Advanced Transition Metal Organometallic Chemistry
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Lecture – 30
Transition Metal C 7 H 7 Complexes: Preparation

Welcome to this course on advanced transition metal organometallic chemistry in continuation with our discussion on transition metal complexes of various ligands starting from procanol to butadiene to cyclobutadiene then moving on to cyclo pentadienyl as well as then we spoke about hexane benzene complexes arene complexes to C 7 H 7 or 7 membered ligands ring ligand systems that we are talking about in the last few lectures.

So, in these connections not only we have looked into the homo these arene kind of complexes but also the various heterolytic and combinations in which there is a two different arene rings which can be a 5 membered 7 membered 6 membered 5 membered 7 membered 6 membered and we have looked at all these combinations of various transition metal arene kind of complexes. So, in continuation with our previous discussion on C 7 H 7 ligands what we had seen is that this transition metal forms a wide variety of complexes with C 7 H 7 ligands.

Not only with C 7 H 7 ligands but also with C 7 H 8 ligands and we have looked into some of the complexes their classifications with respect to being the sandwich or half sandwich types. And then in the last lecture we have also discussed about the preparations of this transition metal C 7 H 7 complexes. Now proceeding further along the line in this lecture too we are going to be taking up this topic on various other preparative methods that are available for this synthesis of the transition metal C 7 H 7 complexes.

And then we are going to be talking about reactivity and structure related studies of this transition metal C 7 H 7 complexes. So, coming back to synthesis we are going to be talking about another interesting method which involves the substitution of C 7 H 7 benzene ring by C 7 H 7 range.

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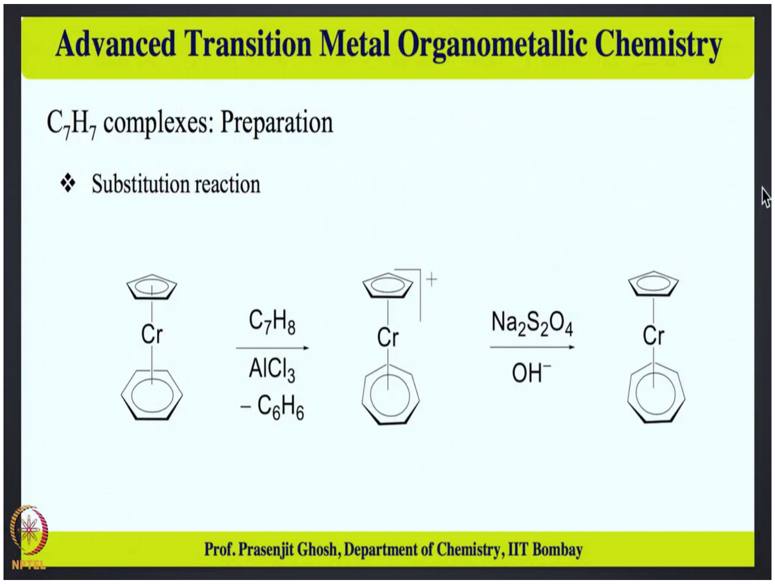

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C_7H_7 complexes: Preparation

- Substitution reaction

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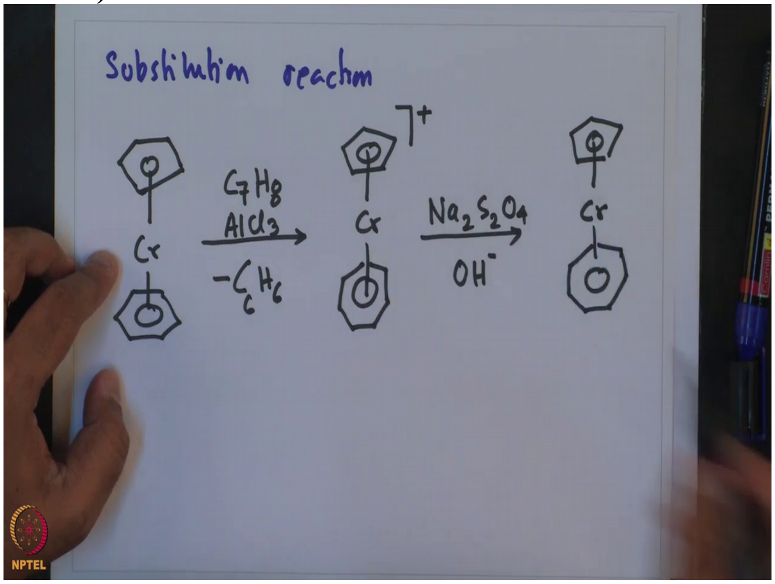

So, this is substitution reaction and this is beautifully illustrated in these particular examples in which there is a chromium C 7 H 8 Al Cl 3 – C 6 H 6, so this arene ring gets substituted or replaced by this C 7 H 8 ring to give this cationic chromium complex that with Na 2 S 2 O 4 and which minus gives the corresponding neutral complex. So, actually what is happening over here is the reduction of chromium over here to chromium 2 over here is observed. So, this is the reduction happening at the metal.

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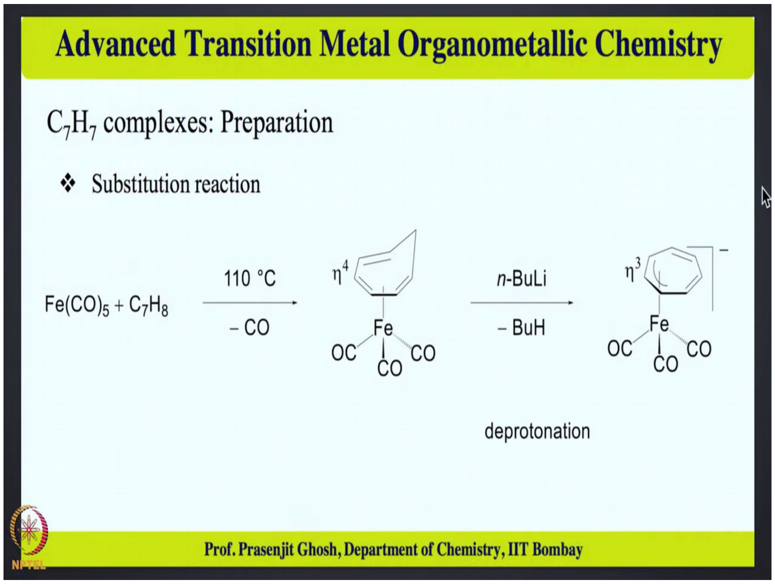

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The next reaction for this involves again another kind of substitution reactions in which a carbonyl of iron carbonyl compound gets substituted with a C 7 H 8 ligand.

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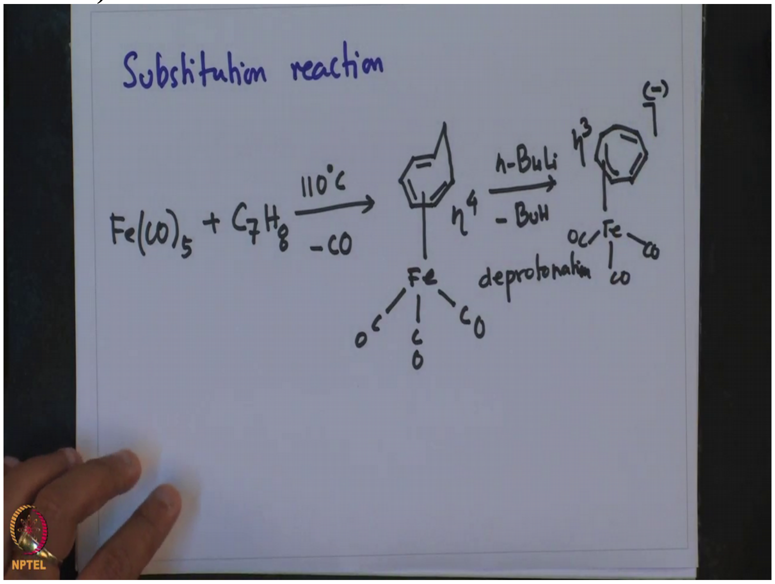

So, the reaction is given over here Fe CO 5 + C 7 H 8 upon heating 110 degree centigrade eliminates a CO give these C 7 H 8 complex and which is bound in eta 4 fashion to a Fe CO 3 that when treated with an butyllithium gives butane and this deprotonation happens in one of the hydrogens of this ring deprotonation to give this eta 3 Fes CO complex. So, the; and this overall after deprotonation becomes anionic complex.

So, there is a lot of scope or varied reactivity of substitution reactions where we had seen that C 7 H 7 or C 7 H 8 can successfully replace a carbonyls of metal carbonyls particularly we have seen that happening in case of vanadium as well as iron carbonyl. And we had also seen that C 7

H 8 can replace the arenes in mixed CP a chromium benzene kind of complex as well as in benzene vanadium CO 4 as our CP vanadium CO 4 kind of complexes.

So, the substitution reaction is suitable not only for metal having carbonyls but also the metal bound to arene moieties. So, we are going to be looking at another new type of reactions these are called reductive complex station which are also used for making these C 7 H 7 type complexes.

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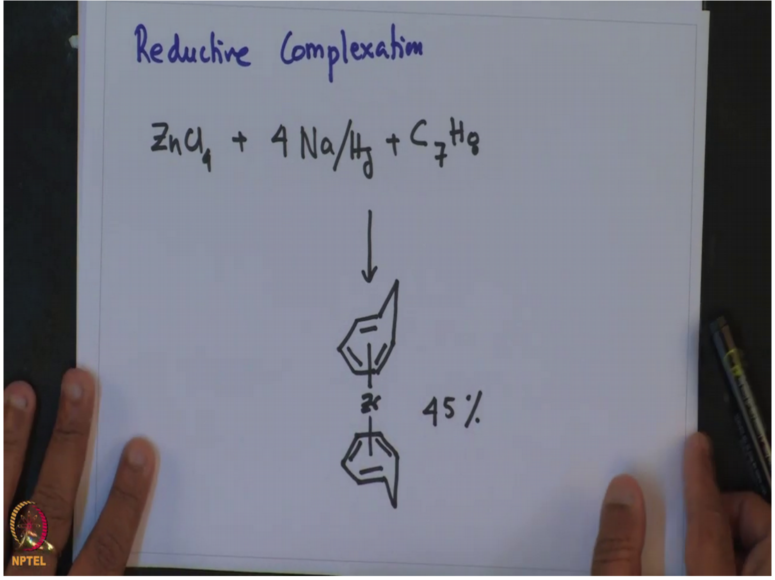

Reductive Complexation

$ZnCl_4 + 4\ Na/Hg + C_7H_8$

So, complex session and the reaction is shown over here.

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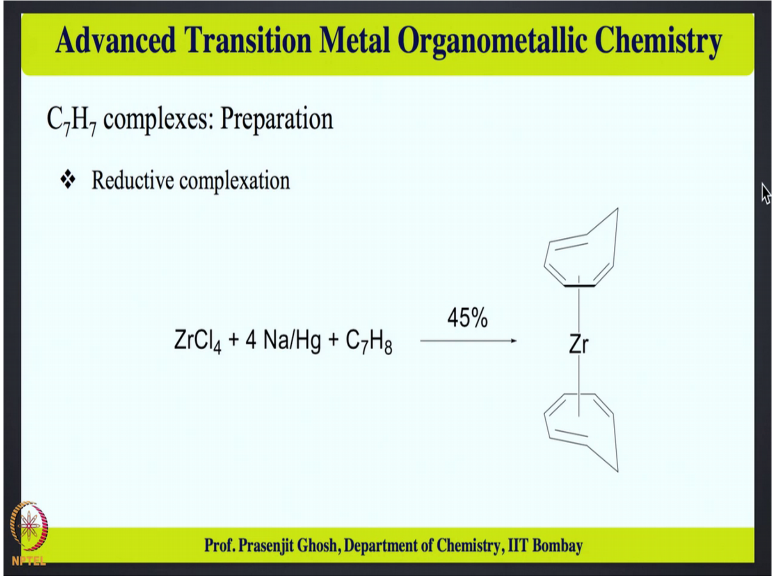

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C_7H_7 complexes: Preparation

- Reductive complexation

$ZrCl_4 + 4\ Na/Hg + C_7H_8 \xrightarrow{45\%}$

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Zinc tetrachloride +4 in a sodium amalgam + C 7 H 8 yields this cyclo hetra tetra triene B's complex of zirconium as is shown over here, as is shown over here now this is produced in 45 percentile what is interesting about here is the name which suggests that there is a reduction which is happening and indeed the reduction is happening in the metal center zirconium which goes on from zirconium 4 to zirconium 0 in this eta 6 bound C 7 H 8.

This zirconium type complex as it is shown over here so there is a reducing agent which is in form of sodium amalgam in presence of the C 7 H 8 ligands and the metal alloy produces this bis C 7 H 8 zirconium complex in which the metal has undergone reduction from +4 oxidation state to its 0 oxidation state. Another example which is slightly more interesting than the one that we had just spoken about in which we will see that not only by the first step at the previous method they will we will produce eta 6 cyclo hepta triene complex of vanadium.

But then with suitable proton abstraction using trityl cation one can generate C 7 H 7 bis vanadium complex and regain its aromaticity. So, we are going to be seeing this nice example as a container of our discussion on reductive complexation and the various methods that are involved in preparing in these C 7 H 7 transition metal complexes.

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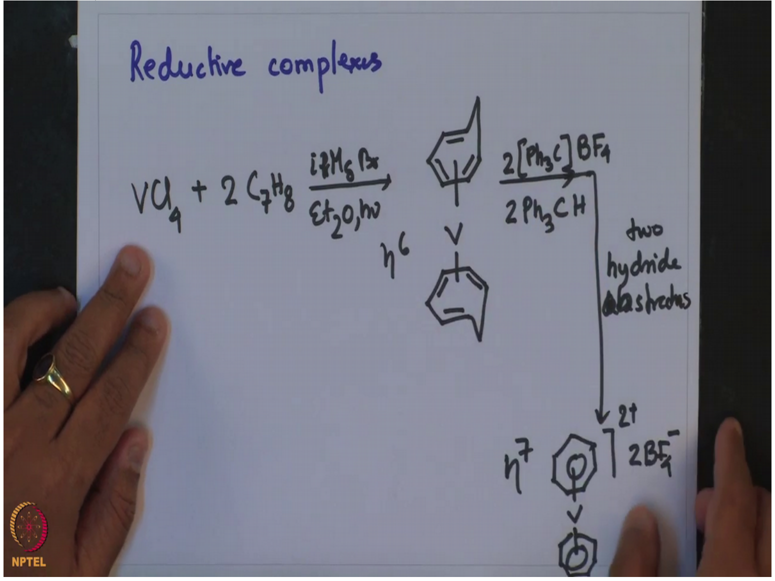

So, in this method what we see that vanadium Cl 4 upon treatment with 2 C 7 H 8 in presence of a grignard isopropyl magnesia isopropyl magnesium bromide ether and light produces these eta 6 C 7 H 8 Bis complex. So, which with clitoral cation abstracts 2 hydrides one from the each of the rings one from the top playing and the other from the bottom ring producing 2 triphenyl methane. And as a result of this hydride abstraction this process is called hydride abstraction or di cationic C 7 H 7 bis tropylium vanadium compound is formed as it is shown over here.

2+ and 2 BF 4 - so the here we say that this is an interesting example where first the; this C 7 H 8 complexes containing eta 6 bound. So, this is eta 6 bound heating cyclo hexa triene is formed which upon abstraction of the hydride there are 2 hydrate abstractions which offer to give this di cationic eta 7 bound C 7 H 8 these complexes of vanadium. So, this reductive coupling method is successfully used in synthesizing this complex.

And over here with what we see a the vanadium undergoing reduction from vanadium +4 to vanadium 0 state as it is shown over her.

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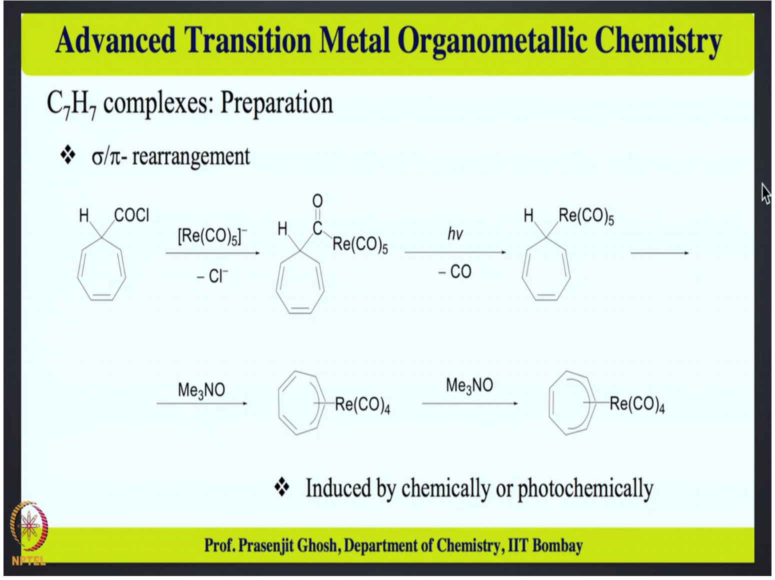

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C_7H_7 complexes: Preparation

- ❖ σ/π- rearrangement

- ❖ Induced by chemically or photochemically

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Another interesting example of reductive complexation involves the reaction of C 5 H 5 MCl 4 M Cl 4 C 5 H 5 M CL 4 + C 7 H 8 with magnesium and THF giving magnesium CP M C 7 H 7 where M equals vanadium niobium and tantalum. So, here in this reductive coupling we see that this MCl 4 which is M is in +5 state getting reduced to +0 state as is shown over here. So, in each of this reductive complexes in examples that we have taken what we saw that the presence of a metal halide presence of a reducing agent and this presence of this C 7 H 8 ligand is there which gives rise to this C 7 H 7 complexes of transition metal by using this method.

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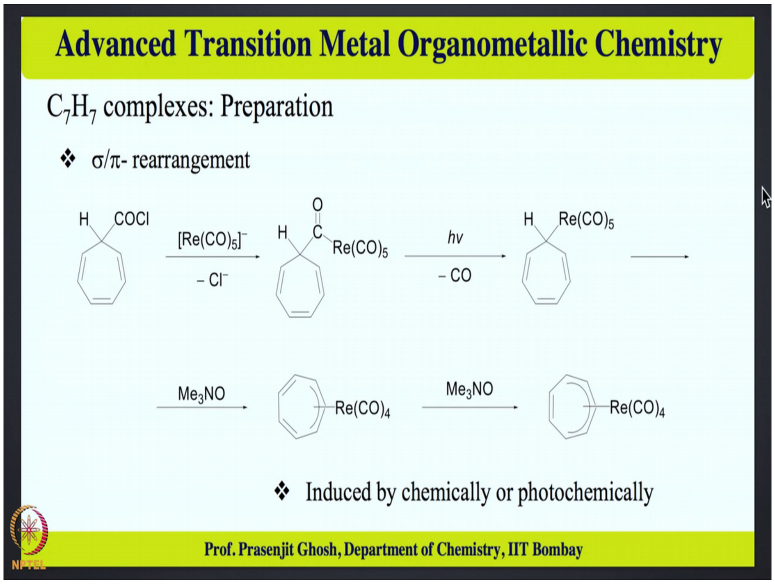

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C_7H_7 complexes: Preparation

- σ/π- rearrangement

- Induced by chemically or photochemically

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The next method is photochemically or chemically induced Sigma Pi here and this is a interest sequence of reaction which uses chemical induction or light based induction of Sigma Pi rearrangement.

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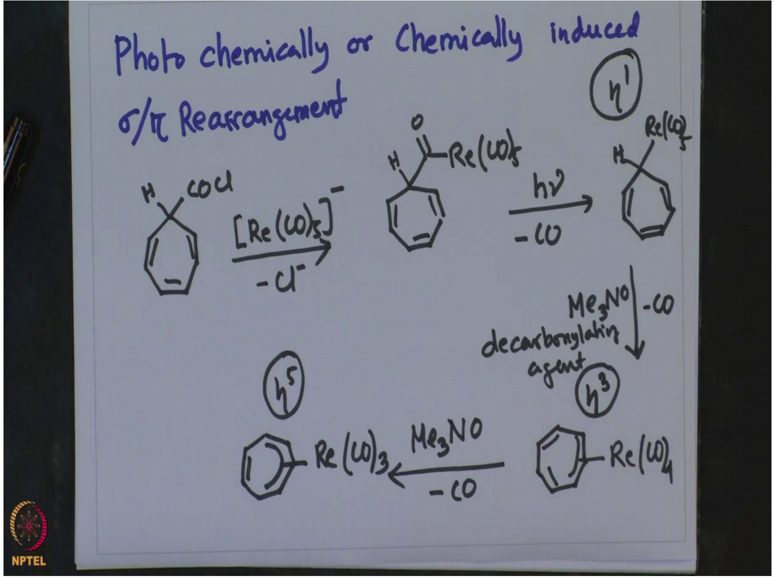

Photo chemically or Chemically induced

σ/π Rearrangement

Photochemically or chemically induced Sigma Pi rearrangement, so in this reaction cyclo iseyl are substituted cyclohexane triene with a metalate Re CO 5- or reacts with this iseyl cation with a loss of chloride anion to give this cyclohexa triene containing CO Re CO 5 which in presence of light loses a CO2 give H Re CO 5 which in presence of Me 3 NO which is a decarbonating agent that sort of favors our loss of carbon monoxide by converting it to C 8 carbon dioxide producing these eta 3 bound.

So, in this case it is eta 1 bound now when a carbon monoxide is lost then it becomes a eta 3 bound Re CO 4 and which in presence of another molecule of Me 3 NO gives eta 5 now another loss of CO happens giving eta 5 bound this complex ligands CO 3. So, what we see is a nice demonstration of change of the simplicity which is Sigma Pi rearrangement. So, this is it eta 1 bound becoming eta 3 bound and finally becoming eta 5 bound system.

And this is promoted by chemically a chemical initiation by providing Me 3 NO which sort of decarbonylation CO making it carbon dioxide CO 2 as well as partly by light the first migratory insertion our loss of CO happens in presence of the light. So, this is photochemically as well as chemically induced Sigma Pi rearrangement where the sigma bonded it one binding gets converted to pi type eta 5 bound C 7 H 7 ligand to the rhenium.

So, this is a very nice example whereby this C 7 H 7 complex was prepared. Now another interesting method obviously is this metal vapor co condensation method which is described right now.

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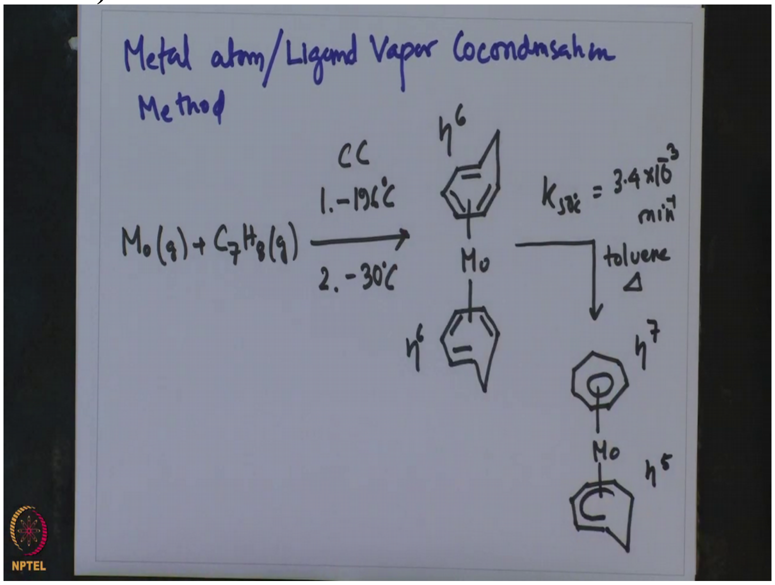

Metal atom/Ligand Vapor Cocondensation Method

So, this is quite a common method for synthesizing various kinds of unusual organometallic compound which otherwise by conventional method it becomes not so easy to prepare. So, these are metal atom ligand vapor co-condensation method and this is illustrated by this beautiful example.

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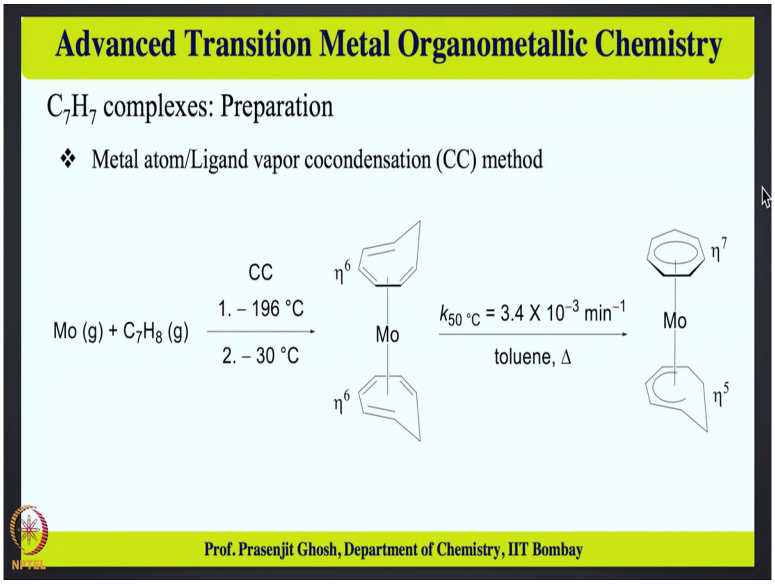

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C_7H_7 complexes: Preparation

- ❖ Metal atom/Ligand vapor cocondensation (CC) method

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In which molybdenum gas is reacted with C 7 H 8 gas by this co-condensation method at -196 degree centigrade and then slowly warming up to -30 degree centigrade gives this eta 6 bound molybdenum complex which 50 degree centigrade decomposes to this eta 7 eta 5 bind complex. So, the rate in which this converts is three point four 10 to power -3 per minute tulvene in and heat molybdenum, so this is eta 7 eta 5 and this was eat 6 eta 6.

So, what we see that these very unstable eta 6, eta 6 combination is formed which upon hitting gets converted to this eta 7 eta 5 forms. So, this is a very interesting method now in which one can see the rear element of the hapticity occurring from eta 6, eta 6 to eta 7, eta 5. Now with these we come to this end of discussion on various synthetic methods that are available for preparing these C 6 H 7 based transition metal complexes.And you are going to be discussing they react the structure of these complexes.

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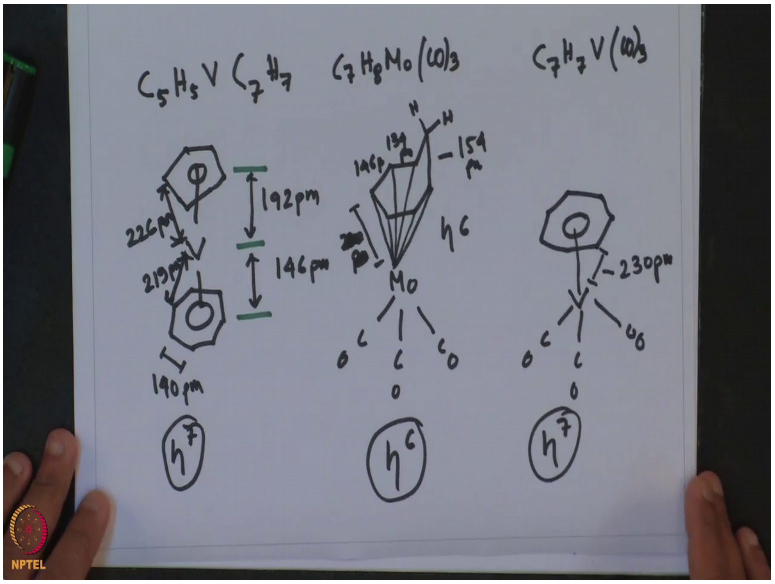

For example the for this particular compound which is C 5 C 5 H 5 vanadium C 7 H 7 the structure is as shown over here. So, this distance between CP to vanadium is 192 picometer whereas vanadium to C 7 H 7 is much shorter and it is at 146 picometer and the vanadium to one of the peripheral ring this is about 226 picometer and vanadium to one of the peripheral ring this is about 219 picometer.

And this carbon-carbon bond is about 140 picometer, so here we have a vanadium complex of the type which is shown there is also eta 6 bound cyclo hepta triene compound as is shown over here. And the x-ray does confirm that one of the ring is not a part of the planar ring and one can sort of see that this is bound in a eta 6 fashion to molybdenum carbonyl and this is a C7 H 8 Mo CO 3, so this the distance is about 134 picometer and the other 1 is 146 picometer.

So, it is between 134 to 146 but as the hydrogen's which are not part of the Ring that is even higher 154 picometer. Now this is eta 6 system similarly one can look at C 7 H 7 V CO 3 which is something like eta 7 bound carbonyl so this distance is 230 picometer and this is eta 7 bound. So, what we see over here that in this one also is eta 7 bound ring. So, what we see over here that in eta 6 bound one of the ch2 is indeed out of plane containing the other 6 carbons and it is projected out as is expected.

So, with this I would like to conclude today's lecture and in this lecture we have looked at various synthetic reparative methods available for preparing these transition metal C 7 H 7 complexes. To begin with we saw that these can be prepared by substitution reactions and these substitution can we actually action can proceed from the transition metal carbonyl complexes then carbon carbonyl moieties getting substituted by C 7 H 7 or C 7 H 8 ligands.

We can also we had also seen examples where mixed CP a metal chromium benzene complexes being reacted with C 7 H 8 and as a result the benzene ligand removing giving away 2 C 7 H 8 incoming ligand. We have also seen the other method apart from substitution are the reductive coupling method in which a metal halide a reducing agent and C 7 H 8 ligand is taken and sometimes these eta 6 cyclo triene complexes are formed which can be converted to eta 7 bound C 7 H 7 complexes by simple apparatus abstraction with usual cation.

We are also seen photochemical as well as chemical induction of Sigma Pi rearrangement in which C 7 H 7 ligand first bind in the eta 1 fashion and then gradually with the carbonyl decarbonylation ends up becoming eta 3 and then finally create a 5 fashion and lastly we see that this can also be produced by metal ligand co-condensation method. We have also looked at the structure and we had seen that indeed for eta 7 is a planar structure.

And whereas in eta 6 that these one of the CH2 system is completely out of the ring containing the 6 carbon atoms in C 7 H 7 moiety, so, with this I would like to conclude today's lecture and we are going to be a talking more on the reactivity aspect of C 7 H 7 transition metal complexes and then subsequent lecture. I sincerely thank you for bearing with or listening to me in this lecture where we have taken up these reparative methods and structure of C 7 H 7 transition metal complexes in quite a detail and we going to be proceeding further by talking about its reactivity in the next class. So, till then goodbye and thank you.