Advanced Transition Metal Organometallic Chemistry
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Lecture – 10
Transition Metal Cyclopentadiene Complexes: Preparation and Properties

Welcome to today's lecture on, Advanced Transition Metal Organometallic Chemistry. Today we are going to be continuing with our topic of, transition metal cyclo pentadiene complexes, their preparation and properties. Now these metal cyclo pentadiene complexes are of historical importance, particularly with the development of organometallic chemistry or development of the field of organometallic chemistry and from that perspective these transition metal cyclopentadienyl complexes that we are discussing over the last two lectures assumes relevance.

In our earlier lecture, we had seen, how these ferrocene the so called representative of transition metal organometallic complexes was first synthesized independently by two groups in 1951 followed by their structure resolution coming in 1952 by Fisher, and which, at that point of time, answer the big question about, as to how to cyclopentadiene and ligands are binding to the transition metal, and these would be interactions of aromatic Pi type orbitals with the metal which will hold these metallocene or ferrocene complexes containing transition metal cyclopentadienyl bonds.

At that point, it was a huge discovery in terms of ligand metal interactions are concerned. And then we have also looked at various ways of preparations that people adopted for preparing these transition metal cyclopentadienyl complexes some of them includes, simple salt metaphysics reactions with CP anions, exchanging with metal halide precursors, or other kind of metal salts, also reactions with of big nerd were chosen for a source of CP anions for methylating it on other metals.

And then continuing further on these various synthetic roots that are available for preparing this metllocene or transition metal CP complexes, we are going to look at few more preparations which are available in today's lecture to begin with.

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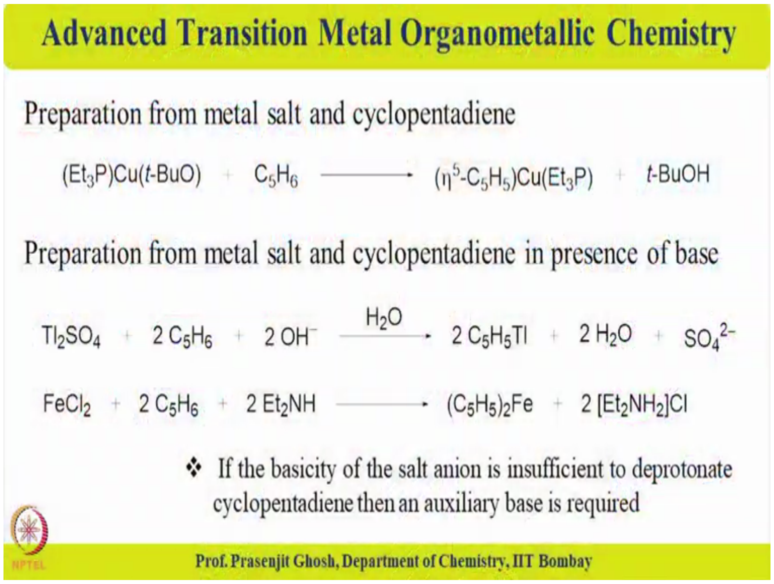

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Preparation from metal salt and cyclopentadiene

$(Et_3P)Cu(t\text{-}BuO) + C_5H_6 \longrightarrow (\eta^5\text{-}C_5H_5)Cu(Et_3P) + t\text{-}BuOH$

Preparation from metal salt and cyclopentadiene in presence of base

$Tl_2SO_4 + 2\,C_5H_6 + 2\,OH^- \xrightarrow{H_2O} 2\,C_5H_5Tl + 2\,H_2O + SO_4^{2-}$

$FeCl_2 + 2\,C_5H_6 + 2\,Et_2NH \longrightarrow (C_5H_5)_2Fe + 2\,[Et_2NH_2]Cl$

❖ If the basicity of the salt anion is insufficient to deprotonate cyclopentadiene then an auxiliary base is required

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Similarly along the same line one can see that reaction of metal salt with cyclo pentadienyl.

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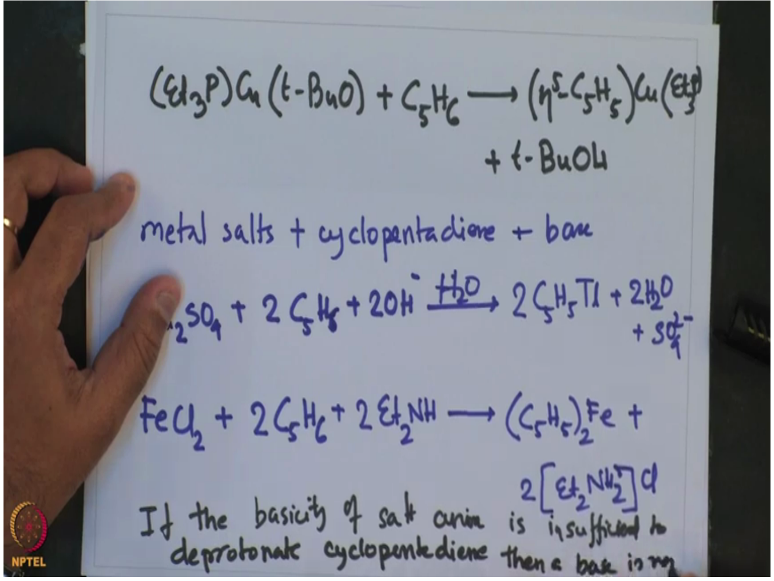

$(Et_3P)Cu(t\text{-}BuO) + C_5H_6 \longrightarrow (\eta^5\text{-}C_5H_5)Cu(Et_3$

$+ t\text{-}BuOH$

metal salts + cyclopentadiene + base

$_2SO_4 + 2C_5H_6 + 2OH^- \xrightarrow{H_2O} 2C_5H_5Tl + 2H_2O + SO_4^{2-}$

$FeCl_2 + 2C_5H_6 + 2Et_2NH \longrightarrow (C_5H_5)_2Fe + 2[Et_2NH_2]Cl$

If the basicity of salt anion is insufficient to deprotonate cyclopentadiene then a base is

In case of copper for example with triethylphosphine copper t-butoxide and cyclo pentadiene gives eta 5 H5 Cu Et3 t along with t-butanol. So, over here this t-butoxide moiety on copper is great and protonated with CP hydrogen. Now the driving force for this protonation arises from the fact that after protonation the CP anion being generated is resonance stabilized because of the attainment of aromaticity and that probably drives this reaction forward to producing the CP eta 5 bound CP copper triethyl phosphine derivatives.

There are reports of such deprotonation affected by using base, for example, there are general reports of using metal salts and cyclo pentadiene in presence of base doing the same thing for example thallium sulphate plus 2C5 H5 +2 OH- is an external bas resulting in water gives this

C5H5 thallium plus water plus sulfate anion, similarly reaction of FeCl2 + 2C5 H6 + 2 Diethyl amine giving ferrocene + 2 NH to Cl.

So, the take home message is if the basicity of salt and iron is insufficient to deprotonate cyclopentadiene, then a base is required and this is illustrated by comparing these two reactions no base was used in the reaction with the copper t-butoxide as this t-butoxide anion the basicity of t-butoxide anion could easily deprotonate cyclopentadiene proton dienyl proton.

Whereas the dienyls like sulfate or chloride in these examples are not basic enough to deprotonate the cyclopentadienyl proton and as a result some ancillary base in the thallium sulfate case, it was hydroxide, and in the iron chloride case, it is diethyl amine was required to produce the cyclopentadienyl anion bound to the transition metal.

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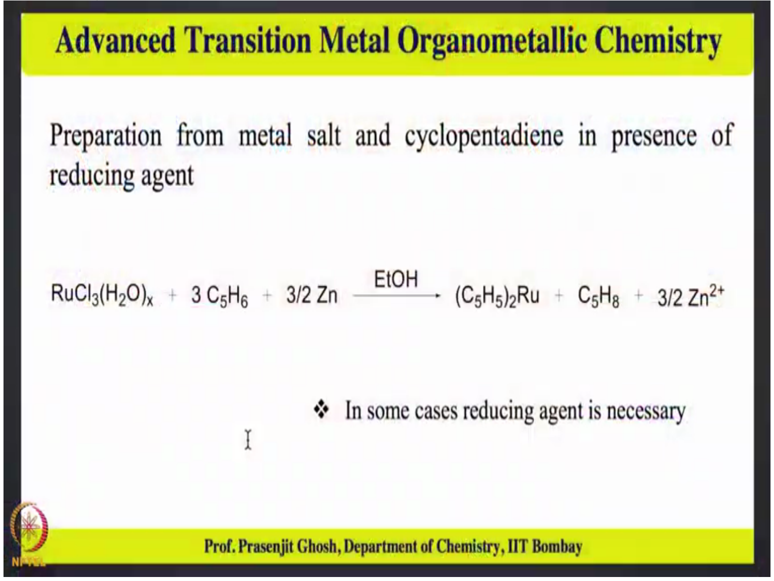

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Preparation from metal salt and cyclopentadiene in presence of reducing agent

$$RuCl_3(H_2O)_x + 3\,C_5H_6 + 3/2\,Zn \xrightarrow{EtOH} (C_5H_5)_2Ru + C_5H_8 + 3/2\,Zn^{2+}$$

❖ In some cases reducing agent is necessary

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In some cases also the presence of reducing agent is required.

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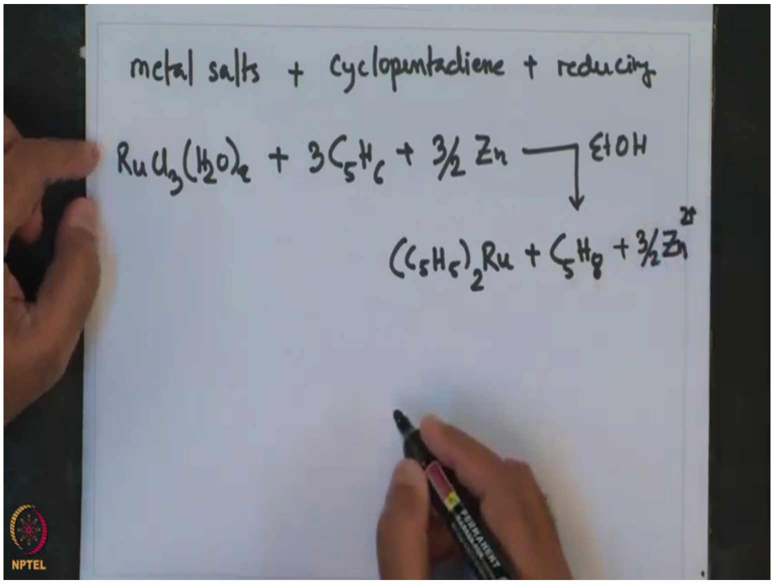

metal salts + cyclopentadiene + reducing

$$RuCl_3(H_2O)_x + 3C_5H_6 + 3/2\,Zn \xrightarrow{EtOH} (C_5H_5)_2Ru + C_5H_8 + 3/2\,Zn^{2+}$$

So, the strategy is similar to what we had seen earlier but that now instead of base the reducing agent is required for example in this strategy it involves metal salts plus cyclo pentadiene plus reducing agent and the reaction is given as 3C5H6 in presence of reducing as agent like zinc in ethanol gives ruthenium + H8 Zinc+ . So in some cases reducing agent is necessary and here is an example where, where zinc was used as a reducing agent for carrying out this reaction.

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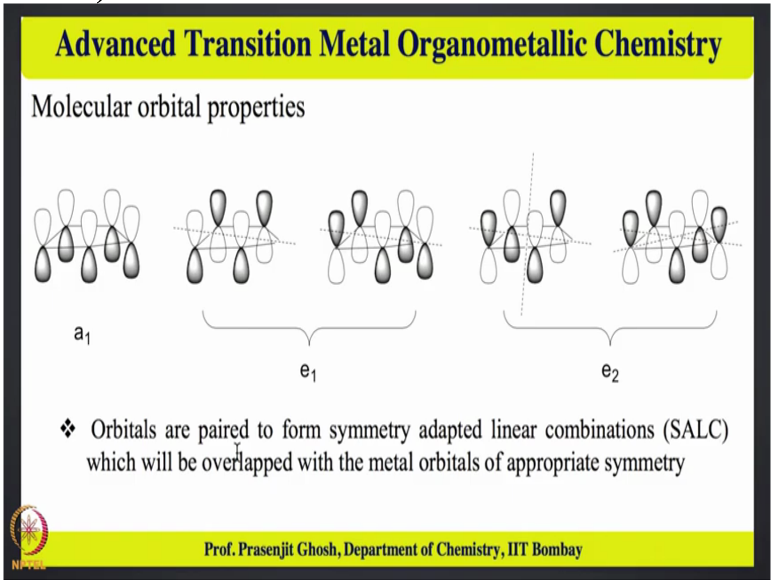

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Molecular orbital properties

- Orbitals are paired to form symmetry adapted linear combinations (SALC) which will be overlapped with the metal orbitals of appropriate symmetry

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Now in order to understand the reactivity or bonding in metal cyclopentadienyl complexes one needs to take a look at its molecular orbital. Now we have been doing this treatment, particularly to understand the reactivity, as well as bonding interaction in various metal ligand that we have discussed so far, we have started with allyl then which is a C3 system, and to butadiene C4 system, again cyclobutadiene C4 system, and now we go on to try and look at the metal ligand interaction in cyclo pentadinyl system.

Now as we go up in the number of carbon atoms so this is the 5 membered rings and hence we will have 5P orbital's so the complexity of these interactions also increases tremendously and to the extent possible I am going to explain this with the help of diagrams which will simplify these interactions to the reader. So, let us take a look at structure and bonding of the cyclo pentadiene ligand, with respect to the transition metal orbitals and to start with we look at their Emo orbital properties.

So, cyclopentadienyl ligand will have 5P orbitals resulting in 5 molecular orbitals of which there will be eh, one of its own type and the two other will be a degenerate.

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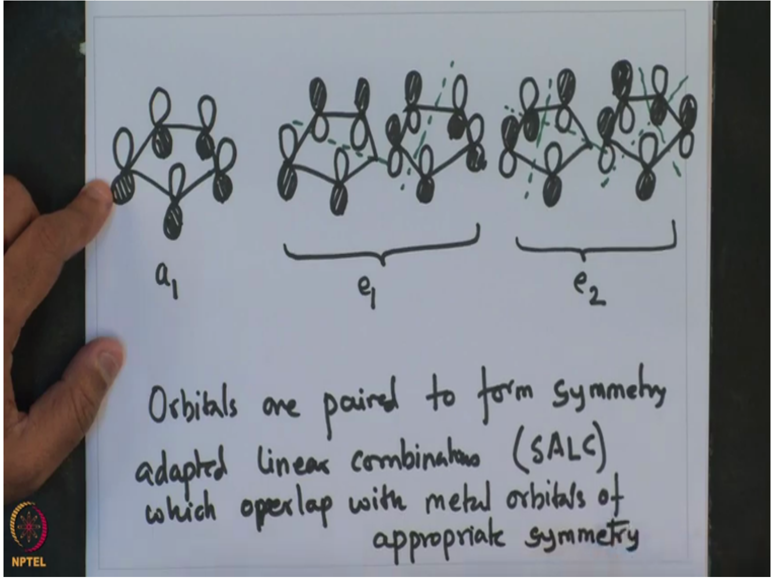

Orbitals are paired to form symmetry adapted linear combinations (SALC) which overlap with metal orbitals of appropriate symmetry

So, they are shown over here. So, this is Psi 1 which is a1 symmetry and this is all bonding. So, now there are 2, e2 types, and another, so this one has one nodal plane and this one has another nodal plane these two are degenerate and is referred to as e1 symmetry. Now this has 2 nodal planes, 1 between this and another between these and the 5th combination is that one also has two nodal planes and these two are also degenerate and enough are called e2 types.

So, these orbital's so what we see that the 5P orbitals they mutually combine in different ways to generate 5 for fragment molecular orbitals of which one is non degenerate and two pairs of degenerate orbitals, e1 and e2. So, orbitals are paired to form symmetry adapted linear combinations or SALC which overlap with metal orbitals with of appropriate symmetry.

So, now the bonding scenario that is presented will gets even complicated further because of the fact that in ferocinal complexes there are two such CP ligands and depending on the orientation of each of the fragment orbitals they would interact differently with the metal orbitals and this I will illustrate with a set of orbitals which is CP.

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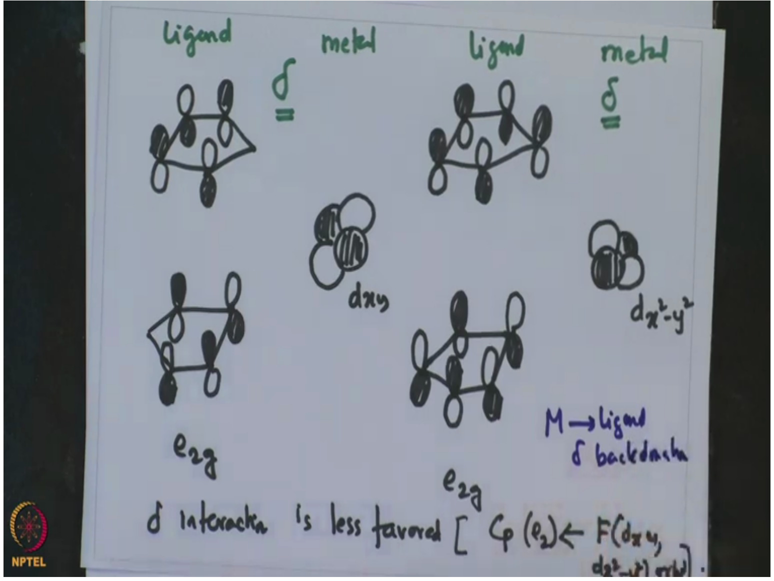

δ interaction is less favored [Cp (e_2) ← F(d_{xy}, $d_{x^2-y^2}$) orbital].

So, there are two CP rings and these two rings are opposite, facing opposite of each other so one is pointing this the other is pointing it and so these two orbitals of the ligand, interacts with the metal orbital, which is dxy this is the metal orbital and such interaction is called Delta type interaction and these combination of ligand orbital is called e2g ligand, similarly the other metal orbital for the e2g group would be like and the corresponding the other CP, so this also is a e2g ligand orbital.

And the metal orbital corresponding to that dx 2 – y 2 and this interaction is also Delta interaction. So what we see is that Delta interaction is a weak interaction and also is less favored, and it involves dative bond between CP e2 ligand from iron dxy or dx 2- y 2 orbitals. So, this is a metal to ligand Delta back donation and hence this is a weak interaction. Let me just go a step further and bring back the earlier slide and what we see that 5 sets of orbitals to e1 e2.

And a1 type is formed from 1 CP and when both of the CP comes, then we have two combinations, because each of the ring appears top and the bottom and what we see that the e2 portion the top most degenerate orbitals, these two are responsible for the Delta interaction, which happens from metal to ligand, metal to ligand interaction happens over here and a1 and e1 are the field cyclopentadienyl anion ligand and ligand to metal, the opposite interaction, ligand to metal interaction would happen over a1 and e2.

So today we have looked into various types of preparative methods that are out there for preparing this transition metal cyclopentadienyl complexes, in addition we have also looked at the structure and bonding particularly from the molecular orbital perspective of these transition metal ferrocenal complexes particularly how the P orbital of the ferrocene cyclopentadienyl ligand rearranges themselves, orient themselves, so that they become ready for interaction with the metal and how they interact based on their energies.

So with this I will conclude today's lecture and we are able to look into, now this bonding aspect of cyclo pentadiene and ligand, with the metal orbital in much more detail in subsequent lecture, where we are to build the CP metal interaction along the same lines in much more detail, looking into ligand to metal sigma and Pi interaction. Today we have built the molecular orbital; the picture and also had looked into metal to ligand Delta interaction which is obviously very weak and also does not happen in many instances.

So, with this I conclude today's lecture and we are able to be taking up this structure and bonding of the transition metal cyclopentadienyl complexes is much more detail in the subsequent lecture till then thank you and good bye.