Transition Metal Organometallic Chemistry : Principles to Applications

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Week - 10
Lecture - 49
Application of Carbonyl Metallates and Metal Halides

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. We have been discussing carbonyl metallates over the last few lectures and looked at the synthesis reactivity and properties of these special kind of transition metal carbonyl complexes, how they were synthesized, what are the reactivity, so on and so forth.

And today we are going to take up and also very important application of transition metal carbonyl metallates particularly of that of Collman's reagent.

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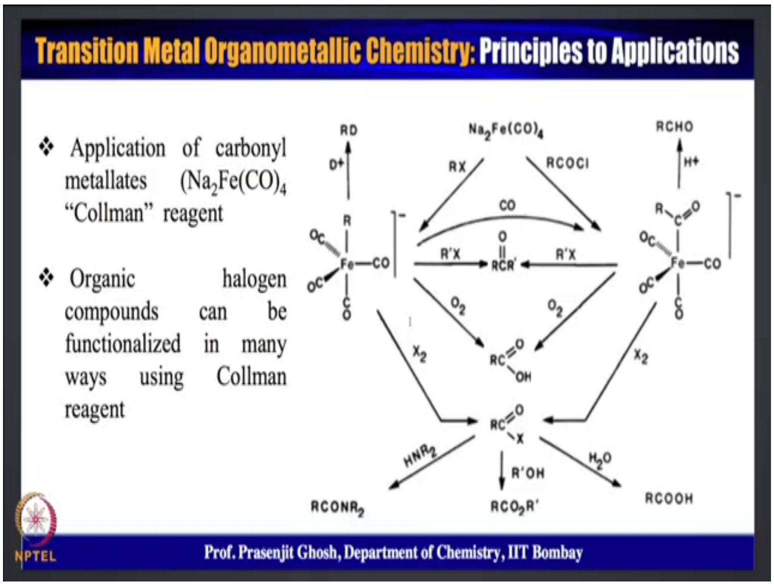

Transition Metal Organometallic Chemistry: Principles to Applications

- ❖ Application of carbonyl metallates ($Na_2Fe(CO)_4$ "Collman" reagent
- ❖ Organic halogen compounds can be functionalized in many ways using Collman reagent

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Now, this is a very useful chemistry which is practice day in and day out in the world of synthetic organic chemistry and this is based on iron based organometallic compound called Collman reagent.

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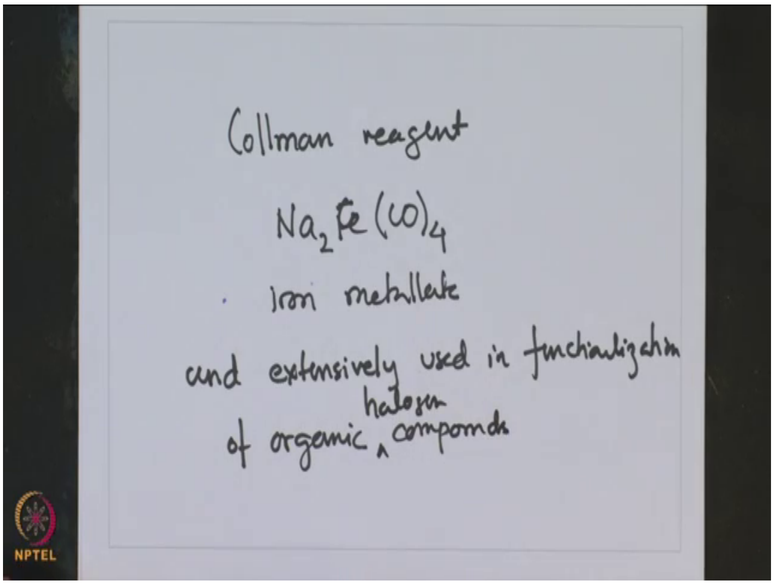

Collman reagent

$Na_2Fe(CO)_4$

Iron metallate

and extensively used in functionalization of organic halogen compounds

And the form of the formulation of this compound Collman reagent is Na 2 Fe CO 4. So, it is the carbonyl metallate, iron metallate complex and used in functionalization of organic halogen compound organic halogen compound. So, here we see a very important application of these iron carbonyl metallate which is called Collman reagent in day to day organic synthesis.

I must note that this application is more on stoichiometric fashion in the sense that Collman reagent is not a catalyst it is just a reagent for performing these functionalization of organic halogen compounds and hence its reactivity is done in stoichiometric fashion. But nonetheless this is the very important reagent as it allows a wide variety of functionalization of organic compounds and we are going to look at these in details right now, in the in this particular lecture.

Now, the interesting iron chemistry is all the more important because iron being naturally abundant there is a significant interest in utility of iron, not only in reagent purpose as we seen in this Collman reagent, but also for its ability to catalyze chemical transformation. So, this iron is a contemporary topic of interest where significant amount of efforts are being directed towards utilizing the chemistry of iron for various catalytic as well as stoichiometric transformations.

So, with that brief introduction about Collman's reagent let us take a look at some of the reactivity that Collman reagent performs.

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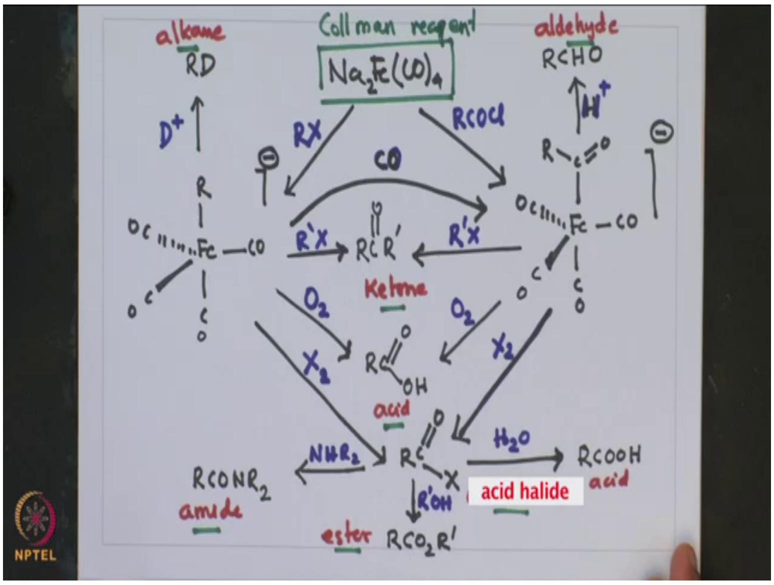

For example Na 2 Fe CO 4 which is the Collman regents when treated with RX provides this anion. Now, in this is the iron and iron with a iron organometallic species formed which when treated with D, D plus gives RD. Similarly when Collman's reagent is treated with acid chloride, then one forms these iron acyl complex this is also metallate aligned and when the same is treated with a H plus gives aldehyde. Now, if this iron alkyl metallate when treated with carbon monoxide then migratory insertion of CO happens in the metal alkyl group which is a very common property of transient metal alkyl complexes giving this transition metal acyl metallate.

So, this is the direct conversion of iron alkyl to iron acyl complex. Similarly if this alkyne is treated with R dash X, then one gets this ketone, where there is a CO inserted one gets this R C O R dash, where one CO has migratory inserted and then R dash X gets in ketone and the same can be obtained from this acyl complex by treating with R dash X. So, here what we see is a nice demonstration of arriving at the same compound by 2 different routes, one is by the right hand side the other is by left hand route, and in one it goes via the formation of the iron alkyl complex for the other it goes via the formation of the iron acyl complex.

Now, the iron alkyl complex similarly when treated with oxygen gives acid, and the acyl complex also when treated with molecular oxygen produces this acid. Similarly when this alkyl complex is treated with halogen X 2 then one gets the acid halide, and similarly the acyl complex when treated with X 2 also give the acid halide. And acid halide when treated with an amine produces amide, as it halide when treated with an alcohol produces ester and acid halide when treated with water produces acid

So, the utility of Collman reagent is nicely demonstrated that when treated with organic halogen compounds and followed by workup one can obtain aldehyde, one can obtain alkane, one can obtain ketone, one can obtain acid, one can obtain acid halide, one can obtain ester, and one can obtain amide. So, what one sees that depending on the treatment so many different for example, alkane aldehyde, ketone, acid, acid halide, ester, amide. About 7 different organic compounds can be obtained from organic halogen compounds using Collman reagent.

So, Collman reagent is a nice demonstration of utility of iron organometallic compound in day to day organic synthesis. The advantage of Collman reagent is high yield and high selectivity, is high yield and high selectivity as organo irons do not, as organo iron anions do not add to carbonyl or nitrile groups.

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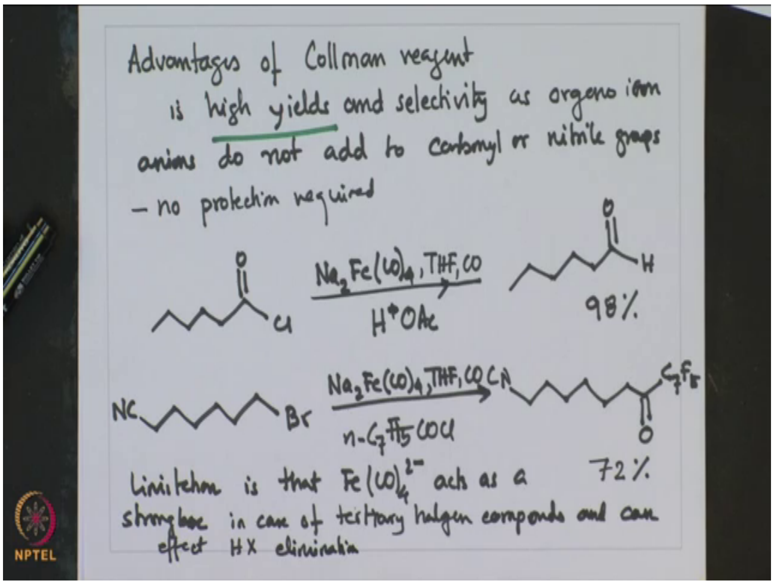

Advantages of Collman reagent is high yields and selectivity as organo iron anions do not add to carbonyl or nitrile groups

– no protection required

Limitation is that $Fe(CO)_4^{2-}$ acts as a strong base in case of tertiary halogen compounds and can effect HX elimination

So, for example, no protection required, for example, reaction of this acid chloride with Na 2 Fe CO 4 in THF, and the molecular and pressure of CO and acidic acid gives high yield of this aldehyde 98 percent yield.

Similarly, the reaction of this bromo nitrile reagent with Na 2 Fe CO 4 THF CO and when treated with acid chloride C 7 F 15 CoCl produces this ketone, nitrile in 72 percent yield. So, here to what we see is this high yields and selectivity here which are the advantages of using Collman's reagent. So, limitations of Collman's reagent entities is that Fe CO 4 2 minus acts as a strong base in case of tertiary halogen compounds, and can affect 8 H X elimination.

So, these the end of discussing this Collman's reagent which is the iron tetracarbonyl dynamic compound and its utility for functionalization of various organic halogen compounds. And what we have seen that the advantages of Collman reagent arises from its high yield and selectivity for these transformations, it can lead to wide variety of functionalized organic compounds.

For example, from acid, ester, alkane, amide, ketone, aldehydes so on and so forth, and that speaks volumes of about how the utility of iron based organometallic compound came into day to day use of organic synthesis. So, where this with this we are going to start another interesting class of organometalic compounds these are carbonyl metal halides and are known for most of the transition metals.

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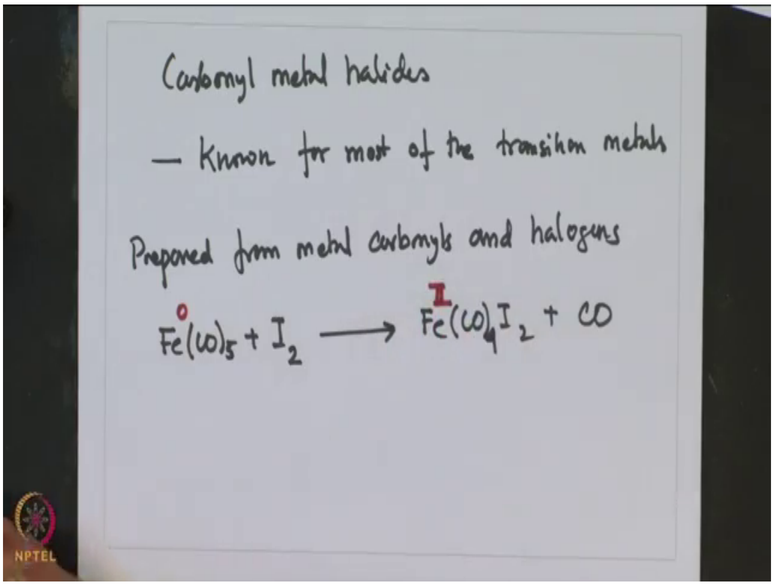

Carbonyl metal halides

— Known for most of the transition metals

Prepared from metal carbonyls and halogens

$$\overset{0}{Fe}(CO)_5 + I_2 \longrightarrow \overset{II}{Fe}(CO)_4I_2 + CO$$

These transition metal carbonyl halides are prepared directly from metal carbonyls and halogen and the reaction is given as Fe CO 5 plus I 2 giving Fe CO 4 I 2 plus CO. So, here we see a reaction of iron carbonyl with iodine giving the iron metal halide and CO.

And iron has been oxidized from its 0 oxidation state over here 2 plus 2 over here by this oxidative addition of iodine.

Now, we are going to take a look at few other examples of these carbonyl metal halides and these two also involves preparations from metal carbonyl with iodine.

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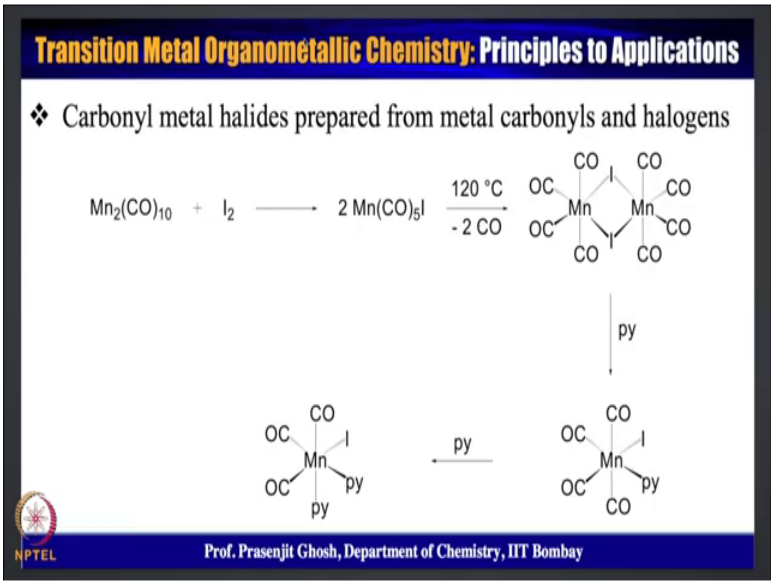

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- Carbonyl metal halides prepared from metal carbonyls and halogens

$Mn_2(CO)_{10} + I_2 \longrightarrow 2\,Mn(CO)_5I \xrightarrow[-2\,CO]{120\ ^\circ C}$

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For example, Mn to similar to the iron carbonyl this one is Mn 2 CO 5 plus iodine gives 2 Mn CO 5 I, which at when heated at 120 degree centigrade loses 2 carbon monoxide molecules to give CO Mn CO, CO, CO, Mn, iodine, CO, CO, CO, CO.

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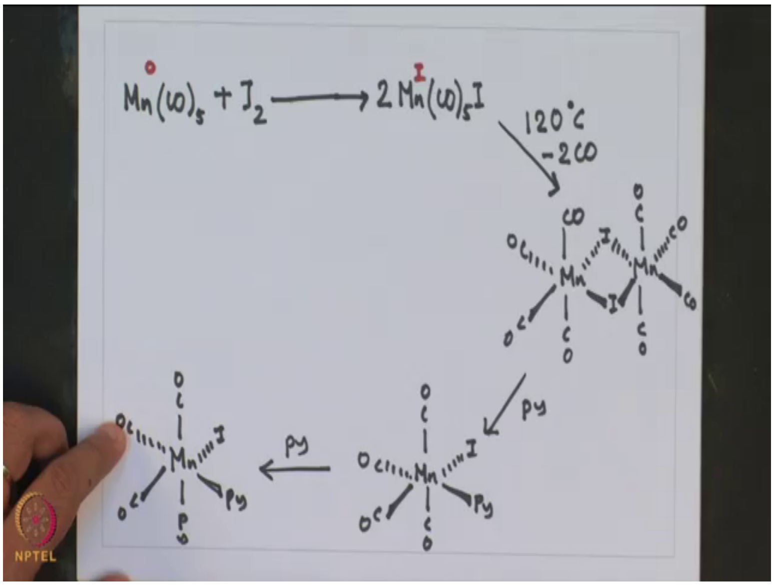

So, here what we see is that iodine has oxidized this dimeric manganese carbonyl compound and each of this manganese center got oxidized by 1 unit. So, they have got turned to manganese one compounds and the when at when heated they dimerize with elimination of CO where we have a dimeric Mn 2 CO 8 compounds with I 2, 2 bleaching iodide.

Now, in presence of pyridine the the diameric bridges of iodine is broken to give the monomeric complex Mn CO, CO, CO, CO Py iodine. So, here this iodine bridge is broken and is replaced by pyridine.

Now, in excess pyridine another of the CO is lost to give the following Mn, CO, iodine, Py, Py, CO, CO complex. So, here we saw the second method or second example of methods for preparing carbonyl metal halides.

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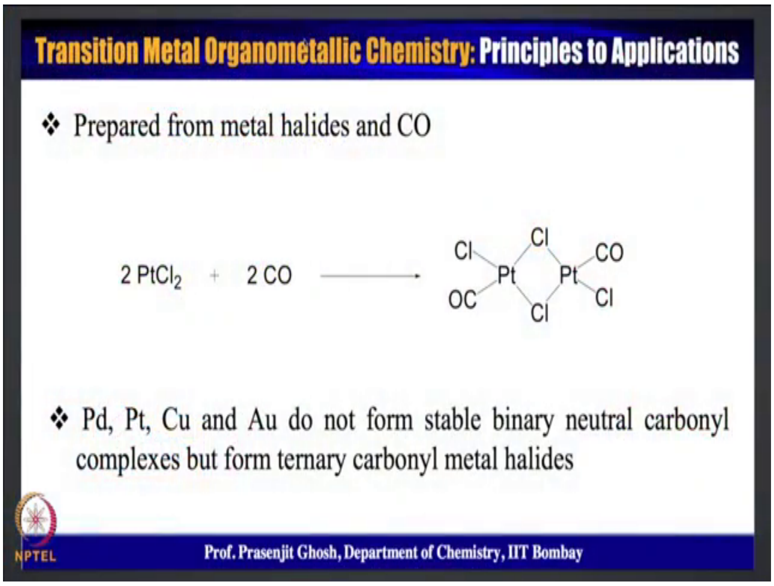

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- Prepared from metal halides and CO

$2\ PtCl_2 + 2\ CO \longrightarrow$

- Pd, Pt, Cu and Au do not form stable binary neutral carbonyl complexes but form ternary carbonyl metal halides

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And these two involve reaction of metal carbonyls with iodine another method is preparation from metal halides and carbonyl that will also give metal carbonyl metal halides prepared from metal halides and carbonyl.

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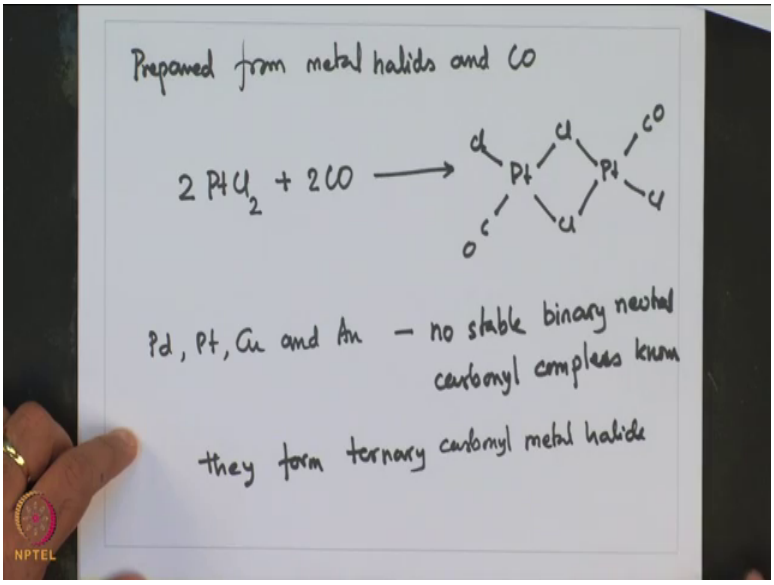

Prepared from metal halids and CO

2 $PtCl_2$ + 2CO ⟶

Pd, Pt, Cu and Au – no stable binary neutral carbonyl complexes known

they form ternary carbonyl metal halide

For example, PtCl 2 plus 2 CO giving this chloro bridge platinum dimeric complex and these platinum compounds containing 2 chloro gage and 2 carbonyl and 2 terminal chloride atoms. It must be noted that for several late transition metals like palladium, platinum, copper, and gold no stable binary, no stable binary neutral carbonyl complexes unknown. They form ternary carbonyl metal halide complexes.

So, with that let me summarize the points that has been discussed in today's lecture. We have looked into a particular reagent which is due to application of transition metal carbonyl metallates, and this is this Collman reagent which is Na to Fe CO 4. And this Collman's reagent is extensively used for transforming organic halogen compounds to functionalized compounds, so this is the extremely good reagent for functionalization.

We have looked into the flow diagrams and we have seen about 7 or 8 different compounds starting from alkane, aldehyde, ketone, amide, ester acid can be formed using Collman's reagent. One important attribute of Collman reagent is that it provides functionalized products in high yields and high selectivity, so that is kind of the advantage for using Collman reagent.

What we had I would I would like to states that Collman's reagent is a beautiful application of iron organometallic compound as a stoichiometric reagent, and in addition to that the utility of iron organometalic compounds in various organic transformation.

But, as a catalyst or in the catalytic fashion is also of significant contemporary interest and currently a lot of work is being done in this area.

Also with that we have concluded our discussion on Collman’s reagent and moved on to carbonyl metal halide compounds and we have looked at various propriety methods available for preparing this carbonyl metal halide compounds and basically the two approaches had been react metal carbonyls with halogens to give the carbonyl metal halides. We obtained in two example one of iron and another manganese for that. And the other approach is about taking metal halides and reacting that with carbonyl this involving platinum.

In this figure it is worth noting that for very late transition metals like palladium, platinum, copper, gold no such binary a neutral carbonyl complexes are known, but for these elements ternary a carbonyl metal halide compounds are known.

So, with that I would like to conclude today’s lecture and I would take up these transition metal carbonyl halides and their properties in bit more details in the subsequent lecture which will follow next. So, thank you for being with me in this lecture and I look forward to the next lecture on transition metal carbonyl halides which will be detailed, which will be studied in more details in the next lecture.

Thank you.