Transition Metal Organometallic Chemistry: Principles to Applications

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Week - 06
Lecture – 26
C - F Activation

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. In the last lecture we have been discussing an very interesting topic on C-F activation.

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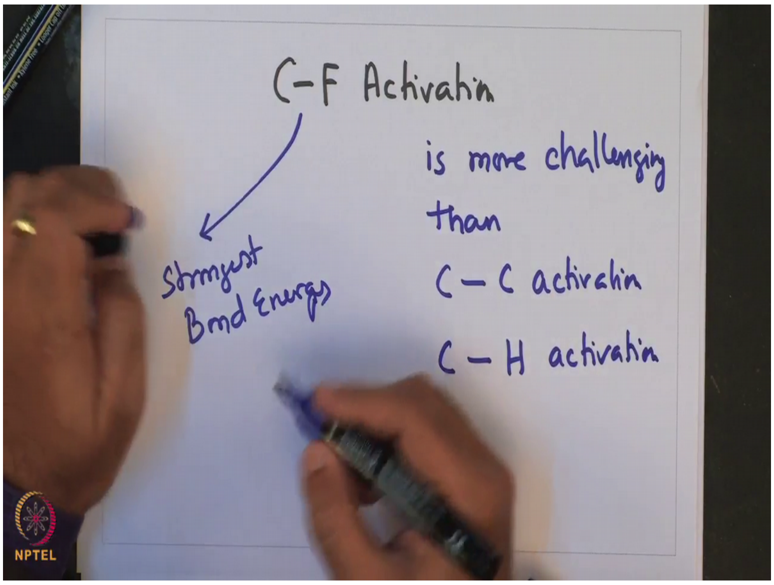

C-F Activation

Strongest Bond Energy

is more challenging than

C-C activation

C-H activation

Now, carbon fluorine bond being among the strongest, being among the strongest this C-F activation is the most challenging of all activation that one we have encountered so far. So, C-F activation is more challenging than for example, C-C activation as well as C-H activation.

However, that being said there are a lot of examples where C-F activation has been achieved. In our last class we have seen how C-F activation has been achieved in form of 2 or 3 examples that we have looked into close details. One was about achieving C-F activation by addition of an electron to a compound making a radical anion and then the radical anion decomposing into anion and a radical species achieving C-F activation.

In another example we had seen that C-F activation was achieved by coordination to electron deficient transition metal that also resulted in C-F activation and lastly we had seen C-F activation in a transition metal perfluoro alkyl sigma complex where when treated with TM S flate one flow C-F activation occurred resulting in the formation of TM S fluoride and transition metal C-F 2 carbon complex.

Now, having say seen that several strategies in place for C-F activation despite the fact that it is one of the most challenging activation to perform with respect to the other activations that we have spoken about like C-C and C-H. In today's lecture we are going to see this in more details. About examples which achieve such C-F activation in a very simplified manner.

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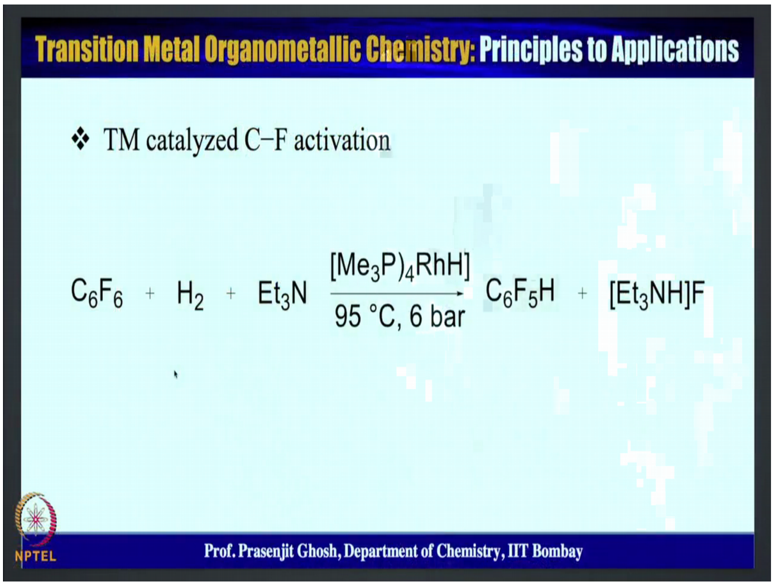

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- TM catalyzed C–F activation

$$C_6F_6 + H_2 + Et_3N \xrightarrow[95\ ^\circ C,\ 6\ bar]{[Me_3P)_4RhH]} C_6F_5H + [Et_3NH]F$$

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So, here is an example where the C-F activation has been achieved in a catalytic fashion.

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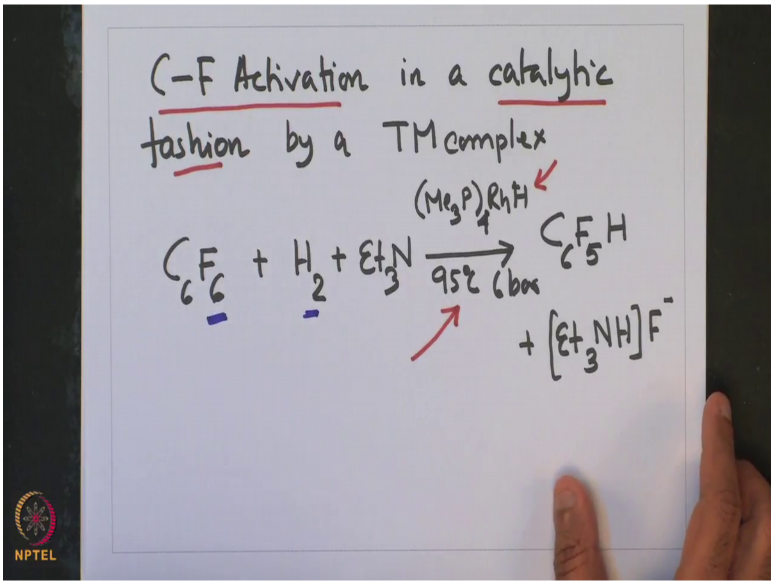

C–F Activation in a catalytic fashion by a TM complex

$$C_6F_6 + H_2 + Et_3N \xrightarrow[95\,^\circ C\ 6\,bar]{(Me_3P)_4RhH} C_6F_5H + [Et_3NH]F^-$$

Transition metal complex, this is illustrated in the examples shown over here reaction of perfluorobenzene C 6 H 6 with the hydrogen in presence of a base triethylamine as catalyzed by a rhodium complex at 95 degree centigrade and 6 bar pressure produces this C-F activated product in terms of giving C 6 F 5 H along with triethyl NH plus and F minus.

To note that these one of the C-F bond of perfluorobenzene has been cleaved and to it a active hydrogen activation has occurred and a hydrogen gets attached to it giving to this C-F activated product C 6 F 5 H and protonated based fluoride which is triethyl NH plus. What is remarkable about this transformation is that not only the C-F a very challenging C-F activation has been achieved, but also this has been achieved in a catalytic fashion by this rhodium catalyst also at not too harsh a condition 95 degree centigrade. So, this is rather considered a very mild condition for achieving C-F activation because of the fact that C-F bonds are extremely strong. So, what we going to do is we are going to now look at how these reaction proceeds in terms of the mechanistic cycle, it undertakes to carry out the C-F activation.

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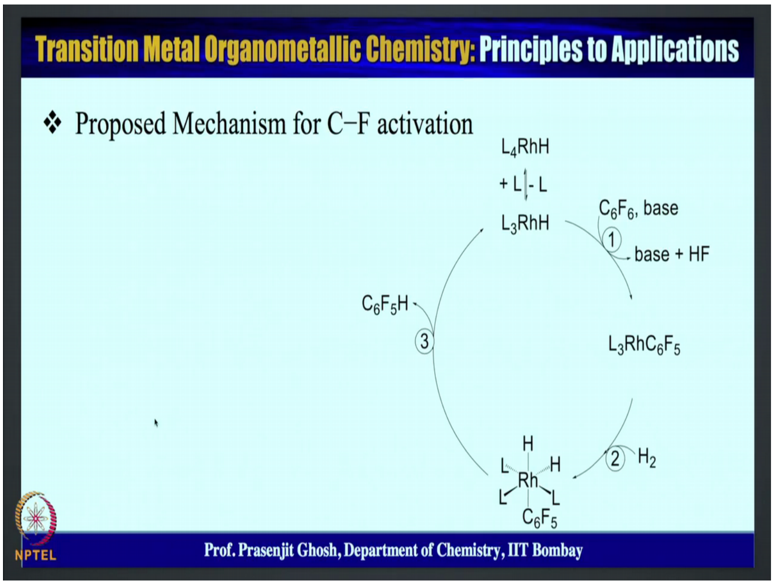
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- Proposed Mechanism for C−F activation

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The catalyst which is L 4 rhodium hydride is one can say both co-ordinatively saturated because it has a coordination number of 5 and electronically saturated because it is a 18 valence electron compound the oxygen state of rhodium is rhodium 1.

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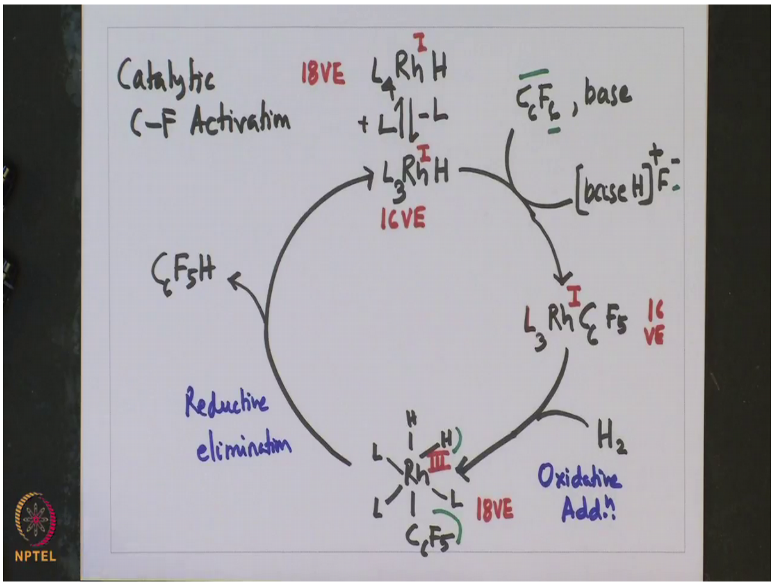

So, that being the case this may be considered as being catalytically inactive. So, these pre catalyst enters the catalytic cycle by elimination of one of the L ligands giving rise to L 3 rhodium hydride complex, here two the rhodium is in plus one oxidation state and it has now become electronically unsaturated as a result of the loss of this L ligands and currently it is a 16 valence electron complex, and also the complex has undergone a loss in its coordination number.

This complex which enters the catalytic cycle reacts with perfluorobenzene C 6 F 6 and the base which is triethylamine to give the C-F activated product in terms of base getting protonated from this hydrogen and the C-F getting cleaved because of the activation giving a fluoride anion and the C 6 F 5 bond then get attached to the rhodium complex. So, this is a C-F activation step where the fluorine gets cleaved and ends up in the anion and the remaining C 6 F 5 binds to rhodium and this proton is gets protonated on the base. This itself is also a rhodium one compound and it is a 16 valence electron complex. So, now, that C-F splitting has had happened the second reagent which is the di-hydrogen reacts with this L 3 rhodium perfluorobenzyl complex giving this rhodium di-hydride complex this is an oxidative addition step in which di-hydrogen molecule (Refer Time: 12:37) adds on the low valent rhodium 1 L 3 Rh C 6 H 5 complex giving the rise to this 6 coordinated rhodium di-hydrogen complex as shown below.

So, here we see di-hydrogen adding on to rhodium giving rhodium di-hydride and the 3 L ligands are occupy the coordinate site and the 6th one being occupied by this C 6 F 5 ligand. So, here the rhodium is in plus 3 oxidation state and this also has become an 18 valence electron complex after the oxidative addition of the di-hydrogen has occurred. So, this step is an oxidative addition step.

The next step which follows this oxidative addition step is a crucial step that eliminates the hydrogenated perfluorobenzene which is C 6 F 5 H and as one can see that this release is because of reductive elimination between this C 6 F 5 and the rhodium hydrogen bond. So, after this oxidative variation the next step which follows is reductive elimination, giving rise to the rhodium 1 L 3 rhodium hydride complex. These complex in presence of this L can give back the precatalyst.

So, what is demonstrated over here is a very efficient catalytic cycle for C-F activation using a rhodium complex. So, we have seen that important and difficult as C the one like C-F activation can be achieved not only in a stoichiometric fashion using stoichiometric reagent, but also can be achieved using catalytic fashion the way by this rhodium complex as has been shown over here. So, this is a nice demonstration of catalytic cycle that carries out C-F activation efficiently. So, with this we sort of finish our discussion on perfluoro alkene complexes.

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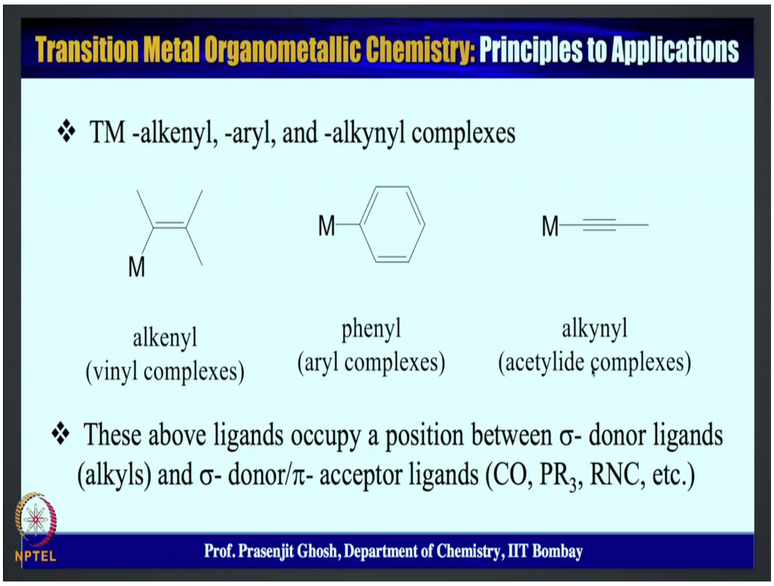

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- TM -alkenyl, -aryl, and -alkynyl complexes

alkenyl
(vinyl complexes)

phenyl
(aryl complexes)

alkynyl
(acetylide complexes)

- These above ligands occupy a position between σ- donor ligands (alkyls) and σ- donor/π- acceptor ligands (CO, PR_3, RNC, etc.)

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Now, to give a brief overview as to how we have been discussing these transition metal sigma alkyl complexes we have seen that we started off with alkyl type complexes and in transition metal sigma alkyl complexes we have covered C H activation as well as C-C activation.

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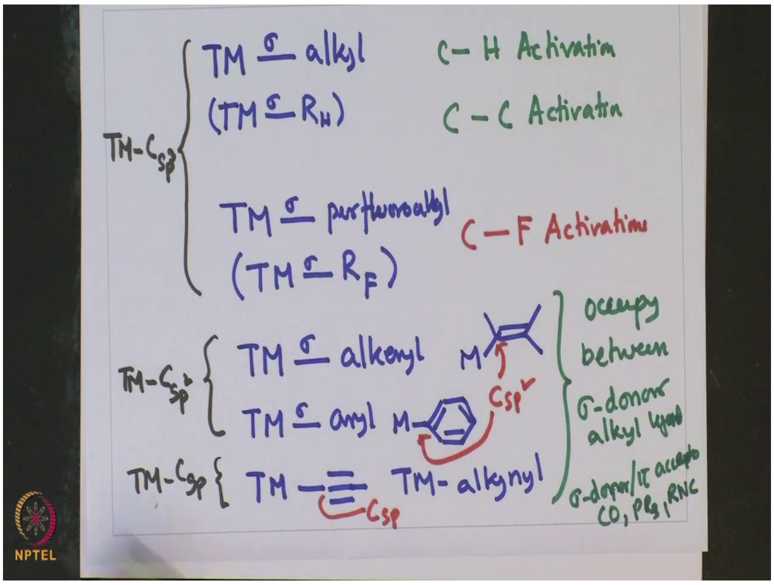

We have also seen how these activations occurred now after considering transition metal sigmaalkyl complexes, we have then looked into this very important transition metal sigma perfluoro alkyl complexes these are represented by TM sigma R F and in this context we have looked at C-F activation reactions.

Now, these are class of compounds which has a commonality. The commonality being that these are transition metal C carbon SP 3 type complexes that we have looked into. Now, we are going to go beyond these SP 3 type complexes and look into some examples of transition metal C SP 2 types in the course of next lectures and to begin with we will look at some of these ligands. Now, in our earlier discussion on type of transition metal sigma alkyl complexes we had shown that sigma alkyl complexes can be of carbon moiety which is of C SP 3 types can also be of carbon moiety which is a which is of C SP 2 type and can also be of carbon moiety which is of SP type.

So, along this now we are going to take a look at two such examples of transition metal complexes one is transition metal sigma alkenyl complexes these can be represented as where the this carbon is C SP 2 we are going to also look at transition metal aryl complexes and these are given by M SP 2 type. So, this is the SP 2 center. So, this would be the type of compounds that we would be discussing now for transition metals C SP 2 type. And as for the transition metal SP type we are going to talk about transition metal alkene alkynyl complexes and these are called alkynyl complexes where this carbon is C SP.

So, over the last few lectures we have covered upto this part and now we are going to go and look into these two kind of systems. As far as these ligands are concerned this alkenyl, aryl, alkynyl, these ligands occupy an intermediate position between sigma donor alkene ligands and sigma donor pi acceptor carbon monoxide P R 3 and R N C ligands. Now, this is a very important statement as far as these ligands are concerned. So, in terms of their in terms of their bonding with the transition metal they thus occupy a position which is between completely sigma donor ligands as well as sigma donor pi acceptor ligands.

So, what does that indicate is that this ligand has intermediate ability to behave as a pi acceptor ligands they are not too strong as a pi acceptor sigma donor, but also they are not fully a sigma donor system we going to look at these in bit more details.

Now, let me summarize what has been covered in this lecture. In this lecture we have looked into C-F bond activation reactions and particularly we have looked into a very nice example of a transition metal catalyzed C-F bond activation reaction using molecular hydrogen under not too harsh conditions rather mild conditions of 95 degree centigrade and 6 bar of hydrogen pressure in presence of a rhodium catalyst that could activate a C-F bond of the perfluorobenzene and replace that with molecular hydrogen to gives C 6 F 5 H under catalytic fashion. We have also looked at the various type of C-F activation reactions and the examples of it and with that we concluded our discussions on transition metal sigma alkyl perfluoro alkyl complexes.

We have also discussed the next set of compounds that we are going to be taking up which are transition metal, alkenyl and alkynyl transition metal arrival complexes which has a transition metal bonded to carbon of C SP 2 hybridization as well as C SP type hybridization.

So, with this I would like to conclude today's lecture and in next lecture we are going to take up transition metal C SP 2 as well as transition metal C SP type compounds. Look at their properties synthesis and the reactivity in much more detail and compare the same with that of the transition metal C SP 3 types compounds that we have covered so far. In the transition metal C SP 3 type compounds we have looked into transition metal sigma alkyl and transition metal sigma perfluoroalkyl complexes. So, till then good bye and see you in the next lecture.

Thank you.