Transition Metal Organometallic Chemistry: Principles to Applications

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Lecture – 25

Preparation of Transition Metal Perfluoroalkyl (RF – TM) Complexes

Welcome to this lecture on transition metal organometallic chemistry from principles to applications. In our previous lecture we have been dwelling upon on very interesting topic on transition metal perfluoro alkyl sigma complexes. These complexes are designated by the type as shown here:

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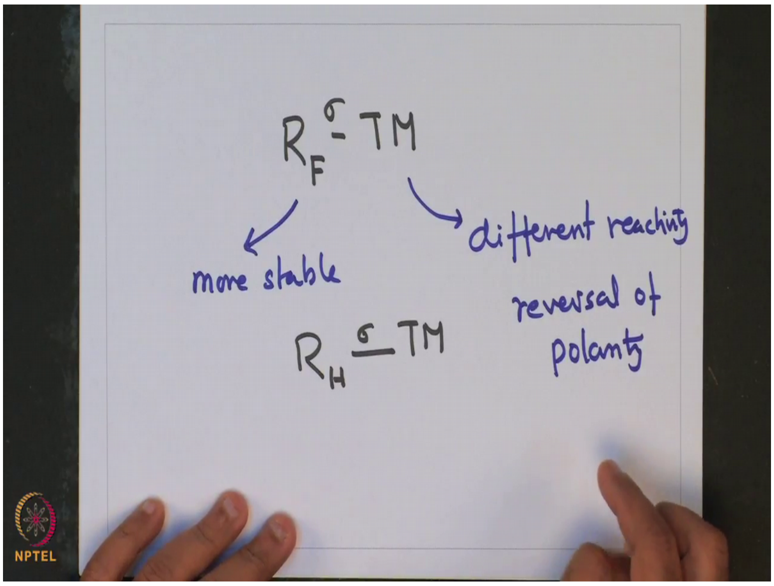

And they are involved in some kind of sigma interaction with the transition metals. This complexes we have discussed show extra stability, as compared to the corresponding transition metal sigma alkyl complexes more stable, as compared to transition metal sigma alkyl complexes which are designated by R H sigma T M.

Also, what we saw is that these complexes show different reactivity as a result of reversal of polarity with regard to these transition metals sigma alkyl complexes. So, because of this reversal of polarity the reactions which would happen naturally for transition metal sigma. Alkyl complexes does not occur or go the opposite way for transition metal perfluoro alkyl complexes that leads to a very interesting complementary comparison between these 2 types of complexes which are both of sigma types, but they show very different reactivity and property as well as their stability, with that we have looked into various methods available for preparation of this transition metal perfluoro alkyl complexes and one the 1 or 2 methods that we have discussed involved replacing of fluoride anion with the metalite anion and in the process making these transition metal perfluoro alkyl complexes.

So, in these lecture, we are going to discuss some more interesting synthetic routes for preparation of these transition metal perfluoro alkyl sigma complexes.

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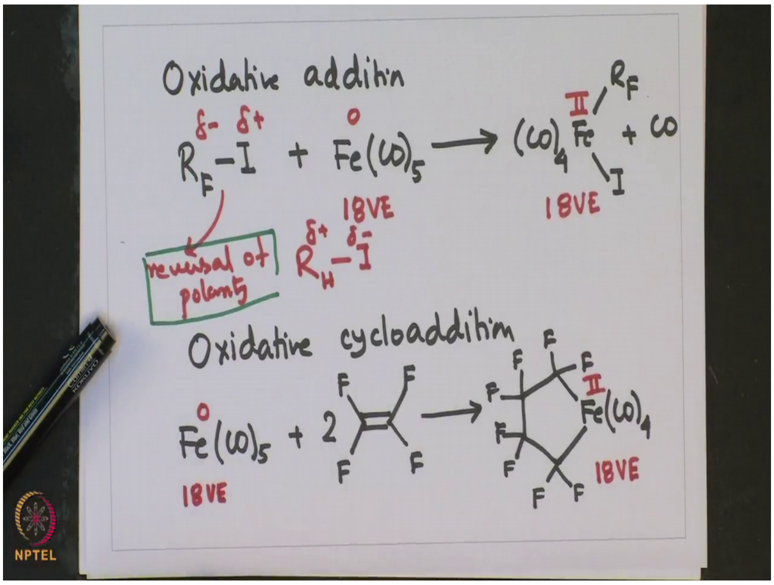

The first and the most common one is the method of oxidative addition. Perfluoro alkyl iodide can be oxidatively added against a low valent metal centered. For example, iron penta carbonyl giving the oxidatively added product plus CO.

Here the iron is in 0 oxidation state and it is a 18 valence electron compound after oxidative variation as expected the iron is in plus 2 oxidation state and it is also a 18 valence electron compound actually it losses a CO to become coordinatively unsaturated to give 16 valence electron compounds which then oxidative add to give the resulting CO4FERFI 18 valence electron compound as discussed in our earlier lecture that the there is a reversal of polarity in this array bound and that RF side is carbon ionic whereas, iodide side is carbo cationic.

This is very different from any alkyl iodide where; the iodide side would be negatively charged and the carbons side would be cationic in nature. We see that there is a reversal of polarity for these perfluoro alkyl type of compounds and that have been used successfully in preparing these perfluoro alkyl transition metal sigma alkyl complexes through this method of oxidative addition.

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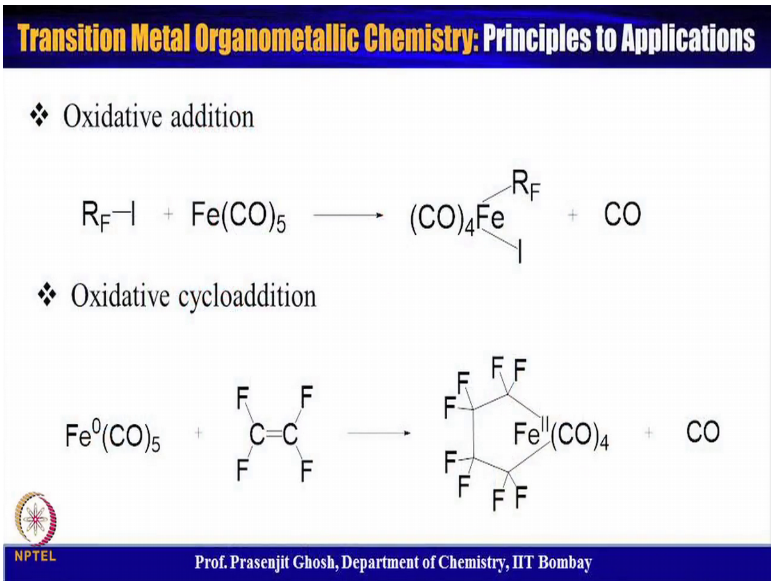

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- Oxidative addition

- Oxidative cycloaddition

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Another method that exist is called oxidative cyclo addition and these involves addition of an olefin of perfluoro alkyl compound resulting in a metalocycle of the type shown. Here too is this low valent iron center reacting with 2 molecules of C2F4 perfluoro ethylene giving this 5-member metal acyclic

Here the oxygen state of iron is in plus 2 and it also has 18 valence electron whereas, in the starting precursor iron is in low valent 0 oxidation state and having a 18 valence electron configuration. Now in the process of oxidative radiation the iron initially like in the previous example releases a CO to become coordinatively unsaturated which then adds undergoes this oxidative cycloaddition with 2 molecules of C2H4 resulting in this perfluoro alkyl cyclo alkyl iron compound as shown over here.

These 2 oxidative addition reactions are kind of related in terms of the fact that the iron center increases it is oxidative state by plus 2 and 1 involves just oxidative addition of an perfluoro halide alkyl halide and in the other, other case it is a perfluoro alkene 2 molecule of this reacting to give the compound another interesting reaction involves insertion of this perfluoro alkene into metal metal bonds

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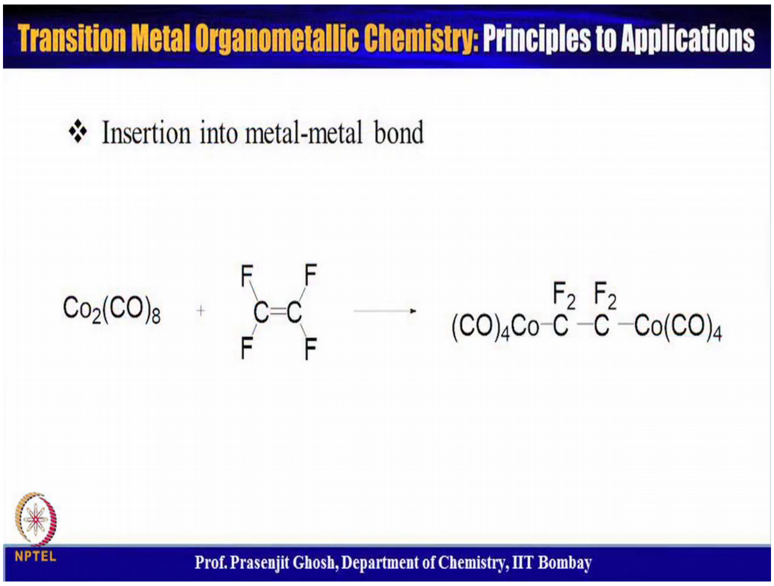

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- Insertion into metal-metal bond

$Co_2(CO)_8 + F_2C{=}CF_2 \longrightarrow (CO)_4Co{-}CF_2{-}CF_2{-}Co(CO)_4$

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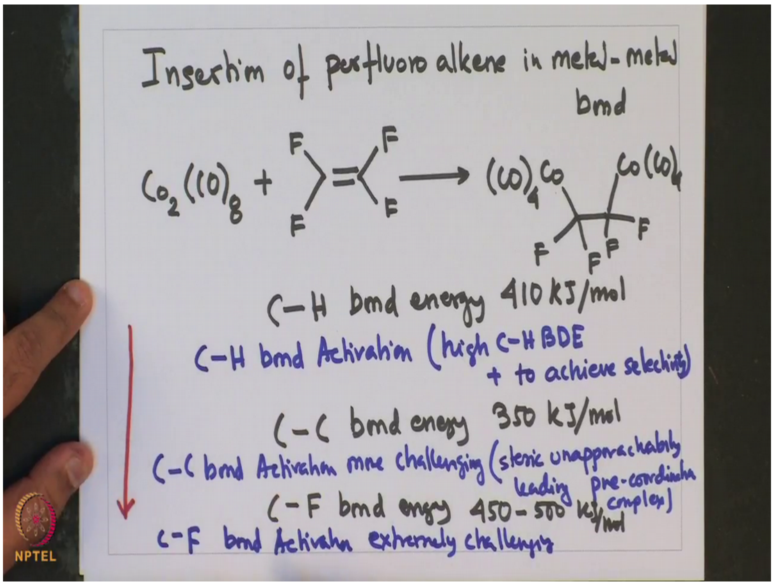

Insertion of perfluoro alkene in metal-metal bond

$Co_2(CO)_8 + F_2C{=}CF_2 \longrightarrow (CO)_4Co{-}CF_2{-}CF_2{-}Co(CO)_4$

C–H bond energy 410 kJ/mol

C–H bond Activation (high C–H BDE + to achieve selectivity)

C–C bond energy 350 kJ/mol

C–C bond Activation more challenging (steric unapproachability leading pre-coordination complex)

C–F bond energy 450–500 kJ/mol

C–F bond Activation extremely challenging

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and this is given by the reaction C cobalt di cobalt octo carbonyl reacting with perfluoro ethylene giving CO4 cobalt CF2CF2 cobalt CO4 here is similar any other insertion reaction of the corresponding alkene, where the alkene insertion into metal metal bond has occurred and the similar path strategy has been successfully employed in preparing this perfluoro alkyl bi metallic cobalt compound as shown over here.

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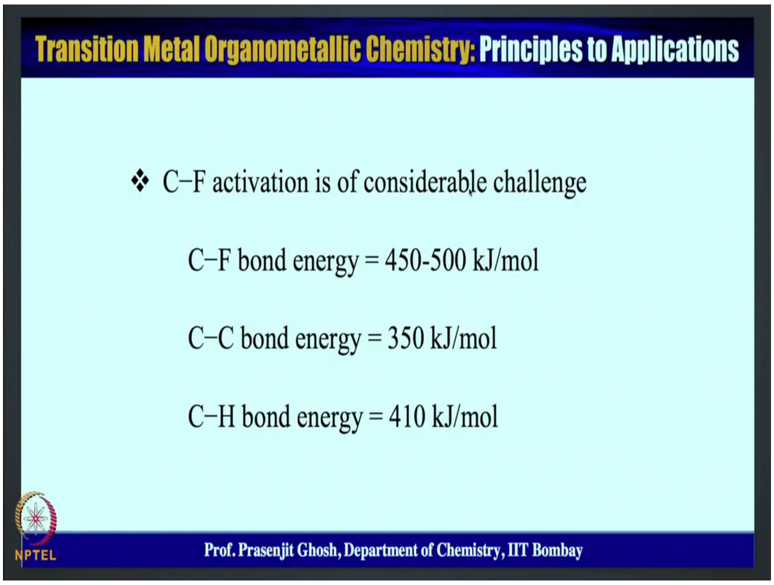

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- ❖ C−F activation is of considerable challenge

C−F bond energy = 450-500 kJ/mol

C−C bond energy = 350 kJ/mol

C−H bond energy = 410 kJ/mol

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Now, we had looked at various kinds of activation reactions particularly, from the utility point of view we started with CH activation and saw that activation was an important reaction leading to various functionalization products which has which would produced value added chemicals from simple hydrocarbons and what we saw is that CH activation was quite challenging as a result of very high CH bond energy the bond was very difficult to break and the CH bond energy was around 410 kilo joule per mole and the challenge as mentioned for CH bond activation had been had been because of high bond energy plus to achieve selectivity.

So, what we saw that CH bond activation was quite challenging primarily because of it is high bond energy as well as of it is very high ubiquitous nature their selectivity becomes the issue. Following that we have looked into CC bond activation and what we found that CC bond is even more difficult to activate despite the fact that CC bond is somewhat easier to cleave a CC bond energy is around 350 kilo joules per mole as opposed to 410, but CC bond activation is more challenging because of steric unapproachability leading to the pre-coordination complex required for initiating the activation reaction is becomes even more difficult.

So, what we saw that even though the CC bond energy was slightly lower than that of CH bond energy it is activation was even more challenging because, these bonds are deeply buried they are outnumbered by CH bonds. As a result, the pre-coordination complex required for initiating the activation reaction is becomes even more difficult and CC bond activations does becomes more challenging then CH bond activation and what we saw that the examples which had CC bond activation had to do with release of ring strength in the sub straight arise resulting in CC bond activation and hence it is more difficult.

Now, when this in in the context of this 2 when we look at CHCF bond activation it becomes on the more challenging primarily because CF bond energy is the strongest and it is way a higher than CC and CH and it is can vary 400 to 500 kilo joule per mole and that is extremely high as compared to CC and CH which makes CF bond activation very extremely challenging. These sort of gives a overall picture that if one goes down the group CH to CC difficulty in bond activation increases as one goes down the group and that primarily for CF is due to the very high CF bond energy which lies between 450 to 500 kilo joules per mole and they are way a higher than that CHCC and CH bond energies as shown over here.

Now, that thing the fact that CF bonds are difficult to activate there are very, very, very many strategies in place which facilitate CF bond activations these are very clever approaches which circumvence this barrier of very high CF bond energy that makes the CF activation very difficult.

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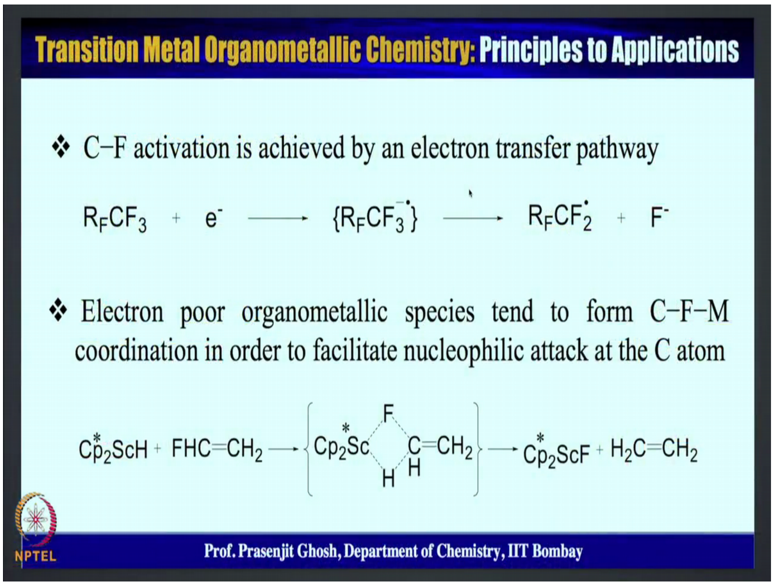

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- C–F activation is achieved by an electron transfer pathway

$$R_FCF_3 + e^- \longrightarrow \{R_FCF_3^{\bullet-}\} \longrightarrow R_FCF_2^{\bullet} + F^-$$

- Electron poor organometallic species tend to form C–F–M coordination in order to facilitate nucleophilic attack at the C atom

$$Cp^*_2ScH + FHC{=}CH_2 \longrightarrow \left\{ Cp^*_2Sc \overset{F}{\underset{H}{\diamond}} \underset{H}{C}{=}CH_2 \right\} \longrightarrow Cp^*_2ScF + H_2C{=}CH_2$$

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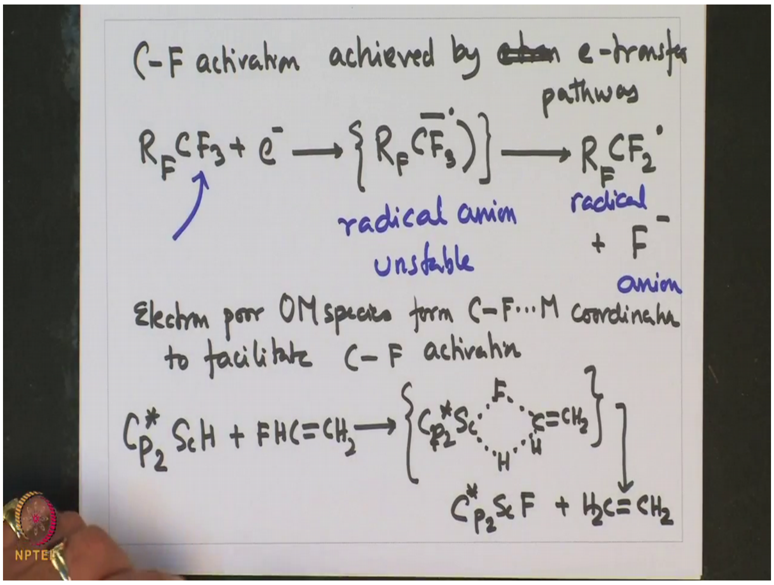

C–F activation achieved by e-transfer pathway

$R_FCF_3 + e^- \longrightarrow \{R_F\dot{\bar{C}}F_3)\} \longrightarrow R_FCF_2^{\bullet} + F^-$

radical anion unstable

radical

anion

Electron poor OM species form C–F···M coordination to facilitate C–F activation

$Cp^*_2ScH + FHC{=}CH_2 \longrightarrow \{Cp^*_2Sc\cdots F\cdots C{=}CH_2 \cdots H\} \longrightarrow Cp^*_2ScF + H_2C{=}CH_2$

And one such strategy that is in place is achieving CF bond activation by electron transfer path way.

This is illustrate in the following example for example, for this perfluoro alkyl compound RFCF3 to which an electron is added to produce this radical anion this is a radical anion and hence unstable and it releases a fluoride anion to give RFCF2 dot radical and an anion F minus. In the process one what one sees that the CF bond in this RFCF3 has been cleaved to CF2 and F. So, that is how the activation has been achieved and activation has been achieved by addition of an electron resulting in the formation of an unstable radical anion and the radical anion stabilizes itself by decompose decomposing from it is radical anion state to give a radical species and anionic species as shown here there by a achieving this CF bond activation.

So, apart from supply of electron sometimes electro organometallic species also helps achieve CF activation through coordination I will illustrate this with an example electron poor or electron deficient organometallic species forms CFM coordination to facilitate CF activation and this is illustrated by this scandium complex CP star 2 scandium hydride reacting with this olefin HFCCH2 to give this compound CP star 2 scandium interacting with fluorine of this alkene that finally, results in the formation of CP star 2 scandium fluoride and ethylene.

Here too, what one observes is that this fluorine is sort of abstracted by this electron deficient species scandium and interchanged with the hydrogen which scandium had leaving to this CF bond activation. So, reviewing the methods available for activating CF bond what one sees that the successful strategy involves either donation of electron resulting in a unstable radical anion species which there by stabilizes by undergoing CF bond activation or by achieving CF bond oxidation by coordination with electron deficient transition metals and this can be also achieved by increased reactivity of transition metal perfluoro alkyl moiety.

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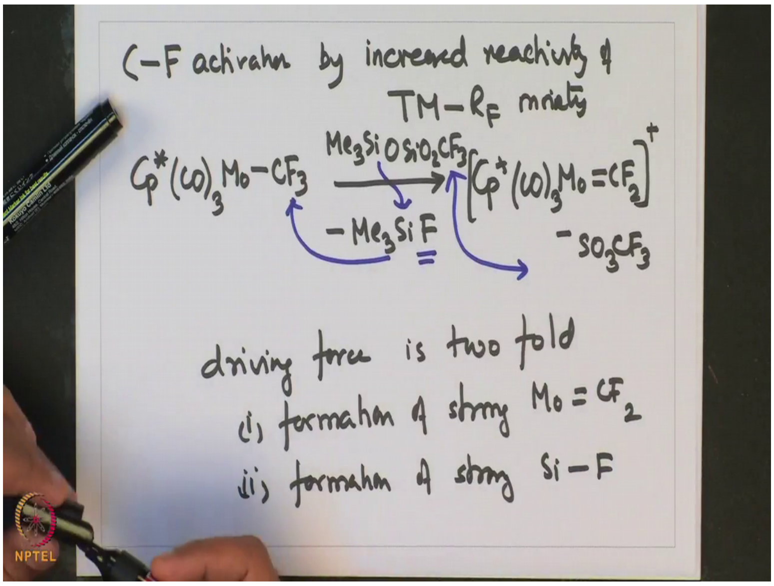

C–F activation by increased reactivity of TM–R_F moiety

$$Cp^*(CO)_3Mo-CF_3 \xrightarrow{Me_3SiOSiO_2CF_3} [Cp^*(CO)_3Mo=CF_2]^+$$

$-Me_3SiF$

$^-SO_3CF_3$

driving force is two fold

(i) formation of strong $Mo=CF_2$

(ii) formation of strong Si–F

For example in this example CF activation achieved by increased reactivity of transition metal RF moiety these is an interesting example in which CP star tri carbonyl molybdenum CF3 compound when treated with MESiO2CF3 gives the eliminates the MeSiF molecule, which abstracts this fluorine from one of the CF molecule by this silicon cation that is coming from ME3SiO moiety and that results in this interesting CP star tri carbonyl molybdenum CF2 di fluoro carbine complex with this SO3CF3 minus anion and this anion is derived from this part of the reagent.

Now, this is a very interesting reaction whereby by using TM must reflect one can abstract the fluoride from a transition metal perfluoro alkyl residue giving rise to CH activation the driving force for this reaction is 2fold first from the formation of strong

MOCF2 moiety where you see a double bond of MOCF2 formed and second thing is formation of strong SIF bond which is in this.

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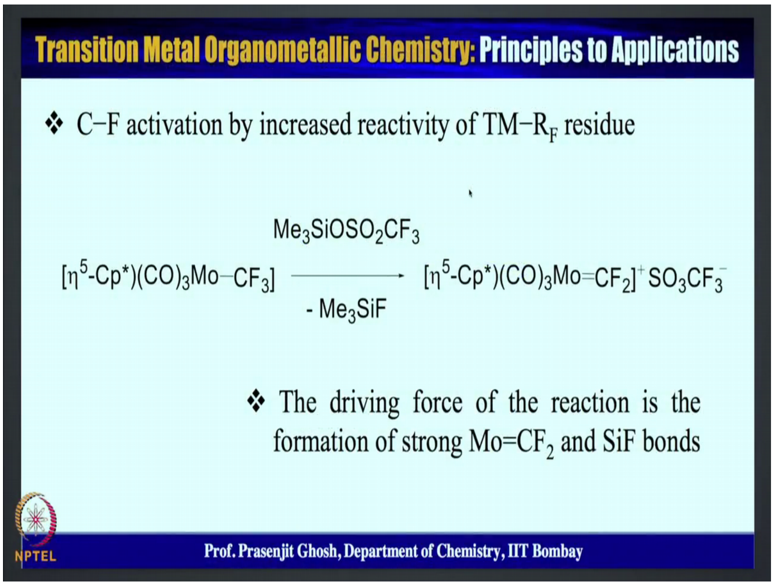

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- ❖ C–F activation by increased reactivity of TM–R_F residue

$$[\eta^5\text{-Cp*})(CO)_3Mo{-}CF_3] \xrightarrow[-\ Me_3SiF]{Me_3SiOSO_2CF_3} [\eta^5\text{-Cp*})(CO)_3Mo{=}CF_2]^+ SO_3CF_3^-$$

- ❖ The driving force of the reaction is the formation of strong Mo=CF_2 and SiF bonds

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So, with this I would like to review what we have discussed in today's lecture we have looked into various synthetic protocols available for preparing transition metal perfluoro alkyl complexes which mainly include oxidative addition reactions and oxidative cyclization reactions. We have also looked at CF activation in the perspective of CH and CC activations owing to very high bond energy of CF bonds which can vary from 450 to 500 kilo joules per mole and are by far more higher a energy, then that of the bond energies of CH and CC bonds CF bond activations are extremely challenging to achieve.

However, we have also seen that few successful strategies that are put in place to achieve c f bond activation which involved electron transfer path way resulting in a anion radical which led to c f bond activation. We have also seen coordination or a fluoride abstraction with electron deficient transition metal complexes resulting in CF bond activation and lastly in this example we have seen that CF activation by increase reactivity of transition metal perfluoro alkyl complexes with these, I conclude todays lecture and look forward to being you being with you in the next lecture where we are going to discuss some more reactivity pattern of CF bond activation reactions and that of perfluoro alkyl transition metal complexes till then, good bye and see you in the next lecture.

Thank you.