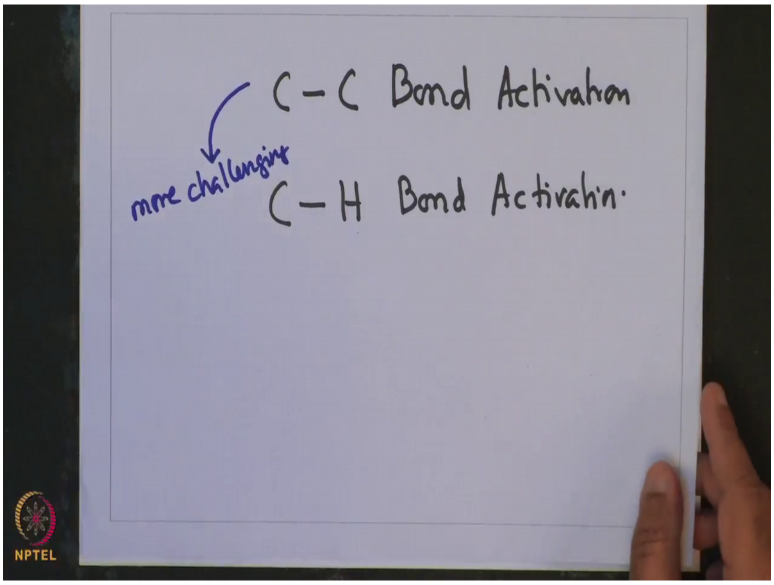
Transition Metal Organometallic Chemistry: Principles to Applications

Prof. Prasenjit Ghosh
Department of Chemistry
Indian Institute of Technology, Bombay

Lecture – 21
C – C Bond activation

Welcome to this lecture on transition metal organometallic chemistry from principles to applications. Today we will be take up a new topic which is C C bond activation reaction.

(Refer Slide Time: 00:36)



C – C Bond Activation

more challenging

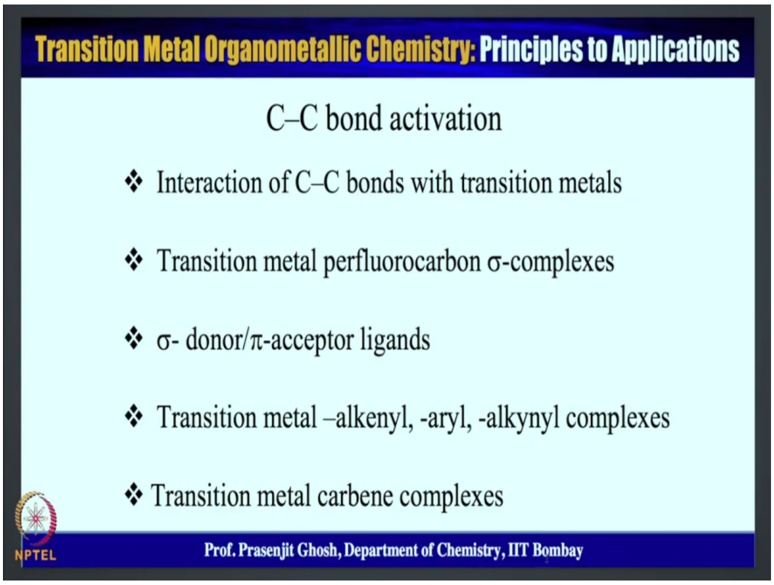
C – H Bond Activation.

And before we take this up which is a more challenging a topic to take up, we have developed the concept of C H bond activation, in our previous lectures. Those C H bond activation is quite challenging by it is own merit, but C C bond activation is even more challenging than C H bond activation. Then C H bond activation and hence I thought that it would be better for us to understand the easier one relatively easier one which is the C H bond activation prior to us taking up the C C bond activation. As the knowledge gained in C H bond activation would help us easily understand the C C bond activation.

In this regard in the last few lectures we have looked at the mechanism of C H bond activation. How it proceeds by intermolecular as well as intra molecular pathways. What how C H bond activation can be favorably utilized for C H bond functionalization by incorporation of functional group on a C H bond. We had seen examples of that we are also looked at various orbital interaction involved between the metal and the ligand in stabilizing the metals C H sigma bond alkane type complexes, which further leads to these C H bond activation.

We had also looked at the free energy a surface space for such C H bond activation processes which can proceed by oxidative addition in the forward direction and by reductive elimination in the reverse direction. Now with these understanding in place we going to look up something more interesting and more challenging a problem which is C C bond activation to understand C C bond activation, we going to look up the following topics.

(Refer Slide Time: 03:31)



Transition Metal Organometallic Chemistry: Principles to Applications

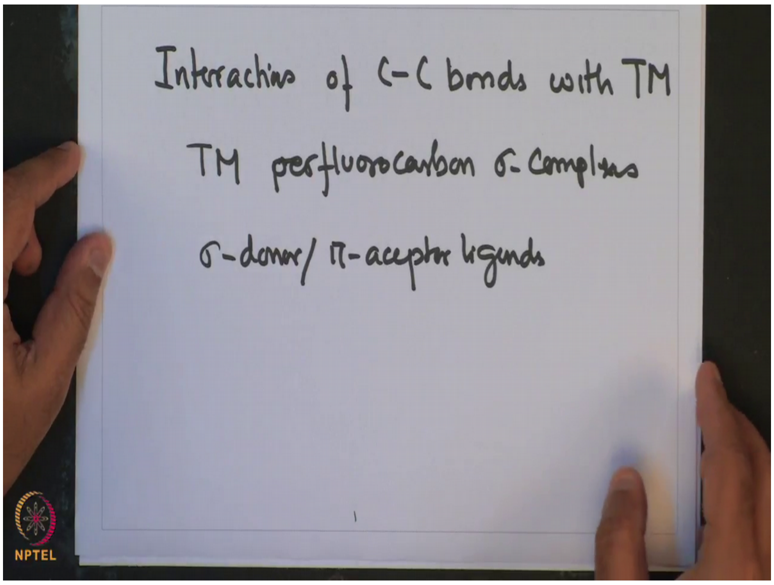
C–C bond activation

- Interaction of C–C bonds with transition metals
- Transition metal perfluorocarbon σ-complexes
- σ- donor/π-acceptor ligands
- Transition metal –alkenyl, -aryl, -alkynyl complexes
- Transition metal carbene complexes

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

Particularly we are going to preview C C bond activation from the perspectives of interactions of C C bonds with transition metals.

(Refer Slide Time: 03:41)



Interactions of C–C bonds with TM

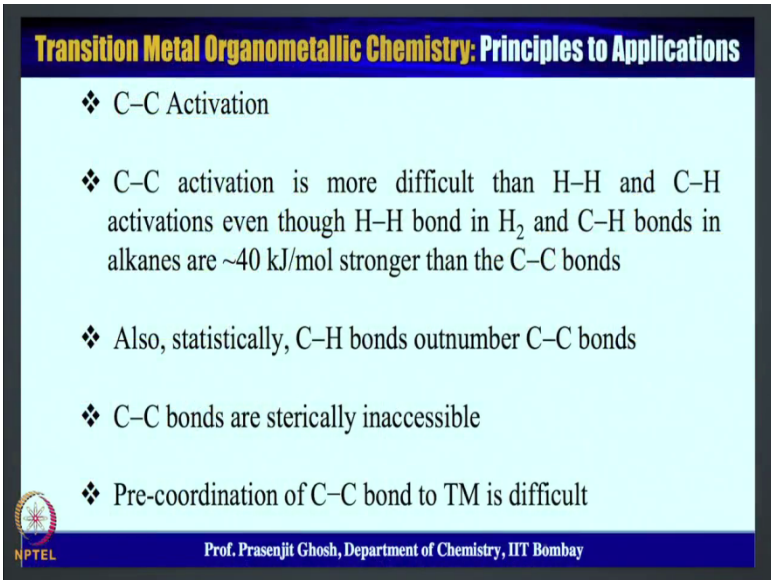
TM perfluorocarbon σ-Complexes

σ-donor/ π-acceptor ligands

Also, we are going to take a look of the C C bond activation from the perspective of transition metal perfluorocarbons sigma complexes. And we will also discuss various other sigma donor and pi acceptor ligands and you would also be looking at transition metal alkynl aryl or alkenyl complexes as well as transition metal carbine complexes.

So, this sort of gives a glimpse of sequence of topics that would be covered with respect to the larger topic that we are discussing in this lecture which is about C C bond activation. Now C C bond activation is more challenging than C H bond activation is more challenging C H bond activation.

(Refer Slide Time: 05:23)

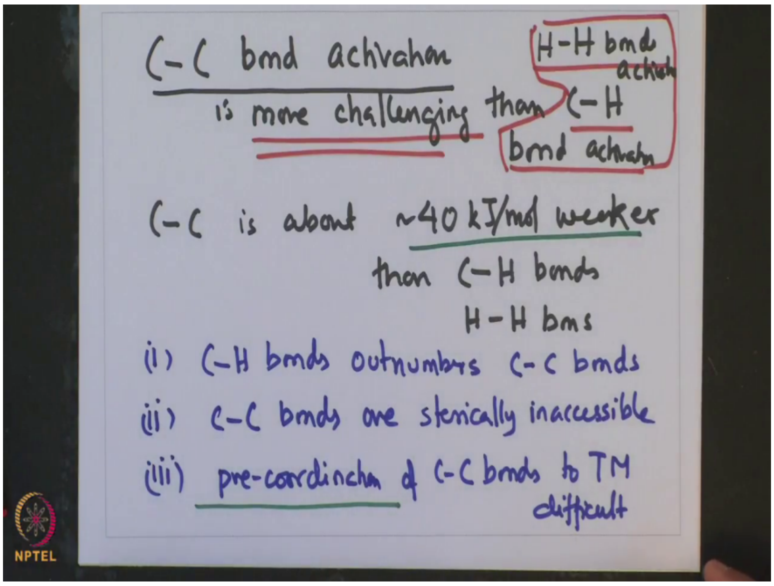


Transition Metal Organometallic Chemistry: Principles to Applications

- C–C Activation
- C–C activation is more difficult than H–H and C–H activations even though H–H bond in H_2 and C–H bonds in alkanes are ~40 kJ/mol stronger than the C–C bonds
- Also, statistically, C–H bonds outnumber C–C bonds
- C–C bonds are sterically inaccessible
- Pre-coordination of C–C bond to TM is difficult

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

(Refer Slide Time: 05:24)



C–C bond activation is more challenging than H–H bond activation C–H bond activation

C–C is about ~40 kJ/mol weaker than C–H bonds H–H bons

(i) C–H bonds outnumbers C–C bonds
(ii) C–C bonds are sterically inaccessible
(iii) pre-coordination of C-C bonds to TM difficult

And that is because that these C C bonds are of C C bonds are weaker than C H bonds to cleave. And what it tells us that this difficulty is not because of the bond energies of C H bond versus C C bond for example, C C bond is about 40 kilojoules per mole weaker than C H bonds or even H H bonds.

So, despite the fact that C C bond is a weaker bond to cleave C C bond activation is more challenging than C H bond activation, as well as H H bond activation. And what it is indicating that despite the fact that these bonds are easier to cleave that the bond energy is about forty kilojoules per mole weaker than that of a C H bond or a H H bond still this is a difficult problem and that is because the challenge is due to statistically C H bond outnumbers C C bonds. So, there are less C C bonds to click for the catalyst to see then the C H bonds out numbers.

So, it is very for a catalyst which is activating a particular sigma bond it will see more number of C H bonds around it then the C C bonds, second reason being C C bonds a less in number and also difficult to approach C C bonds are statically inaccessible, because C C bonds are in the skeleton of a carbon or organic compound framework and they are covered by many hydrogen bonds. And hence they are statically inaccessible as well as there are large more number of C H bonds which is covering the C C bonds.

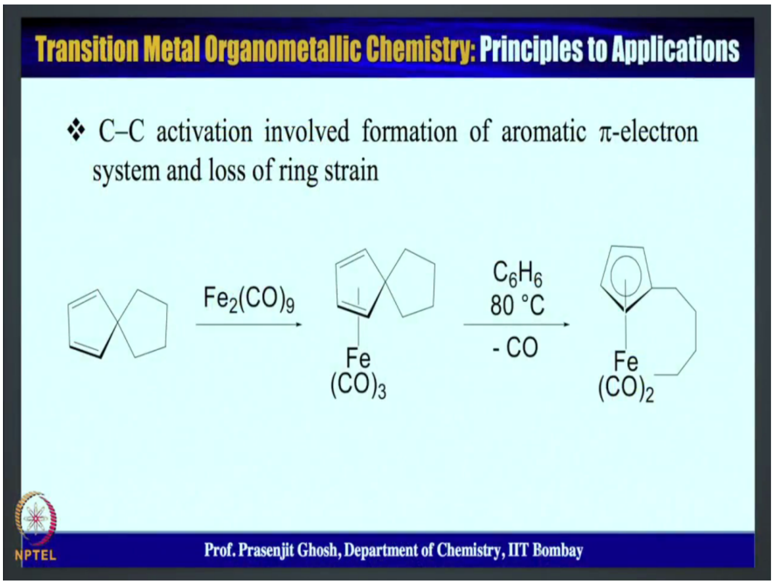
So, C C bonds are statistically outnumbered by C H bonds, and lastly because of these 2 effects that there are large number of C H bonds and fewer number of C C bonds, and whatever C C bonds are present they are statically inaccessible. So, both of this effect sort of work in the same direction and makes a the pre-coordination of C C bond to transition metal difficult.

So, these 2 effect these 2 effect makes pre-coordination of C C bonds to transition metal difficult. Now these is a very important criteria for activation of a bond because with our knowledge in C H bond activation what we had seen that the pre-condition is a necessary requirement for this bond activation to occur. And we had seen pre-coordination in the form of intermolecular sigma alkane complexes or intramolecular acoustic interaction occurring leading to C H bond activation, but from the discussion which we have had right now over C C bond it seems that the pre coordination criteria is not fulfilled or difficult to fulfill in case of C C bond activation and as a result this C C bond activation, becomes all the more challenging then H H bond activation as well as C H bond activation.

So, what is coming out over here that, these activation a it becomes difficult because of there are many numbers of C H bond which outnumbers C C bond and also C H bonds make C C bonds sterically inaccessible, as a result pre-coordination of C C bonds to transition metal becomes very difficult. So, all of these adds to making C C bond more challenging then C H bond and C H, H bond activations despite the fact that C C C bonds are weaker than the C H bonds and H H bonds.

Now, with these in mind there are, but few examples which exists of C C bond activations and we are going to take a look at some of this example and try to understand how despite all of these hurdles the C C bond activation has taken place and how these hurdles have been have been overcome and the require; the desired C C bond activation products were obtained.

(Refer Slide Time: 12:46)



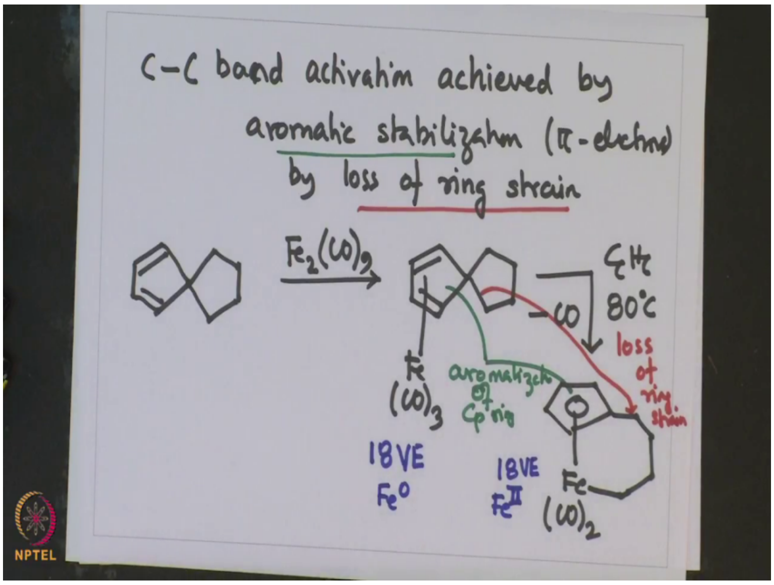
Transition Metal Organometallic Chemistry: Principles to Applications

- C–C activation involved formation of aromatic π-electron system and loss of ring strain

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

So, what has been done is that sometimes removal of ring strain or at stabilization due to aromatization has been successfully used for performing C C bond activation.

(Refer Slide Time: 13:11)



C–C bond activation achieved by aromatic stabilization (π-electrons) by loss of ring strain

So, C C bond activation achieved by aromatic stabilization of these pi electrons as well as by loss of ring strain. For example, in this molecule having lot of ring strain as 2 5 membered rings are bound to each other at this carbon when that is treated with iron carbonyl gives this iron complex.

This is a 18 valence electron compound, and iron 0 compound is 0 valent that when heated in benzene at 80 degree centigrade eliminates a molecule of co and undergoes C C bond activation to give this following compound. So, this also is a 18 electron compound and it is a iron 2 compound.

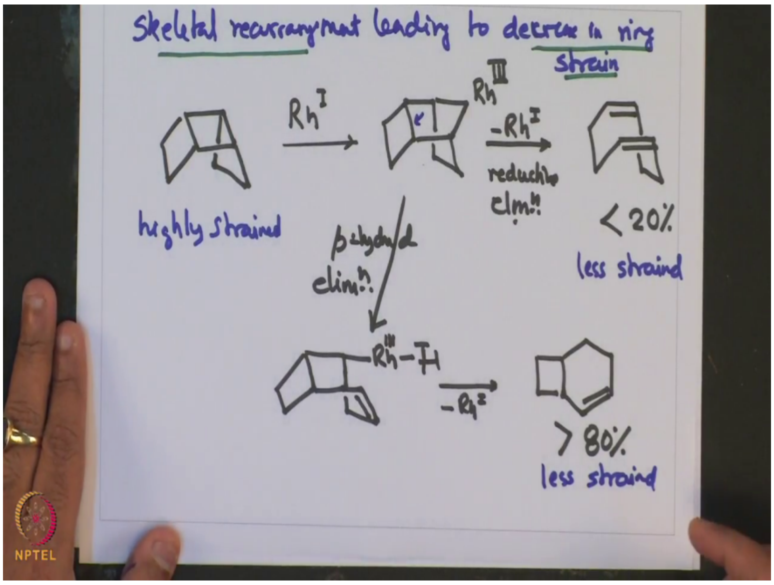
So, what has happened over here is that aromatization of the Cp ring Cp ring has happened which leads to the formation of the compound, as well as release of the ring strain from the spiro compound to this loss of ring strain. So, this loss of ring strain as well as aromatic stabilization in the product complex has resulted in this C C bond activation or cleavage of the C C bond.

Now, over here because chs there is no pre-coordination involved the way pre-coordination had been observed in most of the C H bond activation reaction this is a unique example where the C C a difficult C C bond activation has been achieved by 2 stabilizing effect which is the aromatization of the Cp ring as well as the loss of ring strain using a iron complex. So, the iron complex which itself is a valence 18 electron complex undergoes a loss of CO to give the electronically unsaturated complex to which this oxidative variation happened and it gives back the 18-valence electron compound with iron 2.

So, this is a nice demonstration of how C C bond activation can be achieved through various stabilization techniques similar arrangements have been made in other systems as well where the idea is to decrease the ring strain of a strain molecule through some skeletal rearrangement and that would lead to C C bond activation.

For example, for this highly strained molecule.

(Refer Slide Time: 19:21)



Skeletal rearrangement leading to decrease in ring strain

There are 3 cyclo butane ring highly strained, and hence it would therefore, undergo C C bond activation for the release of strain, when treated with a rhodium one compound gives the C C bond activation of this particular bond leading to the formation of this rhodium 3 compound. Which undergoes reductive elimination giving back rhodium 1 compound to give cyclooctadiene in 20 percent yield. What is seen is in the process of reductive elimination this particular bond has also been cleaved and there has been a conversion of this highly strained molecule into cyclooctadiene and this approach is called skeletal rearrangement leading to decrease in ring strain.

Obviously the cyclooctadiene is less strained then the original molecule which is highly strained. The rhodium 3 complex can also undergo beta elimination, beta hydride elimination to give the following compound and the olefin and this can finally, eliminate rhodium one to give this 6 membered 4 membered fused complex in 80 percent yield. And here also this compound is less strained then the original compound which was highly strained.

Now, what is coming to the 4? So, what is coming to the 4 is that skeleton rearrangement leading to decrease in ring strain plays an important role in C C bond activation reaction with this let me summarize the discussion which we have at today about C C bond activation reaction C C bond activation reaction is more challenging than C H bond activation reaction despite the bond despite the fact that C C bonds are weaker about 40 kilo joule weaker than C H bonds or even the H H bonds and despite the reason the fact that it is weaker they are difficult to activate and that is primarily because of the fact that C H bonds outnumbers C C bonds and hence for a catalyst to activate C C bond it sees less number of statistically it sees less number of C C bonds to activate then the C H bonds it come across.

Furthermore, that C C bonds are less approachable because they are buried deep inside the skeleton and they are covered by various kinds of C H bonds and these both of these statistically less number of C C bonds as well as they are less approachability makes C C bonds have pre-coordination to transition metal very difficult and as a result C C bond activation becomes all the more challenging.

Now, this has been successfully overcome in the 2 examples that we saw in which the loss of ring strain as well as aromatization owing to stabilization were successfully used in strained organic molecules a having a lot of ring strain was successfully used in executing C C bond activation particularly with transition metals we have seen 2 examples of that and we are going to discuss this C C bond activation in some more detail in next lecture where we are going to see how this what are the reasons the behind the C C bond activations or at the molecular level, what kind of inter interactions do take place for such C C bond activations and what are the criteria where these a C C bond activations thrive with that in mind let me conclude today’s lecture and I look forward to being with you in the next lecture.

Thank you.