Transition Metal Organometallic Chemistry: Principles to Applications
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Week – 03
Lecture – 13
Beta - Elimination in detail

Welcome to this lecture on transition metal organometallic chemistry from principles to applications. In the last lecture we have discussed about a very important attribute of transition metal organometallic compounds particularly with respect to their reactivity as to why this compounds are. So, reactive. So, difficult to handle why they decompose and what are the reasons behind that. And while analyzing we came upon the main factor responsible for extremely high reactivity of these transition metal organometallic compounds and that is

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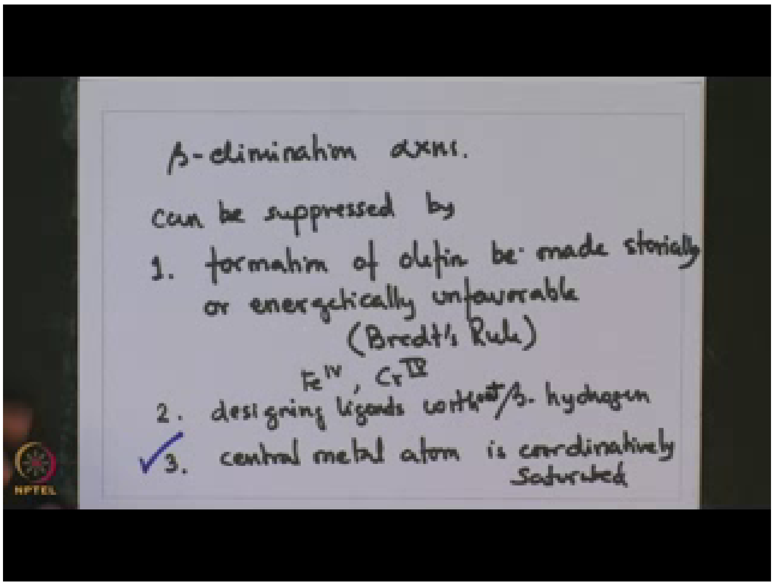

β-elimination rxns.

can be suppressed by

1. formation of olefin be made sterically or energetically unfavourable (Bredt's Rule)

Fe^{IV}, Cr^{IV}

2. designing ligands without β-hydrogen

✓3. central metal atom is coordinatively saturated

Called beta elimination reactions in the course of discussing beta elimination reactions, in details in the last lecture we aimed at understanding how this reaction was occurring how this reaction mechanistically was proceeding and what was established was through experiment was the fact that these reactions proceed if there is a hydrogen at the beta carbon of the alkyl group which is attacked by the transition metal leading to the elimination, hence the name beta elimination resulting in a metal hydride and an olefin. And this was established by a classical and isotope modelling experiment in which a beta hydrogen was replaced with a deuterium resulting in the formation of a metal duty right which sort of established the fact that the beta elimination proceeds by elimination of the hydrogen placed at the beta position of the metal alkyl bond.

In the previous lecture we further discussed about the various strategies that are often employed in suppressing beta elimination reactions, these can be done by the following 2 strategies which we had discussed in the last lecture. First one was formation of olefin. Olefin be made sterically or energetically unfavorable. And this was made possible by application of this bredts rule. Whereby formation of olefin at a bridge carbon becomes unfavorable and the example of these are norbornene ligand which does not undergo beta elimination even though there is a beta hydrogen in the ligandat it is beta carbon atom.

We had a fairly detailed analysis of this particular rule and we found that this can be favorably used for stabilizing several high valent oxygen states of metal for example, iron 4 chromium 4 complexes and several others which otherwise would be difficult to stabilize. Now in the previous lecture we also discussed about a string of ligands which does not have beta hydrogen at the beta position and does not form beta elimination reaction. So, designing ligands without beta hydrogen would also suppress beta elimination reaction. The second strategy involved designing ligands without data hydrogen as this ligands in absence of it is beta hydrogen is unable to undergo beta elimination reaction.

Now, with this in background we come to another interesting strategy for today’s topic that is if the coordination of the central metal atom we made saturated. So, the beta elimination can be stopped. So, this strategy is about inhibiting beta elimination by coordinatively saturating the central metal atom.

In this it takes into fact that beta elimination proceeds via transition state in which the simple metal atom attacks the sigma bond of the carbon hydrogen bond placed at the beta position of the ligand and thereby the metal undergoes an increase in coordination number. So, the implementation of the strategy requires such that the metal be coordinatively saturated. So, the metal despite having a vacant d orbital to attack the CH sigma bond of the beta position it is unable to do so, because of coordinated or steric saturation for example, let us analyze this third strategy where this metal atom is coordinatively unsaturated for example, let us look at thermal stability.

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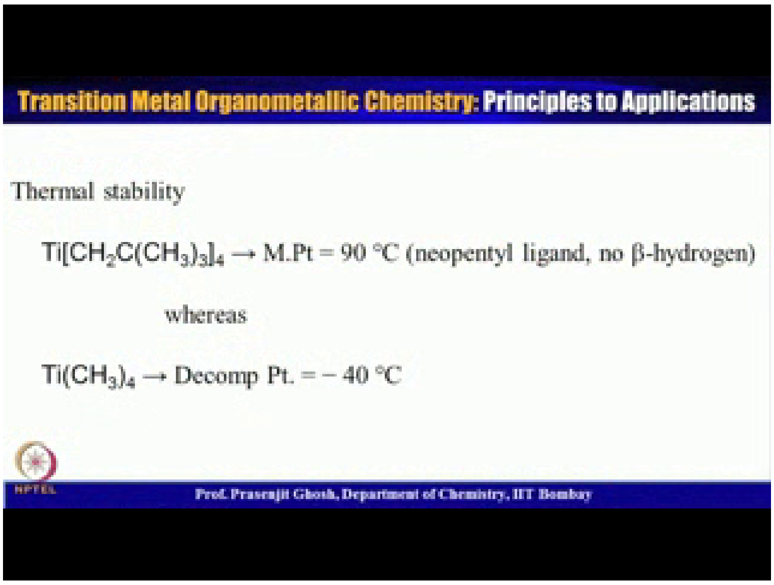

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Thermal stability

$Ti[CH_2C(CH_3)_3]_4$ → M.Pt = 90 °C (neopentyl ligand, no β-hydrogen)

whereas

$Ti(CH_3)_4$ → Decomp Pt. = – 40 °C

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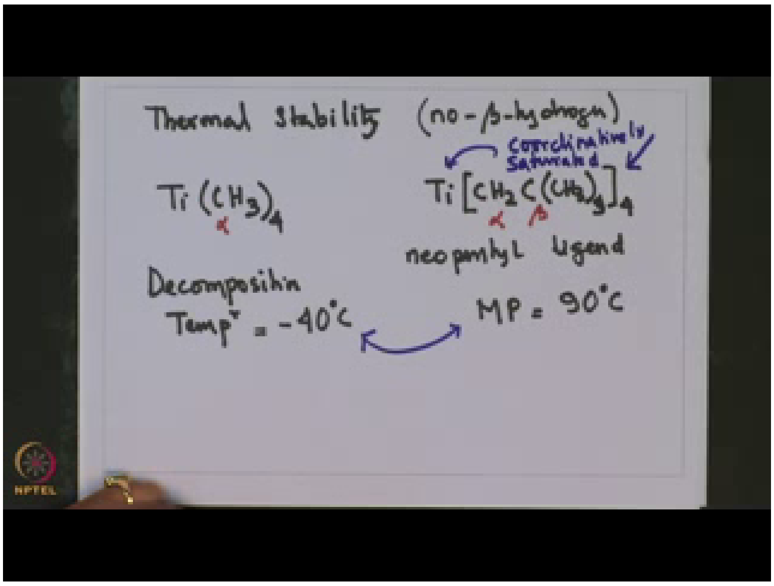

Thermal stability (no-β-hydrogen)

$Ti(CH_3)_4$

Decomposition Temp^r = $-40^\circ C$

coordinatively saturated

$Ti[CH_2C(CH_3)_3]_4$

neopentyl ligand

MP = $90^\circ C$

Now, thermal stability of these 2 compounds let us say titanium tetra methyl and titanium tetra CH2 CCH3 whole 4. Now both of these does not have beta hydrogen. This only has alpha hydrogen and this at beta carbon does not have a beta hydrogen, this is a neopentyl group.

And as both of these ligands do not have beta hydrogen. So, one would think that they may be equally stable, but actually that is not the case as titanium tetra methyl shows a decomposition temperature of minus 40 degree centigrade whereas, platinum tetra neopentyl compound gives a melting point of plus 90 degree centigrade. So, what can see that there is huge difference in stability between titanium tetra methyl and titanium tetra neopentyl despite the fact that both titanium tetra methyl and titanium tetra neopentyl does not have beta hydrogen.

So obviously, there has to be some other effect responsible for extra stability of this titanium tetra neopentyl complex, and that extra stability is comes from this coordinative saturation coordinatively saturation environment around titanium. So, titanium being flanked by all this bulky neopentyl group 4 of them is very much coordinatedly saturated and hence it does not decompose. So, this is in tune with the strategy of the third one that we are discussing that coordinative saturation at the metal center.

For example, again let us take a look at another set of complexes for example, if we look at thermal stability of the following 2 compounds.

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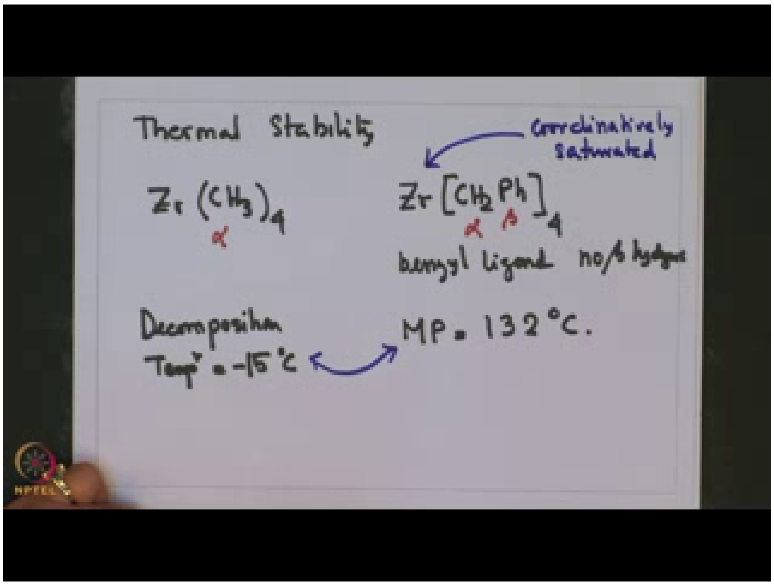

Thermal Stability

Coordinatively saturated

$Zr(CH_3)_4$ α

$Zr[CH_2Ph]_4$ α β

benzyl ligand no/β hydrogen

Decomposition Temp^{r} = -15 °C

MP = 132 °C.

In this case zirconium tetra methyl similar to titanium tetra methyl we had discussed earlier and zirconium tetra benzyl both does not have beta hydrogens. So, this does not have a beta hydrogen and this also does not have a beta hydrogen. So, this is the benzyl ligand no beta hydrogens. So, in this case what we see decomposition temperature in this case is minus 15 degree centigrade whereas, zirconium tetra benzyl the melting point is 132 degree centigrade. So, there is a tremendous increase in stability despite the fact that both of this compound does not have beta hydrogen and there is a significant increase in stability a on the tetra benzyl and this is also explained by the fact which we are discussing as a part of the third strategy that the central metal atom is coordinatively saturated.

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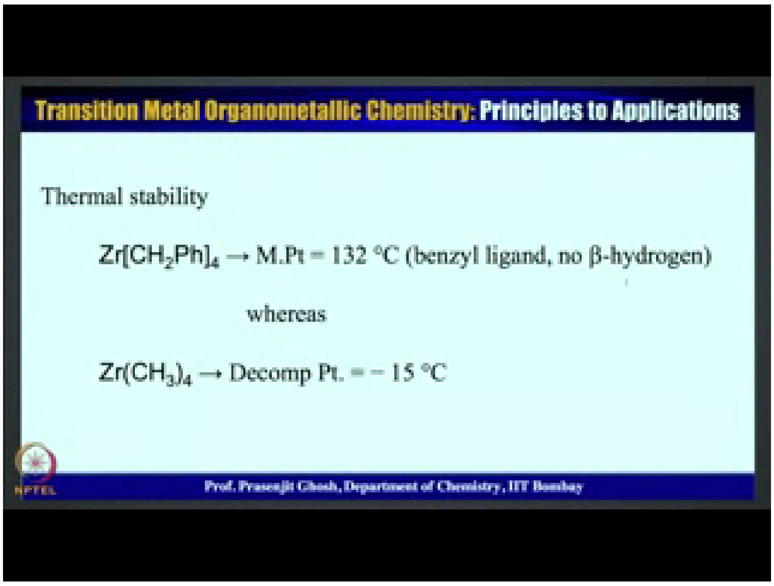

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Thermal stability

$Zr[CH_2Ph]_4$ → M.Pt = 132 °C (benzyl ligand, no β-hydrogen)

whereas

$Zr(CH_3)_4$ → Decomp Pt. = − 15 °C

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So, what we are seeing right now is the manifestation of this third strategy of how coordinatively saturated metal center may increase or impart extra stability to transition metal complexes in addition over and above of the what comes from the ligand which it does not have a beta hydrogen.

So, let us sort of understand the fact that how come coordinatively saturated central atom leads to extra stability to understand this we need to understand.

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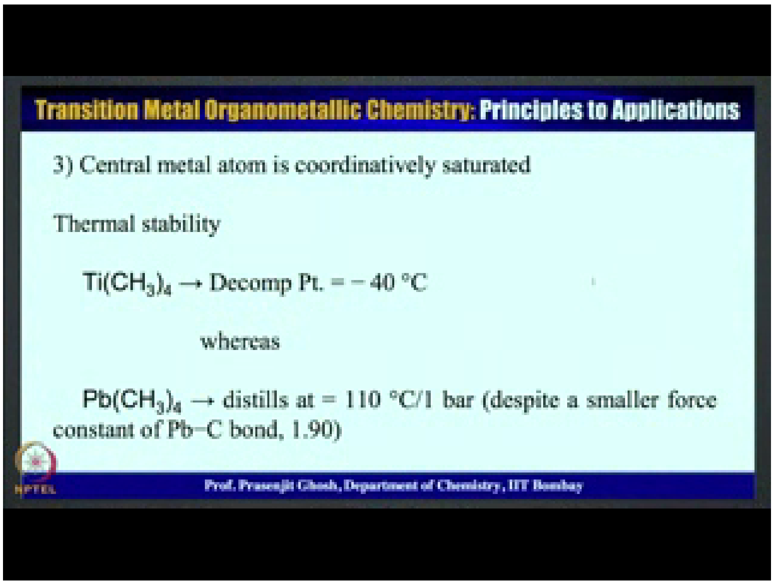

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3) Central metal atom is coordinatively saturated

Thermal stability

$Ti(CH_3)_4$ → Decomp Pt. = − 40 °C

whereas

$Pb(CH_3)_4$ → distills at = 110 °C/1 bar (despite a smaller force constant of Pb−C bond, 1.90)

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Or take a look at the unstability of compounds like zirconium tetra methyl. So, for stability thermal stability

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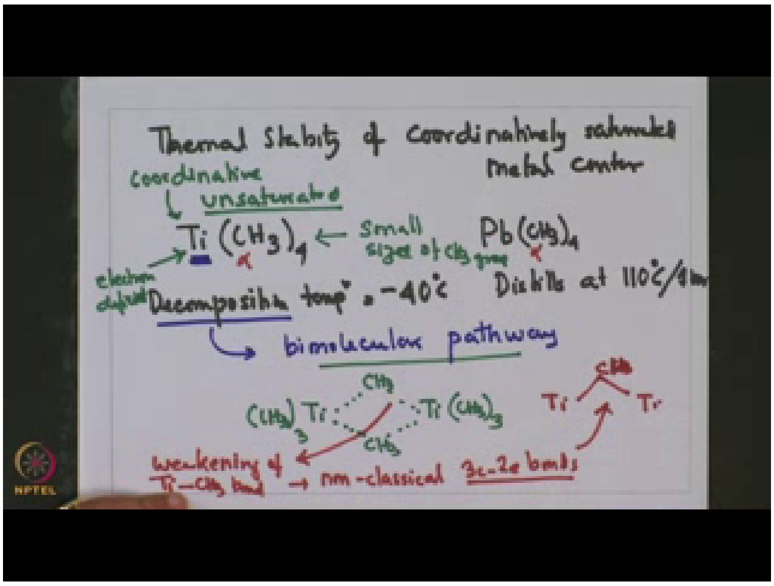

Of coordinatively saturated metal center as mentioned to understand this we need to take at the following 2 compounds for example, titanium tetra methyl which does not have a beta hydrogen decomposes at minus 40 degree centigrade whereas, the corresponding late tetra methyl which is a main group sigma alkyl metal complex that also does not have a beta hydrogen only has alpha hydrogen distills at 110 degree centigrade in one bar pressure. So, this shows that this main group late tetra methyl is exceptionally stable that one can distill it. So, what is the reason why this titanium tetra methyl is. So, reactive that it decomposes at minus 40 degree

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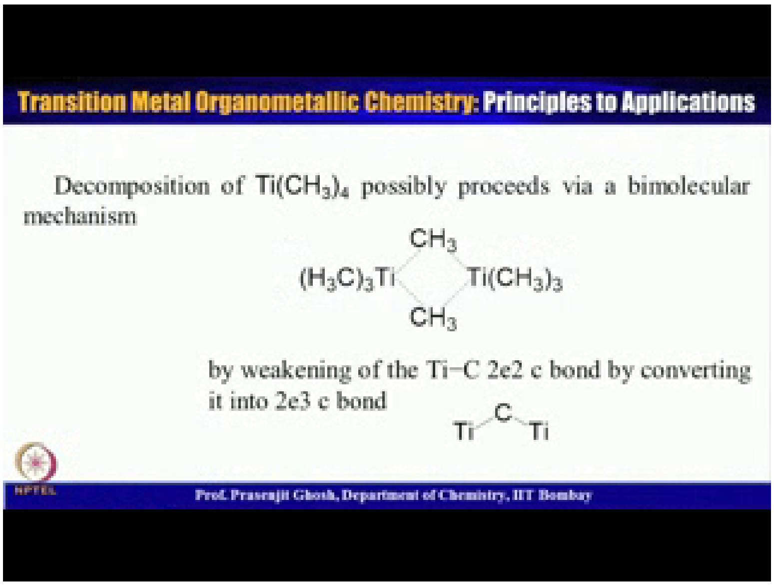

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Decomposition of $Ti(CH_3)_4$ possibly proceeds via a bimolecular mechanism

by weakening of the Ti–C 2e2 c bond by converting it into 2e3 c bond

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Centigrade and the reason comes from the fact that decomposition arises via ab by molecular pathway. What is this by molecular pathway resulting in the decomposition to understand this that titanium tetra methyl is coordinatively unsaturated. This unsaturation comes from small size of the methyl group. As a result, titanium being early transition metal and extremely electron deficient; can undergo this by molecular pathway by attacking the titanium methyl bond of the neighboring molecule. As a result, this titanium methyl bond becomes weak as they convert from classical 2 centered 2 electron bond to a non-classical, 3 center 2 electron bonds leading to their decomposition.

So, what is very interesting is that for electron deficient element like titanium, if it remains coordinatively unsaturated then it can interact with the titanium methyl bond of a neighboring titanium tetra methyl compound thereby weakening it and resulting in decomposition of the

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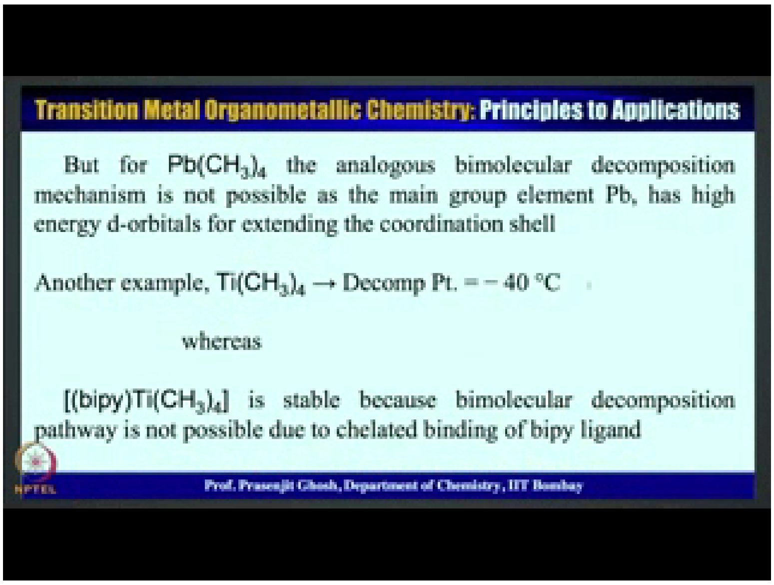

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But for $Pb(CH_3)_4$ the analogous bimolecular decomposition mechanism is not possible as the main group element Pb, has high energy d-orbitals for extending the coordination shell

Another example, $Ti(CH_3)_4$ → Decomp Pt. = − 40 °C

whereas

$[(bipy)Ti(CH_3)_4]$ is stable because bimolecular decomposition pathway is not possible due to chelated binding of bipy ligand

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Compound whereas, inlaid electron rich main group element such by molecular decomposition pathway is not possible.

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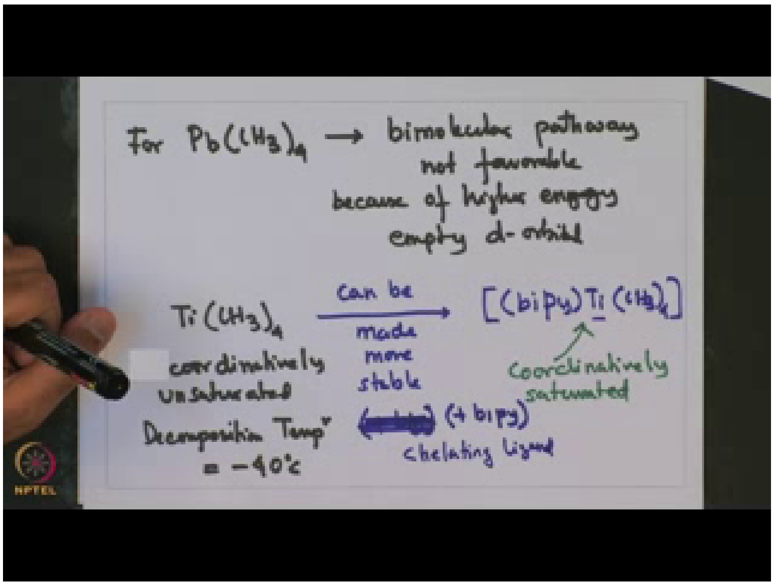

For $Pb(CH_3)_4$ → bimolecular pathway not favorable because of higher energy empty d-orbital

$Ti(CH_3)_4$ $\xrightarrow{\text{can be}}$ $[(bipy)\underline{Ti}(CH_3)_4]$

coordinatively unsaturated

made more stable

coordinatively saturated

Decomposition Temp^r = −40°C

(+ bipy)

chelating ligand

For tetra methyllaid by molecular pathway not favorable because of higher energy empty d orbital. For it for undergoing such decomposition pathway whereas, titanium tetra methyl which is coordinatively unsaturated and decomposes at minus 40 degree centigrade can be made can be made more stable if it is made coordinatively saturated and that can be done by adding a bi pyridine ligand. For example, plus bi pyridine to give this compound which now has become coordinatively saturated due to collation so, what is observed that by addition of this bi pyridine ligand, which is a chelating ligand the coordinate of saturation of the titanium center is increased in this titanium tetra methyl complex and hence these become very stable. So, what is emerging out of this third

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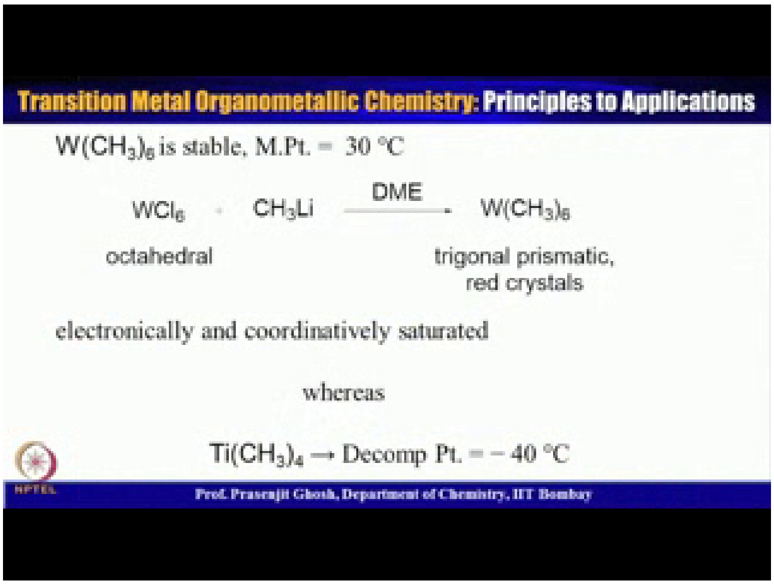

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$W(CH_3)_6$ is stable, M.Pt. = 30 °C

$$\underset{\text{octahedral}}{WCl_6} + CH_3Li \xrightarrow{DME} \underset{\text{trigonal prismatic, red crystals}}{W(CH_3)_6}$$

electronically and coordinatively saturated

whereas

$Ti(CH_3)_4$ → Decomp Pt. = – 40 °C

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Strategy is that the third strategy is a very potent approach for increasing stability of transition metal sigma alkyl complexes and that can be achieved by increasing the coordinatively saturation of the central metal atom.

Here is another example of coordinatively saturated central metal atom in this tungsten hexamethyl complex.

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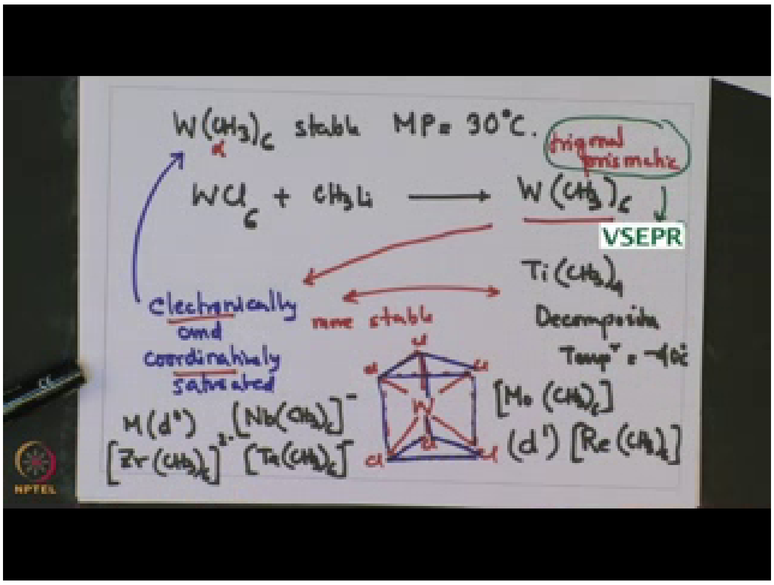

$W(CH_3)_6$ stable MP = 30°C.

trigonal prismatic

$WCl_6 + CH_3Li \longrightarrow W(CH_3)_6$

VSEPR

electronically and coordinatively saturated

more stable

$Ti(CH_3)_4$

Decomposition Temp = -40°C

$M(d^0)$ $[Nb(CH_3)_6]^-$

$[Zr(CH_3)_6]^{2-}$ $[Ta(CH_3)_6]^-$

$[Mo(CH_3)_6]$

(d^1) $[Re(CH_3)_6]$

This is very stable relatively and has a melting point of 30 degree centigrade. Now this is one of the home electric rare complexes where the metal methyl home elective complex is. So, stable that it is molting point is around 30 degree centigrade. This can be prepared from the reaction of tungs10 hexachloride with methyl lithium giving to tungsten hexamethyl. This complex is electronically as well co ordinarily saturated. And also, it does not have a beta hydrogen and hence it is stable of 2 plus 30 degree centigrade and in contrast the titanium tetra methyl has a decomposition temperature of minus 40 degree centigrade.

These tungsten extra methyl being both electronically and co ordinatively saturated becomes significantly more stable than the corresponding titanium tetra methyl and also this exhibits unique kind of coordination geometry. For example, the most common coordination geometry for a metal complex having a coordination number 6 is octahedral where as tungsten hexamethyl shows trigonal prismatic geometry. Which is very different and the structure of it can be shown over here. So, this is kind of can be seen as a prison whereby the 3 vertices occupied by 3 chlorine atom the top one and the bottom ones tungsten sits in the middle.

Now, in this there are several other complexes which shows similar trigonal prismatic geometries and these are mainly metal d 0 centers like zirconium hexa methyl, niobium hexa methyl, tantalum hexa methyl, molybdenum hexamethyl and d one complex like rhenium hexamethyl. So, this trigonal prismatic is a very unique geometry which is explained by quantum mechanical calculations and even VSERP fails to explain the reason for this. So, with this let me summarize todays lecture the main point that we have been dwelling upon today is that; how coordinatively saturated central metal atom may affect beta elimination and we saw that transition metal which is coordinatively saturated does not undergo beta elimination reactions that easily resulting in suppression of beta elimination pathway and enhancing the stability of transition metal organometallic compound.

And with this we are going to still study in a bit more detail that what happens when all of these strategies that we have been discussing put together in the same example how the stability of these compounds may be enhanced. We are going to discuss all of these and many more in the next lecture and I hope that you would you found this todays lecture very interesting one with that I look forward to being with you in the next lecture.

Thank you.