Transition Metal Organometallic Chemistry : Principles to Applications

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(Week 9)

Lecture - 42

Transition Metal Carbonyls

[noise]

Welcome to this lecture on transition metal organometallic chemistry from principles to applications. We have been discussing ah an important [vocalized-noise] class of organometallic compounds in the last few [vocalized-noise] lectures, and this is about transition metal carbonyls.

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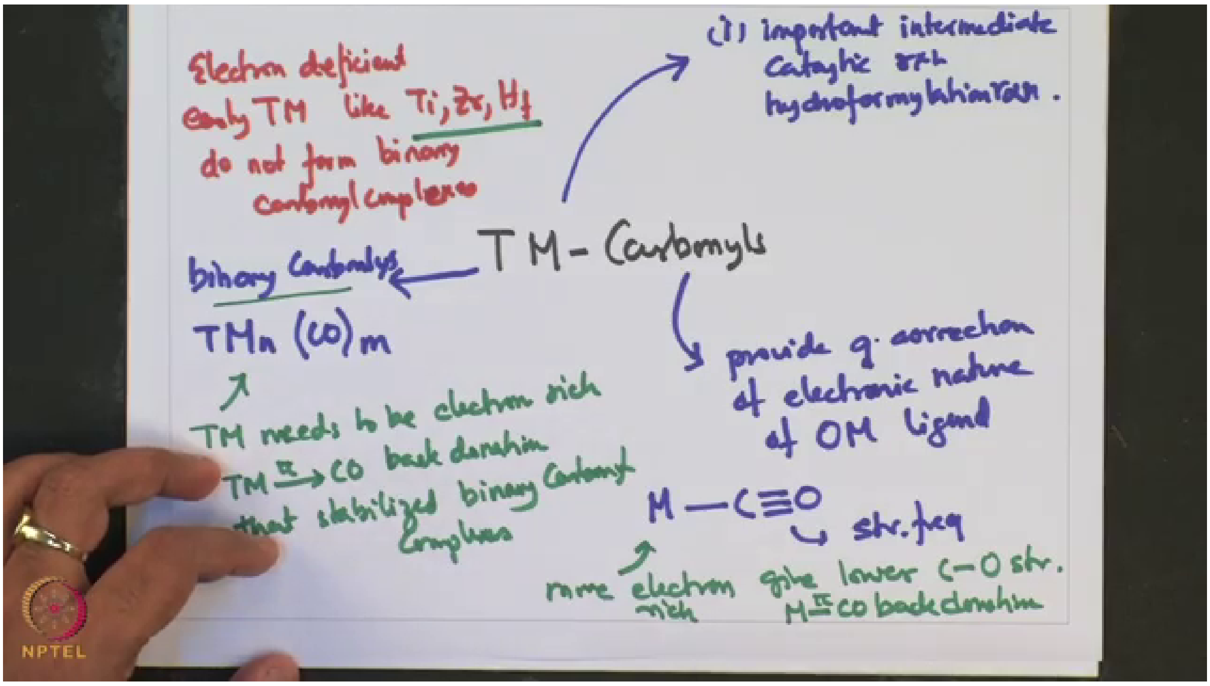

The transition metal carbonyl complexes [noise] are long known in the area of organometallic chemistry over a century, and is sort of an old class of compounds which have been studied really lot as compared to the other class of compounds that we had discussed in the earlier lecture for example, transition metal carbene or transition metal carbyne complexes, which only came to existence 30 or 40 years ago.

So, transition metal [vocalized-noise] ah carbonyl complexes have been studied a a lot particularly for their ah applications [noise] in homogeneous catalysis ah as this transition metal carbonyl compounds are important intermediate [noise] [vocalized-noise]. In ah several catalytic reactions [noise] for example, ah hydroformylation reaction,[noise] also ah these transition metal carbonyl compounds have been studied ah to get a quantitative estimation of electronic ah nature of other ah ah ligands, provides [noise] correlation of electronic [noise] nature of [noise] organometallic ah ligands. And this is done by infrared [vocalized-noise] spectroscopy and probably this is a very useful tool engaging ah different electron [vocalized-noise] donating ability of different polygons that appear with a carbonyl compound in the organometallic ah complex, and that arises because of these m [noise] MCO bond, where one measures ah the ah stretching frequency of [noise] ah of this CO ligands.

Now, if the metal is more electron rich more electron rich, metal [noise] gives lower [noise] CO stretch more electron rich metal [vocalized-noise] gives lower CO stretch as a [vocalized-noise] as a result of may M 2 o CO pi back donation. [noise] And [vocalized-noise] that sort of helps one ah ah to get an idea of the nature of ah or electron density on the metal by looking at the CO stretch and this is successfully employed in uh getting the getting an insight on the extent of ah electron richness that a metal possess by virtue of being bound to all other ligands ah ah around it.

So, this is has been used as an useful tool for ah getting a correlation of the electronic nature of various organometallic ligands, that combines with carbon monoxide in organometallic complexes. The apart from this in the last lecture we have also ah looked at binary carbonyls [noise] and these are of the formula Mn [noise] CO m.

Now, ah what we have ah discussed in the previous ah lecture was that that [vocalized-noise] this for the binary carbonyls to occur the transition metal has to be electron reach [noise] be electron reach [noise] ah such that, [noise] tm to CO pi back donation occurs [noise] that stabilized this [vocalized-noise] transition metal carbonyl complexes ah that stabilized [noise] binary [noise] carbonyl complexes [noise].

Now, ah these ah also we have seen that [noise] this is an important hypothesis and metals which are electron deficient metals for example, ah [noise] early transition metals, [noise] electron deficient [noise] early [noise] transition metals like [noise] titanium, zirconium, hafnium [vocalized-noise] do not [noise] form binary carbonyl complexes [noise].

So, this is an important ah observation because ah binary carbonyl [vocalized-noise] complexes are mainly stabilized by the ligand to metal as well as metal to carbonyl pi back donation, and the transition metals which are not efficient in ah ah displaying significant amount of transition metal to ligand pi back donation, for those complex ah transition metals the binary carbonyl complexes do not exist. And therefore, example ah in this ligand being ah titanium zirconium ah and hafnium which are group 4 elements ah and the our electron deficient enough ah not facilitate the transition metal to [vocalized-noise] ligand pi back donation.

On the other hand for electron rich electron transition metals where there is significant amount of ah electron density are the metal, these elements do ah have a significant component of transition metal to carbyne pi back donation as a result several binary [vocalized-noise] complexes of these electron transition metals starting from group 6 ah ah to group 9 are ah known. And with that ah brief background we are going to take a look at various methods ah which are available for synthesising these transition metal carbonyl complexes.

Now, as transition metal carbonyl complexes ah required ah metal to ligand pi back donation ah for the stabilisation of the carbonyl moiety uh its. So, it is important that the metal be at low oxidation state for it to stabilize transition metal carbonyl complexes [vocalized-noise].

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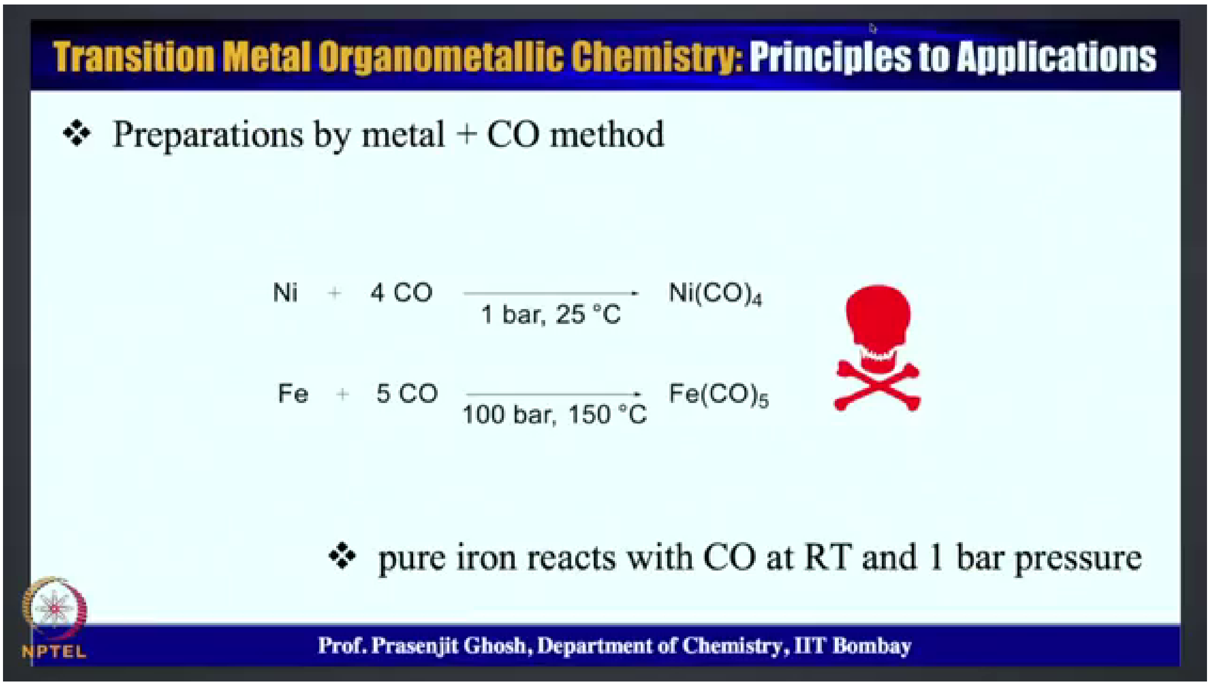

And ah these being the theme ah of ah these methods which are available for preparation ah we would see that the most of the methods ah confirmed to this idea of [vocalized-noise] the metal being at low oxidation state, such that the metal is electron rich enough ah, as to ah part take in metal to ligand pi back donation.

So, in that theme in mind we are going to take a look at the first method of preparing binary [vocalized-noise] metal carbonyls, and this is the simplest ah ah approach whereby this binary metal carbonyls are prepared by direct reaction of metal with carbon monoxide [noise].

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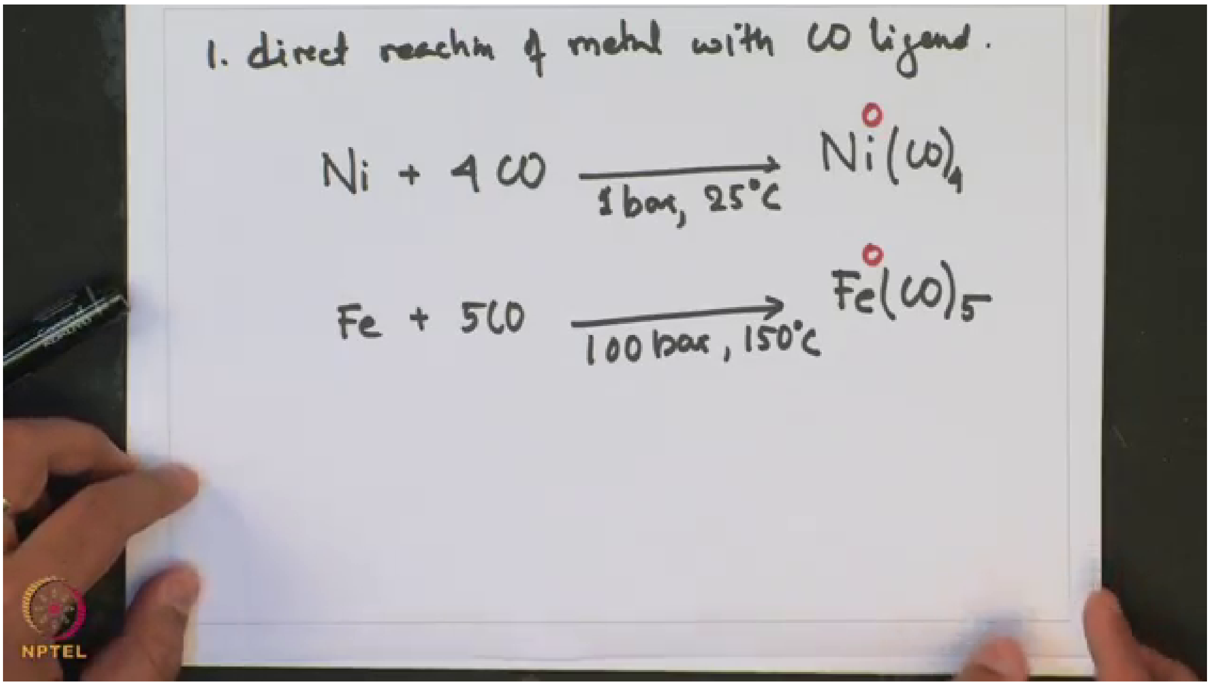

And these ah are ah sort of ah a very difficult ah compound to make some of the ah ah ah is volatile and also very toxic.

For example nickel [noise] plus 4 CO [noise] one bar of pressure [noise] 25 degree centigrade give this nickel tetracarbonyl. [noise] Similarly direct reaction of iron [noise] plus CO [noise] at much higher pressure [noise] of 100 bar and higher temperature of 150 degree centigrade give this iron [noise] pentacarbonyl. And ah this ah shows that one can ah indeed make binary uh transition metal carbyne complexes of late transition metal by direct reaction of the metal with the carbonyl gas.

The high electron density of the metal because of its low oxygen state in the if the oxygen state uh of the metal ah is 0 for both of the examples and that facilitate metal to the ligand pi back donation, as a result this binary alkaline carbene complexes are stabilised. Apart from the direct reaction of the metal with carbon monoxide, the other approach ah involved ah reducing a metal salt ah by ah suitable reducing agent and then treating that reduce metal salt with carbon monoxide to give transition metal binary a carbonyl complexes.

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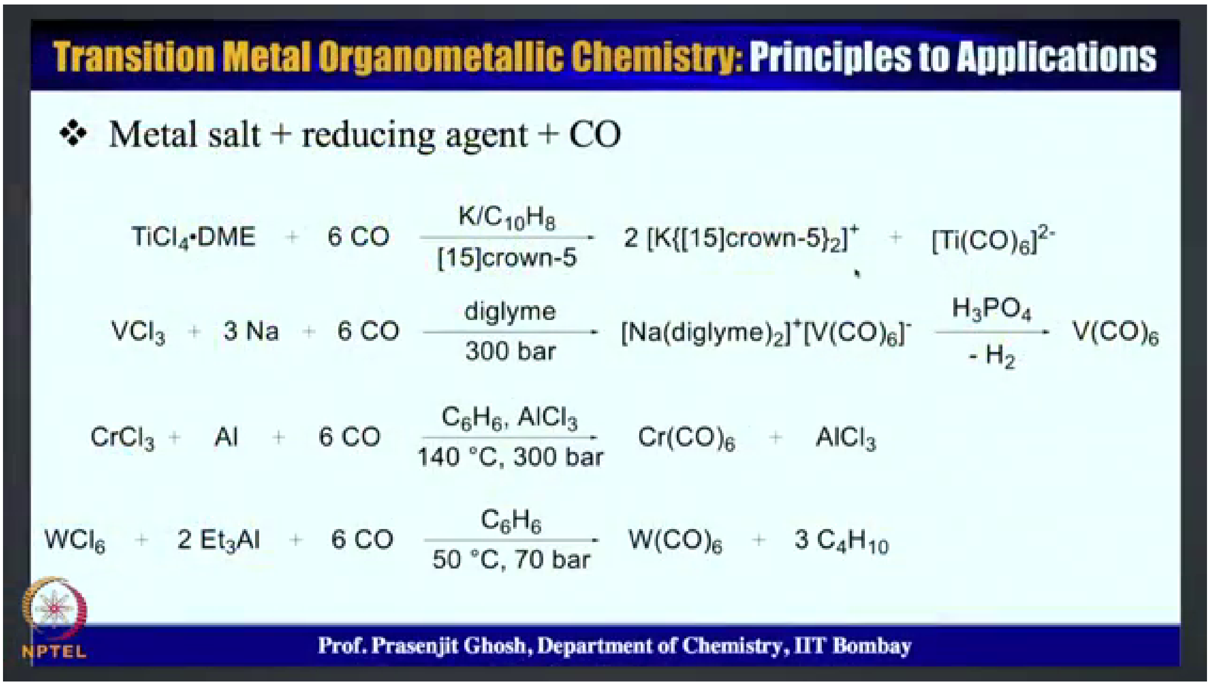

Some of the examples for this method are [noise] ah shown ah here [noise].

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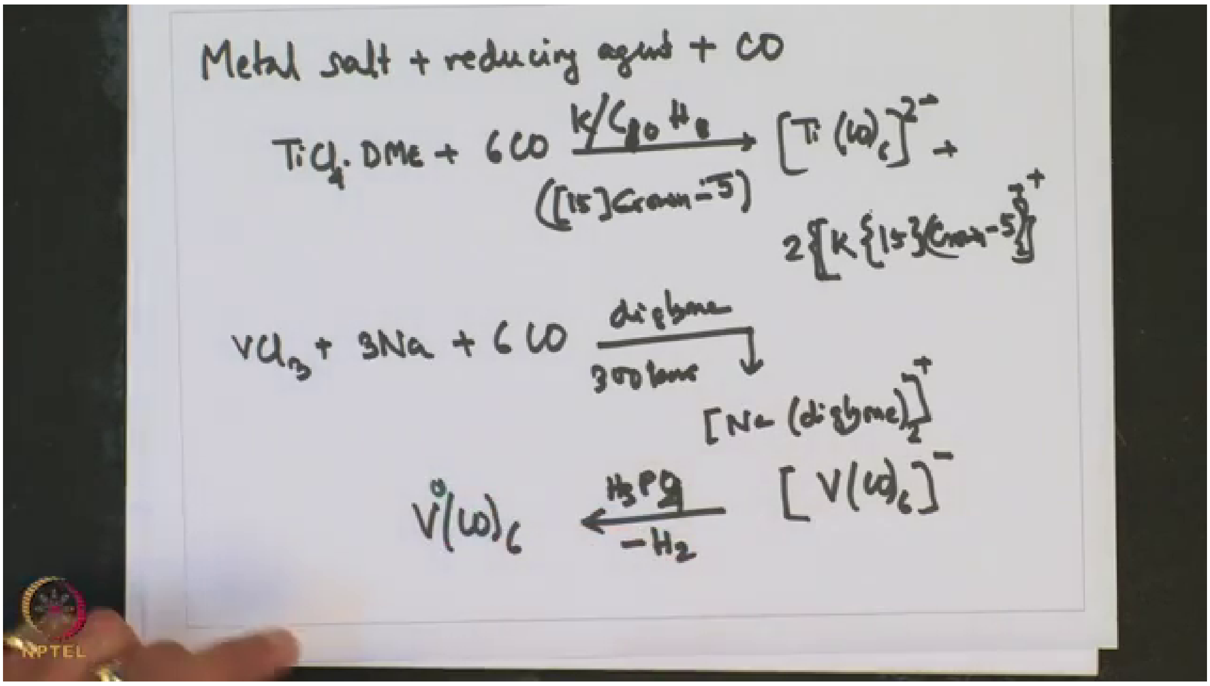

Metal salt plus reducing agent [noise] plus CO. So, the examples are [noise] 6 CO [noise] C [noise] C 10 [noise] H 8 [noise] 15 crown 5 [noise] gives [noise] titanium [noise] CO 6 [noise] 2 minus [noise] plus [noise] k [noise] 15 crown [noise] 5 whole 2 plus [noise].

So, here is a reaction where [vocalized-noise] metal salt is reduced by reducing agent where reducing agent is potassium, and then the carbonyl complexes of the same is obtained similarly [noise] VC l 3 plus 3 Na [noise] plus 6 CO [noise] in diglyme [noise] at 300 bar pressure [noise] gives sodium diglyme m e 2 plus V CO 6 [noise] minus that [noise] in presence of H 3 PH 3 PO 4 [noise] eliminates a hydrogen [noise] to give V CO [noise] 6.

So, here to we see that this [vocalized-noise] vanadium trichloride in presence of a reducing agent with a sodium and carbonyl compound gives vanadium carbonyl compound where the oxidation state of vanadium has reached ah ah 0 [noise]. So, the other examples in this category is reaction of ah chromium trichloride with aluminium [noise].

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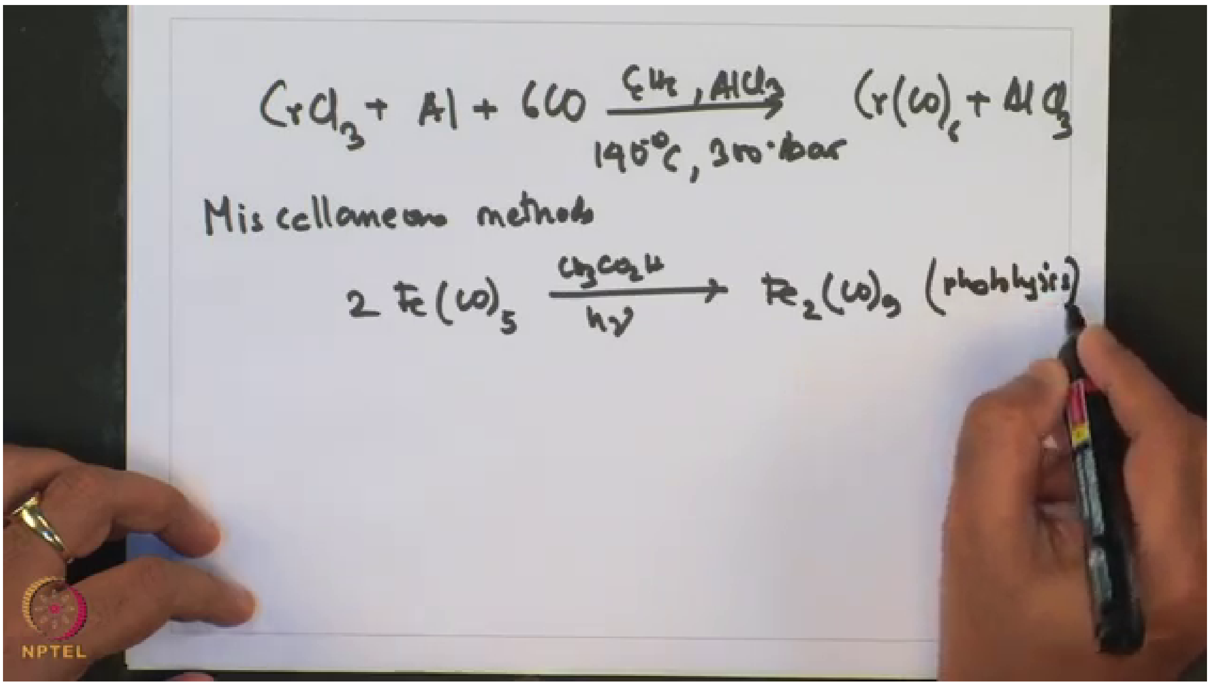

CrCl 3 plus al plus 6 CO gives [noise] C 8 H 6 AlCl 3 [noise] 140 degree centigrade [noise] and 300 atmospheric pressure [noise] ok.

So, that gives the chromium hexacarbonyl [noise] plus AlCl 3.

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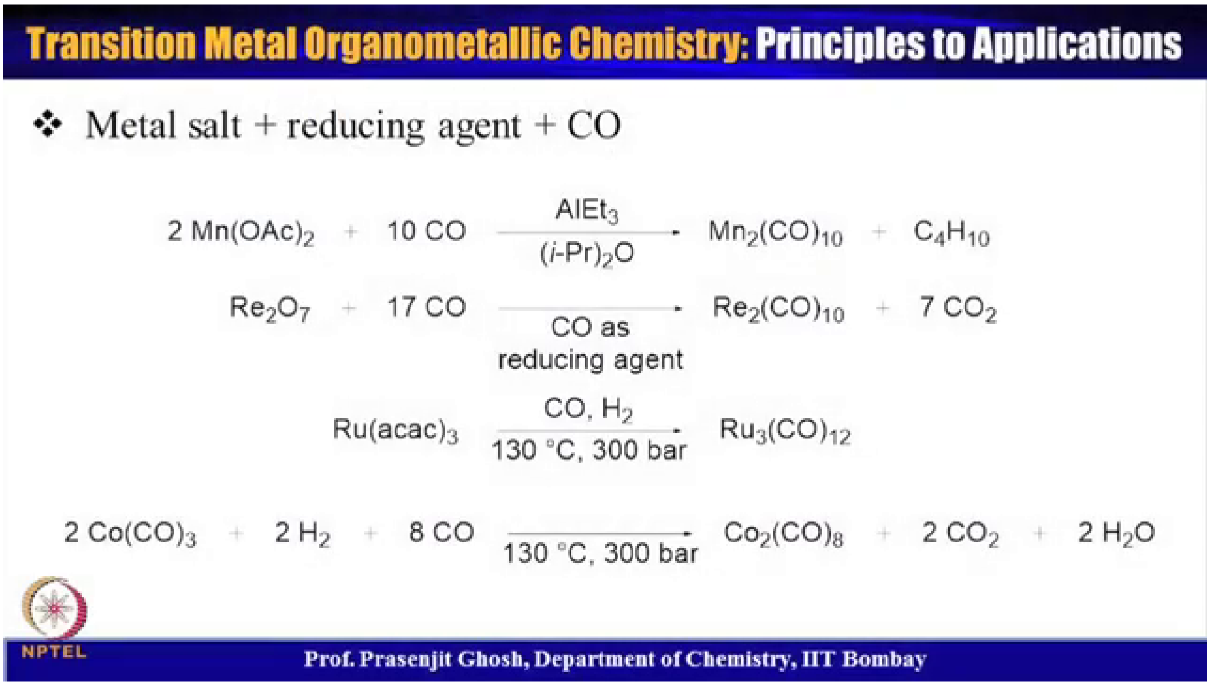

So, what we got is a flavour of ah this strategy which involved the metal with reducing agent and carbonyl, the this is the very effective method with a lot more ah ah number of transition metal carbonyl complexes been prepared ah by using this method.

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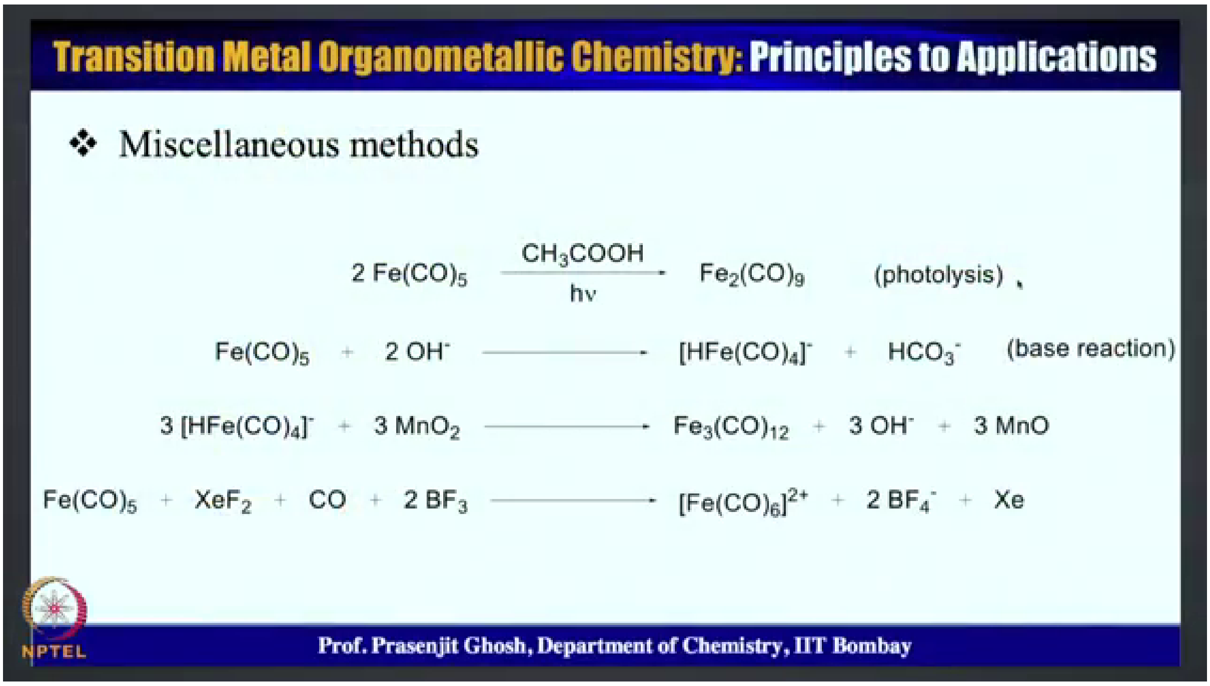

Some of the representative examples ah of these a I have ah discussed uh here.

Similarly, uh there are several miscellaneous methods available for preparing this ah transition metal carbonyl complexes, and this methods are [noise] for example, 2 F e CO 5 [noise] in presence of light, and acetic acid [noise] produced [noise] F e 2 CO 9 and this reaction has been obtained as shown over here by photolysis reaction [noise].

The other involved also F e CO 5 plus 2 h minus giving h F e CO 4 minus plus H CO 3 minus then these 3 H F e CO 4 minus plus 3 MnO 2 gives F e 3 CO 12 plus 3 OH minus plus 3 MnO. Another reactions also involved this iron pentagonal complex as if F e CO 5 plus XeF 2 plus 2 BF 3 giving F e CO 6 2 plus plus BF 4 minus plus Xe.

So, what is ah learn from here that they there are other methods apart from going by the convention way of getting the carbonyl in this ah low valent oxidation state [vocalized-noise] eight by a reducing agent or by that direct reaction of the metal ah ah as opposed to [vocalized-noise] that being the conventional there are other methods, whereby ah you can take a metal carbonate and generate this transition metal ah ah other transition metal carbonyl complexes by this method ah discussed here.

Now, with that ah needed to go to some important aspects of these transition metal carbonyl complexes particularly their structure.

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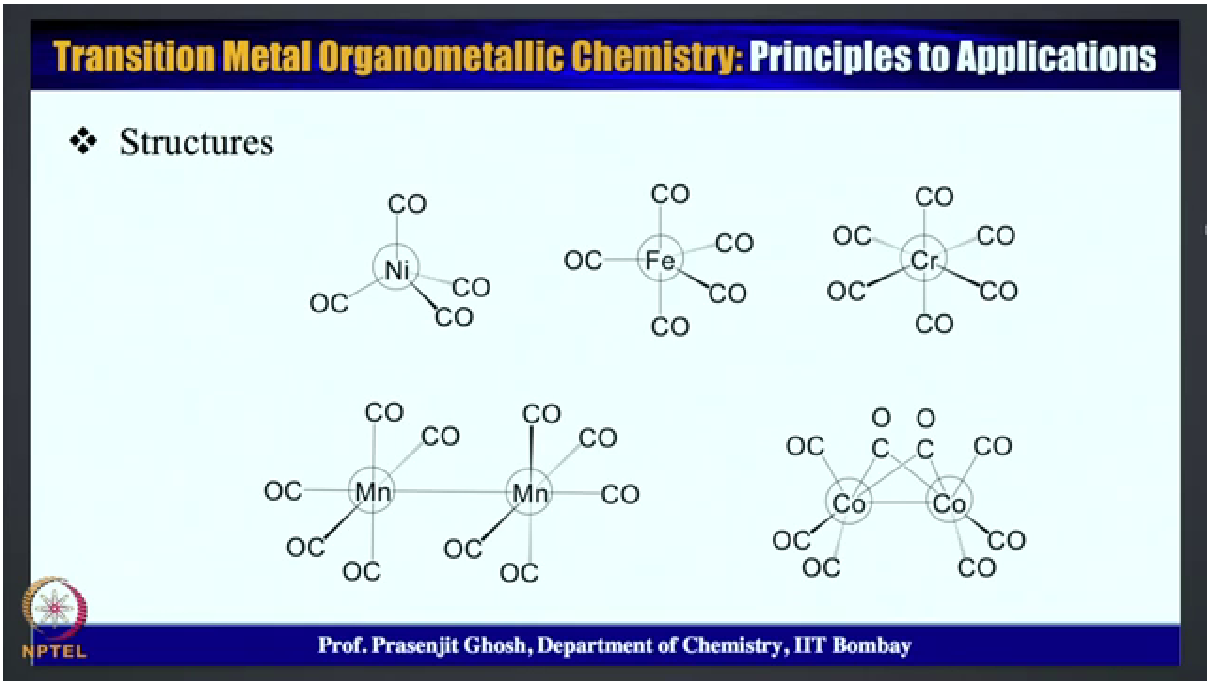

Now, [vocalized-noise] structurally the [vocalized-noise] form of ah diverse class of compounds, where carbonyls are ah depose ah [vocalized-noise] ah around the metal centre they can come occur as a bridging ligand as well as they can occur as a terminal ligands, and the bridging can expand the scope from ah once uh 2 centre to 3 centre ah and so on so forth.

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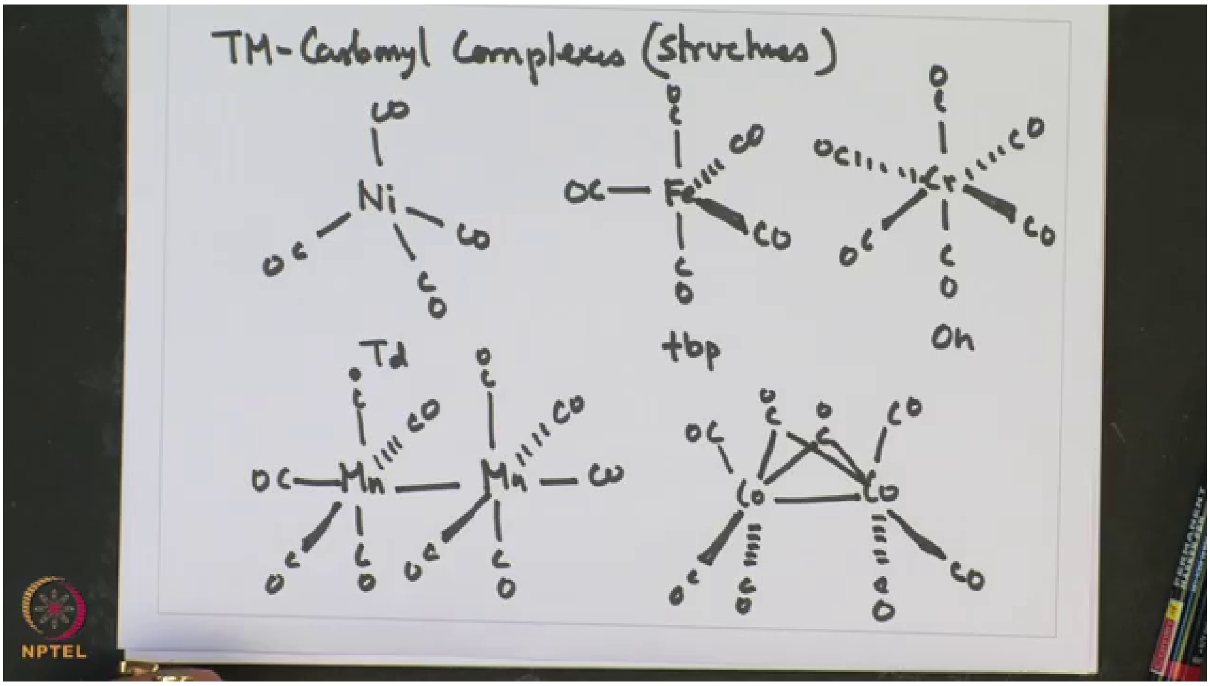

So, we are going to take a look of some of the important ah aj structures of transition metal carbonyl complexes [noise] for example, nickel tetracarbonyl is [noise] tetrahedral structure [noise] it is in zero state, iron pentacarbonyl [noise] is the tbp structure [noise] whereas, chromium hexacarbonyl [noise]. So, this is our tetrahedral structure, this is tbp structure, this is octahedral [vocalized-noise] structure [noise].

So, ah we see that depending on the metal all [vocalized-noise] sorts of ah possible structures are formed, and [vocalized-noise] here is a structure of manganese dimer ah that contains a metal metal bond [noise]. So, each [vocalized-noise] manganese is bonded to 5 ah carbonyl moietys and then there is a metal metal interaction.

Another example of a ah, but all of these carbonyls are terminal in nature here is an example of a compound continuing increasing carbonyl, ah which is dicobalt [noise] C O

2 C O 8 so; that means, that there 3 carbonyls on each cobalt [noise] and there are 2 CO-bridging ah carbonyls [noise].

So,. So, what can be [vocalized-noise] seen over here that ah if the carbonyl display diverse ah structures ah in this binary alkyl kind of compounds, that can range from tetrahedral to ah [vocalized-noise] diagonal by pyramid at 2 octahedral or dinuclear complexes, that contains bridging carbonyl as well as the ones which does not ah form one um and uh. So, this ah diverse um orientation ah is ah hallmark of transition metal carbonyl complexes.

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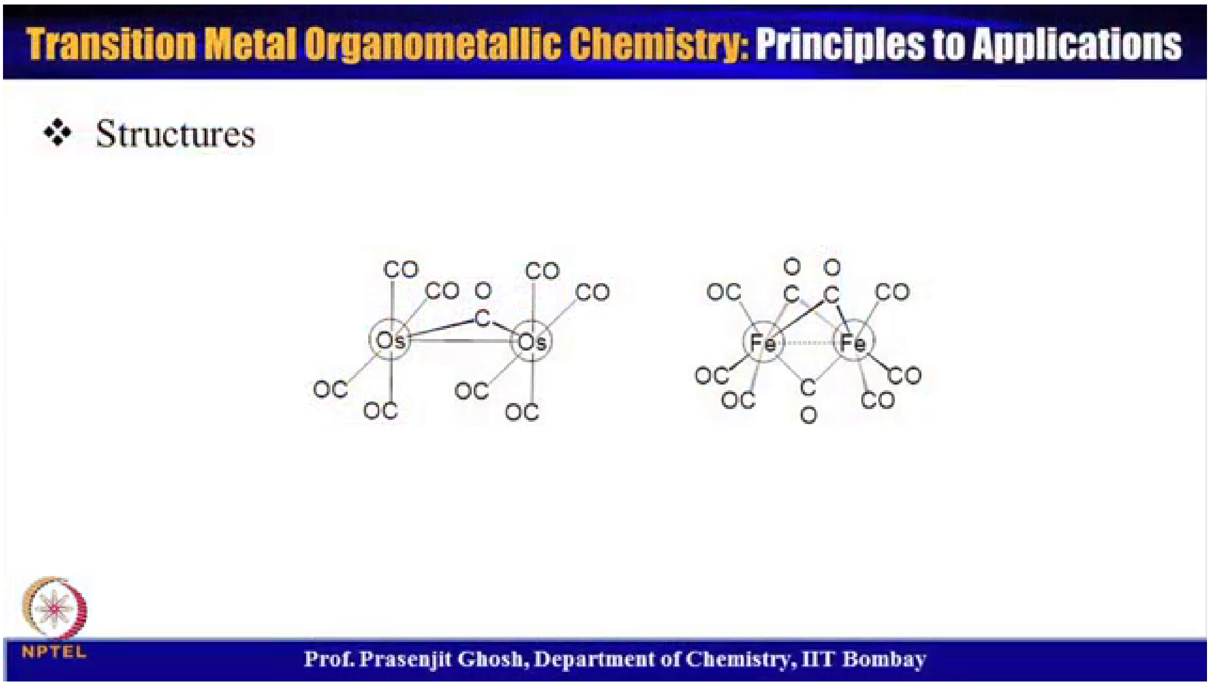

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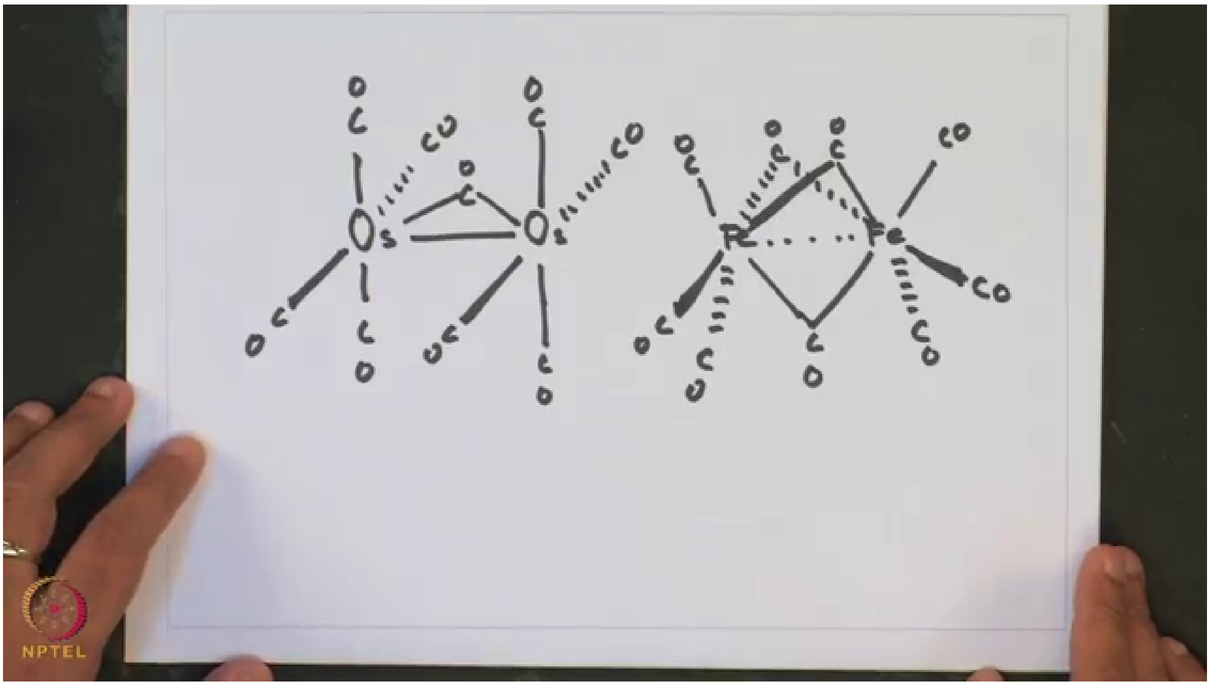

We are going to take a look at 2 more such [noise] ah structures, where ah similar ah ah diversity uh have been observed; and this is osmium [noise] carbonyl complexes where you have [noise] 2 osmium [noise] [noise] also have 2 osmium and ah bridging [noise] carbonyl. Similar ah the structure of the iron ah compound [noise]. So, containing 3 bridging carbonyl [noise] [noise].

So, what we see over here that ah F e 2 C O 9 and this is also ah OS 2 CO o 9, but [vocalized-noise] what we see over here that there are 3 bridging carbonyl as opposed to one bridging carbonyl as seen over here, and that is because that osmium being bigger in size ah ah that the number of bridging terminal carbonyls ah are less as opposed to iron which is smaller in size we see more bridging carbonyl atoms.

So, let me just conclude what ah we have been discussing ah in this ah transition metal carbonyl complexes, we have looked at ah the [vocalized-noise] synthetic strategies ah ah that are place for preparing this complexes, most of the strategy involved using either direct reaction of 0 ln metal with carbonyl or ah metal salts ah getting reduced in presence of a reducing agent to [vocalized-noise] its lower oxidation state followed by direct reaction with carbonyl, and there are few other miscellaneous method that produces transition metal carbonyl complexes, including starting from some ah initial ah ah ah transition metal carbonyl complexes as regions as well.

After that we also looked into ah [vocalized-noise] ah some of the ah [vocalized-noise] structures of the binary transition metal carbonyl complexes, and what ah came to the 4 is that this transition metal [vocalized-noise] complexes display of wide variety of structures, that changes ah from the ah coordination number from 4 to 5 to 6 depending on the metal, and also ah they show ah a various kinds of binding modes of the carbonyl ligand, which mostly are ah terminal as well as bridging and depending on the size of the metal ah the number ah of the bridging ah carbonyl is sort of decided.

So, with that ah I would like to [vocalized-noise] conclude todays lecture on transition metal carbonyl complexes, we going to take it up in more detail with more analysis being done on the geometry structure reactivity and property of this transition metal carbonyl complexes, ah in the subsequent lecture that is going to come up next. ah With that ah [vocalized-noise] let me thank you for being with me and also I look forward to take up this ah detailed ah topic in ah this next lecture, till then ah goodbye.

And thank you [noise].