

**Advanced Transition Metal Organometallic Chemistry**  
**Prof. Prasenjit Ghosh**  
**Department of Chemistry**  
**Indian Institute of Technology-Bombay**

**Lecture – 27**  
**Transition Metal Arene Carbonyl Complexes: Reactivity**

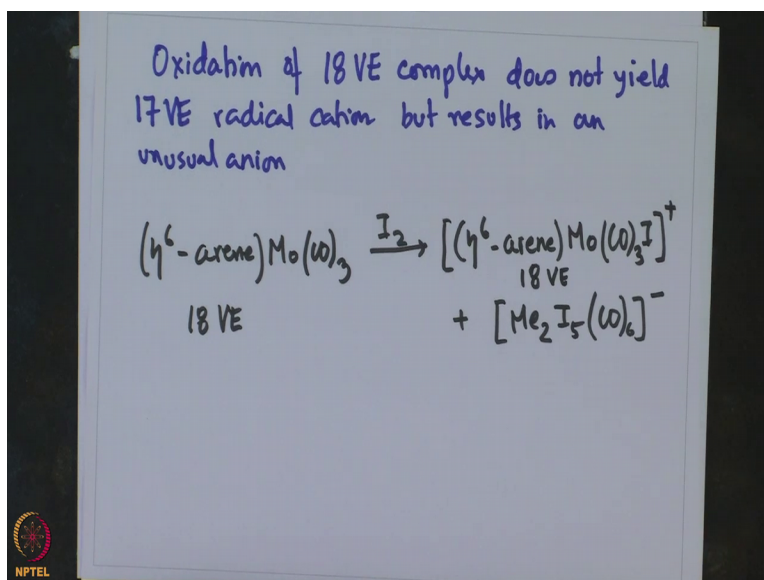
Welcome to the course on advanced transition metal organometallic chemistry, we have been discussing transition metal arene carbonyl complexes. These are half sandwich complexes and also have different kind of different reactivity as well as structure and bonding. In with respect to these transition metal arene carbonyl complexes we have looked at structures they exhibit which can be a the conventional eta 6 mononuclear metal carbonyl complexes to that of it a 2 bound di nuclear metal carbonyls are eta 2 bound tri nuclear metal carbonyl complexes.

We have also looked into the reactivity pattern of these arene metal carbonyl complexes and what we had discussed is the fact that electrophilic substitution reactions do occur but occur at a slower rate as compared to that of free arene's and this has been attributed to the inductive effect of the metal carbonyl bound to that in arene ring in as opposed to the electrophilic substitution reactions. The nucleophilic substitution reactions however are more facile for these are in metal carbonyl complexes.

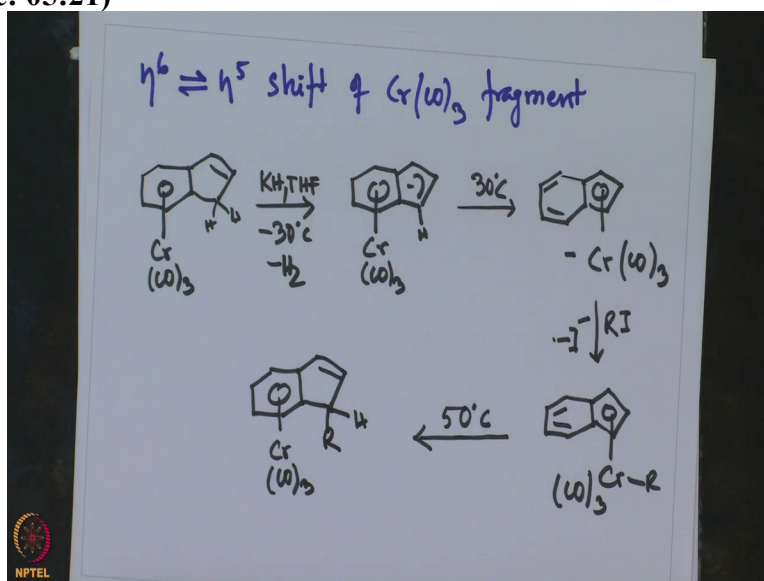
The nucleophile attacks on the link from an extra fashion resulting in the loss of aromaticity followed by the loss of the leaving group from the endow site which we had taken a looked at the example for which the endow loss of the chloride ligand was the regular meaning step of these reaction. We have also seen as a part of this reactivity that these arene metal carbonyl can also be substituted by Sigma donor Pi acidic ligands at elevated temperature.

Continuing further along our discussion on this metal carbonyl arene complexes we look at the oxidation reaction that usually is observed. Now this oxidation reaction is kind of unusual in the sense that oxidation of 18 valence electron compound does not result in an oxidize 17 electron species but instead produces an 18 valence electron compound with a different anion and I will sort of explain that with this example over here.

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So, oxidation of 18 valence electron complex does not yield 17 valence electron radical cation but results in an unusual anion and this is illustrated by the example over here eta 6 arene molybdenum tricarbonyl which is a 18 VE complex with iodine giving eta 6 arene molybdenum tricarbonyl iodide plus and a corresponding anion which is a Me 2 I 5 CO 6 anion. So, this is an interesting example that gives that the oxidation does not lead to the usual 17 valence electron radical cation but results in a very unusual kind of anion which is shown over here.  
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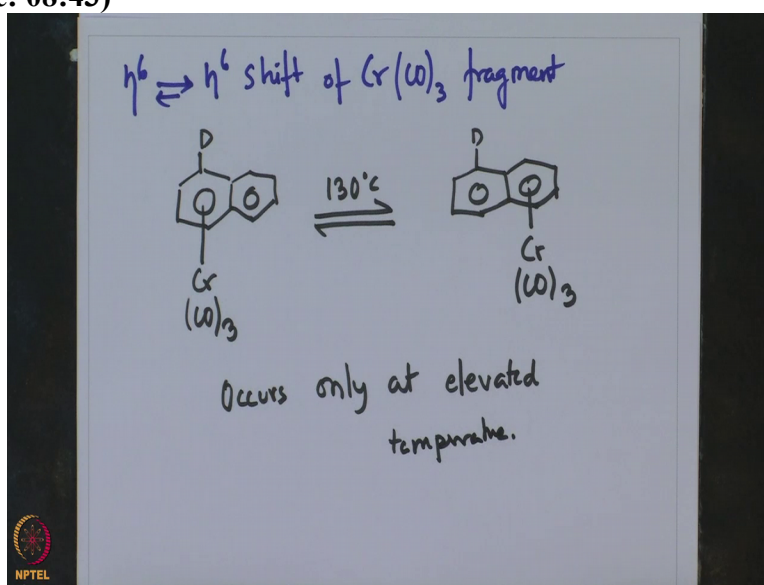
Now the other interesting the activity is a shift of eta 6 to eta 5 hapticity and so that this example would involve eta 6 to eta 5 shift of chromium tricarbonyl fragment and this is beautifully explained in this reaction CH 2 chromium CO 3 reacting with K 8 THF -30 degree centigrade eliminates hydrogen to give this benzene ring bound chromium CO 3 and this anion which came

30 degree centigrade undergoes the shift to give eta 5 bound chromium CO 3 minus which in presence of RI eliminates I minus giving the calculated chromium R CO 3 that at 50 degree centigrade.

You know goes gives back the original eta 6 bound chromium carbonyl R. So, what is observed over here is that it is a demonstration a beautiful demonstration of eta 6 bound arene chromium carbonyl compound giving rise to eta bound by species and then it again goes back to eta 6. So, this is eta 6 to eta 5 and then back to eta 6 the way the conversion very nice example is shown over here.

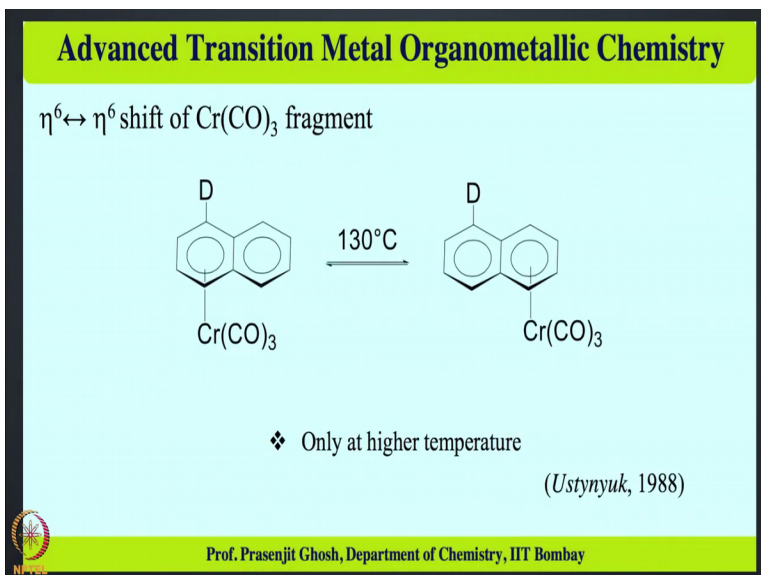
Another such it of shift involves going from one eta 6 ring to the other eta 6 ring. So, the previous one was going from eta 6 to eta 5 back and forth and the subsequent example that we would see would involve shifting from eta 6 to eta 6.

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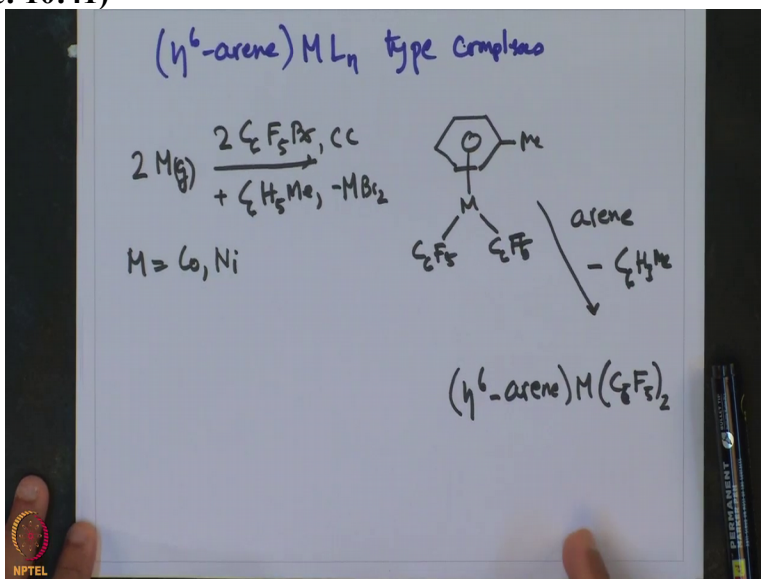


So, this is eta 6 to eta 6 shift of chromium eta 6 to eta 6 shift of chromium tricarbonyl fragment and this is beautifully illustrated by the example over here. If one of the benzene is deuterated chromium carbonyl at 130 degree centigrade giving deuterated chromium carbonyl. Now this shift from one of the ring to are there only occurs at elevated temperature.

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Now you know here is another two interesting reactions which are widely spoken about metal in complexes. And these can be of metal arene  $\text{L}_n$  type of complexes.  
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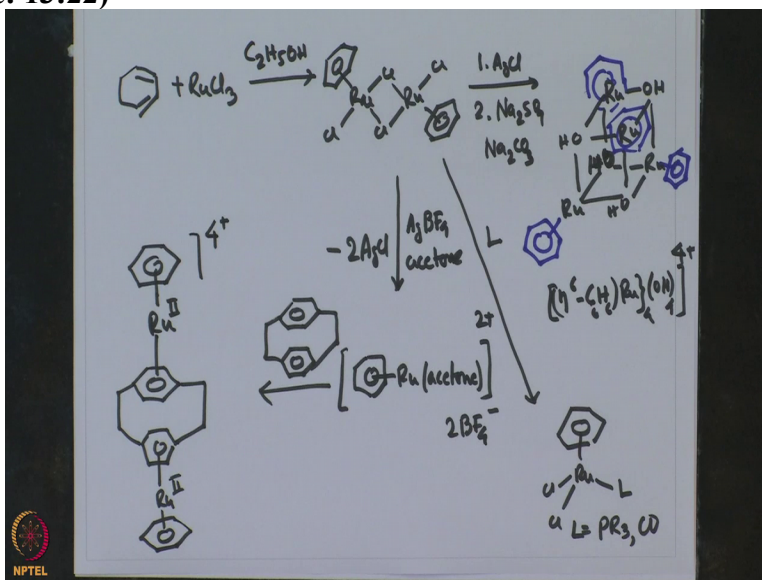
So, these are of the type eta 6 arene metal  $\text{L}_n$  type complexes and some of the two such examples are given over here the first involved preparation of these complexes from let us say magnesium in presence of two  $\text{C}_6\text{F}_5\text{Br}$  and this was co-condensation method in presence of  $\text{C}_6\text{H}_5\text{Me}$  then  $\text{MBr}_2$  is lost giving rise to this benzene substituted metal  $\text{C}_6\text{F}_5$  ligand type complexes and  $\text{M}$  = cobalt and nickel.

So, this is the co-condensation method involving  $\text{Me}$  in the gaseous state with Penta fluoro benzene bromide in presence of methyl benzene leading to the formation  $\text{MBr}_2$  and this allyl di allyl complex which sort of in presence of arene loses the benzene to give eta 6 arene metal  $\text{C}_6\text{F}_5$

C<sub>6</sub>F<sub>5</sub> whole 2 type complex. So, one can see that the co-condensation method or metal vapor synthesis method is successfully is used in synthesizing arene eta 6 arene and C<sub>6</sub>H<sub>5</sub>Br Ln type complexes.

So, here is an interesting example another very interesting example we are going to be talking about that can be used for preparing wide variety of complexes.

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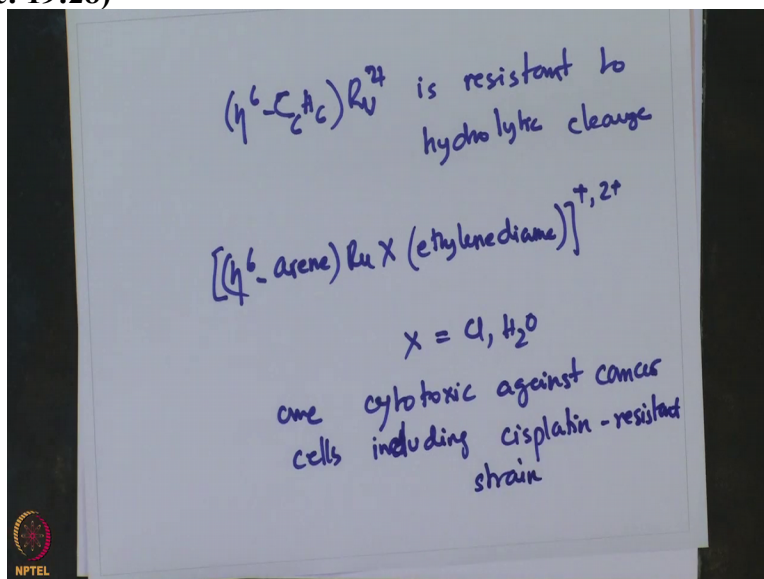


And one such reaction is the reaction of these cyclohexadiene + ruthenium tri chloride in presence of ethanol gives this dimeric compound that with silver chloride and Na<sub>2</sub>SO<sub>4</sub> and sodium carbonate giving this compound this is a ruthenium tetrameric hydroxyl compound bridging hydroxyl on each of this ruthenium this is a OH and each of this ruthenium is bound to 4r benzene rings that is 1, 1 over here and this 1 is bound to 1 benzene ring and this ruthenium is bound to another benzene ring.

So, this gives this tetrameric compound which can be written as eta 6 C<sub>6</sub>H<sub>6</sub> ruthenium 4 OH whole 4 4+ so this is a interesting Q bend kind of compound. The reaction of these two ruthenium dimer with L produces breaks the dimer and the produce is the corresponding monomeric compound L can be PR<sub>3</sub> CO. If one abstracts the halides with AdBF<sub>4</sub> acetone then twice AdBF<sub>4</sub> results and one gets a interesting acetone adduct of this compound 2 + 2 BF<sub>4</sub><sup>-</sup> which reacting with cyclophane gives Bis-arene dinuclear compound interesting dinuclear compound bis-arene kind of the dehydrated mixed cyclophane benzene ruthenium compound 4+.

And what one says that these arene ruthenium Ln kind of complexes can be used to produce wide variety of interesting compounds not only in terms of formulation but also in their leach structure and diversity. And one can see these tetrahedra oxide cubed ruthenium tetramatic structure or the monomeric ruthenium halide phosphine compounds or this interest in ruthenium acetone adduct with this this huge mixed be serene cycle of in benzene kind of dinuclear ruthenium compound.

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So, this is really some very interesting chemistry exhibited by this compound and one thing which comes to the fore is the fact that these ruthenium di cationic species  $\text{C}_6\text{H}_6\text{Ru}^{2+}$  is he is resistant to hydrolysis hydrolytic cleavage and because of which you know or these kind of complexes ruthenium complexes have been found to be a very cytotoxic in nature. So, they have anti-cancer activity a because they do not get hydrolyzed.

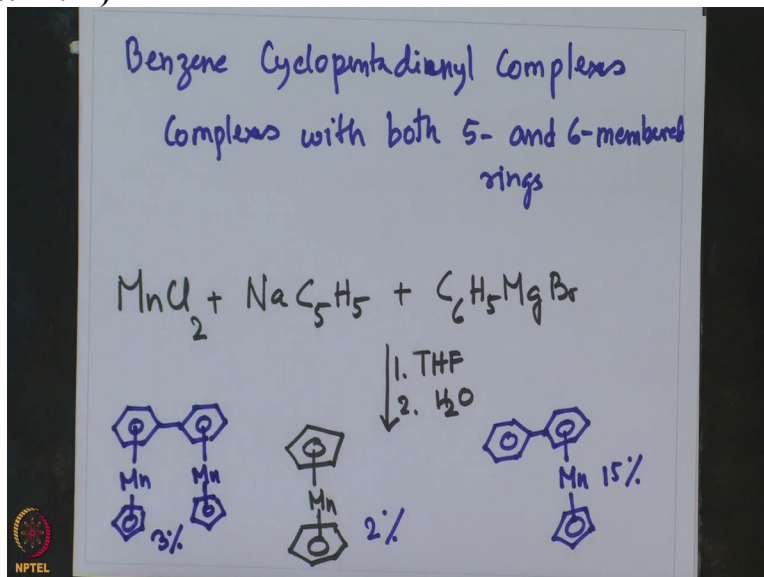
And this one such compounds which is eta 6 arene ruthenium X ethylene diamine + or 2 + okay X can be chloride or water or cytotoxic against cancer cells including the cisplatin resistant strength. So, this is a wide very interesting application of ruthenium eta 6 arene complexes that they not only can form interesting structures but they have also because of their resistance to hydrolysis they have found used as very good anti-cancer agents and not only that they are also quite active against the ones which are which is cisplatin later on the becomes ineffective or these ruthenium compounds are active against cisplatin resistant strain as well.

So, with these we are going to just briefly finish upon the structure our discussion on arene metal Ln type complexes and we move on to something which are more interesting or more intriguing



and these are hetero elliptic bis-arene transition metal complexes to be more precise we are going to be now talking about benzene cyclopentadienyl complexes. So, eta 6 out of eta 5 bound hetero elliptic these are kind of complexes.

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So, the next few minutes of this lecture would be dedicated to benzene cyclopentadienyl complexes and these are complexes with both five and six membered frames this is beautifully illustrated by reaction  $\text{MnCl}_2 + \text{NaC}_5\text{H}_5 + \text{C}_6\text{H}_5\text{MgBr}$  reacting with THF 2 water to give  $\text{CpMnC}_6\text{H}_6$ . So, the thing which is notable of this fact is that the yield of the reaction the yield of the reaction is only a 2% and the major product formed in this reaction is biphenyl  $\text{Mn}(\text{C}_5\text{H}_5)_2$ , so the major product is biphenyl  $\text{Mn}(\text{C}_5\text{H}_5)_2$  which is about 15%.

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**Advanced Transition Metal Organometallic Chemistry**

Benzene Cyclopentadienyl Complexes

- ❖ Complexes with both five and six membered ring

$$\text{MnCl}_2 + \text{NaC}_5\text{H}_5 + \text{C}_6\text{H}_5\text{MgBr} \xrightarrow[2. \text{H}_2\text{O}]{1. \text{THF}} \begin{array}{c} \text{Cp} \\ | \\ \text{Mn} \\ | \\ \text{C}_6\text{H}_6 \end{array} \quad 2\%$$

- ❖  $(\text{Biphenyl})\text{MnCp}$  is the other product (15%)

Prof. Prasenjit Ghosh, Department of Chemistry, IIT Bombay

And there are several other byproducts of the reaction one is this biphenyl bis-arene manganese cyclopentadienyl so that is 3%, so that is also a very interesting compound biphenyl manganese CP is 3% okay. So, one thing which comes out that in this method all possible compounds are formed and the compounds which are of the interest the desired compound is formed only in 2% and there are other compounds for example biphenyl manganese CP 15% or biphenyl biphenyl dinuclear manganese-manganese CP-CP only a 3% can be formed.

So, these reactions can also be used for making the chromium complex but here also the corresponding chromium complex by the same method which gives benzene chromium cyclopentadienyl this is a 17 valence electron compound and by this method this is formed is or informed in only a 3%. So, this method even though it produces the desired compound but what is evident from here that the yield of the reactions are indeed very little which can be about 2 to 3%.

So, now with these I would like to draw a conclusion on today's lecture particularly if we have looked at the reactivity of transition metal arene complexes. And to begin with we have looked into these 3 new kinds of reactions the first one being the oxidation reactions of arene transition metal carbonyl complexes and what we had seen that it does not really give the desired one electron oxidation given the same thing one electron species.

But forms an unusual counter anion of molybdenum then we had taken two other examples where we had seen a reversible shift from  $\eta^6$  to  $\eta^5$  hapticity in arene systems where it goes from a six membered heading to a five membered ring. And then we had seen another example where it went from six membered ring to another six membered ring under elevated temperatures.

In addition to that we have also looked into other types of transition metal arene  $L_n$  type of complexes and these we have looked at from perspective of two reactions and the first one being the formation of these complexes which leads to arene metal Bis  $C_6F_5$  type complexes. And the next one we have seen are the reactivity of arene metal halide kind of complexes. And what we can see is that these complexes depending on the reagents used and the halide abstractions taken and this can they can give rise to many other interesting compounds.



For example we had looked into new at the cube and type a hydroxyl bridge a diene ruthenium tetramer and also we had looked into these mixed cyclopentadiene arene mixed dinuclear ruthenium complexes. We have also discussed that these arene ruthenium species are resistant towards solvolysis and because of which have been exploited in making very good cytotoxic compounds that not only was cytotoxic against cancer cell lines but also against flattened resistant cell lines.

Now we have finished in this lecture on this arene transition metal carbonyl as well as L type complexes and then moved on to discuss these new types of benzene cyclopentadienyl complexes and we have looked into the first synthetic method. And what we saw that these method is not very selective and also very poor yielding in terms of the desired compound which could only be isolated in about 2 to 3% yield in presence of other mixtures which were up to 15% yield.

So, this speaks about the challenges in isolating this kind of mixed Hetero elliptic transition metal bis-arene type complexes. So, more of their synthesis and further discussion will come up in next lecture and I thank you for being with me in this lecture and hope to discuss this in more details when we take up this topic in next lecture, till then thank you and good bye.