Advanced Transition Metal Organometallic Chemistry
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Lecture – 15
Transition Metal Cyclopentadienyl Carbonyl Complexes: Preparation.

Welcome to this course on, Advanced Transition Metal Organometallic Chemistry. In today's lecture, we will be talking about, transition metal cyclo pentadienyl carbonyl complexes; these are popularly known as half-sandwich can complexes primarily from the point of view of havingcyclopentadienyl ligand a metal and the remaining ligand sites being occupied by carbonyl moieties.

So, the name derives from the fact that these cyclopentadienyl complexes which contains two CP rings and the metal are called sandwich complexes whereas cyclo pentadienyl metal carbonyl complexes which containssingle cyclopentadienyl ligand are called half sandwich complexes. Also these half sandwich complexes are transition metal cyclo pentadienyl carbonyl complexes differ from their metallocenes counterpart by being heteroleptic in nature, means, it contains two different kind of ligands.

As oppose to the metallocenes which are by aryl, binary compounds of cyclopentadienyl ligands and their homoleptic complexes and also called sandwich complexes. So, in our last class on these half sandwich complexes of transition metal cyclo pentadienyl carbonyl complexes, we have looked into the preparative methods availablefor synthesizing this compound. The method that we looked at was, direct reaction of transition metal carbonyls with cyclo pentadiene resulting in formation of this half sandwich cyclo pentadiene transition metal carbonyl complexes.

So,we would be discussing, more on various synthetic methods available,for preparation of these complexes as well as on their structure and reactivity. So continuing along the discussion we were having on the synthesis of transition metal cyclo pentadienyl carbonyl complexes, we want to look at some other exampleswhich are available for preparation of thesecompounds.

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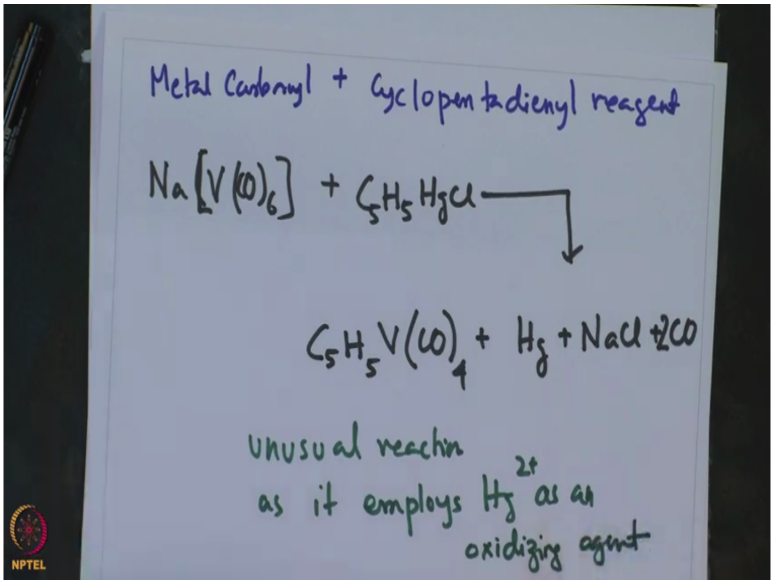

Metal Carbonyl + Cyclopentadienyl reagent

$Na[V(CO)_6] + C_5H_5HgCl \rightarrow$

$C_5H_5V(CO)_4 + Hg + NaCl + 2CO$

unusual reactin
as it employs Hg^{2+} as an
oxidizing agent

The other method involves metal carbonyl plus cyclo pentadienyl reagent, for example reaction of in a Na V CEO 6 + C5 H5 Hg Cl giving rise to C5 H5 V CO 4 + Hg + Na Cl + 2 CO. Now this is an unusual reaction as itimplies Hg2+ as a an oxidizing agent resulting in the preparation of C5 H5 VO 6 along with the precipitation of elemental mercury.

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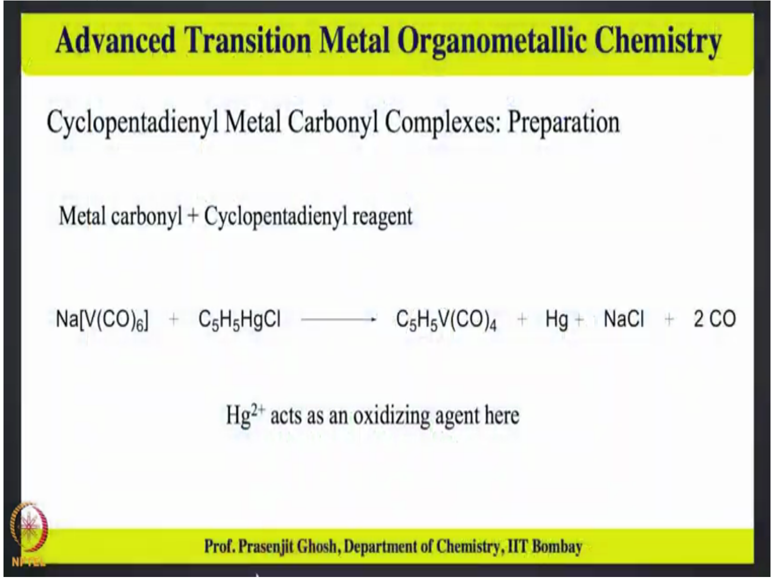

Advanced Transition Metal Organometallic Chemistry

Cyclopentadienyl Metal Carbonyl Complexes: Preparation

Metal carbonyl + Cyclopentadienyl reagent

$Na[V(CO)_6] + C_5H_5HgCl \longrightarrow C_5H_5V(CO)_4 + Hg + NaCl + 2\,CO$

Hg^{2+} acts as an oxidizing agent here

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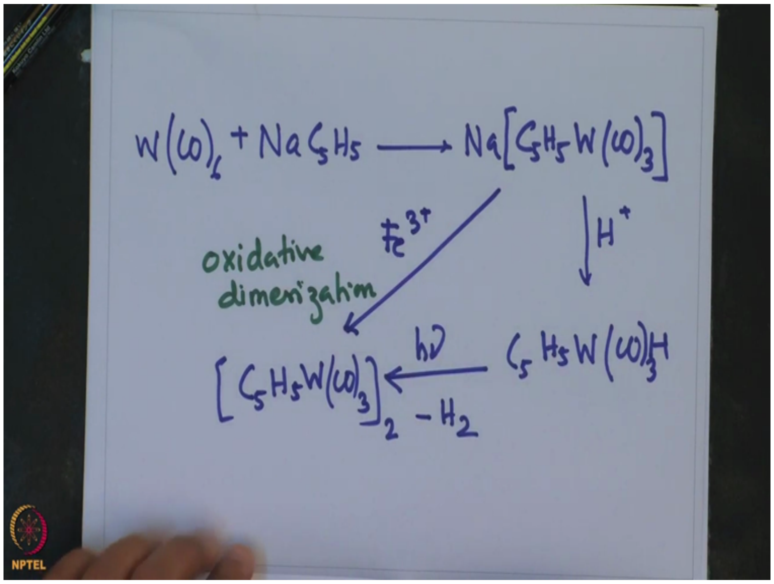

The next method also is along the similar line, reaction of tungsten extra carbonyl plus sodium CP whichresults in the formation of sodium C5 H5 tungsten Co 3 and that is a methylated ion, when protonated, gives the corresponding type tungsten hydride complex, C5 H5 tungsten CO3 and these hydride complex decomposes in light, eliminating hydrogen to give the dimer C5 H5 tungsten CO3 andthe same dimer can be directly obtained by treating the sodium C5 H5 tungsten tri carbonyl with Fe3 + ion, thatitself will get reduced and resulting in the formation of the C5 H5 tungsten tri carbonyl dimer.

So, this methodof getting this dimer from this tungsten metalate is called oxidative dimerization and is triggered by the presence of iron 3 which acts as an oxidizing agent. So, this is a interesting way of synthesizing cyclopentadienyl iron tricarbonyl kind of complexes by direct reaction of tungsten hexacarbonyl with the cyclopentadienyl reagent. In this case it is sodium CP.

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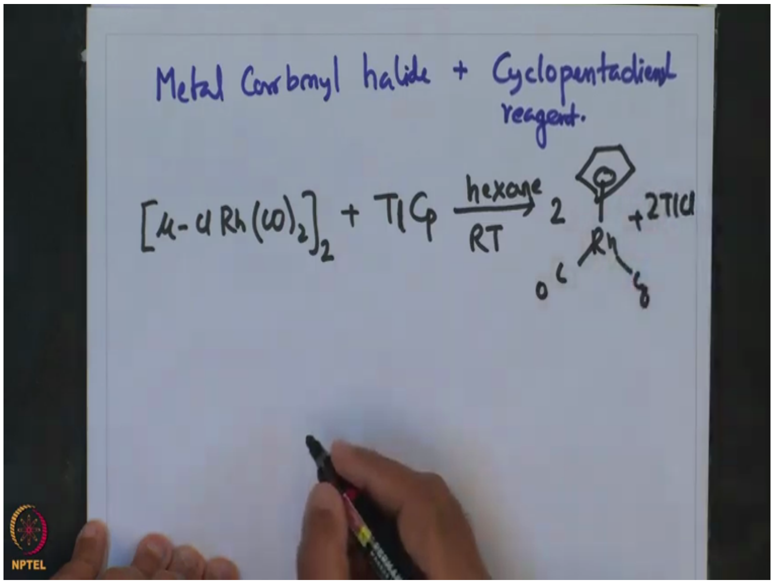

Metal Carbonyl halide + Cyclopentadienyl reagent.

The next reactionis the reaction of metal carbonyl halide with cyclo pentadienyl reagent. So, this is illustrated as follows: Cl Mu Cl, rhodium dicarbonyl dimer plus thallium CP cyclopentadinyl thallium in hexane, at room temperature gives two equivalents of CP rhodium dicarbonyl plus twice thallium chloride. Subsequent reaction involves cyclopentadienyl metal halide being reduced with a reducing agent in presence of carbonmonoxide that will also give cyclo pentadienyl carbonyl complexes.

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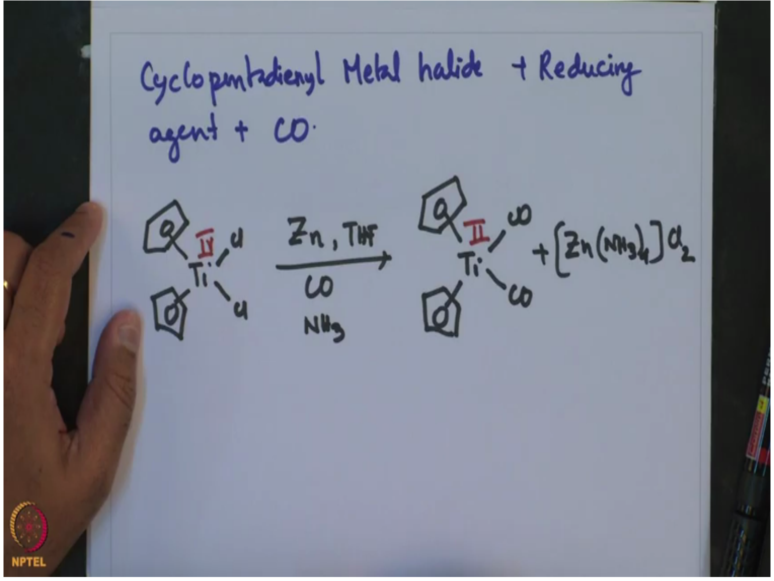

Cyclopentadienyl Metal halide + Reducing agent + CO.

So, the next method involves metal-halide plus reducing agent plus carbon monoxide. The nice example of this is shown over here. This is BCP titanium dichloride this in this case titanium is in plus 4 oxidation state the reducing agent is zinc in THF, in presence of carbon monoxide and NH3, gives the desired BCP titanium di carbonyl compound plus zinc tetramine dichloride. So in this casethe titanium has been reduced from +4 oxidation state to +2 oxidation state usingthe reducing agent which is zincin this case.

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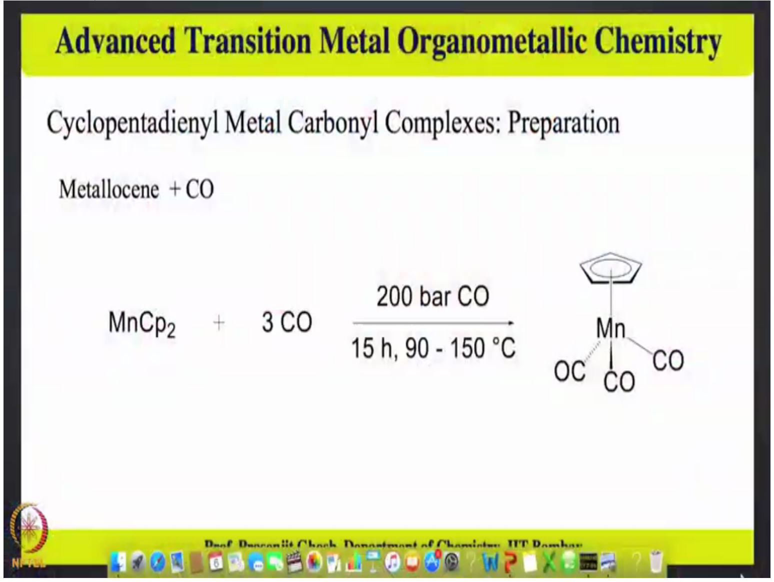

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Cyclopentadienyl Metal Carbonyl Complexes: Preparation

Metallocene + CO

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Another reaction involves directreaction of metallocene with carbon monoxide.

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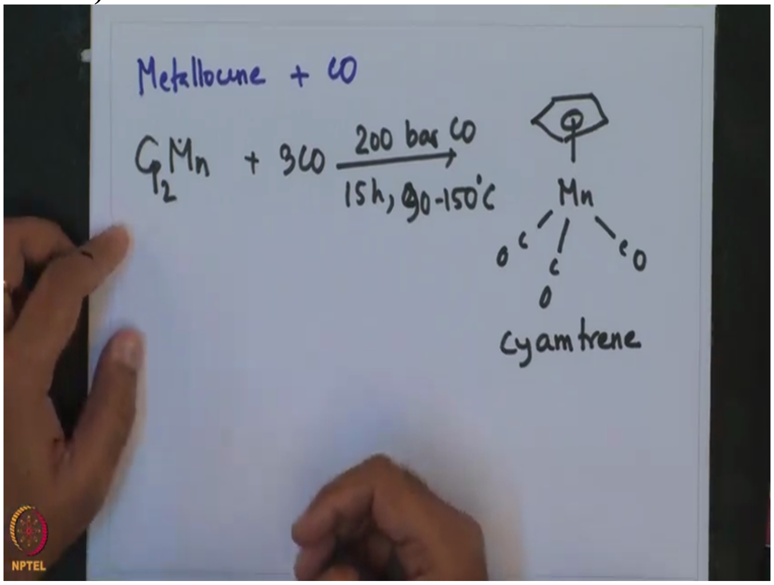

Metallocene + CO

So, in this case no reducingagent is used. This reaction however requires drastic conditions as we see by high pressure and temperature and longer reaction times. For example, CP 2, manganese plus 3 carbonyl in 200 bar of CO 15 hours, 90 to 150 degree centigrade gives this CP manganese tricarbonyl complex which is popularly called Cyamtrene. So, thismethod is a direct method of reacting metallocene with carbon monoxide andat the very elevated pressure and temperature and longer reaction time to produce this manganese CP a tri carbonyl compound which popularly is known as Cyamtrene.

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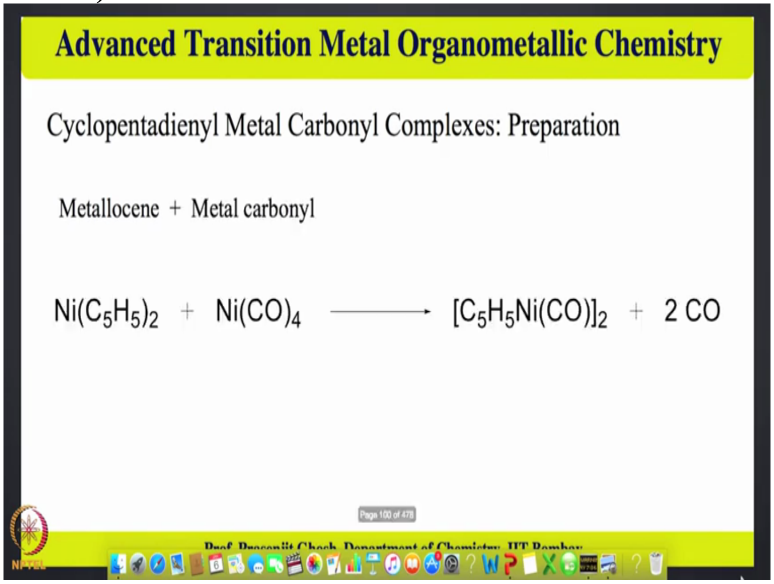

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Cyclopentadienyl Metal Carbonyl Complexes: Preparation

Metallocene + Metal carbonyl

$Ni(C_5H_5)_2 + Ni(CO)_4 \longrightarrow [C_5H_5Ni(CO)]_2 + 2\,CO$

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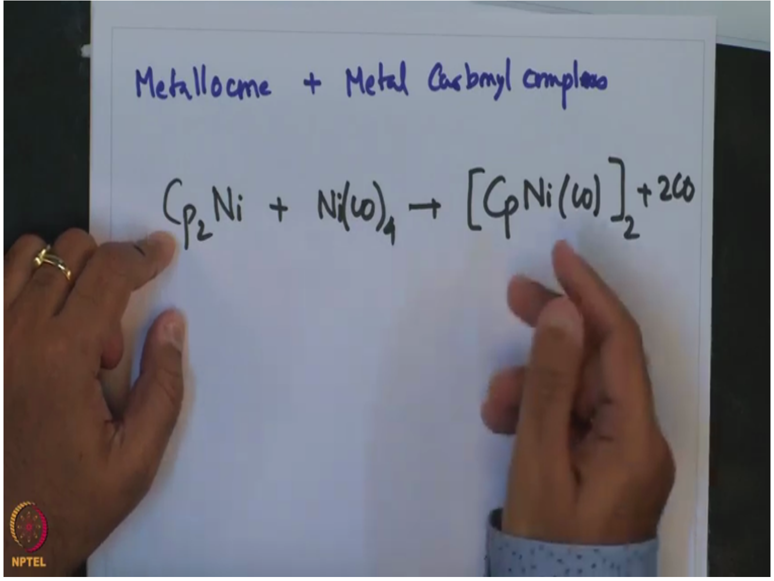

Metallocene + Metal Carbonyl complexes

$Cp_2Ni + Ni(CO)_4 \rightarrow [CpNi(CO)]_2 + 2CO$

The last method involves reaction of metallocene with the metal carbonyl complexes plus metal carbonyl complexes and the reactionis between nickelocene plus nickel tetra carbonyl compound giving CP nickel carbonyl dimer +2CO. So, this also is a viable method for synthesizing cyclopentadienyl metal carbonyl complexes. So, what we saw primarily is the reactionsthat involves the preparation of transition metal cyclo pentadienyl carbonyl complexes involved the reaction ofeither metallocenesdirectly.

We take carbon monoxide or carbonyl compound or with a reducing agent in presence ofof carbonyl compound or it can also be from metal carbonyls and cyclopentadienyl complexes or metal carbonyls with cyclopentadienyl reagents which also lead to the formation of this transition metal cyclo pentadienyl carbonyl complexes.

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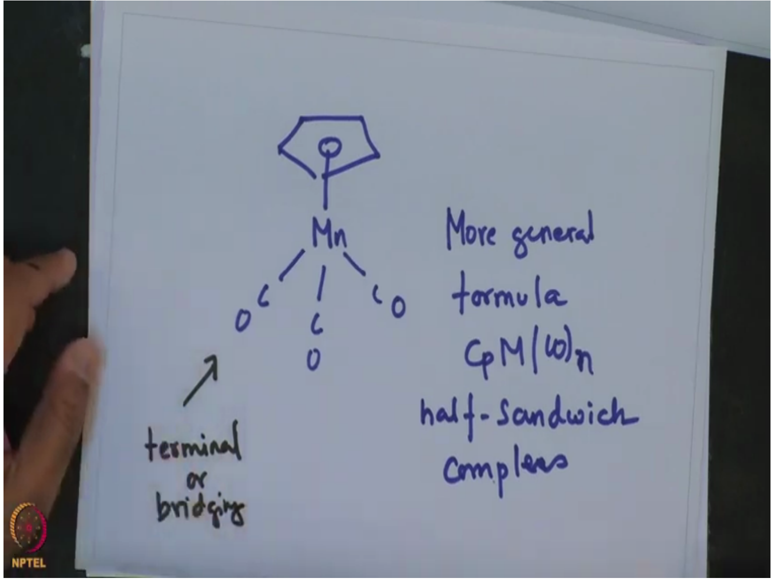

Now we now look at the structure of this cyclopentadienyl carbonyl complexes, for example, the structure of this kind of compounds are primarily of this type where you have a CPM, CO, CO3 MN CO3 or more generally more general formulawould be CPM COnfor depending on the metal, the end may vary and these are called half sandwich complexes as opposed to the full sandwich complexes a feature there in metals in compounds.

Also another notable thing aboutthesetransition metal cyclopentadienyl carbonyl complexes that these carbonyl moieties can act as terminal or bridging. Terminal orbridging depending upon the metal centers they are bound to. So, I will illustratethiswith the following examples for example these carbonyl moieties can act as both bridging and terminal, when they're bound to 3d metals, whereas they can act as mainly terminals when bound to 4d or 5d,metals.

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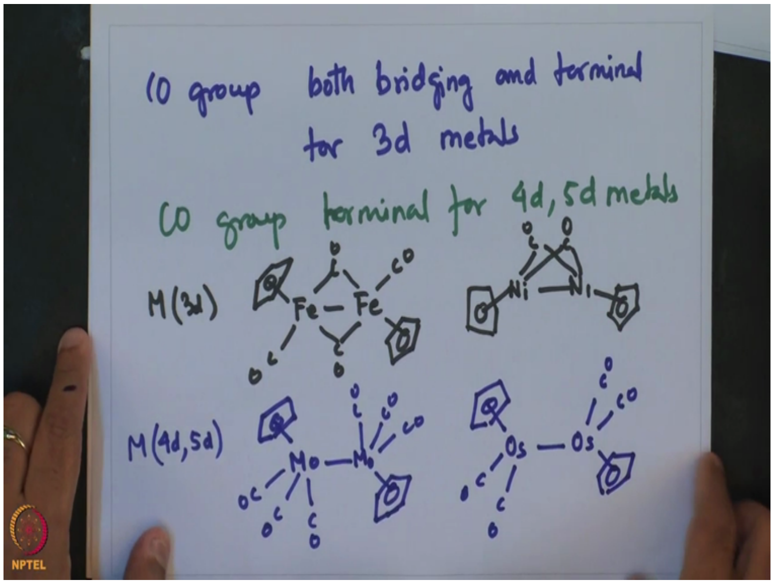

CO group both bridging and terminal
for 3d metals

CO group terminal for 4d, 5d metals

So, CO ligand groups can beboth bridging and terminal for 3d metals whereas the CEO groups may is mainly a terminal for 4d and 5d metals. The reasons are being very simple 4d and 5d bridging bigger than 3d the bridging binding is not favored. So I am going to illustrate this in the following example if M is 3d then FeC dimer can have both bridging carbonyl as well as terminal carbonyl.

Also for the nickel complex, it also hasthe bridging, whereas, when the metal is 4d or 5d, thenit can actmainly as the terminal carbonyls for example, for this CP molybdenum tri carbonyl dimer, this and osmium, CP dicarbonyl dimer, which mainlyhas this time zone moiety. So, over here this being bigger theyhave terminal carbonyls, whereas, in 3d, it being smaller in size, they can have both bridging and terminal moieties.

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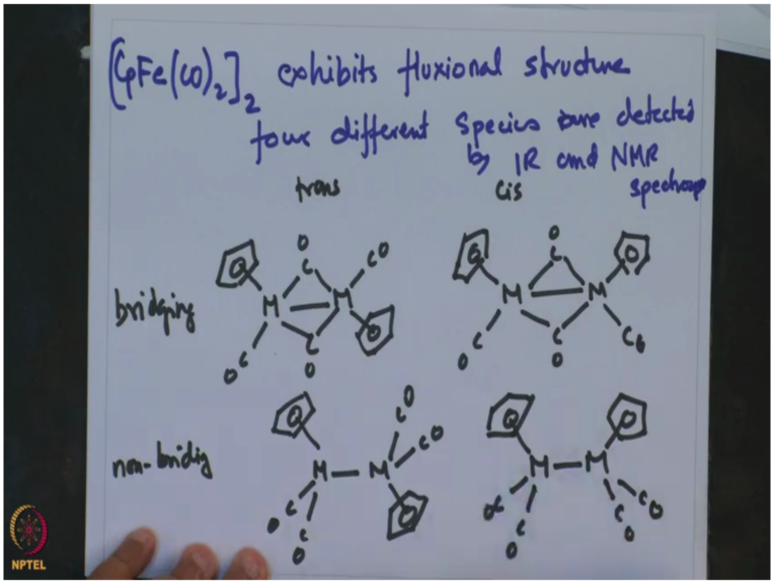
$[CpFe(CO)_2]_2$ exhibits fluxional structure
four different species were detected by IR and NMR spectroscopy

So, this is very much reflected in this iron CP dicarbonyl dimer which has fluxional structure, Fe CP CO2 whole 2 exhibits fluxional fractional structure and 4 different species, species detected by IR and NMR spectroscopy, and that is primarily because of its bridging and non bridging nature, and also because of CIS and trans isomerism, for example, this compound can exist in following bridging, the confirmation which is trans, this is with bridging carbonyls and also in the CIS confirmation.

The way it is shown over here, and non-bridging conformation the way it is shown over here. So, over here, is that, this CP iron dicarbonyl moiety exhibits functionality and that 4 different kinds of species are observed by NMR and IR and this is because various CIS and trans isomeric forms in which thismolecule can exist in which this cyclopentadienyl moiety, can have a trans disposition to each other or they can have CIS disposition to each other.

And also the other possibility is that this carbon moiety can be acting as a bridging ligand in two of the conformation CIS and trans over here as well as at the carbonyl moiety being totally terminal nature in the two other conformation as shown over here, so this speaks aboutthe different properties that one can exist that can arise due to the terminal and the bridging binding of this ironof these iron dicarbonyl CPdimer complexes.

So, with this I would like to conclude today'slecture which had primarily been on various preparative methods available for synthesizing cyclopentadienyl iron carbonyl complexes that these primarily involves two types of synthesis in which metal carbonyls were directly reacted with cyclopentadiene to give and this, the desired complexes, or it can alsobe the reaction of metal carbonyl with cyclopentadienyl reagent.

The otherreactions or the other strategies also involved reacting metallocenes with carbonyl compounds in presence or absence of the reducing agent to generate the striker metal carbonylcyclopentadienyl complexes. Now as well is the structure and the reactivity of these compounds are concerned which was also discussed in this lecture, it was found that they exhibit both as a bridging as well as terminal depending on which kind of metal central they are bound to for 3d transition metals the carbonyl tend to exist in both bridging and terminal forms whereas how the carbonyl ligands exists as terminal ligands in for 4d and 5d.

We have also explained the functional nature of iron CP dicarbonyl dimer which sort of exists in 4 different forms, depending on the bridging cis and trans isomers that can form out of the carbonyl binding. So with this I would like to conclude; now today is a lecture and we are going to discuss more on the reactivity of transition metal carbonyl complexes as well as transition metal cyclo pentadienyl nitrocyl complexes in the next lecture. So, till then thank you forbeing patiently listening to this lecture and I look forward to being with you in the next lecture, till then good bye.