Advanced Transition Metal Organometallic Chemistry

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Lecture – 28

Transition Metal Arene Cyclopentadienyl Complexes

Welcome to this course on advanced transition metal organ mentally chemistry we have been discussing a very important compound or class of compound in this context and these are these arene transition metal heterolytic complexes. And in this regard we have been talking about transition metal arene cyclopentadienyl complexes. These compounds can be thought about as a hybrid of Bis cyclopentadienyl complexes are Bis benzene transition metal complexes.

So, that the transition metal is bound to both of this ligand that is the arene in eta 6 fashion and cyclopentadienyl ligand in eta 5 fashion. So, this makes this a class of compounds very interesting. Now in the previous lecture we have started off by talking about the synthesis of these compounds and the method that we have used involved reaction of metal halides with cyclopentadienyl sodium salt and phenyl magnesium bromide grignard resulting in the formation of and these manganese cyclo pentadienyl benzene complex.

But one of the characteristic feature of the synthesis is that the desired product which is cyclopentadienyl magnesium benzene complex was formed only in 2% yield they were mixture of other combination of products which were obtained but the desired product in this method was very less in amount.

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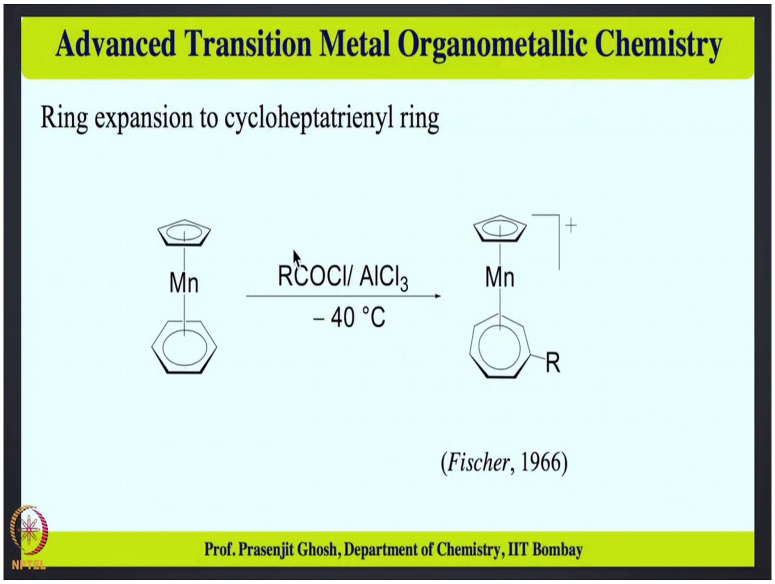

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Ring expansion to cycloheptatrienyl ring

(*Fischer*, 1966)

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Now proceeding further today we are going to take up some more synthesis of these mixed cyclo pentadienyl metal arene complexes and one such method involves doing expansion of benzene to cyclohexane and ring as shown over here.

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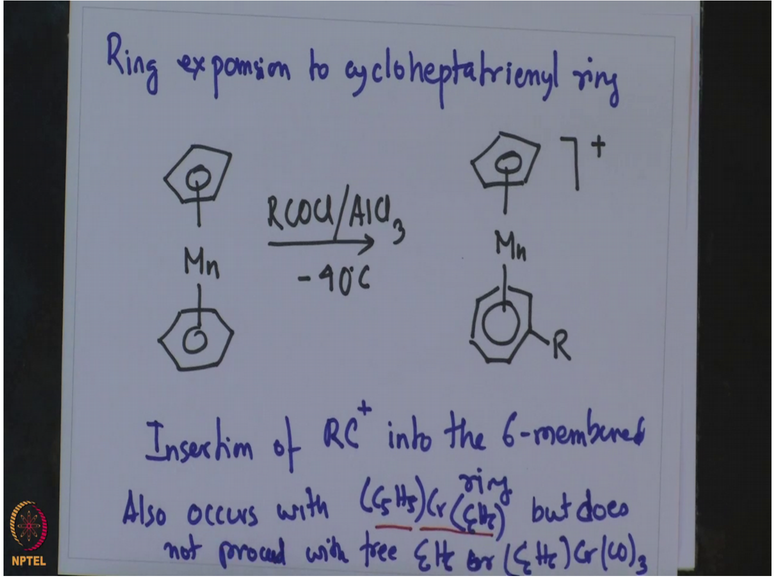

Ring expansion to cycloheptatrienyl ring

Insertion of RC^+ into the 6-membered ring

Also occurs with $(C_5H_5)Cr(C_6H_6)$ but does not proceed with free C_6H_6 or $(C_6H_6)Cr(CO)_3$

This is a interesting reaction as can be seen over here that manganese is bound to two different rings one is cyclopentadienyl ring and benzene ring. Now treatment of this with RCOCl in presence of AlCl 3 at -40 degree centigrades leads to the expansion of the six membered ring to produce a seven membered ring as is shown over here. Now the mechanism of this reaction is not clear but what is evident is insertion of RC+ into the 6 membered, benzene ring.

Now this reaction also occurs with the chromium derivative C 5 H 5 chromium C 6 H 6 but does not proceed with free benzene or C 6 H 6 Cr CO 3, so this reaction is kind of an interesting reaction in which cyclopentadienyl manganese benzene ring gets extended by treatment to a 7 membered ring by treatment with RCOCl with AlCl 3 at -40 degree centigrade resulting in CP manganese 7 membered ring with substituted our cationic species.

Now the mechanism of this insertion though not clear but what is evident is that insertion of RC + actionn into the 6 membered ring takes place and this reaction is not only limited or restricted to this CP manganese benzene compound. But can also be effectively used for another such complex which is CP a chromium benzene compound but cannot be used in case of free benzene or with benzene chromium tricarbonyl so this is an interesting reaction in which one can obtain the cyclopentadienyl metal arene kind of complex.

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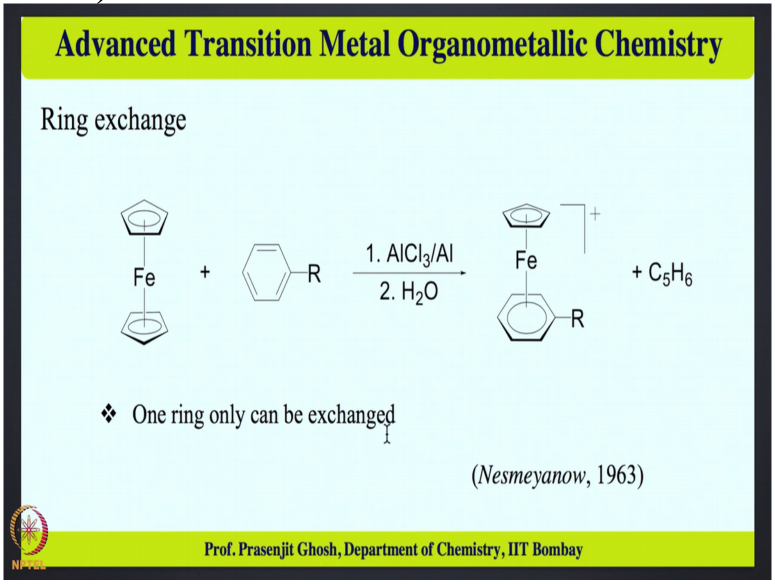

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Ring exchange

- One ring only can be exchanged

(*Nesmeyanow*, 1963)

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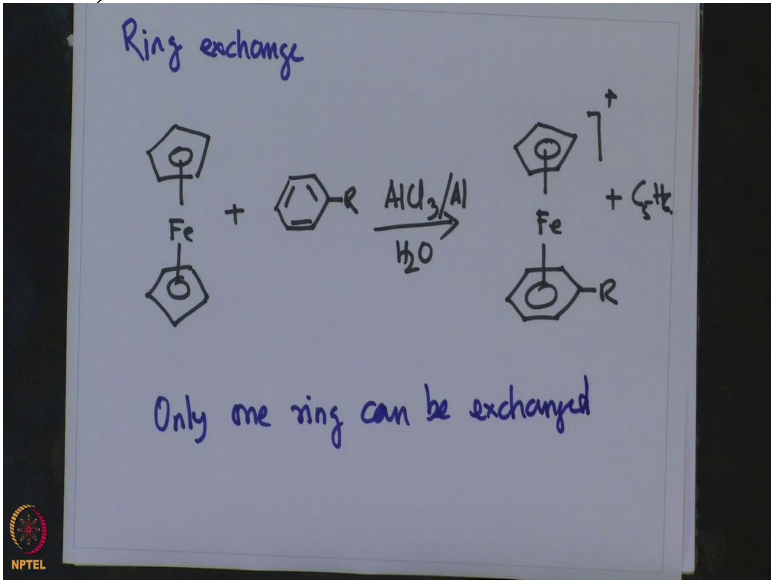

Ring exchange

Only one ring can be exchanged

We are going to take a look at some more reactions to this effect another reaction involves just simple ring exchange and this is seen in this beautiful example involving reaction of ferrocene + arene in presence of AlCl 3 and aluminum followed by water work up resulting in exchanger of one of the CP rings with the arene rings giving this cationic iron complex + C 5 H 6 and the notable feature is that only one ring can be exchanged and cannot be exchanged 2 bis-arene complexes.

So, only one of the cyclopentadienyl ring of these arene ferrocene complex can be exchanged in this ring exchange method. So, what we see so far that there is a wide variety of synthetic techniques that are available for preparing this mixed CP arene complexes and the first one first one obviously involved the simple reaction of taking metal halide with a source of CP a and the arene as a nucleophile.

But the problem with that synthesis was that the yields were very low despite that was probably the direct route of obtaining these compounds. The second method that we had same involved the expansion of being a six membered ring and this we had seen by treatment of CP manganese benzene with RCOCl and AlCl3 led to the expansion of the 6 membered ring to give this cationic CP metal substituted 7 membered ring species.

The third that we had reviewed involved ring exchange in which the ferrocene was treated with an arene and one of the CP rings were exchanged to give this cyclopentadenyl arene compounds.

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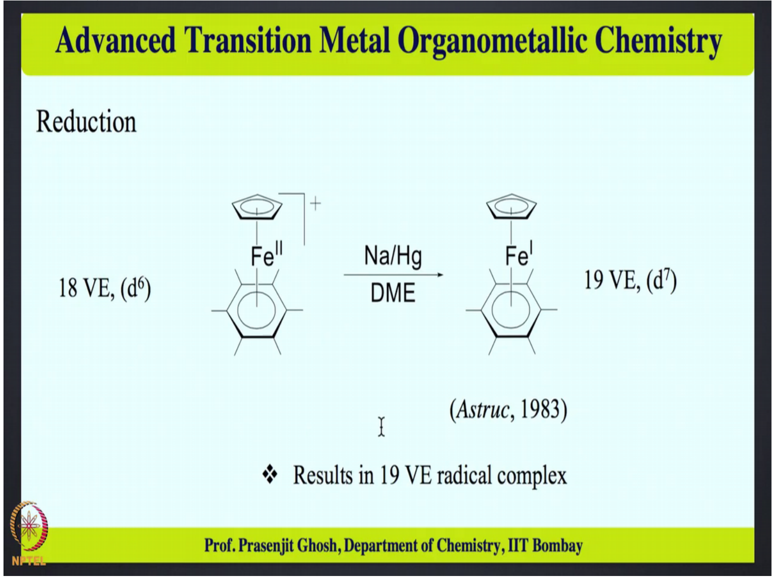

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Reduction

(*Astruc*, 1983)

❖ Results in 19 VE radical complex

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So, another involves the reduction of this cyclopentadienyl iron benzene compounds to form the corresponding 19 electron species which as expected is are radical.

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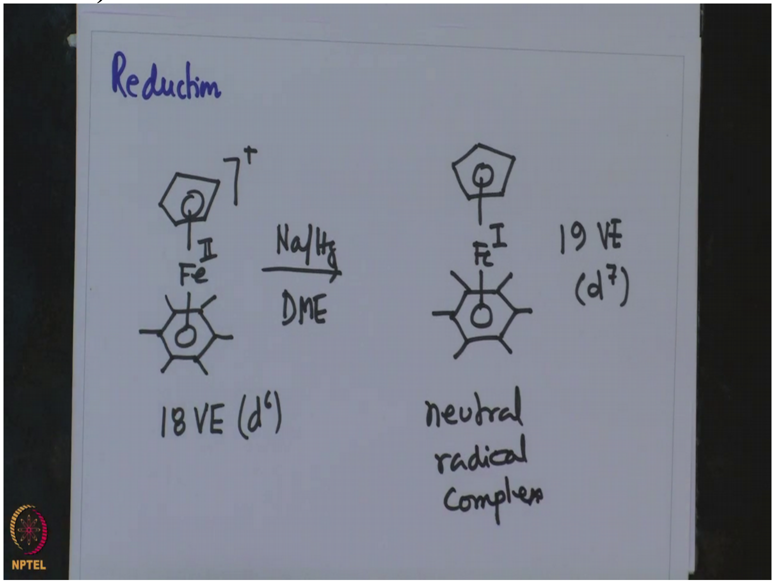

Reduction

So, CP Fe hexa methylbenzene it is a cationic compound when produced with sodium mercury in DME giving this is a 19 valence electron compound d 6 giving the corresponding neutral 9 electron species 19 valence electron d 7 and this is a radical complex neutral. So, this one particular one is a nice example in which one can obtain these 9th electron radical complex of cyclopentadienyl hexa methyl benzene iron by a just simple reduction of another cyclopentadienyl hexa methyl benzene iron - cationic complex by using sodium amalgam in DME.

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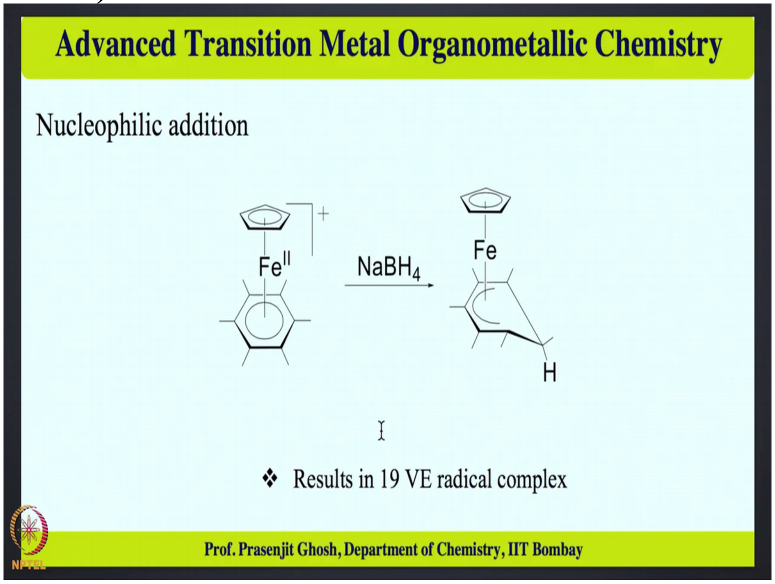

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Nucleophilic addition

❖ Results in 19 VE radical complex

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Similarly the reduction of nucleophiles lead to cyclohexane dienyl complexes.

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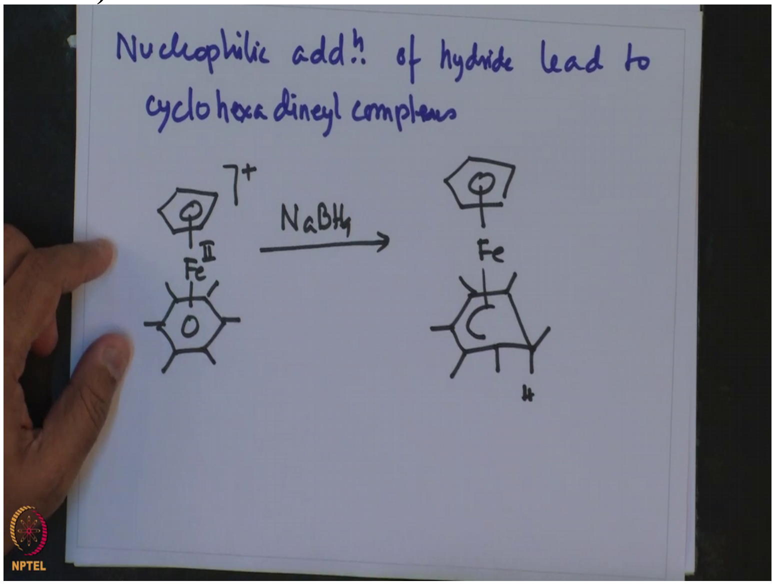
Nucleophilic add^n. of hydride lead to cyclo hexa dineyl complexes

Similarly the nucleophilic addition will lead to addition of hydride lead to cyclo hexa Dienyl complexes. Now this is interesting reaction in which the same complex CP iron 2 hexa methyl benzene is react a cationic complex he is reacted with sodium borohydride and then the hydride goes and attacks at the ring giving rise to these neutral complex. The way it is shown here and which sort of illustrates that the addition of addition of this hydride goes on to attack at these extra methyl benzene ring.

So, far what we had seen that in case of the mixed cyclopentadienyl arene complexes the ring expansion happened at the arene ring whereas the nucleophilic addition to occurred at the arene ring. Whereas a simple reduction with sodium amalgam that only affected the middle center which got reduced from +2 oxidation state to a +1 oxidation state in the previous example.

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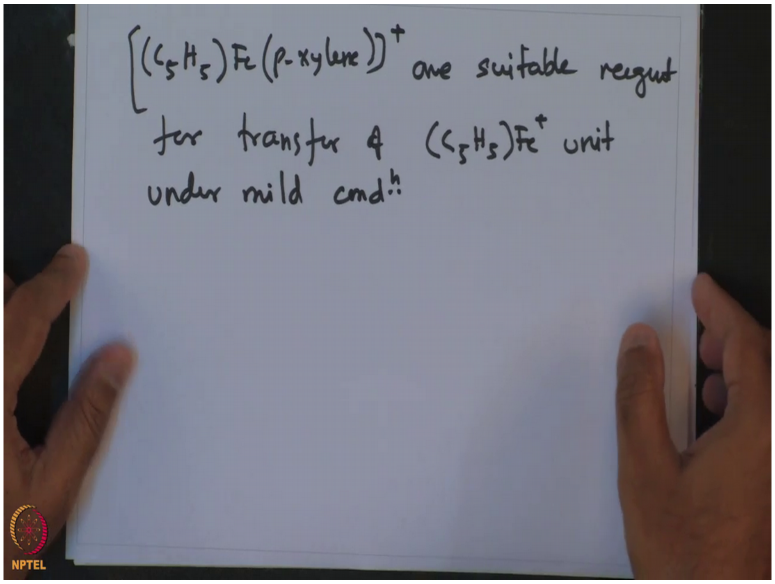

$[(C_5H_5)Fe(p\text{-xylene})]^+$ are suitable reagent for transfer of $(C_5H_5)Fe^+$ unit under mild cond^n

So, for complexes like this C 5 H 5 Fe para xylene + are suitable reagent reagent for transfer of C 5 C 5 H 5 Fe + unit under mild conditions;

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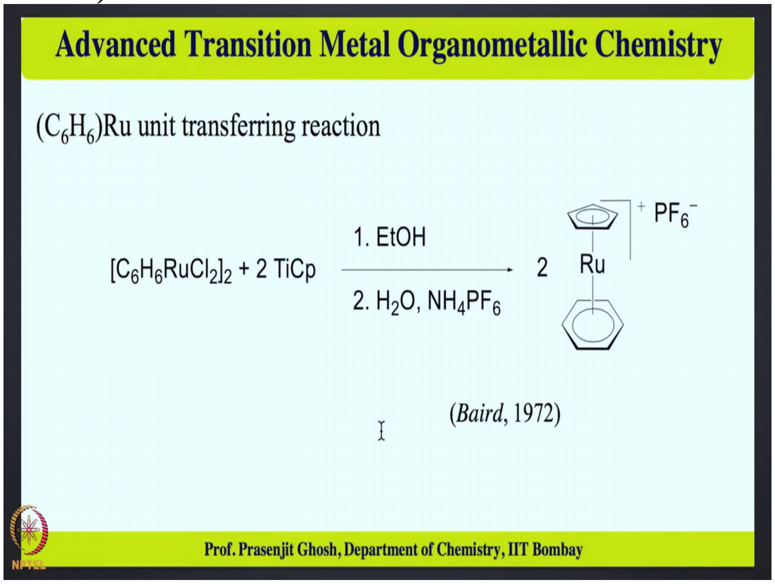

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(C_6H_6)Ru unit transferring reaction

$$[C_6H_6RuCl_2]_2 + 2\ TiCp \xrightarrow[2.\ H_2O,\ NH_4PF_6]{1.\ EtOH} 2$$

(Baird, 1972)

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Here is an another interesting example in which a ruthenium dimer was reacted with thallium CP a to form this mixed CP ruthenium benzene complex and this C 6 h 5 ruthenium unit was transferred from its dimer it complex.

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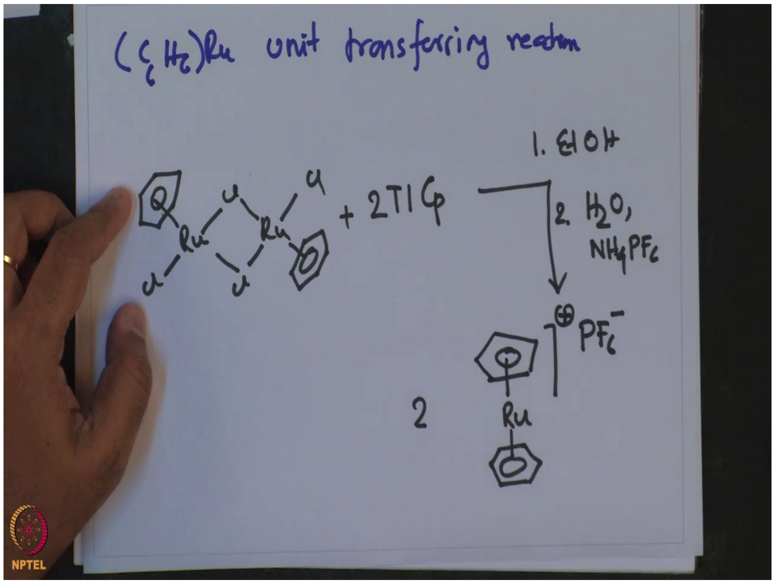

So, we are going to see an example of along the same line C 6 H 6 ruthenium unit transferring reaction. So, this is beautifully illustrated by this example of ruthenium benzene chloro dimer when treated with two talium CP in ethonal and 2 water NH 4 PF 6 then 2 units of this desired CP ruthenium benzene + PF 6 - compound is formed so this is a interesting example where one can see this CP ruthenium unit gets transferred from this dimeric complex by treatment with thallium CP resulting in the CP ruthenium arene cationic complex of the type shown over here.

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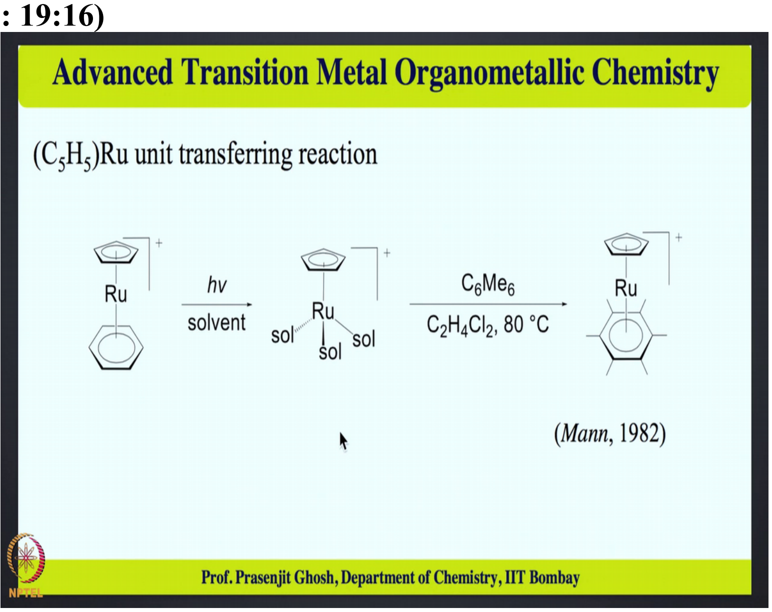

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(C_5H_5)Ru unit transferring reaction

(*Mann*, 1982)

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Now this ruthenium CP unit these compounds ruthenium CP benzene cationic compounds are photo the photo labile and forms solvents.

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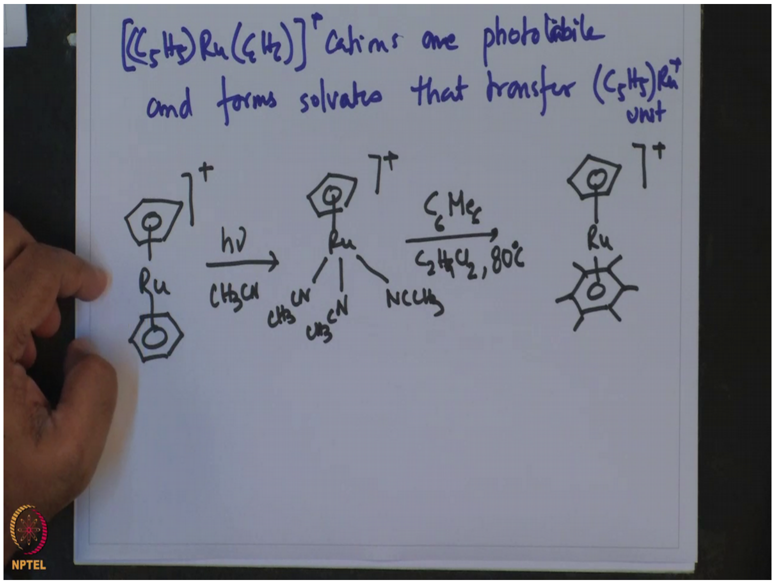

$[(C_5H_5)Ru(C_6H_6)]^+$ cations are photolabile and forms solvates that transfer $(C_5H_5)Ru^+$ unit

So, one interesting property of this is this C 5 H 5 Ru C 6 H 6 + cations are photo libile and from solvents that transfer for the C 5 H 5 Ru + unit this is beautifully example exemplified provided in the example we ran over here where you have CP ruthenium benzene + in presence of H Nu in acetonitryl giving ruthenium Cn and complex.

And that in presence of hexa methyl benzene C 2 H 4 Cl 2 solvent at 80 degree centigrade gives the desired ruthenium benzene complex. So, one can see that these compounds can be used particularly the CP ruthenium benzene cationic compounds can be used as a source of CP ruthenium cation unit transfer and that is affected by a light in which the benzene ring falls apart and then the vacant site is occupied by dative solvents like acetonitride and subsequently a react treatment of that solvated ruthenium CP cationic species with arenes gives this ruthenium arene, arene CP a cationic compound.

So, this is an interesting example whereby one can make these mixed arene CP metric metal complexes. Another example involves abstraction successive elimination of two hydride ions lead to the formation of such kind of CP a metal arene complexes.

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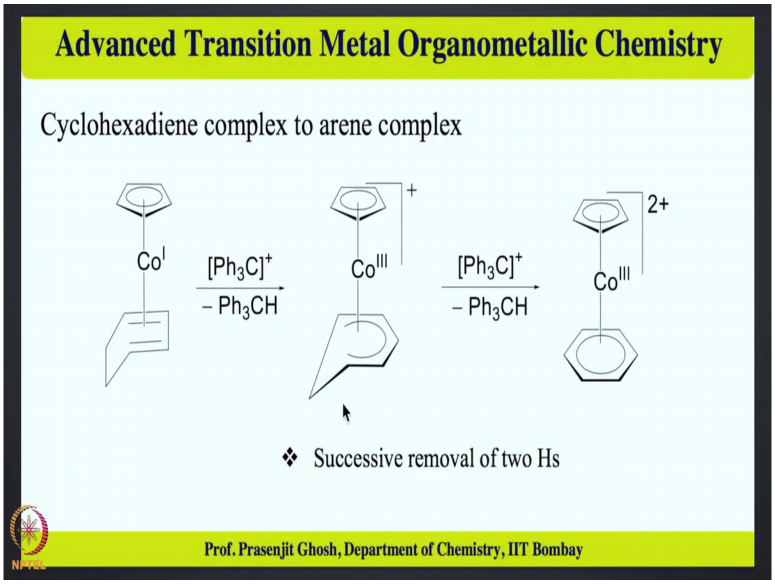

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Cyclohexadiene complex to arene complex

❖ Successive removal of two Hs

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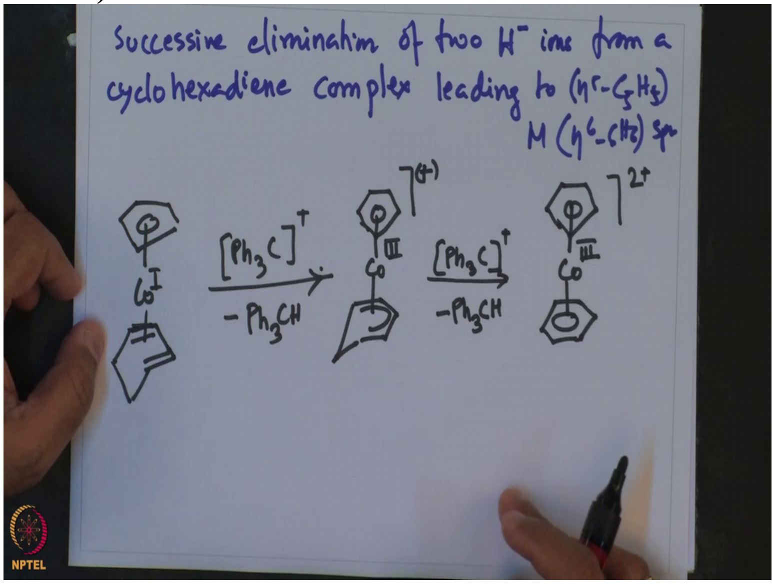

Successive elimination of two H^- ions from a cyclohexadiene complex leading to $(\eta^5\text{-}C_5H_5)$ $M(\eta^6\text{-}C_6H_6)$ sp.

So, this is another very interesting example that involves successive elimination of 2 hydride ions from cyclohexadyne complex leading to to the formation of the eta 5 C 5 H 5 M eta 6 C 6 H 6 species. So, this is beautifully a example shown in this cobalt compound cobalt that the hydride abstraction is affected by triphenyl fatale cation triphenyl carbon cation which gives Ph 3 CH giving CP this is cobalt 1 cobalt 3 followed by second abstraction.

Again by the same reagent minus giving CP cobalt 3 so this after abstraction it becomes mono cationic species and after the second abstraction it becomes even di cationic species and the desired cobalt 3 cyclo pentadienyl benzene 6 complex. So, this is a interesting approach where hexa diene can was converted to arene by abstraction of two of the hydrogen sitting hydrogen’s using total cation.

Let me just reiterate here that we had seen the reverse of it when just a few examples back when we had seen that the iron arene arene complex when treated with sodium borohydride led to the formation of this hexadiene where the hydride nucleophile attacked on the ring. So, just exactly opposite of what we have been talking about over here was discussed a couple of examples back where the reduction was a ring reduction was carried out with sodium borohydride.

And in the present case that hexadiene is converted by abstraction of the hydride with metal cation to give the metal arene complex and in the earlier example a metal arene moiety was converted to metal hexadiene complex by reduction with sodium borohydride where the hydrate attacked the metal bound arene ring. So, what we come across right now is just two opposing reaction which was discussed back to back into to show the type of versatility that one can get in these methods that we have been discussed discussing.

So, with that we would like to talk about stop today's conclude today's lecture which had primarily been on various methods that are available for preparing this transition metal cyclo pentadienyl arene complexes and among the things that we have discussed the one that stands out the most is that these compounds are probably the most versatile in terms of the synthesis is concerned because we have discussed a second different approaches that were involved in the preparation of this complex that you started start with.

We discussed the conventional approach where one can start thinking about preparing this mixed ligand compound by taking the metal halide and each of the ligand nucleophile and then the problem of that method was that these were very low in ending and there were also side products however they could give rise to the desired mixed cyclopentadienyl benzene type of complexes. The next method in this today's discussion was the ring expansion method.

Where we saw that the ring of a metal cyclo pentadienyl benzene or arene ring was expanded from a 6 membered arene to a 7 membered arene by the treatment with RCOCl in presence of LCL 3, so this ring expansion method also is a very unusual method in which a 6 membered metal bound ring was converted to a 7 member metal bound ring and whereas the 5 membered metal bound ring remained intact the third approach that we had spoken about involved the displacement of one of the cyclopentadienyl ring and with another 6 membered benzene ring.

And this example looked into the reaction of ferrocene with total reagent in which one of the CP ring got discarded displaced replaced by another benzene ring. The next we discussed was just the formation of by reduction the simple reduction the formation of 19 electron species in which cationic iron CP benzene complex was treated with sodium mercury amalgam to make this 19 electron neutral iron CP benzene compounds.

We had also seen same that the treatment of the same cationic iron CP a benzene ring with sodium borohydride led to the formation of of these hexadiene bound iron cyclopentadienyl complex. We are also seen that the reaction of of benzene ruthenium chloride dimer in presence of thallium CP gives this mixed thallium CP benzene ruthinium benzene compounds. And lastly we had also seen two examples in which one can see the cyclopentadienyl ruthenium benzene a catana compound being photo lab photolabile.

And also form solvate can be used to make this mixed cyclopentadienyl benezene complexes and last person of the list we have also seen that if one can starts with a metal hexadiene CP compound by suitable abstractions of the hydride one can go to the target CP benzene cobalt 3 di cationic compounds. So, what comes to the fore is the fact which I have already mentioned that these compounds have a quite a bit of versatility in terms of the synthetic methods that are available towards their synthesis.

So, I am going to discussed about 6 or 7 of them in today's lecture I am going to continue further look further in the next few lecture next lecture and see why makes these compounds so unique in terms of being the synthetic targets. We are going to also be looking at the reactivity and the structure and bonding and reactivity of these complexes in the next lecture and so I thank you for being with me in this lecture and also look forward to taking up this topic in bit more detail.

In next lecture where we finish off with the synthesis and look into the structural reactivity of this cyclopentadienyl transition metal arene complexes till then thank you and good bye.