Transition Metal Organometallic Chemistry: Principles to Applications

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Lecture – 01
Week - 01

History of Organometallic Compounds

Welcome to the first lecture on organometallic chemistry. The title of this course is Transition Metal Organometallic Chemistry from Principles to Applications. To begin with let me give you a brief overview of organometallic chemistry. Organometallic chemistry lies at the interface of inorganic chemistry and organic chemistry; and has implications both in the areas of organic as well as in organic domains. One important aspect about these compounds are that they are very difficult to synthesis, very difficult to handle as they are extremely air and moisture sensitive's.

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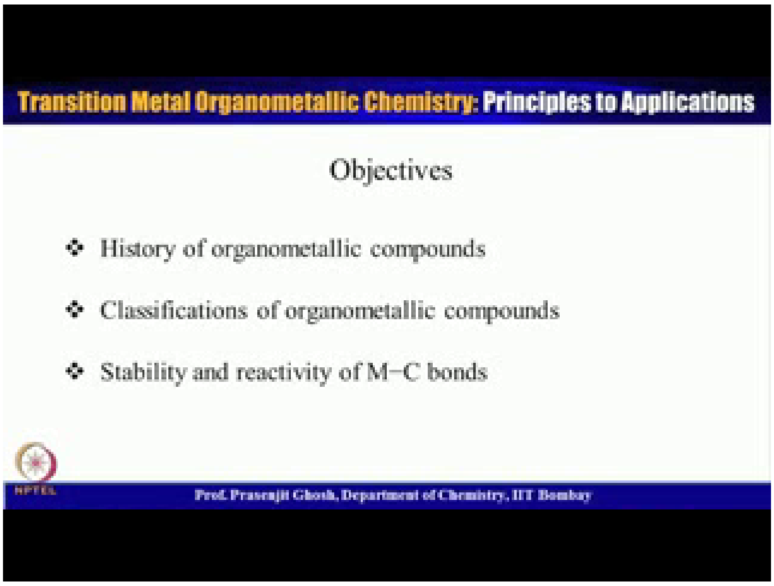

Transition Metal Organometallic Chemistry: Principles to Applications

Objectives

- History of organometallic compounds
- Classifications of organometallic compounds
- Stability and reactivity of M–C bonds

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This compounds thus are prepared handled and reacted in the exclusion of air; and it takes a lot of technical knowhow in dealing with this compounds and that is one of the reason why organometallic chemistry have thus for state confined to very few chemist practicing in this area. In the beginning of the course, what I have thought is that I would give you a brief overview of the history of organometallic compounds. I believe this is very important as to give you a perspective as to how these compounds evolved over time with discoveries made along centuries.

This would also give you a view as to which compounds were discovered first and which came next, and obviously it would be important to stress that the easier ones got discovered earlier and the more challenging and rigorous ones are coming off late only when we have number of technical knowhow about handling them. So, in this first week we will give you a brief history of organometallic compounds and then we move to various classifications of organometallic compounds and then from there we would well on the stability and reactivity of metal carbon bonds.

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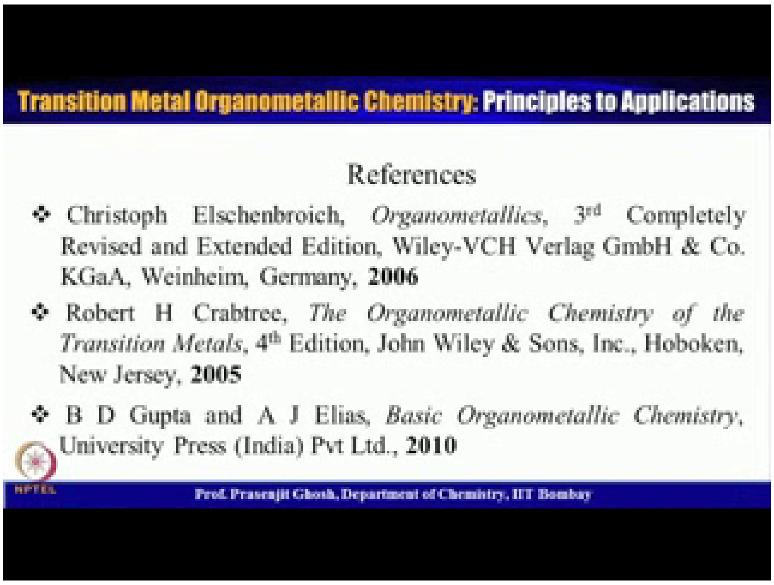

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References

- Christoph Elschenbroich, *Organometallics*, 3rd Completely Revised and Extended Edition, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2006**
- Robert H Crabtree, *The Organometallic Chemistry of the Transition Metals*, 4th Edition, John Wiley & Sons, Inc., Hoboken, New Jersey, **2005**
- B D Gupta and A J Elias, *Basic Organometallic Chemistry*, University Press (India) Pvt Ltd., **2010**

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The reference book for this course is three of them, one is Elschenbroich Organometallics 3rd edition, Robert Crabtree - The Organometallic Chemistry of Transition Metals, and B D Gupta and A J Elias - Basic Organometallic Chemistry. These books as well as any other books on the subject we will do.

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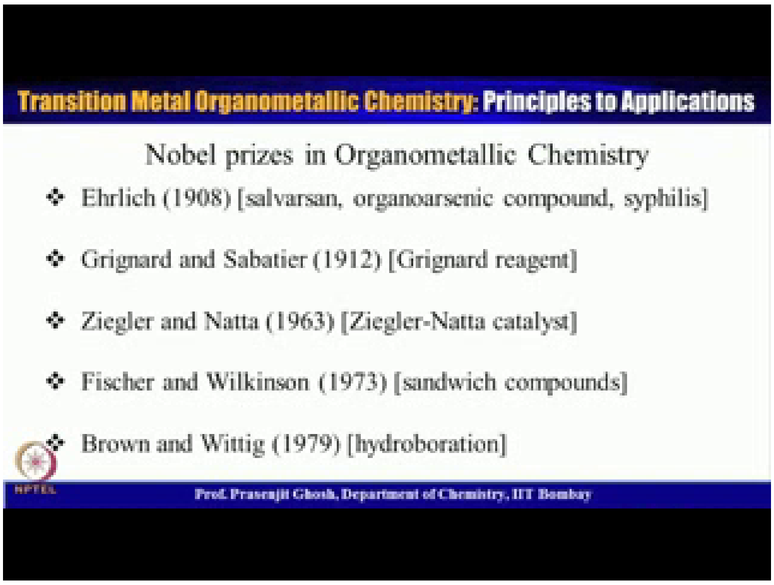

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Nobel prizes in Organometallic Chemistry

- Ehrlich (1908) [salvarsan, organoarsenic compound, syphilis]
- Grignard and Sabatier (1912) [Grignard reagent]
- Ziegler and Natta (1963) [Ziegler-Natta catalyst]
- Fischer and Wilkinson (1973) [sandwich compounds]
- Brown and Wittig (1979) [hydroboration]

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Now to give you a feel for how important this field is I would say that 9 Nobel Prizes have been awarded to the area of organometallic chemistry that starts with 1908, Ehrlich for organarsenic compounds. Followed by Grignard and Sabatier for Grignard reagent in 1912; Ziegler Natta in 1963 for Ziegler-Natta catalyst that is let the wall in polymerization. Fischer and Wilkinson in 1973 for sandwich compounds, brown in 1979 hydroboration reaction.

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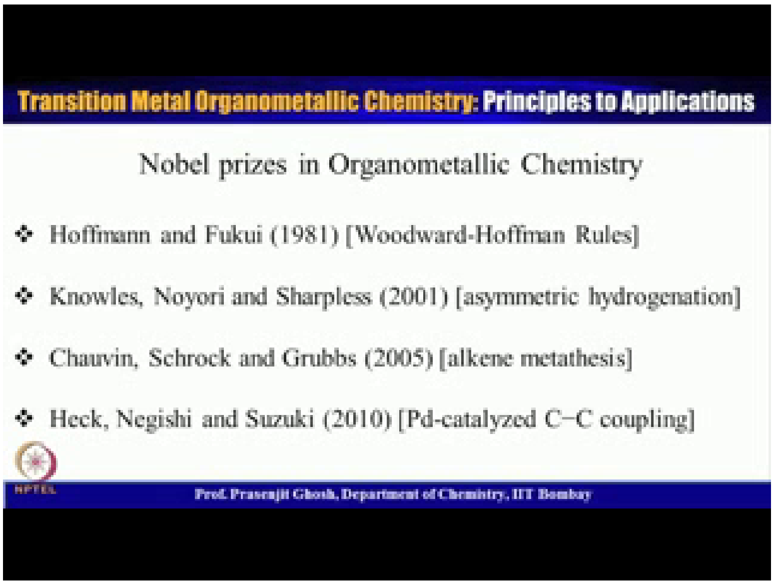

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Nobel prizes in Organometallic Chemistry

- Hoffmann and Fukui (1981) [Woodward-Hoffman Rules]
- Knowles, Noyori and Sharpless (2001) [asymmetric hydrogenation]
- Chauvin, Schrock and Grubbs (2005) [alkene metathesis]
- Heck, Negishi and Suzuki (2010) [Pd-catalyzed C−C coupling]

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Hoffmann and Fukui in 1981 for Woodward-Hoffmann rule, Knowles, Noyori and Sharpless in 2001 for asymmetric hydrogenation, Chauvin, Schrock and Grubbs in 2005 for alkene metathesis. And lastly Heck, Negishi and Suzuki in 2010 for palladium catalyzed cross coupling reactions. So, these give you a feel for the significance of this field which is only about a 100 or 200 years old, but it has may tremendous impact in our society. And also the diversity in the area tells you about the depth and the breath of the fields which organometallic chemistry posses.

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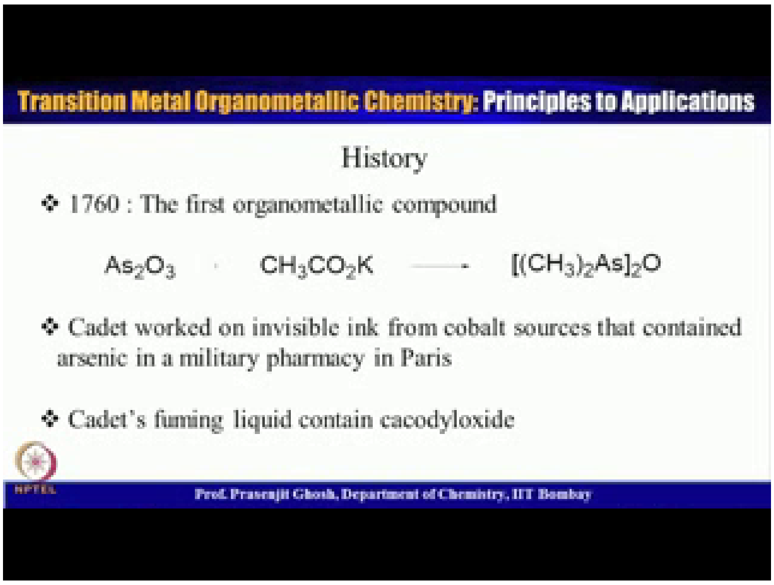

Transition Metal Organometallic Chemistry: Principles to Applications

History

- 1760 : The first organometallic compound

$$As_2O_3 + CH_3CO_2K \longrightarrow [(CH_3)_2As]_2O$$

- Cadet worked on invisible ink from cobalt sources that contained arsenic in a military pharmacy in Paris
- Cadet's fuming liquid contain cacodyloxide

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To back at the history the first organometallic compound gets back to 1760, when the first organometallic compound in form of dimethyl arsine oxide was prepared. This compound dimethyl arsine oxide is called cacodyl oxide because it has a very bad smell. It was prepared by Charles Luis cadet working in a military pharmacy in Paris in an attempt to make invisible ink for military use. So, this is the first reported organometallic compound that one can trace back.

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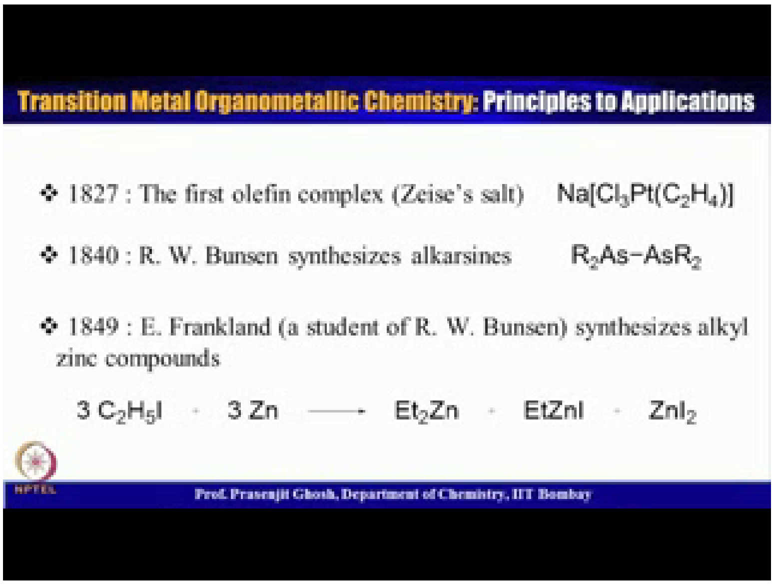

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- 1827 : The first olefin complex (Zeise's salt) $Na[Cl_3Pt(C_2H_4)]$
- 1840 : R. W. Bunsen synthesizes alkarsines $R_2As\text{-}AsR_2$
- 1849 : E. Frankland (a student of R. W. Bunsen) synthesizes alkyl zinc compounds

$$3\ C_2H_5I + 3\ Zn \longrightarrow Et_2Zn + EtZnI + ZnI_2$$

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To subsequent to this about in 1827, the first olefin complex called Ziese's salt having the formulas sodium Cl 3 Pt C 2 H 4 was prepared. Now, this complex is not a very simple complex because this complex has a binding of gaseous ethaline molecule on to platinum. So, one important attribute of organometallic chemistry is the ligand metal interaction. The metals interacts with ligands in various ways, and this is a representative compounds which has led to development of lot of theory in how gas or olefin in a form of a gaseous atom by into a metal like platinum. Subsequent to this, in 1840, R. W. Bunsen synthesis di-alkene di arsine R 2 As-As R 2. Then in 49 E. Frankland a student of bunsen synthesis alkene zinc this was done from the reaction of ethylenehalide with zinc giving diethyl zinc ethyl zinc hydride and zinc hydride.

Now if you recall that this reaction is some are similar to oxidative addition reaction where alkyl halide adds to a zero valent metal center. Now, probably the first or among the first methods that were used to synthesis organometallic compound starts with this oxidative addition reaction. And what we see later on that in many catalytic processes oxidative addition reaction becomes an important step.

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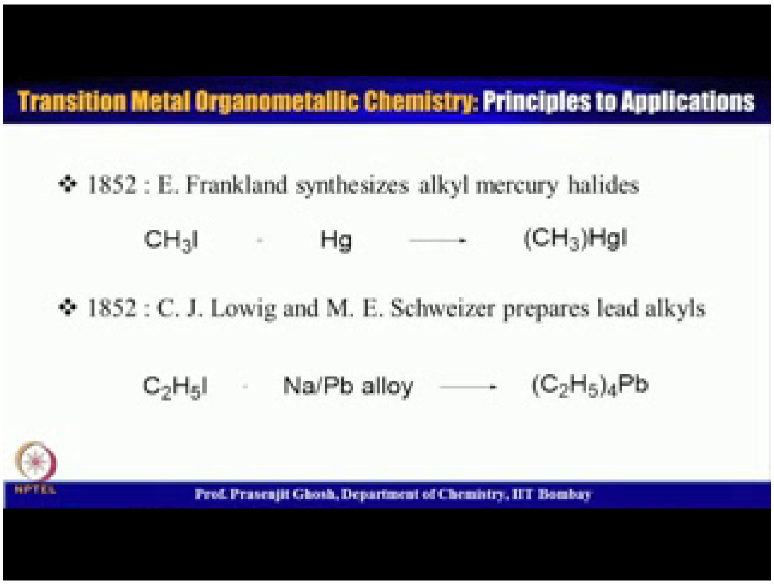

Transition Metal Organometallic Chemistry: Principles to Applications

- 1852 : E. Frankland synthesizes alkyl mercury halides

$$CH_3I + Hg \longrightarrow (CH_3)HgI$$

- 1852 : C. J. Lowig and M. E. Schweizer prepares lead alkyls

$$C_2H_5I + \text{Na/Pb alloy} \longrightarrow (C_2H_5)_4Pb$$

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And hence we see the origin of this step lies in synthesis of some of very important compound at very early stages of the history. Now, in 1852 E. Frankland synthesis alkyl mercury halides, again we see the similar kind of oxidative addition reaction occurring here between methyl halide and mercury giving methyl mercury halide. So, these seems to be time when lot of new organometallic compounds were being synthesized. In 1852 C. J. Lowing and E. Schweizer prepares lead alkyls again following the similar method of oxidative addition were by ethyl halide was added to sodium lead alloy giving tetraalkyl lead.

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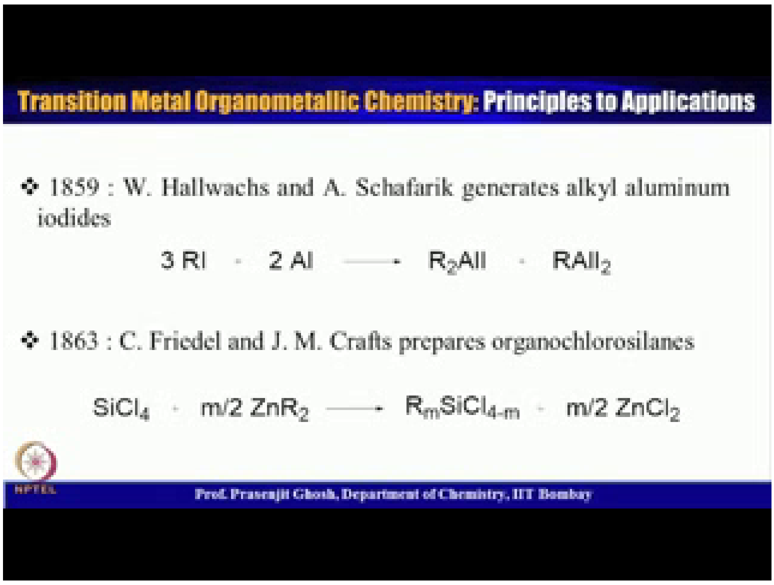

Transition Metal Organometallic Chemistry: Principles to Applications

- 1859 : W. Hallwachs and A. Schafarik generates alkyl aluminum iodides

$$3\,RI + 2\,Al \longrightarrow R_2AlI + RAlI_2$$

- 1863 : C. Friedel and J. M. Crafts prepares organochlorosilanes

$$SiCl_4 + m/2\,ZnR_2 \longrightarrow R_mSiCl_{4-m} + m/2\,ZnCl_2$$

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1859 W. Hallwachs and A. Schafarik generated aluminum alkyl halide. Again, following the same method of oxidative addition, happening between alkyl halide and metallic aluminum giving dialkyl aluminum hydrate and alkyl aluminum di hydrate. 1863 solve the famous Friedel C. Friedel and J. M Crafts prepares organochlorosilanes compounds by the reaction of cylen tetra chloride with di alkyl zinc giving alkyl cyline chloride and zinc dichloride. Now, this we see is a different reaction then that of the oxidative reactions that we have been seen so far. This reaction is sort of a transmetalation reactions where zinc alkyl migrates on to silicone and zinc itself abstracts the chlorine and becomes zinc chloride.

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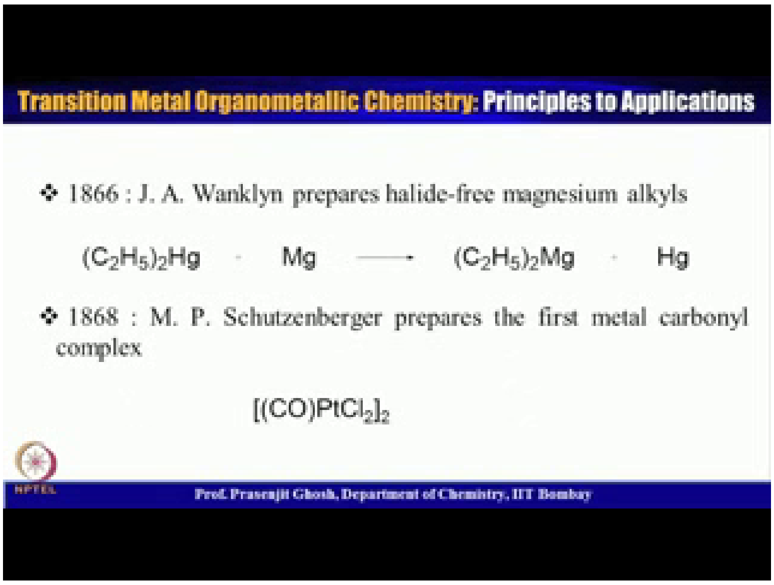

Transition Metal Organometallic Chemistry: Principles to Applications

- ❖ 1866 : J. A. Wanklyn prepares halide-free magnesium alkyls

$$(C_2H_5)_2Hg + Mg \longrightarrow (C_2H_5)_2Mg + Hg$$

- ❖ 1868 : M. P. Schutzenberger prepares the first metal carbonyl complex

$$[(CO)PtCl_2]_2$$

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1866 J. A. Wanklyn prepares halide-free magnesium alkyls, and this was done by reaction of diethyl mercury with magnesium giving diethyl magnesium and mercury. This reactions opens up a new role for alkyl mercury as a transmetalation the agent and that is for not only on this alkyl mercury has been use for transmetalation reactions in preparing transition metal organometallic compounds in many other instances. 1868 saw M. P. Schutzenberger prepare the first metal carbonyl complex in the form of CO Pt Cl 2 dimer. Here a gaseous carbon monoxide molecule by is to platinum. I must say that organometallic compounds offer great opportunity to study variety of interaction with occurring between metal and the ligands. The ligands are a varying types and metal also has different electronic configurations and different orbitals like a s, p, d and f which interact with the ligand.

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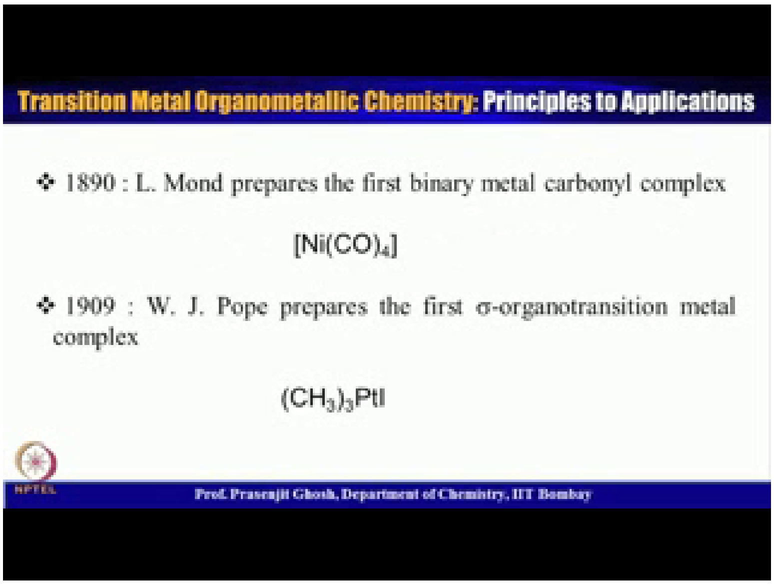

Transition Metal Organometallic Chemistry: Principles to Applications

- ❖ 1890 : L. Mond prepares the first binary metal carbonyl complex

$[Ni(CO)_4]$

- ❖ 1909 : W. J. Pope prepares the first σ-organotransition metal complex

$(CH_3)_3PtI$

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In 1890 L. Mond prepares the first binary metal carbonyl compound in the form of nickel tetra carbonyl. This compound is very toxic and has to be handle with care. This discovery lead to the formation of a big chemical company which came to be later known as ICI. In 1909 W. J. Pope prepared the first sigma transition metal complex in form of tri methyl platinum iodide. See one of the definition of organometallic compound lies in the fact that they contain metal carbon bonds. Now, the metal carbon bonds can be several type; it can be a sigma bond as well as pi bond. And there are lot of examples which were synthesized that had a sigma bond or pi type interaction of the ligand with metal. So, from this instant, this is the first sigma organotransition metal which was formed on platinum.

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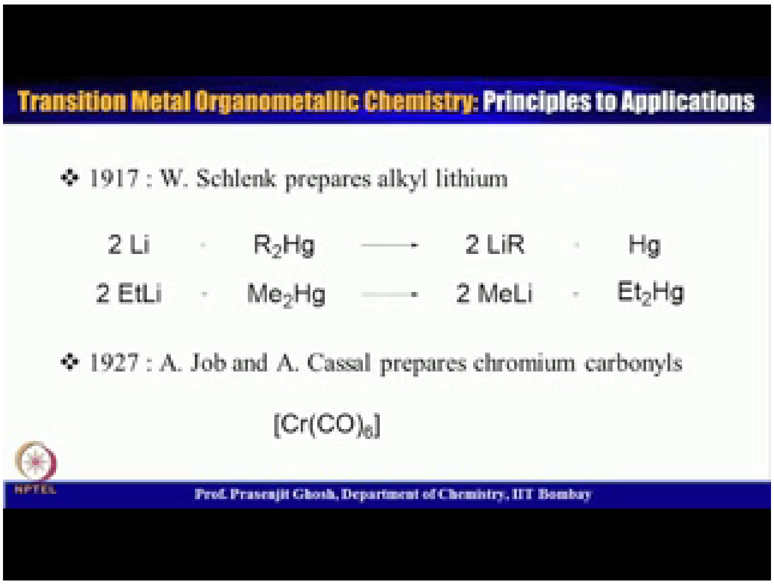

Transition Metal Organometallic Chemistry: Principles to Applications

- 1917 : W. Schlenk prepares alkyl lithium

$$2\,Li + R_2Hg \longrightarrow 2\,LiR + Hg$$
$$2\,EtLi + Me_2Hg \longrightarrow 2\,MeLi + Et_2Hg$$

- 1927 : A. Job and A. Cassal prepares chromium carbonyls

$$[Cr(CO)_6]$$

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In 1917 W. Schlenk prepares alkyl lithium. The reaction used was transmetalation reaction using mercury alkyls. So, lithium with dialkyl mercury give lithium alkyl and mercury and ethyl lithium with dimethyl mercury gives methyl lithium and diethyl mercury this is the ligand exchange reaction. Now, methyl lithiums are extremely difficult compounds to handle as they are pyrophoric, they when expose to air they instantaneously start burning, but these compounds are extremely good compounds as alkylating reagents, and they play crucial role in organic synthesis. In 1927 A. Job and A. Cassal prepares chromium carbonyls.

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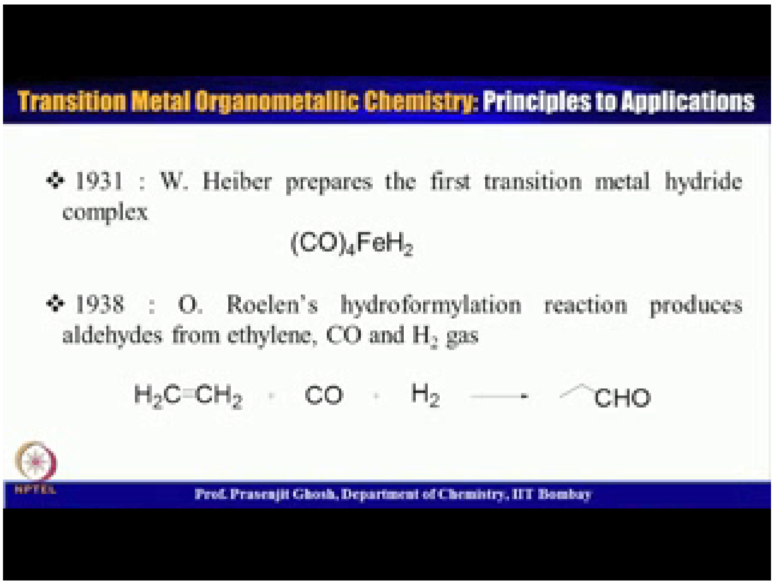

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- 1931 : W. Heiber prepares the first transition metal hydride complex

$$(CO)_4FeH_2$$

- 1938 : O. Roelen's hydroformylation reaction produces aldehydes from ethylene, CO and H_2 gas

$$H_2C{=}CH_2 + CO + H_2 \longrightarrow$$ CHO

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So, in 1931 W. Heiber prepares the first transition metal hydride complex in form of CO 4 Fe H 2. 1938 saw O. Roelen's hydroformylation reaction that produces aldehydes from ethylene carbon monoxide and hydrogen gas. Thus the reaction of ethylene with CO and H 2 gives aldehydes. This was a very important reaction and when turn to be big hit in industry producing tons of aldehyde by using this method and this is came to be known as hydroformylation reaction; various catalyst organometallic catalyst particularly rhodium and cobalt discovered for this transformation.

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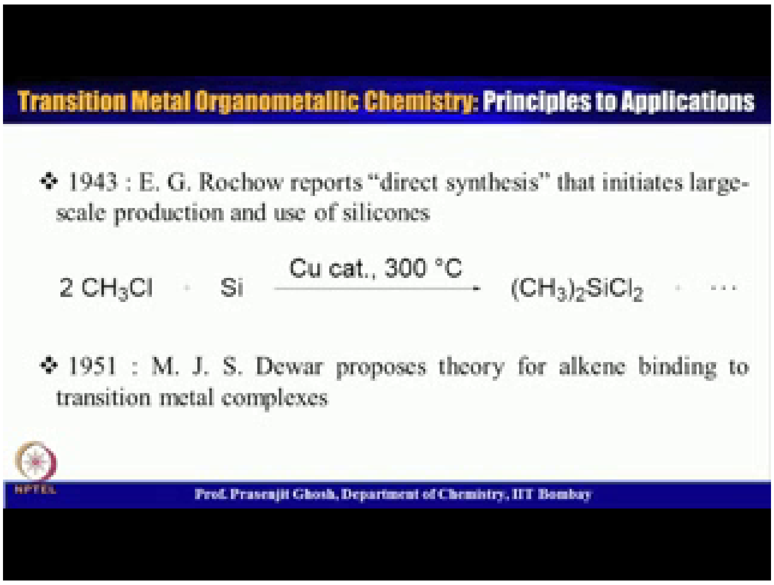

Transition Metal Organometallic Chemistry: Principles to Applications

- 1943 : E. G. Rochow reports "direct synthesis" that initiates large-scale production and use of silicones

$$2\,CH_3Cl + Si \xrightarrow{\text{Cu cat., 300 °C}} (CH_3)_2SiCl_2 + \cdots$$

- 1951 : M. J. S. Dewar proposes theory for alkene binding to transition metal complexes

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In 1943, E. G Rochow reported the first direct synthesis that initiated large-scale production and use of silicones. The reaction used was methyl chloride with elemental silicon copper catalyst as 300 degree centigrade giving dimethyl calycle dichloride and other isomers. Silicon was also commodity, which was produced large-scale in industry. Beginning from 1951 probably what one can say is the golden age of organometallic chemistry started with many new and interesting compound being synthesis at this period. In 1951 M. J. S. Dewar proposes the theory of alkene binding to transition metal complexes. These are really very engaging theory at it involves interactions of ligand orbital with that of the metal ones.

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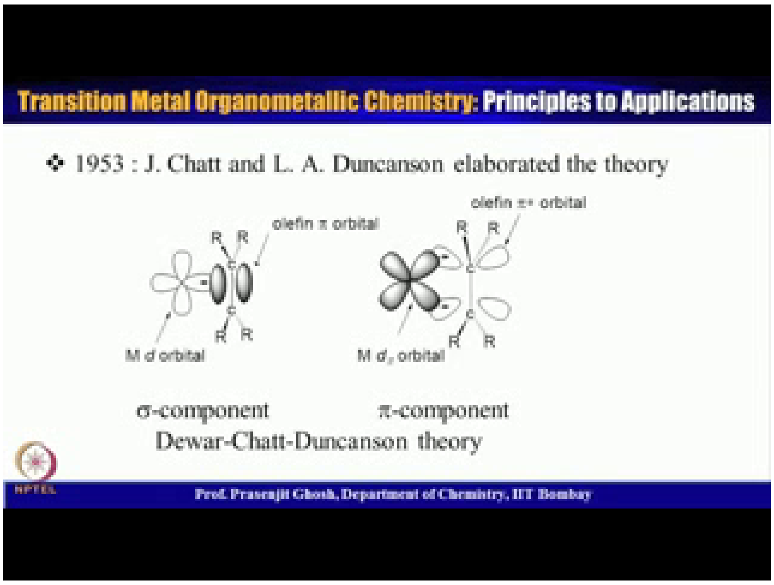

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- 1953 : J. Chatt and L. A. Duncanson elaborated the theory

σ-component π-component

Dewar-Chatt-Duncanson theory

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In 1953, J. Chatt and L. A. Duncanson elaborated the theory and came up with Dewar-Chatt-Duncanson theory. This theory explained how the bonding happened in ziese’s salt that was discovered in 1827 about 100 years later. This was very fascinating discovery at the time because it was found that during the alkene metal interaction; there are actually two interactions which are happening. One a sigma interaction that happened from the metal p orbital olefin p orbital onto a empty metal d type orbital. And the second interaction which is called a pi interaction that happen between field metal d orbital onto a vacant pi star orbital of the polyphonic ligand. And these two interactions occurred in a symbiotic fashion. If the first one reinstated the second one, which reinstated first one; as a result there is metal olefin interaction became very strong. These had a great implication in chemical industry as well as in chemical catalysis. As these metal olefins are important intermediates in various catalytic reactions.

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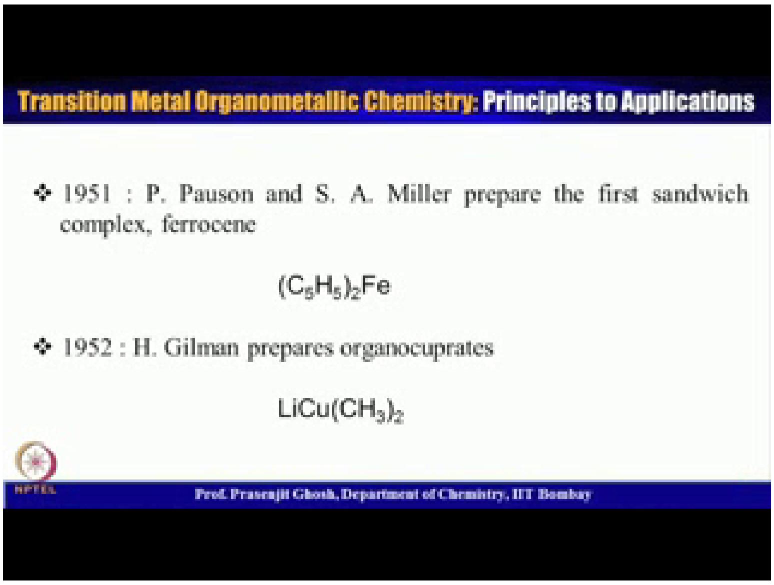

Transition Metal Organometallic Chemistry: Principles to Applications

- 1951 : P. Pauson and S. A. Miller prepare the first sandwich complex, ferrocene

$(C_5H_5)_2Fe$

- 1952 : H. Gilman prepares organocuprates

$LiCu(CH_3)_2$

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In 1951, P. Pauson and S. A. Miller prepared the first sandwich complex in the form of ferrocene, which is di cyclopentadienyl iron. Prior to that it was extremely difficult to believe how two cyclopentadienyl ligands attached to a metal center would. Ferrocene is a very stable molecule where we have two cyclopentadienyl ligands attaching to a metal center and the overall stability of this complex arises from the 18 balance electron of this metal center which leads to a very stable form of this compound. In 1952, H. Gilman prepares organocuprates in the form of lithium copper dimethyl these are very good alchelating agents and have extremely important role in organic synthesis.

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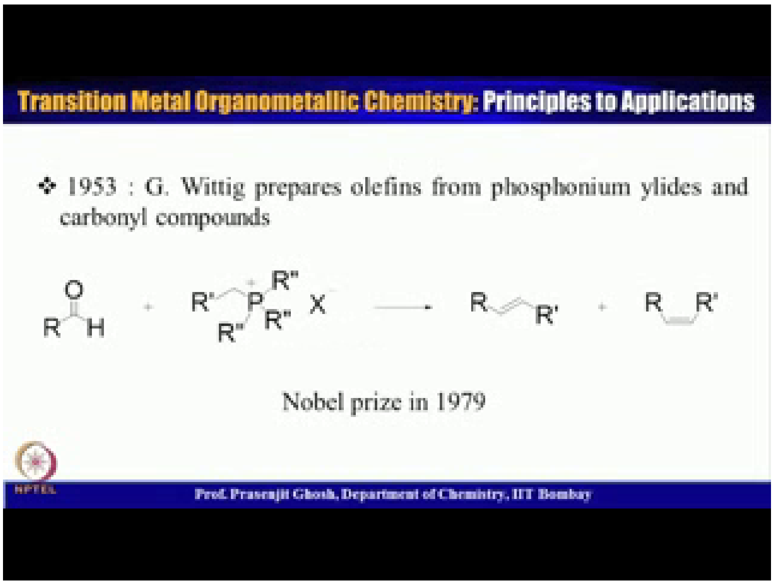

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- 1953 : G. Wittig prepares olefins from phosphonium ylides and carbonyl compounds

Nobel prize in 1979

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Another important discovery was made in the following year in 1953. Wittig prepares the olefin from phosphonium ylides and carbonyl compounds. Actually the reaction of aldehyde with phosphonium ylides leads to this various olefins the Cis and the trans olefins. This was a very important discovery as one could make a olefins from carbonyl compounds; impact of this discovery was recognized by the fact the Nobel prize for 1979 was awarded to this reaction.

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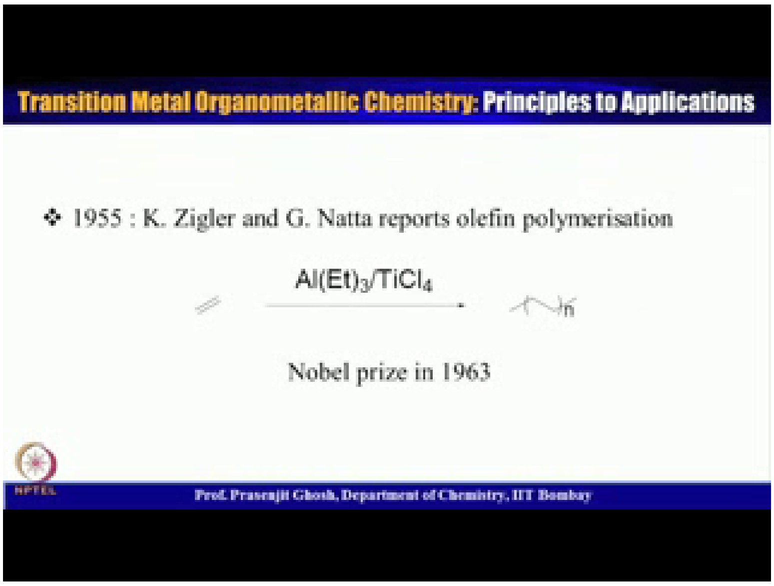

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❖ 1955 : K. Zigler and G. Natta reports olefin polymerisation

$\xrightarrow{Al(Et)_3/TiCl_4}$

Nobel prize in 1963

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1955 saw another important discovery in terms of olefin polymerization with a report from Karl Ziegler and Giulio Natta. What Karl Ziegler and Giulio Natta did was they could see that olefins in terms of ethylene, propylene or other higher order olefins in presence of tri aluminum and titanium chloride could give very long chain polymers. And that was a significant discovery that within 10 years time was awarded a Nobel Prize. And we have seen the polymers have transformed the wall significantly. Actually in the beginning of the century there was a belief that long chain polymers are probably a very difficult challenging or probably never be formed because of entropy factor going against in the formation of polymerization. However, it was later realized that the enthalpy gain due to the formation of the polymers through monomers lead overcomes the loss entropy, and results in overall formation of the polymers.

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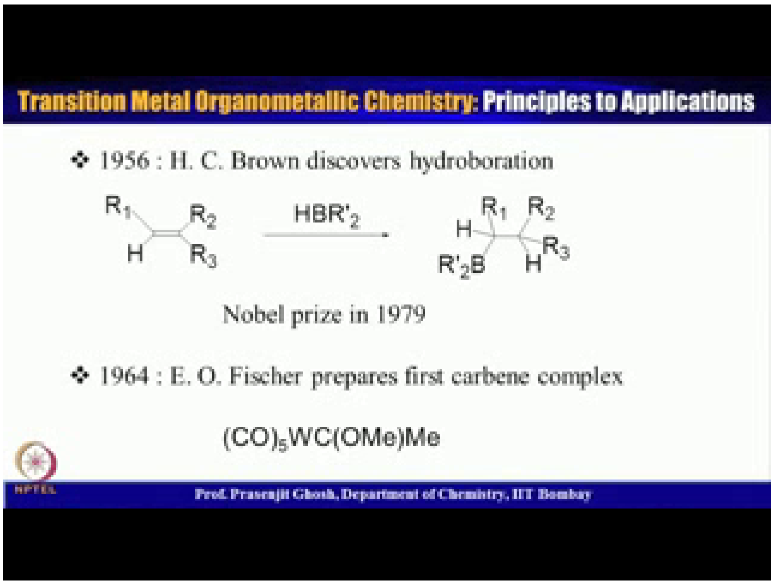

Transition Metal Organometallic Chemistry: Principles to Applications

- 1956 : H. C. Brown discovers hydroboration

Nobel prize in 1979

- 1964 : E. O. Fischer prepares first carbene complex

$(CO)_5WC(OMe)Me$

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In 1956, saw another Nobel Prize awarding discovery by H-C Brown when he discover hydroboration reaction. So, hydroboration reaction became a very important reagents method for under carrying out HB addition in unsaturated compounds. A lot of boro reagents were discovered subsequently, and finally, the reaction was recognized the Nobel Prize in 1979. In 1964, E. O. Fischer prepared the first carbene complex in form of CO 5 WC O Me methyl, this is the compound where there is a double bond between tungsten and the carbon center. This was the first ever multiple bonded metal carbon compound. These are usually known as carbene.

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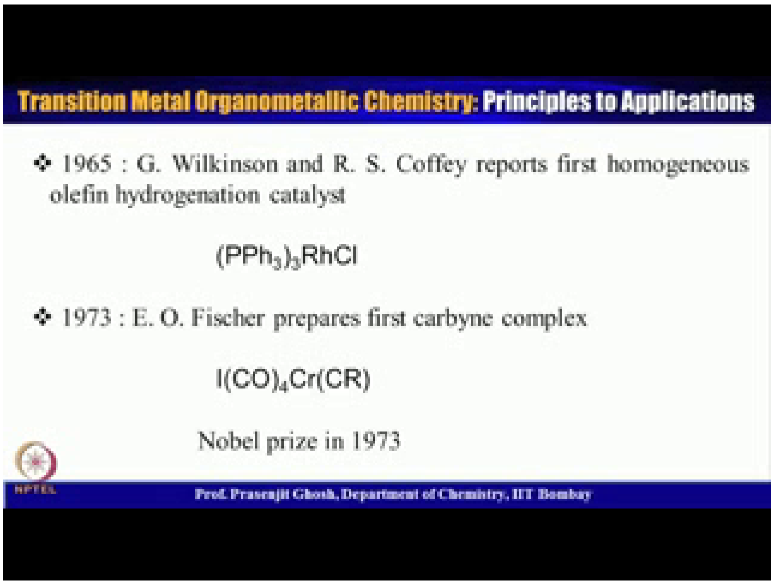

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- 1965 : G. Wilkinson and R. S. Coffey reports first homogeneous olefin hydrogenation catalyst

$(PPh_3)_3RhCl$

- 1973 : E. O. Fischer prepares first carbyne complex

$I(CO)_4Cr(CR)$

Nobel prize in 1973

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Subsequently in 1965 G. Wilkinson and R. S Coffey reported the first homogeneous olefin hydrogenation catalyst in terms of in the form of phenol phosphine rhodium chloride. This is a very active catalyst for carrying out hydrogenation reactions of olefin under homogeneous conditions. 1973 E. R. Fischer prepared the first carbyne complex in I CO 4 Cr CR. So, in that way Fischer was instrumental not only with making metal carbon double bond, but also in making metal carbon triple bond; and this lead to he is receiving Nobel Prize in 1973.

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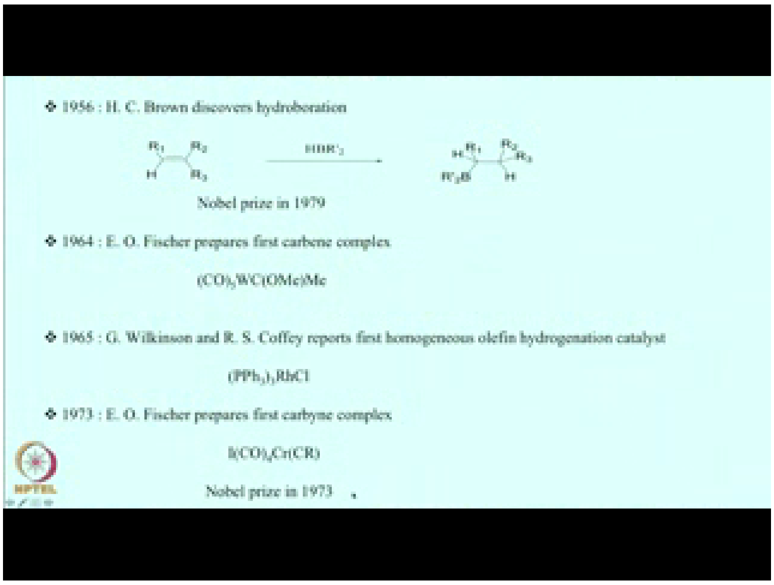

- 1956 : H. C. Brown discovers hydroboration

Nobel prize in 1979

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$(PPh_3)_3RhCl$

- 1973 : E. O. Fischer prepares first carbyne complex

$I(CO)_4Cr(CR)$

Nobel prize in 1973

As I said that beyond 1950 onwards the golden age of organometallic chemistry probably unfolded, these compounds are extremely important and very exciting, and they carry out very important transformations in various catalytic cycles.

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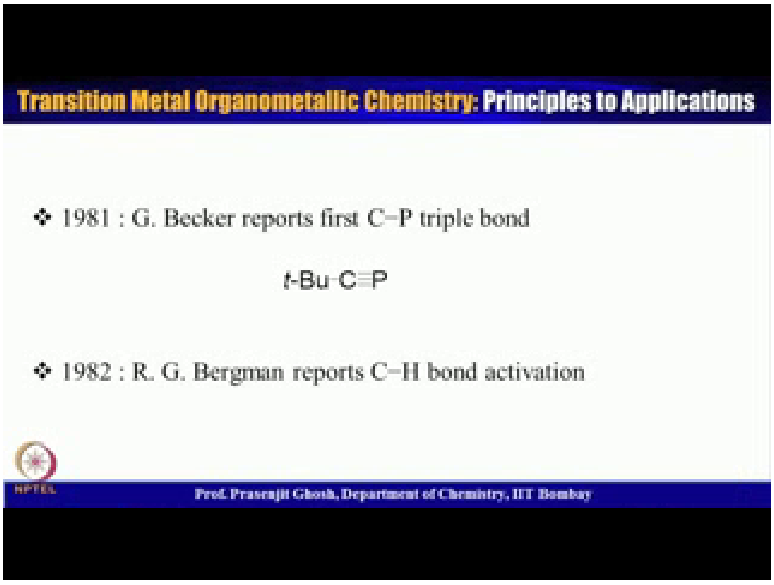

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- 1981 : G. Becker reports first C–P triple bond

$t\text{-Bu}-C\equiv P$

- 1982 : R. G. Bergman reports C–H bond activation

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In 1981, G. Becker reported the first C-P triple bond in terms of utile C triple bond P. 1982, R. G. Bergman reported first C-H activation. C-H activation is an important area of research because if activated and functionalized they can be very useful in producing various compounds having different functional group, but the difficulty in activating C-H lies in the ubiquitousness and very strong carbon-hydrogen bond. So, C-H activation is a topical area of research in present time and this had been initiated by Robert Bergman, first report of C-H activation about 30 years back in 1982.

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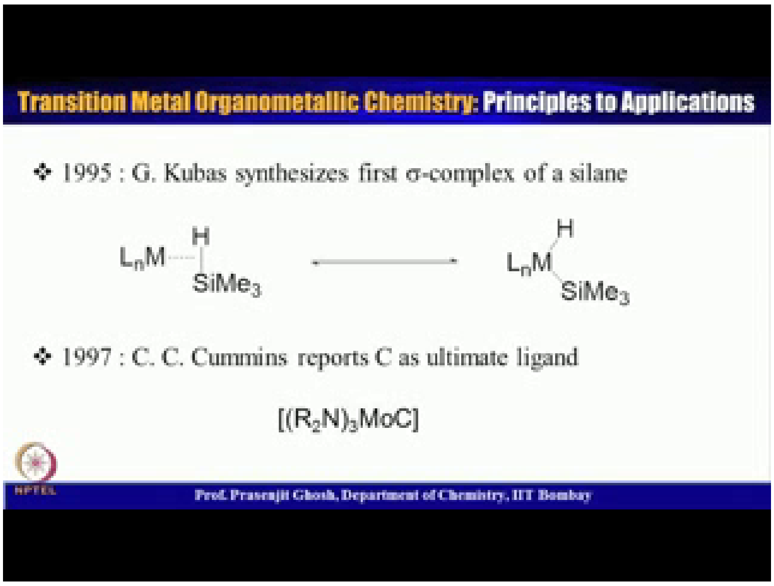

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- 1995 : G. Kubas synthesizes first σ-complex of a silane

- 1997 : C. C. Cummins reports C as ultimate ligand

$[(R_2N)_3MoC]$

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In 1995, G. Kubas reported the first sigma complex of a silane, where a metal is bound to a silicon hydrogen bond through a sigma complex. Now, these are very challenging compounds because the sigma complex may undergo oxidative addition to give metal hydrate and metal tri methyl silyl moiety. In 1997, Cit Cummins reported carbon as the ultimate ligand where carbon moiety was solely bonded to molybdenum. What we saw is that discovery of organometallic compounds started with compounds which are very stable, easy to handle and then gradually as the technique and behavior improved it went on to become something which is very difficult and very sensitive ones even they two are isolated over time.

The field expanded over about 200 years also from somewhere where it was practically non-existence to somewhere where it is becoming important parts in various chemical catalytic reactions. Also what we saw is that oxidize addition was previously probably a the first reaction that came in play in synthesizing this organometallic compound. Later on reaction like ligand metathesis transmetalation reactions were also came brought in to synthesis various organometallic compounds.

Another important aspect which evolved over the years was in the understanding of organometallic compounds; particularly the understanding of the metal ligand interaction. One started appreciating by looking at this compounds that this metal ligand interactions are varying types and they change with the nature of the ligands. So, there were ligands, which are just sigma bonded, they were ligands which are sigma and pi bonded, and all of this had different kind of binding ability and attributes. So, what it chose out chose open is that a huge area with very diverse type of bonding and very diverse kind of compounds with properties that emerged as the field unfolded. Also it became clear that with time one was able to handle the exclusion of air and synthesis of this compounds under such conditions the more and more important compounds came into form.

So, with these I will sort of summarize today’s lecture, which was on historical perspective of organometallic compounds. We saw what kind of methods were used over time to prepare some of the very important compounds like Grignard reagents, Wittig reactions hydroformylation, hydrogenations that as well as sigma complex as well as Zeise’s salt which went onto become very important markers in the field of organometallic chemistry. With this, I would summarize this lecture and we will move onto the next lecture, which will cover the bond polarity and the reactivity of various organometallic compounds.

Thank you.