Transition Metal Organometallic Chemistry: Principles to Applications

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Week – 08
Lecture – 36
Transition Metal Carbene Complexes: Reactivities

Welcome to this lecture on transition metal organometallic chemistry from principles to applications. We have been discussing a very important class of transition metal organometallic compound that is the transition metal carbene complexes over last few lectures and in that; we have developed this concept of the transition metal carbene complexes particularly from the perspective of their synthesis, their classifications and their reactivity.

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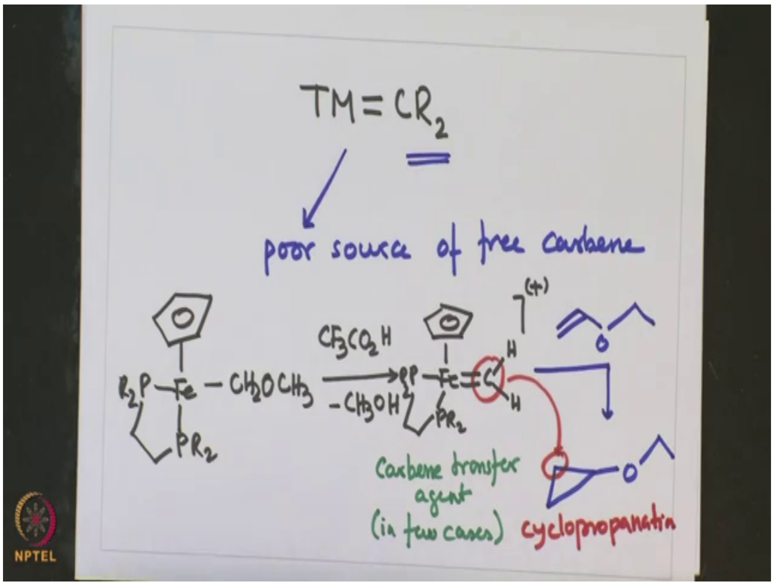

So, these transition metal carbene complexes are extremely important from application point of view because they are important intermediates; in many catalytic cycles and from that perspective understanding them is of crucial importance for designing better and more efficient catalysis. Now with that perspective in mind, we have looked into the synthesis as well as classification of these transition metal carbene complexes in the last lecture, we have also looked into the characterization methods that are often used for characterizing these kind of complexes that includes various spectroscopic techniques like carbon proton NMR as well as ir and also by single crystal x ray diffraction studies we have also discussed about the reactivities of these kind of transition metal carbene complexes.

In the last lecture, we have seen that Fischer carbene complexes are partially positive at the carbonic carbon as a result they undergo reactions with nucleophiles, we have also seen that that because of this reaction of the nucleophile, if any carbon ion gets generated and adjacent to the Fischer carbene center that carbon ion is stabilized by the carbonic moiety and that was established by isotope leveling experiment which we had discussed in the previous lecture.

Now, in this lecture, we going to study in the reactivity of transition metal carbene complexes in bit more detail in terms of various reactivity reactivity that they exhibit and also, we going to try and draw a parallel between the Fischer carbene and the Schrock carbene complexes in terms of complimentary reactivity that they exhibit and try to understand the reasons behind such difference in their reactivity.

Now, it may seen that these carbene moiety a bound to our transition metal should be effective reagent for to be transferred on to other molecules. So, they like they can be thought of as very good carbene transfer reagents ah, but what it turns out that transition metal carbene complexes are poor source of free carbene.

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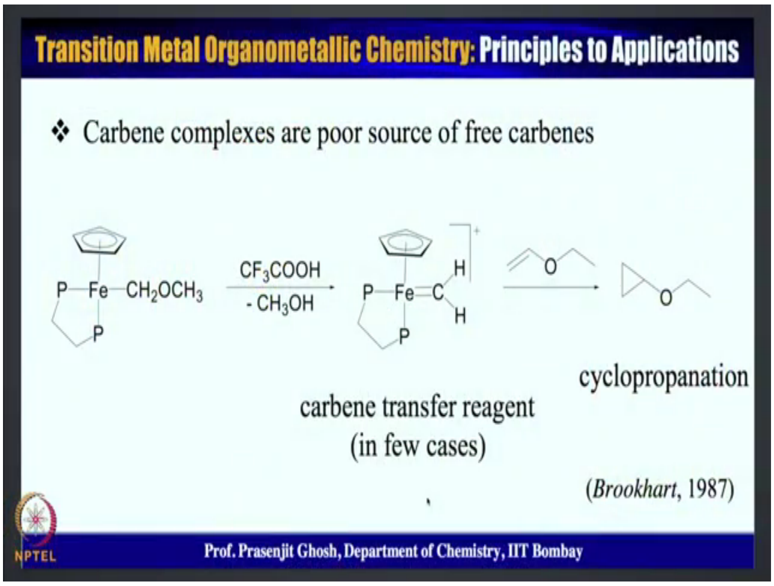
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❖ Carbene complexes are poor source of free carbenes

carbene transfer reagent
(in few cases)

cyclopropanation

(*Brookhart*, 1987)

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And this is illustrated by the example given below.

So, for example, these CPe Fe rn P r 2 CH 2 O CH 3 when treated with CF 3 CO 2 H eliminates methanol which gets protonated OH to give this iron carbene complex and that carbonic moiety bound to this iron can be thought of as a carbene transfer agent and such carbene transfer reactions are not very common, but observed in few cases where transition metal carbene moiety can transfer its carbonic moiety onto another substrate or another transition metal.

So, we are going to look at some of the examples which had shown the transition metal carbene complexes as carbene transfer agents and the first example of this chemistry was shown by Brookhart way; back in 1987 when he treated these iron complex with carbene trapping reagent in terms of an olefin and he was successful in making cyclo propane ether of the type shown which clearly demonstrates that the CH 2 moiety of the carbene center has added onto this olefinic double bond of the olefin substrate resulting in cyclopropanation.

So, this was one of the few examples are few examples of carbene transfer reactions carbene transfer reactions which transition metal carbene complexes exhibit, I must the say that these reactions are not very common though and only in certain specific cases these carbene transfer chemistry seem to work very nicely otherwise these transition metal carbenes are poor source of free carbenes as these carbenes are stabilized only when they are bonded to transition metal, we are going to look at another example of such a carbene transfer reaction where carbene bound to a transition metal in a transition metal carbene complex is effectively transferred onto organic substrate to give a value added product as can be seen in the next example; for example, in these chromium carbene complex.

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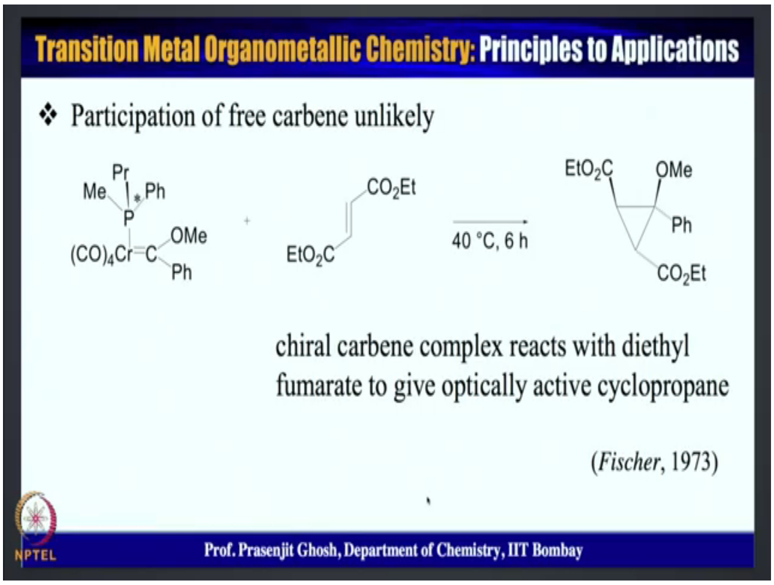

- Participation of free carbene unlikely

chiral carbene complex reacts with diethyl fumarate to give optically active cyclopropane

(*Fischer*, 1973)

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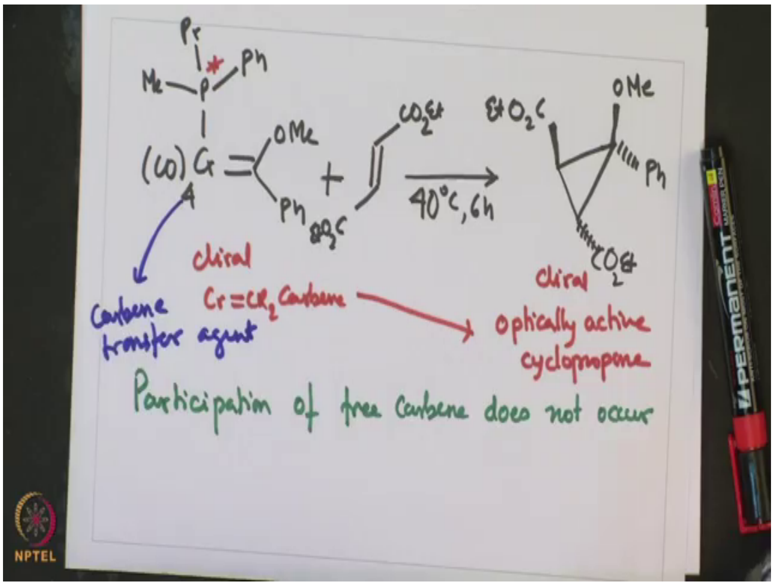

Carbene transfer agent

chiral Cr=CR$_2$ Carbene

chiral optically active cyclopropane

Participation of free Carbene does not occur

CO 4 Cr OMe Ph bound to phenyl propyl methyl.

So, this phosphorus center is chiral phosphorus chiral phosphorus I mean that reacts with diethyl fumarate at 40 degree centigrade and for 6 hours these cyclo propyl ring is formed having OMe Ph O CO 2 Et CO 2 Et. So, now, one may argue that this cyclopropane ring is formed from free carbenes, but that is not true as this product formed also is chiral and hence it gives optically active cyclopropane ring and since this optically active cyclopropane ring comes from chiral chromium Cr 2 carbene complex.

So, one may argue that participation of free carbene is unlikely free carbene does not occur. So, because had free carbene participated then this optically active cyclopropane ring would not have formed because the free carbene could add to this diethyl fumarate from both sides resulting in rhythmic mixture of the cyclopropane ring.

Now, this shows that indeed this chromium carbene complex is acting as a carbene transfer agent because there is a transfer of chirality from the complex onto the substrate along with the transfer of carbene. So, this also is one of the few rare examples where transition metal carbene complexes have been used for carbene transfer reactions onto substrates this has been done in an asymmetric fashion to make cyclopropane ring as well as in a chiral way a chiral way which was discussed with the for the iron complex. So, there is chiral not only if the chirality transfer, but also carbene transfer has carried out by this chromium complex.

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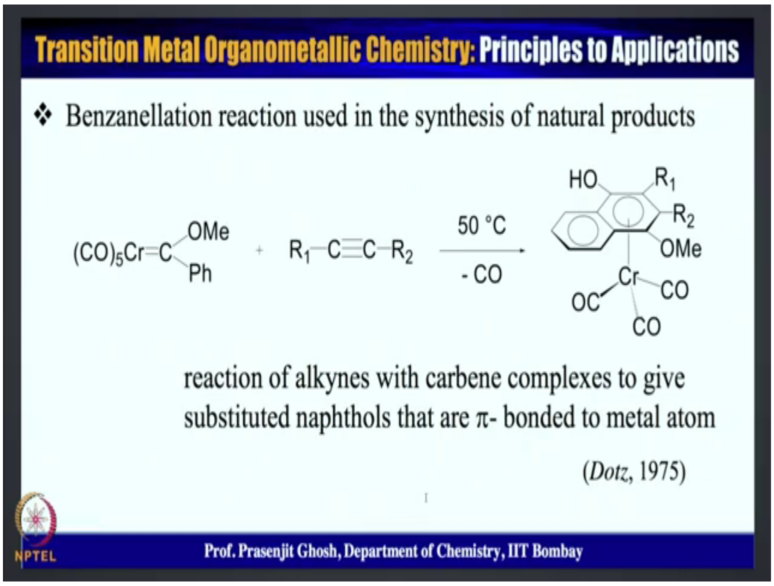

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- Benzanellation reaction used in the synthesis of natural products

reaction of alkynes with carbene complexes to give substituted naphthols that are π- bonded to metal atom

(*Dotz*, 1975)

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Now, we are going to look at another very interesting reactivity of carbene complexes which is used for synthesis of benzanellation reactions; that means, that aromatic rings have been synthesized effectively by the reactions of transition metal carbene complexes where they serve as carbene transport agent which sort of gives further value added chemicals and this has been used in synthesis of natural products.

So, this is a very interesting reaction called benzene.

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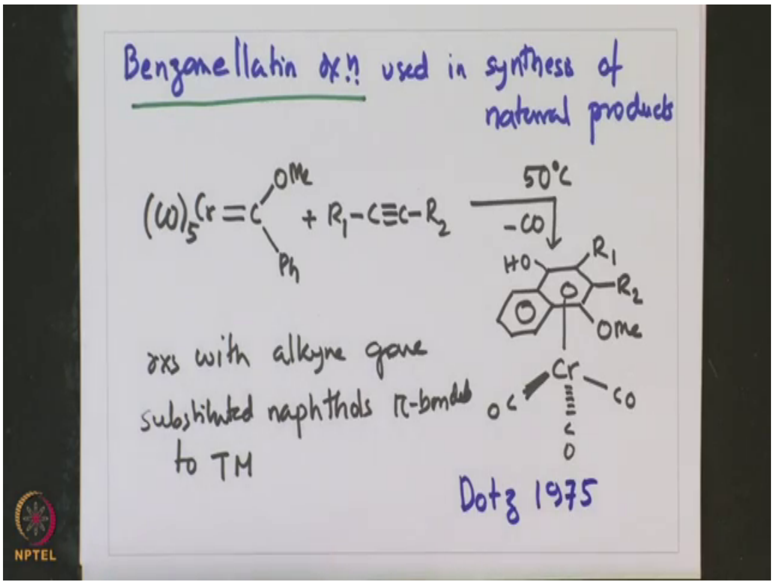

Benzanellation rxn used in synthesis of natural products

rxs with alkyne gave substituted naphthols π-bonded to TM

Dotz 1975

Benzanellation reaction and this is given by the reaction of this carbene complex reacting with alkynes at 50 degree centigrades which eliminates carbon monoxide to give these naphthols weight R 1, R 2 OMe and chromium carbonyl complexes.

So, this reaction of carbene with alkyne gave substituted naphthols pi bonded to transition metal. So, this is a very interesting chemistry where one can see that these aromatic rings are constructed using carbene complexes where carbene complexes are used in a stichometric fashion not in a catalytic fashion and this reaction is popularly called as benzanellation reactions where benzene ring is constructed by the reaction of carbene with acetylenes the way it has been shown over here.

Now, this is a very important application of transition metal carbene complexes and this was discovered by dots way back in 1975 and this popularly is also called dots reaction this particular reaction is popularly named as dots reaction as well now we have seen various.

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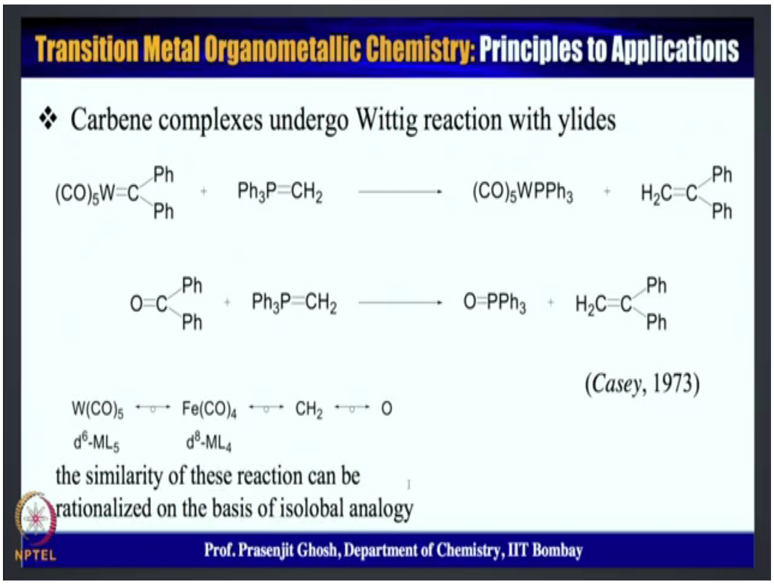

Transition Metal Organometallic Chemistry: Principles to Applications

- Carbene complexes undergo Wittig reaction with ylides

$(CO)_5W{=}CPh_2 + Ph_3P{=}CH_2 \longrightarrow (CO)_5WPPh_3 + H_2C{=}CPh_2$

$O{=}CPh_2 + Ph_3P{=}CH_2 \longrightarrow O{=}PPh_3 + H_2C{=}CPh_2$

(*Casey*, 1973)

$W(CO)_5 \leftrightarrow Fe(CO)_4 \leftrightarrow CH_2 \leftrightarrow O$

$d^6\text{-}ML_5$ $d^8\text{-}ML_4$

the similarity of these reaction can be rationalized on the basis of isolobal analogy

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Reactivity of transition metal carbene complexes; we had seen that the Fischer one undergoing nucleophilic additions that we had seen we have also seen the Fischer one stabilizing carbon ions through isotope experiments in addition to that in today's lecture we have seen that these carbene complexes can under undergo of carbene transfer reactions though these reactions are not too common.

But we had seen it occur for 2 examples, where carbene has been transferred onto olefinic substrate both in a chiral as well as chiral fashion depending on the catalyst which produced. We have also seen that the carbines can be used for making aromatic rings using reactions with alkyne and that we had seems seen in that this reaction produced naphthols which can be used for synthesis of various natural products another we are going to now discuss another very interesting reaction of carbenes which are parallel to Wittig reaction with ylides.

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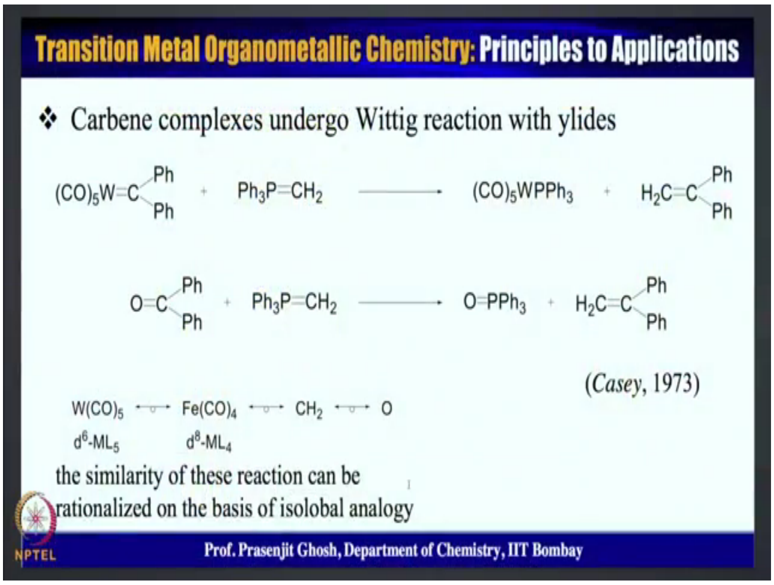

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(*Casey*, 1973)

$\underset{d^6\text{-}ML_5}{W(CO)_5} \longleftrightarrow \underset{d^8\text{-}ML_4}{Fe(CO)_4} \longleftrightarrow CH_2 \longleftrightarrow O$

the similarity of these reaction can be rationalized on the basis of isolobal analogy

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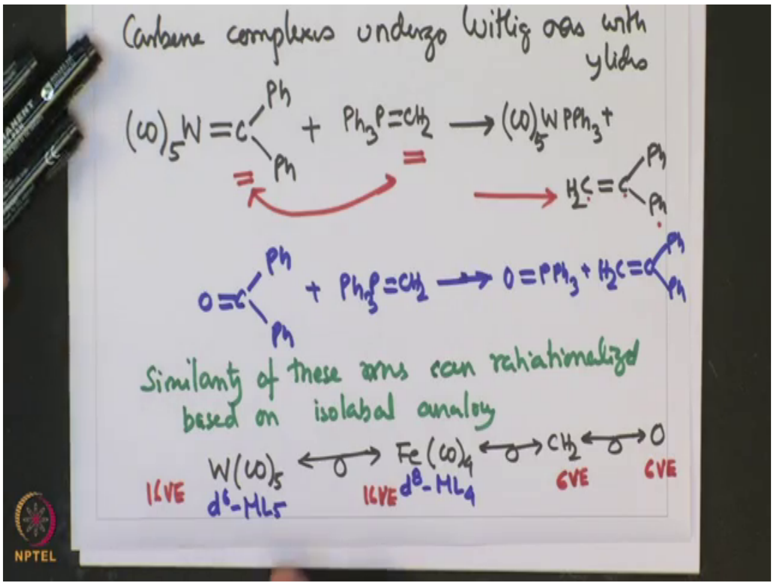

Carbene complexes undergo Wittig rxns with ylides

$(CO)_5W{=}CPh_2 + Ph_3P{=}CH_2 \longrightarrow (CO)_5WPPh_3 + H_2C{=}CPh_2$

$O{=}CPh_2 + Ph_3P{=}CH_2 \longrightarrow O{=}PPh_3 + H_2C{=}CPh_2$

Similarity of these rxns can rationalized based on isolobal analogy

$\underset{16VE\ d^6\text{-}ML_5}{W(CO)_5} \longleftrightarrow \underset{16VE\ d^8\text{-}ML_4}{Fe(CO)_4} \longleftrightarrow \underset{6VE}{CH_2} \longleftrightarrow \underset{6VE}{O}$

So, carbene complexes undergo Wittig with ylides and this is illustrated by the example CO tungsten pentacarbonyl c phenyl phenyl plus this Ph 3 P double bond CH 2 giving CO 5 tungsten P Ph 3 plus CH 2 C Ph; Ph. So, this we see similar to that of Wittig reaction where this CH 2 moiety has added to this carbenic P diphenyl carbene moiety to give this olefin which is C Ph 2 and another side CH 2 which comes from this.

Now, this is very similar to the Wittig reaction which we are aware of for example, instead of the carbene one can think of ketone reacting with the same reagent giving phosphineoxide plus this olefin also exactly similar to that of the Wittig reagent now these similarity of these reactions can be rationalized based on based on isolabal reactions can be rationalized based on isolabal analogy; for example, for tungsten makes a pentacarbonyl is isolabal with iron tetra carbonyl none of these can be explained as such for example, tungsten pentacarbonyl is d 6 ML 5.

So that means, it is sixteen valence electron species and Fe CO 4 is d 8 ML 4. This also is 16 valence electron species and as far as the organic point is a constant concern that this is isolabal with CH 2 with also is isolabal with oxygen both of which has 6 VE. So, these 2 are organic molecules which are isoelectronic and isolabal and these 2 are a transition metal compounds which arise our species which are isolabal and with each other.

Now, the because of the isolabal Wittig principles their reactivity also can be explained. So, Wittig reaction is a very important reaction which is exhibited by carbenes and this is analogues to that of the Wittig reaction that is used with ketones and both of these Wittig reactions results in the formation of olefins as is the case observed for the Wittig reactions of organic molecules we are going to now sort of take a look at some of the examples of Wittig reactions particularly with schrock type of carbene.

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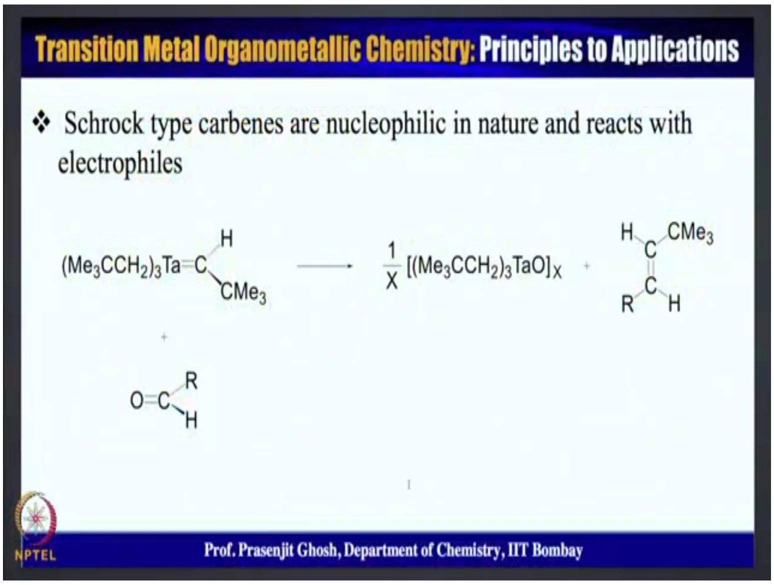

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- Schrock type carbenes are nucleophilic in nature and reacts with electrophiles

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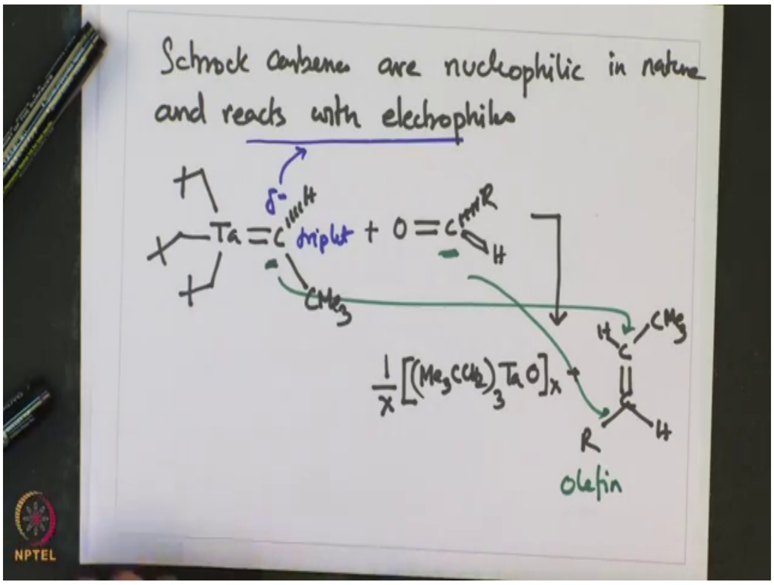

Schrock carbenes are nucleophilic in nature and reacts with electrophiles

So, schrock carbene are nucleophilic in nature and reacts with electrophile. So, let us take a look at the this particular complex tantalum CMe 3. Now as I said their reaction with electrophile arises from the fact that this carbene is negatively charge because of carbene carbon is negatively charged because of this carbon being more electronegative than tantalum and this carbon is engaged this carbon is engaged in 2 types of covalent interaction with the tantalum the carbon to metal sigma bond and the metal to carbon pi bonds and these are simple covalent bond in which a triplet carbene carbonic carbene is in interact with tantalum as a result of which because of high electro negativity of the carbon this carbonic center is negatively charged and because of which if this carbonic center reacts with electrophiles.

So, for example, the reaction of these with let us say carbonyl compound gives the following product Me 3 C CH 2 whole 3 tantalum O x O plus CH C Me 3 double bond R H. So, what one says that this moiety is attached over here and this moiety is attached over here.

So, now this gives in the olefin product as a result similar to that of Wittig reagent where Wittig reagent reacts with a carbonyl compound to give olefin. So, this is a very interesting application of transition metal carbene complexes. So, with this I would like to draw the conclusion about today's lectures which had mainly being on following we have started the lecture by looking into the reactivity of transition metal carbene complexes in this lecture we have we have looked into the nucleophilic addition reactions which are typical of Fischer carbene the source of such reaction reactions we have looked into reason as to why Fischer carbene undergoes nucleophilic addition reactions.

We have also seen in the beginning of this lecture as to how the Fischer carbene complexes can stabilize the formation of carbyne upon deprotonation reaction and this was established using isotope labeling studies experiment, we have also subsequently looked into these applications of transition metal carbene complexes particularly with regard to carbene transfer reactions do the free formation of free carbenes from transition metal carbene complexes are very rare in nature; however, there exist examples were free carbene transition metal carbenes has been used as carbene transfer agents where they transfer their carbonic moiety onto olefins.

And this has been achieved both in a chiral as well as chiral fashion depending on the catalyst which were used we have also subsequently looked at a parallel reactions where carbenic transition metal carbene complexes has a similar reactivity to that of the ylides or of the Wittig reactions. So, these one great applications of transition metal carbene complexes is the Wittig type reactions which these complexes organometallic complexes display, we have also looked at another applications where aromatic rings benzanellation reaction where aromatic rings are formed from the reaction of transition metal carbene complexes with alkyne.

So, with this, I conclude today's lecture we are going to take up this reactivity in bit more detail in the subsequent lecture where we are going to look at the Wittig reactions of transition metal carbene complexes and draw a parallel between them with that of the organic reactions that we are aware of in more details and also few more reactivity of transition metal carbene complexes. So, with that I thank you for being with me in this lecture and look forward to being with you in the next lecture till then.

Good bye and thank you.