Advanced Transition Metal Organometallic Chemistry
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Lecture – 32
Transition Metal C 8 H 8 and C 7 H 7 Complexes

Welcome to this lecture on, Advanced Transition Metal Organometallic Chemistry. As a part of our discussion on transition metals C 7 H 7 complexes, in the last lecture, we have looked at the reactivity of this transition metal C 7 H 7 complexes of the reactivity that we have looked upon that involved different kind of reactions starting from redox processes to metallation reactions to addition of nucleophiles to even hapticity change and so on and so forth.

So all of these reactivity can is kind of observed in a transition metal C 7 H 7 complexes and that sort of showed that these class of compounds represents reach gamut of chemistry. Now there is a little bit more discussion left on transition metal C 7 H 7 complexes and this is particularly with respect to their bindings. Now most of the complexes so far discussed for transition metal C 7 8 7 complexes involved eta 7 binding of C 7 H 7 ligand on to the metal centre giving rise to mono nuclear metal complexes.

However there are also possibilities in which C 7 H 7, can even bridge between, two metal centers giving rise to di nuclear complexes. So one such example is illustrated as follows:

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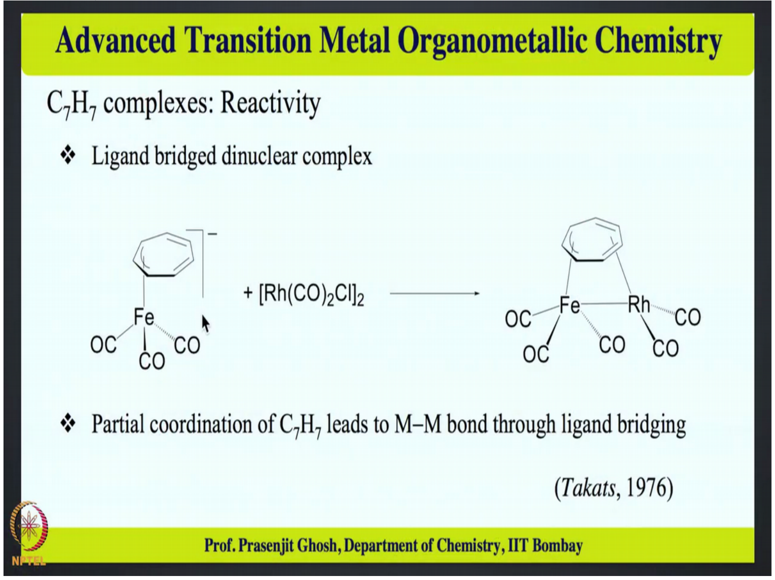

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C_7H_7 complexes: Reactivity

- Ligand bridged dinuclear complex

- Partial coordination of C_7H_7 leads to M–M bond through ligand bridging

(*Takats*, 1976)

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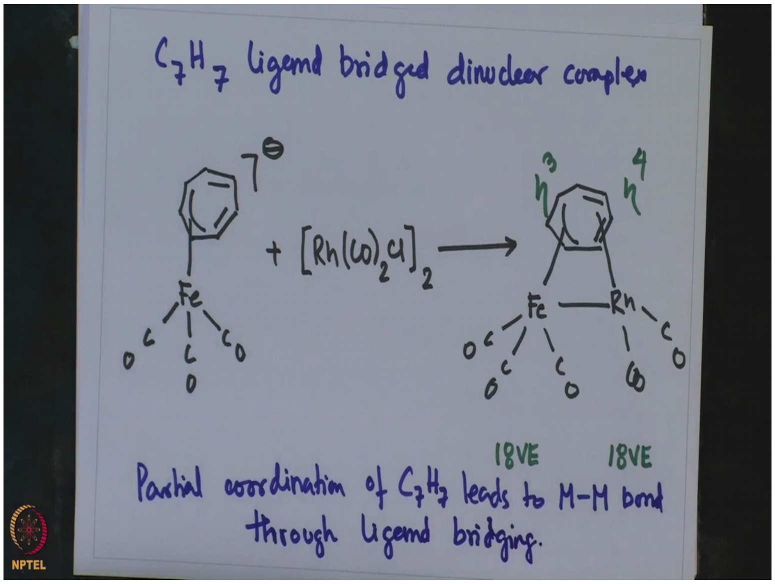

C_7H_7 ligand bridged dinuclear complex

Partial coordination of C_7H_7 leads to M–M bond through ligand bridging.

So, ligand C 7 H 7 ligand bridge di nuclear complex. This is a interesting reaction in which eta 3 bound iron tricarbonyl compound of the type shown over here. In its anionic form reacts with rhodium dicarbonyl chloride, dimer giving rise to this bridging dinuclear hetero bimetallic compound, rhodium. So this is the interesting compound in which you know iron is bound in eta 3 fashion, iron and eta 4 fashion to rhodium.

Now these both are in 18 valence electron configuration 6 + 3 9 1 10 and iron is 8 so 18 and rhodium also is in 18 valence electron configuration. 4 +4 8 1 9 and rhodium is 9 9 + 9 18, so what we see that hapticity of 7 can be split into eta 3 and eta 4 and that can accommodate two different metals one is iron and rhodium and not only it is binding mode of bridging binding mode of C 7 H 7 ligand, it is interesting because C 7 H 7 is split into two binding eta 3 and eta 4, not only that is interesting but also it is interesting in the fact that hetero bimetallic two different metallic man centers have been stabilized because of this bridging binding of C 7 H 7 ligand.

And another interesting fact about this complex is that there also involves one of the rare examples where metal-metal bond is formed. So this particular example is kind of interesting in three ways, first one can see that these C 7 H 7 ligand can indeed breach and the breaching can lead to the splitting of their hapticity pattern into of eta 7 into eta 3 and eta 4 not only that it can bridge but also it can support hetero bimetallic dinuclear complexes and last of all there is also interesting metal-metal bond that has been formed in these hetero bimetallic dinuclear complex, okay.

So, this is a very interesting example where the bridging ability of C 7 H 7 ligand has been observed. So, partial coordination of C 7 H 7 leads to metal-metal bond through ligand bridging. So, this, with this, we sort of closed our discussion on C 7 H 7 ligands in which we have not only looked at the various types of complexes that are formed, we have looked at the various methods that are used for preparing these complexes. And also we have looked at the reactivity of C 7 H 7 ligand in details over the last two lectures.

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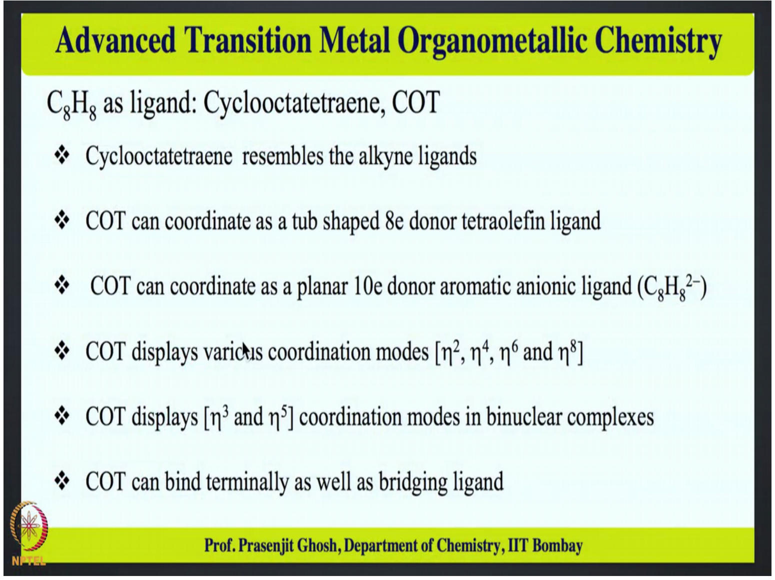

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C_8H_8 as ligand: Cyclooctatetraene, COT

- Cyclooctatetraene resembles the alkyne ligands
- COT can coordinate as a tub shaped 8e donor tetraolefin ligand
- COT can coordinate as a planar 10e donor aromatic anionic ligand ($C_8H_8^{2-}$)
- COT displays various coordination modes [η^2, η^4, η^6 and η^8]
- COT displays [η^3 and η^5] coordination modes in binuclear complexes
- COT can bind terminally as well as bridging ligand

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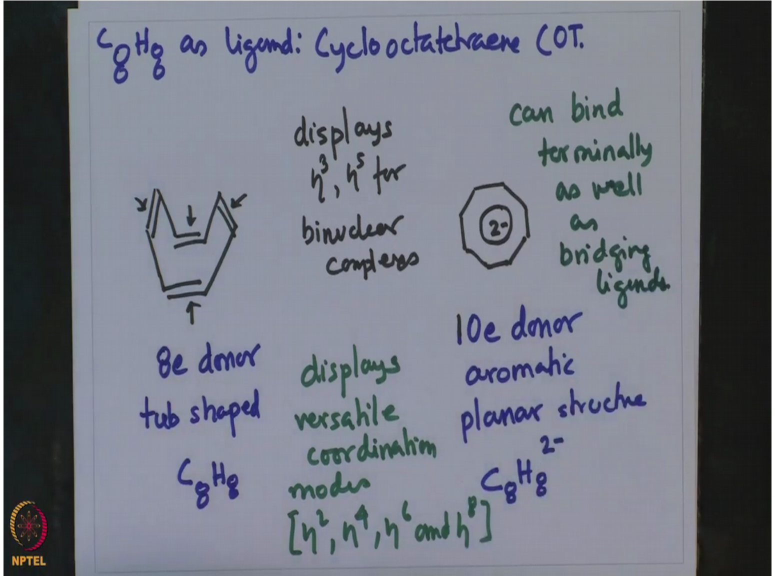

C_8H_8 as ligand: Cyclooctatetraene COT.

displays η^3, η^5 for binuclear complexes

can bind terminally as well as bridging ligands

8e donor tub shaped C_8H_8

displays versatile coordination modes [η^2, η^4, η^6 and η^8]

10e donor aromatic planar structure $C_8H_8^{2-}$

Moving on, we are coming on to another new set of ligands which are C 8 H 8 ligands or better known as cyclooctatetraene, cyclo octa tetraene or COT, okay. Now COT sort of resembles similarly there of an alkyne ligand COT can coordinate in a tub fashion 8 electron donor or it can coordinate as a planar 10 electron donor aromatic ligand as C 8 H 8 2-.

Now this needs a bit of illustration now COT is a cyclo octa tetraene and the structure of that is, so this is this 8 electron donor, donor tub shaped structure. This is this 8 electron donor tub structure, 8 electron donation occurs from here, here, here, here. So there are four double bonds giving rise to 8 electron donor. The other possibility of this COT structure is of obviously the planar 10 electron donor structure which is sort of shown over here.

So, this is a planar structure which is dianionic and this is 10 electron donor, 10 electron donor. So, aromatic planar structure and stoichiometry is C 8 H 8 2- whereas for this one is C 8 H 8. So, the C 8 H 8 ligand can exist in two binding modes one can be tub shaped where it is behave like a tetraene with four double bonds the other it can be a planar structure where it has 10 electrons and it is in dynamic state.

COT displays coordination modes, displays versatile coordination modes that can be eta 2, eta 4, eta 6 and eta 8. So, depending on the number of atom in the C 8 H 8 ligand that binds to the metal it can show hapticities ranging from 2, 4, 6 and 8. These is usually for mono nuclear complexes and COT displays, displays eta 3 and eta 5 mode for bi nuclear complexes, as a results COT can bind terminally as well as bridging ligand as a result can it can bind terminally as well as bridging ligands.

So, what you see is not only in the structure it shows, but also in its ability to bind to the metal where it can act like a 8 electron donor tub structure or a 10 electron donor planar structure it can show a wide variety of band binding modes in mononuclear complexes which can vary from 2, 4 6 and 8 depending on number of the carbon atoms that the metal is bound to or it can even show odd hapticity like 3 and 5 and these are especially observed for dinuclear complexes.

In addition COT can also bind as a terminal ligand as well as, as a bridging ligand. So really all these properties make very rich and versatile and interesting chemistry awaiting for us to look into as we discuss more on this special organometallic complexes. So, with that let me start off with the preparation of COT complexes and depending on the stoichiometry a the different composition of complexes for titanium can be observed and this is best illustrated by the examples which are shown over here.

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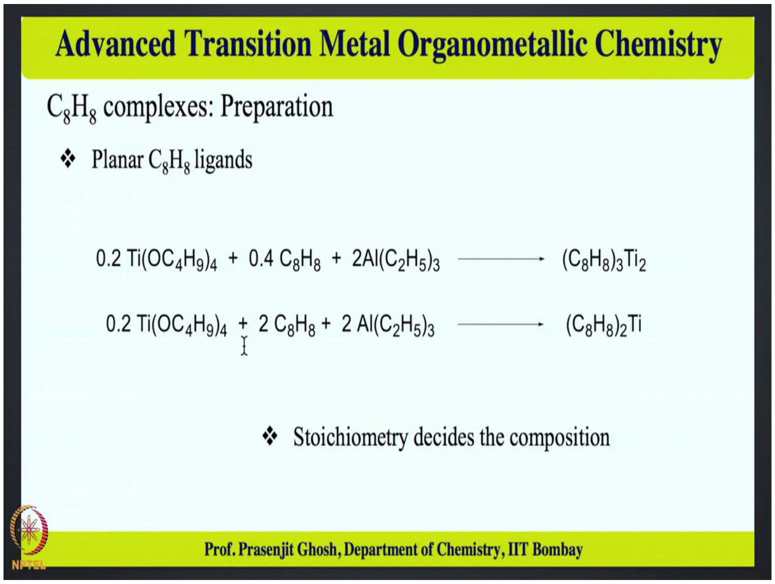

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C_8H_8 complexes: Preparation

- Planar C_8H_8 ligands

$$0.2\ Ti(OC_4H_9)_4 + 0.4\ C_8H_8 + 2Al(C_2H_5)_3 \longrightarrow (C_8H_8)_3Ti_2$$

$$0.2\ Ti(OC_4H_9)_4 + 2\ C_8H_8 + 2\ Al(C_2H_5)_3 \longrightarrow (C_8H_8)_2Ti$$

- Stoichiometry decides the composition

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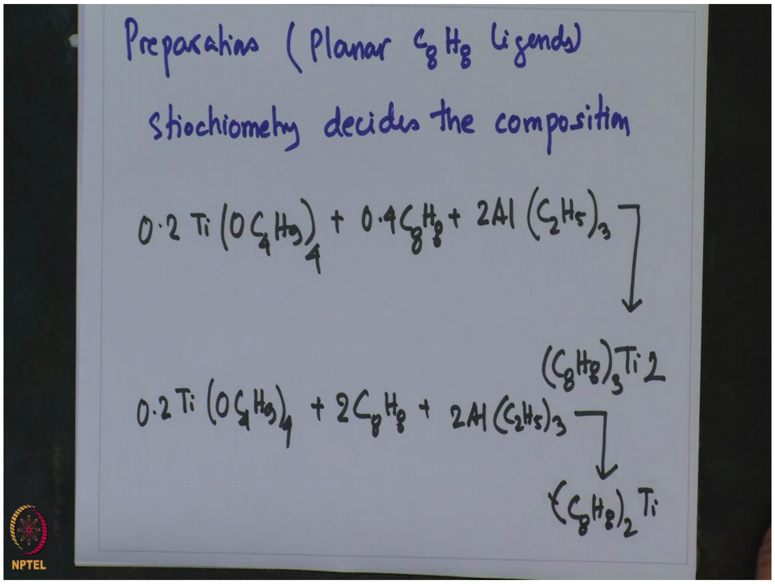

Preparation (Planar C_8H_8 ligands)

Stiochiometry decides the composition

$$0.2\ Ti(OC_4H_9)_4 + 0.4 C_8H_8 + 2Al(C_2H_5)_3 \longrightarrow (C_8H_8)_3Ti\ 2$$

$$0.2\ Ti(OC_4H_9)_4 + 2C_8H_8 + 2Al(C_2H_5)_3 \longrightarrow (C_8H_8)_2Ti$$

Now, the preparations that we are going to be talk about the planar C 8 H 8 ligands and their complexes. So the discussion on these few preparative methods would now focus on obtaining transition metal complexes of planar structure of C 8 H 8 ligand. So, preparations planar C 8 H 8 ligands so this involves preparation of coordination metal complexes, continuing planar C 8 H 8 ligands.

Now the, for these, it is observed that the stoichiometry decides the composition of the complex and this is illustrated by the following two reactions in two different complexes of C 8 H 8 in titanium were obtained. For example for the reaction of 0.2 Ti O C 4 H 9 whole 4 + 0.4 C 8 H 8 +2 Al C 2 H 5 whole 3 gives C 8 H 8 whole 3 Ti 2. Now the other stoichiometric reaction is 0.2

titanium O C 4 H9 whole 4 +2 C 8 H 8 + 2 Al C 2 H 5 whole 3, would give C 8 H 8 whole 2 titanium. So what is observed over here is the fact that the reaction stoichiometry decides on the composition of the product.

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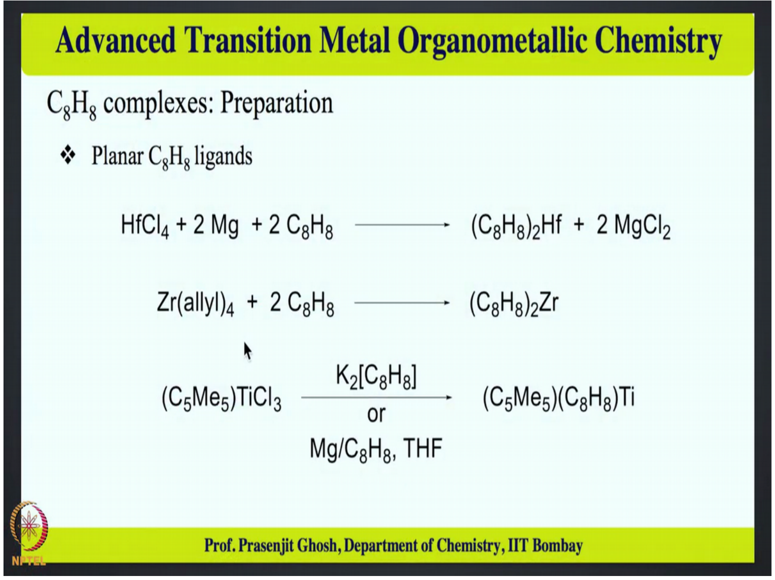

Advanced Transition Metal Organometallic Chemistry

C_8H_8 complexes: Preparation

❖ Planar C_8H_8 ligands

$$HfCl_4 + 2\,Mg + 2\,C_8H_8 \longrightarrow (C_8H_8)_2Hf + 2\,MgCl_2$$

$$Zr(allyl)_4 + 2\,C_8H_8 \longrightarrow (C_8H_8)_2Zr$$

$$(C_5Me_5)TiCl_3 \xrightarrow[\text{or}\ Mg/C_8H_8,\ THF]{K_2[C_8H_8]} (C_5Me_5)(C_8H_8)Ti$$

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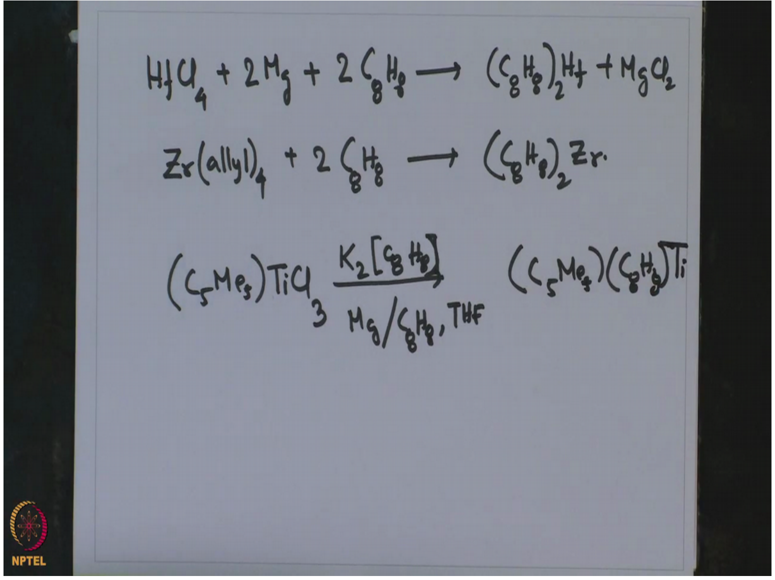

$$HfCl_4 + 2Mg + 2C_8H_8 \longrightarrow (C_8H_8)_2Hf + MgCl_2$$

$$Zr(allyl)_4 + 2C_8H_8 \longrightarrow (C_8H_8)_2Zr.$$

$$(C_5Me_5)TiCl_3 \xrightarrow[Mg/C_8H_8,\ THF]{K_2[C_8H_8]} (C_5Me_5)(C_8H_8)Ti$$

Some more examples are shown over here, for example hafnium tetrachloride +2 Mg + 2 C 8 H 8 would give this complex of C 8 H 8 whole 2 Hf + Mg Cl 2. similarly zirconium allyl +2 C 8 H 8 would give C 8 H 8 whole 2 zirconium and lastly another example involved CP star or C 5 Me 5 which is also popularly called as Penta methyl cyclopentadienyl ligand, complex of titanium Ti Cl 3 in the dianionic form of the COT which is K 2 C 8 H 8 giving magnesium and C 8 H 8 in THF giving C 5 Ma 5 C 8 H 8 titanium.

Now, one thing to note over here, that in, all of these reactions, you know, these reducing agents like magnesium, metallic magnesium are over here, magnesium C 8 H 8 is aided has been added and this is primarily to make the COT into a dianionic form which because COT would take two electrons to become a dianionic form and that then would react with hafnium. So, in this case two COT in dianionic form makes happen hafnium +4 oxidation state in this case also it is 2 dianionic C 8 H 8 making the exact Zirconium plus in plus 4 oxidation state.

And whereas, in this case, it is titanium in + 3 oxidation state 2 from dianionic as well as 1 mono ionic C 5 H 5- but because of this reducing agent magnesium present in the system, that titanium has also undergone a reduction from + 4 over here to +3 over here. So, what we see is the fact that this preparation of the C 8 H 8 complexes of transition metal particularly that of the planar C 8 H 8 complexes of transition metal involves metal halide as well as some reducing agent and C 8 H 8 which will reduce C 8 H 8 2- a dianionic form which will then go and react with the transition metal halide giving the required transition metal halide complexes.

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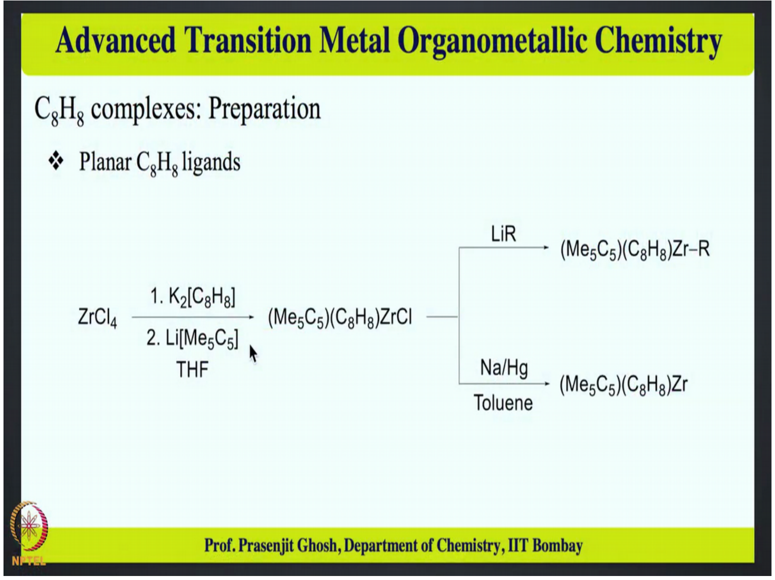

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C_8H_8 complexes: Preparation

- Planar C_8H_8 ligands

$$ZrCl_4 \xrightarrow[\text{2. Li}[Me_5C_5]\ \text{THF}]{\text{1. }K_2[C_8H_8]} (Me_5C_5)(C_8H_8)ZrCl$$

$$(Me_5C_5)(C_8H_8)ZrCl \xrightarrow{LiR} (Me_5C_5)(C_8H_8)Zr{-}R$$

$$(Me_5C_5)(C_8H_8)ZrCl \xrightarrow[\text{Toluene}]{Na/Hg} (Me_5C_5)(C_8H_8)Zr$$

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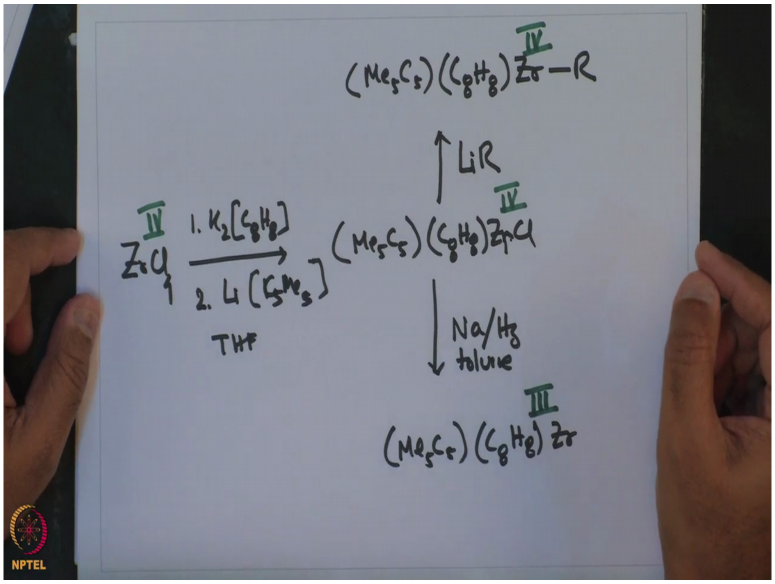

So, here is another interesting example of the synthesis for with zirconium salt and that is illustrated by the reaction discussed here. For example, reaction of zirconium Cl 4 with one K 2 dianionic form of C 8 H 8 and 2 lithium, lithium salt of C 5 Ma 5 pentamethene CP in tetrahydrofuran give rise to this Me 5 C 5 pentametheyl CP then dianionic C 8 H 8 zirconium chloride and that upon reaction with lithium alkyl would alkylate this zirconium giving rise to a Me 5 C 5 C 8 H 8 zirconium alkyl and if one were to do this reduction of zirconium 4 over here with sodium mercury Hg in toluene and then monitoring up when Me 5 C 5 C 8 H 8 zirconium.

We see the oxidation state over here zirconium is in +4 oxidation state, when one makes this pentametheyl CP its dianionic C 8 H 8 zirconium chloride then also zirconium is in +4 oxidation state when the chloride is exchanged with an alkyl to make the zirconium alkyl complex of C 8 H 8 anion dianionic ligand and mono anionic C 5 Me 5 ligand, then overall against zirconium is in +4 oxidation state however when the Kuro complex is treated with or reduced with sodium mercury amalgam to give the C 5 Me 5 C 8 H 8 zirconium, then the zirconium goes back to + 3 oxidation state.

So, this is an interesting reaction where one can see that the zirconium C 8 H 8 dianionic complexes can be formed with zirconium halide in presence of this cp lithium CP star salt giving rise to mixed valence compound which can further be reduced using sodium mercury or it can exhibit salt methods reaction as is observed by treatment with alkyl R to correspondingly synthesize the zirconium R derivative.

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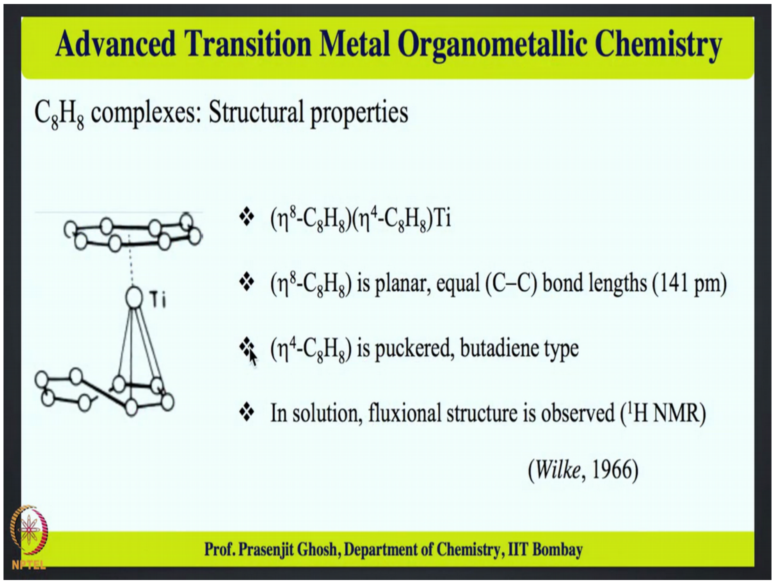

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C_8H_8 complexes: Structural properties

- ❖ $(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)Ti$
- ❖ $(\eta^8\text{-}C_8H_8)$ is planar, equal (C–C) bond lengths (141 pm)
- ❖ $(\eta^4\text{-}C_8H_8)$ is puckered, butadiene type
- ❖ In solution, fluxional structure is observed (^{1}H NMR)

(*Wilke*, 1966)

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So, then after synthesis we are going to move on to the structure and properties of transition metal C 8 H 8 complexes and one such example that we are going to be talking about is this C 8 H 8 complexes, however, the binding of these 2 C 8 H 8 ligands are quite different, and they bind in two different fashion one binding in eta 8 mode and the other binding in eta 4 mode.

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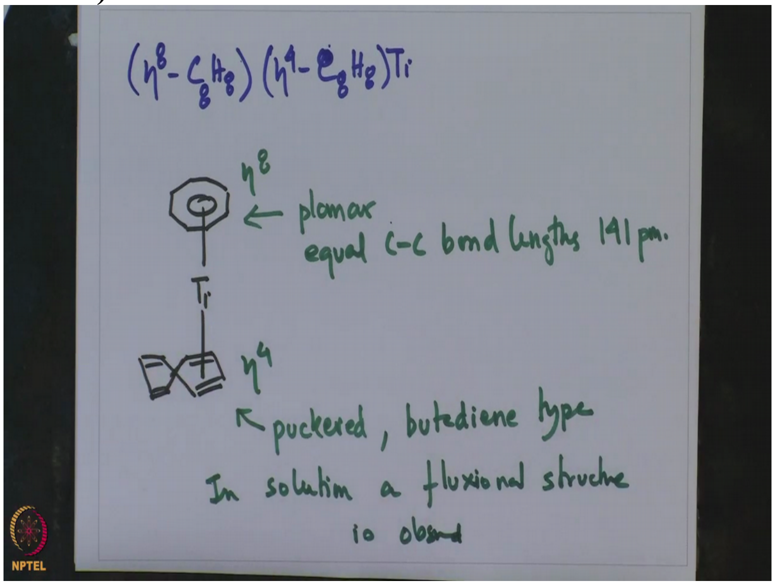

$(\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)Ti$

η^8 ← planar
equal C-C bond lengths 141 pm.

η^4
↖ puckered, butadiene type
In solution a fluxional structure is observed

A very nice example of this is seen for the complex eta 8 C 8 H 8 and eta 4 C 8 H 8 titanium. So this can be illustrated by the structure. So, the bottom one is bound in a eta 4 fashion where the top one is in eta 8 fashion eta 8 is planar, where, whereas this is non puckered eta 4 is puckered and eta 8 is planar contains equal C-C bond lengths of 141 picometer.

Whereas there is no conjugation across the whole ring in the eta 4 fashion because it is puckered, so it does not show equal bond length and this binding is more like a butadiene type and another interesting bit about the structure is that in solution fluxional structure is observed, okay.

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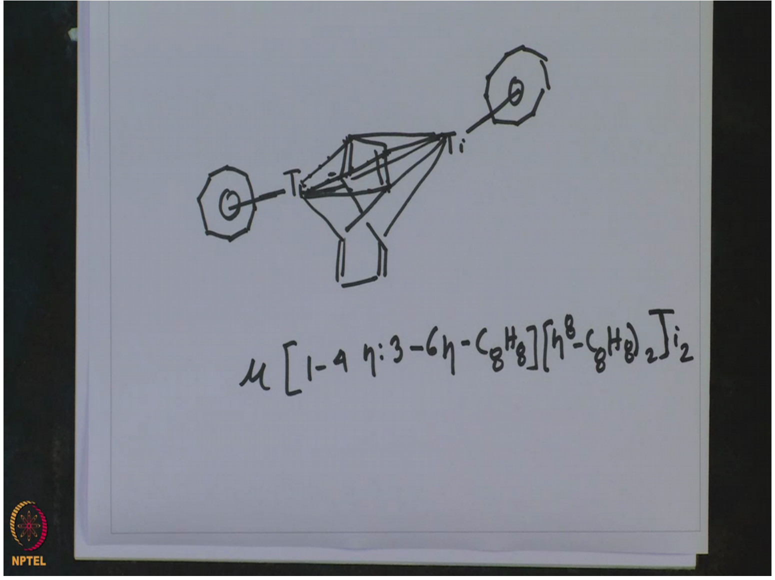

$$\mu[1\text{-}4\eta:3\text{-}6\eta\text{-}C_8H_8][\eta^8\text{-}C_8H_8)_2Ti_2$$

Now another interesting example of this compound is this titanium complex where these binds in a puckered fashion and it bridges across 2 titanium center something like that where each of the phase, 1 phase is bound to titanium and then it is bound, whereas the other side is also bound to another titanium and that is bound to another eta 8, 1 compound. So this is Mu 1 4 eta 3 6 eta C 8 H 8 eta 8 C 8 H 8 whole 2 titanium whole 2. So, this is a interesting compound in which as puckered eta 4 binds to two different titanium each of them is then bound to another planar C 8 H 8 moiety.

So, with this I would like to conclude today's discussion on our of our class and then to summarize we have started looking at the bridging binding of these eta 7 C 7 H 5 ligands and which can bind in a eta 3 and eta 4 fashion in a particular example that you are observed to produce hetro bi metallic compound and not only that and even that compound had a metal-metal bond and then we have looked into these new C 8 H 8 ligands that we have been talking about.

And what we have seen that C 8 H 8 ligand can bind into fashion one in a 10 electron dollar tanner geometry in which it is aromatic and it is dynamic in nature, all the C-C bond lengths are same, and the other is a puckered by binding where it behaves like a tetra olefin and more like a butadiene moiety and then we had also looked into various synthetic procedures available for preparing these complexes the ones that have looked at involves forming planar C 8 H 8 complexes.

And these reactions are primarily dependent on stoichiometry however the strategy is to take transition metal halides with C 8 H 8 in presence of some reducing agents which reduces C 8 H 8 to C 8 H 8 -2 dianion and then forms the complexes we have also looked at some of the structure of these complexes and in this particular we have looked at two titanium complexes one was eta 4 C 8 H 8 and eta 8 C 8 H 8 bound to ruthenium and the other one was di nuclear is titanium C eta 4 bound C 8 H 8, and then each of the titanium is bound in eta 8 fashion C 8 H 8 structure of which is shown over here.

So with this I am going to conclude today's discussion on structure and reactivity of C 8 H 8 complexes and then we are going to be taking the more on the structure and reactivity in C 8 H 8 complexes and the subsequent lecture. I once again thank you for patiently listening to this lecture, and I look forward to take up this topic of C 8 H 8 ligand and in a bit more detail in the next lecture to come. Till then good bye and thank you.