Transition Metal Organometallic Chemistry : Principles to Applications

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Week – 12
Lecture – 60
Summary

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Application. This is the incidentally this is the 60th lecture and the last lecture of this course and I have decided to summarize the topic that has been thought in all the 59 lectures, so as to help us get a perspective of what has been done throughout this course.

In the beginning I have this pleasant duty of acknowledging and thanking the people who had been behind this effort particularly in helping me been preparing for this course. To begin with let me thank mister A. P. Prakasham he is the teaching assistant for these online course and he would be the one who would be a taking exam conducting and grading the creases editing all the videos.

I would also like to thank the whole of NPTEL video team at IIT Bombay, who had been extremely friendly and coach me through these video graphing of this course. And in particular I would like to mention Mister Tushar, Mister Amin, Mister Vijay, and Mister Ravi who had always been smiling in helping me learn how to present in front of the video taking this course.

So, with that let me just start summarizing the topics that we have covered throughout this course. To begin with we started on with the history of organometallic compounds what we had seen that this field of organometallic chemistry is relatively new about 200 years or slightly over that old. And the importance of organometallic chemistry can be gauged by the fact that even though it is relatively a new field many a Nobel prizes have been awarded to recognize the importance of the field so much so that in the last 100 years or so about 9 Nobel prizes have been awarded for various discoveries in the area of organometallic chemistry and these sort of justifies the importance of these topic.

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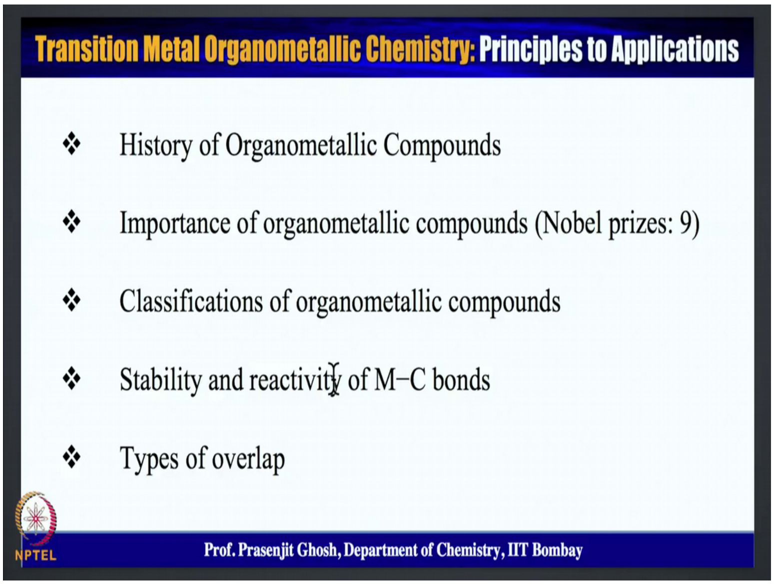

Transition Metal Organometallic Chemistry: Principles to Applications

- History of Organometallic Compounds
- Importance of organometallic compounds (Nobel prizes: 9)
- Classifications of organometallic compounds
- Stability and reactivity of M−C bonds
- Types of overlap

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Now in the earlier classes I have gone into the classification of organometallic compounds. Particularly looking at the stability and reactivity of metal carbon bonds these sort of started with type of overlap they make.

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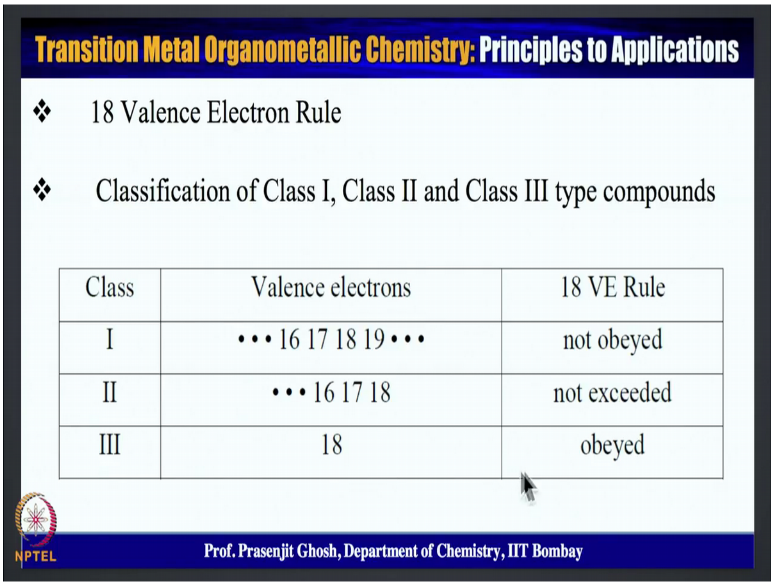

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- 18 Valence Electron Rule
- Classification of Class I, Class II and Class III type compounds

Class	Valence electrons	18 VE Rule
I	• • • 16 17 18 19 • • •	not obeyed
II	• • • 16 17 18	not exceeded
III	18	obeyed

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One of the a basis for classification of organometallic compounds starts with this 18 valence electron rule. And based on these three classes or three types of organometallic compounds can be made which is class 1, class 2, class 3, and they are classified as class 1 are the ones which can have a valence electron more or less than 18 from maybe can have 16 to 19 and these are called class one types which does not obey 18 valence electron rules.

The class 2 types are the ones that can have electrons, but should not exceed 18 valence electron, and class 3 are the ones which actually obey the valence electron rules. So, what we saw that there is so much of space for types of compound to exist beyond 18 electron rule that we are all familiar with.

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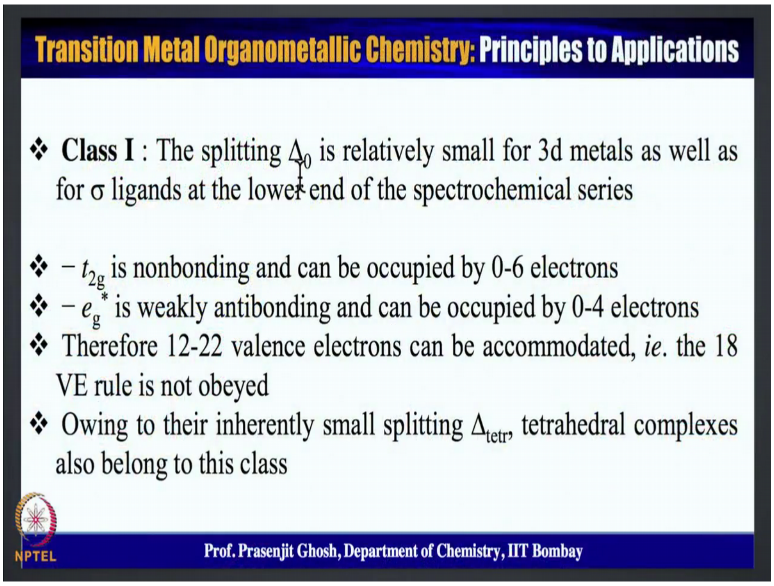

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- **Class I** : The splitting Δ_0 is relatively small for 3d metals as well as for σ ligands at the lower end of the spectrochemical series

- $-$ t_{2g} is nonbonding and can be occupied by 0-6 electrons
- $-$ e_g^* is weakly antibonding and can be occupied by 0-4 electrons
- Therefore 12-22 valence electrons can be accommodated, *ie.* the 18 VE rule is not obeyed
- Owing to their inherently small splitting Δ_{tetr}, tetrahedral complexes also belong to this class

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Now we are also seen that the reason for by fabrication of these are revision for division of these classes organometallic compounds is particularly because of the delta o splitting. And these class one are usually shown by 3d transition metal for whom the delta o splitting is relatively small. And as a result the t 2 g is nonbonding and e g star is weakly anti bonding.

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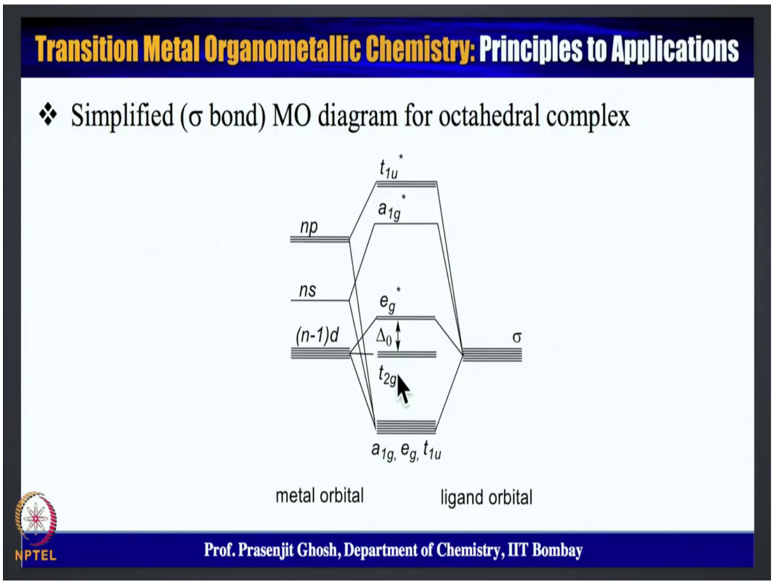

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- Simplified (σ bond) MO diagram for octahedral complex

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So e g star is weakly anti bonding maybe populated t 2 g is nonbonding and as a result can have anywhere between 12 to 22 electrons to populate with. So, they do not obey relating valence electron rule.

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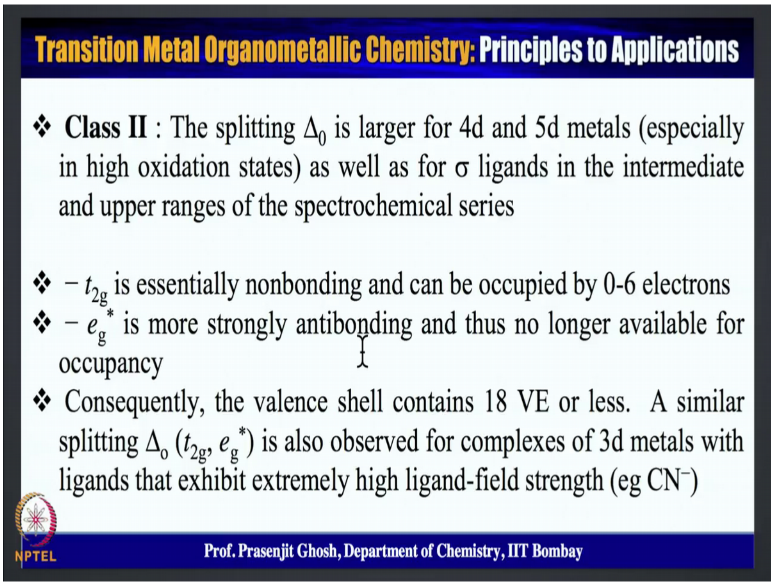

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- **Class II** : The splitting Δ_0 is larger for 4d and 5d metals (especially in high oxidation states) as well as for σ ligands in the intermediate and upper ranges of the spectrochemical series
- – t_{2g} is essentially nonbonding and can be occupied by 0-6 electrons
- – e_g^* is more strongly antibonding and thus no longer available for occupancy
- Consequently, the valence shell contains 18 VE or less. A similar splitting Δ_o (t_{2g}, e_g^*) is also observed for complexes of 3d metals with ligands that exhibit extremely high ligand-field strength (eg CN^-)

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For then next comes the class 2; class 2 are for larger metals mainly 4d and 5d transition metals a for which the t two g is essentially nonbonding and can have 0 to 6 electron. Whereas, e g star is strongly antibonding and that is not populated and this can be seen over here e g star is now very high in energy as a result this mostly remains unpopulated, and as a consequence up to 18 electrons can fit in these type two type complexes.

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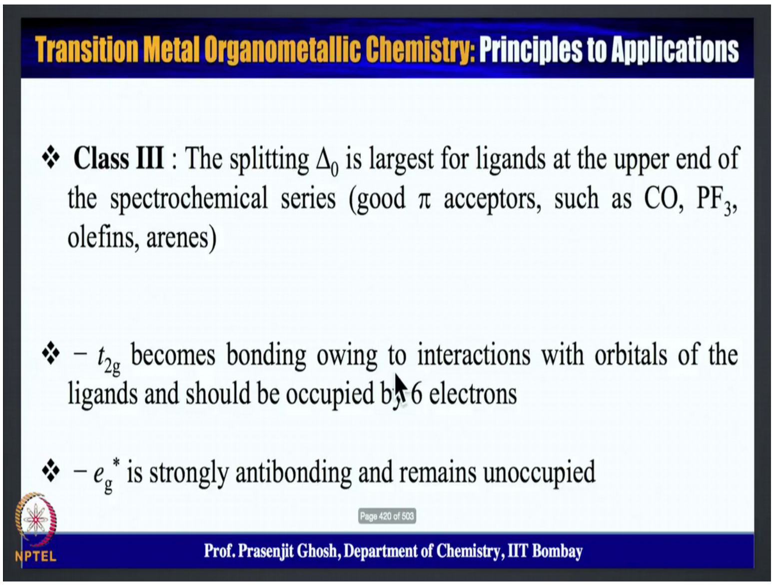

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- **Class III** : The splitting Δ_0 is largest for ligands at the upper end of the spectrochemical series (good π acceptors, such as CO, PF_3, olefins, arenes)
- $- t_{2g}$ becomes bonding owing to interactions with orbitals of the ligands and should be occupied by 6 electrons
- $- e_g^*$ is strongly antibonding and remains unoccupied

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Then comes class 3 types where the splitting is even the largest and this is good for pi acceptor ligands such as carbon monoxide PF 3, and here t 2 g becomes bonding owing to interaction with the ligand orbital's. And they are occupied as a result they are always occupied and e g star is strongly anti bonding and remains unoccupied.

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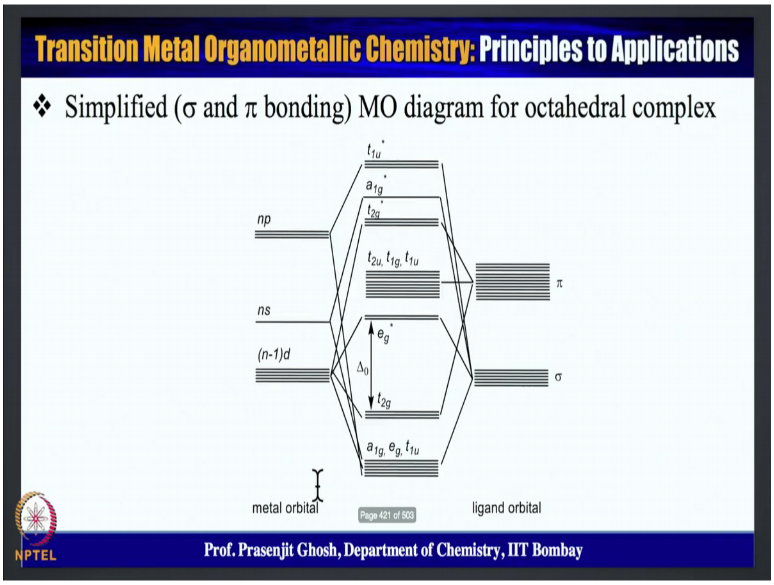

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- Simplified (σ and π bonding) MO diagram for octahedral complex

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So, because of these pi electrons of the ligand interacting with the pi electrons of the metal orbital these t 2 g becomes strongly bonding and that is why an e g star becomes strongly anti bonding. And as a result they do not exceed 8 electron, and hence they obey the interact rule; now with these classification of three types of organometallic complexes based on their molecular orbital correlation diagram.

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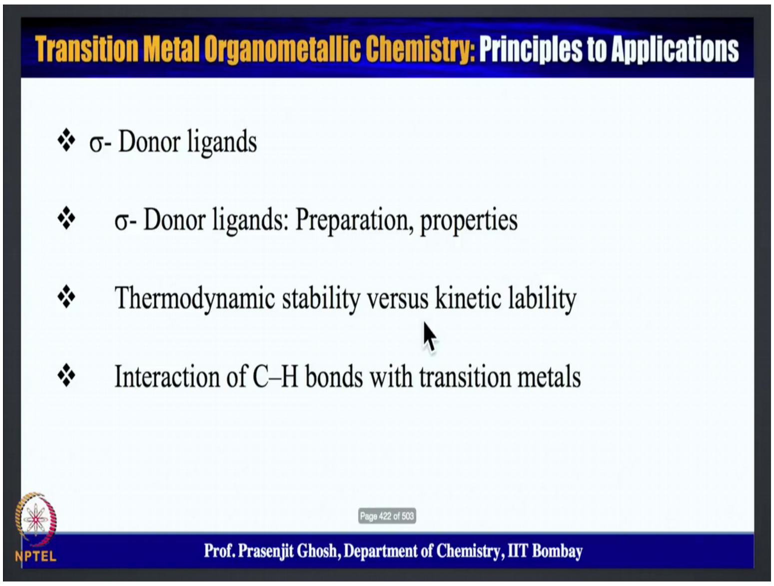

Transition Metal Organometallic Chemistry: Principles to Applications

- σ- Donor ligands
- σ- Donor ligands: Preparation, properties
- Thermodynamic stability versus kinetic lability
- Interaction of C–H bonds with transition metals

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One then understands how these organometallic compounds react. Now that was on the basis of metal orbital now classifications can also be made based on the ligands, and the ligands can be the ones which are of different type they can be sigma donor or pi acceptor and to begin with we looked at sigma donor proper ligands; particularly their properties, thermal dynamic stability, kinetic abilities, interaction of C H.

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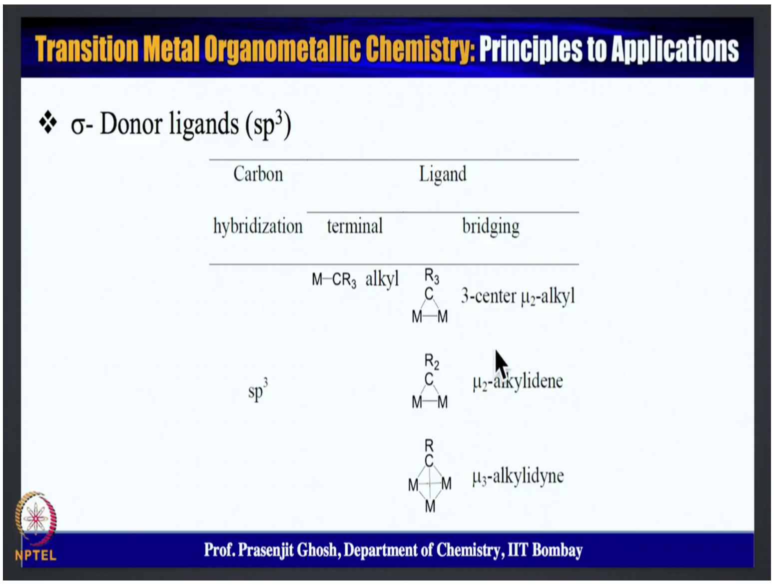

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❖ σ- Donor ligands (sp^3)

Carbon hybridization	Ligand terminal		bridging	
sp^3	$M{-}CR_3$	alkyl		3-center μ_2-alkyl
				μ_2-alkylidene
				μ_3-alkylidyne

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And to start with we looked at various s p 3 hybridized like metal alkyls, the type of bridging they kind of show.

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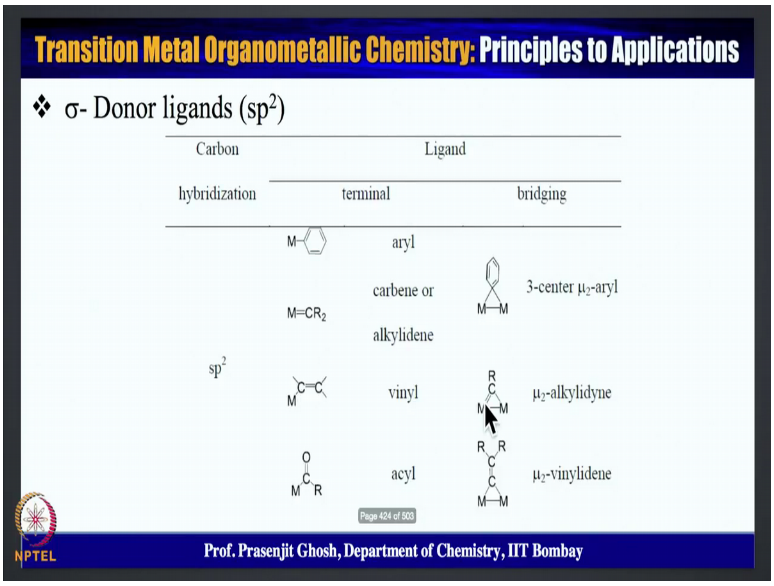

Transition Metal Organometallic Chemistry: Principles to Applications

❖ σ- Donor ligands (sp^2)

Carbon hybridization	Ligand terminal		bridging	
sp^2		aryl		3-center μ_2-aryl
	$M{=}CR_2$	carbene or alkylidene		
		vinyl		μ_2-alkylidyne
		acyl		μ_2-vinylidene

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We looked at s p 2 type sigma donor ligands.

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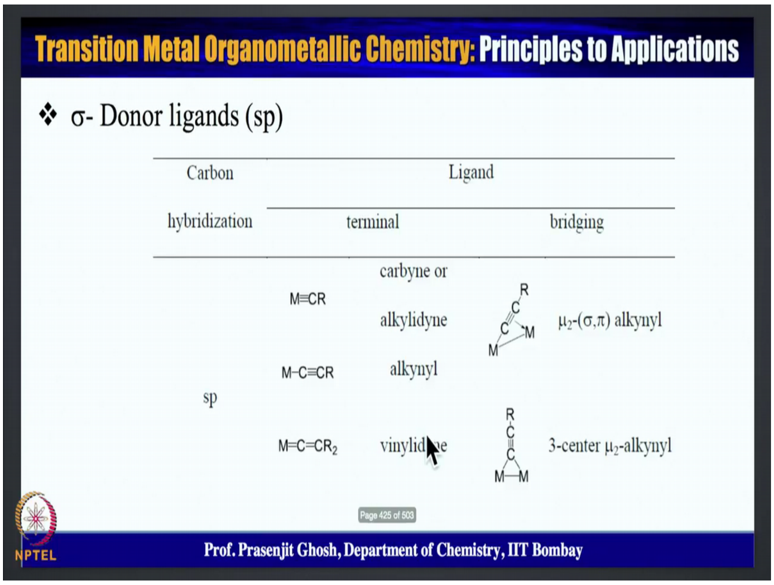

- σ- Donor ligands (sp)

Carbon hybridization	Ligand terminal		Ligand bridging	
sp	$M{\equiv}CR$	carbyne or alkylidyne		μ_2-(σ,π) alkynyl
	$M{-}C{\equiv}CR$	alkynyl		
	$M{=}C{=}CR_2$	vinylidene		3-center μ_2-alkynyl

The aryls, vinyl, acyl and then finally, 2 s p type your carbyne and alkylidyne alkynyl vinylidene so on and so forth. And type was the bridging they undergo.

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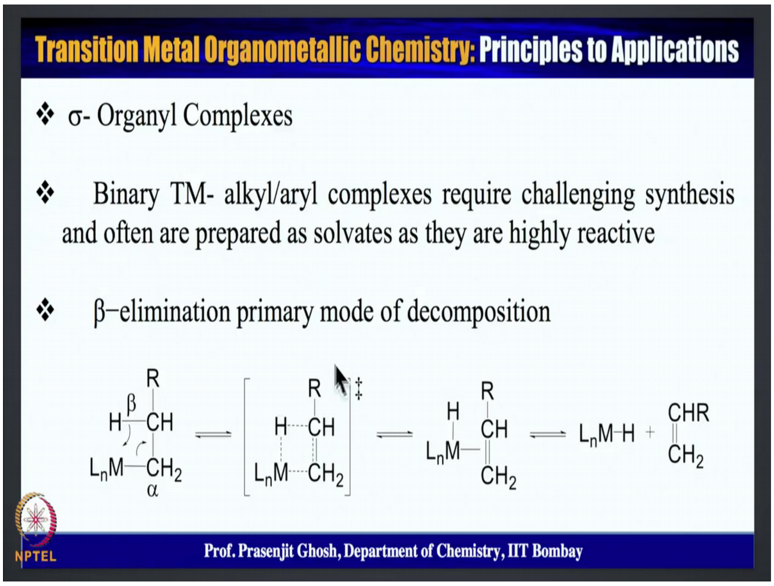

- σ- Organyl Complexes
- Binary TM- alkyl/aryl complexes require challenging synthesis and often are prepared as solvates as they are highly reactive
- β−elimination primary mode of decomposition

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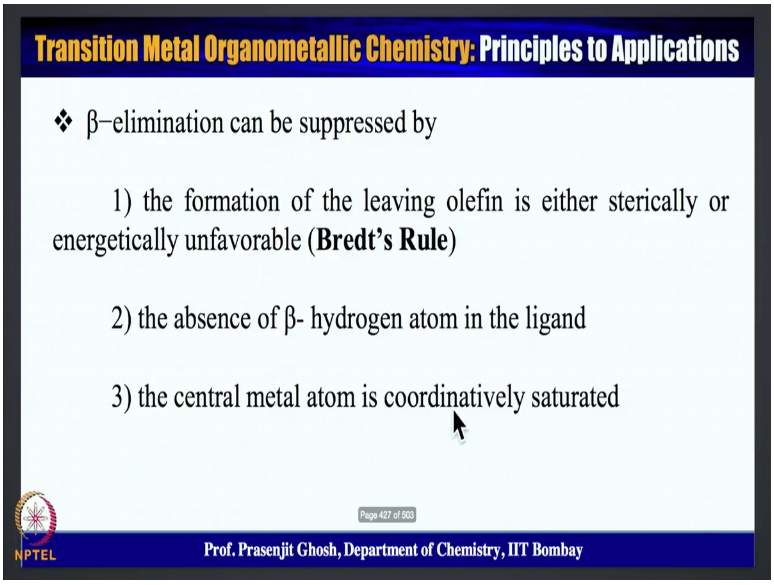

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❖ β−elimination can be suppressed by

1) the formation of the leaving olefin is either sterically or energetically unfavorable (**Bredt's Rule**)

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

3) the central metal atom is coordinatively saturated

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Now, for sigma transition metal organ complexes one phenomenon which is very common is this phenomenon of beta elimination. Now beta elimination is a primary mode of decomposition which sort of leads to the composition of these complexes.

And then we also looked at a discussion as to how to suppress the beta elimination. And if so one can really achieve a very stable organometallic compounds. And for that we have looked in to various strategies in place. For example, formation of olefin that will have either sterically or energetically unfavourable which is Bredt's rule, then absence of beta hydrogen or the central metal atom is co-ordinatively saturated.

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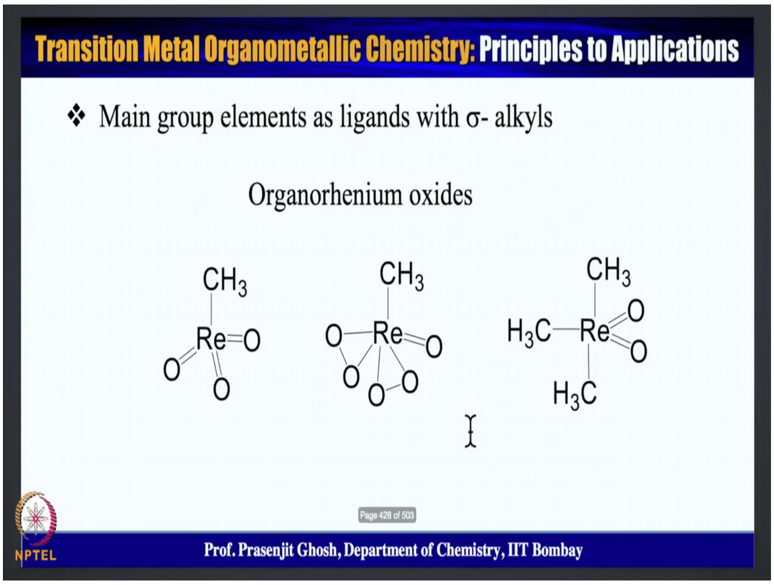

Transition Metal Organometallic Chemistry: Principles to Applications

- Main group elements as ligands with σ- alkyls

Organorhenium oxides

If all of these are put in place then one can well stabilized transition metal complexes we had seen that with examples.

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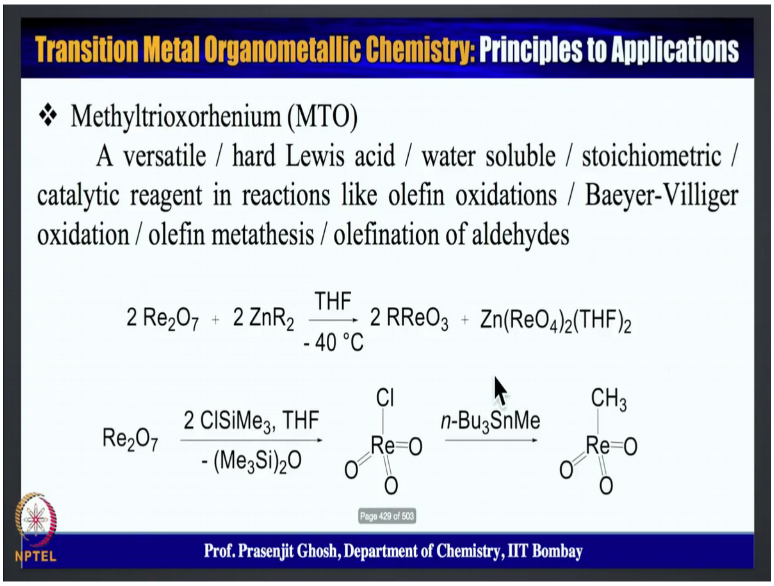

Transition Metal Organometallic Chemistry: Principles to Applications

- 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

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

And then we looked into a main group sigma alkyls, particularly the organorhenium oxides of the type shown over here. These are important versatile, hard lewis acid, water soluble, stoichiometric, catalytic reagents and they are used in various useful reactions like olefin oxidation, Baeyer-Villager oxidation, olefin metathesis, olefination of aldehydes so on and so forth. Some of the examples we have also discussed.

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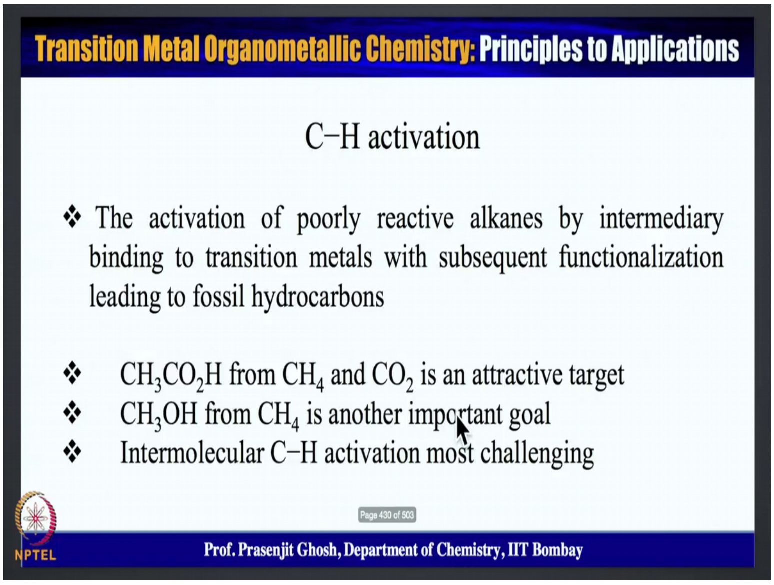

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C–H activation

- 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 moving on from rhenium organorhenium oxide complexes we went to an interesting topic which is very challenging which is and of contemporary interest is this C H activation, the C H activation of poorly reactive alkanes by intermediary binding to transition metal can lead to subsequent functionalization and leading to utilization of fossil fuels.

So, there are some holy grail transformations for example, macitric acid from methane, and carbon dioxide methanol from methane are important goal and we have also discussed about inter and intra molecular C H activations of which the inter molecular C H activation is even more challenging.

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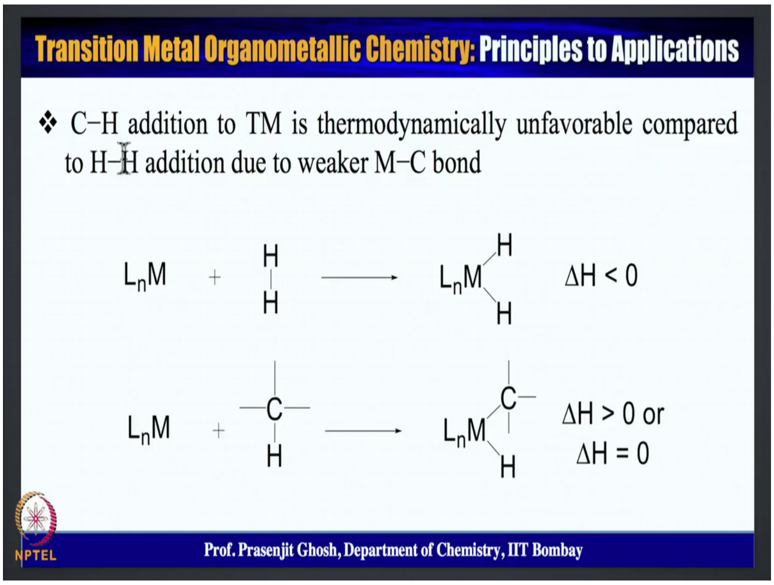

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- ❖ C−H addition to TM is thermodynamically unfavorable compared to H−H addition due to weaker M−C bond

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We have also looked at the thermodynamic criteria for C H activation to transition metal which is unfavorable compared to hydrogen; hydrogen addition to transition metal. Because metal hydro carbon bonds are weaker than metal hydrogen bonds which has a negative enthalpy of formation whereas, metal carbon has positive or almost thermo neutral with enthalpy being 0.

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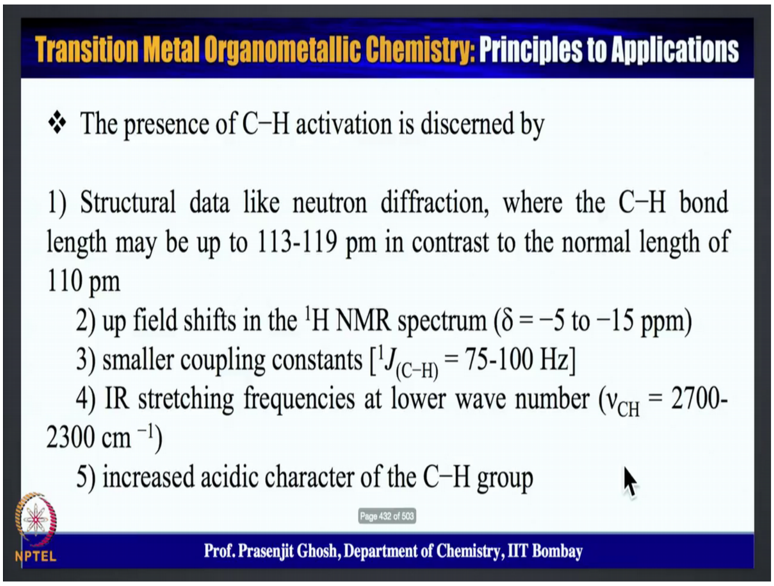

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- ❖ The presence of C−H activation is discerned by

1) Structural data like neutron diffraction, where the C−H bond length may be up to 113-119 pm in contrast to the normal length of 110 pm

2) up field shifts in the ^{1}H NMR spectrum ($\delta = -5$ to -15 ppm)

3) smaller coupling constants [$^{1}J_{(C-H)} = 75\text{-}100$ Hz]

4) IR stretching frequencies at lower wave number (ν_{CH} = 2700-2300 cm^{-1})

5) increased acidic character of the C−H group

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Now, the presence of C H activation is characterized by a structural data as well as NMR data based on the carbon chemical shifts one can sort of discern the extent of C H activation, infrared values gives useful, tool for looking at C H activations and then the increased nature of the acetic C H group. So, proton and the carbon are important criteria for understanding the presence of C H activation.

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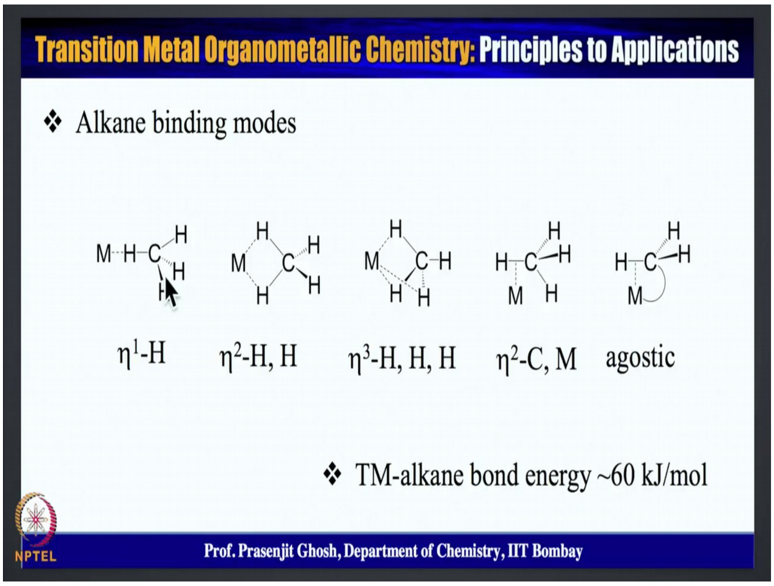

Transition Metal Organometallic Chemistry: Principles to Applications

- Alkane binding modes

η^1-H η^2-H, H η^3-H, H, H η^2-C, M agostic

- TM-alkane bond energy ~60 kJ/mol

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We have looked then we have looked into several binding modes of alkanes, and what is important to note here is that alkene can bind in a varied fashion which can be either on hydrogen, it can be either 2 hydrogen, hydrogen of the type shown here, it can be either 3 3 hydrogens are either 2 carbon hydrogen. And then the acoustic transition metal alkyl bond energy is around 60 kilojoules per mole and this is just the plane sigma interaction.

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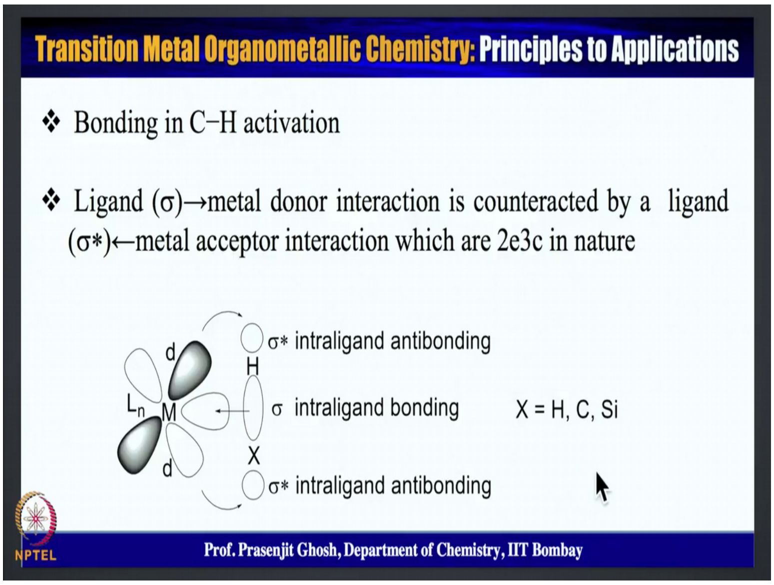

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- ❖ Bonding in C−H activation
- ❖ Ligand (σ)→metal donor interaction is counteracted by a ligand (σ*)←metal acceptor interaction which are 2e3c in nature

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So, this is considerably a weaker interaction, we have looked into the binding mode of transition metal alkane with respect to being two interaction one is the sigma interaction donating on empty metal d orbital. And the other one is the metal field metal orbital donating to the sigma star which is more of 2 electron, 3 centre in nature. So, this is a non classical interaction and so we have one sigma and another pi back donation and this is similar for various C H C H kind of activation where X can be hydrogen carbon and silicon.

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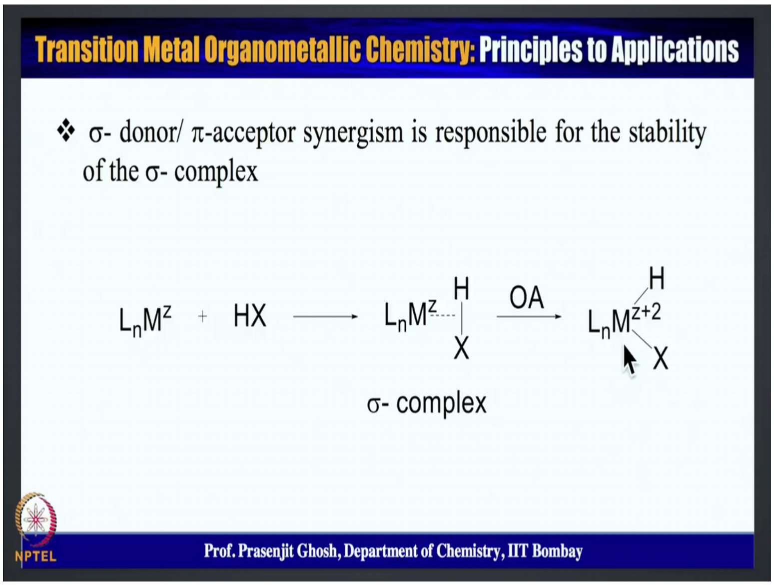

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- ❖ σ- donor/ π-acceptor synergism is responsible for the stability of the σ- complex

$$L_nM^z + HX \longrightarrow L_nM^z\cdots\begin{matrix}H\\|\\X\end{matrix} \xrightarrow{OA} L_nM^{z+2}\begin{matrix}H\\X\end{matrix}$$

σ- complex

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There is also a sigma donor pi acceptor synergism responsible for the stability of the sigma complex. And this sigma complex is followed by oxidative addition where the coordination number as well as the oxidation state of the metal increases by 2 we have seen that.

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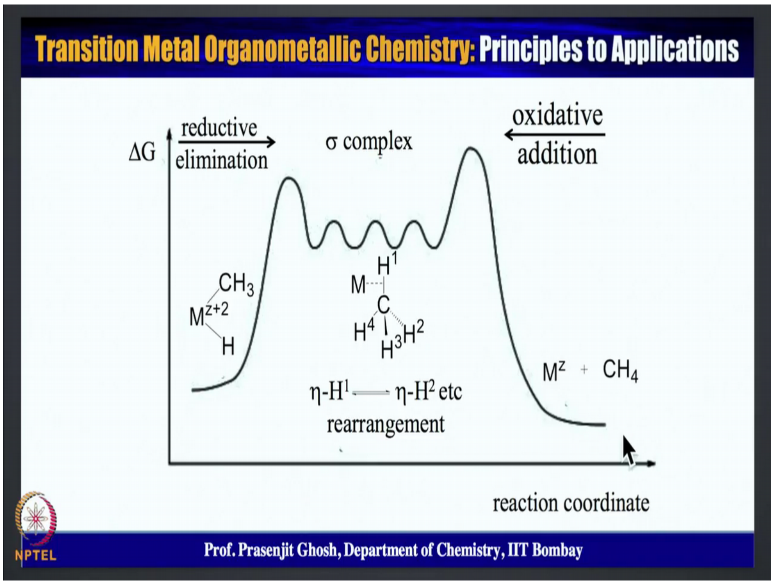

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And finally, with respect to C H activation what we had seen that there are several rearrangements that occur depending on which hydrogen is bound to the metal in a sigma fashion. And in one way if it goes further then oxidatively at this C H 3 hydrogen to give the metal hydrides and if it proceeds the other side then it is a reductive elimination leading to metal and C H 4. So, what we see that sigma complex is sort of sits in the middle between oxidative addition product as well as reactive elimination product in the reaction coordinates and that is an interesting observation.

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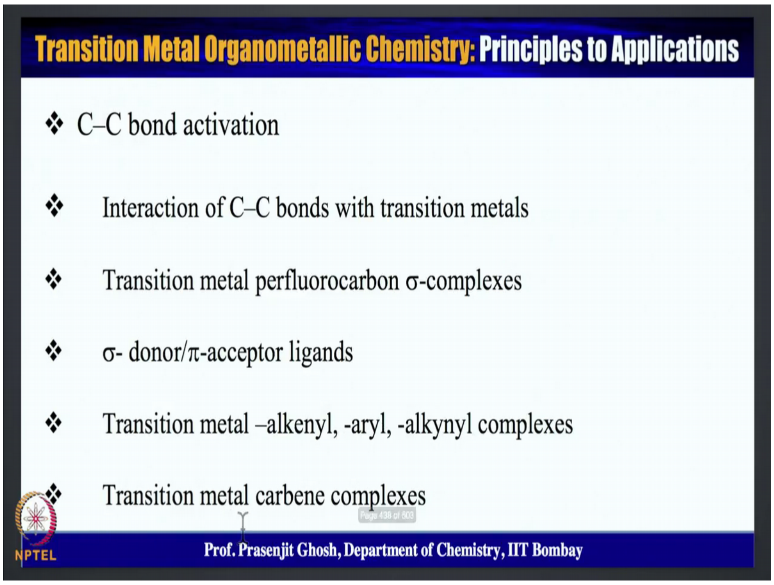

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- ❖ C–C bond activation
- ❖ Interaction of C–C bonds with transition metals
- ❖ Transition metal perfluorocarbon σ-complexes
- ❖ σ- donor/π-acceptor ligands
- ❖ Transition metal –alkenyl, -aryl, -alkynyl complexes
- ❖ Transition metal carbene complexes

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Then after looking at C H bond activation we have looked at C C bond is activations we have seen how the C C bonds interacts with transition metals in perfluoro sigma complexes as well as we have taken a look at sigma donor pi acceptor ligands. And in that perspective looked into alkenyl aryl alkynyl and transition metal carbene complexes.

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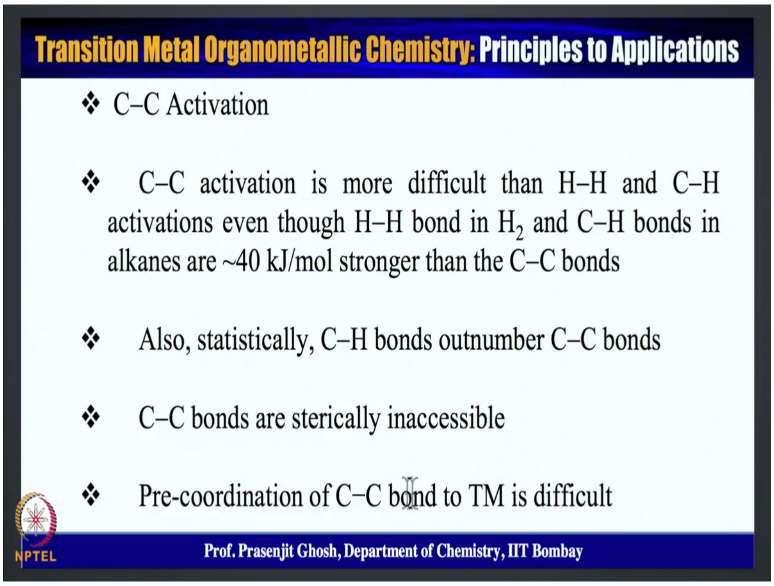

Transition Metal Organometallic Chemistry: Principles to Applications

- ❖ C–C Activation
- ❖ C–C activation is more difficult than H–H and C–H activations even though H–H bond in H_2 and C–H bonds in alkanes are ~40 kJ/mol stronger than the C–C bonds
- ❖ Also, statistically, C–H bonds outnumber C–C bonds
- ❖ C–C bonds are sterically inaccessible
- ❖ Pre-coordination of C–C bond to TM is difficult

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Now, C C activation is more difficult than hydrogen hydrogen and C H activations even though the hydrogen hydrogen bond in H 2 and C H bonds in alkanes are more stronger than C C bonds. But statistically the reason for these challenging activation is C H bonds outnumber C C bonds C C bonds are sterically inaccessible and and furthermore the pre coordination of C C bonds of transition metal becomes difficult.

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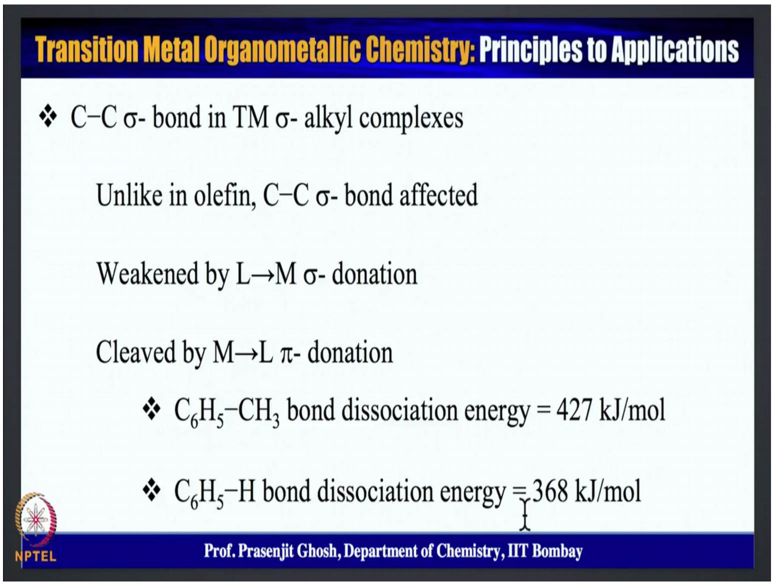

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- C–C σ- bond in TM σ- alkyl complexes

  Unlike in olefin, C–C σ- bond affected

  Weakened by L→M σ- donation

  Cleaved by M→L π- donation

  - C_6H_5–CH_3 bond dissociation energy = 427 kJ/mol
  - C_6H_5–H bond dissociation energy = 368 kJ/mol

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Now, C C bonds in transition metal alkane single bond remains unaffected, and made ligand to metal sigma donation as well weakens the C C bond as well as metal to ligand pi donation cleaves the C C bond. For example, in toluene the bond dissociation energy is 4 twenty 7 kilo joules per mole of cc bond which is more stronger than benzene H C H bond dissociation energy of 368 kilo joules per mole in benzene.

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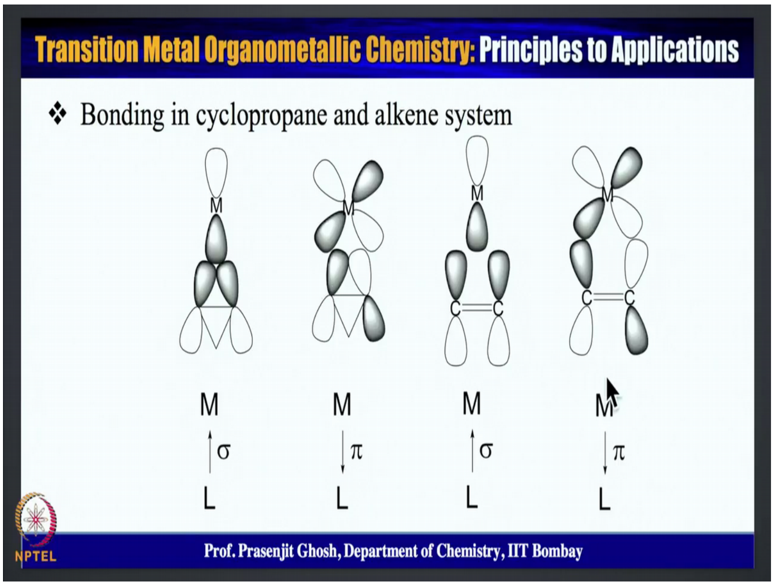

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- Bonding in cyclopropane and alkene system

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Now, in order to understand this bond activation we have looked at the cyclopropane and alkene kind of systems for various C H activations as well as C C activations. And we see that there is a similarity in terms of ligand to metal sigma donation and metal to ligand pi donation these synergism operates not only in the middle of cyclopropane kind of intermediate, but also in alkynes kind of intermediate.

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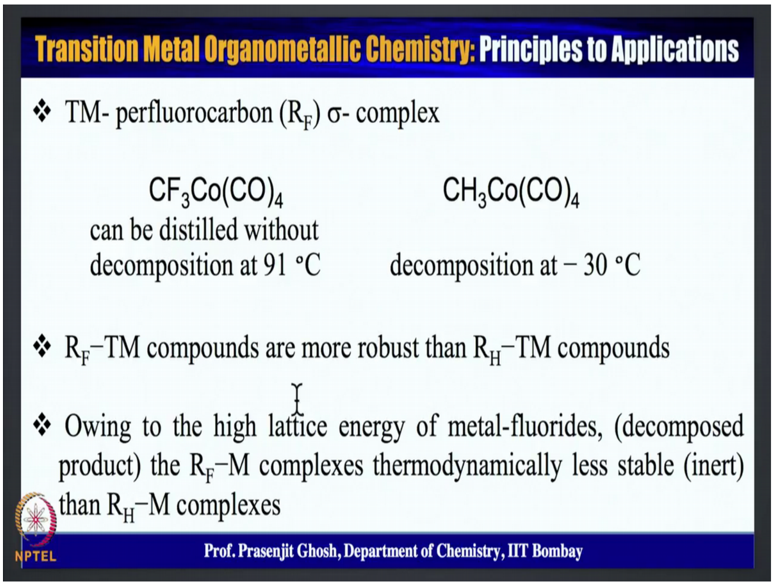

Transition Metal Organometallic Chemistry: Principles to Applications

- TM- perfluorocarbon (R_F) σ- complex

$CF_3Co(CO)_4$ can be distilled without decomposition at 91 °C

$CH_3Co(CO)_4$ decomposition at − 30 °C

- R_F–TM compounds are more robust than R_H–TM compounds
- Owing to the high lattice energy of metal-fluorides, (decomposed product) the R_F–M complexes thermodynamically less stable (inert) than R_H–M complexes

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Then moving on from C C bond activation we have discussed a transition metal perflourocarbon complexes for example, C F 3 C o C O 4, and C H 3 C o C O 4 and what we saw that the perflouro hydrocarbon complexes are more robust.

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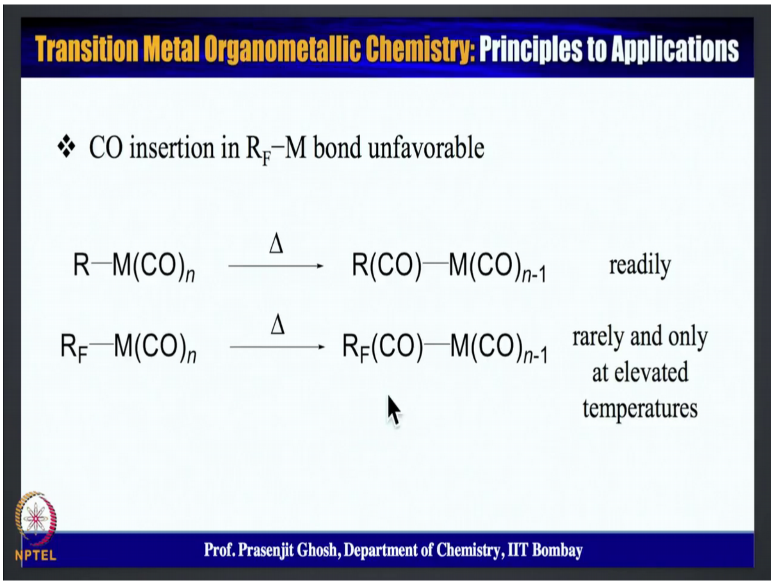

Transition Metal Organometallic Chemistry: Principles to Applications

- CO insertion in R_F–M bond unfavorable

$R{-}M(CO)_n \xrightarrow{\Delta} R(CO){-}M(CO)_{n-1}$ readily

$R_F{-}M(CO)_n \xrightarrow{\Delta} R_F(CO){-}M(CO)_{n-1}$ rarely and only at elevated temperatures

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So, we have looked into various kinds of reactions which are favourable or are unique to this perflouro metal bonds. For example, C O insertion in metal carbonyl occurs readily, but in the perflourated organo carbon and it does not take place.

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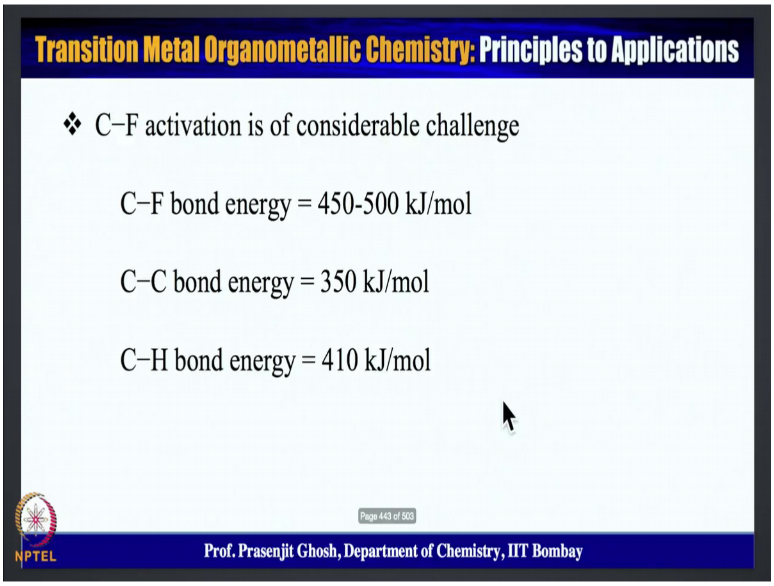

Transition Metal Organometallic Chemistry: Principles to Applications

- C–F activation is of considerable challenge

C–F bond energy = 450-500 kJ/mol

C–C bond energy = 350 kJ/mol

C–H bond energy = 410 kJ/mol

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C F in the tune of C C and C H bond activation T C F bond acceleration probably is by far; the most difficult to achieve with c f bond energy between 400 to 500 kilojoules per mole.

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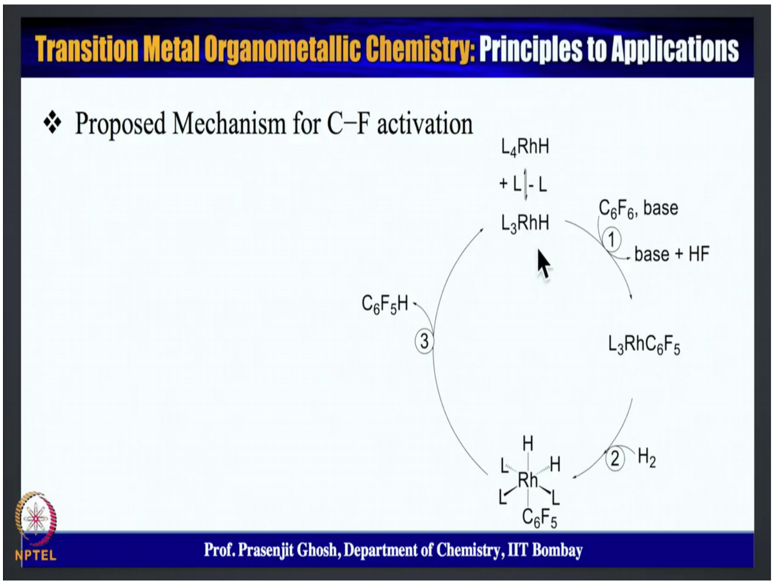

Transition Metal Organometallic Chemistry: Principles to Applications

- Proposed Mechanism for C−F activation

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And we have looked into various catalytic cycles there are in place that they undergo C H bond activation. Now despite the fact that the C H bond activation is difficult there are several examples we have discussed which are shows C H bond activation, moving on from that we have moved into transition metal alkynyl, and aryl complexes.

And here also we have seen that sigma donor s p 2 center as well as s p ones now transition metal alkynyl aryl, and alkynyl complexes they occupy position between sigma donor alkyl and sigma donor pi acceptor ligand like carbon monoxide, phosphine, RNC etcetera. We have compared the reactivity of transition metal aryl versus transition metal alkyl and then what we concluded that transition metal aryl complexes are slightly more stable than the alkyl complexes and that is because their bond dissociation energy is only 10 percent higher than the methyl ones.

For example, that you have tetra phenyl decomposes above 0 degree whereas, tetrameter decomposes as minus 40 degree. From then we have moved into transition metal alkenyl complexes these are isoelectronic with cyanide carbon monoxide. These acetyls are strongly basic undergo hydrolytic cleavage and what it says that interaction with the metal makes the complex is more stable towards hydrolysis, coordination of these acetyls to metal make them less reactive moving.

Then we moved on to another important aspects which a transition metal carbene complexes that shows that has a metal carbon double bond. In this regard we have covered Fischer carbine, as well as Schrock carbene and then we have looked into Arduengo's carbene where by a free a carbene species was isolated stabilized and structurally characterized. We have looked into various synthetic methods that are available for preparing that is this cabene complexes.

We have looked into type of the spin states each of the carbons signify for example, singlet and the triplet. We have looked into the interaction that occurs in the singlet Fischer kind of carbene between the metal and the ligand as shown by sigma donation and pi back donation and the same type for the triplet Shrock kind of carbene which is a covalent bond between the metal sigma bond between the metal and the carbon orbital as well as a metal pi d pi and the carbene Fischer orbital.

so, with that we have looked into various canonical structure feasible and the characterization of the carbene moiety. After that we have looked into various reactivity of the Fischer and the Shrock type of carbine kind of applications of the carbene particularly with respect to wittig reactions, and the tepees reagent abuse reagent is alternative to wittig wittig reagent; and carry out many a reaction similar to that.

And moving on from carbene we have looked into carbine there spin steps are Fischer type doublet, and the quartet of the Shrock type, and the kind of interaction that goes on in the Fischer type carbine as well as in the Shrock type carbine. Aafter moving from carbine we went to metal carbonyls these are important compound one of the longest known compounds.

We have looked into various kind of binary carbonyls that are present for various metal and these are mainly the late transition metal particularly the structures of these carbonyl complexes can be very interesting where which contain metal metal bond or bridging carbonyl. We have looked into some of the examples as well as the type of bridging that the carbonyl display which can be eta 1, eta 2, and eta 3.

Moving on from there we have looked into the semi bridging which is another mode of the double carbonyl complexes and the kind of examples that stabilize it, lot of unsymmetrical sigma pi bridging metal carbonyls with 4 or C electron donor side. Donors were also discussed and that shows side on coordination to understand these metal carbonyl we have looked into the orbital diagram responsible for the carbon monoxide.

And then looked into the interaction of the carbon monoxide frontier orbital with the metal d orbital's and we had looked at various kind of carbon monoxide to metal sigma carbon monoxide to metal pi and metal to carbon monoxide back pi interactions. We have seen how these carbonyl metal carbonyl stretching frequency can be justified to look into the type of bonding and the type of bonding carbon monoxide display.

We have done a detailed analysis of transition metal carbonyl complexes particularly with respect to the trans effect. How the ligand which is opposite to c o become weaken when the electron density on the metal is pulled away toward by this pi acidic carbon monoxide ligands. We have looked into another class of compounds for carbonyl matallates, these are (Refer Time: 19:19) compounds.

We have looked into a carbonyl metal hydrides these are important intermediates in many catalytic reactions and what we have seen that metal hydrides can function as a hydrating donor, or a proton donor depending on the ligand and the metal they are binding to we have seen how the characterization of the metal hydride moiety is achieved using X ray diffraction as well as neutron diffraction coupling constants by NMR.

With regard to utility of carbonyl metallates we have looked into Collman reagent similar to that of the (Refer Time: 19:53) reagent that we had seen where a large number of organic compounds were formed from these iron carbonyl metallates. We have looked into carbonyl metal halides from the metal hydrides and then into various kind of sigma pi donor, pi acceptor ligands particularly the olefin and alkyne complexes.

The olefin complexes are important particularly in respect to catalysis and we have looked into the type of bonding the display a say the sigma donation and the pi back donation particularly with respect to Dewar Chatt Duncansan model. And that can be rationalized with respect to the infrared C C stretching frequencies observed for these complexes. We have also drawn a analogy in the past discussion between the epoxide and the nikela cyclopropane complexes and how these two sort of match each other. We have looked at how the orbital interaction of the metal orbital with the ligand orbital takes shape in explaining the Dewar Chatt Duncanson model.

Moving on from olefin we have looked at the diolefin complexes like butadiene, and looked at how the ligand orbital interacts with various forms of metal orbital. And then we have looked mainly on the alkyne type complexes particularly with respect to cyclooligomerization, reactions of acetylene metal alkyne display a versatile mode of binding which can be monodentate, bidentate, bidentate, tetradentate.

We have looked into how these can be characterized using X ray as well as I r studies, and then finally, what we have looked at is the various kinds of interactions that we have studies in these thing. So, over all let me just brief you as to what we have done these course started off with this theory underlying the organometallic complexes. We have looked at how what are the compounds? How they were discovered based on their reactivity over of course, of 200 years or so.

And then we saw that how the development of the organometallic chemistry gradually came into being with understanding of the theory a that emerge alongside it. And these all started with (Refer Time: 22:16) oxide followed by zeises salt which was synthesized in 1827. But the theory of fate of the Dewar Chatt Duncansan model came much later in 1950s and then we looked into the reactivity of this transition metal organometallic compounds and what we saw that the reactivity is dependent on two kinds of interaction, mainly a ligand to metal sigma donation and metal to ligand pi back donation and these are, but common for most of the transition metal organometallic complexes.

And depending on their interplay or extent of forward donation, or backward donation the structural parameters of the organometallic moiety bound to the transition metal vary. We have also a looked at the characterization aspects of all these transition metal organometallic compound particularly the characterization of the organic moiety a bound to the transition metal with respect to X ray, neutron diffraction, infrared, and proton, and carbon NMR spectroscopy’s.

And what also we have seen is the application aspects of these now organometallic compounds are important particularly with respect to chemical catalysis, and they form excellent catalysts for various catalytic transformations. Alongside, organometallic reagents can be extremely useful for various transformations and we have seen that with regard to Collman reagent, to be debris reagent. So, not only on the catalytic front where these organometallic compounds are of tremendous importance, but also on the utility from stoichiometric reagent purpose they also play a wonderful role.

Now, another important aspects which to be mentioned with regard to organometallic compound is their leach bonding interaction. Now the bonding chemistry like particularly the interaction of the metal and the ligand is extremely reach diverse versatile and moves on from the domain of classical 2 center, 2 electron bonds to non classical 3 centered, multi centered multi electron bonds, so that is something which is extremely challenging, intellectually, particularly in academics to understand how these multi nuclear and non classical bonds are formed.

What leads to the formation of them what how the ligand interact with the metal with regard to this kind of bonding. So, not only from the utility aspects these organometallic compound particular in the chemical catalysis as well as inorganic synthesis as stoichiometric reagents they are useful. Their bonding is something which is unique to these compounds and they provide a rich area for understanding the interaction of an ligand to the metal. Now in that you take like you know usually there is this concept that ligand always denotes electron and metal accepts, but here we have organometallic compounds which show oh extensive and significant metal to ligand pi back donation, where the ligand accepts and metal the acidic metal gives.

So, actually these sort of apart from this classical 2 center 2 electron bonds we also see a that kind of interactions where metal provides electron to the electron rich ligands. Now we have also looked at impala reactivity that arises because of forward donation, and backward pi pi back donation, so apart from you chemical utility, apart from this interesting bonding aspect.

Another important aspect of organometallic chemistry which comes to the 4 is the fact that these compounds require very ingenious way of synthesizing them. These are extremely difficult and challenging compounds which need to be prepared in the exclusion of air and moisture. And stored in that environment and that requires tremendous amount of skills in manipulating these compounds.

So, from the perspective of organic synthesis or from the perspective of synthesis of these a compounds they are extremely challenging and requires extremely specialized a set of skills which take a long time to develop. So, from the front of synthesis organometallic chemistry poses a host of challenges for their preparations. And the kind of strategies that have been implied to achieve those compounds are indeed very inspirational.

In this regard it is important to note that synthesis of a transition metal carbene complexes carbine complexes are one of the most difficult ones to achieve. Similarly a one can take like the handling of the Grignard. So, lot of reagents Grignard is also lithium alkanes are important reagents that have been developed with organometallic chemistry in the four.

Now apart from these another important aspect of organometallic chemistry which is of note is the reactivity of these compounds these are extremely reactive compounds, but also can be utilized to once benefit and we have seen that aspect upheld in the last discussion of transition metal alkyne complexes. What we had seen that the extremely unstable cyclic alkynes like cyclohexane or benzene or benzenedyne which are difficult to stabilize by themselves can be stabilized when they are coordinate to transition metal metals, and they make the transition metal alkyne complexes.

So, those also mark another important aspects of transition metal chemistry whereby one can one can synthesize compounds which otherwise are difficult to obtain. In that regard I would also like to note the synthesis of that a cyclo butadiene and 2 minus dianion stabilized by lithium. Here also to acetylic moiety where dimerized to form the cyclo butadiene and then lithium was used to reduce it to make the aromatic dianion which was stabilized with lithium to lithium cations as was discussed in the last lecture.

Now overall this has been and this still is an exciting emerging field which a has a long way to go and the field has good amount of challenges that it offers it also provides a solution too many catalytic reactions as has been mentioned that 8 or 9 type of 9 Nobel prizes has been comfort conferred for this particular area. And the reactions which is emerged from these the field of organometallic chemistry are as follows.

For example, the Grignard reagents Grignard reactions, lithium, alkyls, then these hydrogenation reactions, polymerization reactions, oligomerization reactions, (Refer Time: 29:51) metathesis reactions, asymmetric hydrogenation shown epoxidation reactions. So, very many important reactions have emerged out of these compounds that we have a discussed in this last in all throughout these 59 lectures. And we are summarizing in this 60th lecture today.

So, with these I want to say that these course started from principles and moved on to various applications. The course would be useful for undergraduate, as well as masters degree students, as well as the people in industry particularly working in the area of homogeneous catalysis. And organometallic synthesis they would find this course extremely useful particularly in understanding the concepts.

Also the course a will provide a basis for how the catalysts have been developed for particular reactions and how they have been used in industry. So, this would find a tremendous use in both the masters academia, master students, undergraduate students. Even engineering students interested in catalysis would find this course very useful along with the industry people industry researchers who are carrying out research on the area of homogeneous catalysis.

Now, these course has thrown outs the concept has thrown in the concepts has also showed how the concept evolved, it has given stress on each of the classes of compounds particularly from understanding their reactivity. Particularly from understanding their bonding and trying to particularly from exploring the various synthetic reactions, which are made available for preparation of these compounds, and also took a look at the various kind of reactivity each of the compounds classes of compounds specializes in.

So, with that let me once again thank you for listening to this lecture patiently, listening to this all of this lecture. And I hope that the concept of organometallic chemistry a would seem very a interesting to you and the field would be something that you would may want to pursue later on. Then in your career and I would also like to once again thank the TA Mister A.P. Prakasham who has put sincere effort in making this course through. And also all of the IIT Bombay NPTEL video team for helping may carry out this lecture.

With that I thank you for being with me in this course transition metal organometallic chemistry from principles to applications.