Transition Metal Organometallic Chemistry: Principles to Applications
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Week - 04
Lecture – 19
Characterization of C-H activation

Welcome to this lecture on transition metal organometallic chemistry from principles to applications. In the last lecture we have looked into a very special kind of transition metal organometallic complexes, these are called sigma alkyl complexes. We have looked into these complexes in the perspective of a very important area which is CH activation, leading to CH functionalization.

In the last lecture we have also looked into two very good example of sequence of reactions, involving this transition metal sigma alkyl complexes that include CH activation as well as CH functionalizaion protocols and with this, these complexes have been used to produce methanol methyl chloride from methane which is a highly inert molecule in a catalytic as well as stoichiometric fashion.

We have also seen conversion of an alkane and two alkane bonicastir, using these again CH activation and CH functionalization sequence in a catalytic video selective and thermal fashion. So, what this method allows us, is that they use value added chemicals from very inert alkanes, which have very strong CHA bonds. In this lecture, we are going to take up a bit more detail, the various characterization techniques at present, at disposal that are there to understand transition metal sigma alkyl complexes. So, in this class we are going to talk about.

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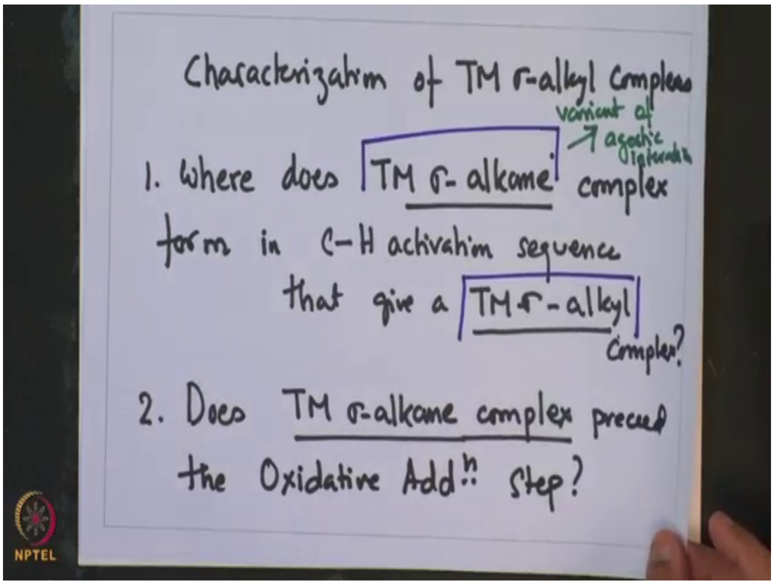

Characterization of TM σ-alkyl Complexes

variant of agostic interaction

1. Where does TM σ- alkane complex form in C–H activation sequence that give a TM σ-alkyl Complex?

2. Does TM σ-alkane complex precede the Oxidative Add^n step?

Now, what is important to note is that in the course of CH activation where does sigma alkane complex occur, and does it precede the oxidative an addition step. So, the first question one asked is, where does transition metal sigma alkane complex form in CH activation sequence that give a transition metal sigma alkyl complex. So, please note that there are two different complexes over here. One is transition metal sigma alkane complex, the other one is transition metal sigma alkyl complex. Now, in this alkyl complex what is interesting to note, is that oxidative addition has occurred.

Whereas, in the transition metal sigma alkane complex, the splitting of C H bond for activation of CH bond has not occurred, but weakening of CH bond has occurred. So, transition metal alkane complex is akin to or maybe a variant of agostic type interaction that we had encountered earlier. So, based on these two complexes, the question comes that where transition metal sigma alkane complex occurs in the course of CH activation that gives a transition metal sigma alkyl complex. So, does it occur, does it precede the oxidation as the addition step complex precede, the oxidative addition step, and what electronic properties of metal and the alkane promote the oxidative addition step?

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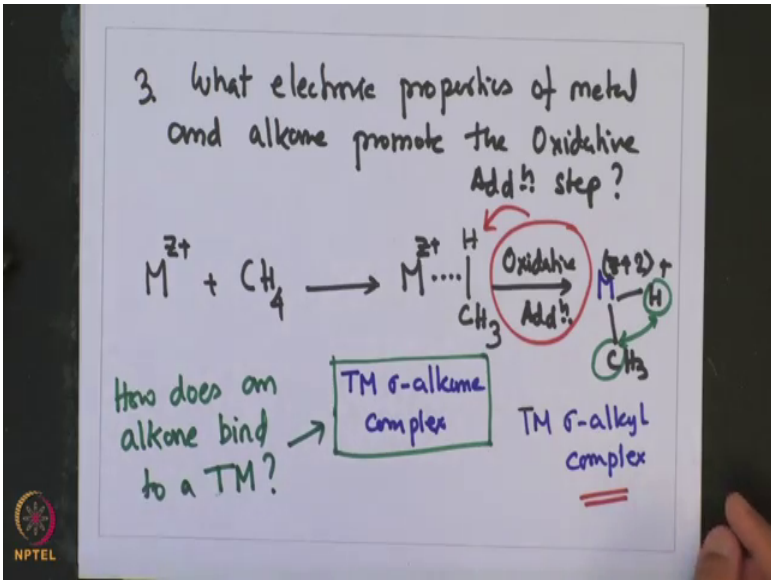

3. What electronic properties of metal and alkane promote the Oxidative Add^n step?

$M^{z+} + CH_4 \longrightarrow M^{z+}\cdots H\text{–}CH_3 \xrightarrow[\text{Add}^n]{\text{Oxidative}} M^{(z+2)+}(H)(CH_3)$

How does an alkane bind to a TM? ↗ TM σ-alkane complex

TM σ-alkyl complex

Now, before we go in details trying to look at this, I would like to note that we have discussed some aspect of the properties of the requirement as far as the metal is concerned. What we had seen in the earlier discussion that for the CH activation to proceed, the metal has to be sterically as well as electronically unsaturated, and that the metal also has to be electron rich, so as to undergo the oxidative addition steps. We had mentioned this with regard to formation of various transition metal sigma alkane complexes in our previous discussion.

Now, if one were to look at all these three questions as to where the transition metal alkane reside in the trajectory of transition metal alkyl complex, which is formed after oxidation addition, what are the requirements of the metal, as well as the alkane for it to undergo oxidative addition reaction. So, one can sort of conceive of these C H activation or formation of transition metal alkyl complex, proceeding via following to reactions. For example, a metal Z plus cation reacting with methane to give this metal Z plus interacting with CH bond of methane. So, this leads to the formation of TM alkane complex T M sigma alkane complex, which then undergo oxidative addition to give the following transition metal, alkyl complex.

Here, the CH activation of this hydrogen and carbon has occurred, as we have seen in other cases. So, this complex formed over here is, a transition metal sigma alkyl complex. The difference being between that over here it is a alkane complex and over here it is an alkyl complex and alkyl complex is formed after the alkane complex has undergone oxidative variation. After this alkane complex has undergone oxidative addition that the transition metal alkyl complex is formed. Let us look in more details at this transition metal sigma alkyl complex. With regard to understanding as to how does alkane interact with transition metal? So, let us take a look at transition metal sigma alkane complex in bit more details.

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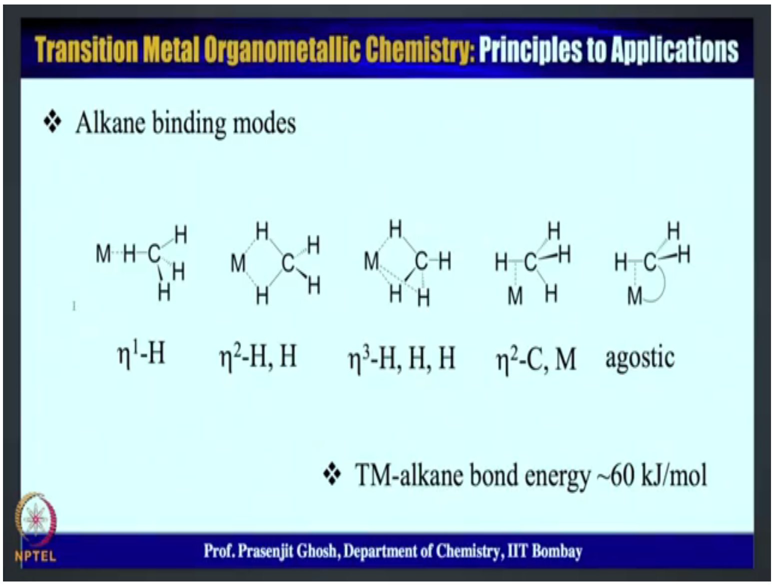

Transition Metal Organometallic Chemistry: Principles to Applications

❖ Alkane binding modes

❖ TM-alkane bond energy ~60 kJ/mol

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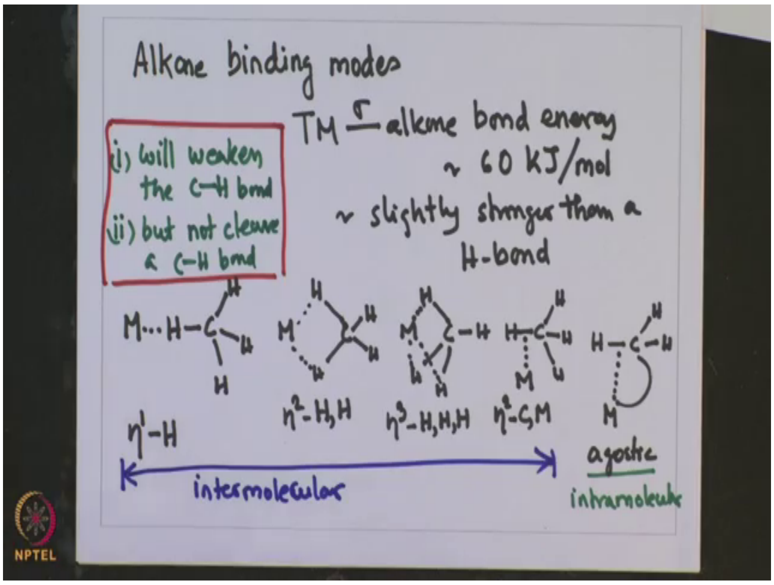

Alkane binding modes

TM σ alkane bond energy ~ 60 kJ/mol

~ slightly stronger than a H-bond

(i) will weaken the C–H bond

(ii) but not cleave a C–H bond

It is interesting to note that alkane has different binding modes to transition metal. Transition metal sigma bond energy is very weak, not very strong. For example, the transition metal sigma alkane bond energy is around 60 kilojoules per mole, which would be slightly higher than a hydrogen bond; stronger. So, what it shows that alkane binds very loosely to transition metal, not only that the binding of alkane to transition metal occur by different modes. At least 5 different modes have been observed. For example, it can bind in a linear fashion, and these are described by as eta 1 binding. It can bind by interaction with two different hydrogens of an alkane.

This is defined as eta 2 H H, H H, because two different hydrogens are involved. A metal can also interact with 3 different hydrogens of alkane, so this molecule just flipped over. Similar to something like that and this is represented as eta 3 H H H type of bun binding. These are all non classical kind of binding. It can also bind to a sigma bond, and this is written as eta 2 CM binding. And lastly, this can bind in a fashion shown here, and this is called agostic interaction. Now, if one were to look at it, one can see that all of these is intermolecular binding; whereas, this agostic one is intramolecular. That is kind of very interesting observation.

So, what its source is that alkane or C H of an alkane can bind in several ways, in which the metal would interact with the hydrogen atom, it can interact with more than one hydrogen atom up to 3, and also it can interact in an intermolecular as well as intramolecular fashion. When it is interacting in a intramolecular fashion it is called a agostic interaction. Also all of these interactions will at most weaken the CH bond, but never cleave it, will weaken the CH bond, but not cleave it, cleave a CH bond, and that can be characterized by various spectroscopic techniques as we had seen in case of agostic interaction. So, these sort of summarizes the various binding modes, by which alkane can bind to a transition metal. The alkane binding in solution has been characterized by UV visible spectroscopy.

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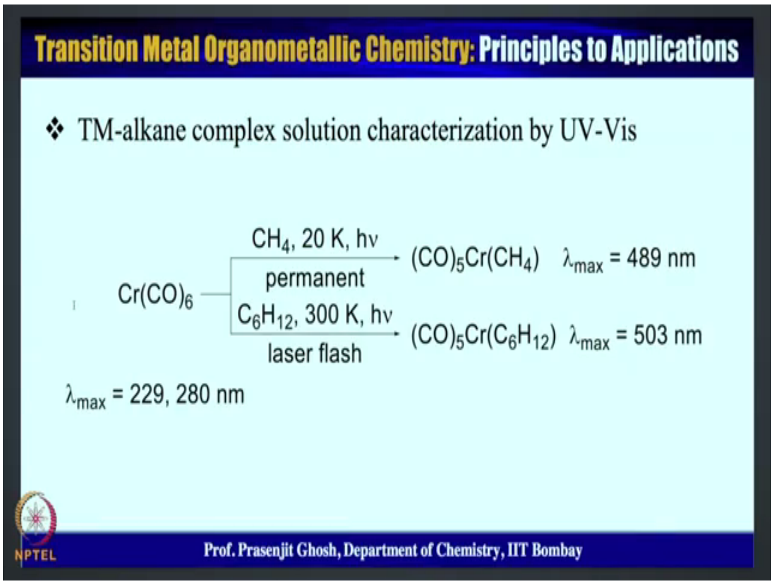

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- TM-alkane complex solution characterization by UV-Vis

$Cr(CO)_6 \xrightarrow[\text{permanent}]{CH_4,\ 20\ K,\ h\nu} (CO)_5Cr(CH_4)$ λ_{max} = 489 nm

$Cr(CO)_6 \xrightarrow[\text{laser flash}]{C_6H_{12},\ 300\ K,\ h\nu} (CO)_5Cr(C_6H_{12})$ λ_{max} = 503 nm

λ_{max} = 229, 280 nm

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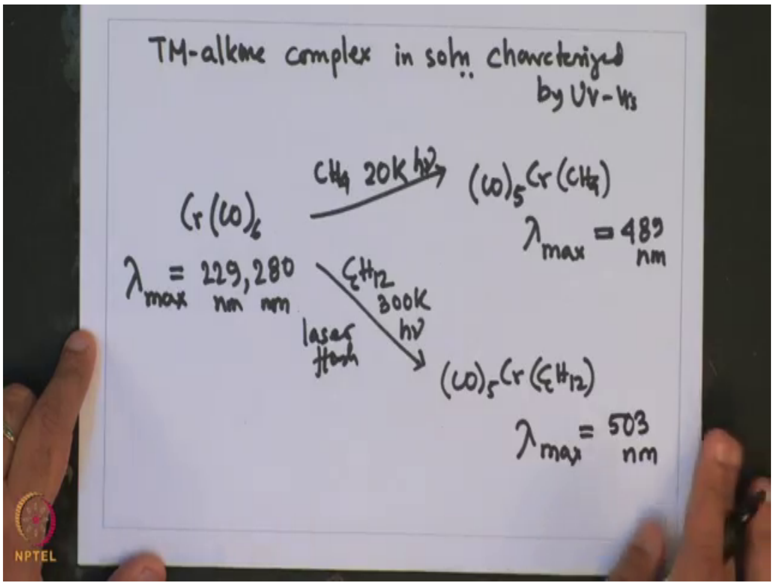

TM-alkane complex in soln characterized by UV-Vis

$Cr(CO)_6 \xrightarrow{CH_4\ 20K\ h\nu} (CO)_5Cr(CH_4)$ λ_{max} = 489 nm

λ_{max} = 229, 280 nm nm

$Cr(CO)_6 \xrightarrow[\text{laser flash}]{C_6H_{12}\ 300K\ h\nu} (CO)_5Cr(C_6H_{12})$ λ_{max} = 503 nm

For example, this chromium hexacarbonyl which shows lambda max at 229 and 280 nanometer forms the alkane complex with methane at very low temperature in light, giving C o 5 Cr methane which shows a distinct lambda max, at 489 nanometer. The same complex in C6H12 at 300 kelvin in presence of light, in laser flash, gives the corresponding alkane complex that display a lambda max at 503 nanometer. Apart from UV-vis the transition metal alkane complex can also be characterized by 1H NMR.

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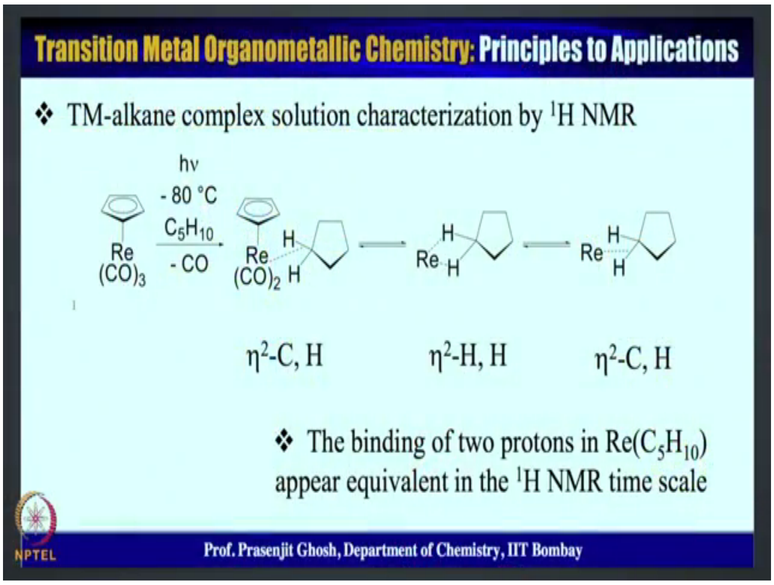

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- TM-alkane complex solution characterization by ^{1}H NMR

- The binding of two protons in $Re(C_5H_{10})$ appear equivalent in the ^{1}H NMR time scale

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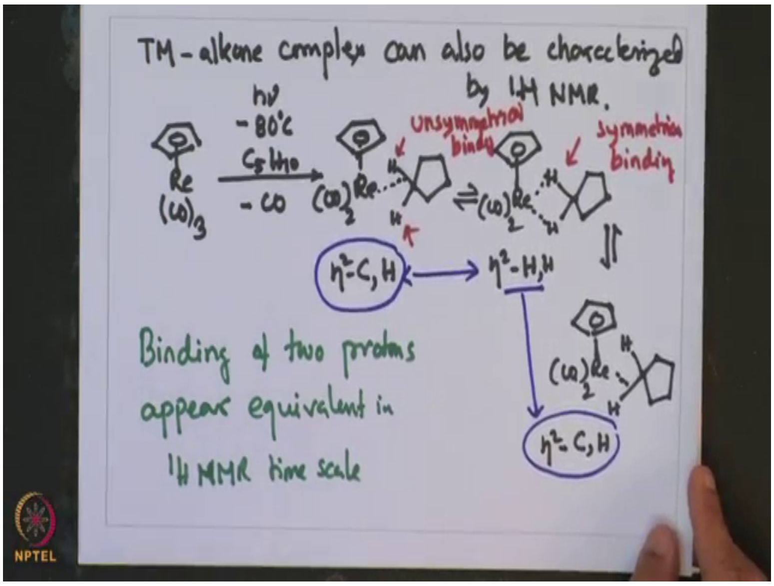

TM-alkane complex can also be characterized by ^{1}H NMR.

Binding of two protons appear equivalent in ^{1}H NMR time scale

For example, this CP rhenium tri carbonyl compound in low temperature, in presence of light at minus 80 centigrade, in presence of C5H10 eliminates a carbonyl, to give the corresponding C5H10 complex which shows this kind of CH sigma interacting with the metal. Now, and this has been characterized by eta 2CH kind of binding. As this is very low energy interaction they undergo various exchange processes, and can also be seen to interact with other modes of binding. For example, of this type which is eta 2HH and that can also undergo exchange to show a binding something, like of this type which also is eta 2CH.

So, what we see that these alkane transition metal bond being very weak, undergoes various exchange processes in the type of binding. It can start with eta 2CH, end up in a eta 2HH and then finally, go back to eta 2CH and they would exchange very rapidly that in NMR time scale, the binding looks equivalent, appear equivalent in 1HNMR time scale. So, let me explain, means that for binding of this type eta 2CH and eta 2CH, these are unsymmetrical. As a result, there are two different kind of proton over here. Whereas, for eta 2HH this is unsymmetrical binding; whearas this is a symmetrical binding and a symmetrical binding would predict a single proton resonance for the 2 hydrogens.

Whereas, the unsymmetrical binding would predict two different resonance for this two hydrogens, but as this exchange is very rapid only one set of resonances appear in the NMR time scale. What is important over here is that various modes of binding can be picked up using proton NMR, particularly by looking at the chemical shift of the proton reasonance. Structural characterization of alkane complex has also been achieved using X-ray diffraction studies, and this has been achieved for the heavier analog SiH4.

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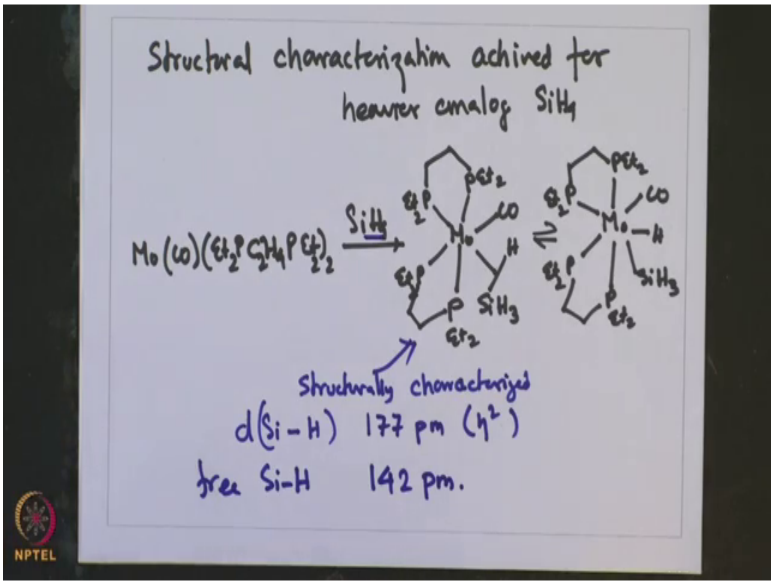

Structural characterization achived for heavier analog SiH_4

Structurally characterized

d(Si - H) 177 pm (η^2)

free Si-H 142 pm.

For example, for this molybdenum complex which reacts with SiH4 giving this molybdenum P2 complex, that binds with SiH4 to give this silone complex, and that finally, equilibrates another gross oxidative variation to give the correspondingly silane hydride complex. Now, these silane complex have been structurally characterized, as has been said that, because of this interaction the silicon hydrogen distance would increase, because this interaction weakens the alkane C H bond. So, d Si H bond length is 177 picometer and this is eta 2 type of binding; whereas, in free silane this bond is about 142 picometer.

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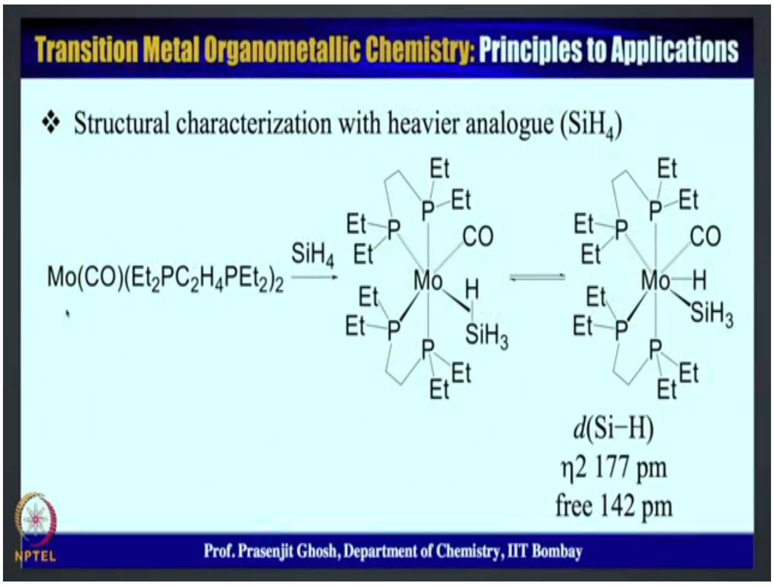

Transition Metal Organometallic Chemistry: Principles to Applications

- Structural characterization with heavier analogue (SiH_4)

$Mo(CO)(Et_2PC_2H_4PEt_2)_2 \xrightarrow{SiH_4}$

d(Si–H)
η2 177 pm
free 142 pm

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So what is becoming clear that this transition metal sigma alkyl complex can be characterized by various techniques including UV NMR X- ray, and all these complexes had the prominent signature that this transition metal sigma alkyl complexes has weakened CH or SH bond. As a result, they have longer SH bonds or they have weaker stretching frequencies which can be picked up by various spectroscopic techniques. We have discussed in this lecture is how an alkane transition metal complexes are formed, in what part of the trajectory of an CH activation followed by CH functionalization does this alkane complexes exist. What are their natures, what are their binding modes when they interact with the metal? How many hydrogens can these alkanes interact with simultaneously with the metal.

And what has been observed that it can interact with the metal; all the way from 1 hydrogen to 3 hydrogens. And lastly we have looked into structural characterization of these complexes, where we found structurally characterized transition metal alkane complex has a longer bond length then that of the free alkane for the silicon analog that has been structurally characterized. With this we looked into various transition metal alkane complexes, and various characterization method that are available. And in the next lecture we are going to take up something more interesting as to provide a comparison of alkane activation, with regard to silane activation, with regard to dehydrogen activations, what are the molecular level interactions that occur between these interaction between the ligand entity and the metal, is there a commonality that exists between alkane activation, dehydrogen activation, silane hydrogen activation. So, all these and more, lot more will be taken up in the next lecture and I look forward to being with you to discuss this in more detail till then,

Thank you.