Transition Metal Organometallic Chemistry: Principles to Applications
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Week – 03
Lecture – 12
B-Elimination in σ-alkyl compounds

Welcome to this lecture on transition metal organometallic chemistry from principles to applications. In the course of last few lectures we have been discussing a very important class of transition metal compounds these are called the sigma alkyl complexes we were looking into reactivity of this complexes particularly their property of extremely sensitive to air and moisture, and one of the reason for them being. So, reactive is a particular class of reaction that they exhibit which is better known as beta elimination.

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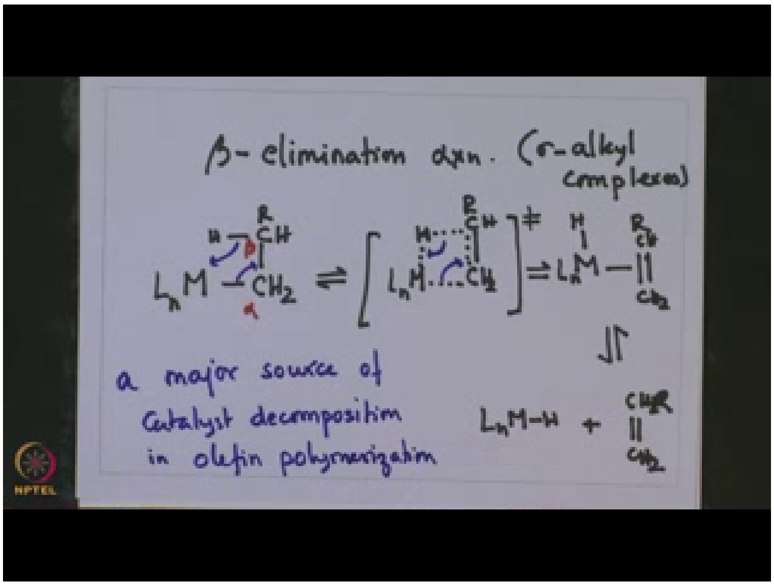

β- elimination rxn. (σ-alkyl complexes)

a major source of catalyst decomposition in olefin polymerization

So, we are looking into a very important reaction that accounts for high reactivity of transition metal sigma alkyl complexes and these are called beta elimination reaction. These reactions particularly observed in sigma alkyl complexes. So, one is to understand the reason for or the mechanism of how this reaction works.

For example transition metal complexes having beta hydrogen for let us say if I have a transition metal bound to a ligand containing a alkyl moiety which has a beta hydrogen, beta hydrogen meaning the location of the hydrogen is on the beta carbon this is alpha carbon beta carbon it undergoes an interaction of this carbon hydrogen sigma bond with a vacant metal d orbital that goes via at 4 numbers transition state of the one shown here, leading to the formation of an alkyl bound complex.

So, this beta elimination results in migration of beta hydrogen from the beta carbon on to the metal and netlinkage of this carbon bond leading to an olefin which sort of happens in a concentrate pathway resulting in a metal hydride, and a coordinated olefin. These can finally, eliminate the olefin plus a metal hydride. So, these results in decomposition of metal alkyl compounds having beta hydrogen, this is the very spontaneous reaction leading to decomposition of many metal alkyl complexes.

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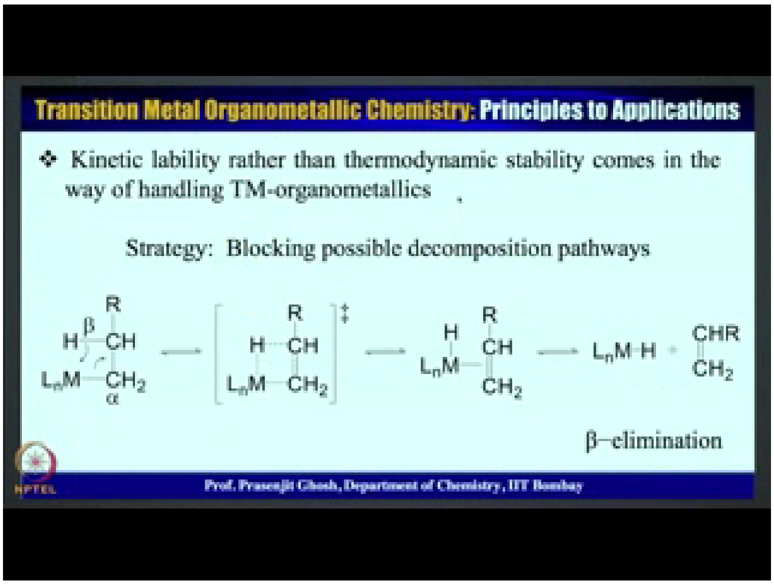

Transition Metal Organometallic Chemistry: Principles to Applications

- Kinetic lability rather than thermodynamic stability comes in the way of handling TM-organometallics

Strategy: Blocking possible decomposition pathways

β–elimination

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This beta hydride elimination is also part of catalyst decomposition in many important transition metal catalyst reactions for example, it is a major decomposition pathway for olefin polymerization reaction catalyze by transition metal that proceeds via coordination insertion pathway. Catalyst decomposition in olefin polymerization reaction.

Now, one may wonder whether this reaction is reversible or irreversible well beta elimination can be reversible.

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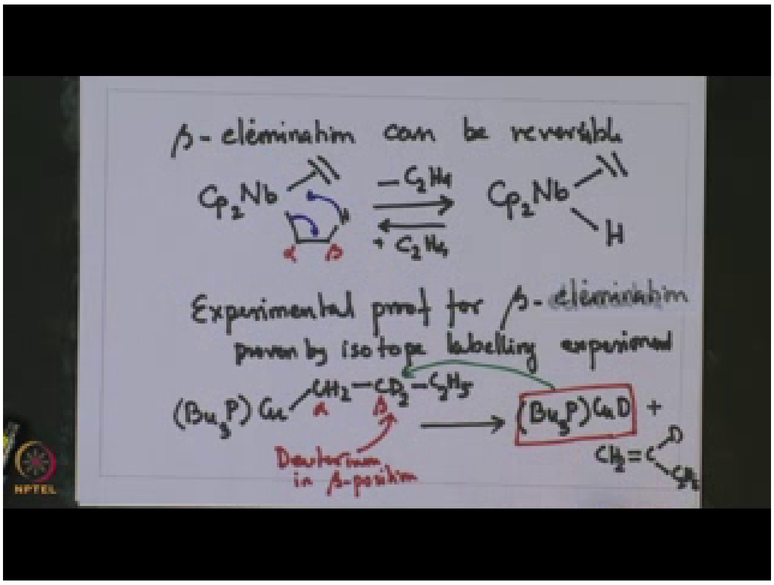

β- elimination can be reversible

Experimental proof for β- elimination proven by isotope labelling experiment

For example, in this Cp2 Nb C2 H4 ethyl complex it loses this olefin to give the corresponding hydride complex, in which the olefin is last from the ethyl moiety and this beta hydrogen gets incorporated into the norbornene now this complex when treated back with olefin gets back the ethyl complex for beta elimination can be reversible and

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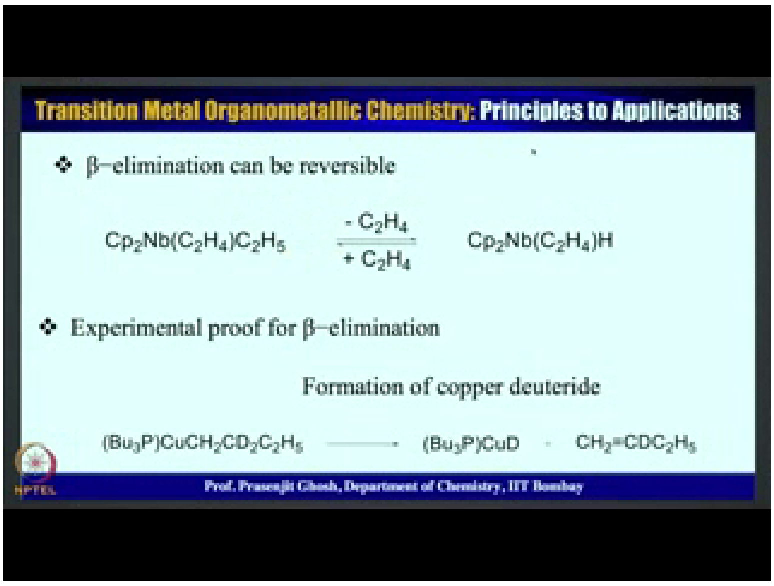

Transition Metal Organometallic Chemistry: Principles to Applications

- β–elimination can be reversible

$$Cp_2Nb(C_2H_4)C_2H_5 \underset{+\,C_2H_4}{\overset{-\,C_2H_4}{\rightleftharpoons}} Cp_2Nb(C_2H_4)H$$

- Experimental proof for β–elimination

Formation of copper deuteride

$$(Bu_3P)CuCH_2CD_2C_2H_5 \longrightarrow (Bu_3P)CuD + CH_2{=}CDC_2H_5$$

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Important experimental proof for beta elimination came from a seminal experiment using deuterium studies. For example, this was proven using isotope leveling experiment. For example, for thus tributile phosphorus copper CH2CD2C2H5 complex which had cleverly incorporated deuterium in it is beta position as expected gave the copper dutrite complex plus the corresponding alkyl. So, this formation of copper dutrite convincingly proves that elimination occur from the beta position. So, this was a convincing proof which sort of establish the fact that in beta elimination reaction the hydrogen is evolved from the beta position. They were no formation of copper hydride which would have resulted from alpha elimination.

And hence the name beta elimination derived from for this reason. Now as beta elimination is a major pathway leading to the decomposition of transition metal sigma alkyl complexes now one of the important challenge in this area is to suppress beta elimination.

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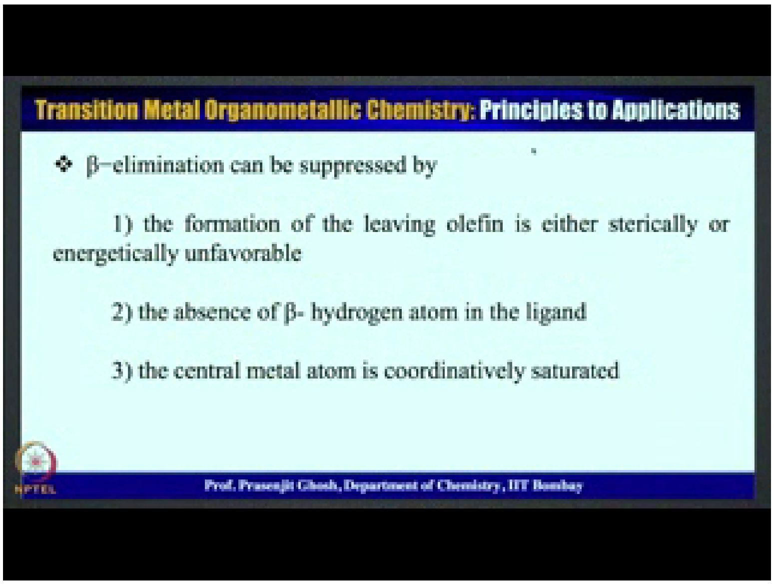

Transition Metal Organometallic Chemistry: Principles to Applications

- β−elimination can be suppressed by

1) the formation of the leaving olefin is either sterically or energetically unfavorable

2) the absence of β- hydrogen atom in the ligand

3) the central metal atom is coordinatively saturated

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So, that longevity and stability of transition metal organometallic compounds can be improved.

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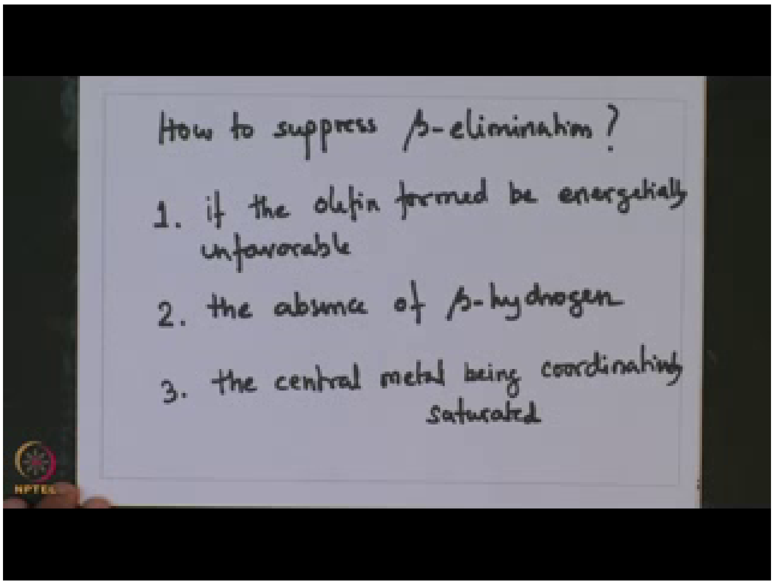

How to suppress β-elimination?

1. if the olefin formed be energetically unfavorable
2. the absence of β-hydrogen
3. the central metal being coordinatively saturated

So, these became a important topic of research and several strategies were evolved towards this challenge. And one of the major one was for example, if the formation of olefin is blocked or suppressed for some reason or other then in principle we should be able to suppress beta elimination. So, the first strategy was in if the olefin formed be energetically unfavorable. So, that was a nice strategy because beta elimination will always lead to the formation of olefin and if one designs the alkyl moiety as such that the olefin that forms from it becomes energetically unfavorable then probably the beta elimination will not proceed.

This was a very clever and ingenious way of stopping beta elimination the other the other strategy is; obviously, include designing ligands for example, if the ligand does not have any in a beta position probably beta elimination would never proceed. So, the second strategy is about the absence of beta hydrogen and third one also involved a clever technique where the beta hydrogen was suppressed because of coordinative saturation

Now, if one were to look back at the 4-member transition state that we had drawn earlier for beta hydrogen elimination reaction then it may be noticed that beta hydrogen was interacting with the metal as a result of metal undergoing increase in coordination number. So, the logic in this particular strategy is that if the central metal atom is coordinatively saturated then the metal atom cannot interact with the beta hydrogen and hence would not participate in beta elimination reaction. The this strategies about the central metal atom being coordinatively saturated.

So, what we have seen that after understanding how the beta elimination occurs one can come up with several strategies which will suppress this beta elimination process the first one being that if somehow the formation of olefin is made unfavorable be that be because of whatever reasons we will discuss in more details then probably beta elimination will be suppresses even though the metal sigma alkyl moiety may have a beta hydrogen.

The second approach was if the beta hydrogen is absent in a particular metal sigma alkyl complex; obviously, it cannot undergo beta hydrogen elimination and lastly since the beta hydrogen elimination requires participation of the metal and an increase in coordination number at the metal. So, if the metal is coordinatively saturated then; obviously, it will not be able to attack the beta hydrogen of the ligand and hence the beta elimination will be suppressed we are going to discuss each of this strategies in much more details and see how they really affect these process of beta elimination favorably in terms of suppressing the elimination process.

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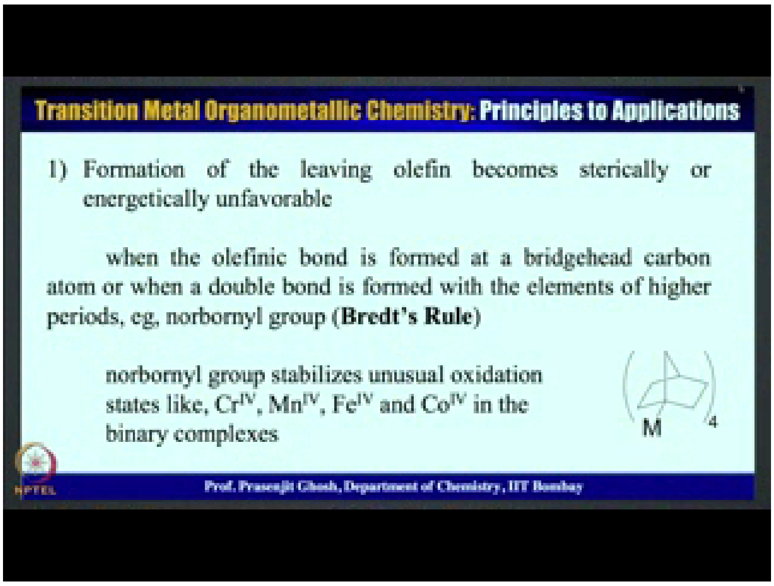

Transition Metal Organometallic Chemistry: Principles to Applications

1) Formation of the leaving olefin becomes sterically or energetically unfavorable

when the olefinic bond is formed at a bridgehead carbon atom or when a double bond is formed with the elements of higher periods, eg, norbornyl group **(Bredt's Rule)**

norbornyl group stabilizes unusual oxidation states like, Cr^{IV}, Mn^{IV}, Fe^{IV} and Co^{IV} in the binary complexes

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Let us look at this first strategy of formation of leaving all olefin become sterically or energetically unfavorable.

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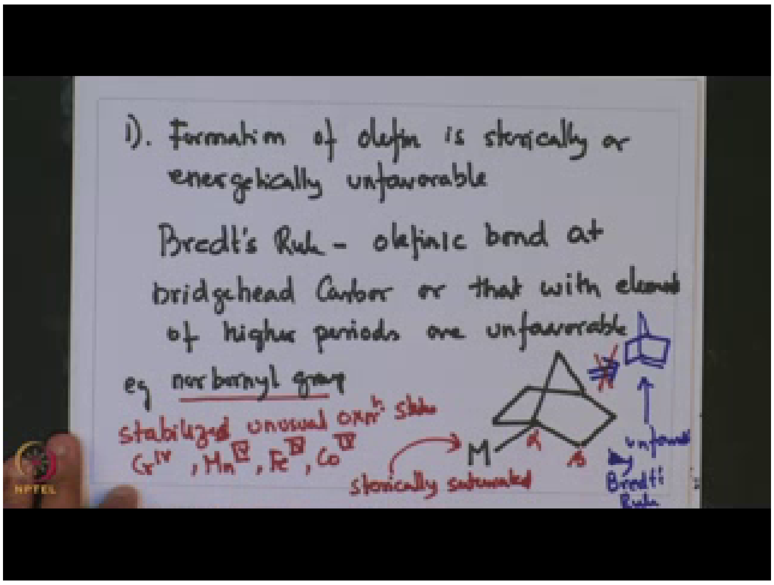

1). Formation of olefin is sterically or energetically unfavorable

Bredt's Rule - olefinic bond at bridgehead Carbon or that with element of higher periods are unfavorable

eg norbornyl group

stabilized unusual oxdn. state Cr^{IV}, Mn^{IV}, Fe^{IV}, Co^{IV}

This brings us back to a famous rule call bredts rule which states that olefinic bond formed at the bridgehead carbon or double bond formed with higher elements in the period are unfavorable or with elements with higher in period are unfavorable for example, the norbornyl group. So, the norbornyl group does not undergo beta elimination because of the reason that olefinic bond will be a formed at the bridgehead carbon let us sort of take a look. So, if a olefin were to form then the olefinic bond would be. So, this has the beta hydrogen.

So, this is alpha this is beta and this hydrogen if it were to get attacked the resultant olefin would be unfavorable and would have a structure something like this, which is unfavorable according to bredts rule. And hence this type of compounds does not undergo beta elimination, and as a result this norbornyl group is very good in stabilizing unusual stabilizes unusual oxidation states of metal like chromium 4 manganese, 4 iron 4, cobalt 4 in binary alkyl complexes where there is only metal and the ligand and norbornyl being very big in size it is it also makes the metal center sterically saturated.

And hence we see that successful utilization of the first strategy of making the formation of olefinic bond unstable leads to transition metal sigma alkyl complexes having very high oxidation states unusual oxidation state which otherwise became extremely difficult to stabilize. Also, what is interesting in this particular example is that even though the norbornyl does have beta hydrogen, but because of the steric bulk of the ligand as well as because of the formation of the olefin being unstable this norbornyl despite having the beta hydrogen does not undergo these so facile beta elimination process. So, this is a very successful implementation of the strategy that we have been talking about. Now let us look at the next strategy which was absence of beta hydrogens now.

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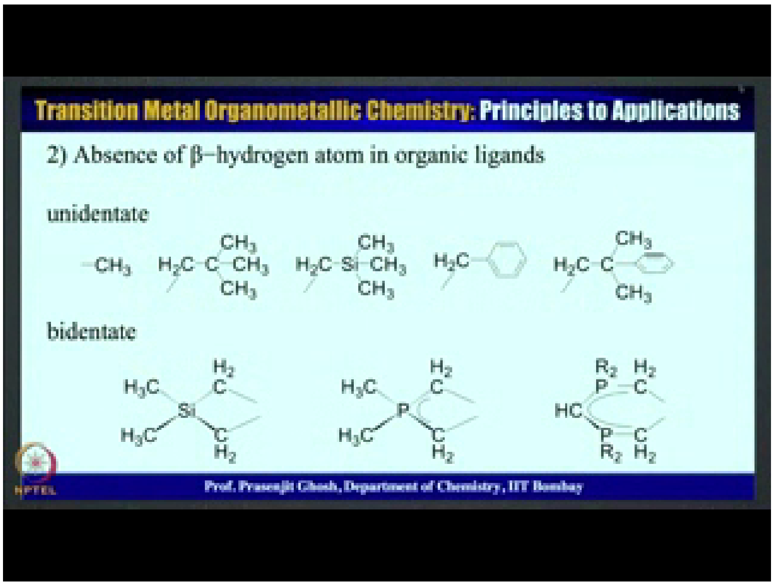

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2) Absence of β–hydrogen atom in organic ligands

unidentate

bidentate

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These strategy revolves around the fact that if there is no beta hydrogen in the sigma alkyl complex then; obviously, beta elimination may not happen. So, the second strategy is about.

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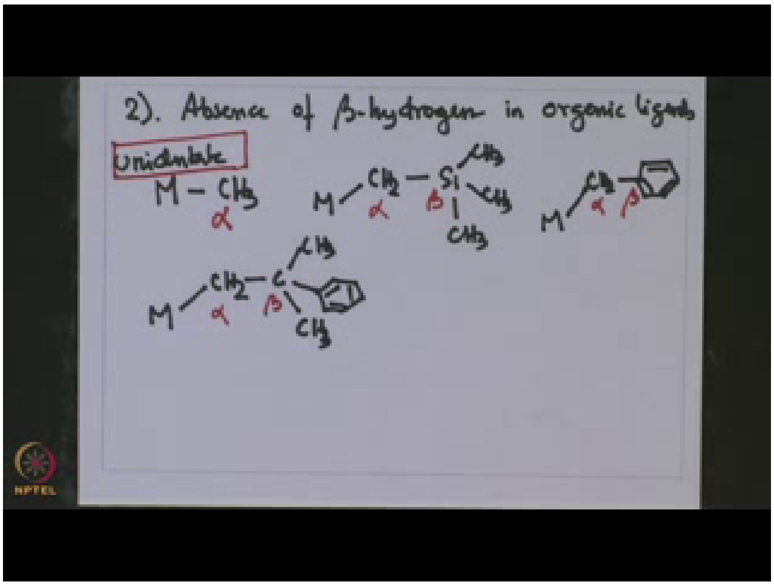

2). Absence of β-hydrogen in organic ligands

Unidentate

Now this also is an effective approach toward suppressing beta elimination and as a result several new types of ligands have been developed using this strategy we are going to take a look some of these ligands and when this ligands are attached to the metal in transition metal organometallic complexes those metal complexes with this particular type class of ligands tend to be more stable than the ones which had beta hydrogen so; obviously, a this is a very effective approach in enhancing the stability of transition metal sigma alkyl complexes and as a result several new types of ligands have been developed. For example, one can have a methyl moiety these are unidentate ligand.

So, methyl moiety has only alpha hydrogen there is no beta hydrogen for it to eliminate one can have these CH2 t m s group this also does not have a beta hydrogen for it to eliminate hence the beta elimination pathway would be unfavorable. One can have a benzyl group this itself also does not have a beta hydrogen for it to eliminate and one can have another variant of this CH2 dimethyl phenyl group this also does not have a beta hydrogen these all belong to the monodentate class of this special ligands which does not have beta hydrogen and impulse to get a stability of the complex.

There are some bidentate chelating ligands as well these ligands being chelating in nature they impart extra stability because of chelation apart from imparting stability with respect to not having beta hydrogens.

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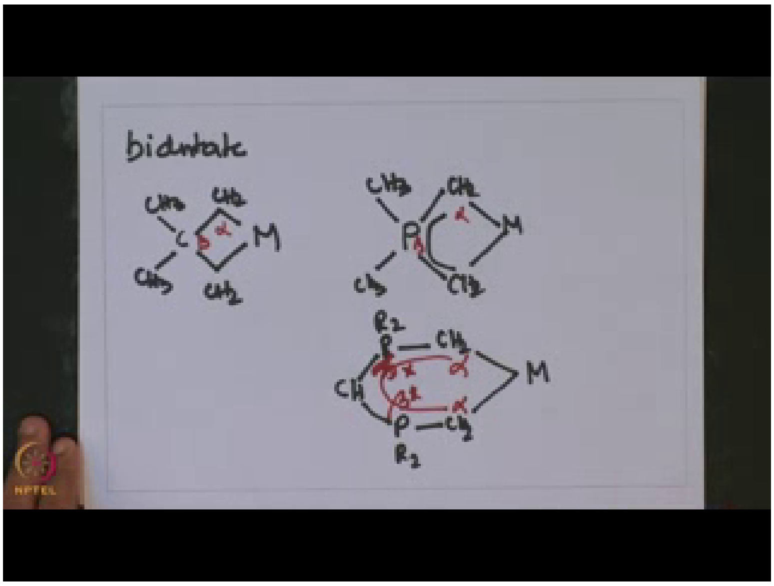

So, this bidentate ligand includes the following. So, one can see that the beta hydrogen does not have a ligand hydrogen similarly the variation with phosphorous. This has a phosphorous atom and also there is no beta hydrogen at the phosphorous. So, this also does not have any hydrogen at the beta and these are bidentate ligands that impart stability to the transition metal sigma alkyl complexes. So, what we have seen to summarize in this lecture is that we have looked at various reasons which inhibit beta hydrogen elimination reaction and that results in extra stability to transition metal sigma organometallic complexes, and to this fact we have looked at 2 such strategies one that involve that absence of beta hydrogen in the metal alkyl ligand as we have been discussing and that comes in 2 types unidentate and bidentate one.

And the first one that we have discussed is about making the formation of the olefin unfavorable either sterically or energetically that will also successfully inhibit beta elimination pathway and impart stability to the transition metal sigma alkyl complexes. So, with this we are still continuing on an interesting topic of beta elimination that results in decomposition of many transition metal organometallic complexes and in our next lecture we will look into few more reasons to how to suppress this beta elimination reaction in transition metal sigma alkyl complexes to our advantage and impart stability to this, otherwise very unstable transition metal organometallic complexes. Thank for being with me in this lecture and I look forward to an interesting one particularly on this topic in the following lecture.

Thank you.