Transition Metal Organometallic Chemistry : Principles to Applications
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Week - 03
Lecture - 15
TM σ – alkyl complexes and its application

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. In the last few lectures we have been discussing an important class of transition metal organometallic compounds mainly the transition sigma alkyl complexes and were looking at various facets of this particular chemistry. We looked at how these compounds were synthesized, what are the reactivity, what is the stability issues with respect to the compounds and how these issues can be resolved by understanding the mechanism by which these compounds decompose.

We also looked in the last few lectures as two methods which are available in enhancing the stability of this sigma alkyl complexes and with that in the background we are going to discuss something very interesting in today's lecture which are the applications of these transition metal sigma alkyl complexes.

To begin with I am going to talk about organorhenium oxides.

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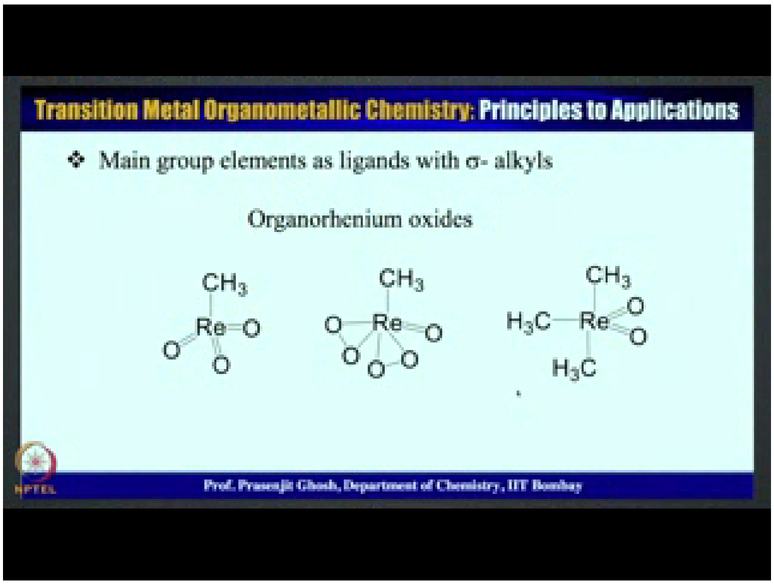

Transition Metal Organometallic Chemistry: Principles to Applications

- Main group elements as ligands with σ- alkyls

Organorhenium oxides

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These are mainly sigma alkyl complexes having main group elements in ligands as ligands along with the sigma alkyls.

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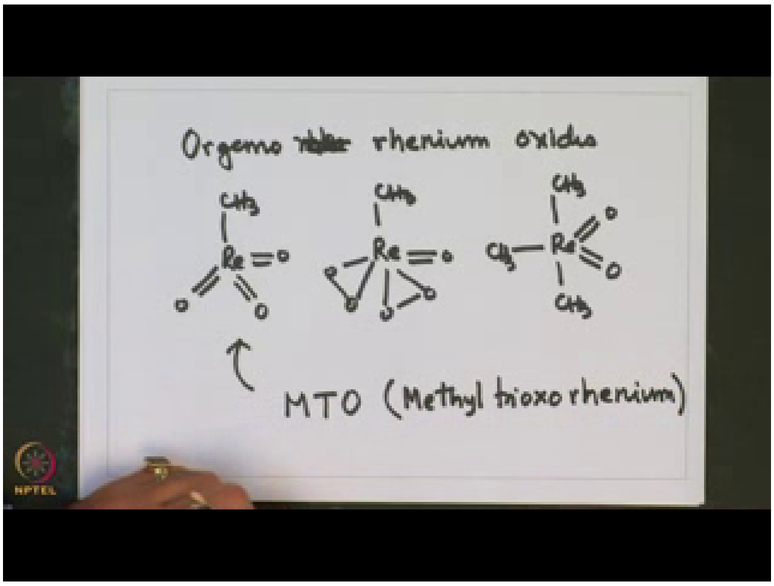

As discussed in our previous class, this can be rhenium try out some methyl or rhenium methyl oxo per oxo or tri methyl rhenium oxo. These alkenes are present along with various kinds of oxo trioxo complexes trioxo ligands attached to rhenium. Now, these compounds sort of gives rise to a special kind of compounds particularly the one discussed over here these are called MTO or methyl tri oxo rhenium. These empty MTOs are versatile compounds that are stable in water and also acts as catalyst for various important oxidation reactions.

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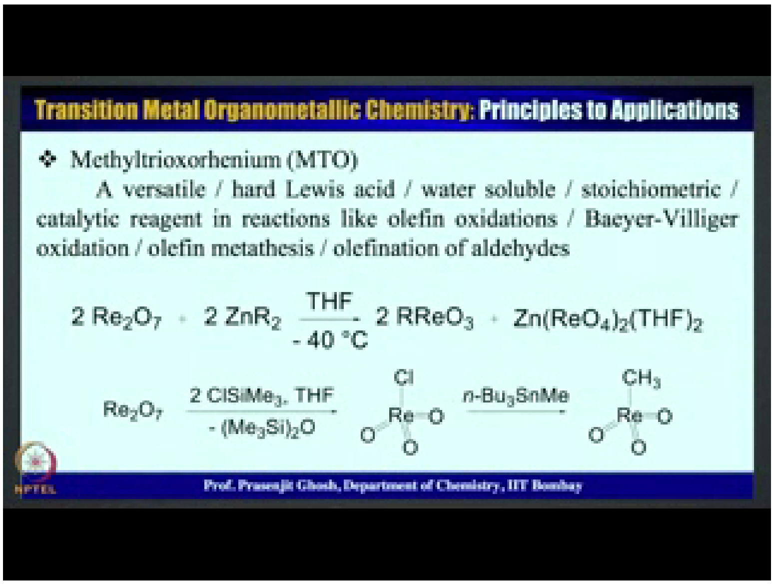

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- Methyltrioxorhenium (MTO)

  A versatile / hard Lewis acid / water soluble / stoichiometric / catalytic reagent in reactions like olefin oxidations / Baeyer-Villiger oxidation / olefin metathesis / olefination of aldehydes

$$2\ Re_2O_7 + 2\ ZnR_2 \xrightarrow[-40\ ^\circ C]{THF} 2\ RReO_3 + Zn(ReO_4)_2(THF)_2$$

$Re_2O_7 \xrightarrow[-(Me_3Si)_2O]{2\ ClSiMe_3,\ THF} ClReO_3 \xrightarrow{n\text{-}Bu_3SnMe} CH_3ReO_3$

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So, MTOs are versatile hard Lewis acids as the metal is in very high oxidation states water soluble.

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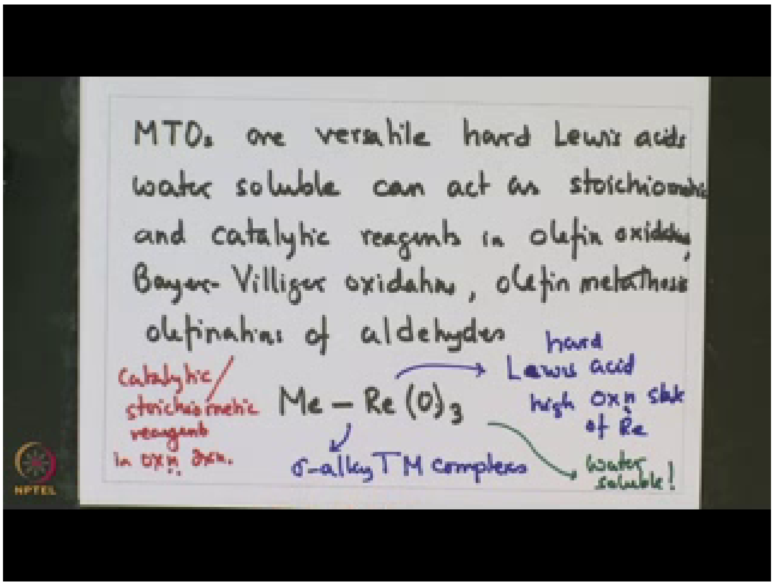

MTOs are versatile hard Lewis acids water soluble can act as stoichiometric and catalytic reagents in olefin oxidation, Bayer- Villiger oxidation, olefin metathesis olefination of aldehydes

Me – Re(O)$_3$

catalytic/ stoichiometric reagents in oxn. rxn.

hard Lewis acid high oxn state of Re

σ-alkyl TM complexes

water soluble!

This is also kind of interesting that organometallic compound where there is a mid rhenium methyl group still the compound is soluble in water and can act as both stoichiometric as well as catalytic reagents in important reactions like olefin oxidation Bayer villiger oxidation olefin metathesis olefination of aldehydes.

So, what we see that methyl rhenium trioxides compounds of this formula are a very important reagents these are sigma alkyl transition metal complexes. They are hard Lewis acids because of high oxygen state of rhenium and they act as catalysts catalytic as well as stoichiometric reagents in oxidation reactions and another important property of these compounds are that they being bound to 3 hetero atoms are also water soluble. This is something which is unthinkable for many organometallic compounds because we think tend to think that organometallic compound with it will instantly or immediately a decompose in water. So, this class of compounds are extremely good catalysts as well as reagent for various oxidation reactions, they are hard Lewis acids a very nice application of transition metals sigma alkyl complexes is in form of these compounds.

Let us take at look at how these MTOS are synthesized usually by two methods, the first one being with the dialkyl of zinc, zinc being the alkyl transfer reagent at low temperature giving.

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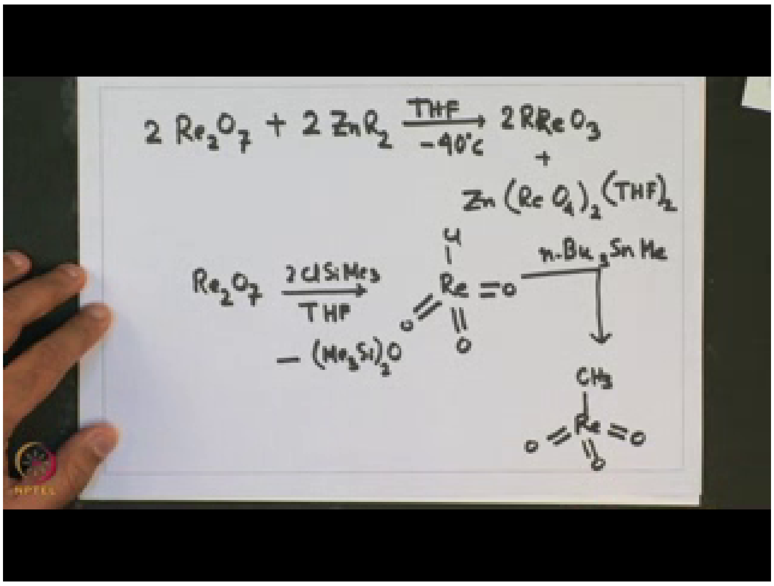

Similarly the other method involved treating of rhenium oxide with Cl Si Me 3 in THF eliminating giving the chloro rhenium trioxide which when alkylated with tri n butyl tin methyl gives this methyl rhenium trioxide.

So, these two methods are very useful methods for preparing these compounds.

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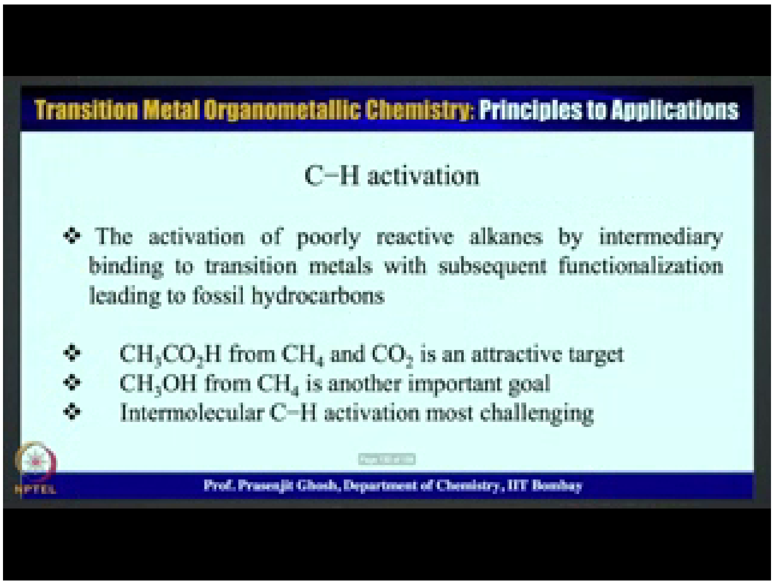

Transition Metal Organometallic Chemistry: Principles to Applications

C–H activation

- The activation of poorly reactive alkanes by intermediary binding to transition metals with subsequent functionalization leading to fossil hydrocarbons
- CH_3CO_2H from CH_4 and CO_2 is an attractive target
- CH_3OH from CH_4 is another important goal
- Intermolecular C–H activation most challenging

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Now, having seen the application of transition metal sigma alkyl complexes we are going to take up another very interesting topic in terms of application of this complex which is the C-H activation.

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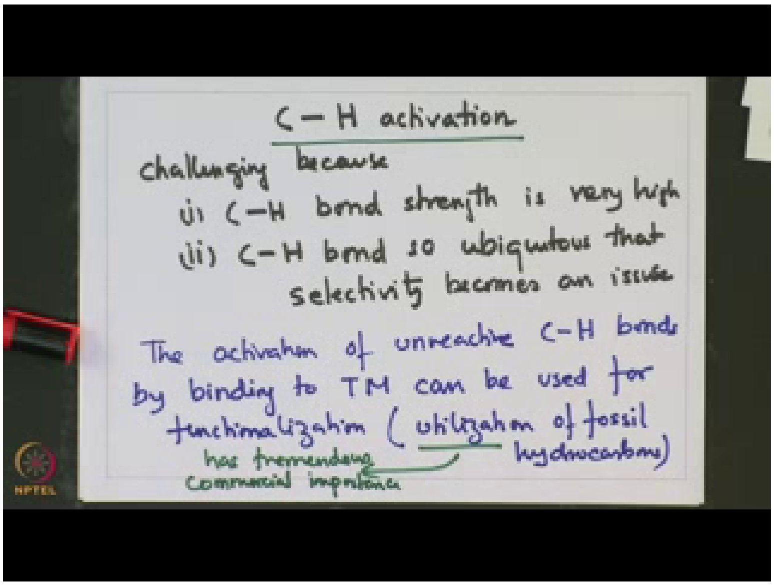

C – H activation

challenging because

(i) C–H bond strength is very high

(ii) C–H bond so ubiquitous that selectivity becomes an issue

The activation of unreactive C–H bonds by binding to TM can be used for functionalization (utilization of fossil hydrocarbons)

has tremendous commercial importance

C-H activation is the topic of contemporary research and is a very challenging area and it is challenging because one C-H bond is very high; that means, that C-H bond is very strong bonds and difficult to believe. Second thing C-H bond is so ubiquitous that selectivity becomes an issue so that is why C-H activation is a problem which is yet to be solved fully.

Now, C-H activation offers certain advantages and that has been achieved by binding of transition metal to the C-H bonds leading to functionalization. So, the activation of unreactive C-H bonds by binding to transition metals can be used for functionalization and; that means, utilization of fossil hydrocarbons. So, this has tremendous this aspect has tremendous commercial value and hence C-H activation is a topic which is of contemporary interest. Let me illustrate the various possibilities exciting possibilities that C-H activation can give.

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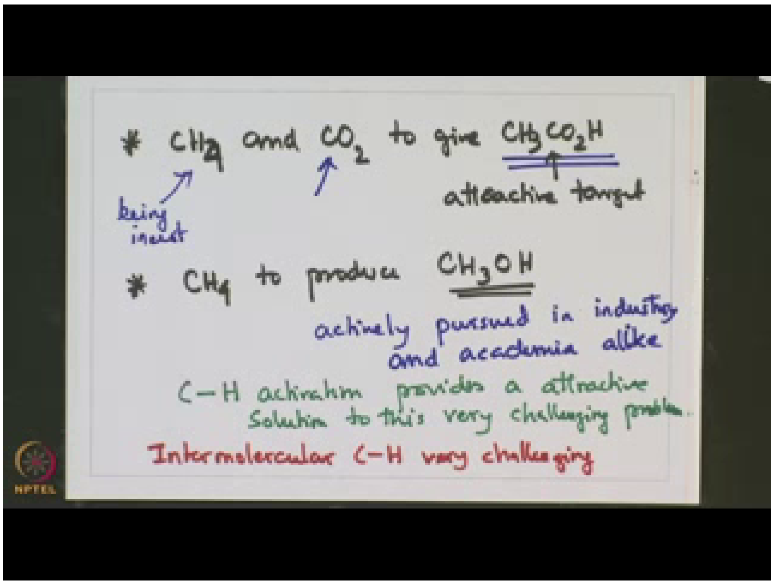

* CH_4 and CO_2 to give CH_3CO_2H

being inert

attractive target

* CH_4 to produce CH_3OH

actively pursued in industry and academia alike

C–H activation provides a attractive solution to this very challenging problem.

Intermolecular C–H very challenging

For example it can convert C-H 4 and carbon dioxide to give acetic acid which is an attractive target.

So, methane being inert is difficult to find functionalize and carbon dioxide is produced a lot in the industry. So, these can give rise to utilization of C-H 4 and CO 2 to produce something useful in the form of acetic acid and that can be used for making many other value added chemicals. Similarly one can obtain another important compound for example, from C-H 4 to produce methanol. So, all of these have tremendous commercial interest in terms of let us say production of methanol from methane or acetic acid from methane and are being actively, actively perceived in industry and academia alike and for this reaction C-H functionalization provides attractive solution to this very challenging problem. And in this context it can be stated that intermolecular C-H functionalization is even more more is very challenging and difficult as compared to the entire intramolecular C-H functionalization.

Now, with this background in mind we are going to look at C-H functionalization both at the intramolecular as well as inter molecular levels and study some of the examples related to it in order to get a appreciation of how difficult this particular area is.

At the outset one must say that C-H activation to transition metal is thermodynamically unfavorable as compared to hydrogen hydrogen addition to a weaker metal carbon bond.

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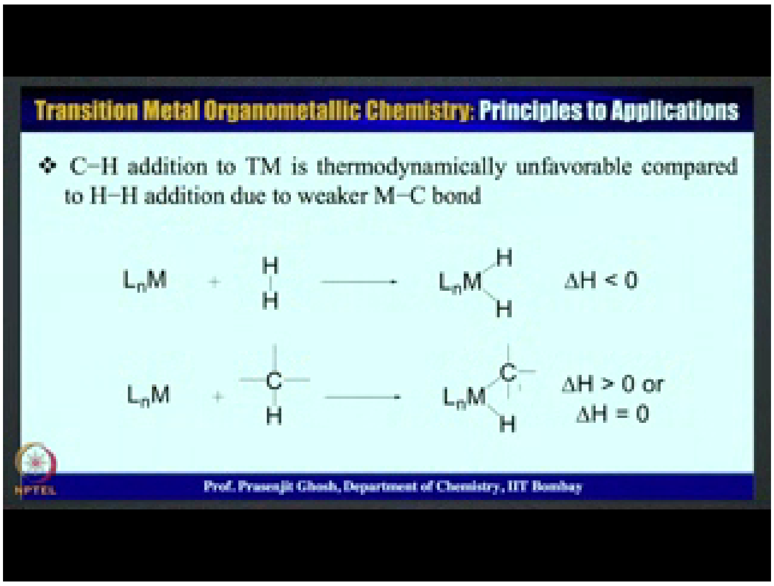

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- C–H addition to TM is thermodynamically unfavorable compared to H–H addition due to weaker M–C bond

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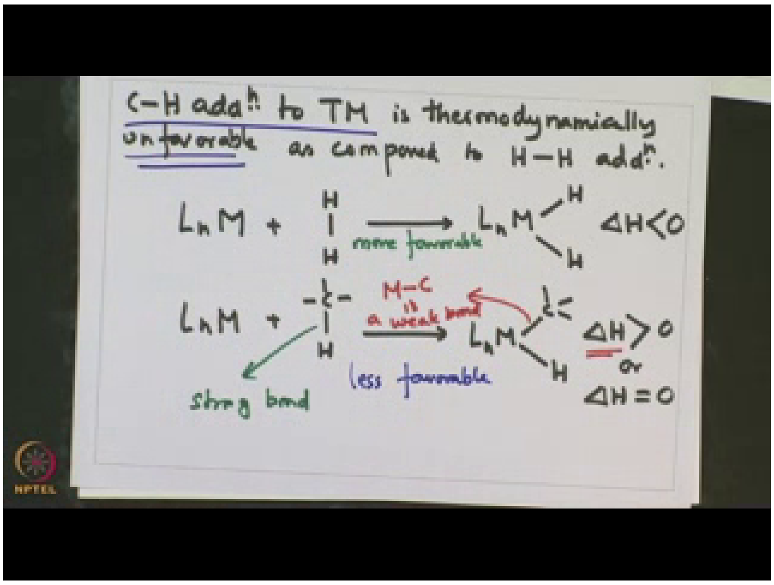

C-H add^{n} to TM is thermodynamically unfavorable as compared to H-H add^{n}.

H-H to bond and this can be illustrated for example, if there is L M and it activates dihydrogen then one forms dihydride the enthalpy is negative for such reaction stating that this is enthalpically favored. Whereas, the same reaction for a C-H bond leading to metal alkyl hydride has delta H greater than 0 or delta H equal to 0 and; that means, that this addition is less favorable and H-H addition is more favorable.

And the primary reason for this H addition being less favorable is that m bond is a weak bond and hence not much of enthalpic gain is realized when a metal carbon bond is formed as opposed to a metal hydride bond. So, metal carbon bond is a weak bond that sort of cannot compensate for the strong bond that is broken when a metal hydrogen bond is cleaved. So, this C-H bond which is very strong is broken and a weak image bond is formed as a result the delta H is usually positive or at the best thermodynamic neutral. And hence this indicates that this C-H addition to transition metal is thermodynamically unfavorable.

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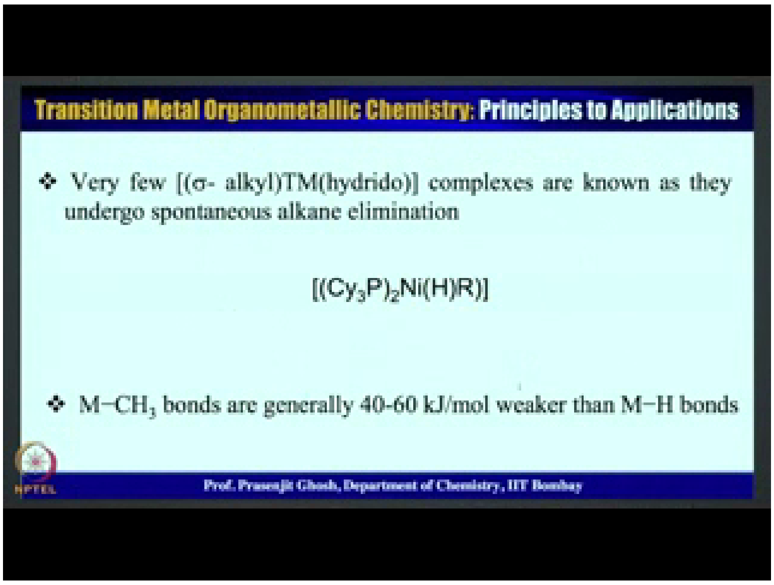

Transition Metal Organometallic Chemistry: Principles to Applications

- Very few [(σ- alkyl)TM(hydrido)] complexes are known as they undergo spontaneous alkane elimination

$[(Cy_3P)_2Ni(H)R)]$

- M−CH_3 bonds are generally 40-60 kJ/mol weaker than M−H bonds

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There are few sigma alkyl transition metal hydrido complex which undergoes spontaneous alkane elimination; that means, that this alkyl hydride complex is so unstable that they eliminate to give back an alkane.

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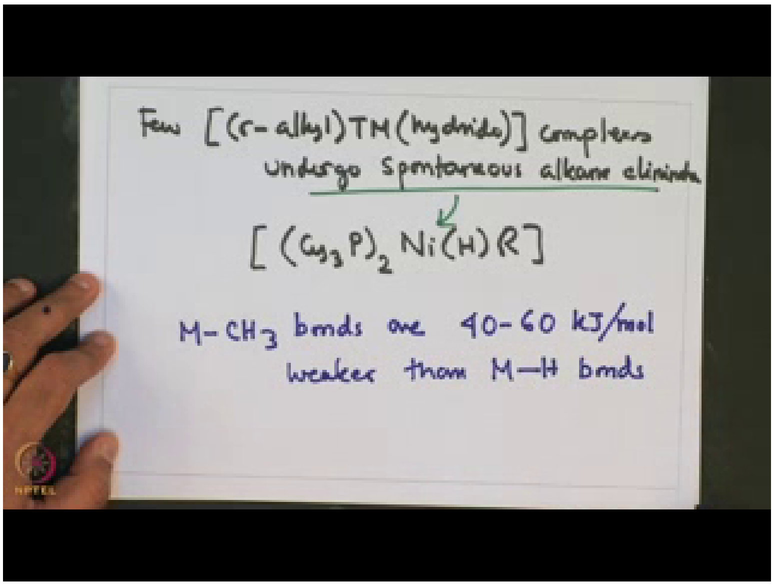

Few [(σ-alkyl)TM(hydrido)] complexes
undergo spontaneous alkane eliminatn

$$[(Cy_3P)_2Ni(H)R]$$

M−CH_3 bonds are 40-60 kJ/mol
weaker than M−H bonds

For example, this cyclohexane phosphine nickel hydride alkyl complex spontaneously undergo alkane elimination. Meaning that this complex is very unstable in the hindsight the metal carbon bond in metal methyl moieties are generally 40 to 60 kilo joule per mole weaker than metal hydrogen bonds.

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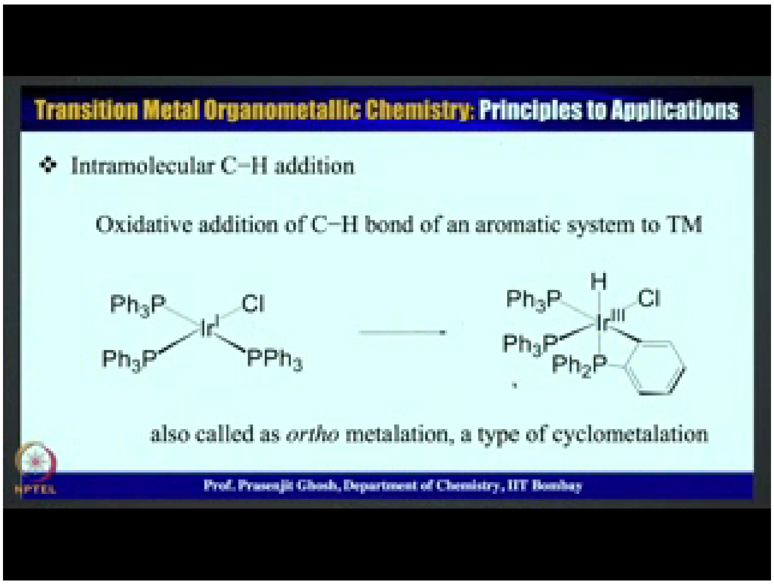

Transition Metal Organometallic Chemistry: Principles to Applications

- Intramolecular C–H addition

Oxidative addition of C–H bond of an aromatic system to TM

also called as *ortho* metalation, a type of cyclometalation

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Now, of the C-H activation which itself is very challenging because of extremely weak metal carbon bonds which are formed and because of the fact that extremely strong metal hydrogen bonds are broken. Let us take a look at different types of C-H activation that may possibly occur.

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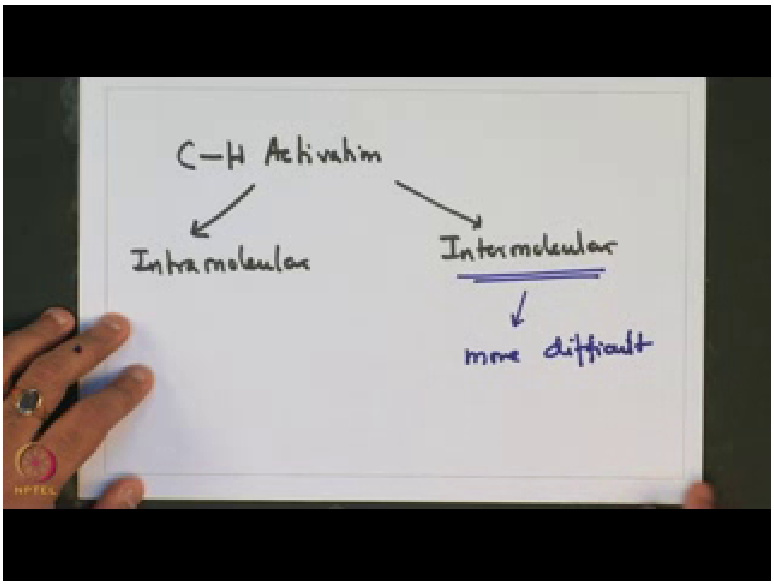

C–H Activation

Intramolecular

Intermolecular

more difficult

It can be intramolecular as well as it can be intermolecular. Of these the intermolecular C-H activation are more difficult as compared to the intramolecular one and in this discussion we are going to take up in more details each of these type of in C-H activation processes. To begin with let us talk about intramolecular had C-H activation.

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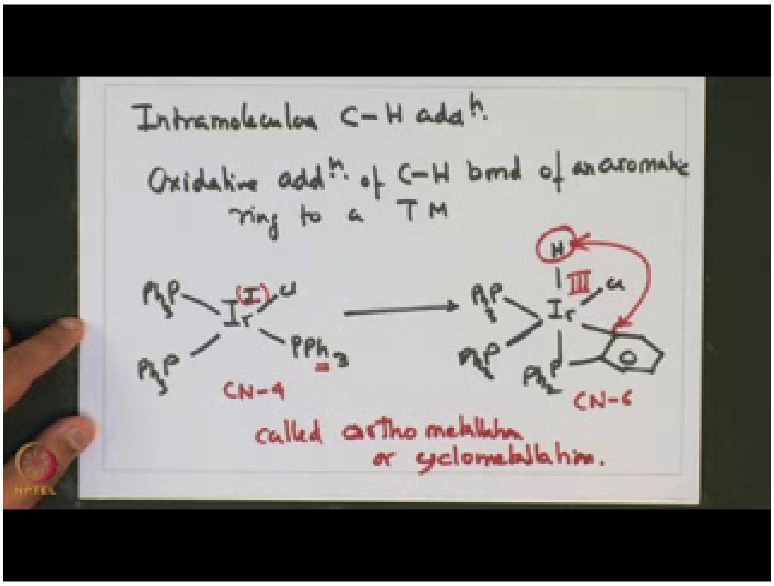

Intramolecular C-H addn.

Oxidative addn. of C-H bond of an aromatic ring to a TM

called ortho metallation or cyclometallation.

This mainly is observed in oxide derivation of C-H bond of an aromatic ring to transition metal an example is given over here. So, iridium one complex chlorine and 3 phosphate iridium undergoes intramolecular C-H activation to give the following iridium 3 complex. So, since the C-H here the oxygen state of iridium has changed from iridium 1 to iridium 3 because it underwent the octave addition and also one of the phenyl rings of this P, P H 3 moiety got activated. So, this hydrogen and this carbon this C-H bond is sort of got activated the coordination number increased from 4 over here to coordination has numbered increased to 6 over there. And since the C-H bond which got activated is ortho to the phosphine this kind of reactions are called also called ortho metallation or cyclo metallation.

So, with this I would like to summarize the point that we have discussed in today's lecture. We have looked into applications of various sigma alkyl complexes. To start with we looked into organo rhenium trioxide type complexes, we have looked into how these complexes were synthesized and also the various kind of applications of these rhenium alkyl tri oxo complexes. Following that we looked into the C-H activation processes which can result in C-H functionalization which is a very challenging area and then we have looked into various kinds of C-H activation processes that are involved to start with we looked into intra molecular C-H activation particularly that of cyclo metallation or ortho metallation that is shown over here.

With this we come to the end of today’s lecture and we are going to take up this interesting topic of C-H activation in bit more detail in next lecture and look into various possible reactions and discoveries made in this area of C-H activations which is of tremendous industrial as well as academic interest. With that I thank you for being with me in this lecture and I look forward to being with you in next lecture discussing various nitty gritty details of this interesting C-H activation reactions of transition metal sigma alkyl complexes.

Thank you.