Transition Metal Organometallic Chemistry: Principles to Applications
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Week - 04
Lecture – 18
C-H activation in details

Welcome to this lecture on transition metal organomettallic chemistry from principles to applications. We have been discussing a very important topic of sigma alkyl transition metal complexes which is about C H activation. Now in the last lecture we had seen that C H activation originates with a C H M agostic interactions.

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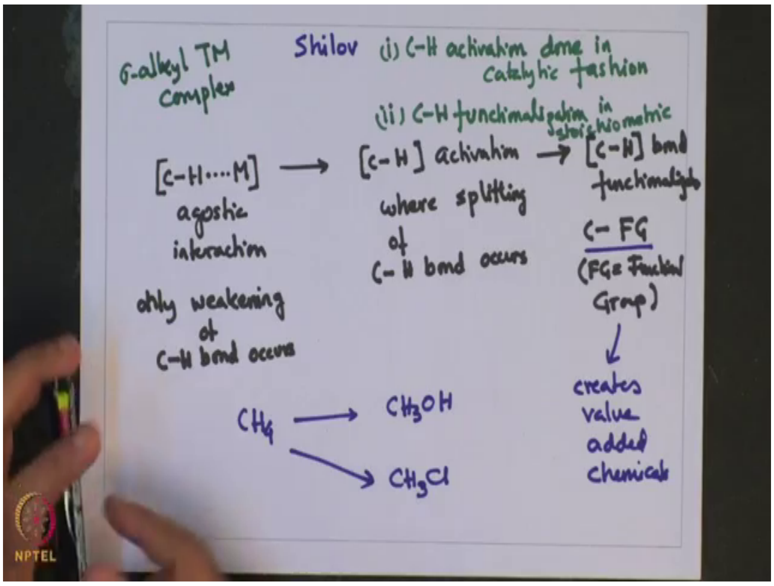

σ-alkyl TM complex

Shilov (i) C-H activation done in catalytic fashion

(ii) C-H functionalization in stoichiometric

$[C-H\cdots M] \longrightarrow [C-H]$ activation $\longrightarrow [C-H]$ bond functionalization

agostic interaction

only weakening of C-H bond occurs

where splitting of C-H bond occurs

$\underline{C-FG}$

(FG= Functional Group)

↓

creates value added chemicals

$CH_4 \longrightarrow CH_3OH$

$CH_4 \longrightarrow CH_3Cl$

This C H M agostic interaction leads to C H activation, where splitting of C H bond occurs; whereas, in agostic interaction only weakening of C H bond occurs. Finally, proper chemical manipulation at the stage of C H bond activation will lead to C H bond functionalization, where C F G, F G equal functional group, bond is found. Now, this has lot of utility in chemical industry, because it creates value added chemicals. In our last class we have seen a very nice example of this whole path way from agostic interaction to C H activation to C H functionalization as demonstrated by Shilov, who using this following sequence of strategy was able to convert methane to methanol, as well as methane to methyl chloride. In the previous lecture we have also seen that between these two sequences of C H activation as well as C H functionalization.

C H activation was performed in a catalytic fashion; whereas, C H functionalization was done in a stoichiometric fashion. Now with that we are going to take a some more examples with regard to these variation C H activation, I am subsequently reading to C H functionalization. Now before we do that let us focus on the initial stages of the reaction, which is about agostic interaction, which sort of is, can we defined as alkane metal complex, or similar to this interaction there can be sigma alkyl transition metal complex which would also initiate C H activation reaction.

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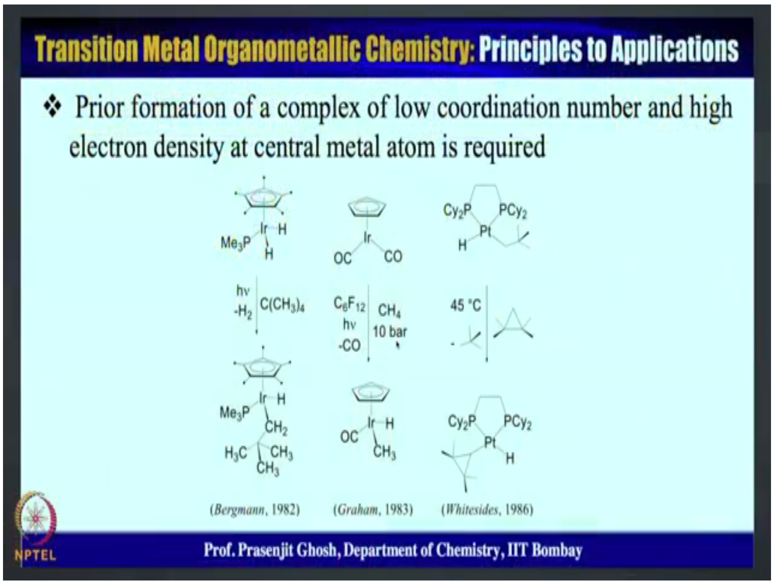

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- Prior formation of a complex of low coordination number and high electron density at central metal atom is required

(Bergmann, 1982) (Graham, 1983) (Whitesides, 1986)

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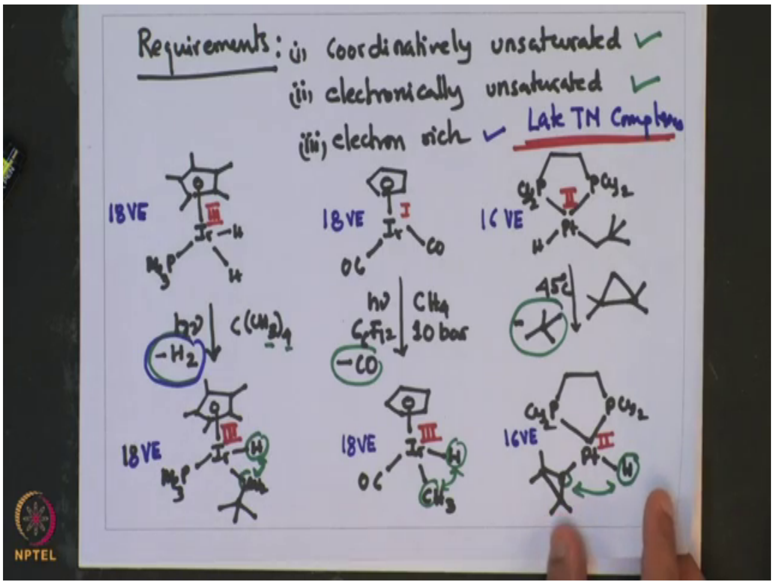

Now, as for the formation of sigma alkyl complexes leading to C H activation, the prior requirements are that the transition metal complex has to be coordinatively unsaturated, so that there is a room for addition of the alkane to the transition metal. It also has to be electronically unsaturated, so that the metal complex is not inert by witching the inert gas configuration in it valid shell, and the last condition is that the transition metal has to be electron rich. This is an important criteria for stabilizing transition metal sigma alkyl complexes.

Let me illustrated this with an example. For example, this C P star iridium hydride complex. This is an iridium plus 3 oxidation state, and it has 18 valence electron. So, this is both, coordinatively saturated as well as electronically saturated, and hence would not be forming a alkyl complex. So, the way to get about it, is reacting this 18 electron electronic coordinative saturated complex with an alkane under light, results in elimination of hydrogen, which will make the compound coordinatively as well as electronically unsaturated.

And to this, this alkane would bind and alkane while binding would undergo oxidative addition reaction, resulting in the corresponding iridium 3 complex as shown below. So, iridium, in this complex a methyl iridium as undergone C H activation over here and has produced this iridium hydride complex, which also is iridium 3 complex having 18 valence electronic.

What is important in this reaction is that, for this reaction to proceed elimination of hydrogen is critical, because it will make the electron iridium complex both coordinately and electronically unsaturated, and after that the oxidative addition of C H of the substrate would occur leading to the correspondent iridium complex.

The same strategy is applied for another iridium complex, is cyclopentadienyl iridium dicarbonyl. This also is 18 valence electron compound; hence electronically inert, it has an oxidative state of iridium plus 1. These in presence of light under high pressure of methane 10 bar in CS 6 F 12 medium eliminates one carbon monoxide to give the corresponding 16 electron complex, which is electronically unsaturated. And to that oxidative addition of methane occur, giving raise to this iridium complex. Here iridium is in plus 3 oxidative state, and it also has 18 valence electron.

So, comparing this two examples, what one see is, that electronically as well as coordinatively saturate compounds in presence of light becomes, both coordinative and electronically unsaturated by release of any of its existing legands, after which it undergoes C H activation of the alkane producing metal hydride alkyl complex as shown over here. Here also we see that the C H of this carbon and hydrogen undergo oxidation addition, similar to what was shown over here.

Another example is seen, in a platinum complex of the types shown over here. These is the square planner platinum complex, having oxidation state of plus 2, And it has 16 valence electron at 45 degree centigrade, it eliminates neo pentene and produces a platinum 2 species, which then activates the C H bond of cyclopropene substrate, giving rise to corresponding platinum hydride complex of the type shown here, here to Olson state of platinum is plus 2, and in the final product platinum has 16 valence electron.

The oxidative addition of the C H bond between the cyclopropene carbon and these hydrogen occurred to give the platinum hydride complex similar to the iridium hydride complex, and as well as this iridium hydride complex. So, comparing this example what becomes clear is, that sigma transition metal alkyl complexes containing activated C H bonds may be obtain even for transition metal complexes that are coordinatively as well as electronically saturated, but which undergoes a loss of legand either by heat or by light, leading to intermediate coordinatively as well as electronically unsaturated, and which then subsequently undergoes C H activation by oxidative reaction by alkane. Now if you look at all of these example and look how this reaction proceeded, what becomes cleared is, that the first two criteria has been reached by loss of all these legands, that would ensured electronic and coordinative unsaturation occurring for these complexes

Now, as for the third criteria electron richness is concerned, it becomes clear that all of these transition metal alkyl, hydride alkyl complexes that have shown C H activation occur for lak transition electron rich lak transition metal complexes. So, these is an interesting observation, that apart from electronic and coordinary unsaturation electron richness is required for making this alkane complex of transition metal. As can be seen that most of the alkane complex of transition metal are observed for lak transition metal complexes which are inherently electron rich.

When we look at more detail as to the interaction, molecular level interaction occurring in stabilizing this C H activation reactions, we would see in greater detail, the reason for electron richness affecting this reaction significantly. Now, the first catalytic application of C H bond leading to, bond activation leading to functionalization was demonstrated by Hartwig as late as in the year 2000 by Hartwig, John Hartwig.

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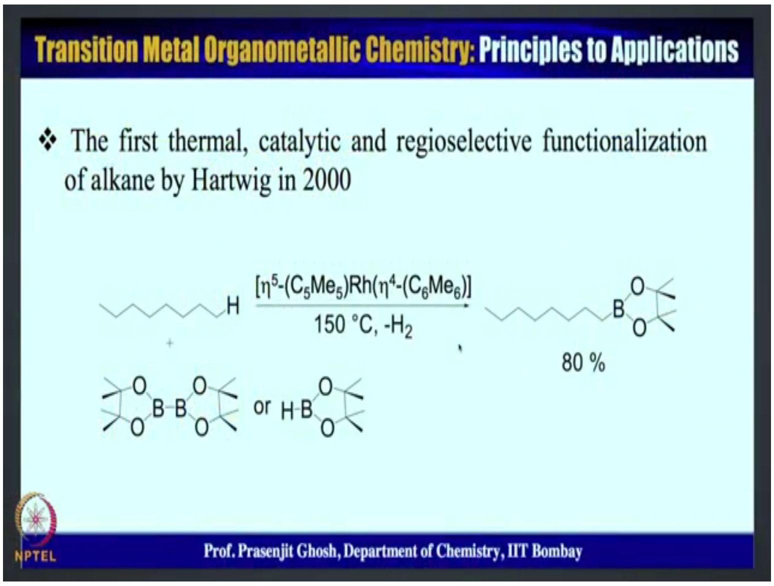

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- The first thermal, catalytic and regioselective functionalization of alkane by Hartwig in 2000

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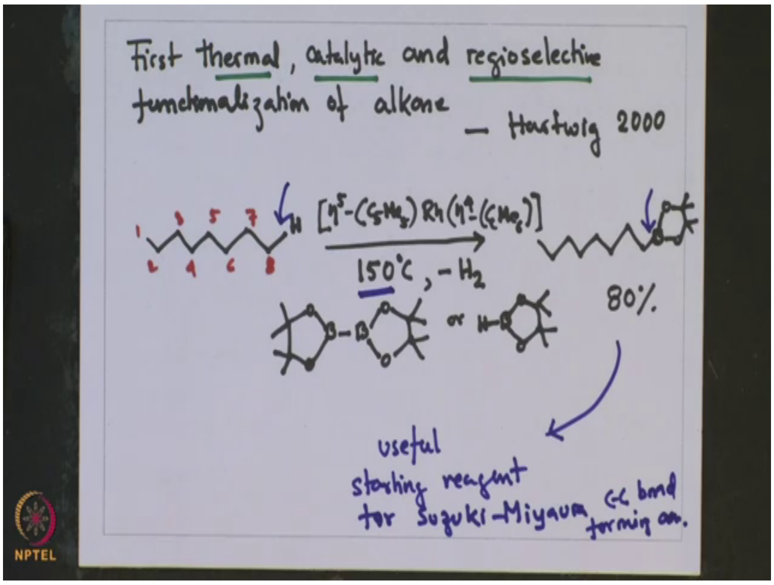

First thermal, catalytic and regioselective functionalization of alkane – Hartwig 2000

useful starting reagent for Suzuki-Miyaura C-C bond forming rxn.

Now these also is a seminal work in the sense that three important criteria's were fulfilled; one is thermal, then thermal way of carrying out C H functionalization, not only that this fair functionalization has an achieved in a catalytic fashion and that too in a regioselective fashion, where selectivity is a major challenge in C H functionalization reaction.

Let me provide the example of this reaction, for these long chain alkane, this is an octane. The terminal C H bond is functionalized, first activated and then functionalized with this catalyst rhodium data 4 C 6 M e 6 equates high temperature of 150 degree centigrades and boral reagents, this and this are its monomer giving the corresponding chronic ester in very high yield 80 percent yield.

So, and in the process elimination of hydrogen is observed. So, this reaction has selectivity, because only this terminal C H is replaced by the chronic ester, done in a catalytic fashion and also requires high thermal conditions. So, gradually with understanding of how C H bond is activated, the subsequent utility of C H bond activation is manifested in C H bond functionalization through the conversion of alkane to various functionalized product; for example, this bionic ester. I must note that this bionic ester is a useful starting precursor for Suzuki Miyaur across coupling reaction, bond forming reaction.

So, one of the limitation for Suzuki had been that though this Suzuki cross coupling reaction, is a very useful synthetic tool for making various cross coupling product, but the challenge had been that synthesis of bionic esters were not easy and very challenging. So, here in that prospective, this reaction by Hartwig gives easy access to bionic ester with high regio selectivity in high yields of support 80 percent using the simple concept of C H activation followed by C H functionalization reaction. Now one needs to sort of understand that how does C H activation and functionalization occur.

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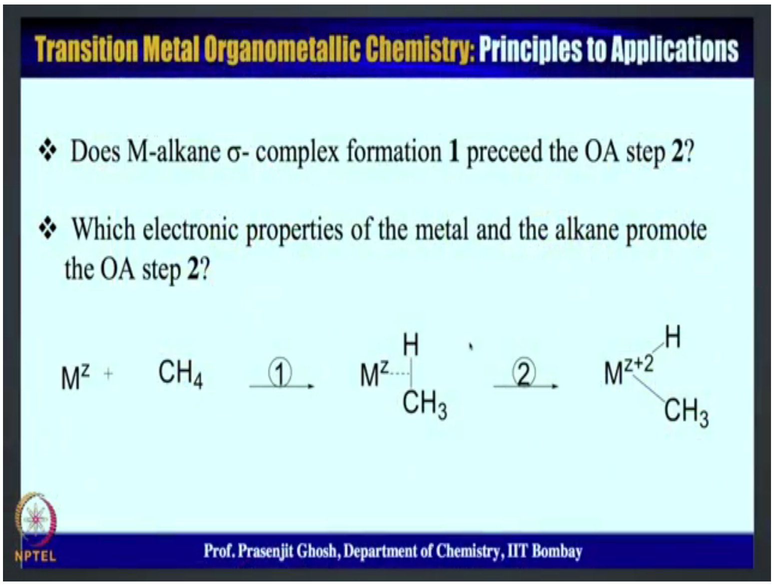

Transition Metal Organometallic Chemistry: Principles to Applications

- Does M-alkane σ- complex formation **1** preceed the OA step **2**?
- Which electronic properties of the metal and the alkane promote the OA step **2**?

$$M^z + CH_4 \xrightarrow{①} M^z\cdots H{-}CH_3 \xrightarrow{②} M^{z+2}(H)(CH_3)$$

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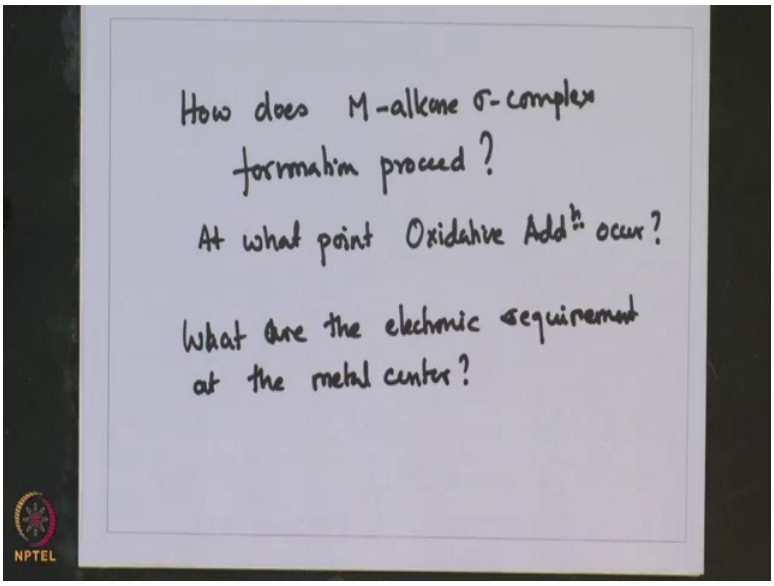

How does M-alkane σ-complex formation proceed?

At what point Oxidative Add^{n} occur?

What are the electronic requirement at the metal center?

So, at what point does this oxidation state occur. So, what are the electronic requirement at the metal center. These had been the key features that we have been trying to understand through this lecture. In this regard in this particular lecture we have looked at two such examples; one was this C H activation as well as functionalization using Shilovs work where methane could be converted to methanol and methyl chloride. And second such example was the conversion of long channel alkane to alkane bionic ester using Hartwigs watt which achieved this conversion under regio selective catalytic and thermal conditions.

So, gradually as the understanding of C H activation and C H functionalization are happening a lot and lot more applications of such strategy are being seen in place. And in this class let me just summarize, that apart from the requirement for formation of this kind of sigma alkane complexes, we have also looked at some of the examples where this sigma alkyl complexes have been isolated. And in such cases what came to the fore is that the metal has to be both electronically as well as sterically a unsaturated, and also it has to be that the metal center is electron rich and which can be ascertain by the fact that the most of the transition metal sigma alkyl complexes which have been isolated, they are for a very electron rich red transition metal ones.

Now with these we are going to take a look at some very interesting topic proceeding C H activation and functionalization, particularly how does an alkane bind, if after it has undergone a C H activation, how does it bind to the transition metal, what are its mode of interaction with a transition metal, how does that affect the C H activation and subsides functionalization pathways. All of these would be discussed in more detail in the lecture which is a succeeding this one, and with that I thank you for being with me in this lecture, and look forward to be being with you in the next lecture, discussing on various modes of binding of alkanes to the transition metal in the context of transition metal sigma alkyl complexes

Thank you.