# Transition Metal Organometallic Chemistry : Principles to Applications
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## Week - 11
## Lecture - 51
## Transition Metal Olefin Complexes

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. We have been discussing an important class of organometallic compounds particularly the transition metal olefin complexes in the last few lecture and what we had seen is the these transition metal olefin complexes are important in important as catalysts for many a transformations.

For example, hydrogenation polymerization, oligomerization, cyclization reactions and these are really important complexes and it is important to know their reactivity as well as their bonding. With respect to transition metals with that perspective we have also looked at and the various preparative procedures available for transition metal olefin complexes.

And we have looked at two or three methods in the past lecture one involved the reaction of transition metal carbonyl halides with halide abstracts abstracting reagents in presence of olefin that led to the carbon in transition metal olefin complex. We have also looked at the reactions with isomerization of a olefinic backbone as a result of reaction with transition metal carbonyl compounds with the elimination of carbon monoxide. We have also seen the method in whereby under forcing conditions forcing thermal conditions the transition metal carbonyl complexes eliminate C O s and in its wired these olefinic ligands are bound.

So, these dissociation of C O O can be achieved under thermal conditions thermal forcing conditions as well as under photo cat photo catalytic conditions where in presence of light the transition metal carbonyl complexes loses carbon monoxide and the void space is then occupied by the olefin.

So, with that in the background we are going to discuss some more of the examples that are available for synthesizing this transition metal olefin complexes in today's lecture.

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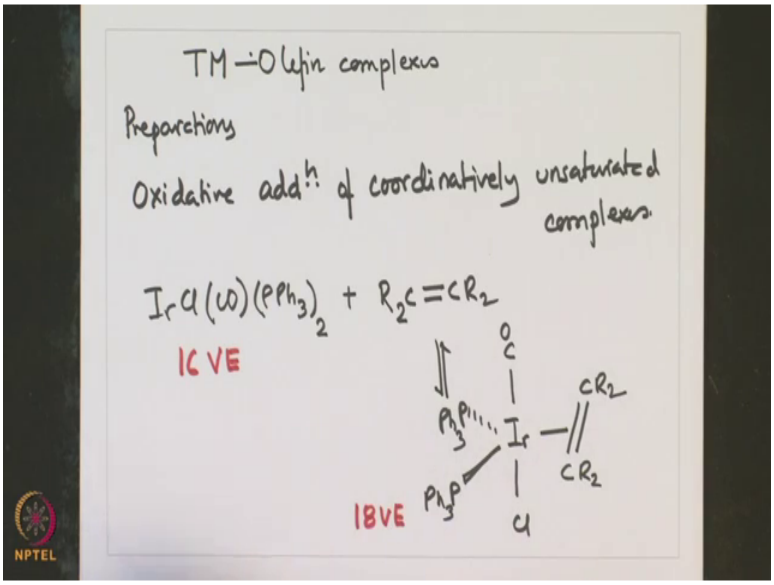

TM – Olefin complexes

Preparations

Oxidative add$^n$ of coordinatively unsaturated complexes

$IrCl(CO)(PPh_3)_2 + R_2C=CR_2$

16 VE

18 VE

So, another important reaction is oxidative addition of coordinatively unsaturated complex complexes. So, for example, iridium chloro carbonyl P P h 3 plus alkane this is a 16 valence electron complex. So, this is both coordinatively as well as electronically unsaturated and these can add against this olefin to give the product C o C l P P h 3 P P h 3.

So, oxidative addition of quadratically unsaturated complex also gives rise to this metal olefin complex and these as a result of this addition of olefin. This has become an eighteen valence electron compound, but one thing to note over here that this olefin is still bound as an olefin and it has not become a metallo cyclopropane and where by a sigma bonds are formed over here.

And as a result the iridium center over here is still in plus 1 oxidation state. So, the complete oxidation oxidative addition has not really truly happened over here to some extent some back bonding from iridium to dolphin exists, but this moiety is predominantly olefinic in nature being bound to iridium. So, this coordinatively unsaturated complex has added on to an olefin to give this coordinatively saturated complex in this example.

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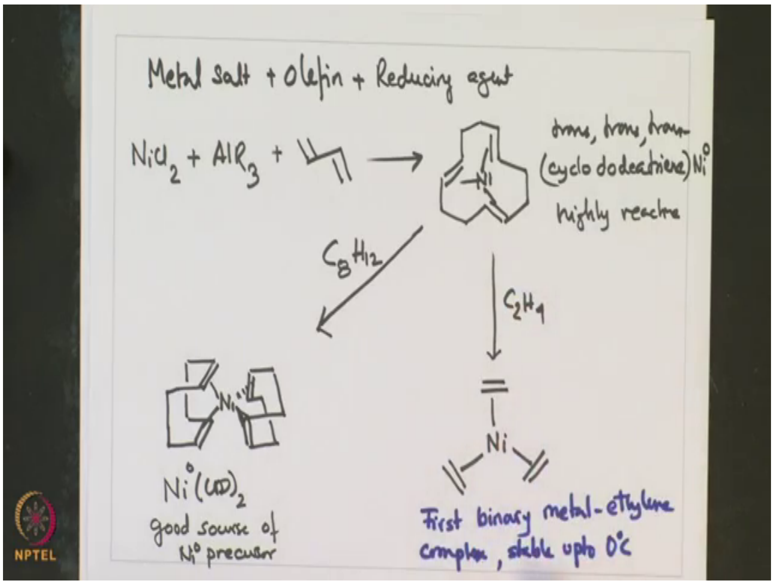

The other common method is the reaction of metal salt plus olefin plus reducing agent. For example, reaction of N I C l 2 plus tri alkyl aluminum in presence of this diene gives this trans, trans, trans cyclo dodeca triene nickel 0 complex which is highly reactive. And the structure of this compound is this where these 3 olefinic bond is coordinated to nickel and this is sort of trimmerization of this butadiene unit to give this cyclododecatriene here and in presence of nickel.

So, this can be seen as a template trimerization process which was this compound was made long back in 1960 by Wilke which when fitted with olefin gives the first binary metal and nickel olefin complex.

So, this is the first binary metal ethylene complex and stable up to 0 degree centigrade I am prepared way back in 1973. Now reaction of this cyclododecatriene with C 8 H 12 COD gives the nickel COD complex and this is nickel COD and it is a good source of nickel zero precursors.

So, what we see is that this metal salt with olefin and some reducing agent over here nickel chloride is the metal salt reducing agent reducing tri alkyl aluminum and olefin butadiene gives this do cyclododecatriene whatever to nickel and then this is a highly reactive complex which can be replaced by COD as well as a ethylene 2 of the code unit and 3 of the ethylene unit to give the very good nickel zero binary olefine different complexes.

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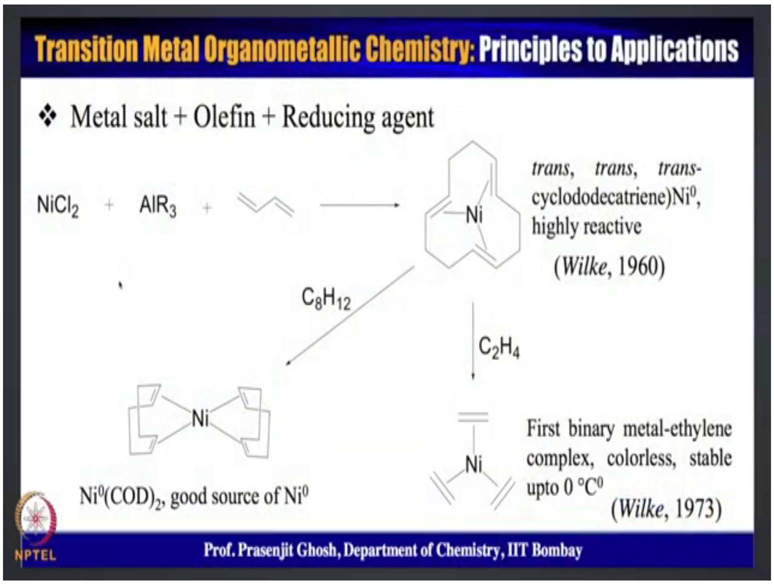

Transition Metal Organometallic Chemistry: Principles to Applications

- Metal salt + Olefin + Reducing agent

$NiCl_2$ + $AlR_3$ +

(*trans*, *trans*, *trans*-cyclododecatriene)$Ni^0$, highly reactive

(*Wilke*, 1960)

$C_8H_{12}$

$C_2H_4$

$Ni^0(COD)_2$, good source of $Ni^0$

First binary metal-ethylene complex, colorless, stable upto 0 °$C^0$

(*Wilke*, 1973)

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So, this is a very effective way of making transition metal olefin complexes where you take a metal salt an olefin under reducing agent.

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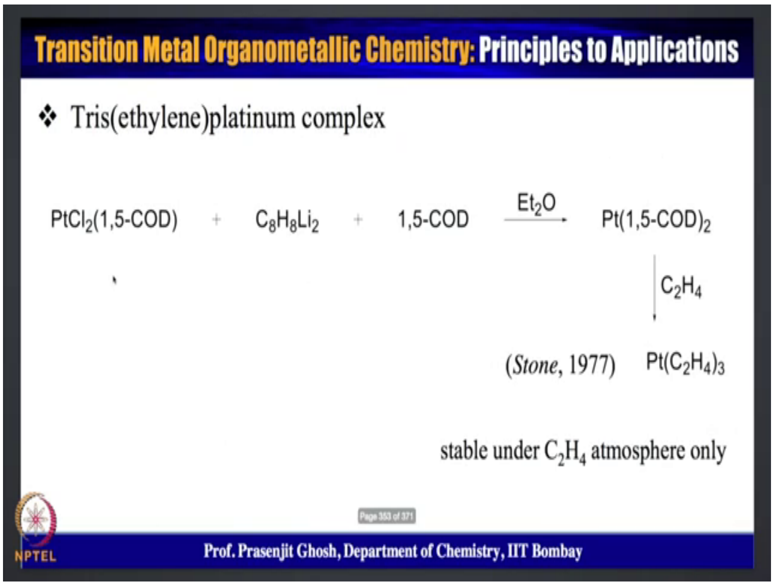

Transition Metal Organometallic Chemistry: Principles to Applications

- Tris(ethylene)platinum complex

$$PtCl_2(1,5\text{-}COD) + C_8H_8Li_2 + 1,5\text{-}COD \xrightarrow{Et_2O} Pt(1,5\text{-}COD)_2 \xrightarrow{C_2H_4} Pt(C_2H_4)_3$$

(*Stone*, 1977)

stable under $C_2H_4$ atmosphere only

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Similarly, the tris ethylene platinum complex was made in which the corresponding the platinum counterpart.

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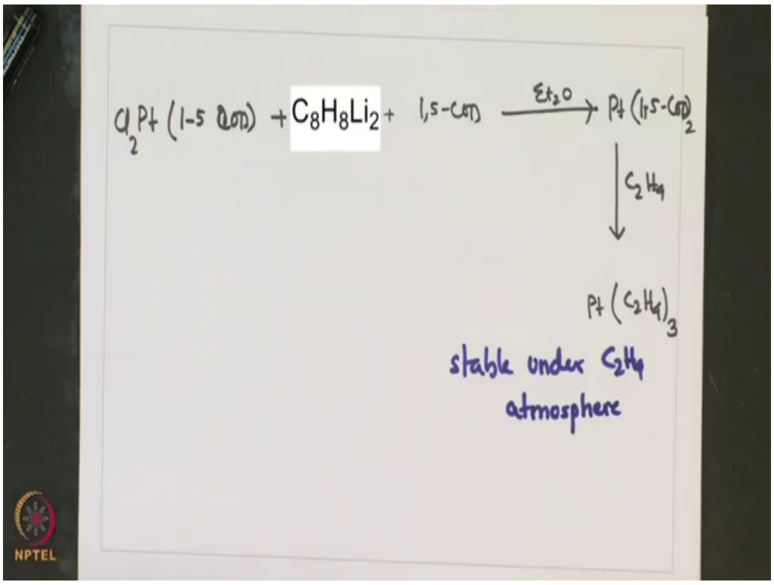

$Cl_2Pt(1\text{-}5\ COD) + C_8H_8Li_2 + 1,5\text{-}COD \xrightarrow{Et_2O} Pt(1,5\text{-}COD)_2$

$\downarrow C_2H_4$

$Pt(C_2H_4)_3$

stable under $C_2H_4$ atmosphere

So, it is taken by platinum dichloride 1 5 COD plus C 8 H 8 L i plus 1 5 COD in ether gives P t 1 5 COD to diamond which when treated with C 2 H 4 gives P t C 2 H 4 whole thrice. This also is a reactive compound and stable under only C 2 H 4 atmosphere.

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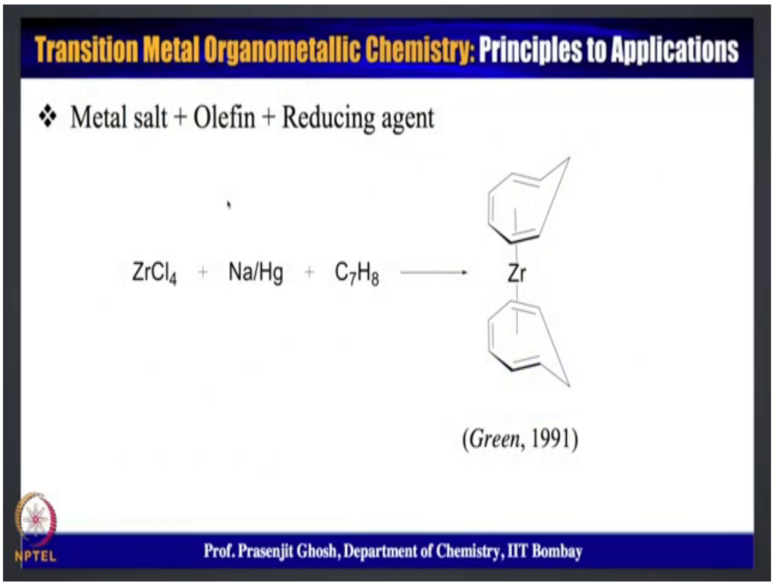

**Transition Metal Organometallic Chemistry: Principles to Applications**

- Metal salt + Olefin + Reducing agent

$ZrCl_4 + Na/Hg + C_7H_8 \longrightarrow$

(*Green*, 1991)

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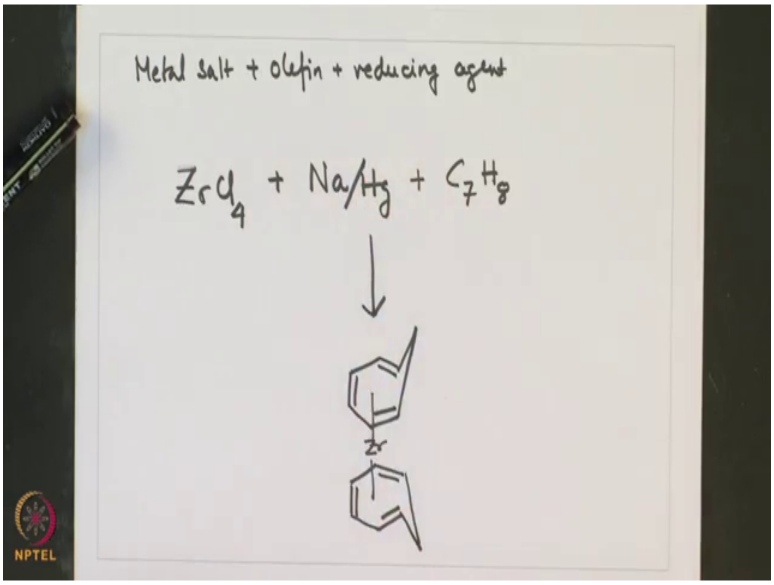

Metal salt + olefin + reducing agent

$ZrCl_4 + Na/Hg + C_7H_8$

The same strategy can be extended for making the zirconium olefin complex this strategy of metal salt plus olefin plus a reducing agent. For example, zirconium tetrachloride plus sodium mercury plus C 7 H 8 gives this 3 7 8 8 piece sandwich kind of complex zirconium and this was are prepared by Green in 1991. So, here this is the metal salt this is the olefin and this is the reducing agent.

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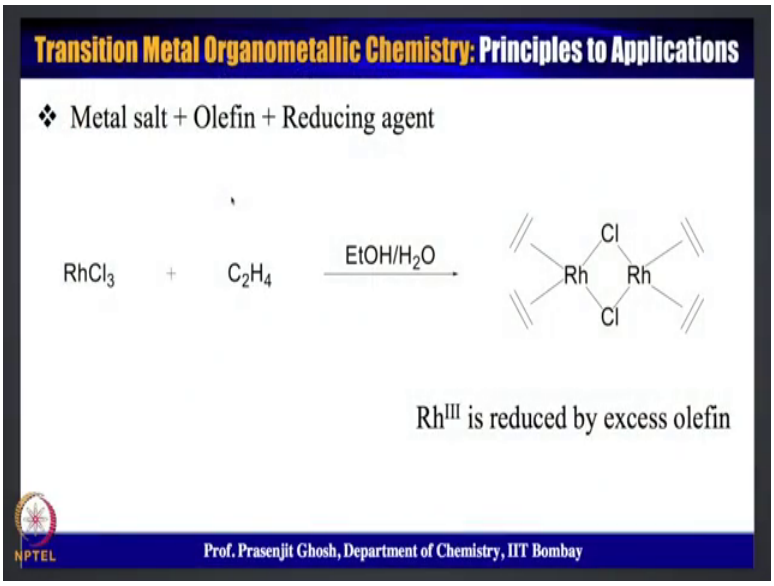

Transition Metal Organometallic Chemistry: Principles to Applications

- Metal salt + Olefin + Reducing agent

$RhCl_3 + C_2H_4 \xrightarrow{EtOH/H_2O}$

$Rh^{III}$ is reduced by excess olefin

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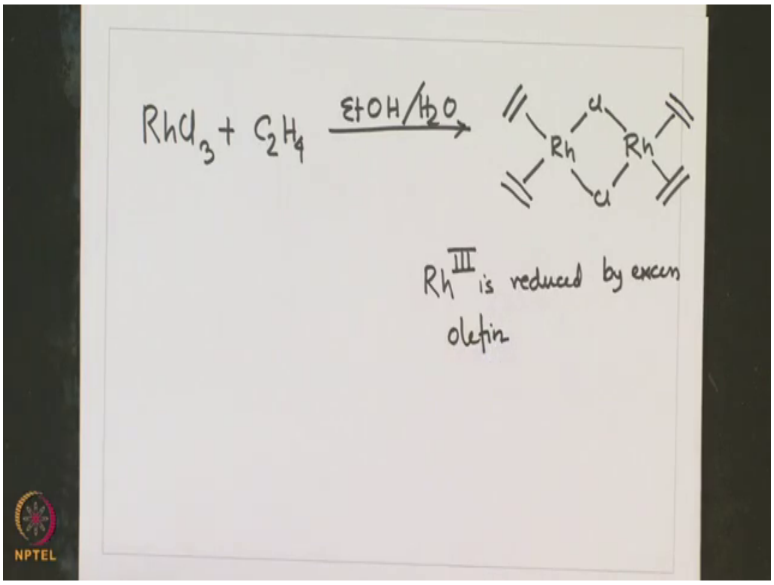

$Rh^{III}$ is reduced by excess olefin

Here is another Example reaction of rhodium trichloride plus C 2 H 4 in ethanol water giving this di rhodium tetra olefin this bridging chloride complex cl cl cl cl di rhodium and the rhodium 3 over here is reduced by excess olefin. So, there is no additional reducing agent for this particular reaction, but the reducing agent comes from electron rich olefin itself is reduced by excess olefin.

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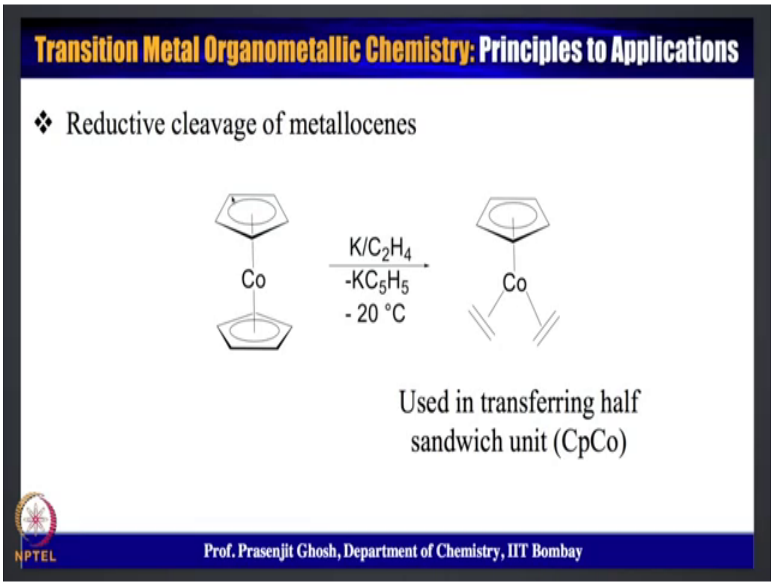
**Transition Metal Organometallic Chemistry: Principles to Applications**

- Reductive cleavage of metallocenes

Used in transferring half sandwich unit (CpCo)

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So, we are saying that there is really a lot of methods which are available for preparing these transition metal olefin complexes they are called quite diverse. And there are a lot of examples of this of them right beginning with this thermal and fertility cleavage of carbonyls from transition metal carbonyl compounds in presence of olefin to all these metal salts plus olefin plus reducing agent by the ligand isomerization reactions and so on and so forth.

So, what it sort of shows that there are a large number of methods available synthetic tools available for preparing these transition metal olefin complexes. Here is another such new example new methods of making it which involves reductive cleavage of metallocene.

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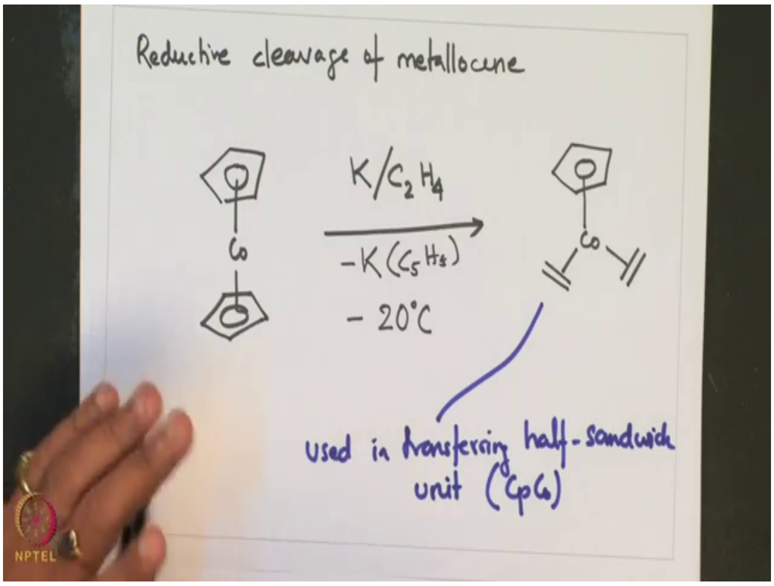

Reductive cleavage of metallocene

Used in transferring half-sandwich unit (CpCo)

Cobalt with potassium C 2 H 4 potassium is the reducing agent in presence of olefin and this gives replaces one of the metallocene as its potassium salt gives potassium C 5 H 5 at low temperature of minus 50 degree centigrades to give this cp cobalt olefin complex. And this is used in transferring half sandwich this particular reaction or this reagent is used in transferring half sandwich unit of C p C o.

So, these being weak bounds they can be replaced by other ligand and this is how this unit can be seen as C p C o transfer or C p C o called half sandwich metal complex transfer unit.

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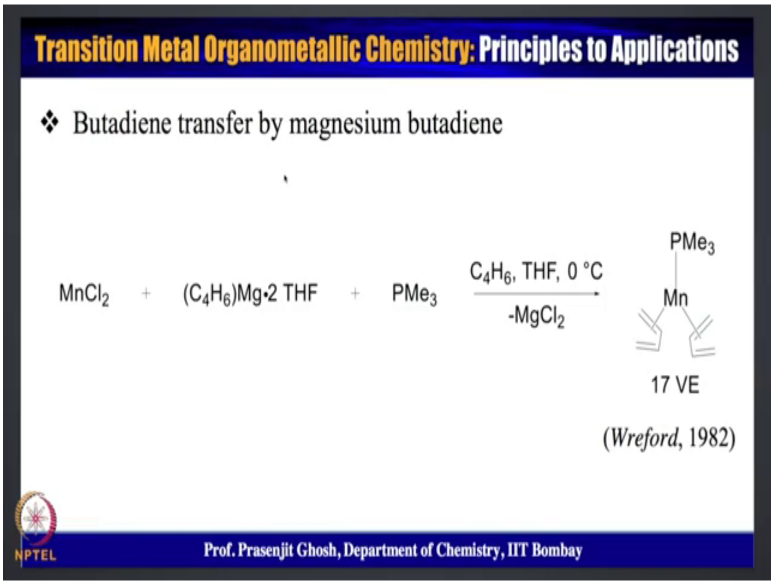

**Transition Metal Organometallic Chemistry: Principles to Applications**

- Butadiene transfer by magnesium butadiene

$MnCl_2 + (C_4H_6)Mg{\cdot}2\,THF + PMe_3 \xrightarrow[-MgCl_2]{C_4H_6,\ THF,\ 0\ °C}$

17 VE

(*Wreford*, 1982)

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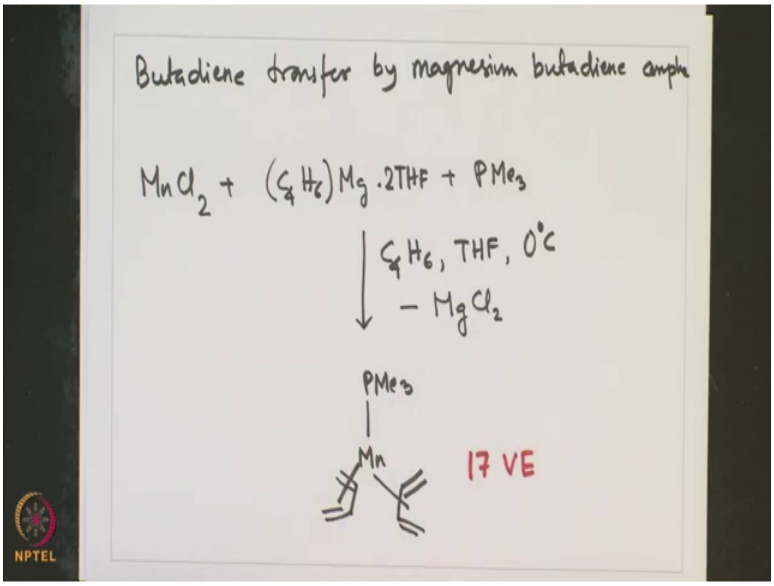

Butadiene transfer by magnesium butadiene compl

$MnCl_2 + (C_4H_6)Mg.2THF + PMe_3$

$\Big\downarrow \ C_4H_6,\ THF,\ 0°C \quad -MgCl_2$

17 VE

Similarly butadiene transfer by magnesium butadiene complex by magnesium butadiene complex M n cl 2 reacts with C 4 H 6 M g dot 2 T H F plus P M e 3 in presence of C 4 H 6 T H F at 0 degree centigrade gives minus M g C l 2 giving this manganese 0 P M e 3 M n butadiene complex which is a 17 valence electron complex.

So, here the butadiene is transferred on to manganese from this magnesium butadiene complex. This is a very nice example where a manganese di olefin is prepared from magnesium butadiene complex and the rest of the coordination sphere and manganese is sort of occupied by P M e 3. So, the reaction is done in presence of P M e 3.

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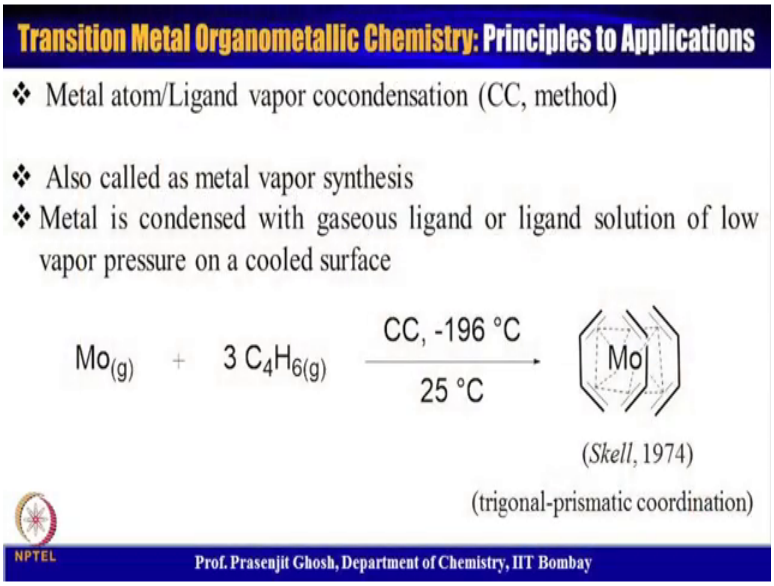

Transition Metal Organometallic Chemistry: Principles to Applications

- Metal atom/Ligand vapor cocondensation (CC, method)
- Also called as metal vapor synthesis
- Metal is condensed with gaseous ligand or ligand solution of low vapor pressure on a cooled surface

$$Mo_{(g)} + 3\,C_4H_{6(g)} \xrightarrow[25\,^\circ C]{CC,\ -196\,^\circ C}$$

(*Skell*, 1974)

(trigonal-prismatic coordination)

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Another metal vapor synthesis m v p and that is a new method that involves metal atom ligand vapor co condensation or these are also called as metal vapor synthesis ok.

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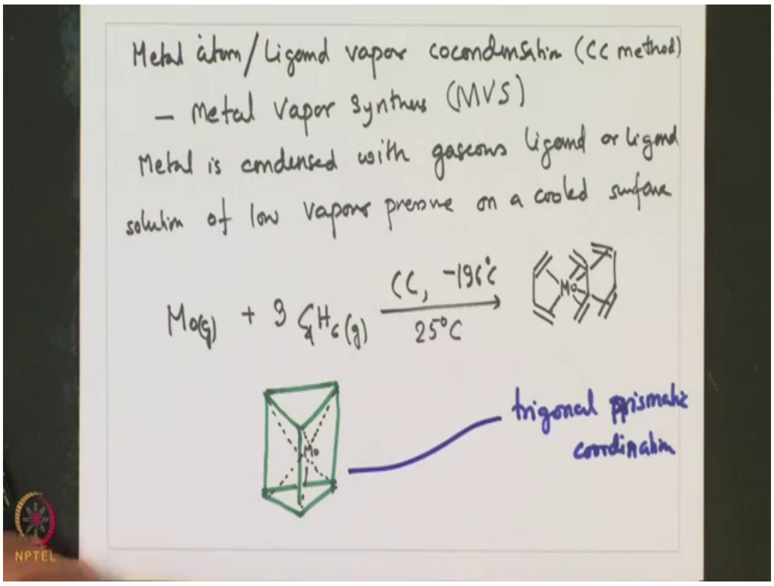

Metal atom/Ligand vapor cocondensation (CC method)

– metal vapor synthesis (MVS)

Metal is condensed with gaseous ligand or ligand solution of low vapors pressure on a cooled surface

$$Mo_{(g)} + 3\,C_4H_{6(g)} \xrightarrow[25^\circ C]{CC,\ -196^\circ C}$$

trigonal prismatic coordination

So, in this is a special technique required special reacting vessels in which the metal is condensed with gaseous ligand or ligand solution of low vapor pressure on a cooled surface and that will produce the organometallic compound directly. A very good example of this is given by molybdenum atom in the gaseous state plus 3 C 4 H 6 there is also in the gaseous phase this is co condensation method CC method or also called m M V S metal vapor synthesis method.

So, we are writing CC minus 196 degree centigrade. So, it is heated and then vaporized and then cooled and then blocked (Refer Time: 22:03) temperature gives this tris butadiene molybdenum complex well tris butadiene units are coordinated to molybdenum and this geometry molybdenum is called trigonal prismatic coordination. And this is similar to a trigonal prism with molybdenum coordinated to olefin and along the 3 edges of a trigonal prism and hence this is trigonal prismatic coordination and it is different from that of the regular octahedral coordination geometry.

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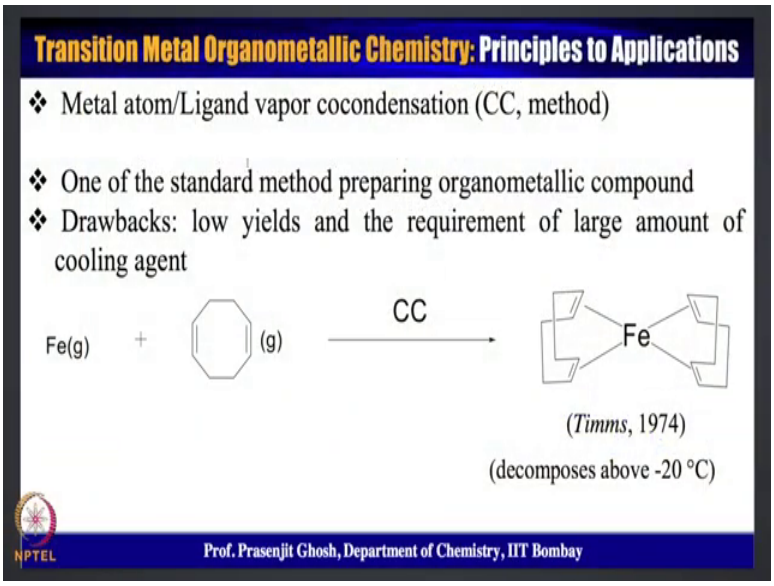

**Transition Metal Organometallic Chemistry: Principles to Applications**

- Metal atom/Ligand vapor cocondensation (CC, method)
- One of the standard method preparing organometallic compound
- Drawbacks: low yields and the requirement of large amount of cooling agent

(*Timms*, 1974)

(decomposes above -20 °C)

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In a metal vapor synthesis is a very useful method for a preparing transition metal compounds M V S or co condensation method is useful for preparing organometallic compounds.

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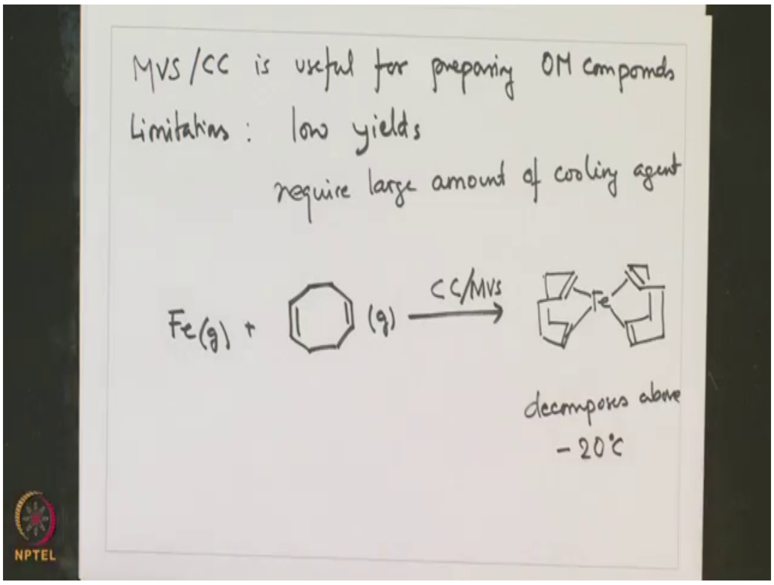

MVS/CC is useful for preparing OM compounds

Limitations : low yields

require large amount of cooling agent

Its limitations are low yields, and require large amount of require large amount of cooling agent general liquid nitrogen in many case. So, here is another example iron gas that ligand also in gaseous phase cc or M V S produces this iron COD complex which decomposes is very unstable above minus 20 degree centigrade.

So, with these let me conclude the points that have been discussed in today's lecture particularly we started looking at a various methods available for synthesizing these transition metal olefin complexes. And what we have discussed to begin with was this reaction of transition metal salts with olefin and presence of a reducing agent that seemed like a very general method for producing these transition metal olefin complexes.

We have also looked into reactions like metal vapor synthesis like which require special equipments to vaporize all the metal and then reacting with the vapor phase of the ligand and then all of them co condensing on a very cold surface and this is a very useful method for synthesizing important organometallic low valent in compounds. And we have seen two examples of that however, the yields of these reactions are usually low and also requires large number amount of cooling agents which are sort of the limitations for this method.

We have also seen the formation of transition metal olefin complexes by addition to a coordinatively unsaturated compounds as well as we have seen transition metal olefin complexes prepared from a reductive cleavage of a metallocene compounds and so on so forth.

So, with that we have discussed several 7 or 8 methods of synthesis for various transition metal olefin complexes in this particular lecture. And we would also take these metal transition metal olefin complex in bit more details look at the bonding and also the reactivity and property study in the subsequent lectures that is going to follow up on this. And I have with that I thank you for being with me in this lecture and I look forward to being with you the next lecture we are going to look up or take up these transition metal olefin complexes and their reactivity study and their bonding properties till then goodbye.

Thank you.