Transition Metal Organometallic Chemistry : Principles to Applications

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Week - 10
Lecture - 50
Application of Metal Halides and Metal Alkenes

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. We have been discussing about transition metal carbonyl halides in the last lecture and there we have looked into various preoperative methods for transition metal carbonyl halides. And in this lecture we are going to look at some of the applications of these kind of complexes transition metal carbonyl halides, and then look into another very interesting class of compounds these are transition metal alkene complexes.

As we sort of look at the compounds that we have discussed so far what which seems that these are extremely important compounds particularly from the catalytic a point of view, in the sense that they are active catalyst for many important and useful transformations which are being routinely used in industry as well as in academia alike.

So, that is what is the hallmark of organometallic chemistry and that we have started appreciating as we have looked at some of these transition metal carbine, transition metal alkane, transition metal carbonyl complexes, transition metal carbonyl hydrides, transition metal halides that we have been discussing.

Apart from that what strikes out is the fact that apart from chemical catalysis which organic metallic compounds are usually known for, they can also be used as good reagents for carrying out various organic transformations.

And one very good example that we had discussed about the reagent applications of transition metal organometallic compound is the Collman reagent which is the iron based metallate disodium iron tetracarbonyl metallate which is extensively used for functionalization of organic halide compounds to various functionalized organic compounds. And we saw that the hallmark of Collman's reagent is that it produces this functionalized carbon compounds from organic halogen compounds in very good yield high yield and high selectivity, we have discussed extensively on that in the previous lecture.

We have also looked into another important organometallic compound which serves as a reagent for various important organic transformation and this had been the tabias reagent which was a titanium carbine complex which we had discussed in our earlier lectures.

So, what we see that from the applications of transition metal organometallic compounds there are two phases to it, one is obviously, the catalytic applications which is predominantly occupying the greater space in application space and the next big thing about organometallic chemistry is these applications at stoichiometric reagents for which we have just looked at Collman's reagent as well as teddies reagent. And we see that these are no less important and they are equally useful and are being extensively used for their utility purpose.

So, with that we are going to discuss some more applications of transition metal carbonyl halides in this current lecture.

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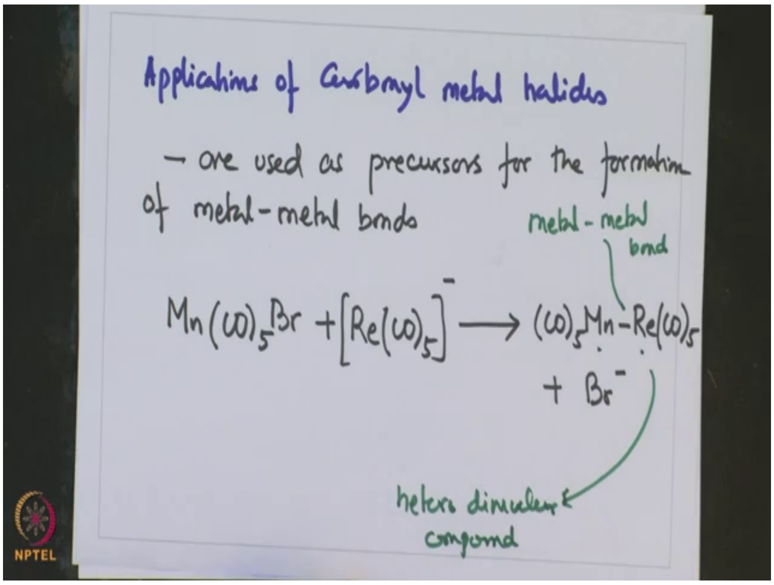

Applications of Carbonyl metal halides

- are used as precursors for the formation of metal-metal bonds

$$Mn(CO)_5Br + [Re(CO)_5]^- \longrightarrow (CO)_5Mn-Re(CO)_5 + Br^-$$

metal-metal bond

hetero dinuclear compound

And one important thing about these carbonyl metal halides that they can be used as precursors for preparing metal metal bonds, are often used as precursors for the formation of metal metal bonds. A good example of this is given in the reaction below, Mn CO 5 bromide reacting with rhenium CO 5 metallic anion, gives CO 5 Mn rhenium CO 5 plus Br minus.

So, this is the interesting reaction where our interesting application of carbonyl metal halides where this is nicely used for preparing these metal metal bond. And another interesting bit over here that this is heterodyne nuclear compound, in the sense that there are two different metals in this dinuclear compound and that is synthetically very challenging compound to make as far as the synthesis is concerned.

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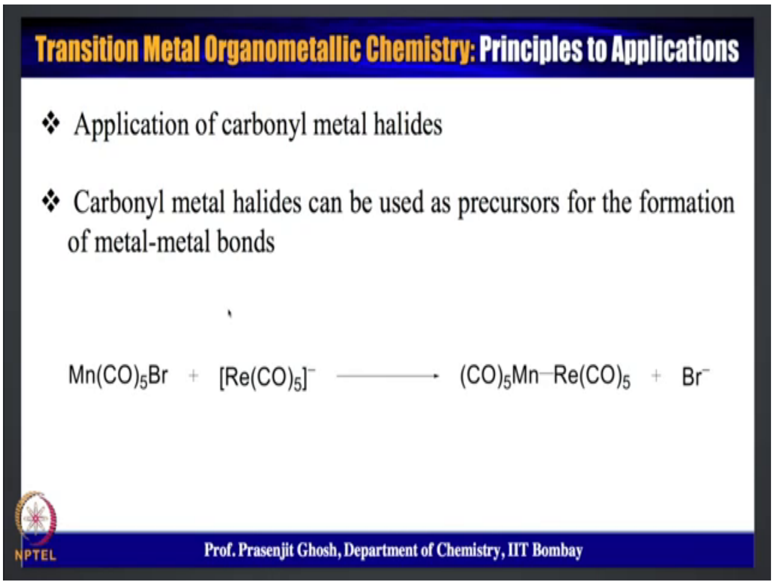

Transition Metal Organometallic Chemistry: Principles to Applications

- Application of carbonyl metal halides
- Carbonyl metal halides can be used as precursors for the formation of metal-metal bonds

$$Mn(CO)_5Br + [Re(CO)_5]^- \longrightarrow (CO)_5Mn{-}Re(CO)_5 + Br^-$$

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And these are a very important compound particularly in chemical catalysis perspective because these two metals will have different affinity or will exhibit different affinity for different kind of substrates. And as a result it can activate more ah more variety of substrate simultaneously giving catalytic products which otherwise are difficult to obtain using the homo die nuclear counterparts or homo metallic complexes.

So, from that perspective this method is a very nice application of transition metal halide complexes to produce this hetero dinuclear bimetallic species containing metal metal involved. And obviously, understanding the molecular orbital picture of this metal metal bond itself is a very interesting problem by itself and that also is extensively studies as being studied as to how or what kind of orbitals are involved information of this metal metal bond.

So, with that we conclude our discussion on transition metal carbonyl halide complexes and move on to another very interesting set of ligands which are sigma pi donor pi acceptor ligands.

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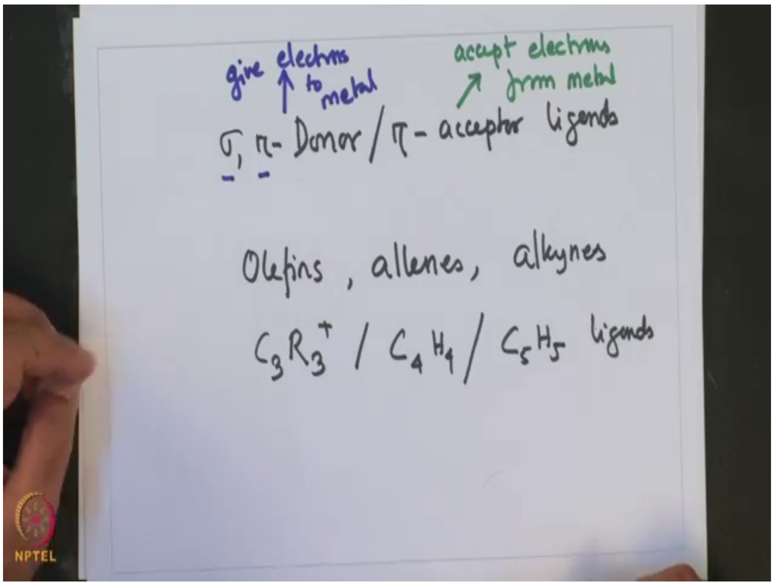

give electrons to metal

accept electrons from metal

σ, π- Donor / π- acceptor ligands

Olefins, allenes, alkynes

$C_3R_3^+$ / C_4H_4 / C_5H_5 ligands

Now, these are interesting class of ligands first of all that make bonds to transition metal by interesting amine these are electron rich species which has filled orbitals like the homos, at the homo minus 1 which can interact both in a sigma and pi fashion with the metal with appropriate orbital symmetry. And also it has empty or vacant lumo or pi star accept orbitals which can accept electron density from the metal and hence is the pi acceptor nature of this ligand.

So, one good thing about this ligand that they can give electrons give electrons to metal which is very common for any ligand that they give electron to the metal and this giving of electron occurs by can occur from sigma a sigma or pi fashion hm. But the other interesting aspect of these ligands are they can accept accept electrons from metal.

Now, this is counterintuitive a concept for a ligand because ligands are known to be electron rich species which donates electron to a electron deficient metal. So, how can electronically species accept electron from election electron deficient entity like metal.

So, in that way this pi acceptor concept is sort of concept which is counterintuitive to to the normal definition of ligand and that is why this kind of sigma pi donor pi acceptor ligand are so special. So, these the examples of these ligands include compounds like olefins, or allenes even alkynes. So, these entities make a bond with ancient metal can bond in similar fashions where they can donate electron through sigma and pi donation and also accept electron as a pi acceptor ligand. The other examples of these ligands are C 3 R 3 a plus or C 4 H 4 or C 5 H 5 ligands. So, cyclopentadienyl, cyclobutadiene denial or cyclopropenyl frameworks or belongs also to this category of ligands.

So, with that said we are going to focus begin our discussion on this sigma pi, donor pi acceptor ligands right from its first example which are the olefins.

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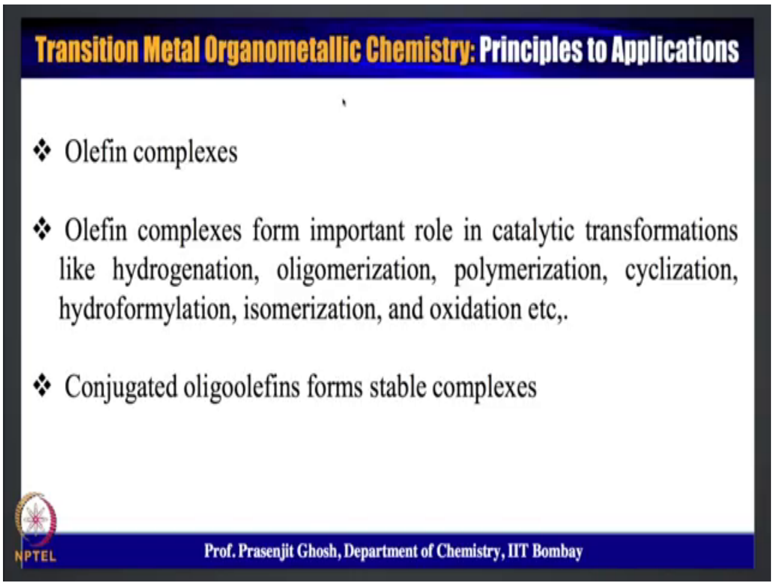

Transition Metal Organometallic Chemistry: Principles to Applications

- Olefin complexes
- Olefin complexes form important role in catalytic transformations like hydrogenation, oligomerization, polymerization, cyclization, hydroformylation, isomerization, and oxidation etc,.
- Conjugated oligoolefins forms stable complexes

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Now, transition metal olefin complexes are important complexes and they a catalytic intermediates in hydrogenations, oligomerizations, polymerizations so on and so forth, important catalytic intermediates, in hydrogenation.

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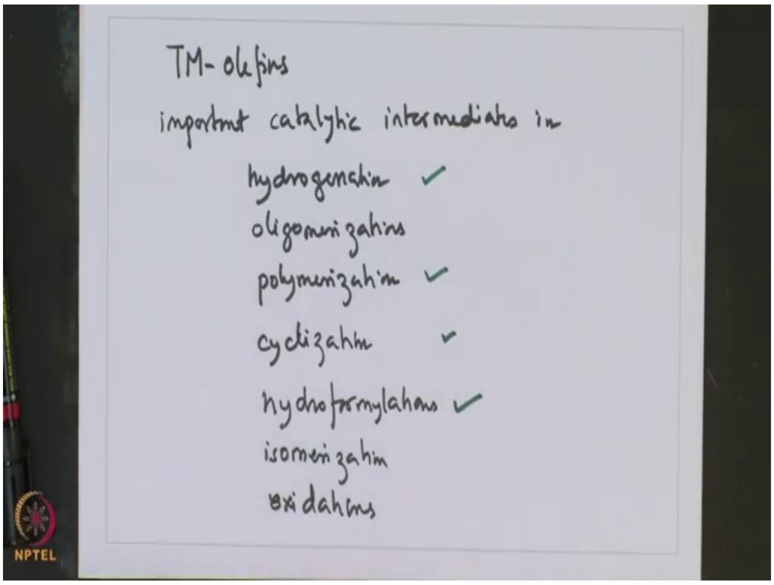

TM- olefins

important catalytic intermediates in

- hydrogenation ✓
- oligomerizations
- polymerization ✓
- cyclization ✓
- hydroformylations ✓
- isomerization
- oxidations

This is an very important reactions where olefins are converted to alkanes oligomerizations or polymerizations reactions, cyclization reactions, hydroformylation reactions, isomerization reactions, and oxidation reactions.

So, what we see that these are extremely important species or compounds or class of compounds which can carry out whole gamut of very important reactions and as to highlight that many of these reactions have been recognized for their utility by the conformant of Nobel Prize. So, for example, hydrogen hydrogenation has been given the Nobel Prize, polymerization, this ring opening chlo metathesis reactions, cyclizations, hydroformylation.

So, at least what we see that 4 of these, so 8 or 9 applications that we have been discussing 4 or 5 of them have been recognized by for their utility by conformant of Nobel Prizes. So, these are extremely important compounds and these transition metal olefin complexes and that can be seen from the kind of utility the transition metal olefin complexes exhibits.

So, with that let us discuss in bit more details about these transition metal olefin complexes. Particularly, a about their stability their propriety methods and also their reactivity a along with some of the applications of these transition metal olefin complexes that we are going to be discussing. So, preparations usually the first this transition metal olefin complexes was prepared long back. The first one was dices salt.

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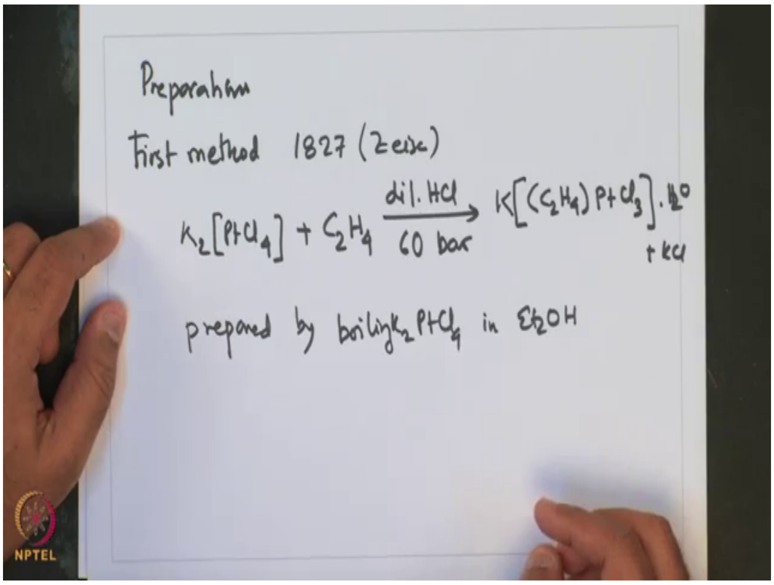

Preparation

First method 1827 (Zeise)

$$K_2[PtCl_4] + C_2H_4 \xrightarrow[60\ \text{bar}]{\text{dil. HCl}} K[(C_2H_4)PtCl_3].H_2O + KCl$$

prepared by boiling K_2PtCl_4 in EtOH

The first method was discovered way back in 1827, like the that is about like 150 years or more earlier by Zeise. And, the reaction was done by taking K 2 PtCl 4 plus C 2 H 4 with dilute HCl and 60 bar pressure gives K C 2 H 4 PtCl 3 KCl.

So, this was prepared by boiling by boiling PtCl 4 in K 2 PtCl 4 in ethanol. And one interesting thing is that this reaction was improved on several accounts and one interesting thing to note about that this compound even though discovered in 1827.

Its understanding of this compound as to how it binds as to what are the bonding interaction that this ethylene displays with the metal that only came to be known about more than 100 years later of his discovery in 1950s and 1960s when the (Refer Time: 16:02) model was proposed to explain the bonding of transition metal olefin complexes.

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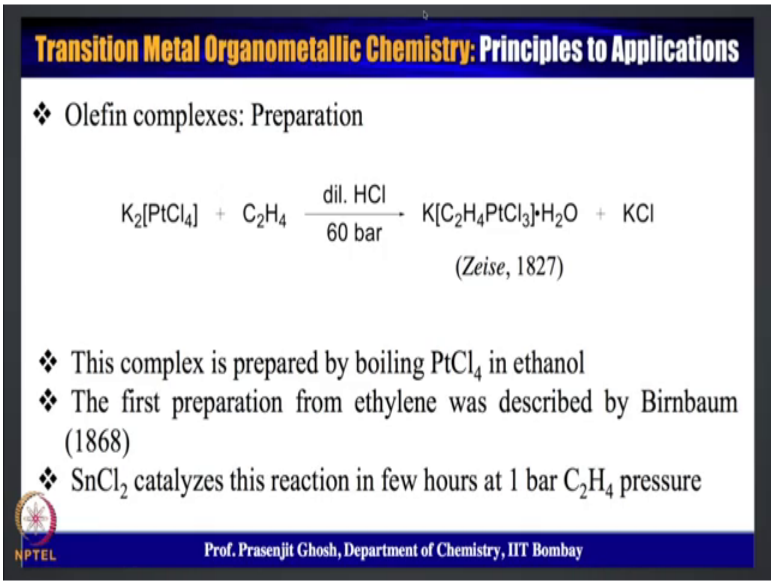

Transition Metal Organometallic Chemistry: Principles to Applications

- Olefin complexes: Preparation

$$K_2[PtCl_4] + C_2H_4 \xrightarrow[\text{60 bar}]{\text{dil. HCl}} K[C_2H_4PtCl_3]\cdot H_2O + KCl$$

(*Zeise*, 1827)

- This complex is prepared by boiling $PtCl_4$ in ethanol
- The first preparation from ethylene was described by Birnbaum (1868)
- $SnCl_2$ catalyzes this reaction in few hours at 1 bar C_2H_4 pressure

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So, here is an interesting example which was understood really about 130 or 140 years after its synthesis and then like the various other it applications of these complexes or these class of complexes emerged.

So, what is interesting to point out with regard to (Refer Time: 16:28) solve that here is the compound which has never lost his (Refer Time: 16:32) right from its discoveries so long back and then it could engage, could engage the community for such a long time and provide an interesting bonding theory that so only develops on these developed on this complex.

So, in that way this is very landmark interesting compound which was not only interesting from its synthesis point of view, but also was equally interesting from the theory it developed for the understanding of the binding of the olefin to the metal center which to which was done in 1950s about one-third 30 years after.

So, there are other methods also available for preparing these transition metal olefin complexes the one involves using Al Cl 3, AlCl 3 is the Lewis acid and that abstract Cl minus to form AlCl 4 minus and the corresponding metal olefin complex.

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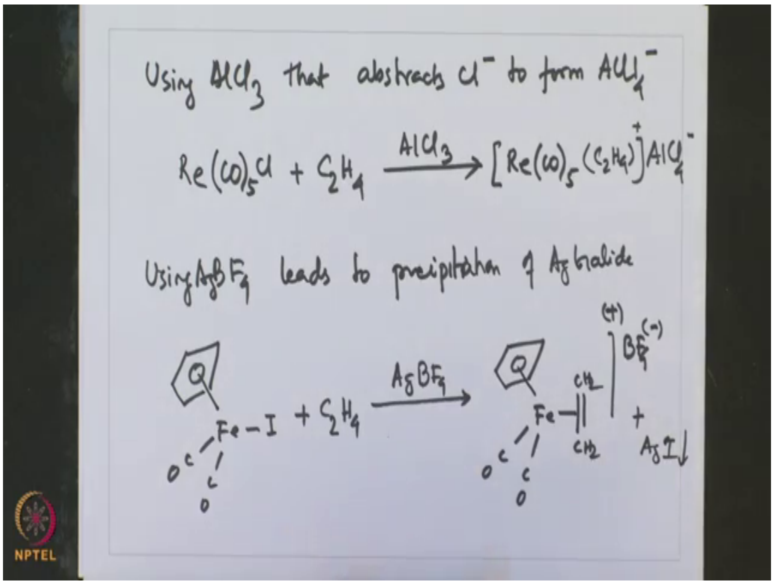

Using $AlCl_3$ that abstracts Cl^- to form $AlCl_4^-$

$$Re(CO)_5Cl + C_2H_4 \xrightarrow{AlCl_3} [Re(CO)_5(C_2H_4)]^+ AlCl_4^-$$

Using $AgBF_4$ leads to precipitation of Ag halide

And this is nicely demonstrated in this reaction of Re CO 5 Cl plus C 2 H 4 giving AlCl 3 and Re CO 5 C 2 H 4 AlCl 4 minus. So, what happened over here this chloride got abstracted by AlCl 3 to give AlCl 4 minus and the vacant space produced over here got occupied by this olefin or ethylene C 2 H 4.

The way AlCl 3 was successfully used in forming this rhenium olefin in complex similarly Ag Br 4 can also be effectively used for making the metal olefin complex leads to precipitation of as Ag halide and the complex. So, these can be seen nicely in this iron example, where Fe iodine plus C 2 H 4 in presence of Ag BF 4 gives Fe CH 2 BF 4 minus plus Ag I which is precipitated out.

So, the counter anion the abstractions of this iodide by silver giving AgCl produces a iron cationic iron species containing this coordinated olefinic compound and then the anionic charge balance is done by the BF 4 moiety here using to this formation of this ionic compound.

Now, apart from this abstraction reactions with Lewis acids or silver salts thermal ligand substitution is equally effective for producing this transition metal olefin complexes.

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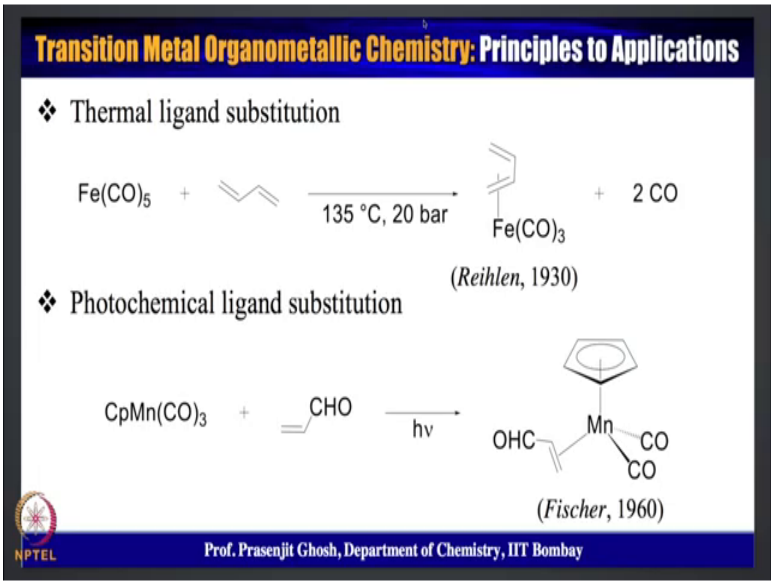

Transition Metal Organometallic Chemistry: Principles to Applications

- Thermal ligand substitution

$Fe(CO)_5$ + $\xrightarrow[\text{135 °C, 20 bar}]{}$ $Fe(CO)_3$ + 2 CO

(*Reihlen*, 1930)

- Photochemical ligand substitution

$CpMn(CO)_3$ + CHO $\xrightarrow[h\nu]{}$ OHC Mn CO CO

(*Fischer*, 1960)

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An example of this is shown here.

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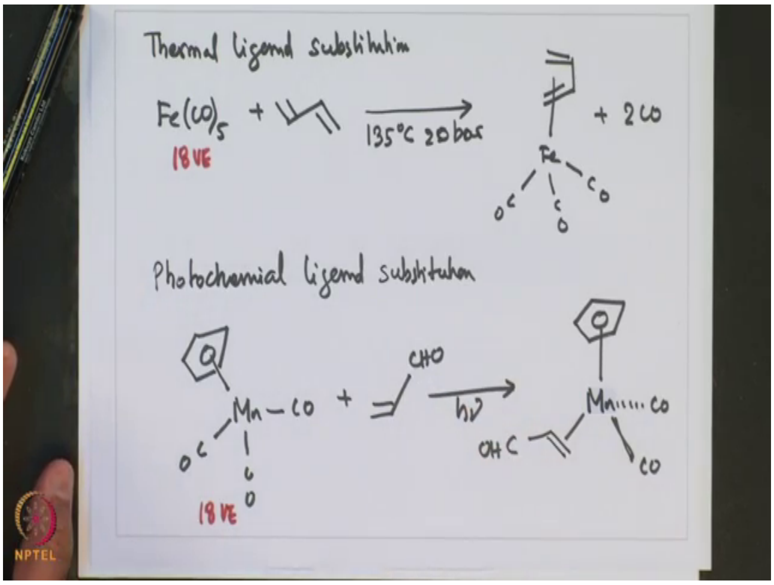

So, Fe CO 5 plus this diolefin at 135 degree centigrade and 20 bar of pressure gives this diolefin iron plus CO. So, here what we saw that this carbonyl got replaced by these olefin leading to these olefinic compounds. Now, usually it is known that the carbonyl binds very tightly to the olefin and that has been achieved.

So, the dissociation of the carbonyl from the iron has been achieved by heating under forcing conditions, forcing conditions I mean the temperature is about 135 degree centigrades.

So, through heat or through thermal conditions that these carbon lanes are made to dissociate otherwise carbon is very bind very strong neutral iron and also the olefinic condition is 20 bar, it is like extremely high pressure of olefin then only you can replace our one can replace carbonyl with olefin because olefin does not bind as strongly as that of a carbonyl.

So, under very forcing conditions of about 135 degree centigrades of heating and 20 bars of olefinic pressure that one can replace this 2 carbonyl moiety is by this diolefin to give this butadiene Fe CO 3 moiety.

The way carbonyls can be substituted by a heat the same can be achieved by photochemical reactions and the example of this is given below. The example is a cp Mn CO 3 plus this olefin in presence of light gives Mn CO. And one of the carbonyl is replaced by n aldehyde. So, here also we see that this dissociation of the carbonyl is achieved by light and in this case this has been achieved by heat and so, one must sort of note take a note of this fact that this is a 18 VE complex.

So, for this addition to happen it has to undergo a dissociative mechanism before the olefin combined and for that the dissociation of the carbon monoxide is very crucial and that is achieved under forcing conditions, because carbon monoxide being a pi acidic ligand binding very strongly to the middle and that it requires forcing condition to be replaced by some weak ligands like olefin.

Similarly the case over here also these complexes is also a 18 elect from complex and for it to react with this olefin is difficult. So, it also goes by dissociative path way and this dissociation is achieved in presence of light photochemically a where one of the CO is dissociated it goes to the 16 electron and when the olefin comes and bind.

So, another two methods which are there for producing this transition metal carbonyl olefinic complexes one such method is called metal induced ligand isomerization.

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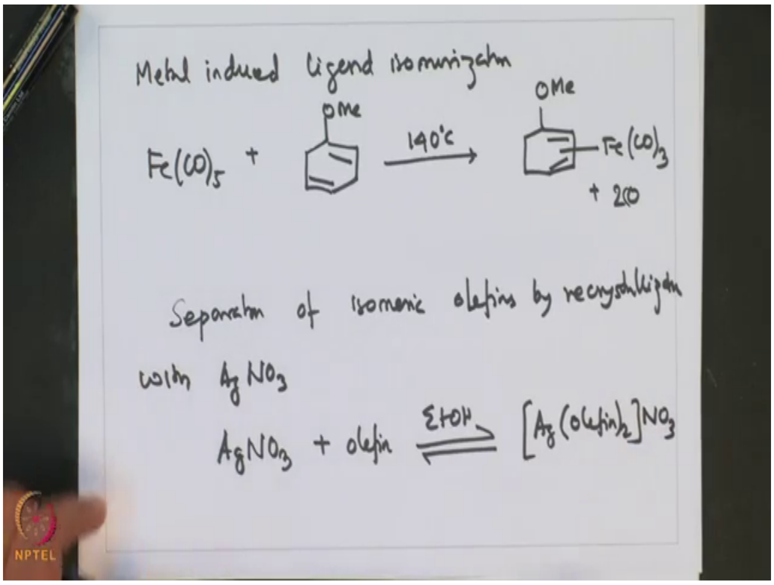

Metal induced ligand isomerization

Separation of isomeric olefins by recrystallization with $AgNO_3$

$AgNO_3 + \text{olefin} \overset{EtOH}{\rightleftharpoons} [Ag(\text{olefin})_2]NO_3$

An example of this is Fe CO 5 plus this OMe when this is heated at 140 degree centigrade, it these diolefinic compounds isomerizes and become conjugated to give the more stable one and that binds to Fe CO 3 plus 2 CO. So, they are here also we see that metal induced ligand isomerization this ligand is isomerizing and the loss of CO has been achieved under very high thermal conditions of 140 degree centigrade.

Sometimes a separations of isomeric olefins by recrystallization with Ag No 3 and that also gives the metal olefin complex example of this is given Ag No 3 plus olefin in ethanol gives the silver olefinic complex and No 3 has the outer sphere.

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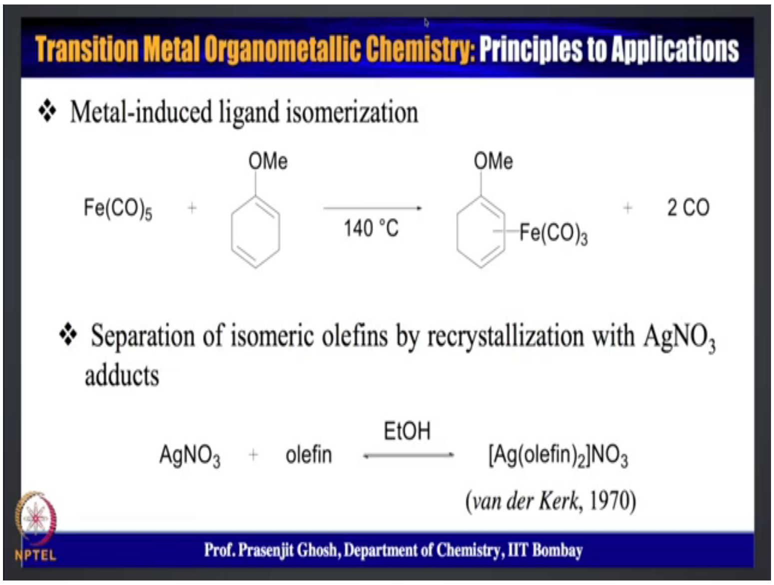

Transition Metal Organometallic Chemistry: Principles to Applications

- Metal-induced ligand isomerization

- Separation of isomeric olefins by recrystallization with $AgNO_3$ adducts

$$AgNO_3 + \text{olefin} \xrightarrow{EtOH} [Ag(\text{olefin})_2]NO_3$$

(*van der Kerk*, 1970)

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So, this is a very useful and convenient method for making this olefin complex with late transition metal by liquid slicing silver nitrate and olefin from ethanol leading to these silver disolefin nitrate complex.

So, with that let me conclude the discussion that we have had in today's lecture. We have looked into studied in this lecture by looking into one of the utility of transition metal carbonyl halide complexes. And what we see that these have been extensively used for predict, preparing dinuclear heterodyne diatomic transition metal complexes which are very challenging compounds to make and this transition metal carbonyl halide provides an effective method route for producing these dinuclear heterodyne nuclear complexes by reaction with transition metal carbonyl metalate anions.

So, we have looked into that utility aspect of this transition metal carbonyl halide. Apart from that we have also looked into this a new class of sigma pi donor pi acceptor kind of ligands like these ligands include alkene alkine as well as this cyclic olefins like cyclopropane, cyclobutane, cyclopentane rings. And we have looked into the propel various preoperative methods available for preparation of these transition metal olefin complexes.

We have looked in some of the examples. One thing I must note in the perspective this perspective transition metal olefin complexes that they are important intermediates and they in various catalytic reactions about 8 or 9 of them and 5 or 6 of them have been recognized further utility with noble prize. So, that sort of speaks volumes about how important these class of transition metal olefin complexes are.

So, with that I would like to conclude today’s lecture. And we are going to be discussing more on this transition important class of compounds this transition metal olefin complex in the subsequent lecture. Till that time, goodbye, and look forward to being with you in the next lecture.

Thank you.