Transition Metal Organometallic Chemistry: Principles to Applications.
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Week – 03
Lecture – 11
Properties of sigma – alkyl compounds

Welcome to this lecture on transition metal organometallic chemistry from principles to applications. In the last few lectures we have been dwelling on very important topic which is on transition metal sigma alkyl complexes these complexes are of prime importance as they are important intermediates in many catalytic cycles and we were looking at various synthetic strategies required for preparing these complexes.

In the last lecture we looked at 4 different methods that are used in making these complexes they involved oxide devidation metallic acylation reaction as well as sigma pi rearrangement type reactions. These reactions were; however, slightly different from the first 4 reactions that we had discussed which involved metathesis reactions, insertion reactions as well as metallic alkylation reactions.

Now, having covered all of the synthetic methods available for preparation of transition metal sigma alkyl complexes we are going to move over to something very interesting in this part of the lecture.

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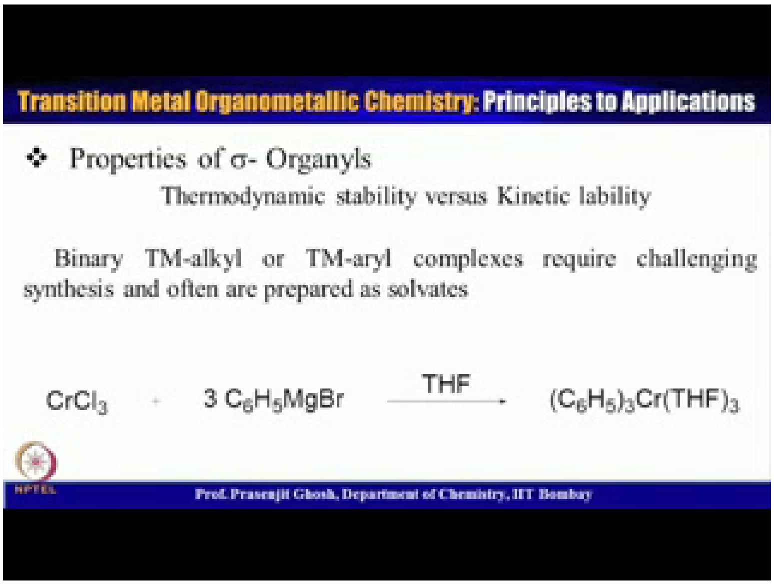

Transition Metal Organometallic Chemistry: Principles to Applications

❖ Properties of σ- Organyls

Thermodynamic stability versus Kinetic lability

Binary TM-alkyl or TM-aryl complexes require challenging synthesis and often are prepared as solvates

$$CrCl_3 + 3\ C_6H_5MgBr \xrightarrow{THF} (C_6H_5)_3Cr(THF)_3$$

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We are going to talk about properties of transition metal sigma alkyl complexes.

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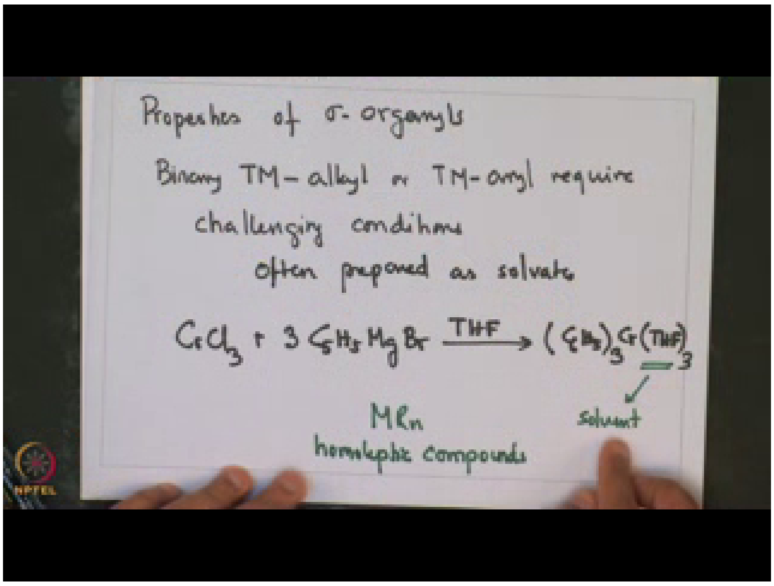

Properties of σ- organyls

Binary TM – alkyl or TM - aryl require
challenging conditions
often prepared as solvate

$$CrCl_3 + 3\,C_6H_5MgBr \xrightarrow{THF} (C_6H_5)_3Cr(\underline{THF})_3$$

solvent

MR_n
homoleptic compounds

Now these complexes initially were thought that they are thermodynamically unstable as they were very difficult to prepare, but later on it was found that they are indeed thermodynamically stable, but their unstability arises from their excessive kinetic reactivity. Hence, preparation of binary transition metal alkyl or aryl requires a challenging conditions or transition metal aryl.

So, having discussed all the synthesis method in this we are going to talk about properties of transition metal sigma organic complexes, initially the transition metal sigma organic complexes were thought to be thermodynamically unstable, but later it was found that these complexes are indeed thermodynamically stable, but their reactivity arises from their kinetic liability and that it is a challenge for preparing them in this regard binary transition metal alkyls and binary transition metal aryls pose a great challenge preoperatively.

However, they are often prepared as solvents. For example, ClCl3 reacts with grignard reagent in presence of THF as solvent giving; this triphenyl chromium twist THF where THF is a solvent molecule.

Now these reaction without the solvent only compounds of this type MRn are homoleptic are called homoleptic metal alkyls. These are indeed very difficult to prepare and as a result these cannot be prepared in many most of the cases and in many of them metal sigma alkyl or sigma allyl complexes are prepared along with the solvents as has been shown over here.

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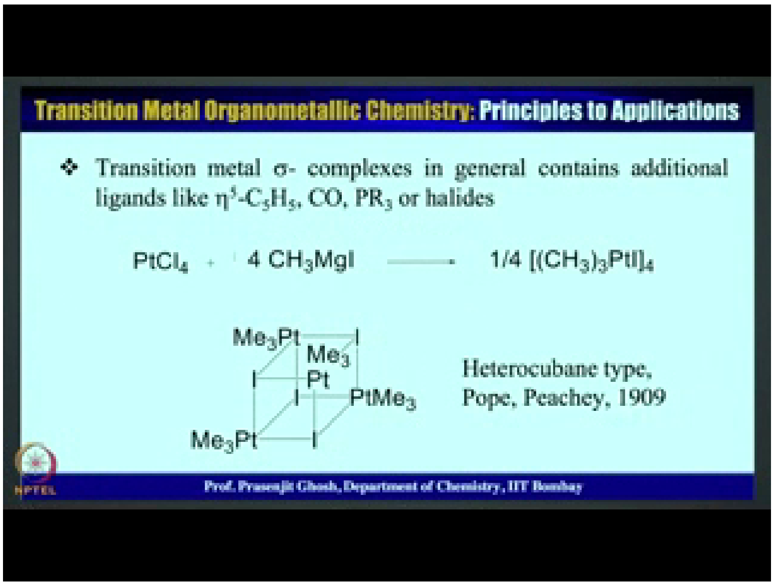

Transition Metal Organometallic Chemistry: Principles to Applications

- Transition metal σ- complexes in general contains additional ligands like η^5-C_5H_5, CO, PR_3 or halides

$$PtCl_4 + 4\ CH_3MgI \longrightarrow 1/4\ [(CH_3)_3PtI]_4$$

Heterocubane type,
Pope, Peachey, 1909

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Apart from the solvent molecule as was seen in the last slide transition metal compounds sigma allyl complexes can also contain other ligands.

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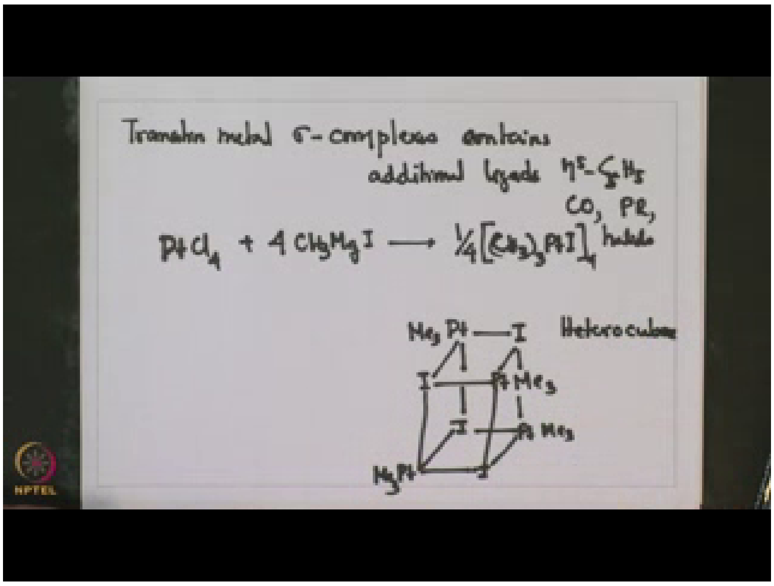

Transitn metal σ-complexes contains additional ligands η^5-C_5H_5 CO, PR_3 halides

$$PtCl_4 + 4\ CH_3MgI \longrightarrow 1/4[(CH_3)_3PtI]_4$$

Heterocubane

Contains additional ligands. Like n5 c5 h5 carbon monoxide PR3 halides for example, Pt Cl 4 with this grignard reagent methyl magnesium iodide gives this 4 Pt Ch 3 whole 3 Pt I tetra more compound the structure of this is of a cuban type of this, this is called hetero cuban type cluster.

Now, what is coming out that home electric sigma allyl complexes of transition metal are indeed a challenge to make and most of the attempt in making them results in transition metal sigma allyl complexes containing either the solvent molecule or other additional ligands like as in the case observed for platinum compound discussed here.

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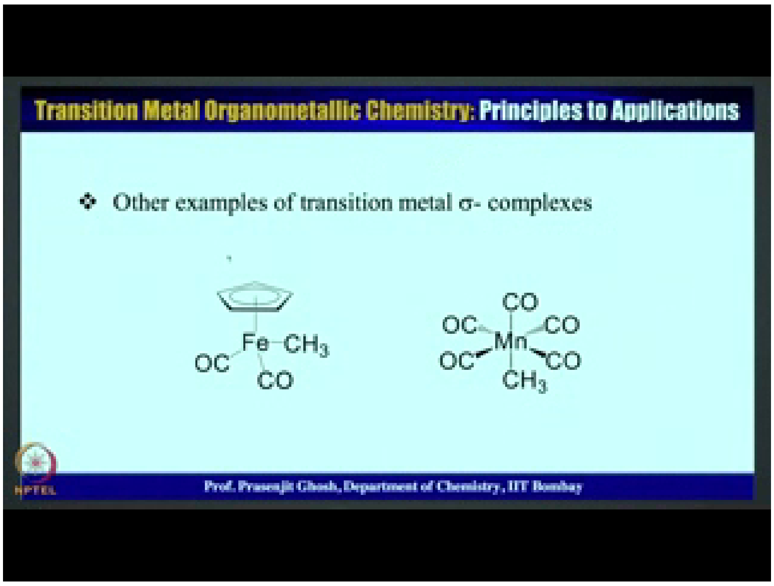

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- Other examples of transition metal σ- complexes

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The other such examples contain other ligands apart from the metal alkyl moiety as shown here.

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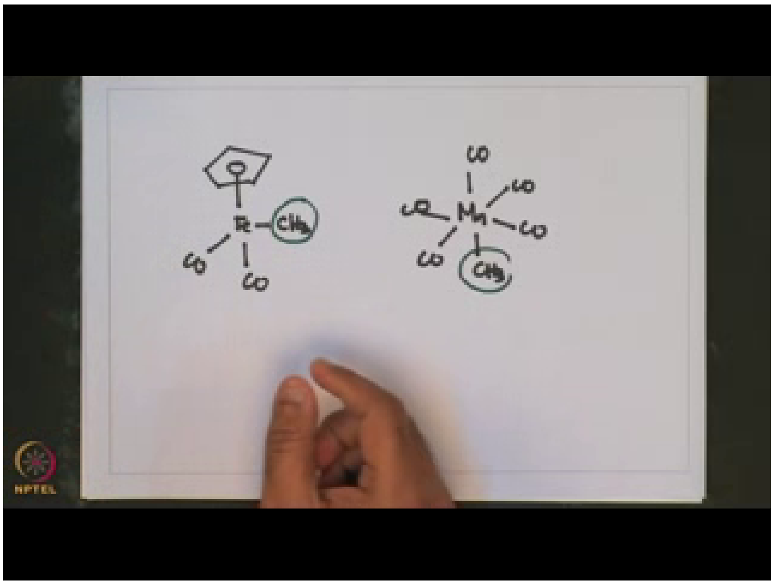

For the following manganese compounds. So, apart from this sigma alkyl ligand there are other types of ligands that stabilize the overall metal complex. Now here is a brief comparison between the transition metal as well as the main group metal carbon

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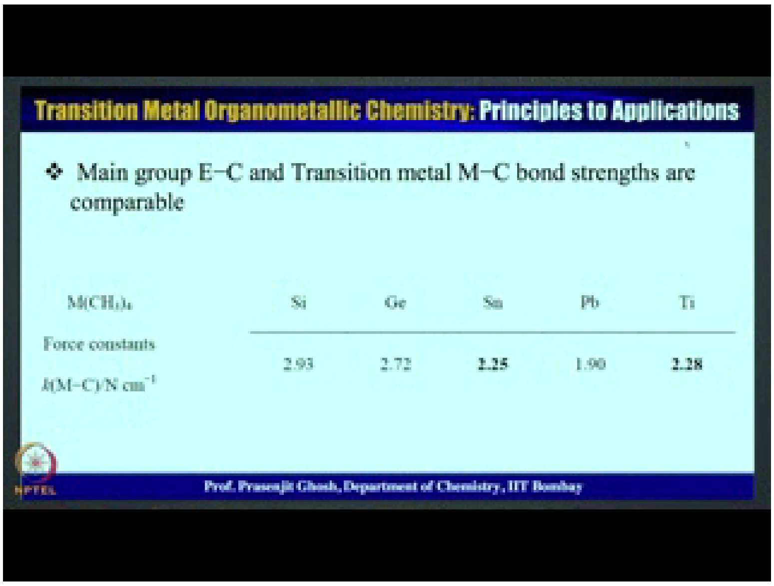

Transition Metal Organometallic Chemistry: Principles to Applications

- Main group E−C and Transition metal M−C bond strengths are comparable

$M(CH_3)_4$	Si	Ge	Sn	Pb	Ti
Force constants $k(M-C)/N\ cm^{-1}$	2.93	2.72	**2.25**	1.90	**2.28**

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Bonds strengths for example, for the main group.

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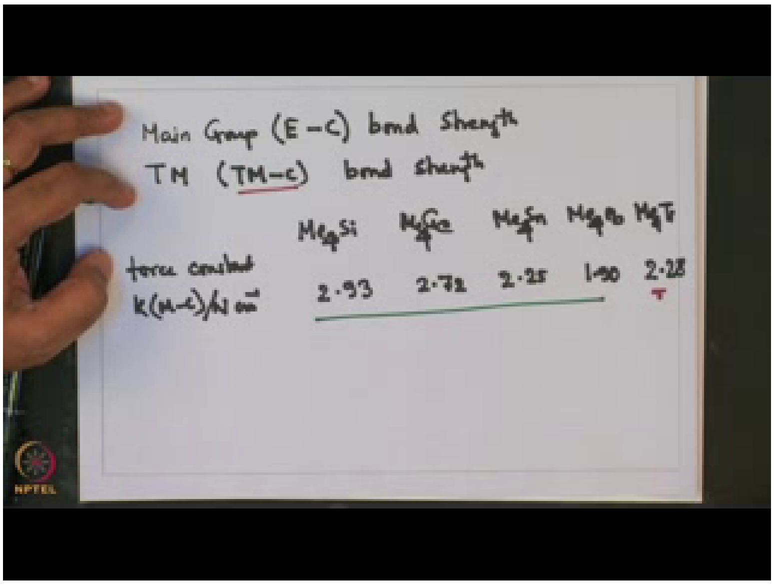

Main Group (E – C) bond Strength

TM (TM – C) bond strength

	Me_4Si	Me_4Ge	Me_4Sn	Me_4Pb	Me_4Ti
force constant $k(M-C)/N\,cm^{-1}$	2.93	2.72	2.25	1.90	2.28 T

E C metal carbon bond strengths are sort of comparable to that of the transition metal bond strength. This can be elucidated by the metal carbon force constant of metal carbon bond for the following main group and transition metal compounds.

For example, for tetra methyl silicon the force constant is 2.93 which is a main group element tetra methyl germanium it is 2.72 tetra methyl teen, 2.25 tetra methyl late 1.90 and tetra methyl titanium it is 2.28. So, these are all main group elements whereas, these is a transient metal and the 4th constant TM C bond of the transition metal is similar or lies within the range observed for the force constants of main group carbon elements. So, that sort of implies that the main group carbon as well astransition metal carbon bond strengths are of comparable capacity. For example, let us take a look at some bond.

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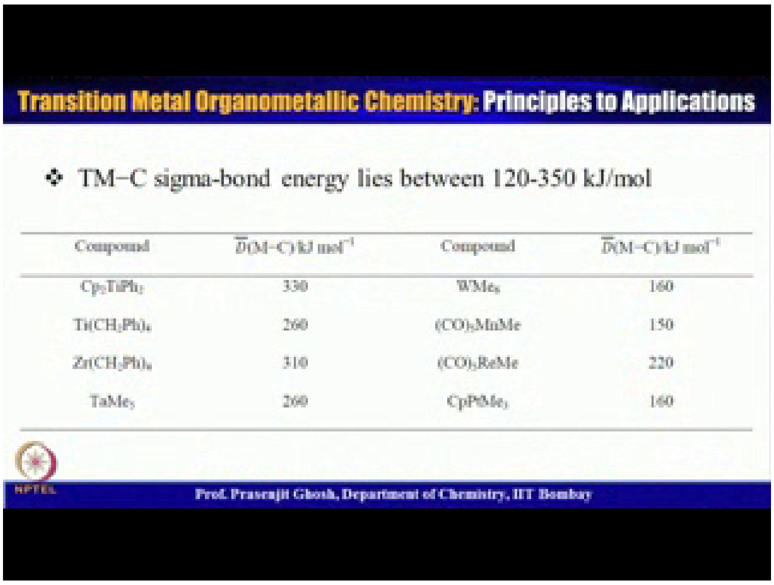

Transition Metal Organometallic Chemistry: Principles to Applications

- TM−C sigma-bond energy lies between 120-350 kJ/mol

Compound	$\bar{D}$(M−C)/kJ mol^{-1}	Compound	$\bar{D}$(M−C)/kJ mol^{-1}
Cp_2TiPh_2	330	WMe_6	160
$Ti(CH_2Ph)_4$	260	$(CO)_5MnMe$	150
$Zr(CH_2Ph)_4$	310	$(CO)_5ReMe$	220
$TaMe_5$	260	$CpPtMe_3$	160

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Energies of transition metal compound sigma alkyl compounds to get a value of their bond strength. So, bond energies are usually designated by

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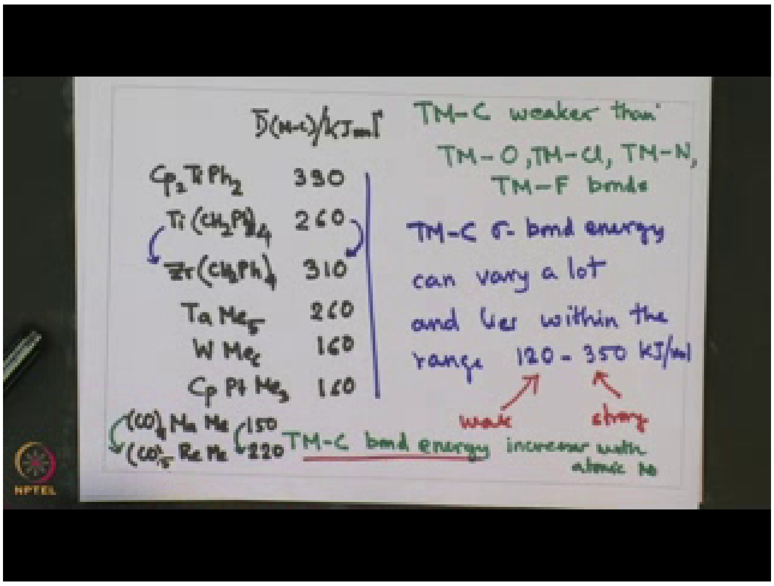

$\bar{D}$(M−C)/kJ mol^{-1}

Cp_2TiPh_2	330
$Ti(CH_2Ph)_4$	260
$Zr(CH_2Ph)_4$	310
$TaMe_5$	260
WMe_6	160
$CpPtMe_3$	160
$(CO)_5MnMe$	150
$(CO)_5ReMe$	220

TM−C weaker than TM−O, TM−Cl, TM−N, TM−F bonds

TM−C σ- bond energy can vary a lot and lies within the range 120 - 350 kJ/mol

weak

strong

TM−C bond energy increases with atomic no

DC in kilo joule per mole Cp 2 titanium diphenyl the mc bond is 330 kilojoules per mole, whereas, for titanium tetra benzyl it is 260 kilojoules per mole, zirconium tetra benzyl is 310 kilojoules per mole tantalum pentamethyl 260 kilo kilojoules per mole, tungsten hexamethyl 160 kilojoules per mole and let us say Cp platinum methyl about 160 kilojoules per mole. So, what it implies is that transition metal carbon sigma bond energy can vary a lot and lie within the range 120 which is a weak bond to about 350 kilojoules per mole. So, the bond strength can be very weak to something which can be very strong as a result transition metal sigma allyl complexes can show varied reactivity.

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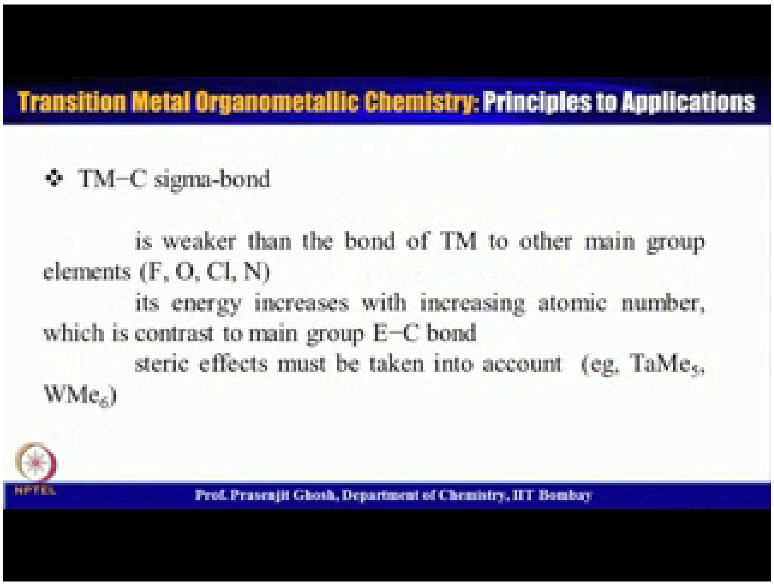

Transition Metal Organometallic Chemistry: Principles to Applications

❖ TM−C sigma-bond

is weaker than the bond of TM to other main group elements (F, O, Cl, N)

its energy increases with increasing atomic number, which is contrast to main group E−C bond

steric effects must be taken into account (eg, $TaMe_5$, WMe_6)

NPTEL

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Another conclusion that can be drawn from this discussion is transition metal carbon bonds are weaker then transition metal heteroatom grounds, transition metal heteroatom main group bonds like transitional metal oxygen, transition metal chlorine, transition metal nitrogen, transition metal fluorine bonds also the transition metal bond energy increases with atomic number increases. So, as one goes down the group the energy increases. For example, if one were to look between titanium and zirconium, zirconium being lower in the group has higher bond energy.

Similarly, one can look at another example for example, between pentane carbonyl manganese methyl which has 150 kilojoules per mole and corresponding the heavier analog pentane carbonyl rhenium methyl analog has 220. Here 2 on going down the group the bond energy increases and this is what has been discussed over here. So, the transition metal carbon bonds are weaker than transition metal other main group elements like the hetero atom halide chlorides and also for transition metal carbon bonds increases with atomic number as one goes down the group.

Now, a lot of debate has gone into understanding the reason for instability of transition metal complexes. As mentioned in the beginning of this lecture that the initial belief of transition metal complexes being thermodynamically unstable was later on proved to be wrong.

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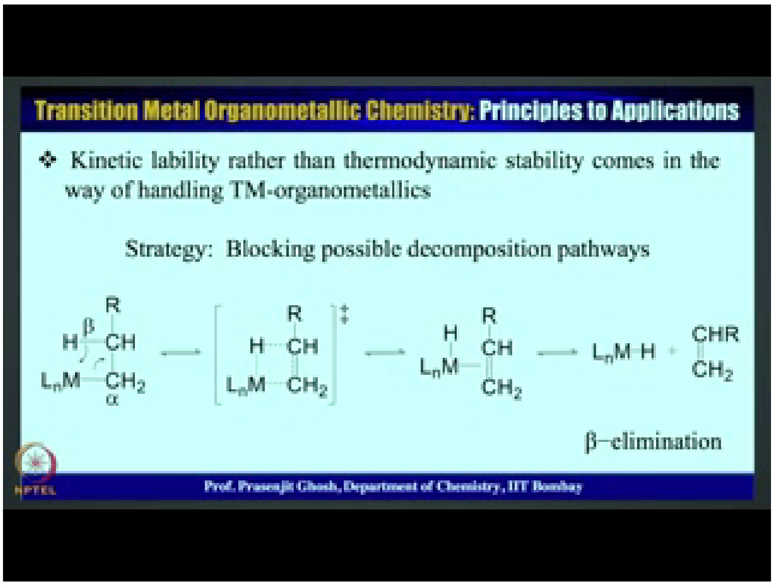

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- Kinetic lability rather than thermodynamic stability comes in the way of handling TM-organometallics

Strategy: Blocking possible decomposition pathways

β–elimination

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And what emerged out was the fact that the extreme unstability of transition metal sigma alkyl complexes arises from their kinetic liability rather than their thermodynamics stability, and that brings us to an important juncture of the need for understanding them. So, the unstability of transition metal compounds can be explained by their kinetic liability.

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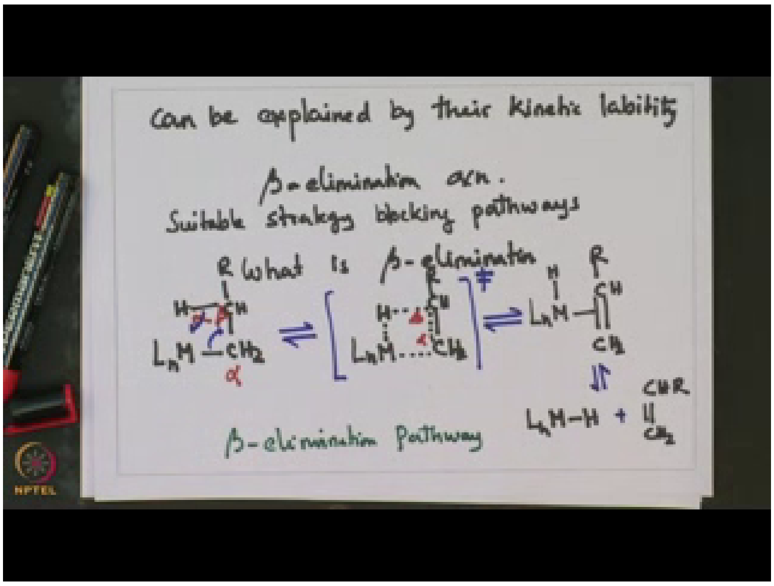

Can be explained by their kinetic lability

β-elimination rxn.

Suitable strategy blocking pathways

What is β-elimination

β-elimination Pathway

And that brings us to this discussion on a very important reaction that results in decomposition of many transition metal complexes. And what I am talking about is this famous beta elimination reaction beta elimination reactions are reactions which occur for transition metal complexes leading to their decomposition hence a suitable strategy involves understanding the beta elimination reaction and blocking pathways that suppress blocking pathways that allow beta elimination reactions. Now let us take a look at what is this beta elimination reaction. Let us say for a transition metal alkyl group that has beta hydrogen. So, this is the alpha hydrogen and this is the beta hydrogen as it is located on the beta carbon chain.

Now, the sigma bond of the hydrogen beta hydrogen or hydrogen located at the beta carbon gets attracted or interacts with m t metal d orbital as is shown here and proceeds to decomposition via a cyclic transition state as being shown here, whereby this beta hydrogen is seen interacting with the metal orbital via a 4 member transition state leading to the formation of a metal hydride, and olyphin bound to the metal and gradually this olyphin bound to the metal eliminates from the metal center leading to a metal hydride complex and free olyphin. And this reaction is called beta elimination.

Beta elimination pathway is present in many transition metal alpha complexes that contains beta hydrogen and which leads to decomposition of many transient metal alkyl complexes giving metal hydride and olyphin and hence results in instability of transition metal sigma alkyl complexes. In this lecture we have looked into various properties of transition metal sigma alkyl complexes we have looked into the bond strengths of transition metal sigma alkyl complexes and they how they vary across the group as well as how they compare along side their main group counter parts. We have also looked into the various decomposition reactions that are responsible for conferring instability to transition metal sigma alkyl complexes and that many of which are of kinetic origin.

Now, with this we are going to go over to some very interesting aspect in the next lecture which would deal about how to suppress beta elimination reactions. Remember if beta elimination reaction be a nuisance as it promotes decomposition of many transition metal complexes well if somebody finds a way to inhibit this beta elimination pathway then that would lead to more stable transition metal sigma alkyl complexes with their that being in mind the next lecture focuses on various strategies aimed at stabilizing transition metal sigma alkyl complexes through separation of beta elimination pathways. We are going to take that up in my next lecture and till then I hope you have enjoyed the current discussion in the present lecture and wish to see you in the next lecture.

Thank you.