# Transition Metal Organometallic Chemistry: Principles to Applications
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## Week - 05
## Lecture – 23
## C – C Bond Activation in Details

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. In the last lecture we have been talking about a very challenging phenomenon which is C-C bond activation reaction.

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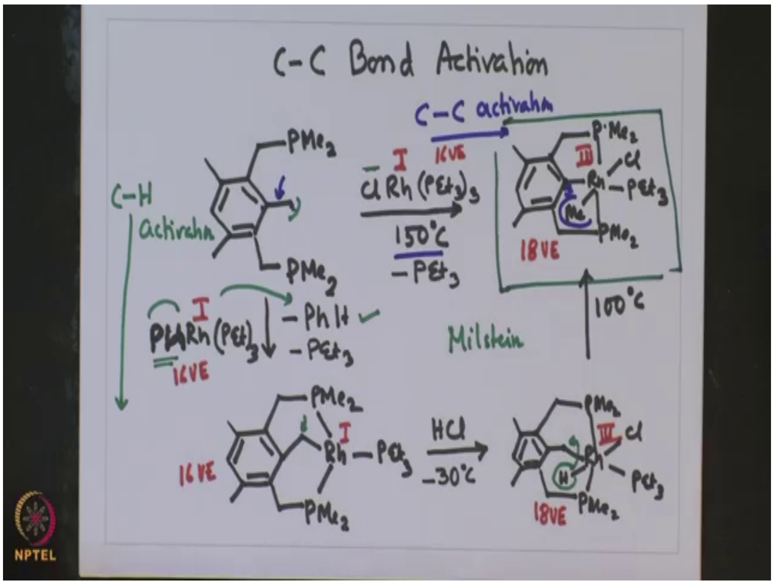

And we have looked into C-C bond activation reaction in the pretext of C-H bond activation or H-H bond activation and what we had seen is that C-C bond activation reaction is very challenging as compared to the other kind of bond activation reactions.

We have also discussed about reason for C-C bond activation reactions being more challenging than C-H and H-H bond activation reactions. We have also looked into the mode of action of various C-C as well as C-H and H-H bond activation reaction. What we have done in the previous lecture is also we have drawn a parallel between cyclo propene ring and alkene.

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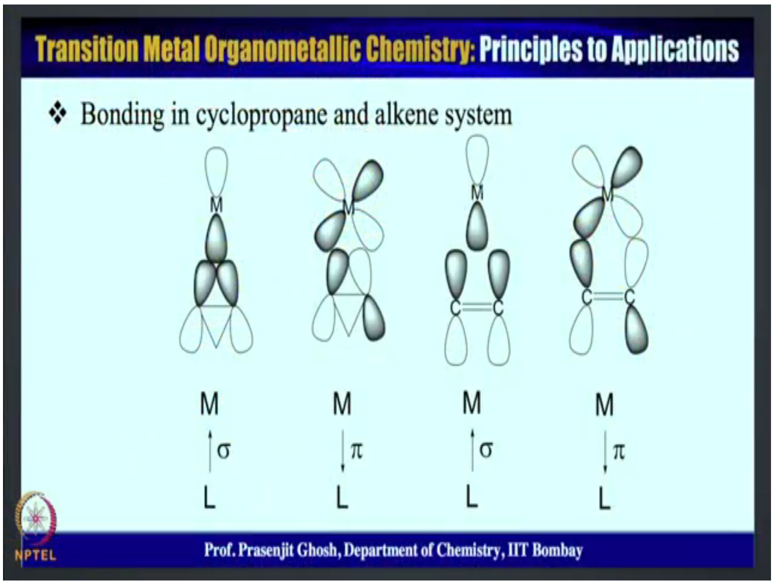

Transition Metal Organometallic Chemistry: Principles to Applications

- Bonding in cyclopropane and alkene system

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And what we had seen that for the C-C bond activation in a cyclo propene ring which is given over here as opposed to C-C bond activation in a alkene where it has a alkene has a double bond. What it was shown that this ligand to metal a sigma donation affects the sigma bond of the cyclo propene which is sort of bent because of the orientation of the orbital whereas, similar composition of C-C bond activation between metal orbital and the pi cloud of an olefin does not affect the sigma bond which sort of remains untouched whereas, it does affect the pi bond. So, there is a sharp distinction in the difference between C-C bond activation of a cyclo propene ring continuing as sigma bond versus C-C bond activation of a alkene containing pi bond.

Similarly the back donation metal to ligand pi back donation competitively cleaves the C-C sigma bond of the cyclo propene whereas, in the alkene case the back donation only happens at the pi star orbital there were there by cleaving the pi orbital and the sigma C-C sigma orbital remains sort of untouched.

So, what we saw is that that C-C bond activation reactions having two different affects if it is done on a strained ring like cyclo propene as opposed to that of an alkene. And some of the examples that we had covered in the last lecture about various types of C-C bond activation reaction. The commonality that ran through all this examples where the fact that these systems where C-C bond activation occurred they were highly strained and as a result of C-C bond activation the ring strength got released favoring the forward reaction and same is true for the cyclo propene ring which is highly strained. However, when they it undergoes C-C activation there is a release of strain when and it gives a metal a cycle with a release of strain which resulting in the stability as well as the forward reaction of cyclopropane in resulting in C-C bond activation.

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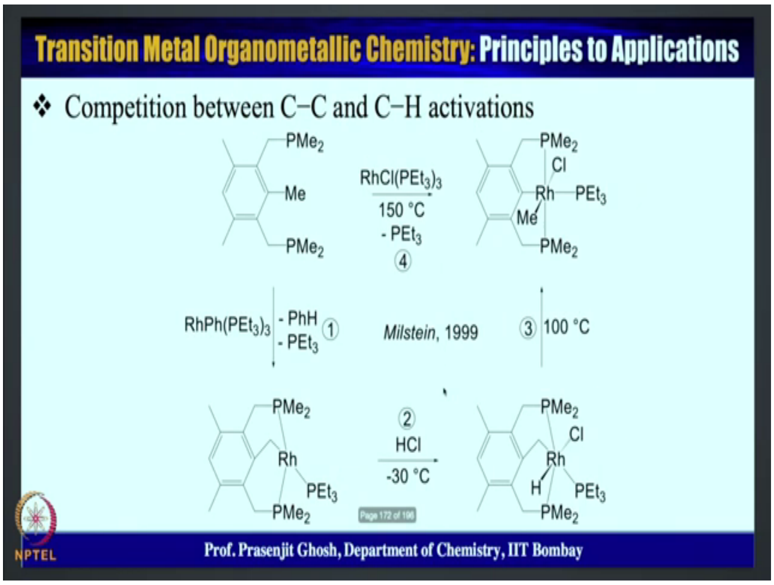

**Transition Metal Organometallic Chemistry: Principles to Applications**

❖ Competition between C−C and C−H activations

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Now, with these background what I am going to do look at is we going to look at another interesting example that where is a competitive activation between a C-C and C-H bond and we would see how one dominates over the other. So, for a particular aromatic moiety of the types shown over here it has 3 methyl group and C-H 2 PMe 2 these reacts with rhodium chloride PEt 3 whole 3 at 150 degree centigrade resulting in a loss of Pet 3 and undergoing a C-C activation giving the corresponding C-C activated product ok.

So, this is a C-C activation occurring as the methyl bond or C-C bond between this benzene ring and the methyl gets cleaved oxidatively at to this rhodium. So, one is over here the other is over here and this is the C-C activated product this see as c activation is very challenging the reaction is carried out at a very high temperature of about 150 centigrade. So, these shows that how challenging the C-C activation is.

Now, as mentioned that there is always a competition between C-C as well as C-H activations primarily for the fact that C-H bonds out numbers C-C bonds and in this case to is no different and that the C-H activation is also observed. So, this molecule reacts with the catalyst and loses react reacts with the catalyst containing rhodium phenyl and losses the benzene, but the C-H of this methyl is lost gets activated and losses as a benzene. So, here C-H activation happens between this hydrogen and this phenyl moiety leading to the elimination of benzene as well as one PEt 3 molecule from the catalyst resulting in this C-H activated product.

So, what one sees over here that in this case the methyl C-H has undergone activation resulting in formation of benzene along with this C-H 2 rhodium bond. So, here is an example of C-H activation preceding with the complex which is phenyl rhodium tri ethyl phosphine and in the C-C activation we had chloro rhodium tri ethyl phosphine the only difference being this chloride is replaced by a phenyl moiety for the C-H activation reaction.

This undergoes this C-H activated product undergoes HCl oxidative variation at very low temperature giving the oxidatively added product which is this. So, HCl is added on this C-H activated rhodium one compound giving the rhodium 3 compound which at 100 degree centigrade completes the cycle and this hydrogen protonates and gives back the gives back C-C activated product. So, this is a very nice demonstration of how the same product which is obtained by C-C activation under very high temperature can also be competitively obtained by more favorable C-H activation followed by oxidative variation and hitting oxidative variation product finally, would give this C-C activation product.

So, to note here is that the protonizaton of this methyl subsequent cleavage of this results in the rhodium methyl group which were obtained by direct by C-C cleavage. So, this work was done by (Refer Time: 12:50) and this is a nice demonstration of arriving at the same product by two different pathways. Now, if one looks at the oxygen state here the rhodium is in plus 1 oxidative state and this is a 16 valence electron complex in the oxidatively added product rhodium is in plus 3 oxidation state and it is 18 valence electron compound and this is what one expects if the oxidative addition of C-C bond occurs.

Similarly, this compound PH rhodium tri ethyl phosphine rhodium is in plus one oxidation state and it has a 16 valence electron in the C-H activated product rhodium is still in plus one oxidation state and it still has 16 valence electron that is because the C-H activation has happened over 2 molecules, one is this, the other is the phenyl, phenyl group leading to the elimination of benzene. And similarly the oxidative addition of HCl results in this rhodium 3 compounds having eighteen valence electron which rearranges on hitting to gives this C-C activated compound.

So, this is a nice demonstration where two pathways can be utilized that is C-C activation as well as C-H activation followed by other to obtain this C-C activated product by two different means.

Now, the reason for higher harsher condition for obtaining this C-C activation comes from the fact that carbon carbon bond or methyl benzene bond in toulene is more difficult to cleave then a benzene hydrogen bond. For example, of one looks at the bond dissociation energy of C c H 5 C-H 3 bond dissociation energy is 427 kilo joule per mole whereas, that of benzene C c H 5 H the corresponding bond dissociation energy is much lower at 368 kilo joule per mole.

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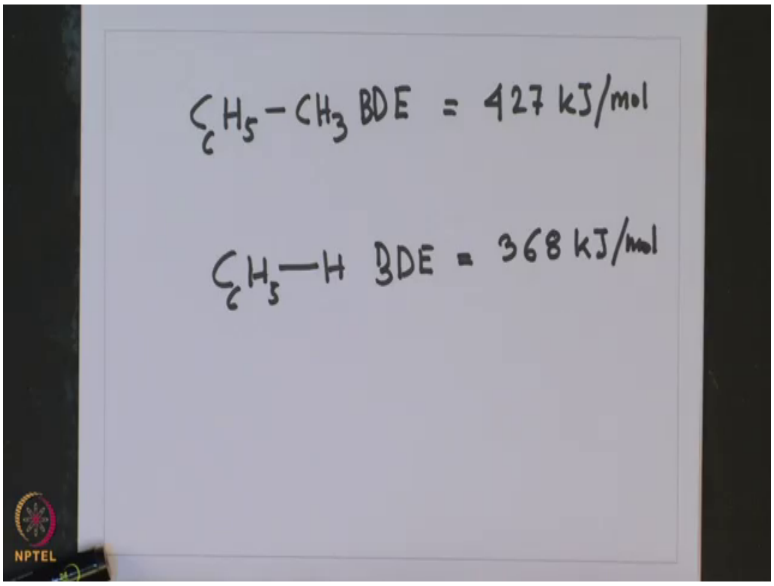

$C_6H_5-CH_3$ BDE = 427 kJ/mol

$C_6H_5-H$ BDE = 368 kJ/mol

So, these explains the difficulty that we had observed in bond activation reaction in our earlier example.

Now, we come to an very interesting topic with regard to this activation chemistry and these are a set of compounds which has very interesting properties and these are called transition metal perfluoro carbon sigma complexes.

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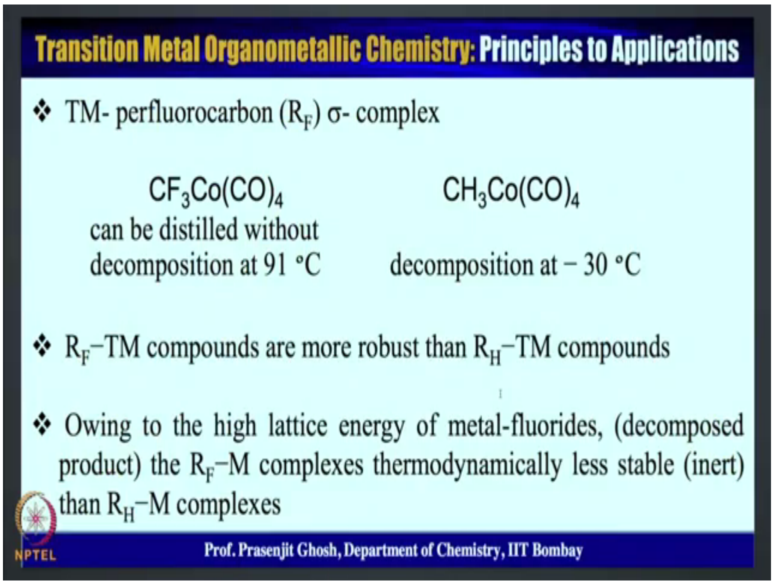

**Transition Metal Organometallic Chemistry: Principles to Applications**

- TM- perfluorocarbon ($R_F$) σ- complex

$CF_3Co(CO)_4$ can be distilled without decomposition at 91 °C

$CH_3Co(CO)_4$ decomposition at − 30 °C

- $R_F$–TM compounds are more robust than $R_H$–TM compounds
- Owing to the high lattice energy of metal-fluorides, (decomposed product) the $R_F$–M complexes thermodynamically less stable (inert) than $R_H$–M complexes

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Now, these are designated by TM R f, where F is the perfluoro carbon complexes sigma complexes.

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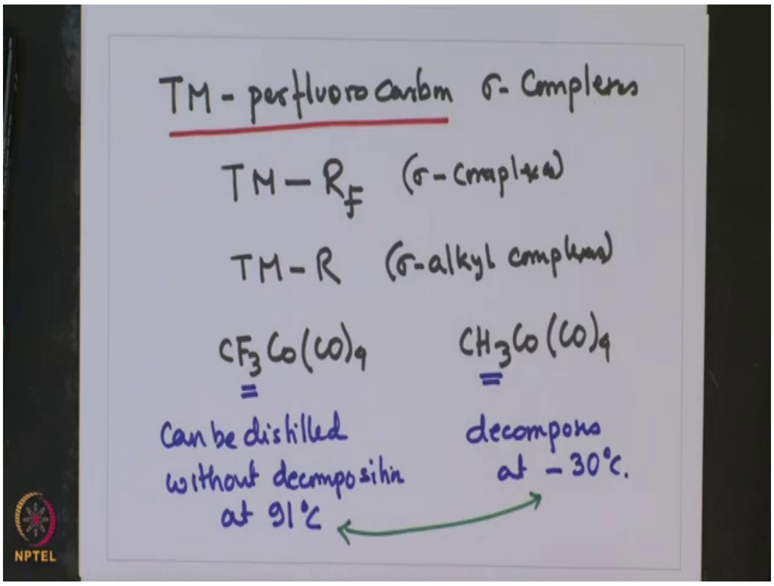

TM - perfluoro carbon σ- Complexes

TM – $R_F$ (σ-complexes)

TM – R (σ-alkyl complexes)

$CF_3Co(CO)_4$ — Can be distilled without decomposition at 91 °C

$CH_3Co(CO)_4$ — decomposes at – 30 °C.

Now, one may think that these are quite related to the other transition metal alkyl, sigma alkyl complexes that we have already discussed, but the point to note is that even though structurally transition metal sigma alkyl complexes very much resemble transition metal perfluoro alkyl complexes, but there is a tremendous difference in their reactivity and properties and that leads us to study this transition metal perfluoro sigma alkyl complexes in greater details.

To illustrate my point for example, for this molecule CF 3 cobalt tetra carbonyl in comparison to C-H 3 cobalt tetra carbonyl then may isostructural and they may look that they would be behaving similarly the only difference that one observed is that C-H 3 has been replaced by CF 3 rest of the molecule remaining the same. And property wise it is same that there is a significant difference in the property. For example, this molecule can be distilled without the composition at 91 degree centigrade whereas the simple alkyl counterpart is very unstable and decomposes at minus 30 degree centigrade.

So, one can see that there is a huge difference in stability when one replaces the hydrogen with fluorine and that is why the interest in perfluoro transition metal alkyl complexes arises from. See even though this complexes are very much structure is similar to the transition metal alkyl complexes their properties are significantly different and that is what makes them interesting to study vice a vice this transition metal alkyl complexes to understand why and how they behave differently from their related transition metal sigma alkyl counter parts.

So, with this in mind we are going to discuss in more detail the bonding reactivity and their procedures that are in place for this transition perfluoro carbon complexes and compare them with the examples which we had covered for transition metal sigma alkyl complexes just to see how these differences arise from.

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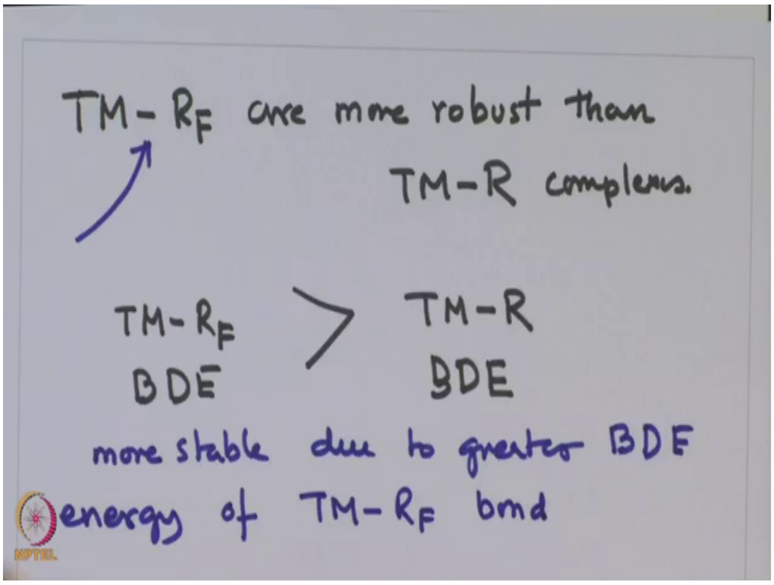

$TM-R_F$ are more robust than $TM-R$ complexes.

$TM-R_F$ BDE > $TM-R$ BDE

more stable due to greater BDE energy of $TM-R_F$ bond

Now, by comparing the two examples what we had seen that transition metal perfluoro alkyl complexes are more robust than transition metal sigma alkyl complexes. The reason for this is interesting in the sense that because of high lattice energy of metal fluorides it may seen that transition metal perfluoro alkyl complexes are less stable. However, the stability has other components as well which is arises because of interactions between the transition metal and the perfluoro alkyl moiety and what it transpires is that this transition metal perfluoro alkyl compounds have greater bond dissociation energy then transition metal alkyl compounds and which makes the transition metal perfluoro alkene more stable.

So, what we have discussed or in this lecture is that this transition metal alkyl perfluoro compounds behave differently compared to transition metal sigma alkyl complexes furthermore what we had seen is that this difference in behavior arises because of higher bond dissociation energy of transition metal perfluoro alkyl complexes with respect to the transition metal alkyl ones. And we have also discussed in this lecture about competitive C-C and C-H activations resulting in the same product where we had seen that C-C activation is more difficult than the C-H activation and required harsher conditions. However, if this two activations can be judiciously applied on a particular system by varying different reagent as well as reaction conditions one can steer these two activation reactions towards the same product and this was finally, demonstrated by a seminal work by Milstein which we are also discussed in this lecture.

So, with these I would conclude this lecture and we will take up the next lecture looking at the more details at these transition metal perfluoro alkene interaction, looking at the source of their extra stability, by looking at the interaction that occurs between the transition metal and the perfluoro alkyl group. And then we would also discuss the various synthetic procedure available for synthesizing this complexes and in the next lecture, till then good bye and hope to see you in the next lecture.

Thank you.