Advanced Transition Metal Organometallic Chemistry
Prof. Prasenjit Ghosh
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Lecture – 29
Transition Metal Arene Cyclopentadienyl and C 7 H 7 Complexes

Welcome to this course on advanced transition metal organometallic chemistry we are discussing an interesting class of compounds these are transition metal arene cyclopentadienyl complexes. Now in the last class we had looked into preparation of these mixed arene cyclo pentadienyl transition metal complexes and what had come to the fore is the fact that there are quite many approaches for synthesis of this compound.

So, synthesis wise these compounds provide very versatile approaches for preparation of these compounds. Now these among these approaches one involved the conventional method which included reaction of metal halides with these arene and cyclo pentadiene and nucleophiles respectively however the limitation of this method was that the desired mixed transition metal arene cyclo butadiene complexes were obtained in extremely low yields about 2 to 3% even less much less than even 5%.

So, even though the method the direct conventional approach did give the product but the yield was problematic and then what came to the fore is the fact that actually there are several other ways in which one can synthesize this kind of transition metal mixed arene complexes. And to start with we looked at a method that involved ring expansion of a metal bound 6 membered benzene ring to a metal bound 7 membered benzene ring in a cyclo pentadienyl metal benzene complex resulting in cyclopentadienyl metal 7 membered arene type of complexes.

We have also seen ring exchange in which a ferrocene compound of was taken and reacted with arene ligand was seen observed that the one of the CP rings was exchanged with the ring to give the metal arene complexes. We have also seen the reduction now with nucleophile in this arene metal cyclopentadienyl complexes giving rise to cyclo pentadienyl metal cyclo hexapenta dienyl

type complex. We are also seen reduction and the metal then we had also discussed about these arene ruthenium cation unit transfer reactions.

In which this arene ruthenium cation unit was transferred from arene ruthenium chlorine dimer by treatment with thallium CP he and also lastly we had seen that if one takes a cyclopentadienyl metal cyclo hexa diene complex and then performs sequential hydride abstraction which tutile cation then one can generate this transition metal arene cyclopentadienyl complex. So, the versatility of the synthetic methods for preparing this mixed arene cyclopentadienyl complex is something that we had discussed in great depth.

And then we are going to look at the structure and binding of these kind of complexes. Now as the name suggests that the cyclopentadienyl ligand can bind in at a 5 fashion whereas the arene would bind conventionally you know you know eta 6 fashion to the transition metal however these mixed ligand complexes can have examples in which these arene's can act as a bridging ligand.

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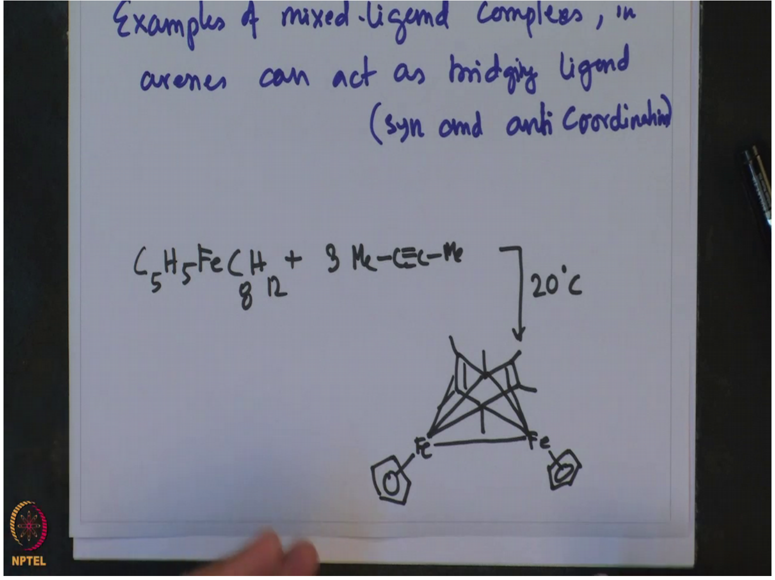

Examples of mixed-ligand complexes, in arenes can act as bridging ligand (syn and anti coordination)

$C_5H_5FeC_8H_{12} + 3\ Me{-}C{\equiv}C{-}Me \xrightarrow{20^{\circ}C}$

So, this is kind of interesting examples of mixed ligand complexes, now the conventional binding of this arena and cyclopentane and against in this transition metal complexes involved arene binding in eta 6 fashion and cyclopentadienyl ligand binding in eta 5 fashion. We be the prominent way method of binding however there exist examples of this mixed ligand complexes the complexes in which the arene's can act as bridge bridging ligands can act as bridging ligands in sync and anti coordination both.

Now this is illustrated by this beautiful example that involved trimerization of acetylenes in which the benzene ring so form is found to be bridging between two iron centers H12 + 3 Ma Ma at 20 degree centigrade gives this beautiful compound, Fe Fe and then each of the Fe is bound to cyclopentadienyl ligand. So, here is a example where the arene is bound as a bridging ligand and they are happening to two iron center.Now each of the iron center is bound in a bound two cyclopentadienyl system.

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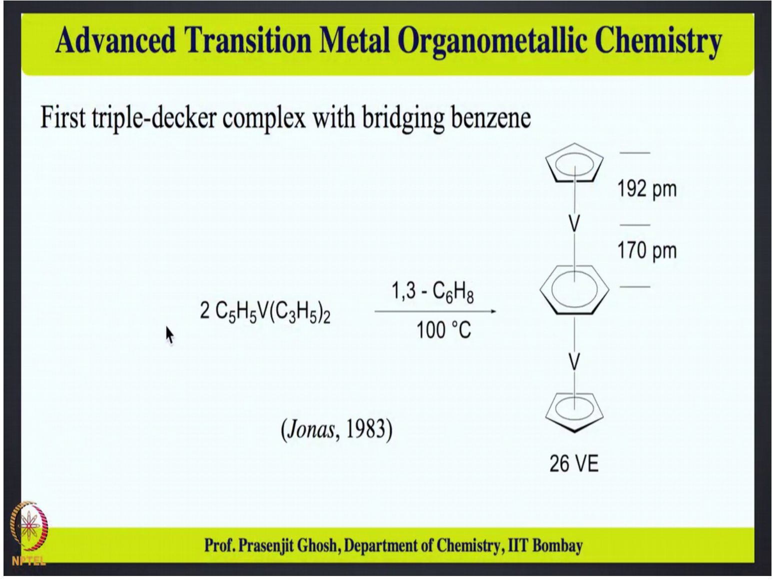

Advanced Transition Metal Organometallic Chemistry

First triple-decker complex with bridging benzene

2 $C_5H_5V(C_3H_5)_2$ $\xrightarrow[100\ °C]{1,3-C_6H_8}$

(*Jonas*, 1983)

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Now the triple-decker complexes of these mixed arene cyclopentadienyl transition metal complex have been synthesized and the first examples of the first triple double complex involved bridging benzene.

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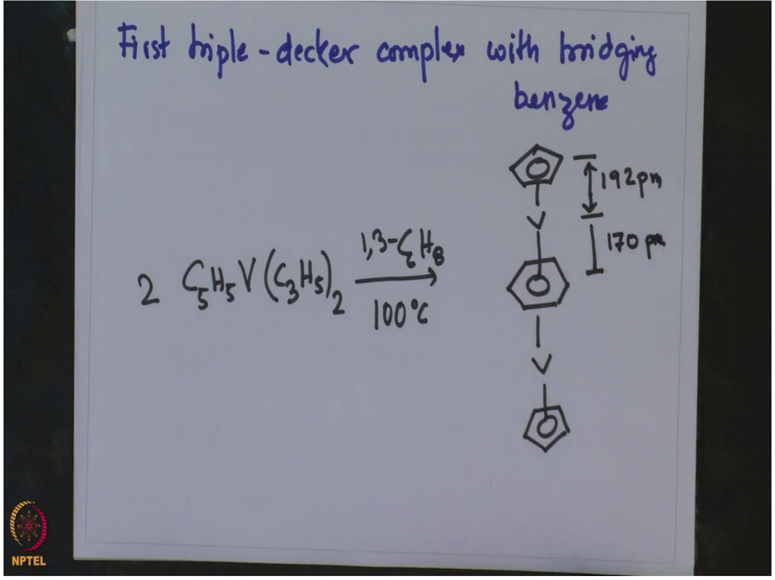

First triple-decker complex with bridging benzene

2 $C_5H_5V(C_3H_5)_2$ $\xrightarrow[100°C]{1,3-C_6H_8}$

First triple-decker complex with bridging benzene this is illustrated by this beautiful synthesis which involved reaction of to C 5 H 5 V C3 H5 whole 2 in presence of 1,3 C 6 H 8 at 100 degree centigrade giving rise to this benzene being bridged between 2 vanadium center one at the top the other at the bottom vanadium bound ligand CP as it shown over here. And the distance between the vanadium to CP is 192 picometer whereas vanadium to benzene is 170 picometer.

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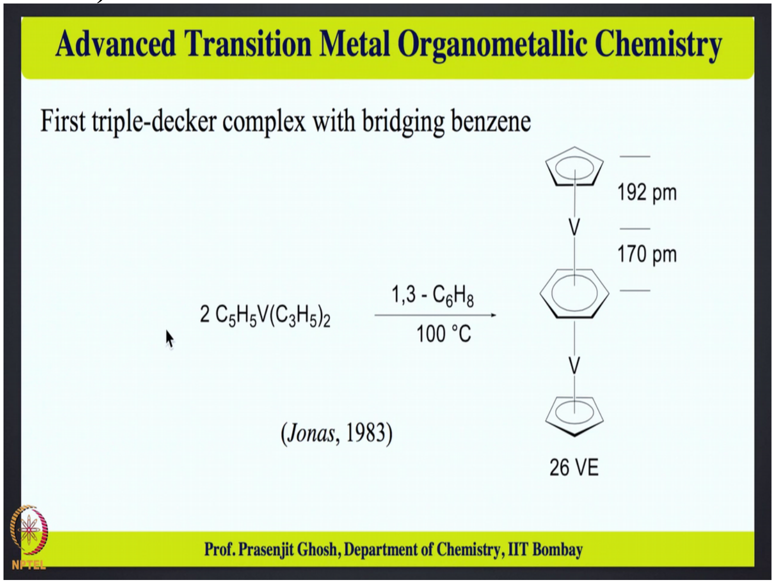

Advanced Transition Metal Organometallic Chemistry

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Another triple-decker complex was prepared for chromium in co-condensation method.

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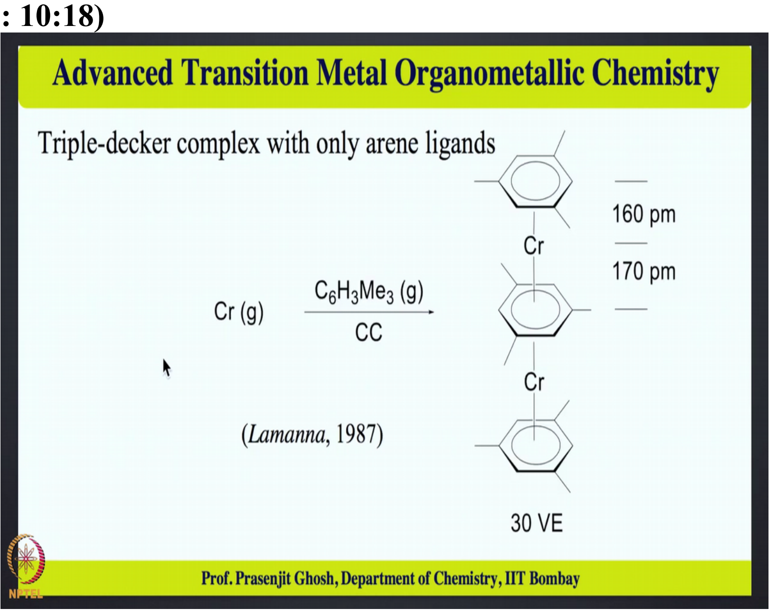

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Triple-decker complex with only arene ligands

$$\mathrm{Cr\ (g)} \xrightarrow[\mathrm{CC}]{C_6H_3Me_3\ (g)}$$

(*Lamanna*, 1987)

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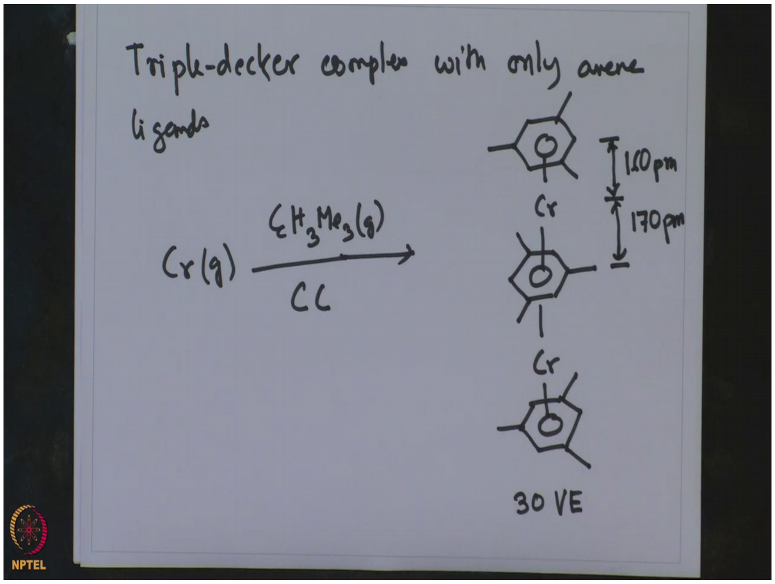
Triple-decker complex with only arene ligands

As is shown over here and this is an example of triple-decker complex with only 3 ligands and this was emphasized by reaction of chromium gas with C 6 H 3 Me 3 gas and this co-condensation method giving rise to this beautiful triple-decker complex of arene as it is shown over here and this is a 30 valence electron compound and the distance between benzene and chromium is 160 pecometer.

Whereas from chromium to the bridging arene is 170 pecometer so with these we had come to the end of our discussion on transition metal cyclo pentadienyl arene complexes and what we had observed so far is that these methods these compounds are indeed special because they are mixed ligand complexes containing CP and arene bound to the metal. The one interesting thing about this class of compound is the fact that there is white versatility in the synthetic approach which exists in the preparation of these complexes.

They not only be prepared from a simple conventional route but also can be prepared by ring expansions reductions as well as abstractions high hydrate abstractions the arene the the ring exchange as well as the unit transfer type of reaction. So, there exists a wide variety of approaches that can give these desired compounds and that is demonstrated by a beautiful piece of chemistry each of these examples is demonstrated by brief use of chemistry.

Also with regard to the structure and bonding what we have seen is that apart from the conventional eta 5 binding of the cyclopentadienyl ligand a eta 6 binding of the arene ligand to the transition metal these arene ligands can also exist as bridging and sync or anti fashion and we have seen a beautiful example of dinuclear iron CP a complex in which the arene ring hexamethyl benzene ring so formed.

And during the part of the reaction is in bridging between the two metal CP units so it not only can exhibit the conventional eta 6 kind of binding but they also can exist in bridging a type of coordination. Another interesting fact about these mixed arene cyclopentane ligand is what we have seen is that they can be used even to undertake lateral expansion and as a result triple-decker complexes in which the arene moiety was sandwiched between the two metal CP units or between two metal arene units are also synthesized and that gives a glimpse of the rich chemistry that these mixed ligand containing CP and arene moieties to the transition metal can exhibit.

So, with these we are going to finish talking about our this particular topic of transition metal CP arene complexes and move on to another very interesting ligands which are C7 H 7 ligands.

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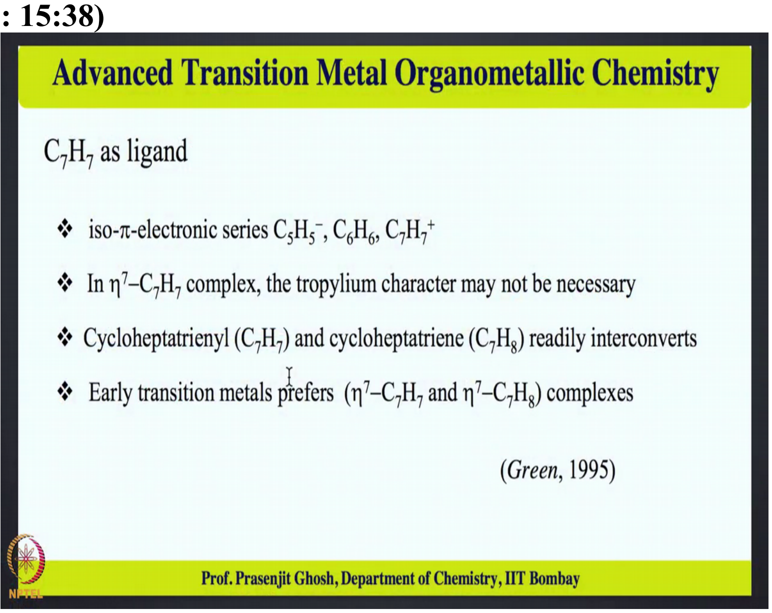

Advanced Transition Metal Organometallic Chemistry

C_7H_7 as ligand

- iso-π-electronic series $C_5H_5^-$, C_6H_6, $C_7H_7^+$
- In η^7–C_7H_7 complex, the tropylium character may not be necessary
- Cycloheptatrienyl (C_7H_7) and cycloheptatriene (C_7H_8) readily interconverts
- Early transition metals prefers (η^7–C_7H_7 and η^7–C_7H_8) complexes

(*Green*, 1995)

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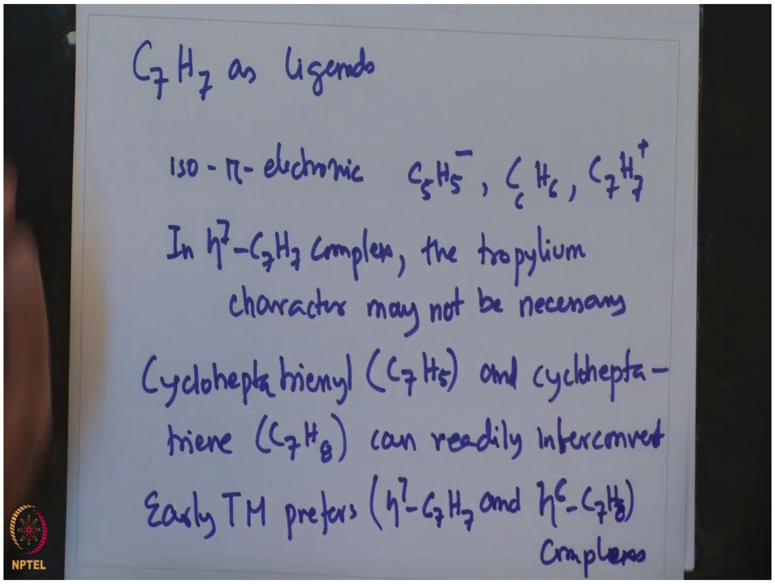

C_7H_7 as ligands

iso-π-electronic $C_5H_5^-$, C_6H_6, $C_7H_7^+$

In η^7-C_7H_7 complex, the tropylium character may not be necessary

Cycloheptatrienyl (C_7H_5) and cyclohepta-triene (C_7H_8) can readily interconvert

Early TM prefers (η^7-C_7H_7 and η^6-C_7H_8) Complexes

So, these C 7 H 7 as ligands now they are 7 membered rings so we started off by looking at 5 membered CP then we looked at benzene C 6 H 6 and then moving on to look at C 7 H 7 as ligands and these are iso Pi electron electronic series with C 5 H 5 - or C 6 H 6 or C 7 H 7 + now all of these are having the 6 PI electrons which makes the ring aromatic and that is why it is C 5 H 5 - C 6 H 6 or C 7 H 7 + and it is why these systems are called iso Pi electronic series.

In also interesting in the fact that in eta 7 bound C 7 H 7 complex the tropylium character that means the cationic may not be necessary. So, this is an interesting thing that they can bind in an aromatic planner way or otherwise as well so the tropylium character may not be necessary the cyclohepta trienyl and cyclo hepta triene so there are 2 forms what is called cyclo hepta trienyl which is C 7 H 7 and cyclo hepta triene which is C 7 H 8 readily inter converts can readily interconvert and also early transition metal prefers eta 7 C 7 H 7 and eta 6 C 7 H 8 complexes.

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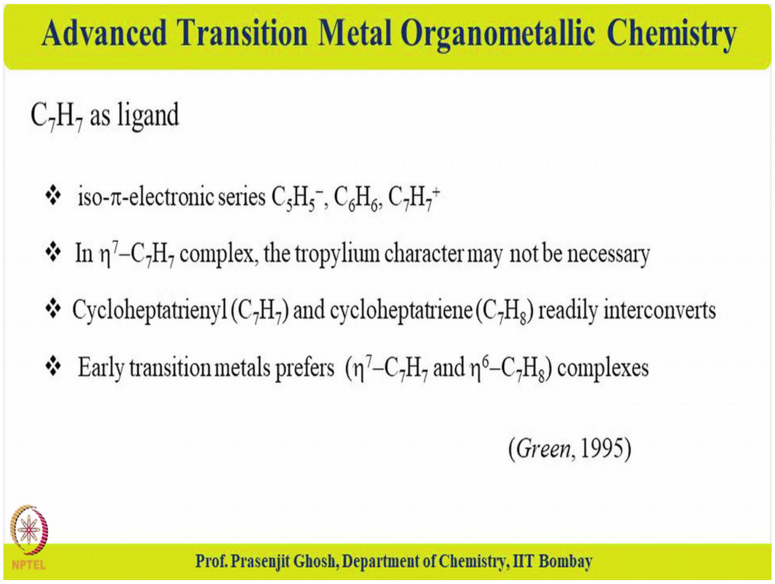

Advanced Transition Metal Organometallic Chemistry

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(*Green*, 1995)

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So, these are just some of the salient features which are characteristics of C 7 H 7 ligands that they are isoelectronic with other systems like CP as well as CP - as well as benzene in unit C 7 H 7 + form the C 7 H 7 binding need not be a tropylium all the way and also there can be a exchange of C 7 H 7 to C 7 H 8 and also early transition metal prefers both C 7 H 7 and C 7 H 8 bound in eta 7 fashion.

So, these complexes come around in many they there are a lot of examples of this we are going to be taking a look at some of them.

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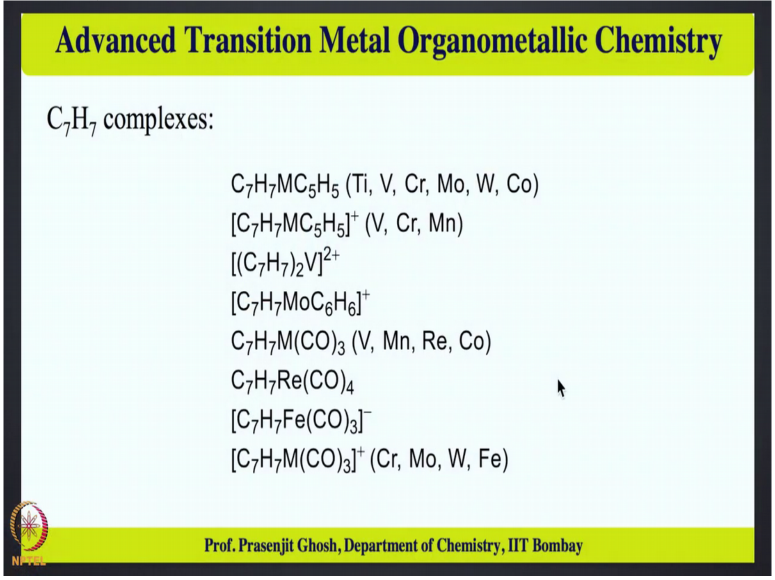

Advanced Transition Metal Organometallic Chemistry

C_7H_7 complexes:

$C_7H_7MC_5H_5$ (Ti, V, Cr, Mo, W, Co)
$[C_7H_7MC_5H_5]^+$ (V, Cr, Mn)
$[(C_7H_7)_2V]^{2+}$
$[C_7H_7MoC_6H_6]^+$
$C_7H_7M(CO)_3$ (V, Mn, Re, Co)
$C_7H_7Re(CO)_4$
$[C_7H_7Fe(CO)_3]^-$
$[C_7H_7M(CO)_3]^+$ (Cr, Mo, W, Fe)

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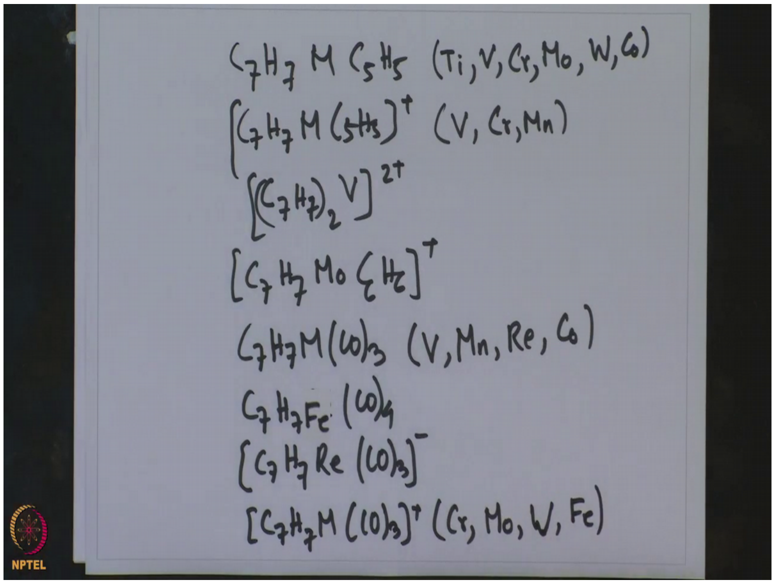

$C_7H_7 M C_5H_5$ (Ti, V, Cr, Mo, W, Co)

$[C_7H_7 M C_5H_5]^+$ (V, Cr, Mn)

$[(C_7H_7)_2 V]^{2+}$

$[C_7H_7 Mo C_6H_6]^+$

$C_7H_7M(CO)_3$ (V, Mn, Re, Co)

$C_7H_7Fe(CO)_4$

$[C_7H_7 Re (CO)_3]^-$

$[C_7H_7M(CO)_3]^+$ (Cr, Mo, W, Fe)

For example C 7 H 7 M C 5 H 5 and now this is exactly similar to the mixed cyclopentadienyl arene complexes of benzene that we have spoken about in this case instead of benzene we have C 7 H 7 this is quite common for titanium, vanadium, chromium, molybdenum, tungsten, cobalt then one can have C 7 H 7 M C 5 H 5 overall cationic species common for vanadium, chromium, manganese then Bis C 7 H 7 whole 2 V 2+ this is the base of C 7 H 7 bound to vanadium 2 + then comes C 7 H 7 Mo C 6 H 6 + so this is 7 membered ring 6 membered ring mixed ligand system with molybdenum C 7 H 7 M CO 3.

Now this is same for vanadium, manganese, rhenium, cobalt, C 7 H 7 iron CO 4 then C 7 H 7 Re CO 3 - and then C 7 H 7 M CO 3 + can be chromium, molybdenum, tungsten, iron. So, what emerges out is the fact that a large number of different types of compounds can be if I observed for this C 7 H 7 ligands. For example it can be a this bis homo aerial kind of system well you have same C 7 H 7 whole 2 vanadium or it can be various hetroecliptic system.

You can have a 7 membered ring 7 membered ring mixed ligand system you can also have a seven membered ring six Ligon ring mixed ligand system you can have C 7 H 7 carbonyl compounds which are half-sandwich compounds of this type. So, basically what all these is pointing to is the fact that C 7 H 7 indeed is important ligand in the area of organometallic chemistry and that they have very many complexes which sort of makes them sufficient in number to be a taken note of and be treated separately as a new class of ligands. So, because of that reasons we are just continuing our discussion on C 7 H 7 type complexes.

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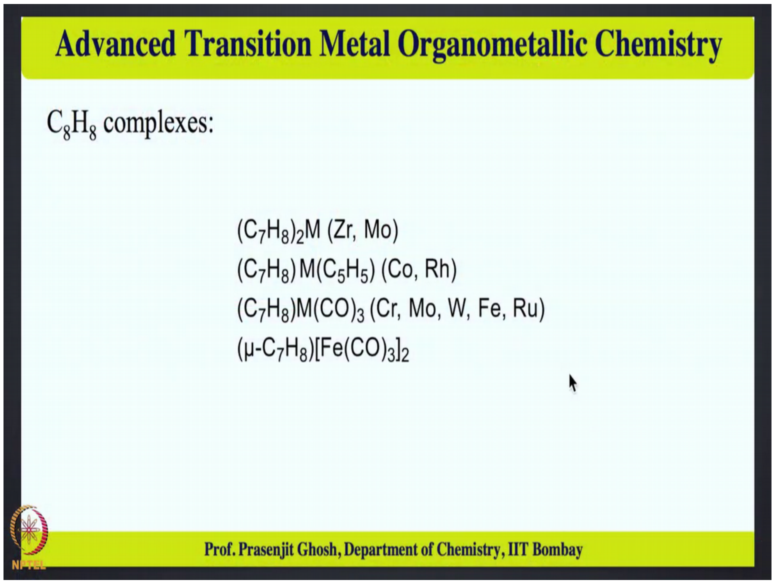

Advanced Transition Metal Organometallic Chemistry

C_8H_8 complexes:

$(C_7H_8)_2M$ (Zr, Mo)
$(C_7H_8)M(C_5H_5)$ (Co, Rh)
$(C_7H_8)M(CO)_3$ (Cr, Mo, W, Fe, Ru)
$(\mu\text{-}C_7H_8)[Fe(CO)_3]_2$

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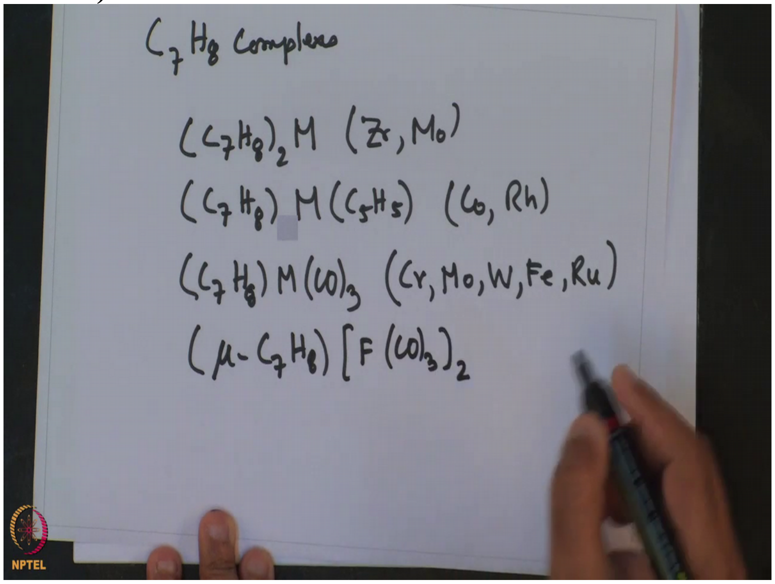

C_7H_8 Complexes

$(C_7H_8)_2M$ (Zr, Mo)
$(C_7H_8)M(C_5H_5)$ (Co, Rh)
$(C_7H_8)M(CO)_3$ (Cr, Mo, W, Fe, Ru)
$(\mu\text{-}C_7H_8)[F(CO)_3]_2$

And now there are some examples of C7 H 8 complexes so the examples of C7 H 8 complexes are whole 2 M is zirconium, molybdenum C 7 H 8 M with C 5 H 5 cobalt rhodium C 7 H 8 M CO 3 that can be chromium molybdenum tungsten iron ruthenium and Mu C 7 H 8 Fe CO 3 whole 2 this is a bridging compound. So, what we see is that C 7 H 7 can have many complexes as well as C 7 H 8 also has similar complexes and that is why these made its proper discussion.

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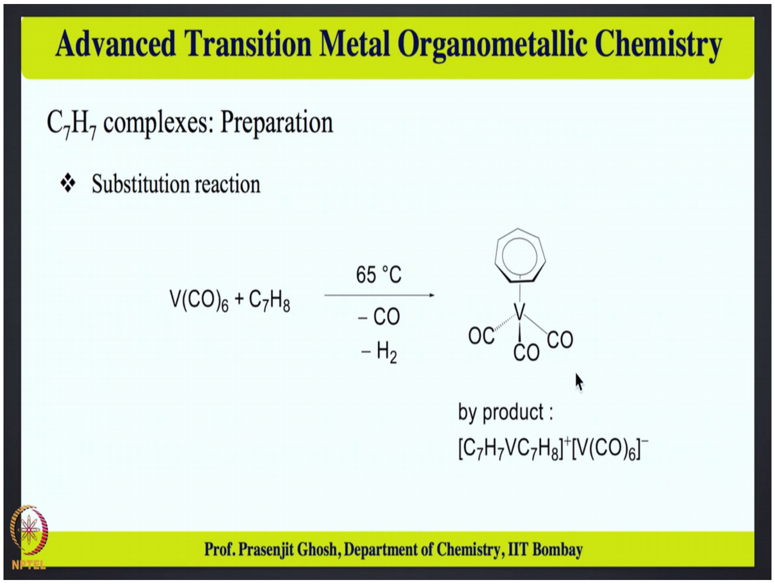

Advanced Transition Metal Organometallic Chemistry

C_7H_7 complexes: Preparation

- Substitution reaction

$$V(CO)_6 + C_7H_8 \xrightarrow[-CO,\ -H_2]{65\ °C}$$

by product : $[C_7H_7VC_7H_8]^+[V(CO)_6]^-$

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So, now let us take a look at the preparations that are available for the C 7 H 7 complexes and one method that is conveniently used over here is this substitution reaction.

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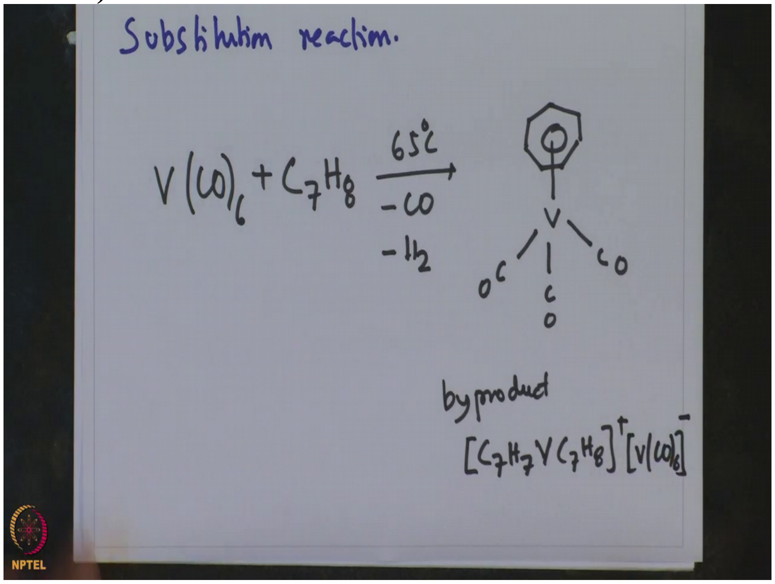

Substitution reaction.

$$V(CO)_6 + C_7H_8 \xrightarrow[-CO,\ -H_2]{65°C}$$

by product

$[C_7H_7VC_7H_8]^+[V(CO)_6]^-$

So, in this case the reaction metal carbonyl like V CO 6 + C 7 H 8 at 65 degree centigrade eliminates CO as well as hydrogen to give this 7 membered C 7 H 7 V CO CO CO compound and some by-product is also formed which contains C 7 8 7 V C 7 H 8 cation and V CO 6 anion.

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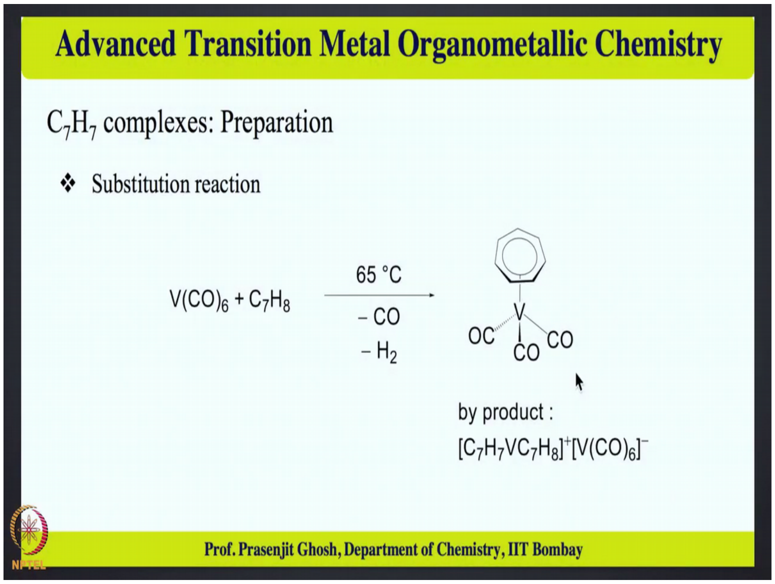

Advanced Transition Metal Organometallic Chemistry

C_7H_7 complexes: Preparation

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by product :
$[C_7H_7VC_7H_8]^+[V(CO)_6]^-$

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Another method involves the reaction of a cyclo pentadienyl vanadium carbonyl with C 7 H 8.

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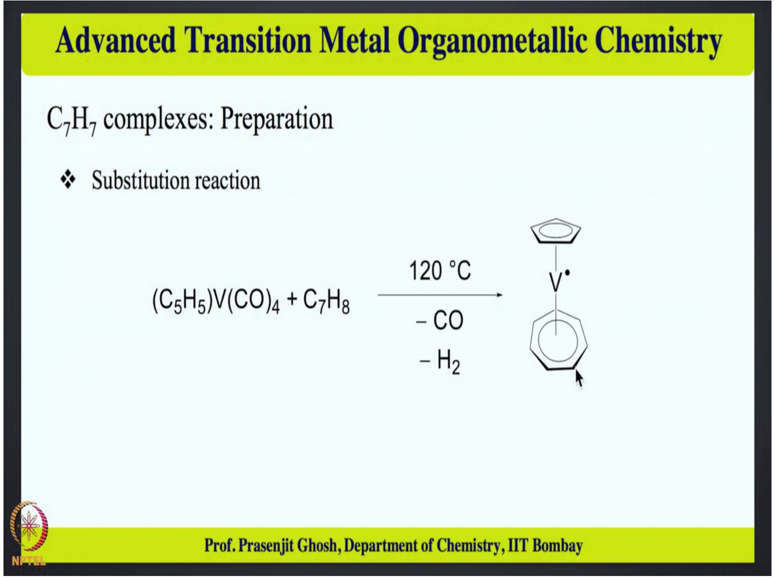

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C_7H_7 complexes: Preparation

- Substitution reaction

$(C_5H_5)V(CO)_4 + C_7H_8 \xrightarrow[- CO \; - H_2]{120\ °C}$

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Giving the rise to CP vanadium cycle C 7 H 7 ligand and this reaction is also part of substitution reaction.

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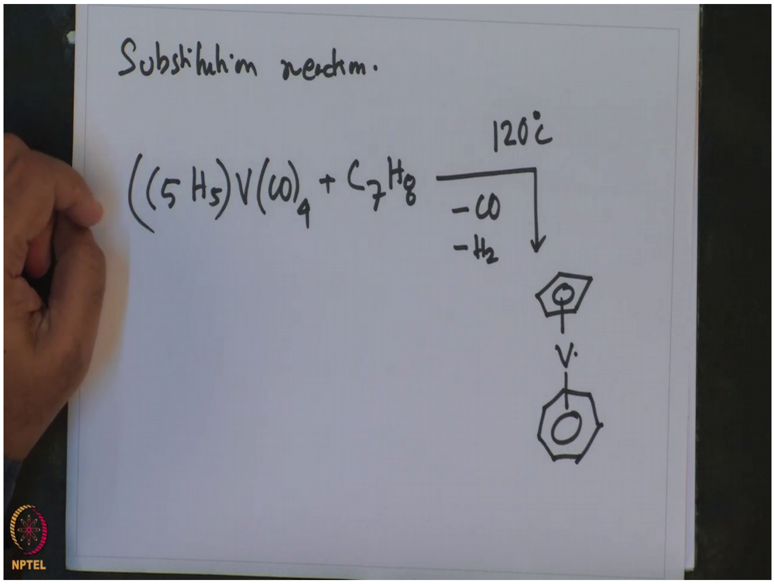

So, this is C 5 H 5 vanadium CO 4 + C 7 H 8 at 120 degree centigrade giving CO – H 2 - CP vanadium this 5 membered 7 membered vanadium compound. So, this also is a very interesting example in which this mixed 5 members remembered compounds of say memory ring compounds of vanadium were synthesized.

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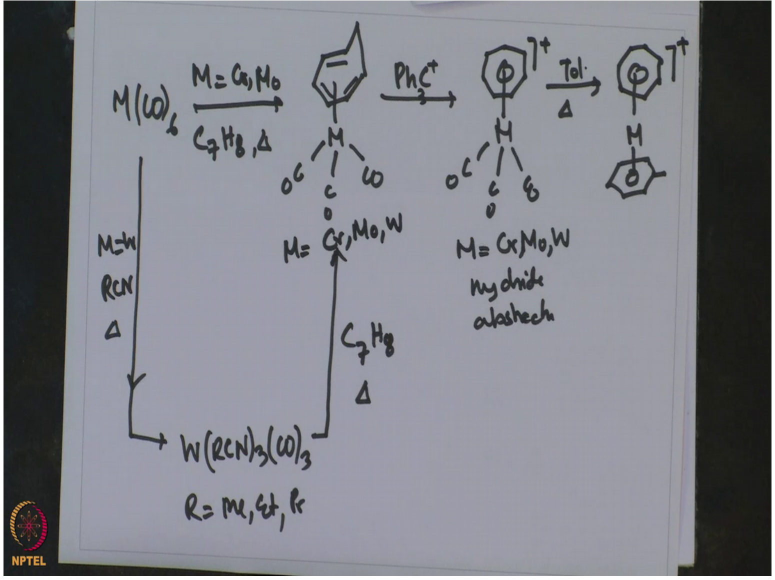

We are going to take a look at another interesting example which involves this reaction of M CO 6 M can be chromium molybdenum C 7 H 8 heat giving rise to this compound M CO CO CO that with the abstraction of hydride Ph 3 + giving rise to the 7 membered metal CO CO CO overall cationic in toluvine heat it gives a tall beam complex M and it is a beautiful example where one can see whole application of these abstractions ring apps hydride abstractions M nickel chromium molybdenum tungsten and then hydride abstraction as well as ring displacement.

And one can take this for tungsten M = W in presence of RCN and heat one can generate this compound WRCN whole 3 CO 3 R can be methyl ethyl prophyl and then treat that with C 7 H 8 giving back to this compound where M can be chromium molybdenum tungsten.

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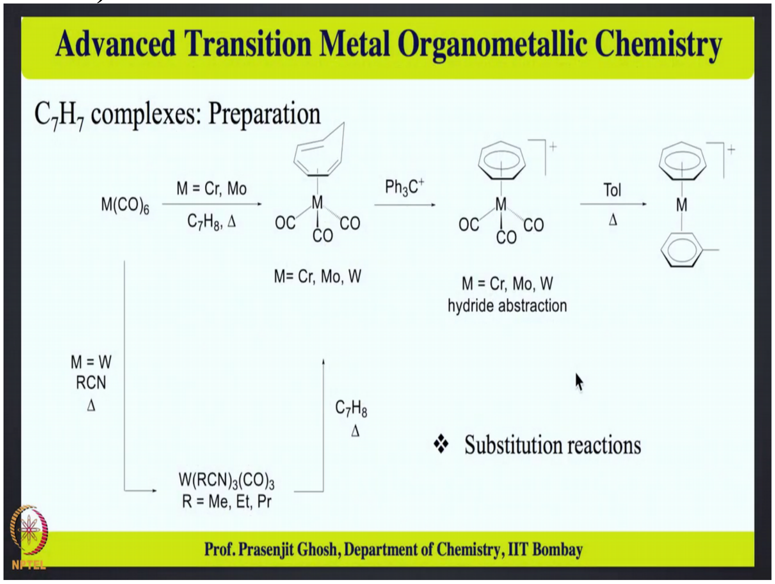

Advanced Transition Metal Organometallic Chemistry

C_7H_7 complexes: Preparation

❖ Substitution reactions

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So, this is a beautiful demonstration of the power of chemistry in which several synthetic approaches some involves thermalatic cleavage some involves the hydride ring hydrate abstractions followed by ligand substitutions giving rise to this mixed 7 membered 6 membered complexes for a series of metal mainly chromium molybdenum and tungsten.

So, with these I would like to include today's next lecture in today's lecture we have discussed about the structure particularly of a transition metal cyclopentadienyl type of complexes. How they can act as a bridging the arene ring can act as a bridging ligand between two metal centers are act as a bridging ligand in a triple-decker complexes. And then subsequently start our discussion on C 7 H 7 complexes.

And what we found that these C 7 H 7 complexes by their own right and merit to deserve a special mention because a wide variety of these complexes are found of these C 7 H 7 ligands not only of that but they can also be observed of C 7 H 8 ligands where there is heptatriene as well as cyclotrienyl C 7 H 7 and then we have looked into various synthetic methods which are available for preparation of these C 7 H 7 and C 7 H 8 complexes of transition metal.

And we have taken up our discussion on particularly the substitution reactions in which we have seen that metal carbonyls can be used for substitute substituting in this C 7 H 7 ligand by virtue of C 7 H 7 in virtue of displacing carbonyl and began giving rise to these C 7 H 7 complexes. And then now we have looked into two such examples and would continue doing so more on the C 7 H 7 preparative methods in the subsequent lecture.

So, till that I thank you again for patiently listening to me in this topic in today's discussion and hope that certainly hope that you join me when we take up our discussion on C 7 H 7 in more detail starting from there other methods of preparation structure and reactivity in the subsequent class, till then goodbye and thank you.