Transition Metal Organometallic Chemistry : Principles to Applications
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Week - 10
Lecture – 47
Transition Metal Carbonyls: Reactivity and Carbonyl Metallates

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. We have been discussing a very important class of organometallic compound in the last few lectures and these are transition metal carbonyl complexes.

And these transition metal carbonyl complexes are important intermediates in many catalytic reactions and that is why they are very interesting. As well as by the fact that these transition metal carbonyl complexes are one of the earlier organometallic complexes that have been synthesized; whereas, their bonding properties particularly a the molecular orbital diagrams involving how they bond with transition metals, they are only recently developed.

So, we have this the we had this compound for a very long period of time over a century, but understanding their bonding only happened may be few decades back. So, from that perspective these are very interesting class of compounds. We have leaked looked at the bonding we have looked at the bonding properties of this kind of transition metal compounds, the way they bond in a terminal fashion to the metal or that they bridge and the kind of bridging's that they may undergo.

All of these were discussed in the last few lectures including the last one also included; the reactivity studies, of this transition metal carbonyl complexes. And what we had seen is that these transition metal carbonyl complexes which are of having 18 valence electron underwent dissociative mechanism, underwent substitution by; whereas, what we had also seen the transition metal complexes which are 17 valence electron underwent substitution by an associative mechanism.

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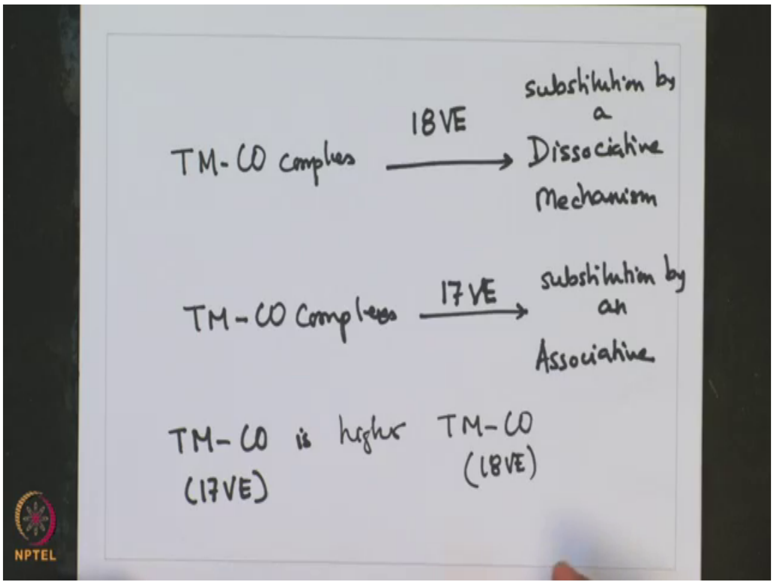

TM-CO complex $\xrightarrow{18VE}$ substitution by a Dissociative Mechanism

TM-CO Complexes $\xrightarrow{17VE}$ substitution by an Associative

TM-CO (17VE) is higher TM-CO (18VE)

And what we had also seen in the last class is that the rate of substitution for the transition metal 17 electron complex is significantly higher or significantly faster than the transition metal carbonyl complexes having 18 valence electrons. And this probably is because of the fact that the 17 valence electron species underwent association of ligand reaching a 19 valence electron species which is highly unstable, giving undergoing the substitution and giving back the substituted 17 valence electron species.

So, because of these in the last lecture we had seen that the substitution reaction was faster for case of 17 valence electron transition metal carbonyl compounds than that for 18 valence electron transition metal carbonyl compound.

Now, with that in background we are going to discuss another interesting type of reaction for transition metal carbonyl complexes and these are addition reaction at the carbonyl and this particularly relates to addition of nucleophiles to CO.

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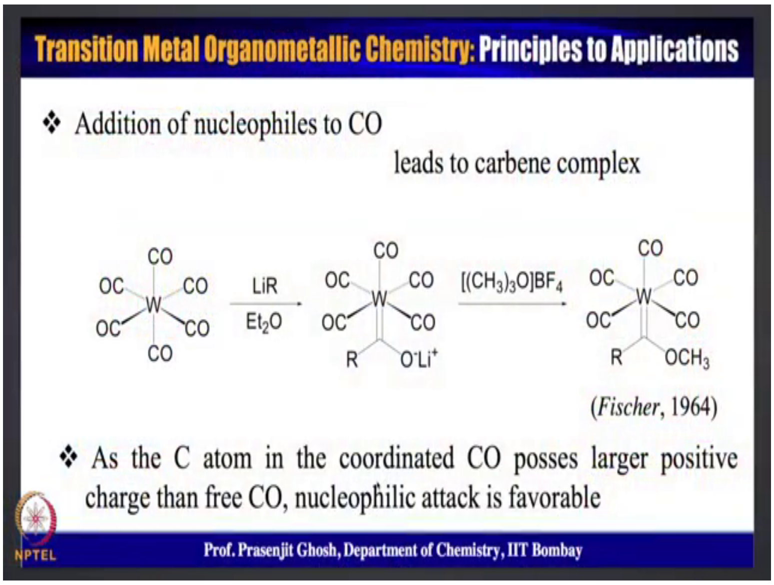

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- Addition of nucleophiles to CO leads to carbene complex

(*Fischer*, 1964)

- As the C atom in the coordinated CO posses larger positive charge than free CO, nucleophilic attack is favorable

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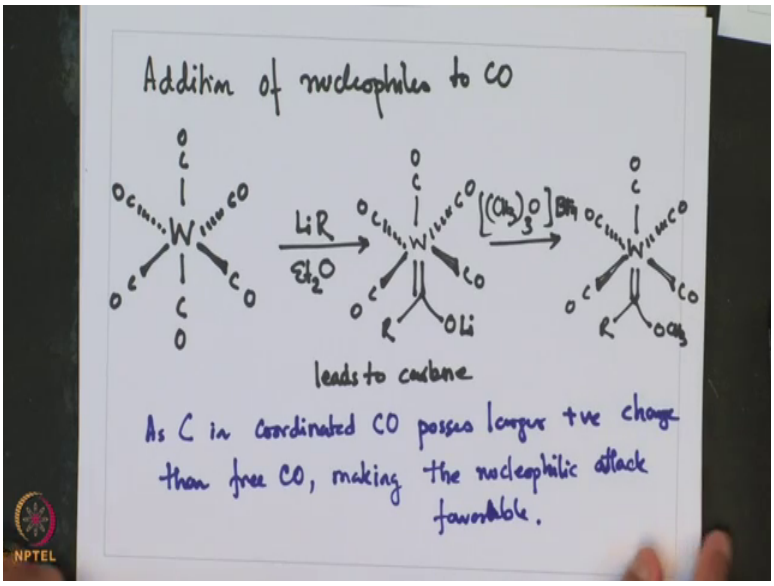

Addition of nucleophiles to CO

leads to carbene

As C in coordinated CO posses larger +ve charge than free CO, making the nucleophilic attack favorable.

So, for Tungsten hexacarbonyl in presence of lithium alkyl, in diethyl ether this R attacks the carbon of a coordinated CO giving rise to the carbon complex the way it is shown.

So, this nucleophilic attack, gives to a carbon complex. Now, we have discussed this synthesis in details particularly with regard to formation of Fischer carbene complexes few lectures back where exactly by following this procedure Fischer synthesize the first Fischer carbene complex where the nucleophilic attack of of R minus on to a coordinate CO occurred.

Subsequently alkylation by CH3 whole 3 O BF4 gives the following carbene complex. And these are this famous Fischer carbene compound made way back in 1964. And the nucleophilic attack is favored as the carbon in coordinated CO possess larger positive charge than free CO, making the nucleophilic attack favorable.

So, because of this carbon monoxide getting coordinated to the tungsten, there is a positive charge at the carbon-carbon and that favors this attack of the nucleophile onto this carbon. So, this is a very well known method of nucleophilic addition to coordinate CO and was first successfully used for producing Fischer carbene complexes from transition metal carbonyl compounds that we had discussed these while discussing the Fischer carbene or transition metal carbonyl complexes few lectures back.

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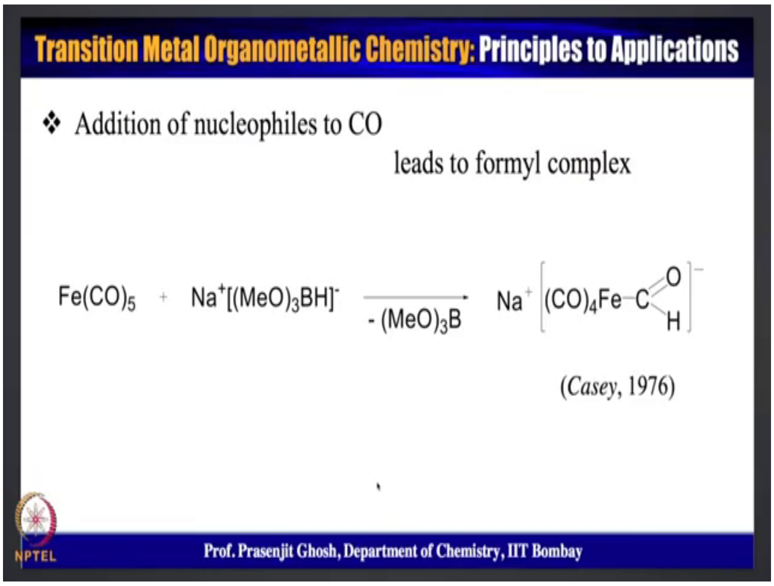

Transition Metal Organometallic Chemistry: Principles to Applications

- Addition of nucleophiles to CO

leads to formyl complex

$$Fe(CO)_5 + Na^+[(MeO)_3BH]^- \xrightarrow[- (MeO)_3B]{} Na^+\left[(CO)_4Fe{-}C\overset{O}{\underset{H}{}}\right]^-$$

(*Casey*, 1976)

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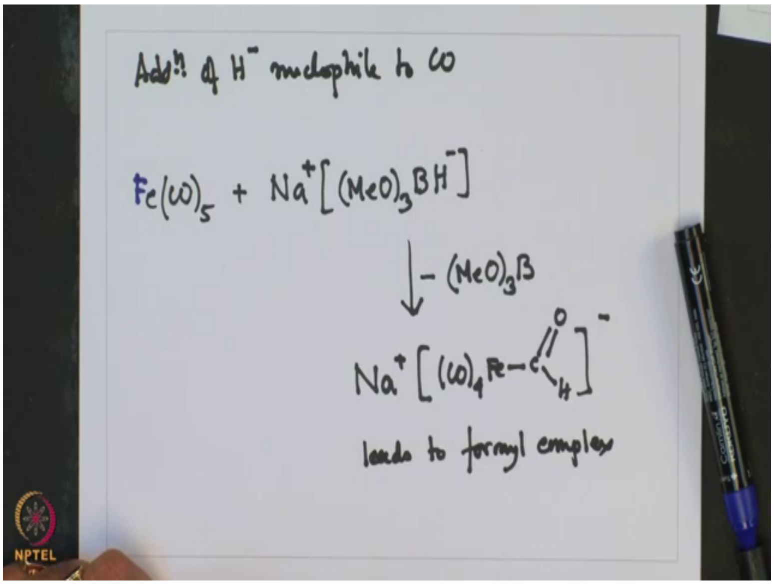

Add^n of H^- nucleophile to CO

$Fe(CO)_5 + Na^+[(MeO)_3BH^-]$

$\downarrow - (MeO)_3B$

$Na^+[(CO)_4Fe-C(=O)H]^-$

leads to formyl complex

Similarly, formyl complexes can also be formed when the reaction of Fe CO 5 plus sodium plus Meo 3 BH minus. So, there is this hydride goes and attacks. So, the nucleophile localism H minus gives minus MeO 3 B, the boron reagent leading to the formation of the formyl complex. So, nucleophilic addition of H minus to CO leads to formyl complex, as is shown over here.

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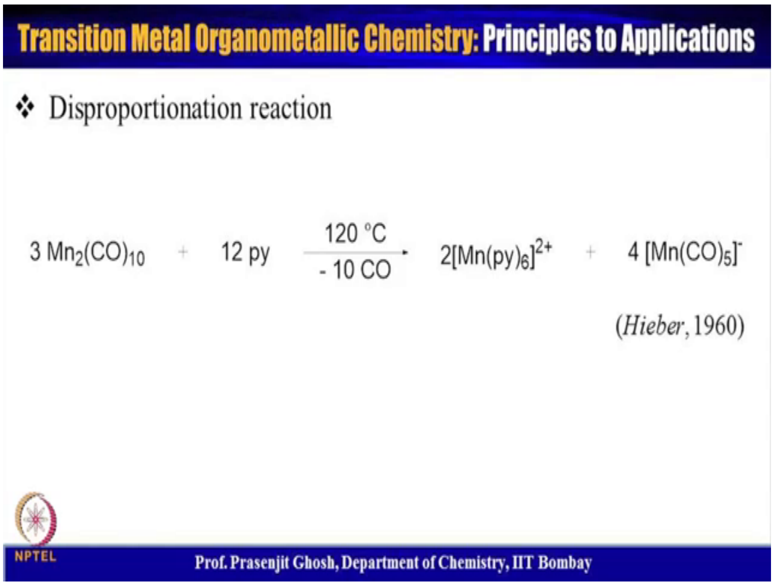

Transition Metal Organometallic Chemistry: Principles to Applications

- Disproportionation reaction

$$3\,Mn_2(CO)_{10} + 12\,py \xrightarrow[-\,10\,CO]{120\,^\circ C} 2[Mn(py)_6]^{2+} + 4\,[Mn(CO)_5]^-$$

(*Hieber*, 1960)

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Now, in terms of the reactivity we had discussed about substitution reactions in the last class and also then about these addition nucleophile addition reactions, that is addition of nucleophiles which can be a carbon based nucleophile or a hydrogen based nucleophile onto the coordinated carbonyl carbon. And now we are going to discuss another interesting reactions, which are disproportionation reactions of transition metal carbonyl complexes.

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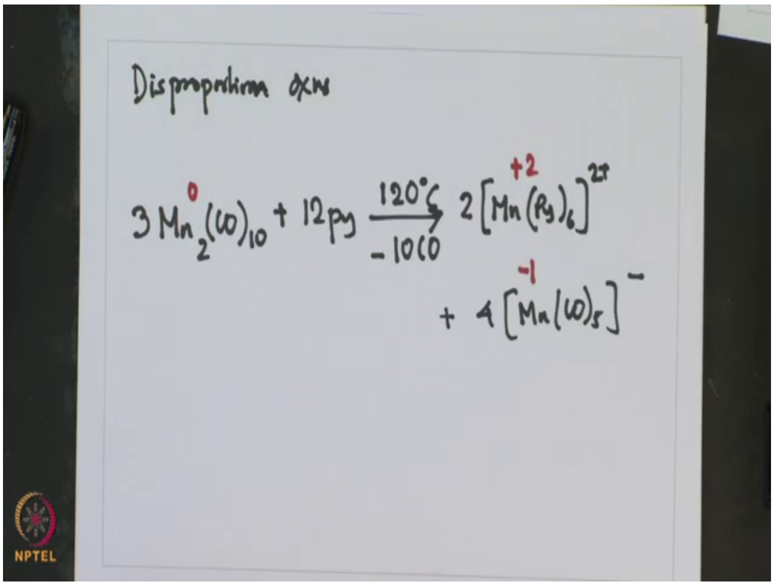

Disproportion rxn

$$3\,\overset{0}{Mn_2}(CO)_{10} + 12\,py \xrightarrow[-10\,CO]{120^\circ C} 2\,\overset{+2}{[Mn(Py)_6]}^{2+} + 4\,\overset{-1}{[Mn(CO)_5]}^{-}$$

For example, 3 Mn 2 CO 10 plus 12 pyridine at 120 degree centigrade results in loss of 10 COs to give Mn Py whole 6 2 plus. So, here the manganese has been oxidized; 2 plus 2 plus 4 Mn CO 5 minus, where the oxidation state of manganese is minus 1; so 0 oxygen state in the starting material; manganese 0 going to plus 2 and minus 1.

And this is an example of disproportionation reactions of transition metal carbonyl complexion. This also is a interesting reaction which transition metal carbonyl compounds show that the metal in the 0 valence state of metal transition metal carbonyl undergoes disproportionation to pro produce manganese in plus 2 as well as manganese in minus 1 oxidation states.

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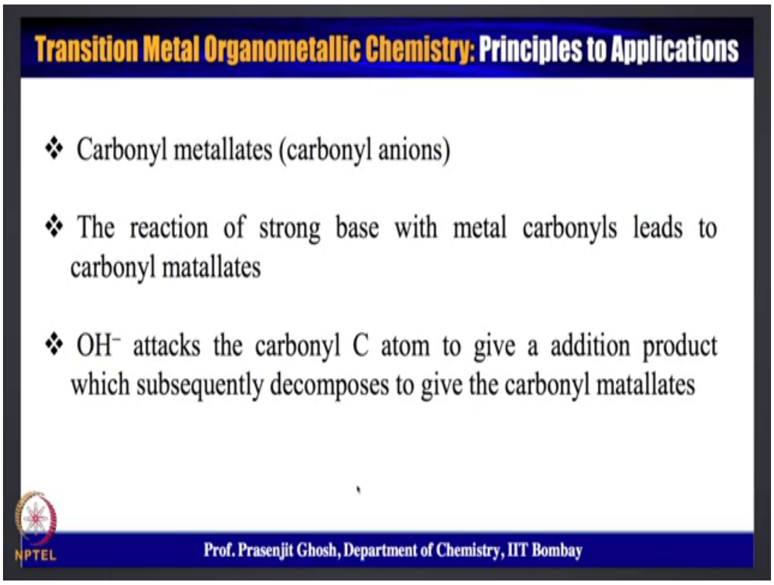

Transition Metal Organometallic Chemistry: Principles to Applications

- ❖ Carbonyl metallates (carbonyl anions)
- ❖ The reaction of strong base with metal carbonyls leads to carbonyl matallates
- ❖ OH^- attacks the carbonyl C atom to give a addition product which subsequently decomposes to give the carbonyl matallates

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Now, with that we are going to discuss another variety of transition metal carbonyl complexes and these are called carbonyl metallates or carbonyl anion. And this metallates are usually formed from the reaction of, of strong base with metal carbonyls.

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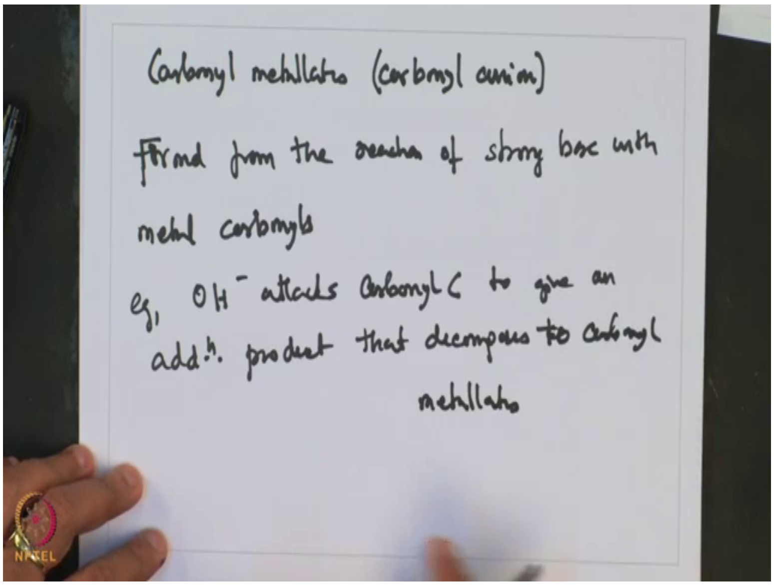

Carbonyl metallates (carbonyl anion)

Formed from the reaction of strong base with metal carbonyls

eg, OH^- attacks carbonyl C to give an add^n. product that decomposes to carbonyl metallates

For example, the OH attack; OH attack carbonyl carbon to give a an addition product that decomposes to carbonyl metallates.

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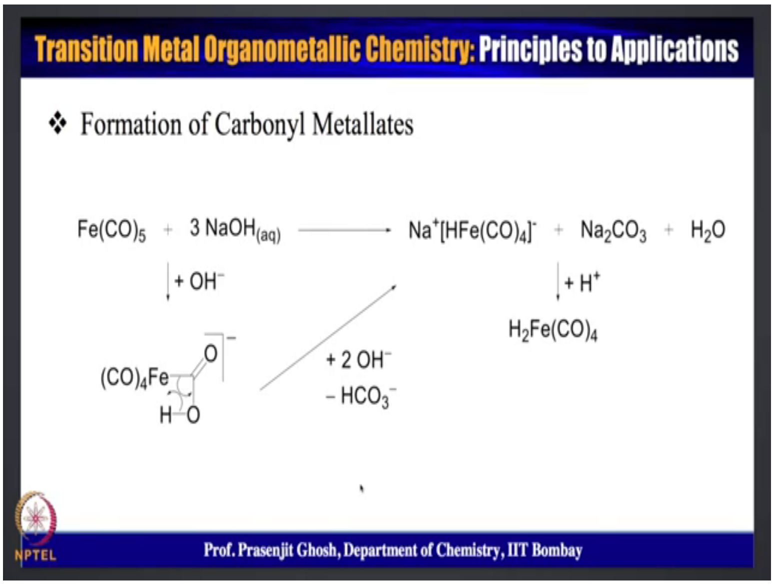

Transition Metal Organometallic Chemistry: Principles to Applications

❖ Formation of Carbonyl Metallates

$Fe(CO)_5 + 3\,NaOH_{(aq)} \longrightarrow Na^+[HFe(CO)_4]^- + Na_2CO_3 + H_2O$

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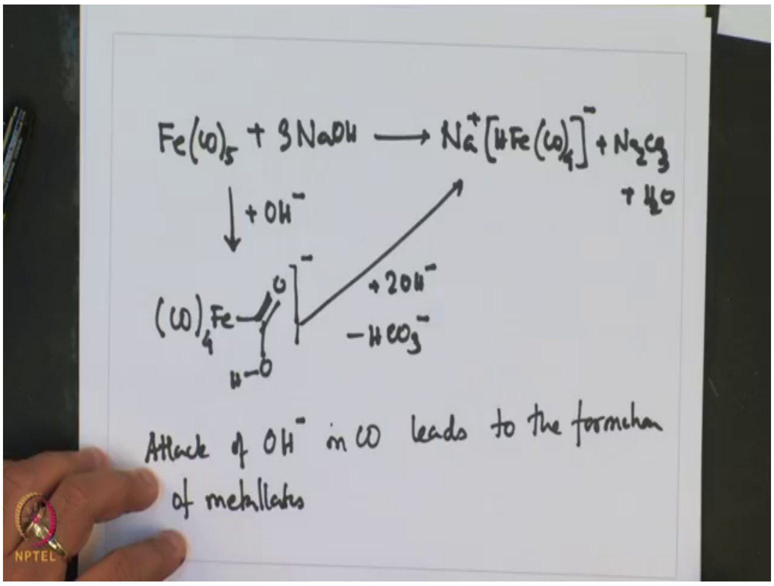

$Fe(CO)_5 + 3NaOH \longrightarrow Na^+[HFe(CO)_4]^- + Na_2CO_3 + H_2O$

Attack of OH^- on CO leads to the formation of metallates

The example of this type of reaction is given; reaction of Fe CO 5 plus 3NaOH gives Na plus H Fe CO 4 minus plus Na 2 CO 3 plus H 2 O. And the reaction proceeds by this hydroxide attacking the carbon atom of the CO moiety giving this. So, CO 4 Fe CO 2 H, which in presence of 2 hydroxide H CO 3 minus to give this sodium hydride Fe CO 4 complex as shown. So, these the attack of nucleophile like sodium hydroxide on attack of sodium hydroxide on iron carbonyl complexes leads to the formation of metallate.

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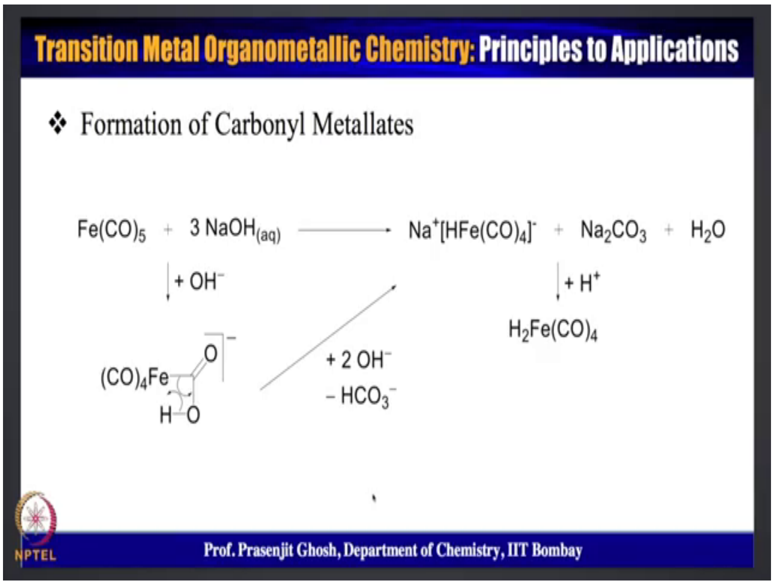

Transition Metal Organometallic Chemistry: Principles to Applications

❖ Formation of Carbonyl Metallates

$Fe(CO)_5 + 3\,NaOH_{(aq)} \longrightarrow Na^+[HFe(CO)_4]^- + Na_2CO_3 + H_2O$

$+\,OH^-$

$+\,H^+$

$H_2Fe(CO)_4$

$(CO)_4Fe$ O H O

$+\,2\,OH^-$

$-\,HCO_3^-$

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So, this reaction is similar to what we had seen for nucleophilics addition reaction and here sodium hydroxide attacks the carbonyl carbon leading to these carbonyl methylate complexes.

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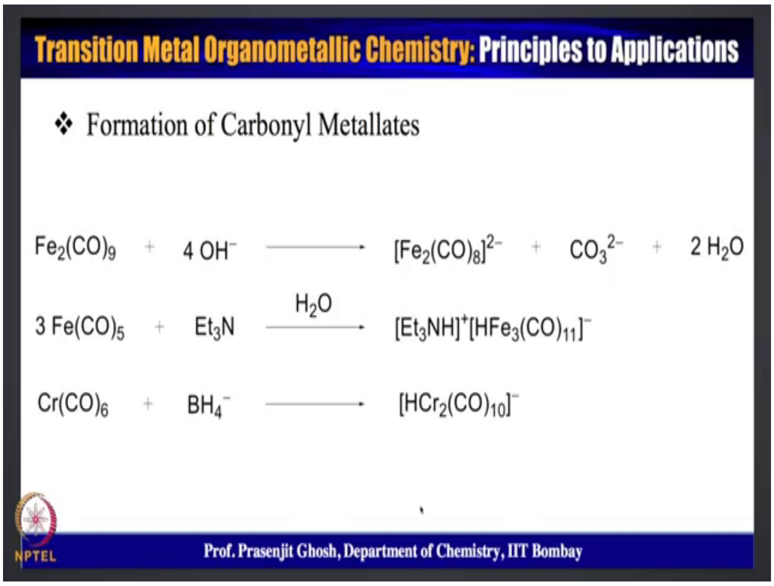

Transition Metal Organometallic Chemistry: Principles to Applications

❖ Formation of Carbonyl Metallates

$Fe_2(CO)_9 + 4\,OH^- \longrightarrow [Fe_2(CO)_8]^{2-} + CO_3^{2-} + 2\,H_2O$

$3\,Fe(CO)_5 + Et_3N \xrightarrow{H_2O} [Et_3NH]^+[HFe_3(CO)_{11}]^-$

$Cr(CO)_6 + BH_4^- \longrightarrow [HCr_2(CO)_{10}]^-$

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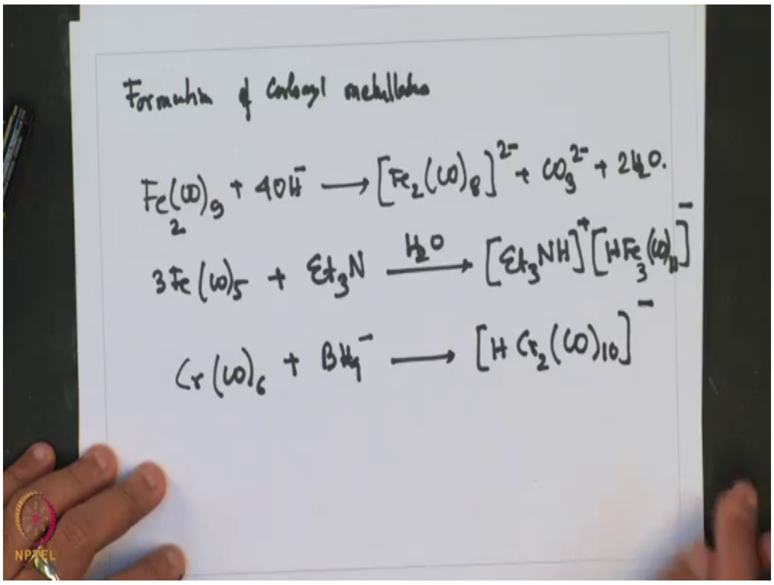

Formation of Carbonyl metallates

$Fe_2(CO)_9 + 4OH^- \longrightarrow [Fe_2(CO)_8]^{2-} + CO_3^{2-} + 2H_2O.$

$3Fe(CO)_5 + Et_3N \xrightarrow{H_2O} [Et_3NH]^+[HFe_3(CO)_{11}]^-$

$Cr(CO)_6 + BH_4^- \longrightarrow [HCr_2(CO)_{10}]^-$

So, there are several methods of forming this carbonyl metallates complexes. The first one, we had already seen is about the attack of hydroxide anion 2 Fe CO 5, the same can be done on Fe 2 CO 9 and we will see how the reaction proceeds, formation of carbon in metallates. And we are going to see that several methods, inclusive of the hydroxide attack leading to the formation of carbonyl metallates.

For example, Fe 2 CO 9 plus 4 OH minus giving Fe 2 CO 8 2 minus plus CO 3 2 minus plus 2H 2 O. Likewise, 3 Fe CO 5 3 Fe CO 5 plus Triethylamine in H2 O giving Et 3 NH plus H Fe CO 11 minus. To note here, is that there is triethylamine and water in presence of this base, hydroxide nucleophile would be generated and that would undergo attack at the iron carbonyl resulting in the formation of the metallate.

One can have hydride as a nucleophilic source. An example of that is Cr CO 6 plus BH 4 BH 4 minus giving H Cr 2 CO 10 minus. So, here the nucleophile is H minus from BH 4 attacking the CO.

So, what we see that, there are various ways of preparing this carbonyl metallates and these are mainly low-valent transition metal carbonyl complexes, where the metal center is highly electron rich.

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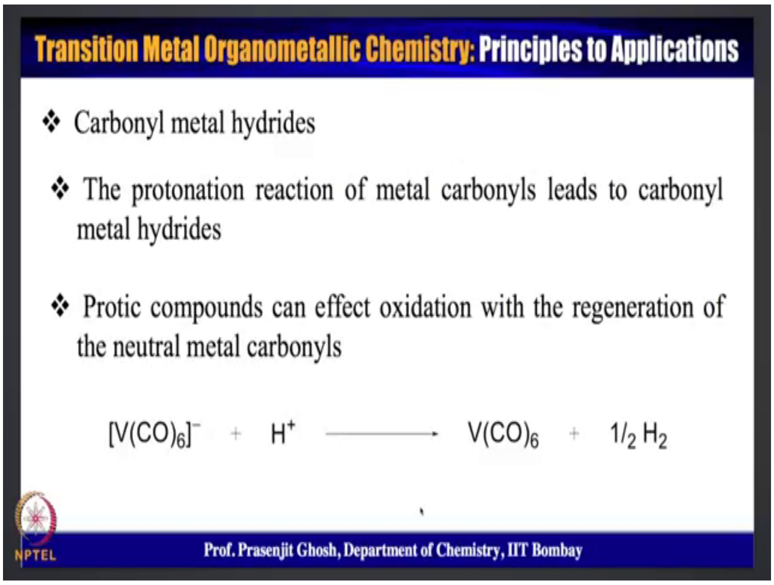

Transition Metal Organometallic Chemistry: Principles to Applications

- ❖ Carbonyl metal hydrides
- ❖ The protonation reaction of metal carbonyls leads to carbonyl metal hydrides
- ❖ Protic compounds can effect oxidation with the regeneration of the neutral metal carbonyls

$$[V(CO)_6]^- + H^+ \longrightarrow V(CO)_6 + 1/_2\, H_2$$

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Now, with that we are going to sort of move on to a new topic which we are going to be discussing in more detail in the subsequent topic and this is about carbonyl metal hydrides. An important class of transition metal compounds or related analog of transition metal carbonyl compounds where you have a carbonyl moiety and transition metal and along with that there is hydrogen also acting as a co-ligand to transition metal. So, usually these transition metal hydride complexes are obtained by protonation reaction of metal carbonyls. The protonation of metal carbonyls leads to carbonyl metal hydride reagents.

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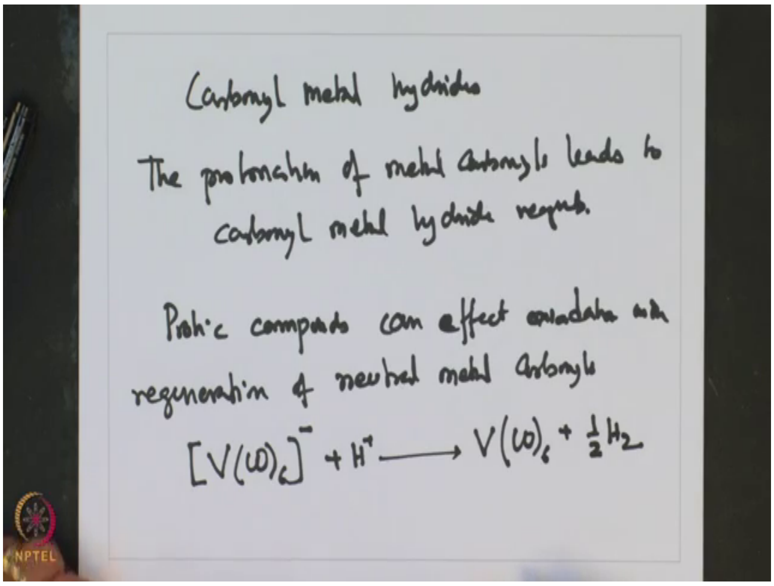

Carbonyl metal hydrides

The protonation of metal carbonyls leads to carbonyl metal hydride reagents.

Protic compounds can effect oxidation with regeneration of neutral metal carbonyls

$$[V(CO)_6]^- + H^+ \longrightarrow V(CO)_6 + \tfrac{1}{2} H_2$$

So, the protic compounds can affect the oxidation; can affect oxidation with regeneration of neutral metal carbonyls. A very good example is given by this reaction where carbonate metallate V CO 6 minus (Refer Time: 21:13) with the acid H plus gives V CO 6 plus half H 2. So, these compounds can affect oxidation with the regeneration of the metal carbonyl complexes.

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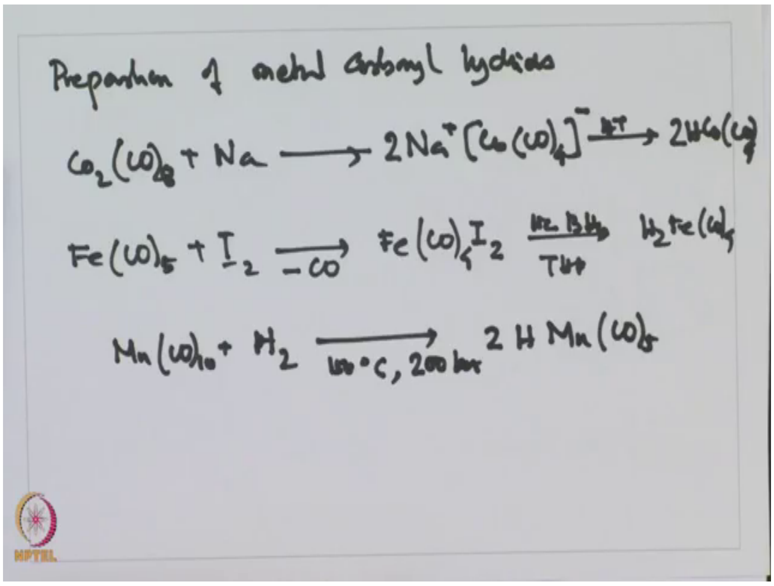

Preparation of metal carbonyl hydrides

$$Co_2(CO)_8 + Na \longrightarrow 2Na^+[Co(CO)_4]^- \xrightarrow{H^+} 2HCo(CO)_4$$

$$Fe(CO)_5 + I_2 \xrightarrow[-CO]{} Fe(CO)_4I_2 \xrightarrow[THF]{NaBH_4} H_2Fe(CO)_4$$

$$Mn(CO)_{10} + H_2 \xrightarrow[150\,^\circ C,\ 200\ bar]{} 2\,HMn(CO)_5$$

So, there are several methods for preparing these carbonyl metal hydrides. And the first one is the reduction of CO 2 CO 8 plus Na giving 2 Na plus plus CO CO 4 minus and that when protonated gives 2HCO CO 4. So, this is cobalt hydrated tetracarbonyl; an important intermediate in hydroformylation reaction.

Similarly, Fe CO 5 plus I 2 gives Fe CO 4 I 2 which one reduced with NaBH 4 in THF gives H 2 Fe CO 4. Reduction can also be done with molecular hydrogen. The example is given here, Mn to CO 10 plus H 2 at 150 degree centigrade and 200 bar give HMn CO 5.

So, with that I would like to conclude today's lecture which we have started with the reactivity of transition metal carbonyl complexes. In this regard, we have looked at a very important reactions of transition metal carbonyl complexes which are nucleophilic addition reactions on CO. And in this class we have read about Fischer carbene complex which was synthesized by addition of a lithium alkyl reagent onto a coordinated CO. We have also looked at the different carbonyl metallates of these transition metal carbon complexes.

And what we have seen is that, these are prepared reaction similar to the addition of the nucleophilic reagents onto the metal coordinated carbon monoxide. We have looked intovarious prepative methods available for producing these metallate complexes. And after that we have looked into, so these new set of complexes which are transitional metal carbonyl hydrides; particularly with respect to various synthetic procedures that are available for preparing these transition metal hydride complexes.

So, with these I thank you for listening to this lecture. And look forward to being with you in the next lecture, when you are going to discuss transition metal hydride chemistry in a bit more detail as we have just started the topic in the a towards the end of this lecture. So, till then goodbye.

Thank you.