Transition Metal Organometallic Chemistry: Principles to Applications
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Lecture – 20
Bonding in C-H activation

Welcome to this lecture on transition metal organometallic chemistry, from principles to applications in the last few lectures, we have been discussing about a very important type of organometallic compounds, these are transition metal sigma alkyl complexes. They are usually designated by R, where these transition metal R alkyl bond is a sigma type bond. So, that is designated by sigma. So, these are called transition metal.

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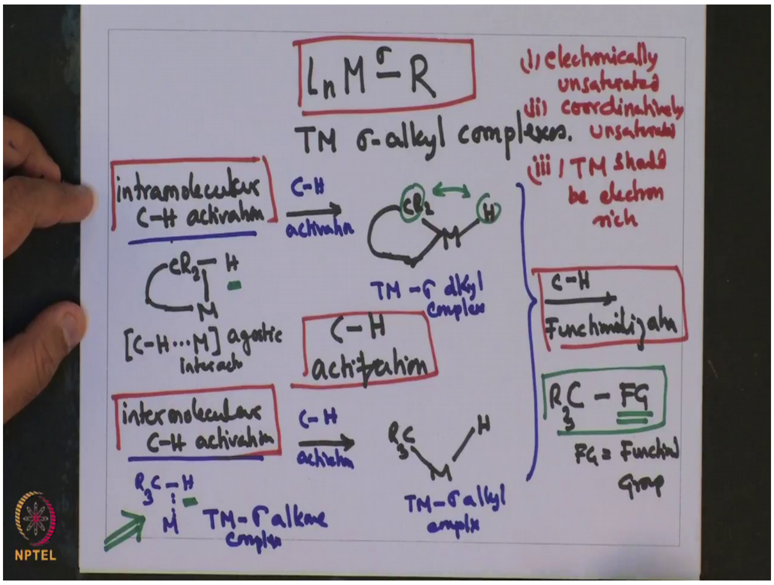

Now, these complexes has tremendous utility, in various industrial processes and hence from that perspective, we were looking at applications of this transition metal sigma alkyl complexes and what we found? That these transition metal sigma alkyl complexes can show, CH activation reactions or can catalyze or participate in CH activation reactions.

CH activation is a very challenging problem, in the sense that the CH bond is very strong. So, to cleave a strong bond becomes a challenge and all the more is the selectivity. So, high bond strength and achieving selectivity are 2 critical points, that one needs to fight over in order to achieve CH activation, the CH activation is a very challenging problem and that, can be solved using this transition metal sigma alkyl complexes.

Now, in the last few lectures, we have looked in details about how CH activation the action proceeds about? How CH activation reaction can be used for utilization purpose? For example, making functionalization of CH and replacing the hydrogen with other functional group and what we had seen is that, this CH activation can be intermolecular as well as intramolecular.

Now, intramolecular as well as intermolecular, the intramolecular CH activation starts with an agostic interaction. So, this is called CH M agostic interaction and then it proceeds to give CH activation. So, this is CH activation and results in a transition metal sigma alkyl complex, where activation of the CH bond at this center and this center has occurred and finally, this can lead to CH functionalization. Similarly, if one were to look at intramolecular CH activation, instead of an agostic interaction, which had been observed in case of intramolecular CH activation, in case of intra intermolecular alkane complex is formed, this is a transition metal sigma alkane complex.

These transition metal sigma alkyne complex, undergoes similar kind of CH activation, to give the transition metal sigma alkyl complex. So, what we see that, both for intramolecular and intermolecular there is a parallel pathway, for CH activation the one preceding with agostic interaction, via the activation CH activation forming sigma alkyl complex, the other starting from a transition metal alkane complex, again likewise proceeding by CH activation to give a transition metal sigma alkyl complex. Now, after this transition metal sigma alkyl complex has been formed, one can do for any of these CH functionalization and that would result in formation of FG, where FG is the functional group kind of complexes.

So, what we see that, these hydrogen for in the intramolecular as well as this hydrogen for intermolecular, can be replaced in this hand by a sequence of reactions for example, intramolecular, intermolecular sigma CH activation, followed by CH functionalization. Leading to a very important type of compound where you have a functional group, in the alkane moiety. Now, this is exactly what we have been studying, in the last few lectures and big picture of which is shown here, this big picture also tells us that this process of CH activation, which is extremely difficult can be achieved catalytically as well as stoichiometrically, using this all-important transition metal sigma alkyl complexes, in carrying out these protocols and hence these compounds are of interest from the perspective of chemical catalysis.

Now, with this brief overview of what we have studied in the last few lectures, about how you have developed this concept of transition metal sigma alkyl complexes, we are going to today focus on something more interesting, particularly looking at bonding interaction in this kind of transition metal sigma alkyl complexes.

Now, by and large what we have seen, that for these CH activation to occur or for that matter the initiating species, which is an agostic interaction our transition metal sigma alkyl complex formation, even to initiate these or to go along this, there are 3 criterias which are required. These criterias are that, the transition metal center has to be electronically unsaturated, the transition metal center has to be coordinatively unsaturated and third the transition metal should be electron rich.

So, these 3 criteria are important for a transition metal sigma alkyl complex, to undergo the CH activation leading to CH functionalization, in this area particularly activation followed by functionalization has been done by shilov, as well as the example of hart wick that we have discussed among many others, that is not in the preview of this course. Now, let us take a look at how the bonding interaction happens in transition metal sigma alkyl complexes?

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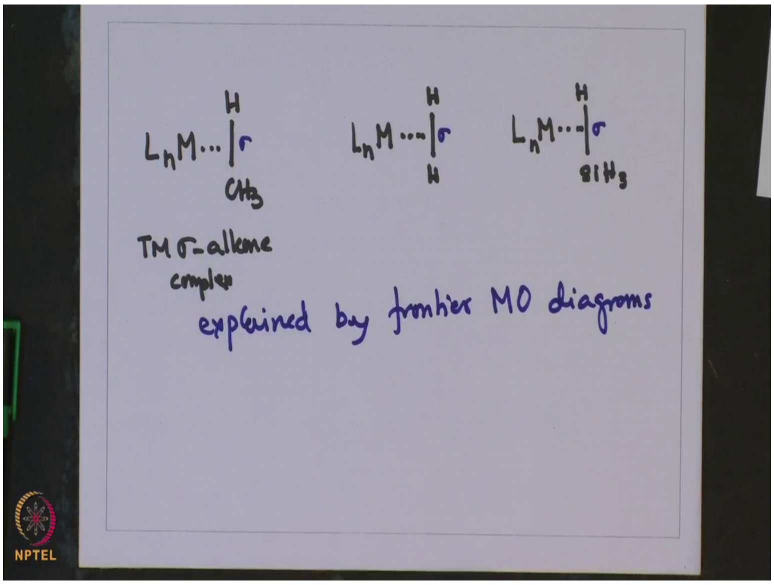

TM σ-alkane complex

explained by frontier MO diagrams

So, the transmission little sigma alkene complexes can be denoted as something like. And for the sigma alkane complex, this is the transition metal sigma alkane complex the related interaction is in the hydrogen complex, which is also given by and for example, in transition metals silane complex.

Now, even though the interaction there is a commonality, if the commonality being that transition metal, is interacting with sigma bonding orbitals or with a sigma bond in each of these and there is also a commonality in the type of interactions, that is required for holding this alkane the hydrogen, as well as the other molecule sigma bonding molecule towards the transition metal and all of these can be explained by frontier orbital energy diagram. Molecular orbital diagrams, to understand the kind of interaction prevalent in these complexes let us now take a look, at how the interaction proceeds for example, for a generic interaction of this sigma type, where x can be hydrogen carbon silicon among other things.

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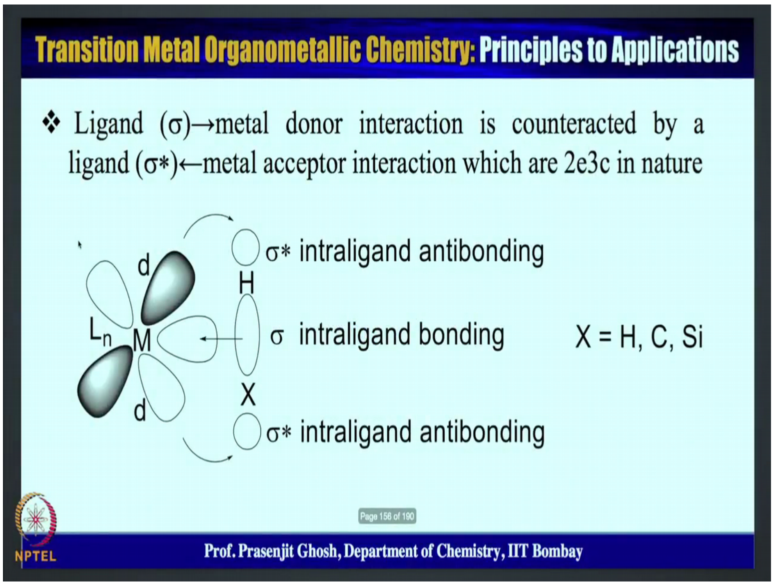

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- Ligand (σ)→metal donor interaction is counteracted by a ligand (σ*)←metal acceptor interaction which are 2e3c in nature

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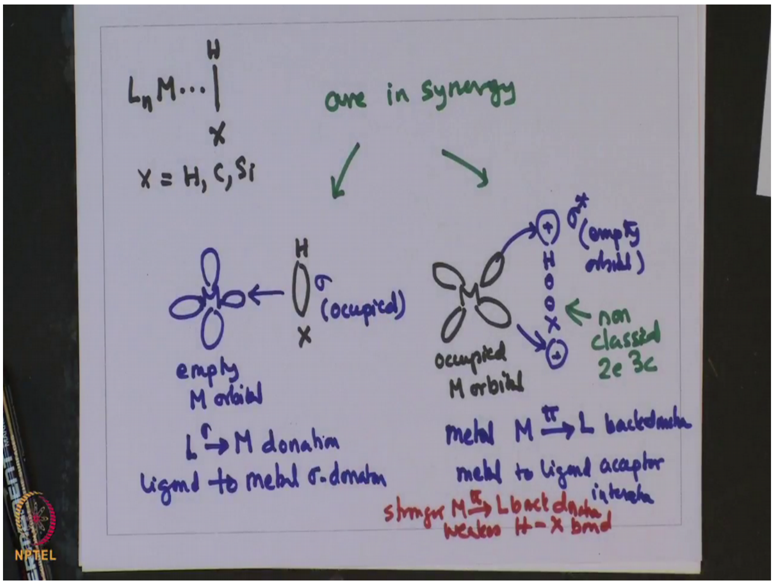

Now, this interaction can be represented by 2 types for example, the sigma bond of this Hx moiety, which is full sigma orbital is occupied donates it is electron to a metal empty D type orbital, this is empty metal orbital and this type of interaction is called a little metal sigma donation, can be expanded as ligand to metal sigma donation and the other type of interaction, that may happen is the metal having field D type orbital, donating to the sigma star of this Hx sigma star, empty orbital and the metal full orbital donating on the back to sigma star orbital and this is called metal or M to L pi back donation or metal to ligand acceptor interaction, this interaction is non classical in nature as involves 3 center 2 electron.

So, non-classical interaction 2e 3c type of bonding, now these 2 are in synergy to each other, one reinforces the other and what we see that, this sigma bonding to 1 M is reinforced by 2 kind of interaction, in the first the sigma electrons or electrons in the sigma bond donates to an empty metal orbital, followed by metal orbital which is already full donates back to the sigma star orbital and more significant is this back donation, the more weakening of the metal to the Hx bond is bond formed. So, another important attribute is stronger M to L back donation weekends Hx bond and the extent of forward donation and back donation that occur, is dependent on the substituent at the ligand at the metal as well as the type of bond that Hx is forming.

So, these sort of gives a unified picture of, how alkane transition metal complexes are formed? What kind of interaction they exist? As well as the same is true for alkane dihydrogen transition metal complex or cillian transition metal complexes, how the kind of orbital interaction occur between the bond of the alkane silane and the hydrogen with that of the empty, as well as filled orbitals of the transition metal. So, unified explanation of this sigma donor and pi acceptor synergism, results in stabilization of sigma complex.

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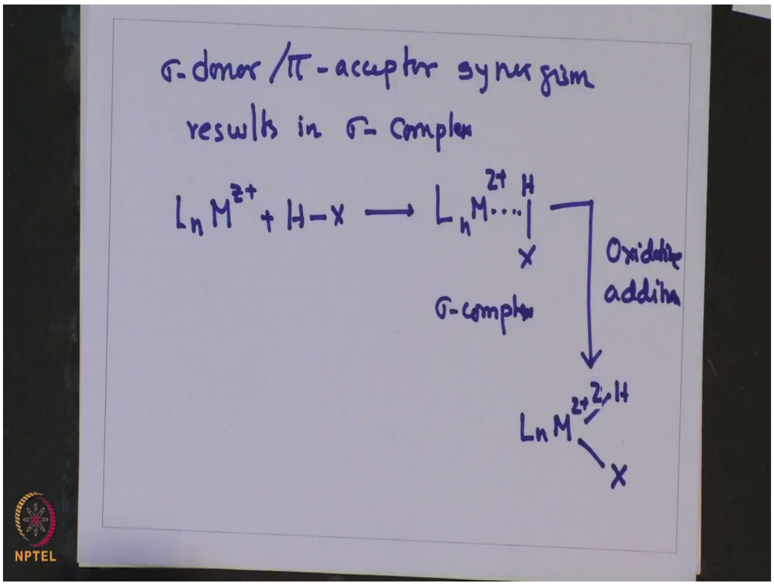

σ-donor/π-acceptor synergism results in σ-complex

$L_nM^{z+} + H-X \longrightarrow L_nM^{z+}\cdots\overset{H}{\underset{X}{|}}$

σ-complex

Oxidative addition

$L_nM^{z+2}(H)(X)$

So, Ln M z plus plus Hx gives Ln M z plus Hx which is the sigma complex and which undergoes oxidative addition, to give the requisite sigma alkyl complex or the Hx complex. So, these gives the pathway in which CH activation occurs and also tells us about, the frontier molecular orbital interaction that leads to CH activation.

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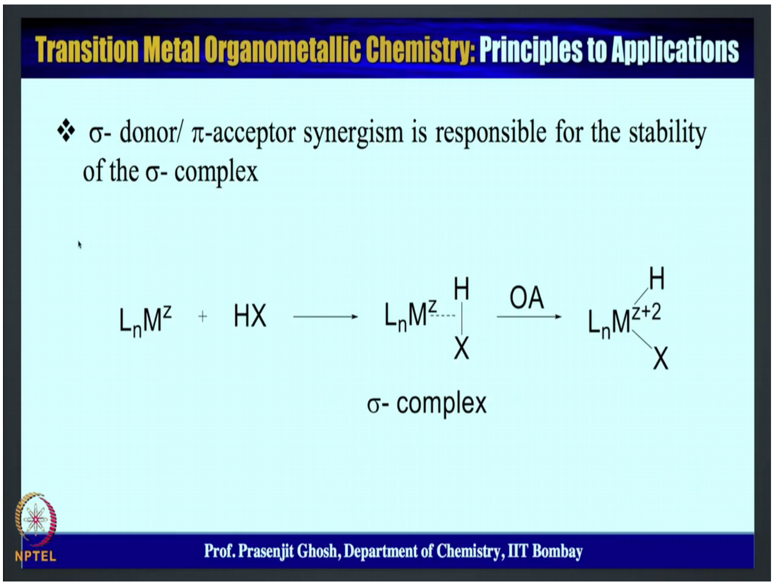

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❖ σ- donor/ π-acceptor synergism is responsible for the stability of the σ- complex

$L_nM^{z} + HX \longrightarrow L_nM^{z}\cdots\overset{H}{\underset{X}{|}} \xrightarrow{OA} L_nM^{z+2}(H)(X)$

σ- complex

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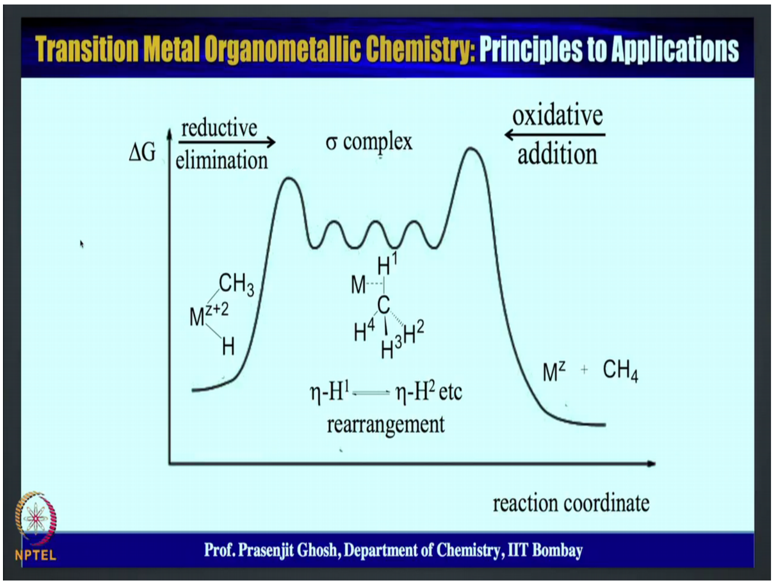

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Now, we will follow this course of CH activation in bit more detail for example, we will follow this as a particular reaction trajectory, and look at how the energy surface looks like for similar CH activation proceeding via alkane complex, and then leading to the transition metal alkyl complex.

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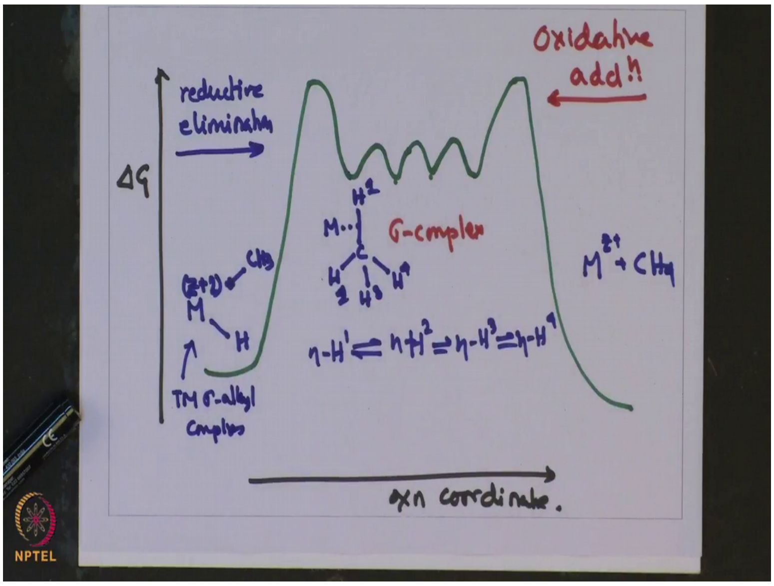

So, let us take a look at this reaction trajectory, y axis designates free energy and x axis gives the reaction coordinate and we will follow this for complex which is already CH activated. So, let us say we have a transition metal as 2 plus oxygen state, having a methyl and hydrogen. So, it is a transition metal sigma alkyl hydride complex, which will undergo reductive elimination, to give transition metal alkane complex, which would be something like and let us say, the energy profile for the same would be something like that, now this transition metal alkane complex can deform with other metal carbon hydrogens as well.

So, there will be eta H1 in equilibrium, with eta H2 and it will be in equilibrium, with eta H3 in further equilibrium in eta H4, all of these will be in equal energy and hence they would be all mutually exchanging with each other, as a result we will get and there will be 4 such complexes, 1 2 3 4 which will be mutually exchanging with each other, resulting in 4 valleys, for this transition metal sigma complex.

And finally, these would undergo oxidative addition, to give back the reactive give back the metal alkyl complex and if it the reaction. So, if by reductive elimination it has formed the metal alkane complex, this metal alkyl complex can go oxidative addition and give the metal alkyl complex, there is another possibility of alkane complex, just leaving the metal and eliminating alkane and metal z plus.

So, if this eliminates alkane the product will be M z plus plus CH 4 and that would be designated by this activation barrier. So, what we have over here is, that if one goes from metal alkyl hydride, to transition metal sigma alkane, to transition metalion plus alkane, this represents reductive elimination pathway. On the other hand, if one goes from metal catayan and alkane forming metal sigma alkyl complex, which undergo oxidative addition to give metal alkyl hydride complex.

So, then when this right-hand side to the left-hand side represents, oxidative addition reaction and when the oxidization products are formed which is this, this is metal sigma alkyl complex and both metal alkane metal ion cation alkane, as well as metal sigma alkyl complex, they go via sigma complex and sigma complex can have several rearrangement between several of it is forms, they are of equal energy and degenerating level.

So, that is why it says that y sigma alkane complex is so crucial, because it is it part of both oxidative addition and reductive elimination. Now, let me summarize what we have discussed in details about these transition metal sigma alpha complexes, we have looked at the molecular orbital frontier energy interaction between the transition metal and the sigma bond of the sigma alkane type compounds, we have also seen in the big picture about how CH activation proceeds, by intermolecular as well as intramolecular pathways, and lastly what we have seen is? That if we go from the reductive elimination side or from the oxidative addition side, how both of these would converge in the transition metal sigma complex?

And it can bifurcate in either direction and we have looked at the free energy diagram, explaining and the big picture of these individual small processes, with that we have come to end of discussion on various kind of CH activation processes, and we look forward to another interesting topic in the next lecture, that would discuss about CC activation reactions, with that I say a goodbye for today and I look forward to being with you in the next lecture.

Thank you.