Transition Metal Organometallic Chemistry: Principles to Applications

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

Lecture - 37

Reactivity of Schrock type Carbene Complexes and Transition Metal Carbynes

Welcome to this lecture on transition metal organometallic chemistry from principles to applications, over the last few lectures we have been discussing important topic, particularly an important class of transition metal organometallic chemistry these are mainly that of transition metal carbene complexes.

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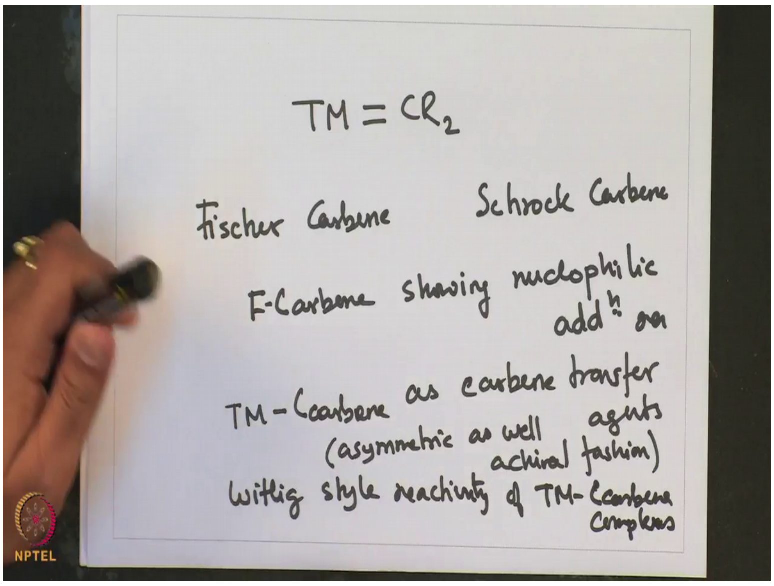

$TM = CR_2$

Fischer Carbene   Schrock Carbene

F-Carbene showing nucleophilic add^n on

TM-Ccarbene as carbene transfer agents
(asymmetric as well achiral fashion)

Wittig style reactivity of TM-Ccarbene complexes

Now, in the last lecture we have looked into reactivity of transition metal carbene complexes, and particularly what we had seen is that there is a difference in the activity that is shown by Fischer carbene complexes, as well as the 1 that is shown by schrock carbene complexes. And in the previous lecture we are also seen the application aspects of this kind of transition metal carbene complexes.

That started by looking at this nucleophilic addition, reactions for Fischer type carbenes. Fischer carbene showing nucleophilic additions, reaction we have also seen these carbene complexes, showing carbon transition metal carbene complexes use as carbene transfer agents..

As carbene transfer agents, and this has been done both asymmetric, as well as achiral fashion. Substitutes mainly for this have been olefins, we have also looked at Wittig style reactivity of these transition metal carbine complexes, and we also had seen utility of transition metal carbene complexes.

In benzene aromatic reactions, where they a are used for where are producing aromatic rings when reacted with alkyne. Now we are going to look into this discussion from the schrock carbene perspective, because as the Fischer carbene was showing in nucleophilic addition reactions, schrock carbene show electrophilic reactions and that we are going to study that in bit more or detail.

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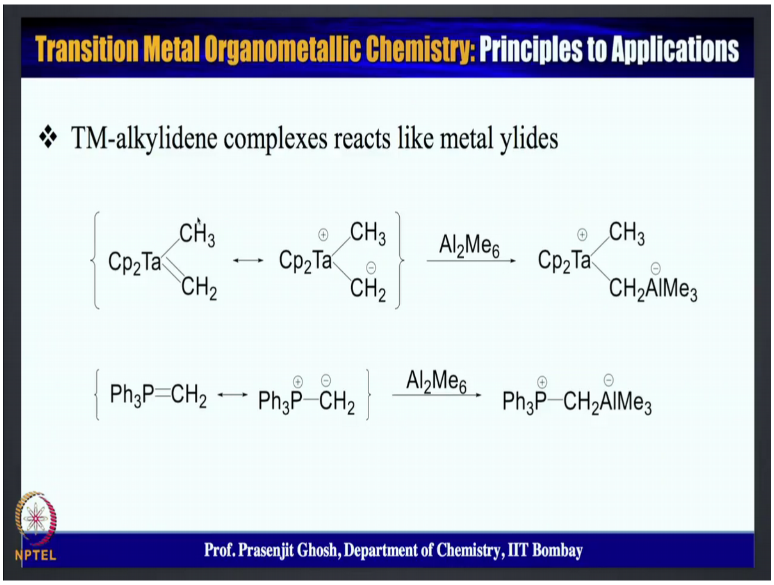

Transition Metal Organometallic Chemistry: Principles to Applications

- TM-alkylidene complexes reacts like metal ylides

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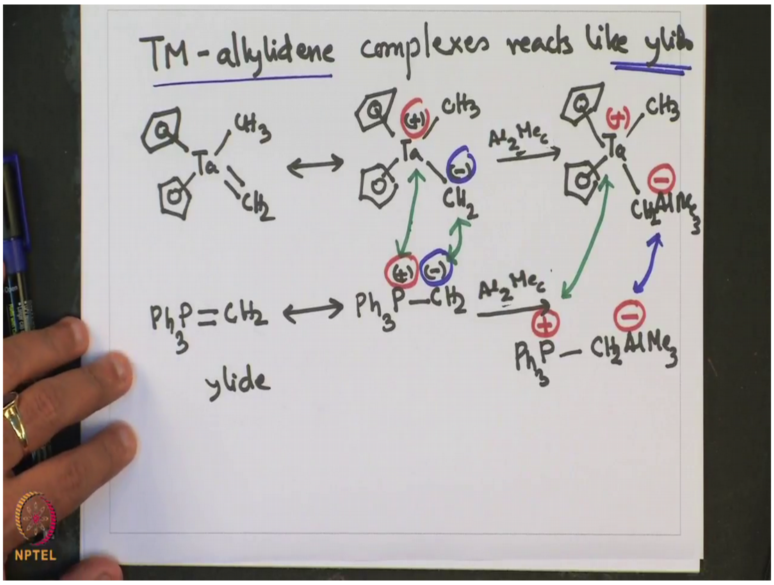

In this lecture, now transition metal carbene complexes usually react like metal ylids. Like ylids for example, ylid let say phosphorus, ylid is given by the formula CH 2, and that has a resonance form of P plus CH 2 minus. Now similarly, the same can be conceived of schrock carbenes..

For example, tantalum pre cyclo pentadienyl methyl's CH 2, which can also exist in a resonance, form in a structure like that often ylid. So, what 1 says that in phosphor ylid that phosphorus is positively charged whereas, in metal ylid with the schrock carbene the metal is positively charged and the carbonic moiety is negatively charged in both the cases as is shown here? And because of this canonical structure of the show similar reactivity for example, when reacted with aluminium alkyl.

Let us say reaction of phosphor ylids with Al 2 Me 6 try methyl aluminium diamond produces Ph 3 P CH 2 Al Me 3, where aluminium is negatively charged. And phosphorus is positively charged analogous reaction with the metal ylid or transition metal carbene complex schrock type complex. Al 2 Me 6 thus gives this bcp to tantalum methyl CH 2 Al Me 3, where again you see the aluminium is negatively charged and tantalum is positively charged, similar to what we had observed in the earlier discussion..

So, basically what it says that transition metal alkyl in complexes reacts like ylids or metal ylids the parallel reactivity is shown here, where the positive charge resides at the metal and the anionic charge resided the carbonic moiety, which then attacks the electron deficient aluminium to give this tetra alkyl aluminium species with a negative charge on aluminium, similar to that of the ylid chemistry that we are familiar with. Now, this is an interesting aspect of the reactivity of schrock carbene.

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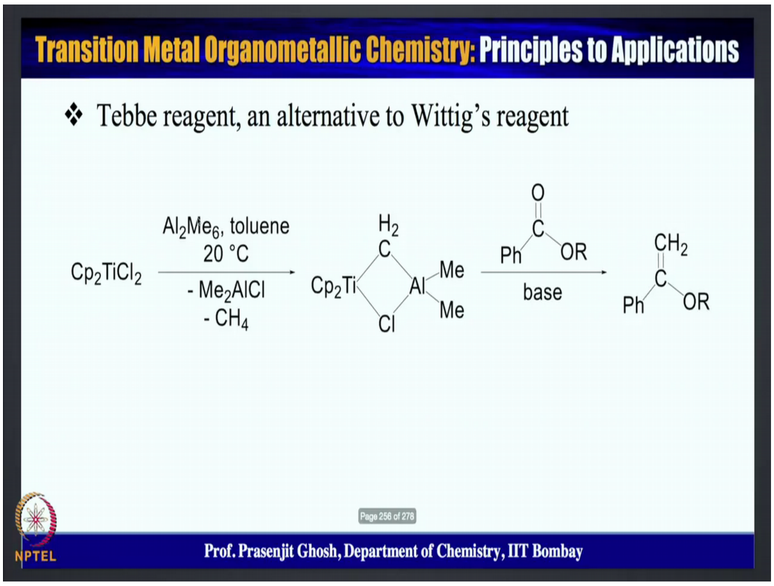

Transition Metal Organometallic Chemistry: Principles to Applications

- Tebbe reagent, an alternative to Wittig's reagent

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And which has found the good use in this developing a particular reagent called tb sb reagent. Now this has come out this application, has come out from this ylid metal ylid chemistry parallel to that of the Wittig reactions that has been observed for carbene a transitional carbene complexes and this has led to the development of tebbes reagents..

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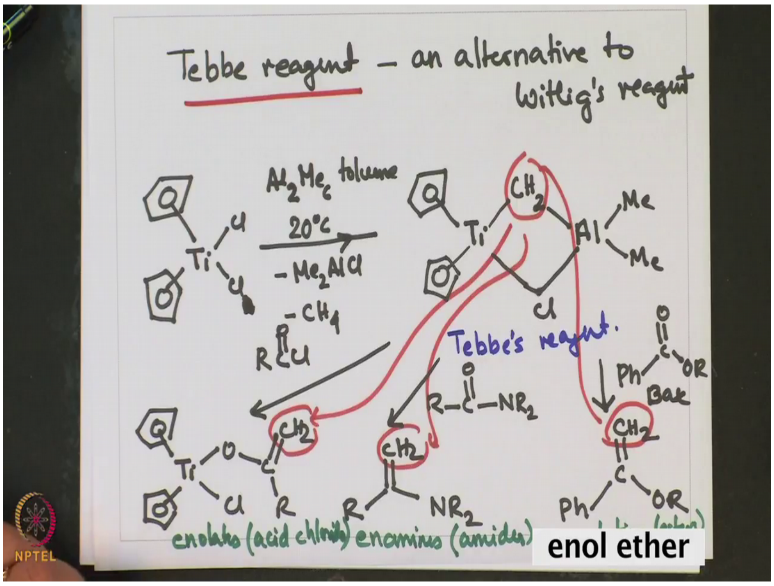

Particularly from schrock carbene, and this tebbes reagent is seen as an alternative to Wittig's reagent. And we are going to see how in what way the parallel Wittig reagent and in what way they go beyond Wittig reagent for example, the reaction of cp 2 titanium dichloride, with try methyl aluminium in toluene at 20 degree centigrade, leads to elimination of dimethyl aluminium chloride..

And methane which happens by alkylation of one of the methyl, which is CH 3 from the tri methyl aluminium from that 1 molecule of Me 2 AlCl, is eliminated resulting in the formation of this particular reagent which is called toluene reagent. cp, cp, cp titanium CH 2 aluminium methyl, methyl and this has chlorine.

Now, this is what is called tebbes reagent, now these when reacted with Esther in presence of base gives Wittig type reaction, and produces and in a (Refer Time: 12:53), where 1 can see that these CH 2 moiety has come from the CH 2 moiety of these tebbes reagent. Now not only it can make an ellipse from Esther's which indeed is a very interesting reaction and the application specific to this reagent..

It can also show other kinds of interesting reaction for example, in reaction for example, its reaction with amides, it produces in a means similar to that of the Esther. Where this CH 2 comes an does. So, these are these two are very specific and interesting applications of tebbes reagents where by olefin can be made out of m amides as well as Esther's. Another interesting reaction after this reagent is that with acid chlorides..

It produces enolates, the reaction with acid chlorides it produces in ylids for example, so a 2 1 can see that CH 2 has been put onto a acid chlorides.

So, here is a interesting compression that with Esther, it produces in the ellipse from Esther's with amides which produces enamines, from amides and with acid chlorides it produces enolates. So, very interesting an application of tebbes reagent is seen and that has developed of this that has developed of this schrock kind of carbine..

And tebbes reagent usually is form from platinum dichloride by reaction with tri methyl aluminium, which results in elimination of a methane and dimethium aluminium chloride, to give this tebbes reagent which is a bcp titanium CH 2 Al Me to and chloride that reacts with different substrates given in a ellipse anamines and enolates, depending on the reaction that it undergoes. So, this is a very nice demonstration and application of these transition metal carbene complexes particularly in terms of their utility in organic synthesis.

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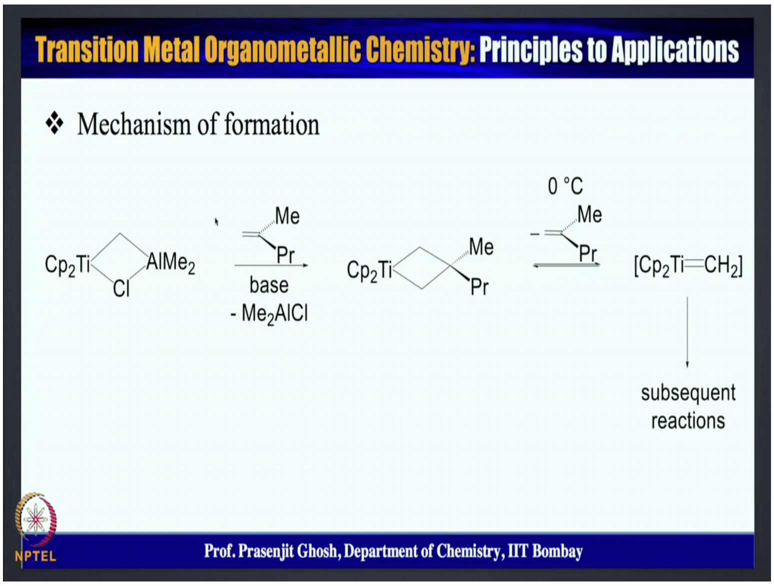

Transition Metal Organometallic Chemistry: Principles to Applications

- Mechanism of formation

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Now we are going to see the mechanism of formation that is a discussed over here.

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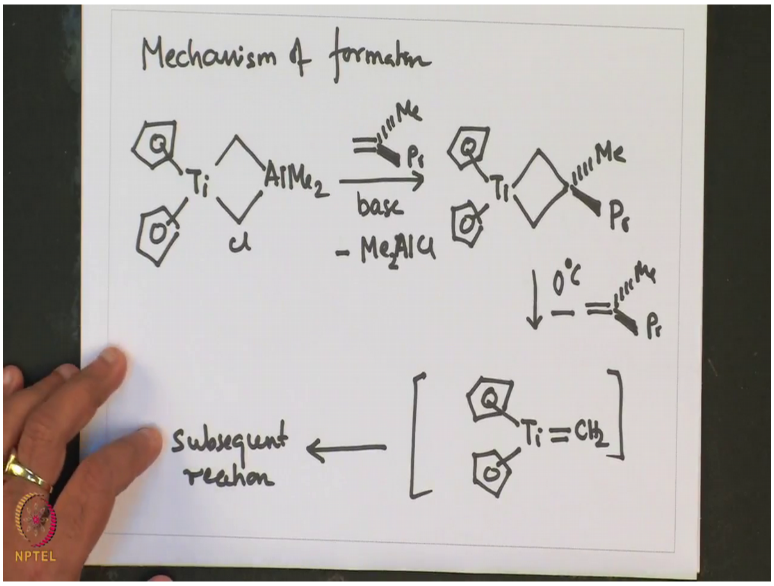

Where of metal carbene species from tabbes reagent for example, this bcp titanium CH 2 Al Me 2, with chlorine which reacts with an olefin in presence of base and minus Me 2 Al Cl, which gives the carbene and the carbon then adds on to this olefin to give this metal of cycle of the type profile, and that at 0 degree centigrade, eliminates back the olefin to give the transition metal carbine intermediate, which undergo subsequent reaction.

So, what it says that these tebbes reagent in presence of an olefin give a metal of cycle, which is probably the resting state and that eliminates back the olefin to generate this important transient and highly active transient metal carbene complexes, which undergo reaction like ylids or show the reactions which are known of tebbes reagent..

So, this gives a glimpse at how the tabbes reagent functions and the important thing to remember is that these functions via transition metal carbine complexes. And that is a important that is the active species for this kind of transformation that is reagent undergo, and that the active species is nothing, but bcp titanium double bond CH 2 that is just a transition metal carbene complex of titanium. Now with that we come to end of discussion on the of these transition metal carbene complexes.

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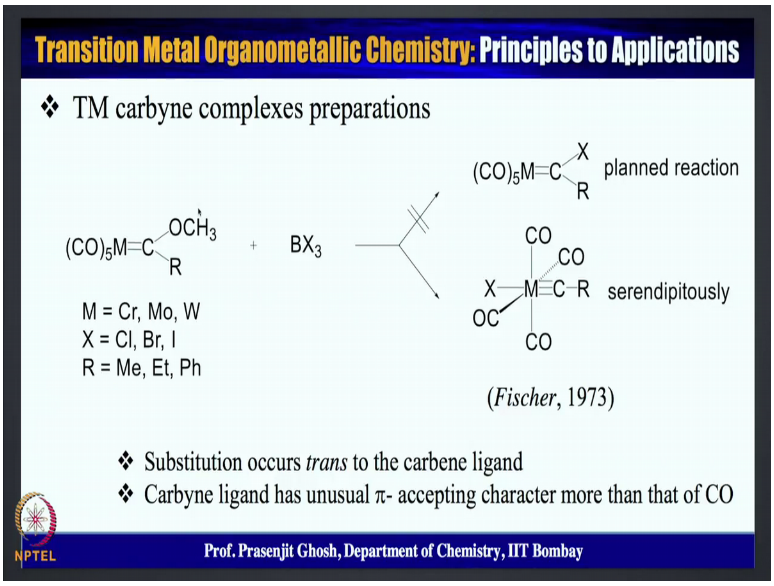

Transition Metal Organometallic Chemistry: Principles to Applications

- TM carbyne complexes preparations

planned reaction

serendipitously

M = Cr, Mo, W
X = Cl, Br, I
R = Me, Et, Ph

(*Fischer*, 1973)

- Substitution occurs *trans* to the carbene ligand
- Carbyne ligand has unusual π- accepting character more than that of CO

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And we are going to take up something more interesting to discuss.

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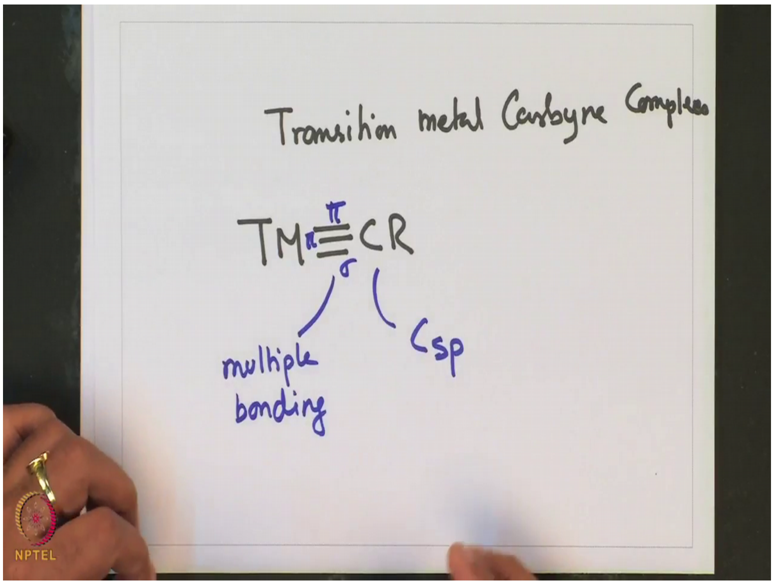

Which follows from this transition carbene complexes; these are transition metal carbine complexes. And these usually are donated by designated by CR moiety, and as we you can see that in transition metal carbine complexes, the carbon is sp hybridized..

And different from the 1 we which we had discussed where it was transition metal carbine complexes, where the carbon center was sp 2 hybridized and then another interesting aspect about this sp hybridized a transition metal carbene complexes are that similar to the transition metal carbyne complexes, there is metal designed multiple bond..

Bonding present between the transition metal and the carbon moiety, which being the sigma and 2 pi type interaction as a result the carbene, and carbyne complexes are very strongly attached to the transition metal and we are going to look take it up in bit more details. Now was 1 sees that what are the types of carbine complexes, and what is their source of utility we are going to discuss that as we precede this topic..

Now to begin with we are going to look at the preparatory of methods available for preparing these transition metal carbine complexes, and what is interesting is the transition metal carbine complexes are prepared serendipitously. So, it was not by design that these complexes where prepared and the first example sort of came out by accident.

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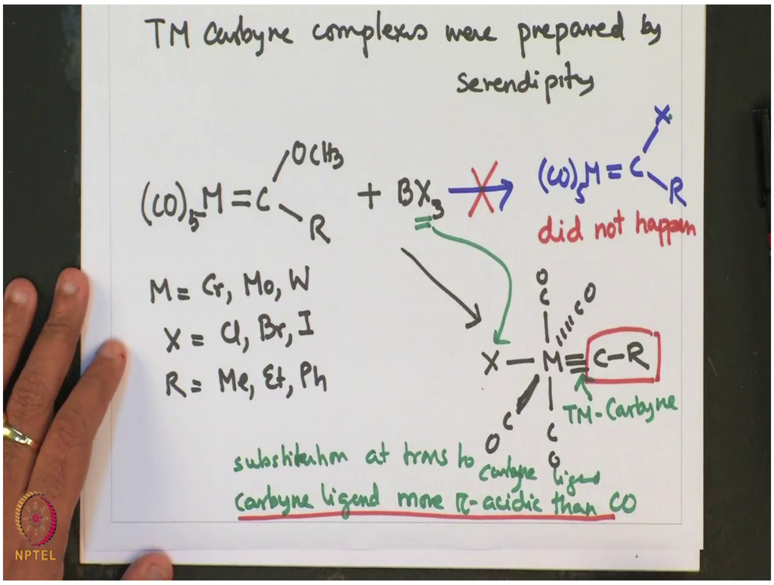

TM Carbyne complexes were prepared by serendipity

substitution at trans to carbyne ligand

carbyne ligand more π-acidic than CO

Transition metal carbyne complexes, where prepared by serendipity and the reaction which was tried was metal c o methyl, with r this is a Fischer carbene where n can be chromium molybdenum tungsten, and when this was reacted with lwies acid BX 3, where X can be chlorine bromine iodine.

And this R is methyl, ethyl, finial, that the purpose was to synthesize these transition metal carbon complex, of the type this were x would undergo a substitution reaction at the carbonyl carbon. Which actually a did not occur and instead the product which was obtained was of this fantastic discovery of a transition metal carbene complex, where the product obtained was CR, and this is a transition metal carbene complex and contains a triple bonded metal carbine moiety and what really has transpired is that substitution occurred.

Occurred substitution at trans to carbene ligand. So, instead of this X ending on the carbon over here the X is found trans to the carbene ligand, and this carbyne ligand has more pi acidic character more pi acidic than co. So, this is an interesting observation for the carbine ligand that it has created a center, which is more pi acidic and also has been formed by substitution opposite to the carbene ligand, which was not planned it was initially planned that the x would end up on the carbonic center..

So, with that I would like to conclude the discussion on today's lecture. What we had done is we had looked at various kinds of a reactivity of a transition metal carbene complexes to begin with and in that respect we have as looked at the tbs reagent ylid type chemistry that transition metal carbine which is play particularly the schlock type carbenes..

And the kind of various organic products that will obtained from various organic reagents, using this tebbes reagent we have also looked into that we have looked into the mechanism of formation of a active species from tebbes reagent responsible for whole lot of a tebbes type ylid type chemistry that we have been discussing.

And with that we concluded our discussion in this lecture on transition metal carbene complexes, and looked up another interesting topic of transition metal carbine complexes..

These are sp center bonded multiply bonded, triply bonded to the transition metal in that perspective, we have looked at the synthesis of transition metal carbene complexes. In which was initially discovered by serendipitously, where they wanted to have a substitution on the heteroatom of a carbonic moiety, but the result which was obtained was that of the formation of a transition metal carbine, moiety with the substitution occurring trans to it this was a very interesting chemistry, a which led to a ligand which is carbine ligand which is more pie acidic character given then that of co.

So, that is kind of also very interesting and probably this acidity arises from the sp nature of the carbon moiety. So, with that I would like to conclude todays discussion on reactivity of transition metal carbon chemistry as well as the preparations on transition metal carbon chemistry.

And we are going to be discussing more on transition metal carbine chemistry in bit more detail from the perspective of synthesis reactivity, and also try to understand their bonding, with respect to them frontier molecular orbital and involved ha in these moiety's and these are many more are to be the topic of next lecture until then good bye.

Thank you.