3 whole 2 with the that elimination hg CHCl 3 and PPh 3 gives this osmium dichlorocarbene PPh 3, Ph 3 that reacts with 2 Ar lithium. So, this is this dichlorocarbene that reacts with 2 Ar lithium by giving aryl chloride and 2 lithium chloride gives this osmium c Ar PPh 3, Ph 3 chloride CO where Ar equaled ortho tolyl.

So, what one says that these dichlorocarbene complex when treated with aryl chloride gives the carbene complex here two what one finds that this is a strategy that implies the earlier method of constructing the transition metal carbene complex on a transition metal carbene complex. So, this reaction is in tune with the other earlier examples that we have been we have discussed at the beginning of this lecture and this is a one that acts highly reactive dichlorocarbene species with aryl lithium.

Transition metal carbene complexes we have we reviewed some of the methods that which are used for preparing these complexes now as for the characterization of this carbene complexes are concerned they are mainly done by various spectroscopic techniques as we had seen in case of the carbenes like NMR, proton and carbon NMR so on and so forth.

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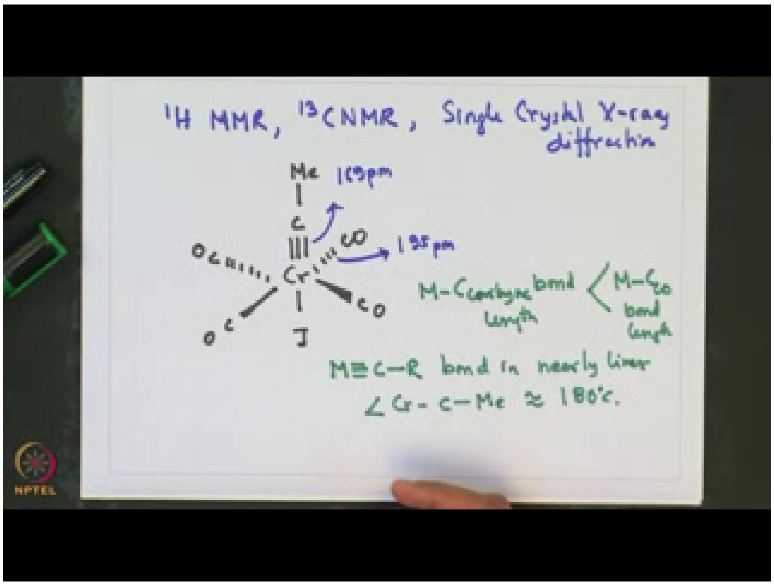

^{1}H NMR, ^{13}C NMR, Single Crystal X-ray diffraction

$M-C_{carbyne}$ bond length $< M-C_{CO}$ bond length

$M\equiv C-R$ bond in nearly liner

$\angle Cr-C-Me \approx 180°c.$

As well as by single crystal X-ray diffraction studies as with the most of the characterization methods X-ray being extremely powerful this has also been used successfully in stabilizing or structurally characterized in many such carbene complexes to gain insight into the nature of bonding that exists between the mill carbene complexes.

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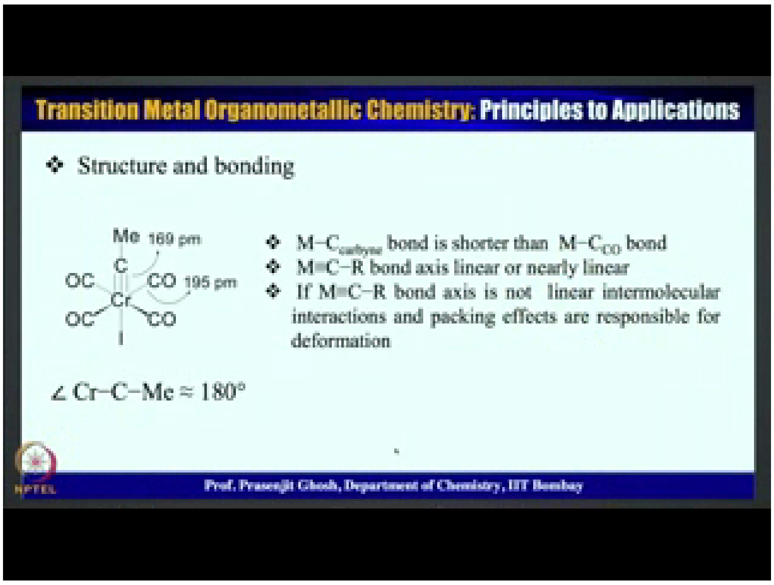

Transition Metal Organometallic Chemistry: Principles to Applications

- Structure and bonding

$\angle$ Cr–C–Me ≈ 180°

- M–$C_{carbyne}$ bond is shorter than M–C_{CO} bond
- M≡C–R bond axis linear or nearly linear
- If M≡C–R bond axis is not linear intermolecular interactions and packing effects are responsible for deformation

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So, here is a structurally characterized example for chromium carbene complex where this metal carbene carbon bond is very short at about 169 picometer whereas, this chromium carbonyl carbon is a very long as compared to this at 195 picometer. So, what is striking is over here that metal C carbene bond length is shorter than metal C CO bond length. The other which is the fallout of sp a natural hybridization of the carbon the metal C R bond is nearly linear.

In this case the chromium C methyl angle is approximately 180 degree centigrade. And sometimes it may so happen therefore, certain metal carbene complexes this M C R bond may not be linear, but that is not due to other reason, but for the fact that many intermolecular interactions like packing effects are res sometime responsible for such a deformation observed little carbene alkyl bond angle.

So, with that let me conclude what we have discussed in today's lecture. We started off by looking at various synthetic preparative methods that were available for synthesizing this important, metal carbene complexes and these methods as most of them are probably all, but one of them involved synthesizing this carbene fragment on from metal carbene for fragments. So, all of this method that we have been looked at involved the initiating species as metal carbene on which by applying certain strategies like alpha deprotonation, alpha elimination, as well as treated it with Lewis acids, as well as by nucleophile like phenyl lithium one could generate this metal carbene complexes. We have also seen that other than this generation of preparation of carbene from metal carbene fragment the only other method that directly prepares metal carbene fragment by other routes involves this metathesis approach where metal metal bond when treated with alkyne results in metal carbene complexes.

Incidentally what is important, what is kind of coincidental is the fact that Fischer prepared not only his method for, not only his carbene complexes, but could successfully a developed method for preparing the corresponding Fischer carbene complexes, similarly a drawing the analogy Schrock not only could come up with synthesis of a method for Schrock carbene complexes, but also could extend the method to prepares his own Schrock carbene complexes. So, these two people develop their own metal carbon double bond as well as metal carbon triple bond routes. And like in metal carbene case metal carbene compounds are also character have been characterized or can be characterized with various spectroscopic techniques including X-ray and we have looked at one such structural character example of chromium tetra carbonyl, methyl carbene and iodide where we saw that transition metal carbine, carbene bond is even shorter than transition metal carbonyl moiety and that the angle at carbene carbon is linear going to sp hybridized a nature of the carbonic carbon moiety.

So, with this I would like to conclude today's lecture and in next lecture I am going to take up the characterization of transition metal carbene complexes in more details and their corresponding reactivity and property study. We are going to look at the orbital interaction involved between the carbene moiety and the transition metal in these complexes in the next lecture. So, till then goodbye. I look forward to being with you in the next lecture.

Thank you.