Advanced Transition Metal Organometallic Chemistry
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Lecture – 33
Transition Metal C 8 H 8 Complexes: Properties

Welcome to this course on, Advanced Transition Metal Organometallic Chemistry. As a part of our discussion on transition metal C 8 H 8 complexes, let me just recapitulate what we have been discussing in the previous lecture. We have been looking at C 8 H 8 ligand in the pretext of other common arene type ligands which are prevalent in organometallic chemistry like cyclopentadienyl or C 6 H 6 or C 7 H 7 and building upon that we have started looking at C 8 H 8 ligands, and its transition metal complexes.

Now as a part of our discussion in the last lecture we have also observed that C 8 H 8 ligand can bind in 2 fashion, it can have a puckered non planar structure, in which, C 8 H 8 more or less exhibits a butadiene type of structure and the whole C 8 H 8 ring has 4 double bonds as opposed to this puckered structure there exist another structures where C 8 H 8 can act as a 10 electron planar and exhibit a planet structure and acts as a 10 electron donor and in that form it is di-anionic in nature.

So, we had also looked into the preparations of the planar form of C 8 H 8 begins with its transition metal complexes and have also looked into various structurally characterized examples in which the transition metal have been found to bind to a planar form of the C 8 H 8 ligand as well and alongside also to the puckered form of the C 8 H 8 ligand. So, we had taken some examples consider some examples in our previous discussion and then coming into this class we are going to be discussing more on various kinds of complexes that C 8 H 8 ligand makes.

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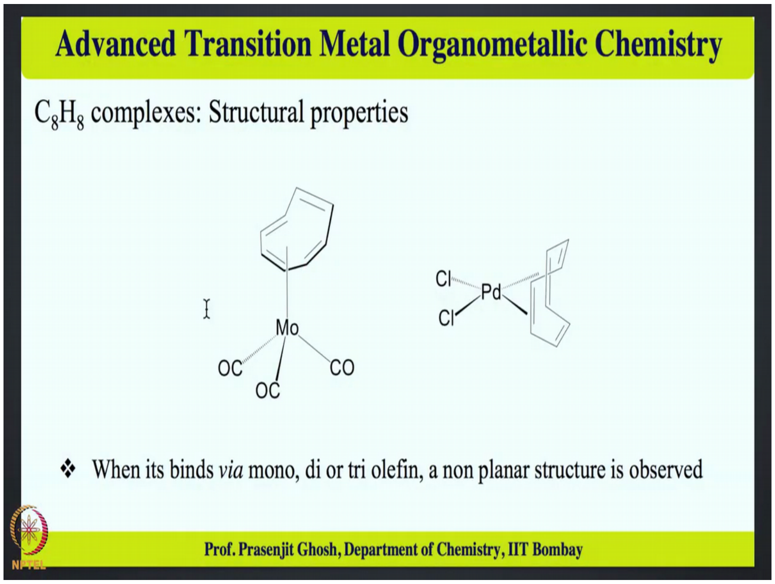

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C_8H_8 complexes: Structural properties

- When its binds *via* mono, di or tri olefin, a non planar structure is observed

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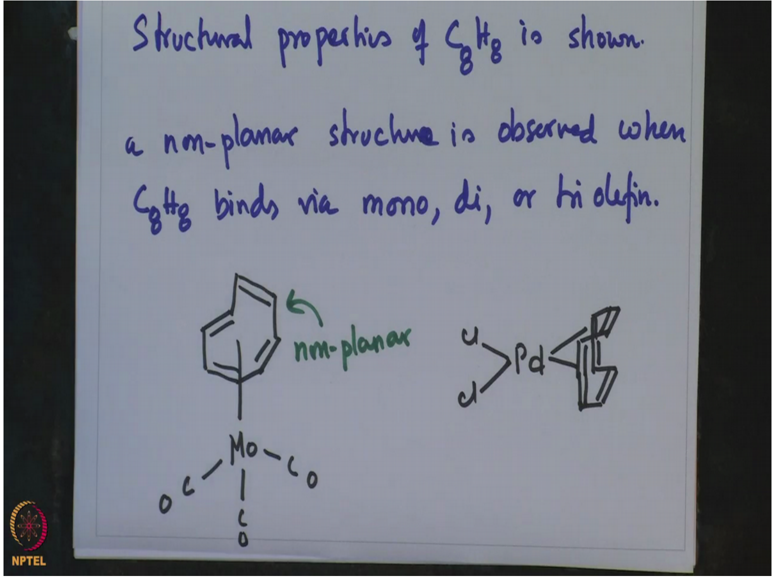

Structural properties of C_8H_8 is shown.

a non-planar structure is observed when C_8H_8 binds via mono, di, or tri olefin.

So, the structural properties of, properties of C 8 H 8 ligand is discussed is shown in the example below. So a non planar structure is observed when C 8 H 8 binds via mono, di or tri olefin and this is illustrated in the example shown over here. This is bound by 1 2 3 4 5 6, eta 6 fashion bound to molybdenum which is which in turn is bound to 3 carbonyl and the structure of the C 8 H 8 ligand is non planar and one can see the but the puckered structure of this complex.

Similarly in COT palladium dichloride, palladium, this C 8 H 8 link is also non planar and tub like, so what one sees is the fact that when these C 8 H 8 ligand binds via mono or di or tri olefins, then these chances are the that they are one obtained pucker one will obtain a pucker or non planar structure.

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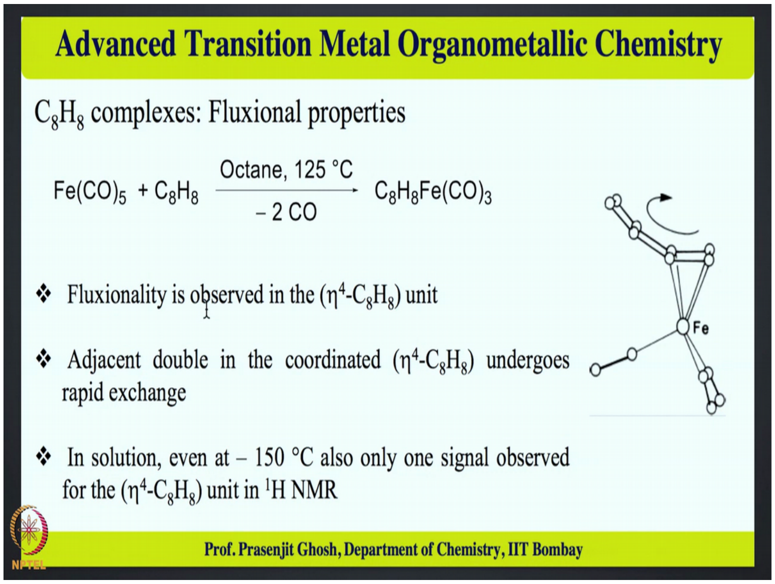

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C_8H_8 complexes: Fluxional properties

$$Fe(CO)_5 + C_8H_8 \xrightarrow[-\,2\,CO]{\text{Octane, 125 °C}} C_8H_8Fe(CO)_3$$

- ❖ Fluxionality is observed in the (η^4-C_8H_8) unit
- ❖ Adjacent double in the coordinated (η^4-C_8H_8) undergoes rapid exchange
- ❖ In solution, even at – 150 °C also only one signal observed for the (η^4-C_8H_8) unit in ^{1}H NMR

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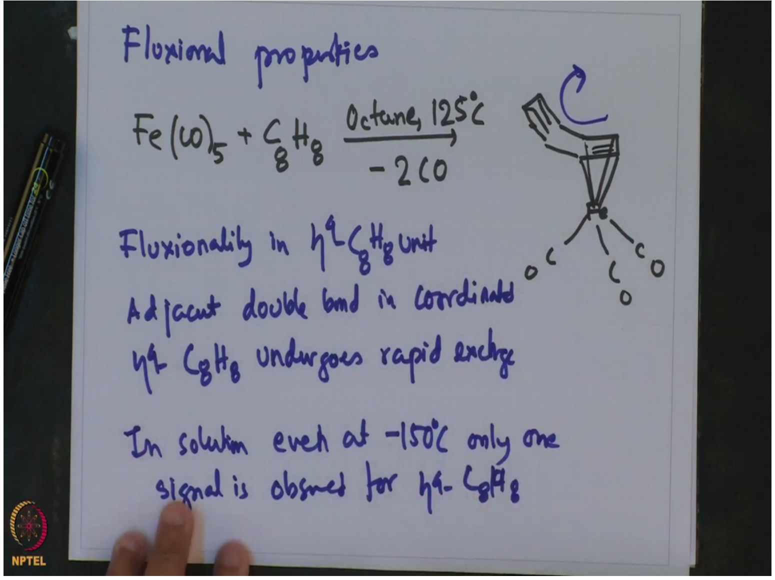

Fluxional properties

$$Fe(CO)_5 + C_8H_8 \xrightarrow[-2CO]{\text{Octane, 125°C}}$$

Fluxionality in η^4-C_8H_8 unit

Adjacent double bond in coordinated η^4 C_8H_8 undergoes rapid exchange

In solution even at -150°C only one signal is observed for η^4-C_8H_8

Another interesting aspect of these complexes are that some of these complexes are fluxional at room temperature. So the fluxional properties of C 8 H 8 complexes are illustrated in the examples given below. In particular, the reaction of Fe Co 5 + C 8 H 8 in octane at 125 degree centigrade eliminates 2CO's to give this kind of complex where this carbonyl is bound in a eta 5 fashion to 3 CO molecules and flexibility is observed in eta 4, C 8 H 8 unit in eta 4, C 8 H 8 unit adjacent double in bond in the coordinated sieve undergoes rapid exchange.

Double bond in coordinated eta 4 C 8 H 8 undergoes rapid exchange. That means, in solution, even at minus 150 degree centigrade, only one signal is observed, for eta 4 C 8 H 8 unit. So, what does that mean is that these will exchange will, with the other C 8 H 8 unit and that there is these 2 things just keep on exchanging amount itself so that at even a temperature above 180 degree centigrade that one could see only one type of C 4 H 8 eta bound C 4 H 8 units.

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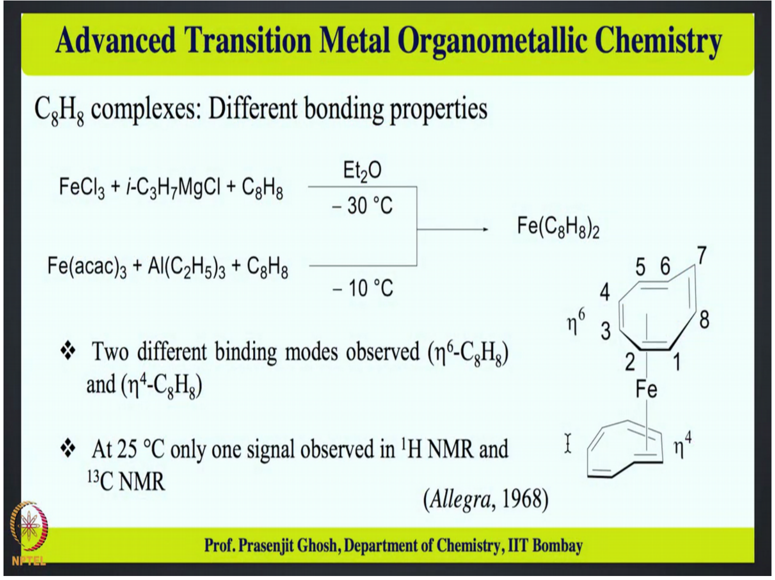

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C_8H_8 complexes: Different bonding properties

$$FeCl_3 + i\text{-}C_3H_7MgCl + C_8H_8 \xrightarrow[-30\ ^\circ C]{Et_2O} Fe(C_8H_8)_2$$

$$Fe(acac)_3 + Al(C_2H_5)_3 + C_8H_8 \xrightarrow[-10\ ^\circ C]{} Fe(C_8H_8)_2$$

- ❖ Two different binding modes observed (η^6-C_8H_8) and (η^4-C_8H_8)
- ❖ At 25 °C only one signal observed in ^{1}H NMR and ^{13}C NMR

(*Allegra*, 1968)

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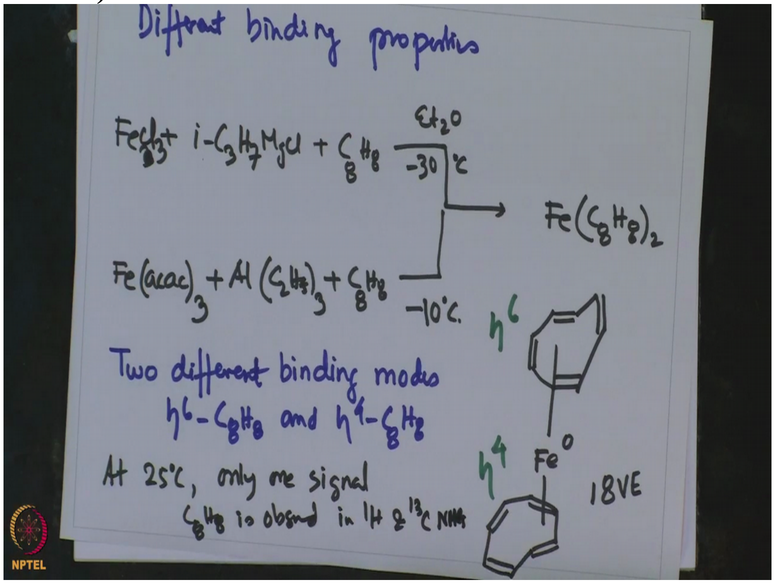

Different binding properties

$$FeCl_3 + i\text{-}C_3H_7MgCl + C_8H_8 \xrightarrow[-30\ ^\circ C]{Et_2O} Fe(C_8H_8)_2$$

$$Fe(acac)_3 + Al(C_2H_5)_3 + C_8H_8 \xrightarrow[-10^\circ C]{}$$

Two different binding modes
η^6-C_8H_8 and η^4-C_8H_8

At 25°C, only one signal
C_8H_8 is observed in ^{1}H & ^{13}C NMR

So, different binding properties of these C 8 H 8 ligand is explained here for example the bis C 8 H 8 iron complex which can be obtained by Fe Cl 3 + i C 3 H 7 Mg Cl + C 8 H 8 in ether, -30 degree centigrade gives Fe C 8 H 8 whole 2, whereas the same compound can also be prepared from a different precursor Fe ac faren acetyl acetonate + Al triethyl aluminum C 2 H 5 whole 3 + C 8 H 8, this at -10 degree centigrade gives this compound that this compound has 2 different binding modes observed.

These iron compounds contain 2 different binding modes, one is eta 6 C 8 H 8 and eta 4 C 8 H 8. So, eta 6 means that there is only the tri olefin is by only binding and eta 4 means di olefin binding, which sort of indicates that the ring definitely was not going to be a planar one, because only in, eta 8 mode that a planar dynamic C4 C 8 H 8 ligand is observed.

So, this sort of gives an idea as to what are the, what are the structures in one structure the C 8 H 8 is bound the way it is shown over here. Fe so again, the iron over here is in iron zero state and these 18 electron compound, this is 1 2 3 4 5 10 + 8 is 18 valence electron compound, and if you see that this needs some kind of reducing agent because the starting precursor is indeed iron 3 iron acetyl acetonate or Fe Cl 3 which is also iron 3 but in the final compound it is iron zero .

So, there some kind of reduction reagent reducing reagent is required, and we see that these bis C 8 H 8 complex does have 2 different kind of C 8 H 8 ring, one is bound in a eta 4 fashion, whereas the other one is bound in a eta 6 fashion, and 2 different binding, also as was seen and for the other complex at 25 this compound is fluxional and at 25 degree centigrade, only one signal of C 8 H 8 ligand is observed in proton and 13C NMR’s.

So, this is kind of interesting that these molecules are indeed non planar and as has been said earlier that if mono, di, tri or tetra olefin just coordinates then one is going to get non planar structure, and this is exactly what is seen over here. Now C 8 H 8 can also act as a bridging ligand and this is illustrated by an example shown over here.

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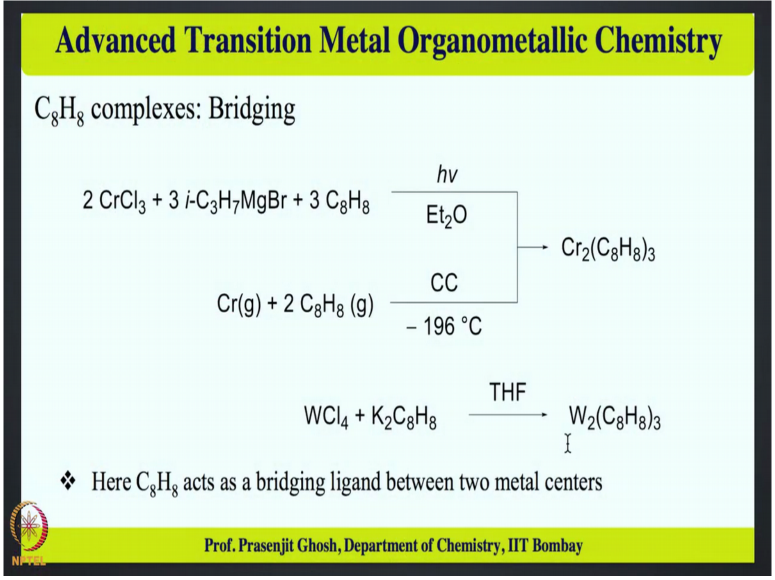

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C_8H_8 complexes: Bridging

$$2\,CrCl_3 + 3\,i\text{-}C_3H_7MgBr + 3\,C_8H_8 \xrightarrow[Et_2O]{h\nu} Cr_2(C_8H_8)_3$$

$$Cr(g) + 2\,C_8H_8\,(g) \xrightarrow[-196\ ^\circ C]{CC} Cr_2(C_8H_8)_3$$

$$WCl_4 + K_2C_8H_8 \xrightarrow{THF} W_2(C_8H_8)_3$$

❖ Here C_8H_8 acts as a bridging ligand between two metal centers

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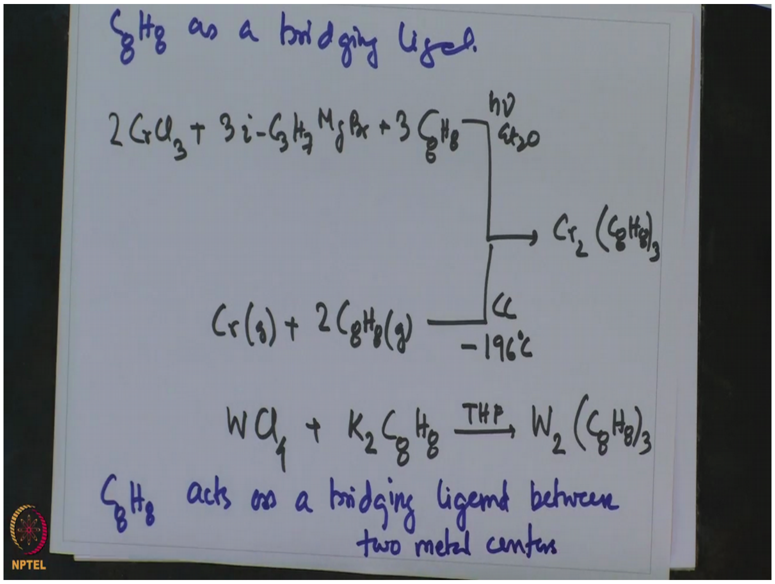

C_8H_8 as a bridging ligand.

$$2CrCl_3 + 3\,i\text{-}C_3H_7MgBr + 3C_8H_8 \xrightarrow[Et_2O]{h\nu} Cr_2(C_8H_8)_3$$

$$Cr(g) + 2C_8H_8(g) \xrightarrow[-196^\circ C]{cc} Cr_2(C_8H_8)_3$$

$$WCl_4 + K_2C_8H_8 \xrightarrow{THF} W_2(C_8H_8)_3$$

C_8H_8 acts as a bridging ligand between two metal centers

So, C 8 H 8 as bridging ligand, now these are bridging ligands are commonly observed or the example that we are going to be talking about are observed for the bis C 8 H 8 complex of chromium and tungsten. So, before I go and talk about the structure of these 2 bis C 8 H 8 ligand chromium and tungsten, which are ISO structure, let me just give the synthesis of these 2 compounds chromium tier 2 C 8 H 8 whole 3 and tungsten 2 C 8 H 8 whole 3 the reactions are given over here, before the structural discussion is initiated on these 2 dinuclear complexes.

For chromium the reaction of chromium trichloride + 3i C 3 H 7 Mg Br + 3 C 8 H 8 in H N u and ether gives Cr 2 C 8 H 8 O3. Similarly one can do see a chromium gas + 2 C 8 H 8 gas and by the co-condensation method -196 degree centigrade one would get this di chromium tri C 8 H 8 ligand and the correspondingly the tungsten compound however is prepared by a slightly different method in which is directly reacted with the dianionic C 8 H 8 ligand.

So, WCl 4 + K2 C 8 H 8 in presence of THF would give to W 2 C 8 H 8 whole 3. Now here C 8 H 8 and act as a bridging ligand between the 2 metal centers, so the interesting thing about these 2 complexes is that, C 8 H 8 acts as bridging ligand between 2 metal centers, okay. Let me illustrate this fact with the structural characterization of these 2 complexes the x-ray data, single physical data indeed show that, these are breathing systems of C 8 H 8 ligands.

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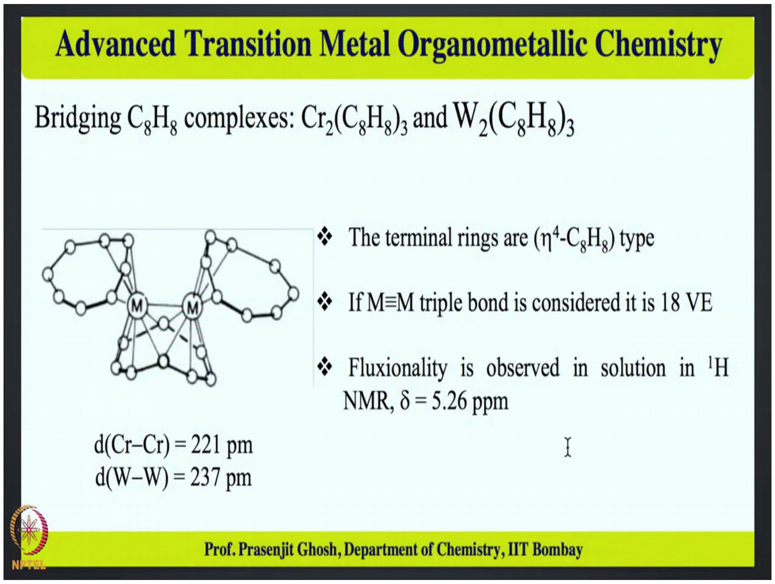

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Bridging C_8H_8 complexes: $Cr_2(C_8H_8)_3$ and $W_2(C_8H_8)_3$

- The terminal rings are (η^4-C_8H_8) type
- If M≡M triple bond is considered it is 18 VE
- Fluxionality is observed in solution in ^1H NMR, $\delta = 5.26$ ppm

d(Cr–Cr) = 221 pm

d(W–W) = 237 pm

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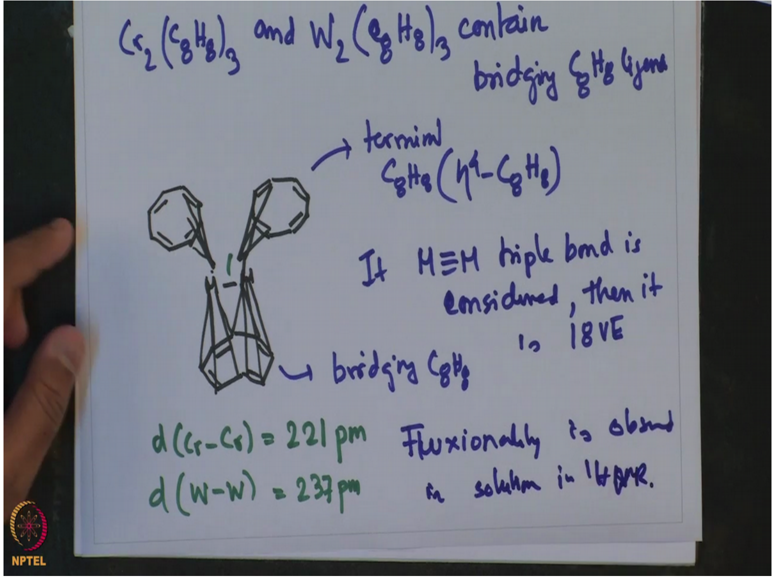

$Cr_2(C_8H_8)_3$ and $W_2(C_8H_8)_3$ contain bridging C_8H_8 ligand

→ terminal C_8H_8 (η^4-C_8H_8)

If M≡M triple bond is considered, then it is 18VE

→ bridging C_8H_8

d(Cr–Cr) = 221 pm

d(W–W) = 237 pm

Fluxionality is observed in solution in ^1H NMR.

So, Cr 2 C 8 H 8 whole 3 and W 2 C 8 H 8 whole 3 contain bridging C 8 H 8 ligands. So, let me just illustrate this with the example and another these 2 unit, is bound to 2 metals and which in turn are bound to this way another the third C 8 H 8 and these are also bound to each other. So, there is a metal-metal bond which is a chromium-chromium bond, and that d Cr is 221 ppm picometer and the tungsten tungsten is 237 picometer.

So, here what we see is that, there are 2 kinds of ligands, these is terminal C 8 H 8 and this one is bridging C 8 H 8, okay. The terminal C 8 H 8 are of eta 4 C 8 H 8 type, and here also, if this metal-metal triple bond is observed is considered then it is 18 valence electron complex and there is a fluxionality is observed in solution in proton NMR is observed in solution in proton

NMR. So these are highly dynamic systems which contains these dinuclear chromium chromium or tungsten types and complexes supported by both bridging and terminal C 8 H 8 ligands.

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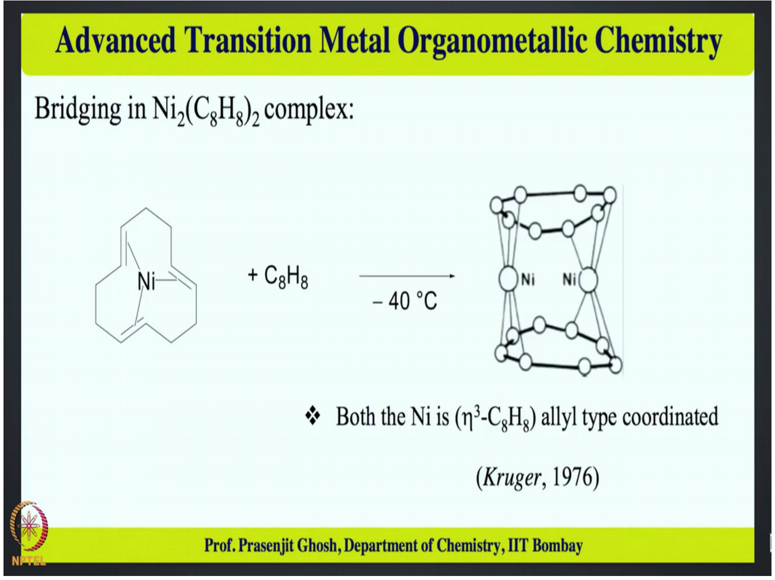

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Bridging in $Ni_2(C_8H_8)_2$ complex:

❖ Both the Ni is (η^3-C_8H_8) allyl type coordinated

(*Kruger*, 1976)

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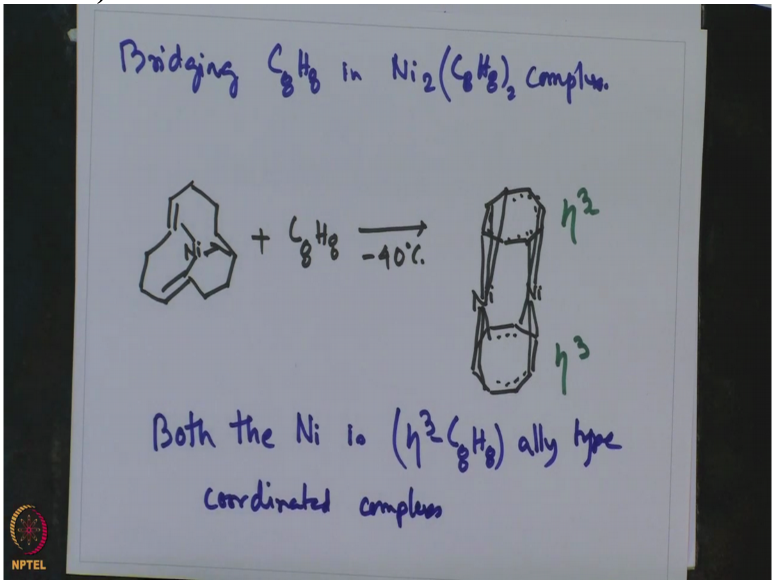

Bridging C_8H_8 in $Ni_2(C_8H_8)_2$ complex.

Both the Ni is (η^3-C_8H_8) ally type coordinated complex

There is another bridging complex in which this C 8 H 8 reaches between 2 nickel Center and this is illustrated by this nice example. So we are going to bridging C 8 H 8 in Ni 2 C 8 H 8 whole 2 complex, and in this, it is prepared by the reaction of, complex of nickel + C 8 H 8 at -40 degree centigrade contains these ring where these are bound in these both are nickels are bound in eta 3 fashion and similarly over here, how so interesting thing is that both of the nickel center is bound in eta 3 fashion and the C 8 H 8 ligand is acting as a bridging ligand supporting a dinuclear such structure.

So both the nickel is eta 3 C 8 H 8 allyl type coordinated complex. So, with this I would like to conclude our discussion of C 8 H 8 type of complexes. Particularly in this lecture, we have looked into, this structure and reactivity of the C 8 H 8 type complexes and what we are saying that the C 8 H 8 type complexes can bind in both the fashions, bridging and terminal, and also it can show change in hapticity which can varies a lot.

What we had observed is that non planar structure is obtained if it binds with mono olefinic, di olefinic or triolefinic form, whereas if we have all the 8 carbon atoms are engaged to the transition metal, then it can bind in a planar form. Now these molecules apart from different binding, it can also; another characteristic is the fact that it is they are also very fluxional, in the sense that at room temp temperatures higher than room temperature Oregon's temperatures which are even lower than room temperatures these compounds show rapid exchange between the ligand and the metal center.

Also, what is came to for that they not only can form mono nuclear complexes, but they also exist, can exhibit dinuclear complexes and in those cases this hapticity, he, can vary from 3 to 5. So apart from 2 4 6 8 kind of other activity, these gamma complexes can also say show activity, hapticity of 3 and 5. So, with these we conclude our discussion on C 8 H 8 ligands complexes of transition metal and these sort of the close down on our discussions of various Sigma donor, Pi acceptor kind of ligands, starting from allyl and going up all the way to C 5 H 5 to then as C 6 H 6 then for following up on C 7 H 7 and finishing with C 8 H 8.

So, these are a very nice set of ligands that we have looked in detail we have tried to understand their bonding, particularly from the level of the molecular orbital and get a glimpse of the electron structure which sort of can help us understand their reactivity, we have looked into various repetitive methods available for preparing these complexes, and also we have looked into the structure and the reactivity replications that come out of these electronic structures that we have discussed.

So, with that in backdrop we are going to finish our topic on C 8 H 8 ligand in this lecture and then we are going to move on to the hetero cycles, these are very interesting, bit of compounds bits of compounds and they also needs a good full-fledged discussion on the structure and reactivity and which as well as their property which will be taken up in the next lecture.

So, with this I once again thank you for patiently listening to this lecture and then look forward to taking up a new topic studying like next lecture where we are going to be talking about hetero cyclic organometallic chemistry. So, till then goodbye and thank you.