Transition Metal Organometallic Chemistry: Principles to Applications
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Lecture – 24
Transition Metal Perfluoroalkyl (RF – TM) Complexes

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications.

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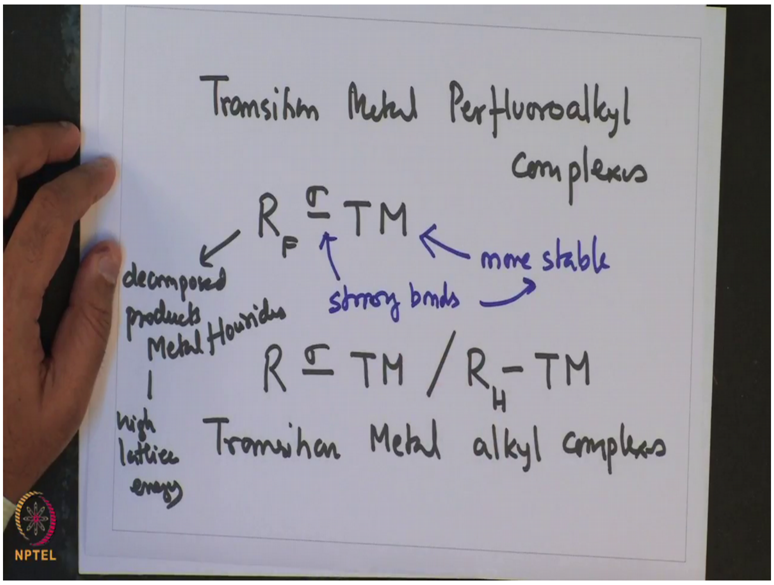

We have been discussing about an interesting area of organometallic compounds an interesting type, these are called transition metal perfluoro alkyl complexes. And these are often designated as R F transient metal type compounds where R F represents the perfluoro alkyl moiety.

Now, these compounds bears analogy to the simple transition metal alkyl complexes, which are also given by R-TM where R is an alkyl group or 1 may also represent the same as R H-TM, where you know all the alkyls have hydrogen substituents on it to be more precise. So, transition metal alkyl complexes are represented as such, both of these compounds may be related in the sense that they are all sigma type bonds with the transition metal, they all make sigma type bonds; however, when 1 looks at these 2 compounds one is the transition metal perfluoro alkene or transition metal alkyl complexes.

So, 1 sees that they differ in their reactivity as well as in property. And that is something which is of interest and needs further discussion, 1 also finds that these transition metal perfluoro alkyl complexes are more stable. Then the corresponding transition metal alkyl complexes, and in today's lecture we will be focusing more on this reason for extra stability of these transition metal alkyl complexes.

Now, there is an counter argument which suggests that transition metal perfluoro alkyl complexes may not be very stable the argument being, that the decomposed product of these complexes should be metal fluorides are metal fluorides, which has high lattice energy. And hence this compound should be less stable, because they would want to dissociate or decompose to metal fluorides having highly lattice energy, but what it turns out is that this transition metal perfluoro bonds are very strong leading to their extra stability. And in this discussion what we are going to focus on is the reason for this extra ah bond strength of perfluoro transition metal alkyl complexes. So, in order to understand this let us take a look at this transition metal perfluoro alkyl bond.

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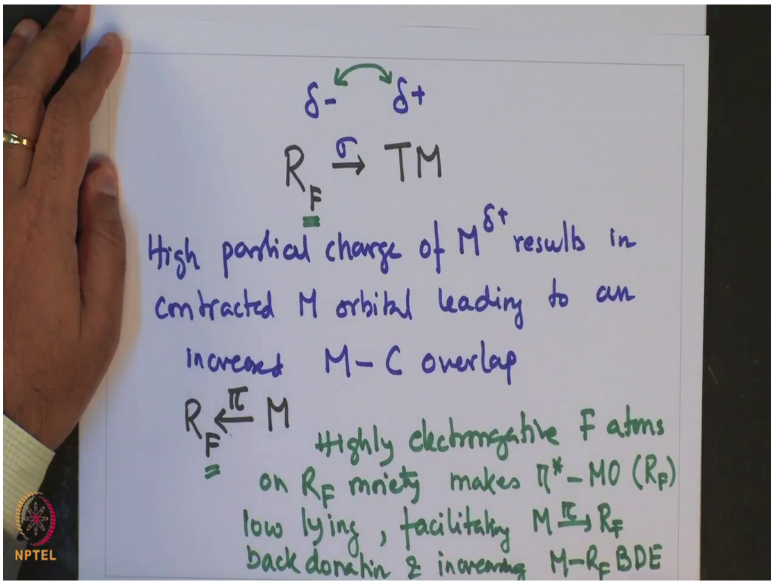

$\delta-$ $\delta+$

$R_F \xrightarrow{\sigma} TM$

High partial charge of $M^{\delta+}$ results in contracted M orbital leading to an increased M – C overlap

$R_F \xleftarrow{\pi} M$

Highly electronegative F atoms on R_F moiety makes π^* – MO (R_F) low lying, facilitating $M \xrightarrow{\pi} R_F$ back donation & increasing $M-R_F$ BDE

Now, perfluoro alkyl has all of the carbon substituted with fluorine instead of hydrogen in the normal alkyl analog.

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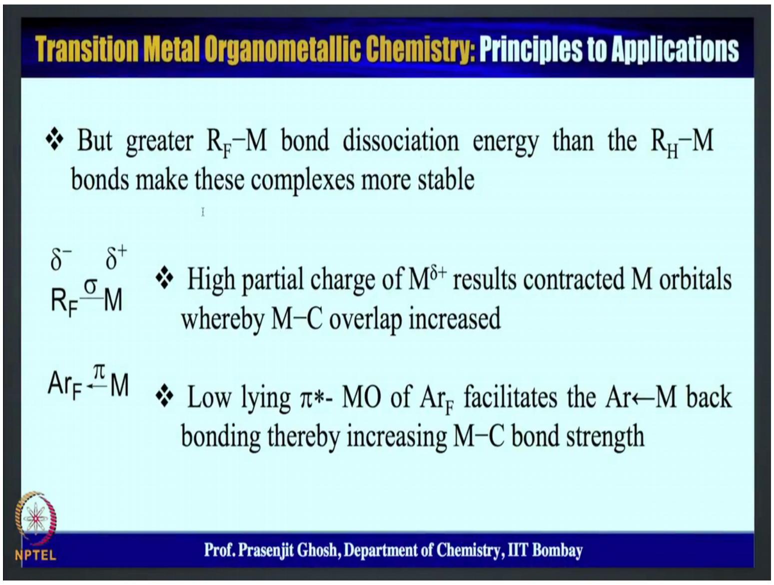

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- But greater R_F–M bond dissociation energy than the R_H–M bonds make these complexes more stable

$\overset{\delta^-}{R_F} \overset{\sigma}{—} \overset{\delta^+}{M}$

- High partial charge of $M^{\delta+}$ results contracted M orbitals whereby M–C overlap increased

$Ar_F \overset{\pi}{\leftarrow} M$

- Low lying π*- MO of Ar_F facilitates the Ar←M back bonding thereby increasing M–C bond strength

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And as fluorine being very electronegative the polarity of this alkyl group thus become del minus, and the metal becomes del plus. And this is a kind of sigma interaction occurring between this perfluoro alkyl group, and the transition metal.

Now, as these difference in polarity or as this bond becomes more polar going to the presence of the fluorine, then the metal becomes partially more positively charged which resolves in contraction of metal orbital thereby increasing the overlap between this metal C bond. So, high partial charge of metal del plus results in contracted metal orbital leading to an increased M-C overlap and which gives greater stability.

Similarly, for the back donation for example, from the metal to the ligand pi type back donation, because of the presence of this perfluoro alkyl fluorine atoms on each carbon the pi star of the R F fragment become low lying, which also increases the metal carbon back bonding, and resulting in a better overlap. So, highly electronegative fluoride atoms on R F moiety makes pi star a MO of R F low lying,, thereby facilitating metal to R F back donation, and increase in R F bond dissociation energy.

So, what comes to the fore is that the greater stability of the R F transition metal arises, because of the greater polarity of the bond. And that affects both the sigma bond as well as the pi bond in the same direction, that is this enhanced polarity due to presence of electro negative fluorodine, affects both the sigma and pi bonds towards increasing the corresponding R F transition metal bond energy.

And this does so, by contraction of the metal orbital as the metal become more partially charged leading to an increased metal M-C overlap for the forward ligand to metal forward sigma donation and the presence of so, many fluoride atoms on the perfluoro alkyl group makes the corresponding pi star molecular orbital low lying. And that also intern facilitates the metal to ligand pi back donation, and both of these factor working together increases the metal to perfluoro alkyl bond dissociation energy, thereby imparting stability to these perfluoro alkyl transition metal complexes.

Now, there are many reactions which are common for simple alkyl a transition metal complex which does not occur, in the peripheral counterparts. And that can be ascribed due to the increased polarity or the presence of fluoride atom in the perfluoro alkyl moiety resulting in difference in reactivity.

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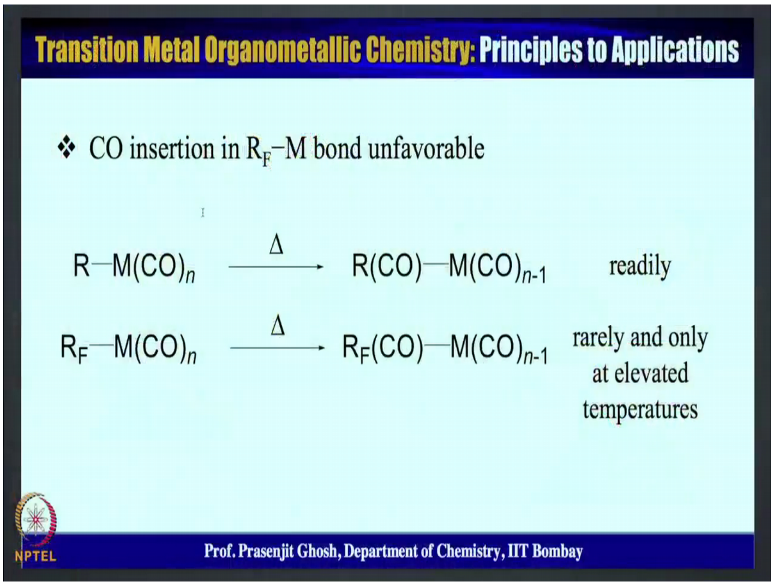

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- CO insertion in R_F–M bond unfavorable

$$R\text{—}M(CO)_n \xrightarrow{\Delta} R(CO)\text{—}M(CO)_{n-1} \quad \text{readily}$$

$$R_F\text{—}M(CO)_n \xrightarrow{\Delta} R_F(CO)\text{—}M(CO)_{n-1} \quad \text{rarely and only at elevated temperatures}$$

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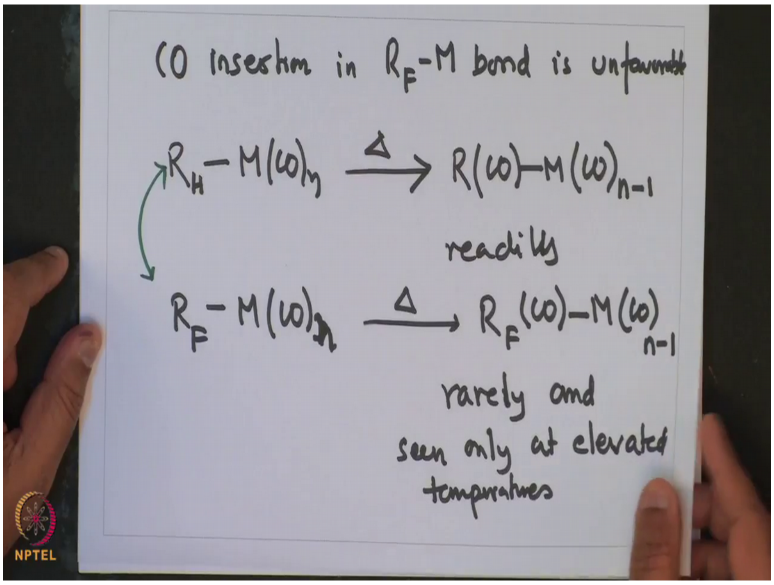

CO insertion in R_F-M bond is unfavorable

$R_H-M(CO)_n \xrightarrow{\Delta} R(CO)-M(CO)_{n-1}$

readily

$R_F-M(CO)_n \xrightarrow{\Delta} R_F(CO)-M(CO)_{n-1}$

rarely and seen only at elevated temperatures

For example CO insertion in R F metal bond is unfavorable. I will illustrate that with an for example, if in a metal alkyl complex of the type M R H-M CO n where R H is a simple alkyl group containing carbon and hydrogen atoms, when heated readily undergoes CO insertion into metal R H bond giving R CO-M CO n minus 1, and this reaction is happens readily upon heating. And is observed in many transition metal complexes whereas, the same reaction in its perfluora alkyl analog as given by R F M CO n is very rare.

So, here 2 such insertion is observed rarely and seen only at elevated temperatures. So, the reaction which is a common for alkyl carbonyl complexes this reaction of CO insertion it a metal carbon bond is absolutely rare for perfluoro metal carbonyl complexes, and proceed at very high temperature.

So, this sort of highlights the difference in reactivity between these 2 classes of compound even though structurally, they may be very similar in resemblance. Now I would come to the various preparative methods available for synthesizing these perfluoro alkyl transition metal complexes.

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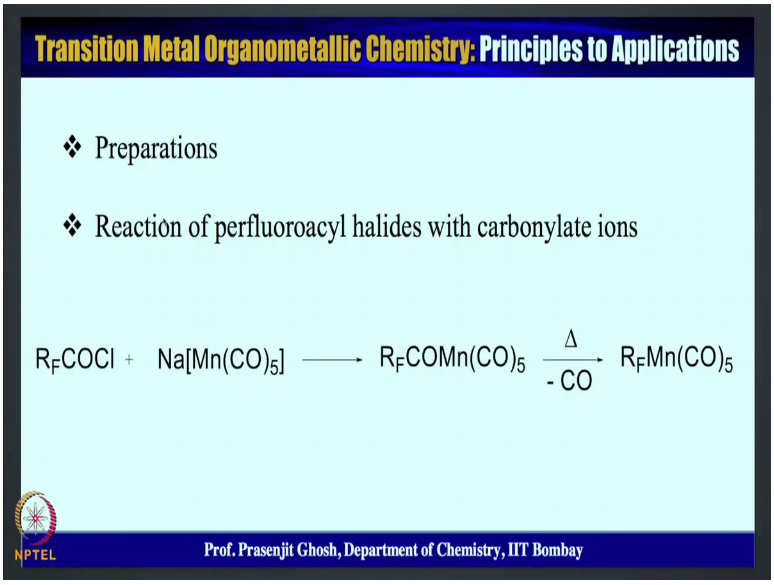

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- ❖ Preparations
- ❖ Reaction of perfluoroacyl halides with carbonylate ions

$$R_FCOCl + Na[Mn(CO)_5] \longrightarrow R_FCOMn(CO)_5 \xrightarrow[-\,CO]{\Delta} R_FMn(CO)_5$$

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And to begin with the most common method for synthesizing this perfluoro alkyl transition metal complexes is to react a is the reaction of perfluoroacyl halide with carbonylate anion plus carbonylate anion.

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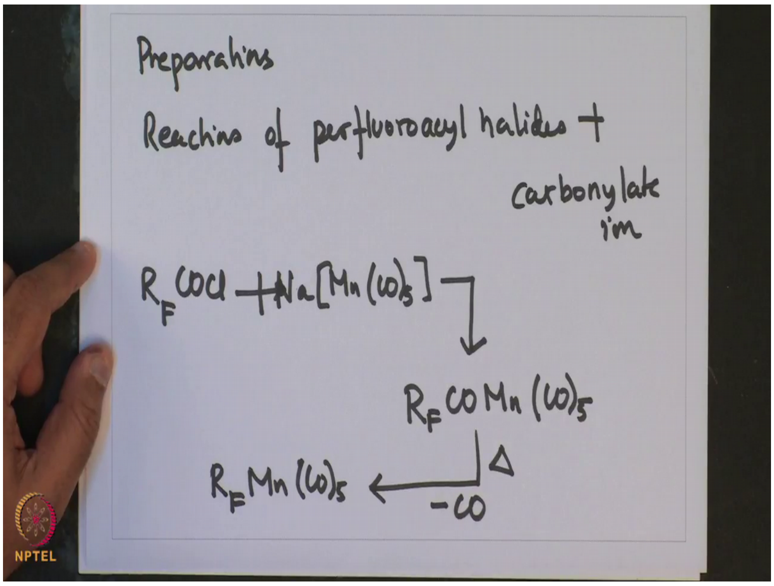

Preparations

Reaction of perfluoroacyl halides + carbonylate ion

$$R_FCOCl + Na[Mn(CO)_5] \longrightarrow R_FCOMn(CO)_5 \xrightarrow[-CO]{\Delta} R_FMn(CO)_5$$

I will illustrate with this following example giving rise to this perfluoroacyl Mn CO 5. Now, here 1 can see that this acyl group has positive charge at the carbon, and the metalite Mn CO 5 has a negative charge at the manganese. As a result the formation of manganese pentacarbonyl perfluoroacyl compound is formed, and this when heated eliminates CO resulting in perfluoro alkyl manganese pentacarbonyl.

So, what we saw is that assign that CO elimination for a acyl bond from a acyl, bond occurs upon heating resulting in the formation of R F Mn CO 5 along with carbonyl moiety. Another interesting feature about this class of compounds is that reversal of polarities are observed in many of its examples.

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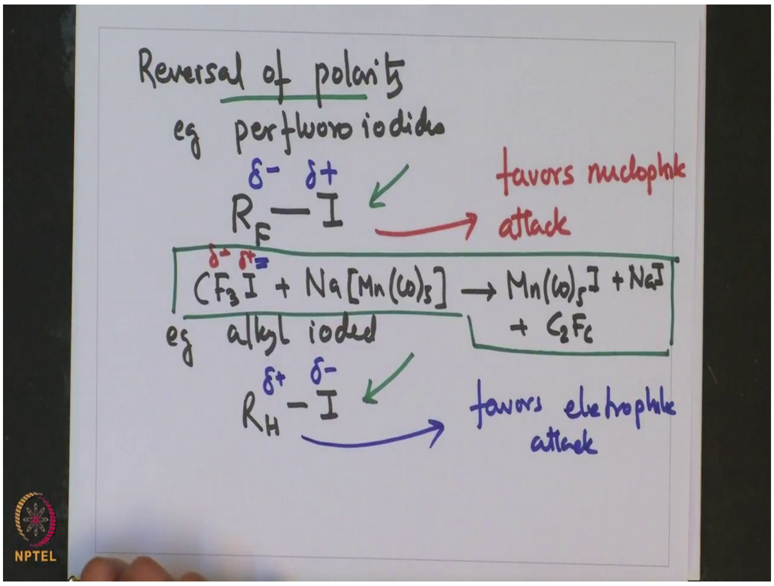

Reversal of polarity

eg perfluoro iodide

$\overset{\delta-}{R_F}-\overset{\delta+}{I}$ favors nucleophilic attack

$\overset{\delta-}{CF_3}\overset{\delta+}{I} + Na[Mn(CO)_5] \rightarrow Mn(CO)_5I + NaI + C_2F_6$

eg alkyl iodide

$\overset{\delta+}{R_H}-\overset{\delta-}{I}$ favors electrophilic attack

Let me illustrate this with perfluoro iodides, for example a perfluoro iodide would have the polarity in the R F-I bond as iodine having the del positive, and the R F minus having the del negative charges. The reason being fluoride being a very strong electron electronegative element would result in accumulation of electron density on the R F moiety resulting in minus del minus on this side, and appropriate del plus on the iodide.

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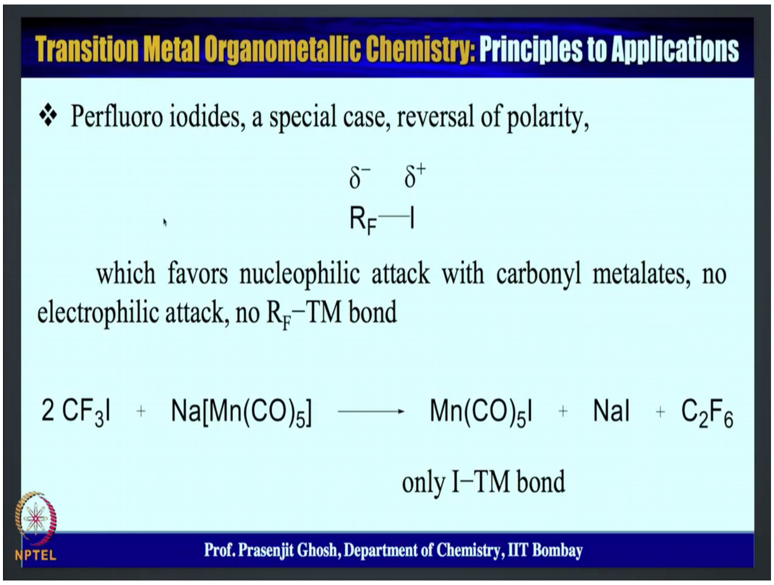

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- ❖ Perfluoro iodides, a special case, reversal of polarity,

$$\overset{\delta^-}{R_F}—\overset{\delta^+}{I}$$

which favors nucleophilic attack with carbonyl metalates, no electrophilic attack, no R_F–TM bond

$$2\,CF_3I + Na[Mn(CO)_5] \longrightarrow Mn(CO)_5I + NaI + C_2F_6$$

only I–TM bond

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However this polarity is completely reverse to that of alkyl halide for example, in alkyl iodide in the corresponding hydrogenated counterpart here in this case what do we see that iodine is del minus and the carbon having all the hydrogen becomes del plus because iodine is more electronegative. So, these to demonstrate that there is a reversal of polarity if 1 were to look at this bond or this bond. And no wonder they show very different reactivity, and that is because this R F iodide type of compound show favors nucleophilic attack at the carbon whereas, our H type of compound favors electrophilic attack.

Let me illustrate this with an example, for the reaction of CF 3 I plus sodium manganese CO 5 here, the iodine is in plus positive charge and the manganese is in the negative charge. And CF 3 has a del minus charge and it does not react with the manganese, and the final product 1 gets is manganese pentacarbonyl iodide plus sodium iodide plus C 2 F 6.

This react reaction is completely different, then what would have what 1 would have expected with the corresponding hydrogenated counterpart. In that case the methylated Mn CO 5 minus would go, and attack the methyl cation cationic fragment of CH 3 and not end up on iodine as shown over here. The another interesting example reactivity of this perfluoro alkyl complexes is that can undergo fluoride substitution with strong nucleophilic metal aids.

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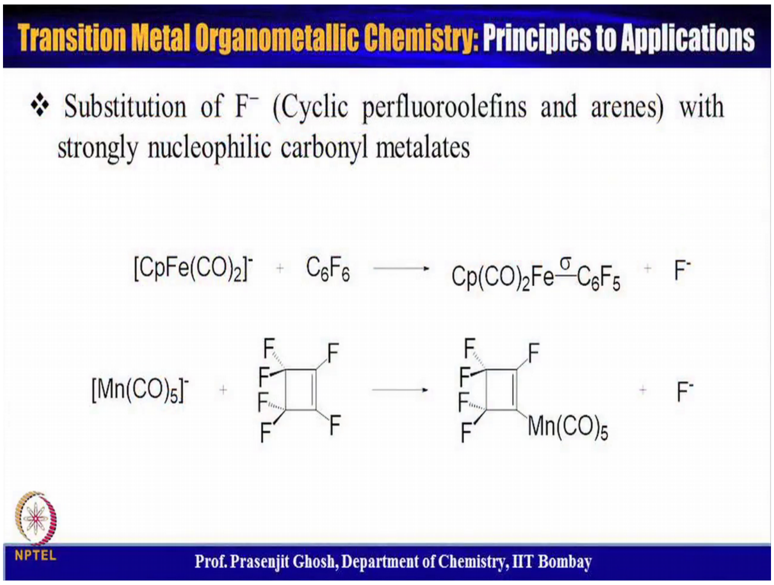

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- Substitution of F^- (Cyclic perfluoroolefins and arenes) with strongly nucleophilic carbonyl metalates

$[CpFe(CO)_2]^- + C_6F_6 \longrightarrow Cp(CO)_2Fe\overset{\sigma}{-}C_6F_5 + F^-$

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With strong nucleophilic carbonyl metalates.

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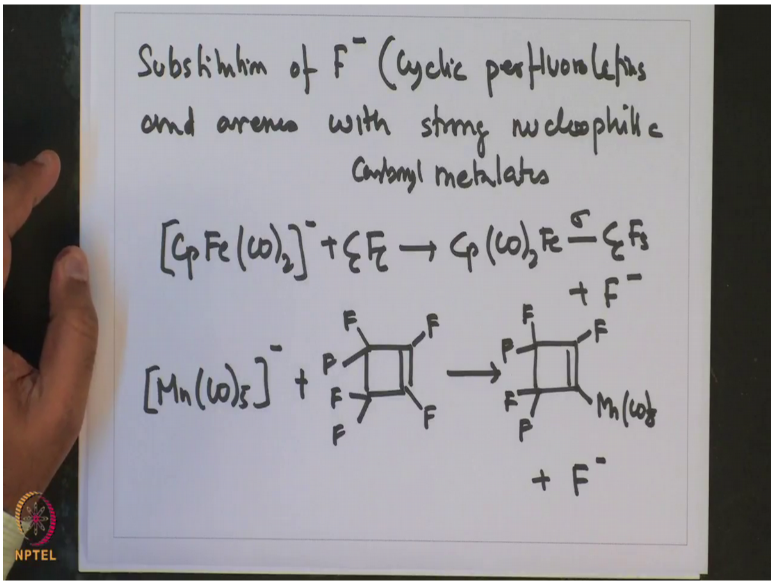

Substitution of F^- (Cyclic perfluoolefins and arenes with strong nucleophilic Carbonyl metalates

$[CpFe(CO)_2]^- + C_6F_6 \rightarrow Cp(CO)_2Fe\overset{\sigma}{-}C_6F_5 + F^-$

For example CpFe di carbonyl anyl plus C 6 F 6 gives Cp CO 2 Fe sigma bonded with C 6 F 5 plus F minus, so here the metal eight anion is substituting a fluoride anion, in this C 6 F moiety the same can be seen over here, where Mn CO 5 minus showing similar nucleophilic attack and replacing the fluoride moiety, in the cyclobutane compound resulting in this cyclo perfluoro cyclobutane fluoride compound and fluoride anion.

With this let me summarize what we have been discussing in today's lecture, we have looked into interesting class of compounds called perfluoro alkyl transition metal complexes. We have looked into their exceptional stability at the for this kind of complexes, which looked for reasons for the source of this exceptional stability. And that arises, because of the polarity of the metal carbon bond containing the perfluoro alkyl moiety. We had also seen that these polarity resolves in stronger ligand to metal sigma donation, and metal to ligand pi back donation which sort of leads to the stable stability of these compounds.

We have also seen that for case of l perfluoro alkyl halide, there is a reversal of polarity leading to different kind of reactions occurring in these perfluoro alkyl transition metal complexes. We have also looked at some of the synthetic procedures available a for this perfluoro alkyl transition metal complexes, with this I conclude todays lecture and look forward to bring with you in next lecture where we are going to take up some more synthetic strategies available for perfluoro alkyl transition metal complexes. And look into the reactivity of these complexes still then goodbye and see you in the next lecture.

Thank you.