Advanced Transition Metal Organometallic Chemistry

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Lecture – 09

Transition Metal Cyclopentadiene Complexes

Welcome to this course on, Advanced Transition Metal Organometallic Chemistry, today we will to be discussing about special type of organometallic compounds namely the transition metal cyclopentadienyl complexes. Now the field of organometallic chemistry per se as such relates to cyclopentadienyl ligand in a big way, because the field sort of developed or emerged around CP systems, particularly a lot of activities based on the organometallic compound in and around cyclopentadienyl ligand were undertaken in 50's and 60's with the aim of greater understanding about transition metal organometallic complex, complexes.

And also with the intention of generating various kinds of transition metal organometallic compounds. So the field sort of develop synonymously with the development of transition metal cyclo pentadienyl chemistry and from that perspective today's lecture which would be centered around transition metal cyclo pentadienyl complexes, assumes significance. Because these compounds by and large are synonymous with organometallic chemistry.

And many people still sort of perceives these compounds to be the unadulterated examples of organometallic compound and all of these probably can again be traced back to ferrocene kind of system sandwich compounds from where the organometallic chemistry or many more of the organometallic chemistry has its deep roots in.

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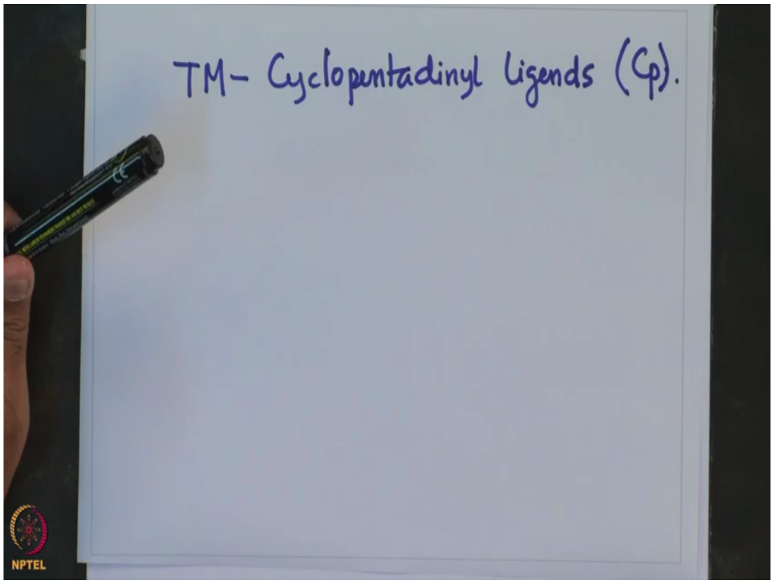
TM- Cyclopentadinyl Ligands (Cp).

So today we to be talking about transition metal cyclo pentadinyl ligand or in shorts they are called CP ligands.

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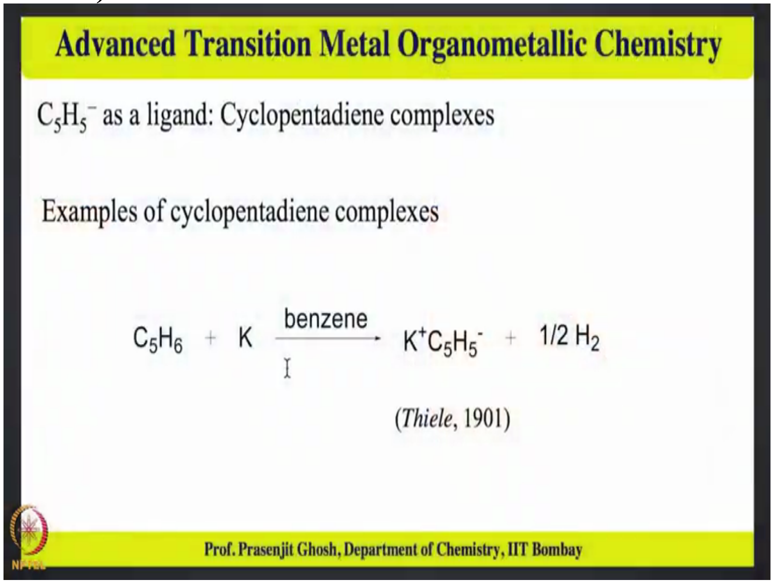

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$C_5H_5^-$ as a ligand: Cyclopentadiene complexes

Examples of cyclopentadiene complexes

$$C_5H_6 + K \xrightarrow{\text{benzene}} K^+C_5H_5^- + 1/2\ H_2$$

(*Thiele*, 1901)

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So the easiest way of preparing these compounds starts from reaction of cyclo pentadiene with inherent nascent metal for example C5 H6 plus potassium in benzene gives K+ C5 H5- along with generation of hydrogen. Now this was done by Thiele, with that in 1901. Now one interesting aspect about organometallic compound is that many of the compounds by reported to have synthesized way long back may be essentially also earlier.

But it was not until, may be essentially or so later that people had found characterization techniques or as well as evolved or developed synthetic protocols that would allow them proper isolation and characterization as well as storage and stabilization of these compounds. So some of the compounds might have been made earlier might have found in many of the earlier literature or differences, however, the understanding of them as well as the characterization of them came way beyond a century or a much later.

And the best example of that is Iso salt does Iso salt was made way back in 1800 but their proper explanation of how olefin is bound to the transition metal the forward Sigma donation from olefin to the and metal back donation from the metal to olefin and was proposed by D Burchard intention in 1950's,and the structural characterization even happened in 60's or 70's. So it is kind of interesting to note that these compounds might have been prepared way back in time, but the proper appreciation and justification or explanation for these compounds came a much longer, sometimes several decades or even a century later.

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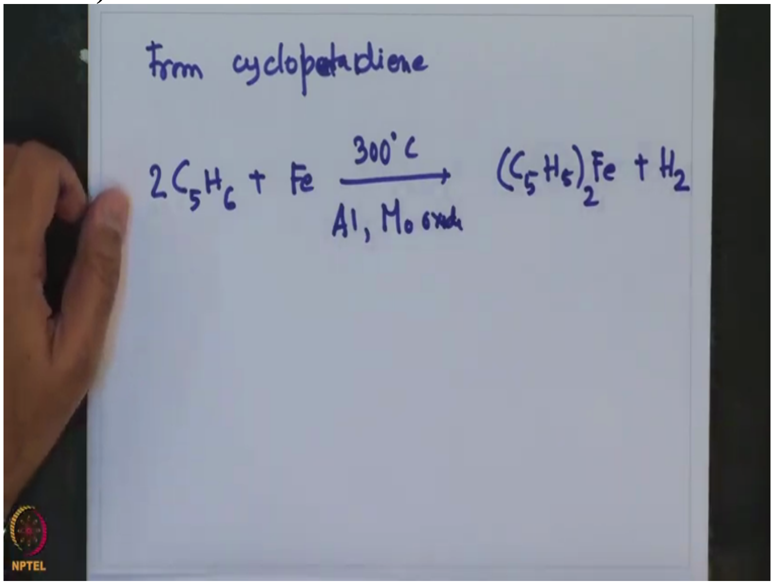

From cyclopentadiene

$$2C_5H_6 + Fe \xrightarrow[Al,\ Mo\ oxide]{300^\circ C} (C_5H_5)_2Fe + H_2$$

Similarly the reaction of a cyclo pentadiene gives plus hydrogen these was also exactly a similar reaction to the one that we had discussed and this is this famous ferrocene molecule which was prepared direct from the cyclo butadiene with iron at very high temperature.

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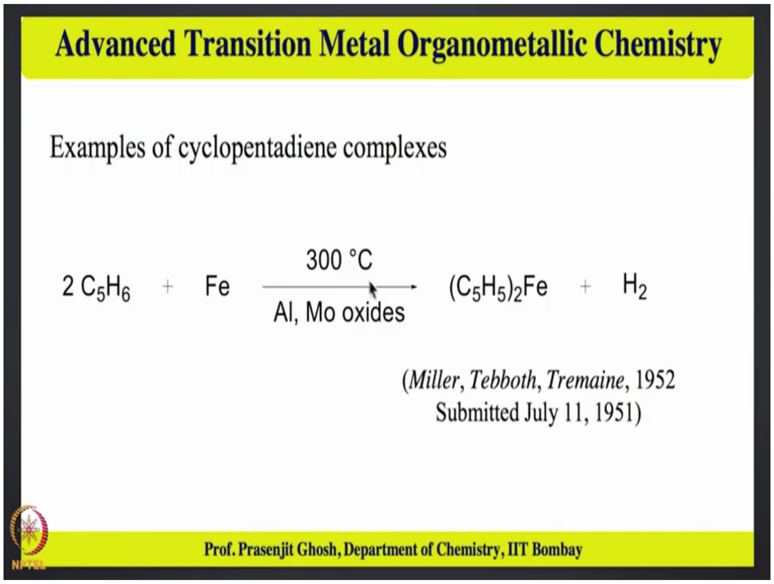

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Examples of cyclopentadiene complexes

$$2\,C_5H_6 + Fe \xrightarrow[\text{Al, Mo oxides}]{300\ ^\circ C} (C_5H_5)_2Fe + H_2$$

(*Miller*, *Tebboth*, *Tremaine*, 1952
Submitted July 11, 1951)

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300, degree centigrade formation of the ferrocene and with the elimination of hydrogen it can also be prepared by the reaction of C5H5MgBr.

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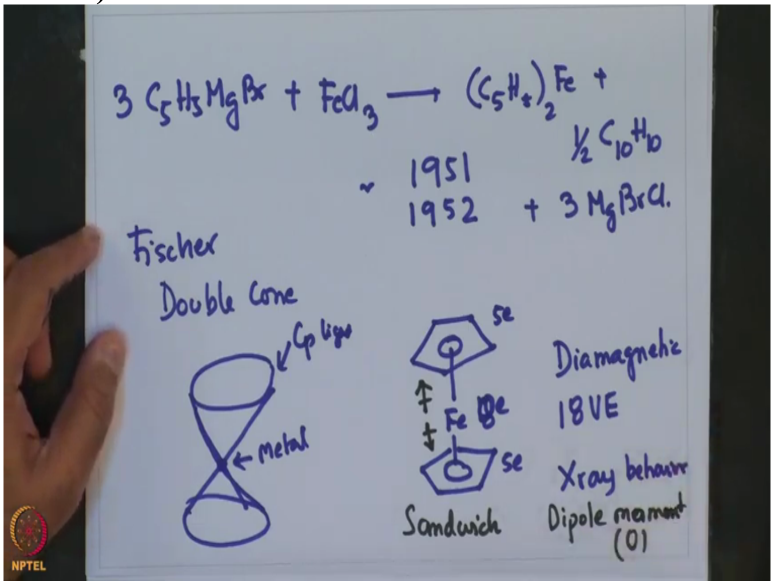

$$3\,C_5H_5MgBr + FeCl_3 \longrightarrow (C_5H_5)_2Fe + \tfrac{1}{2}C_{10}H_{10} + 3\,MgBrCl.$$

~ 1951
1952

Fischer
Double Cone

Diamagnetic
18VE
Xray behaviour
Dipole moment (0)

Three equivalents of it with FeCl3 giving ferrocene + 1/2 of C10 H10 + 3 Mg Br Cl so this was reported by Frosen in 1951.

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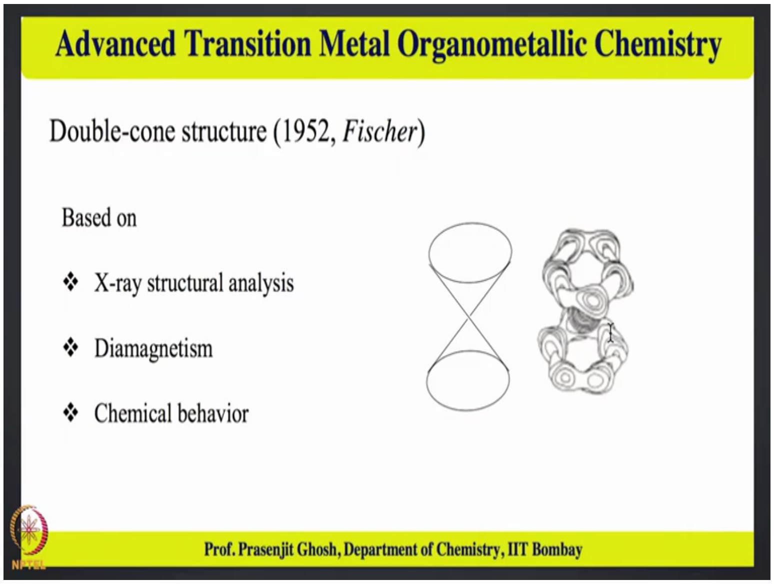

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Double-cone structure (1952, *Fischer*)

Based on

- X-ray structural analysis
- Diamagnetism
- Chemical behavior

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Now at that point of time, there was a greater interest on the structure of ferrocene in the hindsight such debate made sense because there is no Sigma type orbital available to make a direct Sigma bond with the CP ligand or CP anion. So one is left to wonder that how does the aromatic Pi cloud interact with metal orbital and such kind of interaction had not earlier been observed in any other metal complexes. So given the fact that the synthesis of this ferrocene compounds was reported somewhere in 1950's 1951 and 52.

The explanation of the structure was given by Fischer in 1952 and it says that it is a double cone structure, with the base of the cone represented by 2 CP ligands and the metal of being at the center and this was based on structure analysis and the structure of ferrocene was thus given by something like this the magnetism showed that these are diamagnetic compounds and this is obvious from the 18 valence electron count 10 and 5e so overall 18 valence electron compounds and also from x-ray behavior, it is also found that these two CP rings are in staggered confirmations where they are not in eclipse confirmations.

So, their orientations are exactly opposite what would be expected in an eclipsed conformation so this was a very interesting report by Fischer who really solved the structure of ferrocene and found that these two cyclopentadienyl ring are indeed flanking the iron in our trans fashion. Thus the hallmark of the structure become that it is a sandwich structure and the dipole moment of these net dipole moment is zero.

And that is because the iron CP dipole moment each cancel each out in opposite direction such that the nail dipole moment becomes zero. At room temperature the cyclopentadiene is sort of stays as a dimer, the way it is shown over here, and this dimerization is formed as a Diels-Alder reaction.

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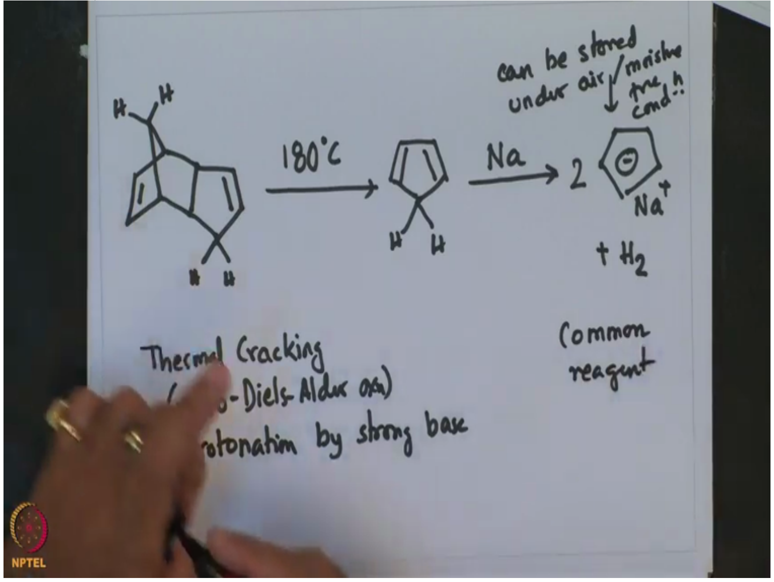

Thermal Cracking

-Diels-Alder rxn)

rotonation by strong base

Now upon heating at 180 degree centigrade the one performs thermal cracking or does a literal Diels-Alder reaction or retro Diels-Alder reaction giving rise to formation of a cyclo pentadiene. Now cyclo pentadiene generated can be deprotonated using sodium metal giving two of sodium CP along with the liberation of hydrogen, can be stored under a moisture free conditions, so sodium CP is a very common reagent in organometallic chemistry.

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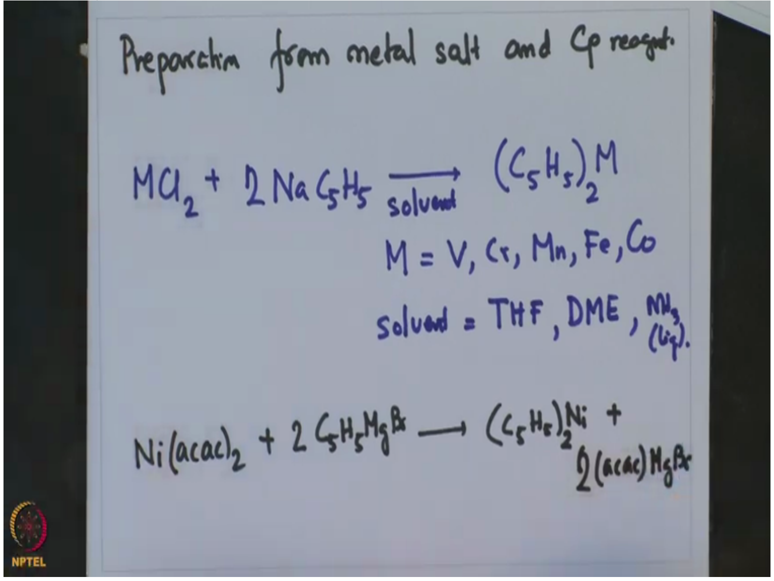

Preparation from metal salt and Cp reagent.

$$MCl_2 + 2NaC_5H_5 \xrightarrow[\text{solvent}]{} (C_5H_5)_2M$$

M = V, Cr, Mn, Fe, Co

solvent = THF, DME, NH_3 (liq).

$$Ni(acac)_2 + 2C_5H_5MgBr \longrightarrow (C_5H_5)_2Ni + 2(acac)MgBr$$

Here is a generic method from salt and CP reagent, so MCl2 + twice Na C5 H5 results in C5 H5 M this is a very common solvent and is a common method and can be used in preparation of various kinds of DCP transition metal complexes where M can be vanadium, chromium, manganese, iron, cobalt and the solvent for this reaction usually are THF, DME, ammonia liquid. This is sort of an example of salt metathesis of salt exchange reactions like instead of MCl2 one can use other salts as well for example this reaction of nickel acac with grignard gives niclocene plus twice Mg Br.

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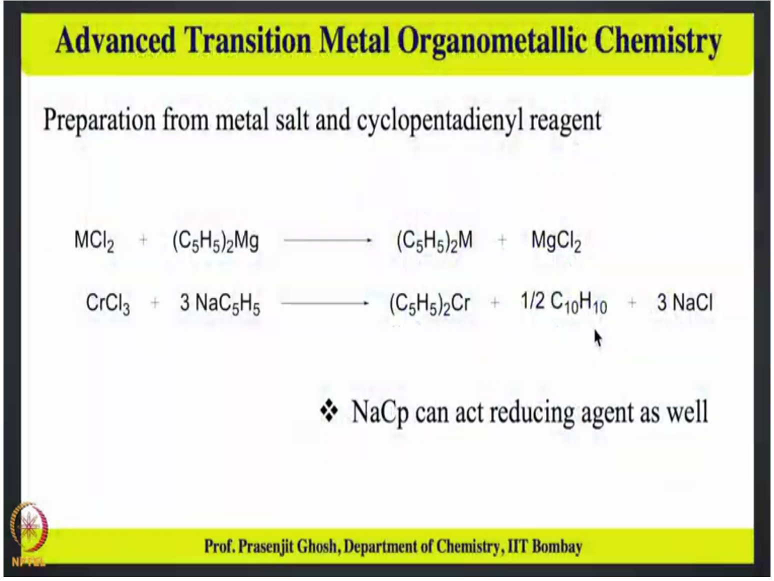

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Preparation from metal salt and cyclopentadienyl reagent

$MCl_2 + (C_5H_5)_2Mg \longrightarrow (C_5H_5)_2M + MgCl_2$

$CrCl_3 + 3\,NaC_5H_5 \longrightarrow (C_5H_5)_2Cr + 1/2\,C_{10}H_{10} + 3\,NaCl$

❖ NaCp can act reducing agent as well

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Similarly dimethyl magnesium or di CP magnesium can also be used for such synthesis.

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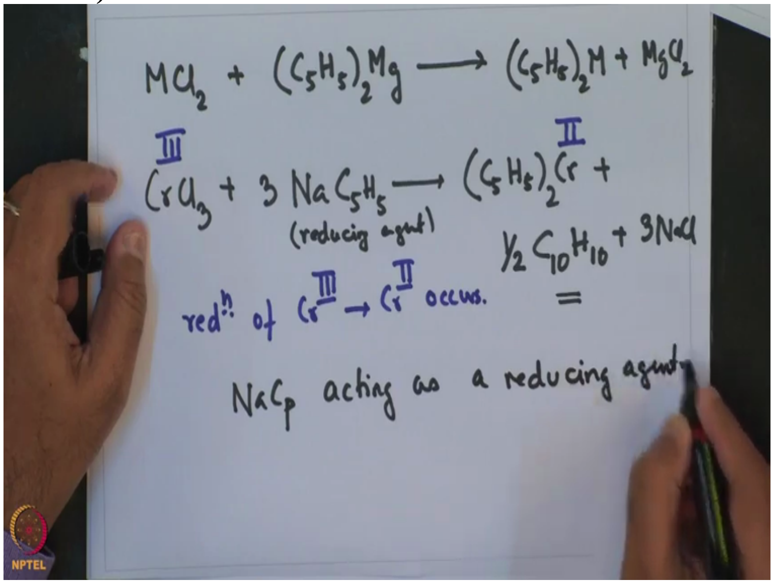

$MCl_2 + (C_5H_5)_2Mg \longrightarrow (C_5H_5)_2M + MgCl_2$

$\overset{III}{Cr}Cl_3 + 3\,\underset{\text{(reducing agent)}}{NaC_5H_5} \longrightarrow (C_5H_5)_2\overset{II}{Cr} + \frac{1}{2}\underline{\underline{C_{10}H_{10}}} + 3NaCl$

red^n of $Cr^{III} \rightarrow Cr^{II}$ occurs.

NaCp acting as a reducing agent

For example, MCl2 + this CP2 Mg giving M+ Mg Cl2 this is very similar reaction of what we had just seen in the earlier discussion and another example includes chromium chloride plus three of sodium M5 giving 5 O2 chromium + C10 H10 plus 3 NaCl. Now over here what one says that chromium goes from plus 3 oxidation state to plus 2 oxidation state and here is a reduction of chromium 3 to chromium 2 occurs to facilitate that process.

Sodium CP is the reducing agent and the CP anion gets C5 H5- facilities disruption and itself gets oxidized to produce this C10 H10. Meson's electron becomes radical and then dimerizes to give C10 H10, so here we see sodium CP, acting as reducing agent. Furthermore the reaction with various kinds of transition metal alkyds.

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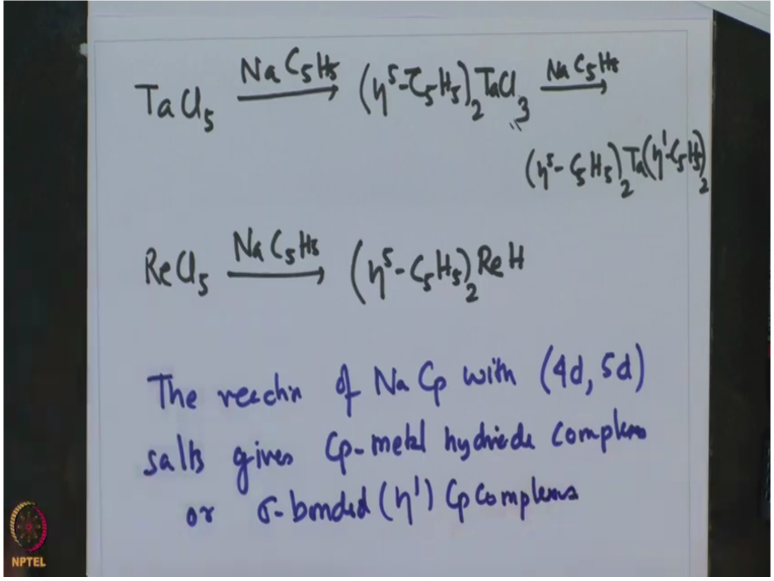

$TaCl_5 \xrightarrow{NaC_5H_5} (\eta^5\text{-}C_5H_5)_2TaCl_3 \xrightarrow{NaC_5H_5} (\eta^5\text{-}C_5H_5)_2Ta(\eta^1\text{-}C_5H_5)_2$

$ReCl_5 \xrightarrow{NaC_5H_5} (\eta^5\text{-}C_5H_5)_2ReH$

The reachn of Na Cp with (4d, 5d) salts gives Cp-metal hydride complexs or σ-bonded (η^1) Cp complexes

For example tantalum pentachloride with sodium CP leads to only replacement of two of the chlorides giving it eta 5 C5 H5 whole 2 TaCl3 and then a subsequent reaction with again sodium CP replaces the two, another two to give eta 5 C5 H5 whole 2 tantalum eta 1 C5 H5 whole 2, similarly for rhenium, ReCl5 with sodium CP one gets eta 5 C5 H5 whole 2, rhenium hydride. So here also rhenium has undergone reduction from +3, a +5 to +3 over here it has undergone reduction from +5 to +4. The reaction of sodium CP with 4d and 5d salt gives CP metal hydride complexes or sigma bonded a eta 1 bound CP complexes.

So, these are two interesting aspects that came to the fore that sodium CP not only can acts as a reducing agent but also can gives rise to formation of metal hydride as well as eta bound CP complexes along with the the reduction, sodium CP performs for itself.

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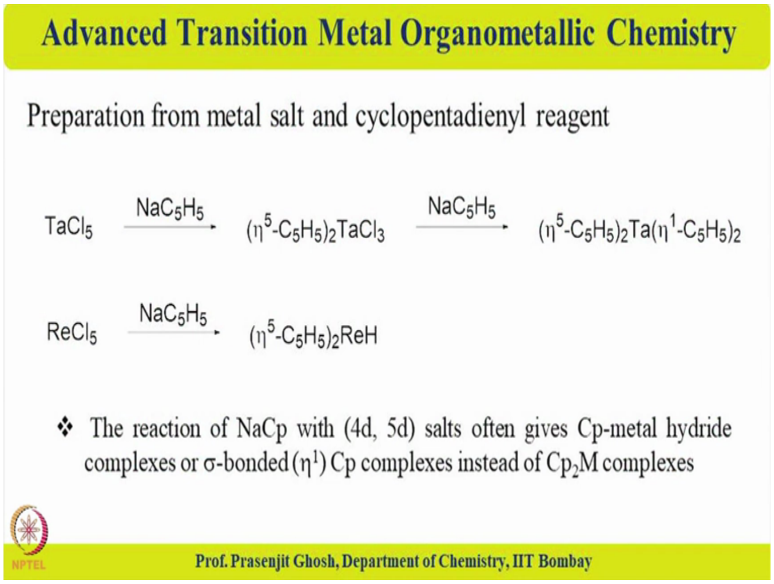

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Preparation from metal salt and cyclopentadienyl reagent

$TaCl_5 \xrightarrow{NaC_5H_5} (\eta^5\text{-}C_5H_5)_2TaCl_3 \xrightarrow{NaC_5H_5} (\eta^5\text{-}C_5H_5)_2Ta(\eta^1\text{-}C_5H_5)_2$

$ReCl_5 \xrightarrow{NaC_5H_5} (\eta^5\text{-}C_5H_5)_2ReH$

- The reaction of NaCp with (4d, 5d) salts often gives Cp-metal hydride complexes or σ-bonded (η^1) Cp complexes instead of Cp_2M complexes

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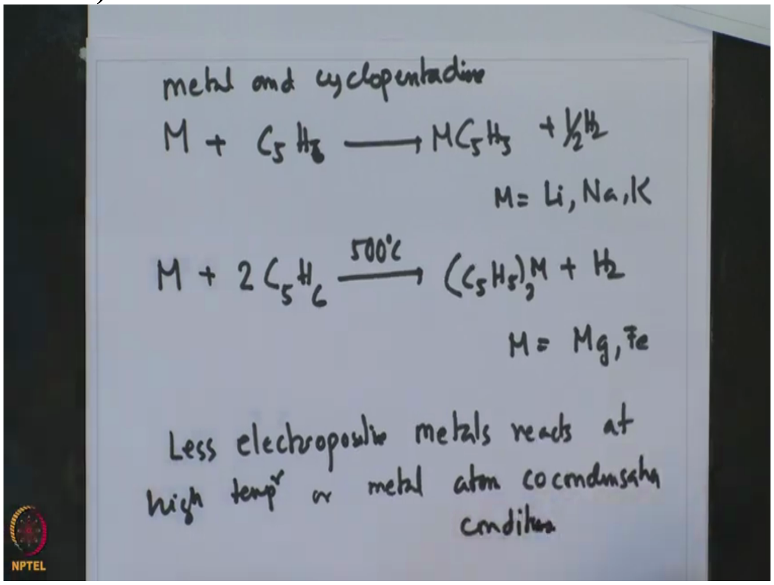

metal and cyclopentadiene

$M + C_5H_6 \longrightarrow MC_5H_5 + \frac{1}{2}H_2$

M= Li, Na, K

$M + 2C_5H_6 \xrightarrow{500^\circ C} (C_5H_5)_2M + H_2$

M= Mg, Fe

Less electropositive metals reacts at high temp^r or metal atom cocondensation condition

Similarly the direct reaction of metal from cyclopentadiene M+C5 H5 giving MC5H5 + 1/2 H2, M can work for lithium, sodium, potassium. As well as, metal can also react with C5 cyclo pentadiene at elevated temperatures, to give plus hydrogen and in this case, this occurs for magnesium and iron. So, what does it say? It says that less electro positive, positive metals react at high temperature or metal atom CO condensation conditions, whereas high electropositive metal reacts immediately or readily with cyclo pentadiene with the elimination of hydrogen.

So, with this I would like to conclude today's lecture, in this lecture, we have looked into the structure and bonding of cyclopentadienyl ligand, the history of its origin, as well as various synthetic methods available for preparing these cyclopentadienyl complexes. We have also seen that these compounds are extremely air and moisture sensitive, particularly, of those of the more electropositive metals and as one goes to the less electropositive metals the reactivity or sensitivity of these cyclo pentadinyl complexes, sort of decrease.

Also that is reflected in the conditions in which they are prepared, for example, for the one reaction discussed over here, they are highly electropositive metal reacts readily a giving very sensitive ionic compounds whereas the list, we have two positive metals like iron and all reacts at elevated temperature and to give a stable complex. So with that, I will conclude today's lecture in which we have looked in depth at various metal transition metal cyclopentadienyl complexes and would continue a little bit more on this topic in the next lecture.

So, with this thank you for being with me in this class and I look forward to being with you in the next class till then good bye.