Transition Metal Organometallic Chemistry: Principles to Applications

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

Lecture – 17
C-H activation in details

Welcome to this lecture on Transition Metal Organometallic Chemistry from principles to applications. We have been discussing a very important topic in this course in over the last few lectures. In the last lecture, we have been speaking about C H activation. C H activation is an important area of research in organometallic chemistry and has tremendous potential for academic as well as industrial applications.

Now what we discussed in our last lecture was how many types of C H activation methods are known and in that context, we looked at intra molecular C H activation reactions, we also discussed at how these C H activation reaction proceeds and what we saw was that C H activation reactions originates with a agostic C H M kind of interactions.

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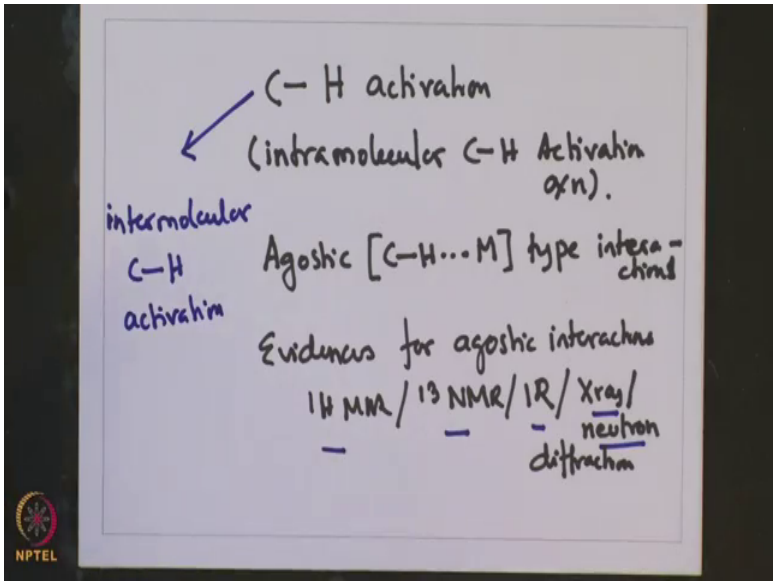

So, in our last lecture, what we had seen is the methods of C H activation reactions and in particular, we have discussed examples of an intramolecular C H activation reaction, we have also came across agostic M type interactions; these agostic interactions are at the source of C H activations and hence, they are of importance and they are useful and

what we have also looked at evidences for agostic interactions. This involves various spectroscopic techniques like proton NMR, carbon 13 NMR, IR as well as X-ray and neutron diffraction studies.

So, what we discussed in the last lecture was the fact that C H activation initiates at agostic interaction. And that agostic interaction weakens the C H bond and does not really fully cleave it and that weakening of the C H bond can be observed in the spectroscopy signature of various spectroscopy like the proton, carbon, IR as well as structural characterization using X ray and neutron diffraction techniques.

Now, between the types of C H activation, we have spoken about intra molecular phase activation and in today's lecture, we are going to talk something more interesting and more difficult which is intermolecular C H activation.

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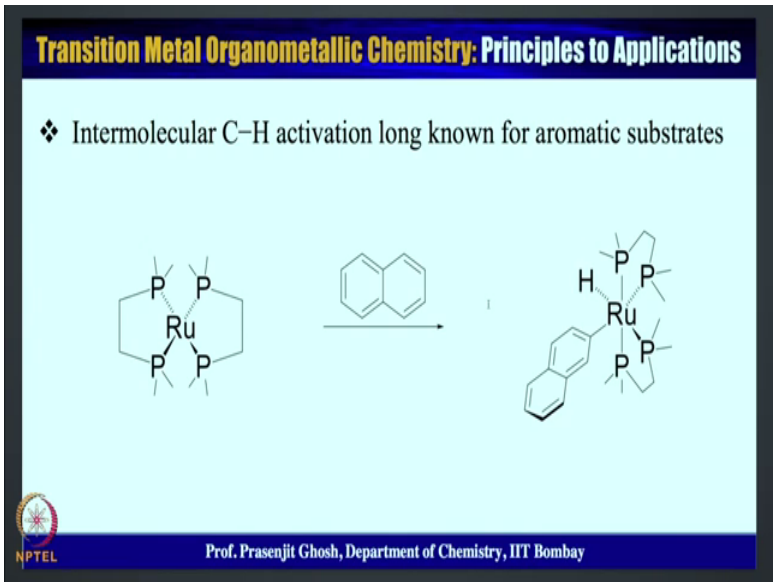

So, in this lecture, we are going to look at intermolecular C H activation and how these proceeds now as for the inter molecular C H activation in term examples of such activation was long known for aromatic substrates.

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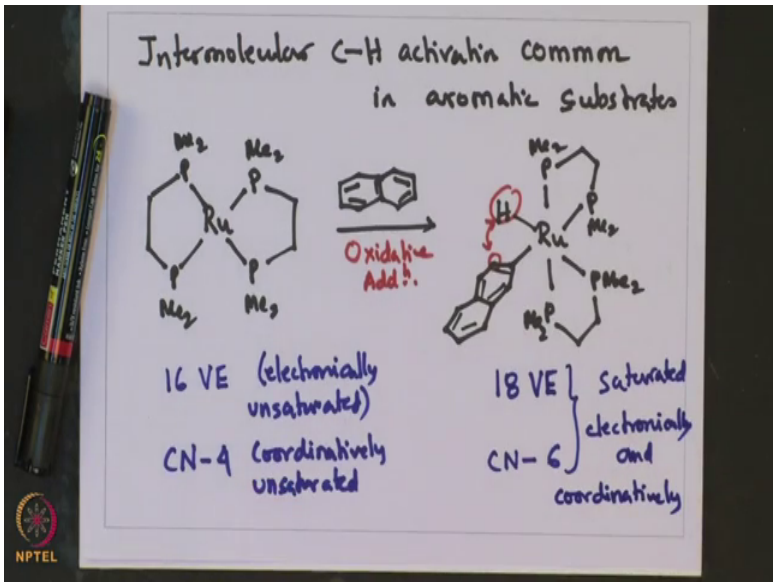

It is important to note that for the intramolecular C H activation, we too have look also looked at a similar aromatic substrate whereby C H bond underwent activation intramolecularly in our as discussed in the last class also for as for intramolecular C H activation, the perquisite criteria was that the metal complex has to be electronically as well as coordinatively unsaturated the same holes for inter molecular C H activation where the metal complex has to be both electronically as well as coordinatively unsaturated to undergo such C H activation this is illustrated in this ruthenium complex.

So, this has 16 valence electrons and hence electronically unsaturated and also the coordination number is 4 and hence coordinatevily unsaturated. So, these complex fulfills the criteria for C H activation. So, when treated with naphthalene again aromatic compound intermolecular C H activation is observed and the product obtained is this C H activated product and ruthenium is bound to this naphthalene moiety as well as the hydrogen. So, here the activation of a C H from this carbon and this hydrogen has happened as a result of oxidative addition hence the coordination number now has increased to 6. So, it is become coordinatively saturated and the valence electron is it has become 18 valence electron complex thus this has become saturated both electronically and coordinatively.

So, the basic criteria for C H activation is common for what was there existed for intramolecular C H activation reactions these are commonly observed for aromatic

substrates as is seen over here and that these proceeds via oxidative variation on a complex which is both electronically and coordinatively unsaturated as a result of this intermolecular C H activation the final complex usually is a ruthenium aryl hydride complex as the C H bond of this a ring got activated resulting in a electronically as well as coordinatively saturated 18 valence electron compound having coordination number of six as shown over here now with these several other examples of C H activation became prominent. Now what is important is to move beyond?

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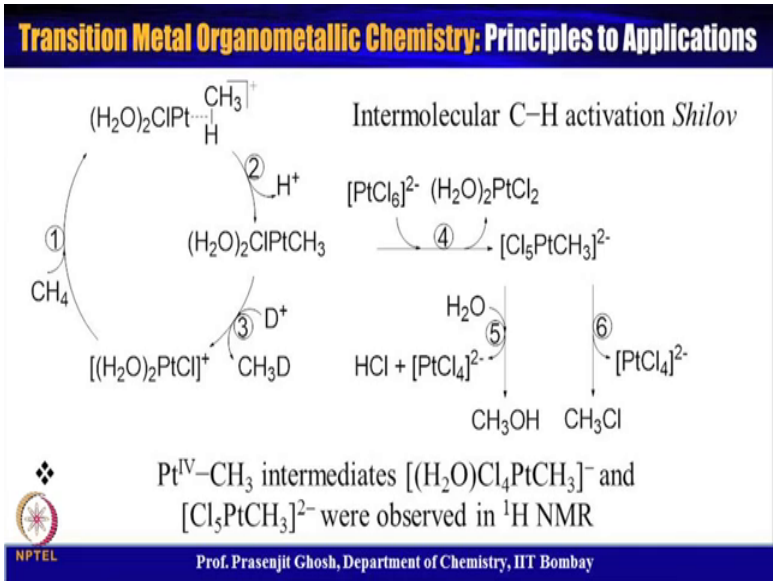

So, the utility of C H activation was further realized in terms of C H functionalization which proceeded after C H activation.

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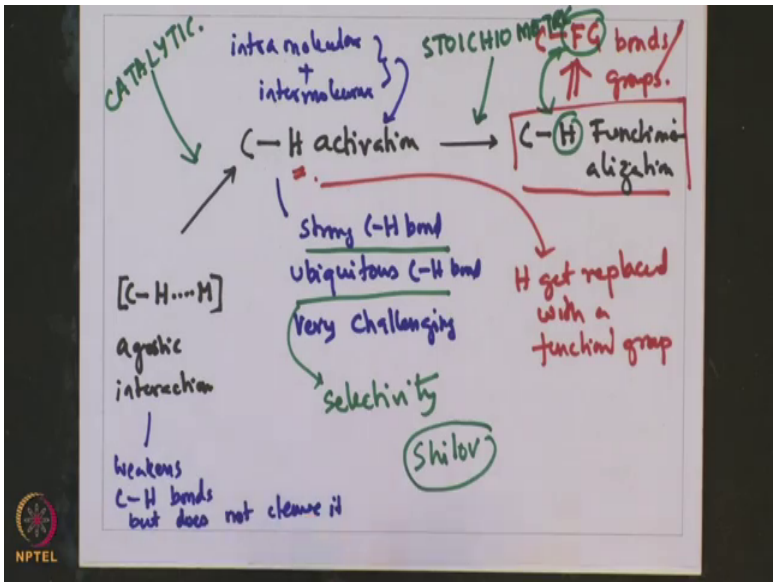

So, let us take a look at how C H activation is very difficult because of strong C H bonds and it is selectivity is a issue and ubiquitous nature very challenging. Now what we saw that these initiates with C H M agostic interaction this C H M agostic interaction weekends C H bonds.

But does not cleave it. Now it is up to this far that we have been seeing we have seen examples of both type intramolecular as well as intermolecular C H activation. Now what I am going to talk about is something beyond this agostic and C H activation and something utility wise very significant is that after the C H activation has happened one can achieve C H functionalization. Now C H functionalization is a very important step whereby this hydrogen of this C H bond after activation get replaced placed with a functional group. So, what it means is that C H functionalization gives C FG bonds or groups.

So, what has been achieved by this is that the hydrogen has been replaced by a functional group and hence, C H functionalization is a very important area of organometallic research. Now as we see; if we take a look at the whole perspective that this C H activation like it starts with a C H (Refer Time: 14:29) agnostic interaction leading to C H activation and followed by C H functionalization where the hydrogen is replaced by a functional group.

Now, this can be done catalytically, this can be done stoichiometrically and this is of immense interest to both industry as well as academia alive why it is interesting to industry because it helped produce different value added substrates if I can functionalize the C H bonds and that will can lead to various valued communities that we use in a day to day life and it is also important from academic perspective because it throws up an a very challenging intellectual problem that one has to solve with regard to carrying this functionalisation that one has to break a strong C H bond and also one has to achieve selectivity in this ubiquitous C H bond that are always present.

Now, the first and the pioneering work in this area has been done by Shilov, who has shown the first example of C H activation followed by C H functionalization whereby he had achieved the C H activation in a catalytic fashion and C H functionalization in a stoichiometric fashion. So, Shilov put together the whole concept in terms of chemical catalysis and achieved all the way from C H activation to C H functionalization in which the first part was achieved in a catalytic fashion and the second part was achieved in a stoichiometric fashion.

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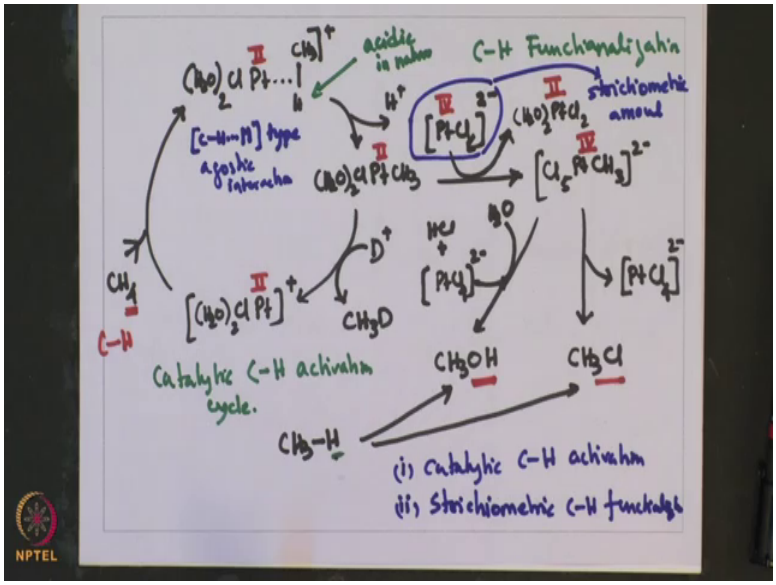

Let me illustrate this pioneering work of Shilov through the example that has been studied. So, these platinum complex these aqua platinum chloromoiety to water one chlorine platinum plus binding an activating a methane molecule; so, these is formed from the cationic fragment p d plus by reacting with methane and this; what is observed

is an agostic interaction type. So, what one can see is that this cationic platinum complex reacts with molecule of methane leading to the first agostic type interaction in from a platinum interacting with C H bond of methane in the cationic species.

Now, this compound as a result of this agostic interaction the hydrogen becomes acidic in nature an eliminates a proton giving rise to this neutral platinum methyl complex. Now this neutral methyl complex can be further protonated using deuterium plus producing C H 3 D molecule am giving back this chlorine chloride platinum plus complex which can again activate a methane molecule.

So, what Shilov attained is a catalytic catalytic C H activation cycle. So, why this is C H activation cycle? So, what we see is that C H more molecule is entering the cycle and it is getting cleaved as H and C H 3 and that the C H 3 is trapped with deuterium.

So, the C H bond is indeed getting cleaved and that cleaving is happening via the initial agostic interaction. So, Shilov attained successfully this catalytic C H activation cycle, but what is more important in this is the next step where he achieved C H functionalization. So, this was C H activation and Shilov achieved further C H functionalization and that is obtained by treating this aqua chloro platinum complex with this platinum 4 compound P t C l 6 to minus.

So, this is a platinum 4 compound and this catalytic cycle is all done with platinum two compound. So, upon treatment of this platinum two methyl with this platinum hexa chloro platinum 4 compound that leads to this platinum 2 compound where this methyl get exchanged with the chlorine, this is a platinum to compound and it produces alongside this alongside a platinum 4 compound.

So, this is a platinum 4 compound and these platinum for this reaction; this platinum 4 compound is used in stoichiometric amount. So, this was a catalytic cycle and this platinum 2 was treated stoichiometrically with platinum 4 compound leading to this platinum 4 compound which is platinum inter chloro methyl. Now this platinum pentachloro methyl when treated with water produces platinum 2 compound plus H C l and this methyl gets hydrolyzed to give methanol and this platinum 4 compound also decomposes to give platinum 2 compound along with C H 3 C l.

So, what is interesting is that C H bond of methane has produced methanol as well as methyl chloride which is C H 3 C l. So, Shilov has selectively converted methane to methanol by replacing the hydrogen with hydroxide group and also it could convert methyl C H 3 H to C H 3 C l where this hydrogen has been replaced by chlorine and it has done by two steps one was this catalytic C H activation followed by stoichiometric C H functionalization and these shows that these compounds are of tremendous use whereas, a inner compound like methane which has very strong C H bond can be made into useful value added chemicals in forms of methanol and methyl chloride.

So, with this let me summarize the discussion on today's topic, what we had discussed today is we have looked at they at the inter molecular C H activation and then we have taken a pioneering example whereby intermolecular C H activation was converted to C H functionalization and this work was done by Shilov who had done the C H activation in a catalytic fashion and then followed it up with C H functionalization in a stoichiometric fashion.

And thereby could functionalized methane to methanol as well as methyl chlorides and another interesting thing that we had discussed is that C H activation catalytic C H activation was performed in a catalytic fashion as I had mentioned by catalytic C H activation, whereas, C H functionalization was done in a stoichiometric fashion also C H activation was achieved with platinum 2 complexes C H functionalization was achieved from platinum 4 complexes and that shows the utility of this method and versatility of platinum as a metal.

Because in 2 different oxidation state it can perform two interesting reactions now with this background we are going to take up something very interesting in next lecture that will discuss more examples of these intermolecular C H activations the ones that followed after Shilov's bond and also would be very useful in terms of understanding the chemistry of this kind of complexes. So, I look forward to take up this topic in the next lecture; until then.

Thank you.