Transition Metal Organometallic Chemistry : Principles to Applications
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Week - 12
Lecture - 59
Transition Metal Alkyne Complexes: Reactivity

Welcome to this lecture on transition metal organometallic chemistry from principles to applications. We have been discussing a very important topic in the last few lectures and this is about transition metal alkyne complexes.

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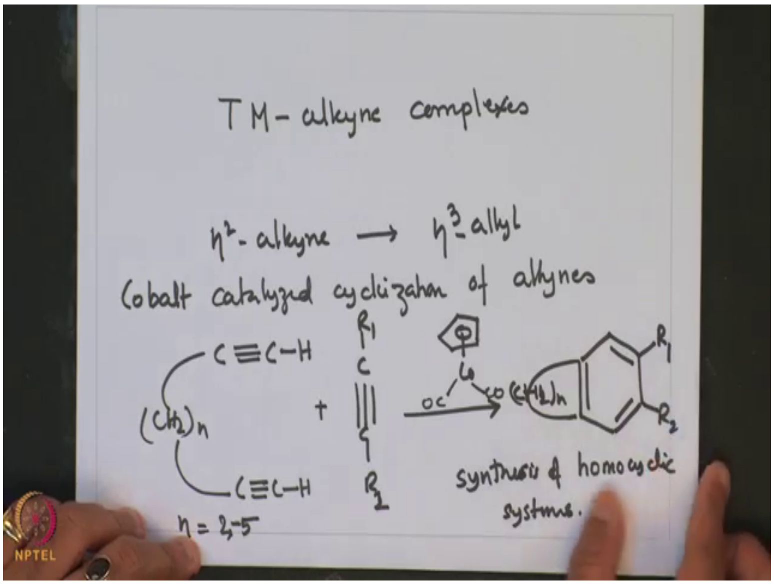

TM-alkyne complexes

η^2-alkyne → η^3-allyl

Cobalt catalyzed cyclization of alkynes

In this regard we have looked into various aspects of these special types of compounds which are right from the synthesis as well as the characterization as well as their reactivity.

Now, one important aspect which emerges from our discussion on transition metal alkyne complexes is that these are very important compounds not only a from the fact that they stabilize many alkynes which otherwise are difficult to stabilize in the free state. For example, cyclohexane, or benzene, or benzedrine which are extremely unstable molecules by themselves.

But when they coordinated to transition metals and make the transition metal alkyne complexes these unstable alkynes are stabilized. We have also seen that these transition metal alkyne complexes also stabilize not only unstable alkynes which we just spoke about, but also alkynes which are extremely reactive and explosive particularly the haloacid acetylenes which by themselves in the free state are extremely reactive are stabilized when upon coordination to transition metal.

So, what we come to see is that this transition metal alkyne complexes are extremely interesting type of orgometallic compounds. We have as far as the reactivity of these interesting compounds are concerned what we have seen that they show diverse range of reactivity for example, transition metal either to alkyne can be converted to eta 3 allyl complexes. So, one can see that eta 2 alkyne can be converted to eta 3 allyl complexes by a series of rearrangements that we had seen.

We had also seen that in presence of transition metals and alkynes there were all kinds of dimerization, trimerization, as well as cyclooligomerization reaction take place and these have been achieved by kinetically libel organo cobalt or organo palladium complexes. So, this all of this has been discussed in the last lecture where we looked at various kinds of useful reactivity that are seen for this transition metal alkyne complexes.

So, with that in the background we are going to take up some more interesting reactions of transition metal alkyne complexes in this lecture that we are going to talk about and discuss today.

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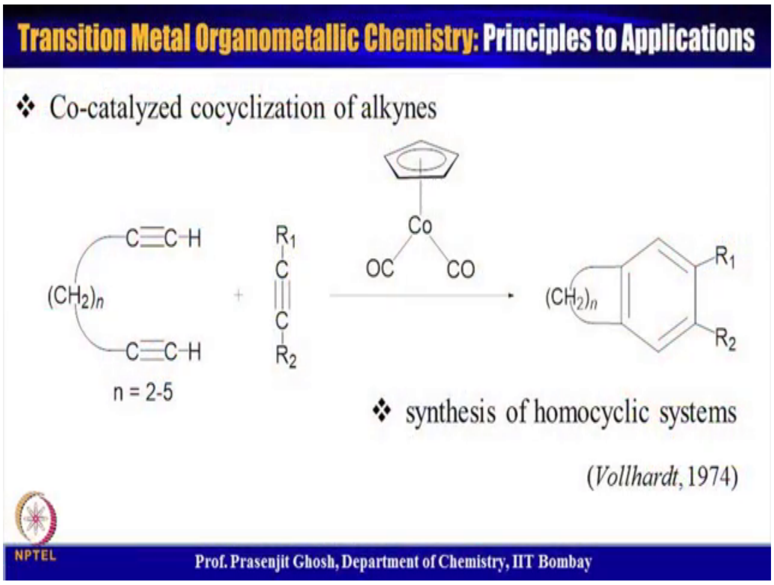

Transition Metal Organometallic Chemistry: Principles to Applications

- ❖ Co-catalyzed cocyclization of alkynes

- ❖ synthesis of homocyclic systems

(*Vollhardt*, 1974)

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So, one such interesting reaction is these cobalt catalyzed cyclization of alkynes. Now, this is an interesting reaction where acetylene of in the terminal chain ends terminal acetylenes n equals 2 to 5 in presence of another alkyne and catalyzed by the cobalt carbonyl complex gives this cyclic compound. And where this cyclization has been achieved between this alkyne and these two terminal acetylene and this R 1 CC R 2 or this alkyne to give this homocyclic a compound.

So, these synthesis of homocyclic systems and these are reactions which are very specific to organo cobalt reagents cobalt is acting as a catalyst to carry out this kind of 2 plus 2 plus 2 cyclization reactions generating aromatic rings. So, this is a very nice demonstration of reactivity of transmit metal alkyne complexes as is observed. This is sort of related to the oligomerization, dimerization reactions that we had seen we have discussed in the earlier lecture.

And here we see that instead of its oligomerization or dimerization or trimerization of the same acetylene unit over here what we see cyclization of two different acetylene unit resulting in this homocyclic systems.

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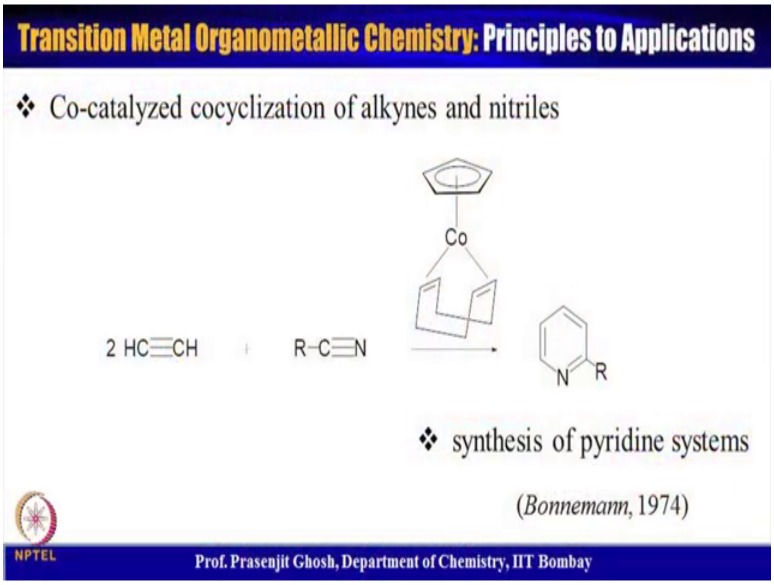

Transition Metal Organometallic Chemistry: Principles to Applications

- Co-catalyzed cocyclization of alkynes and nitriles

$2\ HC\equiv CH + R{-}C\equiv N \longrightarrow$

- synthesis of pyridine systems

(*Bonnemann*, 1974)

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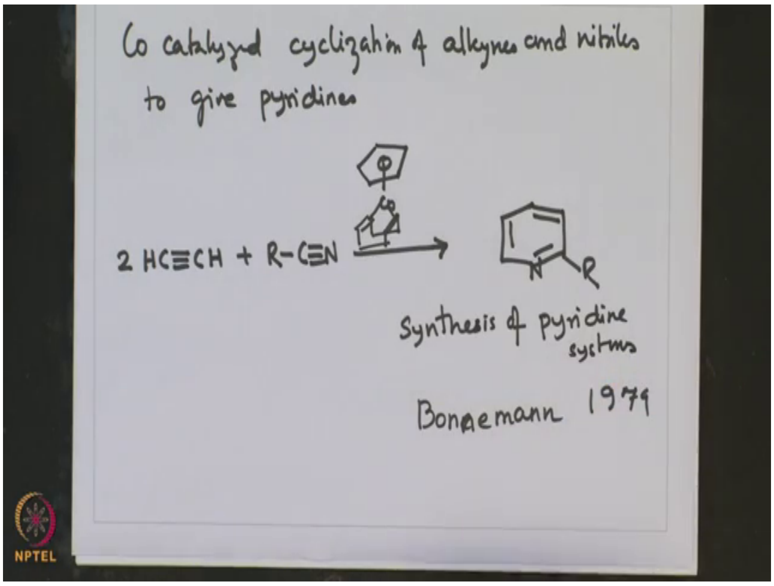

Co catalyzed cyclization of alkynes and nitriles to give pyridines

$2\ HC\equiv CH + R{-}C\equiv N \longrightarrow$

Synthesis of pyridine systems

Bonnemann 1974

So, another example of a very famous example of cobalt catalyzed cyclization of alkynes and nitriles and this is an important reaction because this cyclization leads to the formation of pyridine which are useful value added chemicals to give pyridine.

And the reaction is between two acetylene reacting with R C N in presence of the cobalt C O bond to give this pyridine moiety substituted pyridine; and this is an named reaction this is called Bonnemann reaction and has been developed by Bonnemann in 1974, and has been successfully used for preparation of pyridine or substituted pyridine.

So, here is another example where we see that cyclizations of the c triple bond c as well as c triple bond n results successfully a performed with C p cobalt cord catalyst giving like rise to this pyridine where this nitrogen comes nitrogen C R comes from the nitrile substituted nitrile and this comes from the two acetylic moiety.

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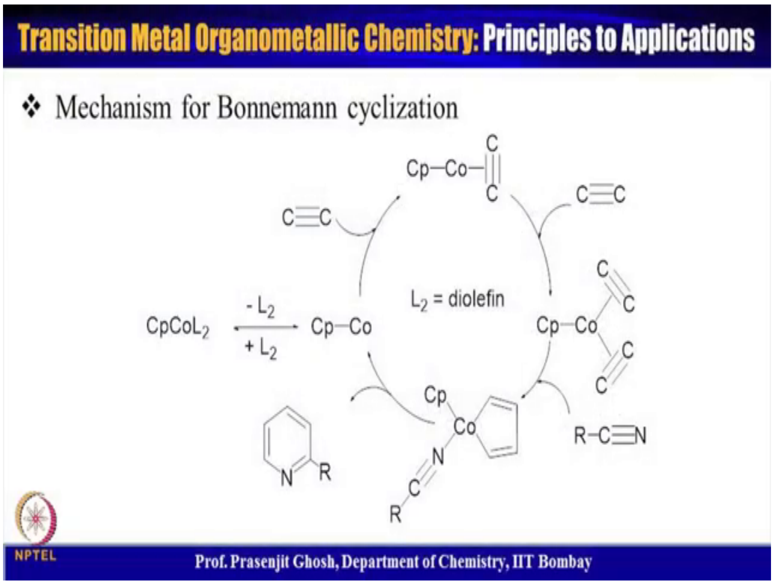

Transition Metal Organometallic Chemistry: Principles to Applications

- Mechanism for Bonnemann cyclization

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Now, let us take a look at the mechanism for this Bonnemann cyclization in bit more detail.

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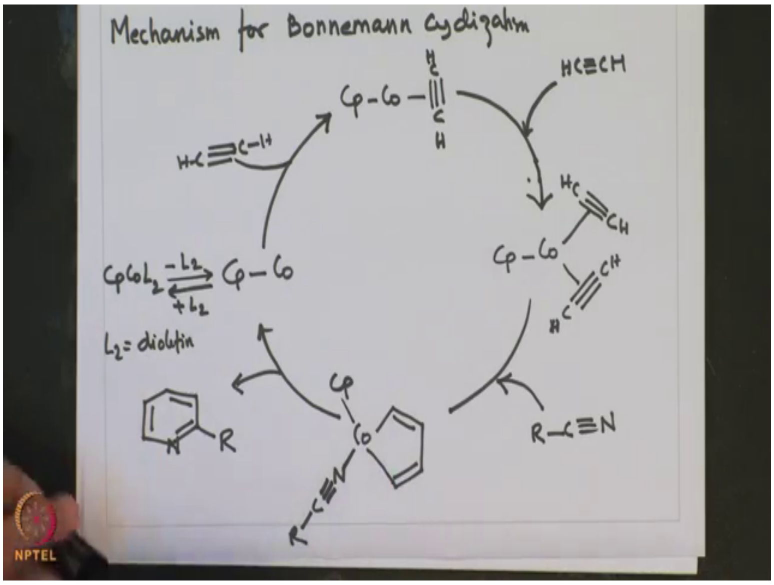

Mechanism for Bonnemann Cyclization

Mechanism for Bonnemann cyclization so C p cobalt C h C h reacts with another molecule so we have a cobalt complex of acetylene reacts with another molecule of acetylene.

So, this is the active species where cord of the C p cobalt has been replaced by an acetylic moiety and then this second acetylene comes in to give this C p cobalt diacetylic compound which again reacts with nitrile C N to give a metalocyclopentadine intermediate of the type shown.

So, this intermediate is formed by cyclization of these two acetylene unit to give this cobalt metalocyclopentadine and then this nitrile is coordinated to cobalt from this intermediate these nitrile inserts into the ring eliminating this pyridine substituted pyridine as shown here and giving back C p, cobalt, as the intermediate.

Now, C p cobalt can take up another molecular acetylene to give this as many compound. Now, this C p cobalt can be generated from C p C O l 2 by loss of 2 l 2 or in presence of 2 l 2 it will give that l 2 is diolefin. So, this clearly states a very nice catalytic cycle whereby the cyclization of a 2 acetylenes and nitrile results in the formation of much value added substituted pyridine, but it goes through metalo cyclopentadiene intermediate containing cobalt in the metalocyclopentadiene having scaffold.

So, this is a very nice demonstration and the value utility evaluated reaction of transition metal alkyne complexes. There by highlighting why these are so important class of organometallic compound. Now, we have seen examples of dimerization, trimerization as well as we have seen cyclization of various alkyne.

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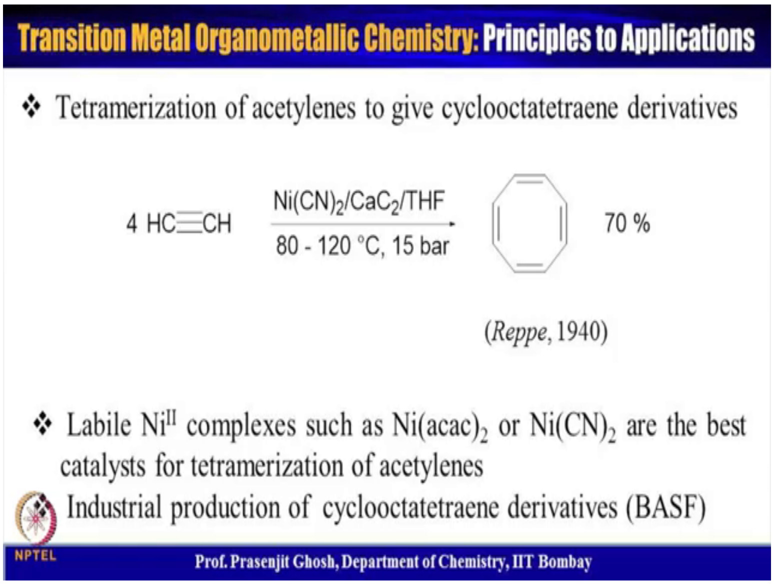

Transition Metal Organometallic Chemistry: Principles to Applications

- Tetramerization of acetylenes to give cyclooctatetraene derivatives

$$4\ HC{\equiv}CH \xrightarrow[80-120\ ^\circ C,\ 15\ bar]{Ni(CN)_2/CaC_2/THF}$$ 70 %

(*Reppe*, 1940)

- Labile Ni^{II} complexes such as $Ni(acac)_2$ or $Ni(CN)_2$ are the best catalysts for tetramerization of acetylenes
- Industrial production of cyclooctatetraene derivatives (BASF)

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So, the next example that we are going to talk about is tetramerization of acetylenes to give cyclooctatetraene derivatives by nickel complexes.

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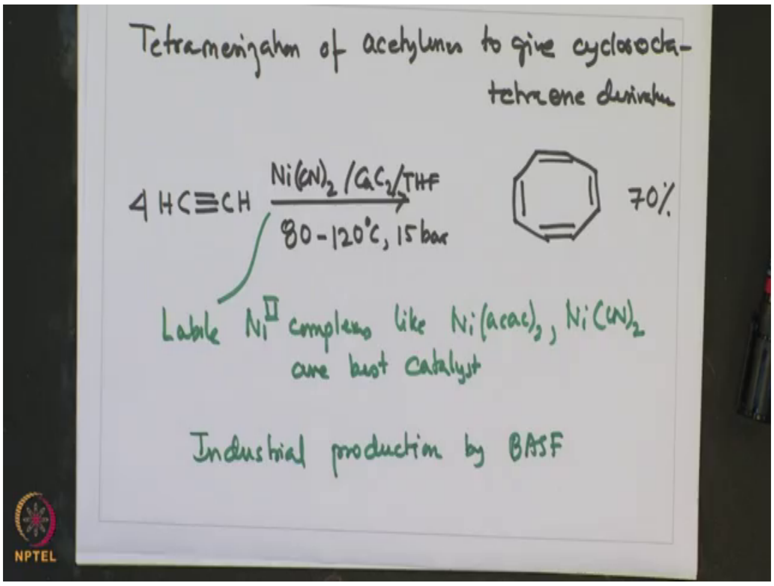

Tetramerization of acetylenes to give cycloocta-tetraene derivative

$$4\ HC{\equiv}CH \xrightarrow[80-120^\circ C,\ 15\ bar]{Ni(CN)_2/CaC_2/THF}$$ 70%

Labile Ni^{II} complexes like $Ni(acac)_2$, $Ni(CN)_2$ are best catalyst

Industrial production by BASF

So, this reaction of acetylene to give cyclo octa tetra ene derivatives. So, the reaction can be given by 4 molecules of acetylene in presence of nickel cyanide and C a C 2 THF 80 to 120 degree centigrade 15 bar of pressure gives this cyclooctatetraene in 70 percent yield.

And what has been found that labile labile nickel 2 complexes like nickel acac 2 or nickel C N 2 are best catalyst and for all these particular reactions and these are used in industrial production by BASF. So, here we see a real practical utility of this tetramerization reaction giving cyclooctatetraene in derivative by reaction acetylene with the nickel cyanide.

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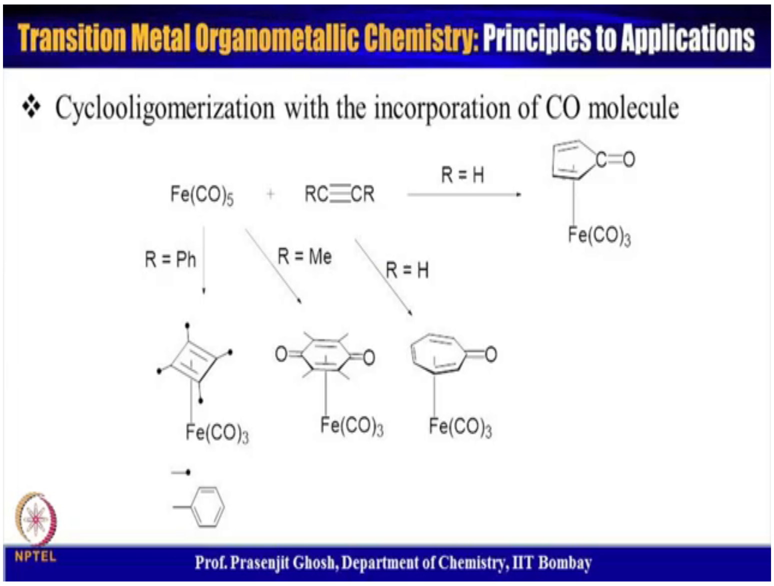

Transition Metal Organometallic Chemistry: Principles to Applications

- Cyclooligomerization with the incorporation of CO molecule

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So, there are other useful reactions of acetylene particularly, the cyclooligomerization with incorporation of carbon monoxide molecule this also an another interesting reaction.

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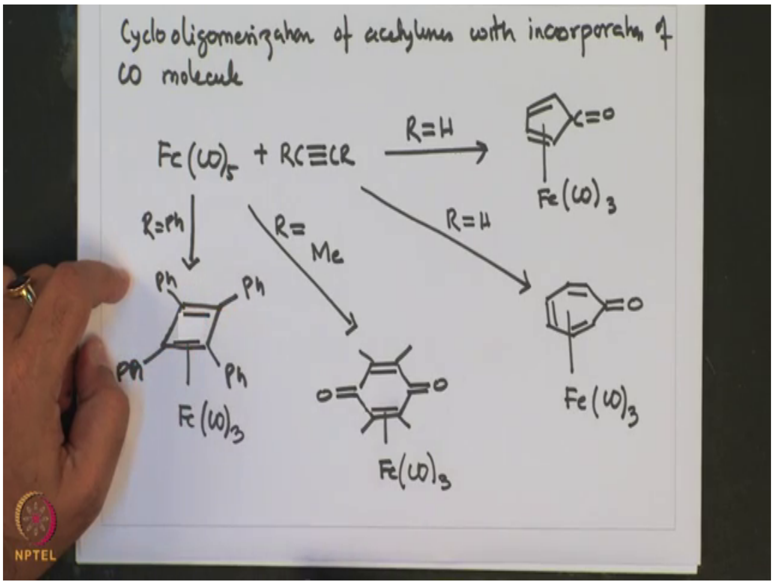

Cyclooligomerization of alkyne with incorporation of carbon monoxide molecule and the best example of this is a Fe C O 5 reacting with R C C R when R equals H gives this C double bond o. So, this is a 5 membered ring containing the C O and this C O has got inserted from the iron carbonyl.

So, we see this cyclo 5 membered ring with ketones cyclo pentenons coordinate to iron tricarbonyl now when R equals P h then one gets these cyclo butadiene complex as shown when R equals methyl equals mythyl then 1 C is benzoquinone some kind of compound. Here the carbonyl got inserted from F e C O 3 from iron pentacarbonyl two of the C os got inserted and also the other product when R equals H is the 7 membered ring containing carbonate and here also F e C O 3.

So, what is being prominent over here that the cyclo oligomerization gives versatile range of products some containing the carbon monoxide incorporated in the cyclooligomerization reaction and in case of phenyl it does not.

But what is to be stressed out over here that a wide versatility of the cyclooligomerization products were obtained by the cycloologomerization of acetylenes with the incorporation of C O molecules when the acetylene is reacted with iron pentacarbonyl and depending on the substituent of the alkyne large number of different products can be obtained and this is shows how versatile this cyclooligomerization reaction is towards producing various kinds of important compound.

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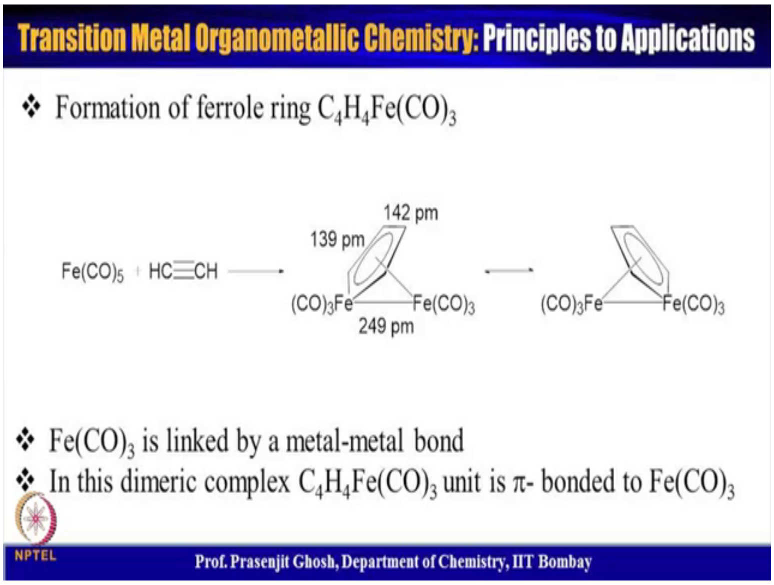

Transition Metal Organometallic Chemistry: Principles to Applications

- Formation of ferrole ring $C_4H_4Fe(CO)_3$

- $Fe(CO)_3$ is linked by a metal-metal bond
- In this dimeric complex $C_4H_4Fe(CO)_3$ unit is π- bonded to $Fe(CO)_3$

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Another important reaction in this context is the formation of ferrole ring where iron itself is part of the 5 membered ring.

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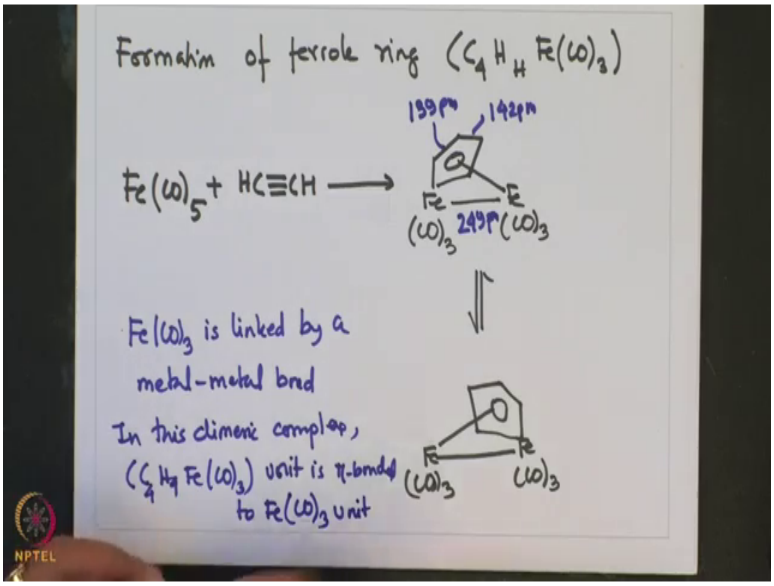

Formation of ferrole ring ($C_4H_4Fe(CO)_3$)

$Fe(CO)_3$ is linked by a metal-metal bond

In this dimeric complex, ($C_4H_4Fe(CO)_3$) unit is π-bonded to $Fe(CO)_3$ unit

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So, formation of ferrole ring C 4 H 4 F e C O 3. So, iron C O 3 is part of the ferrole ring and one can see interesting bonding. We will look at the bonding after we see the reaction F e C O 5 plus H C C H to give F e C O 3 F e C O 3 which can be in equilibrium with the other center F e C O 3 F e C O 3 and these have been structurally characterize so one has full metrical data for it. So, this bond is 139 picometer, this 142 picometer and this is 249 picometer.

So, what is evident from here is that these F e C O 3 is linked by a metal metal bond which is kind of extremely interesting. And in this dimeric complex this C 4 H 4 F e C O 3 unit is pi bonded to another F e co 3 unit. So, this is interesting reaction what we have seen where this ferrole ring is formed by reaction of F e C O 5 with a acetylenes.

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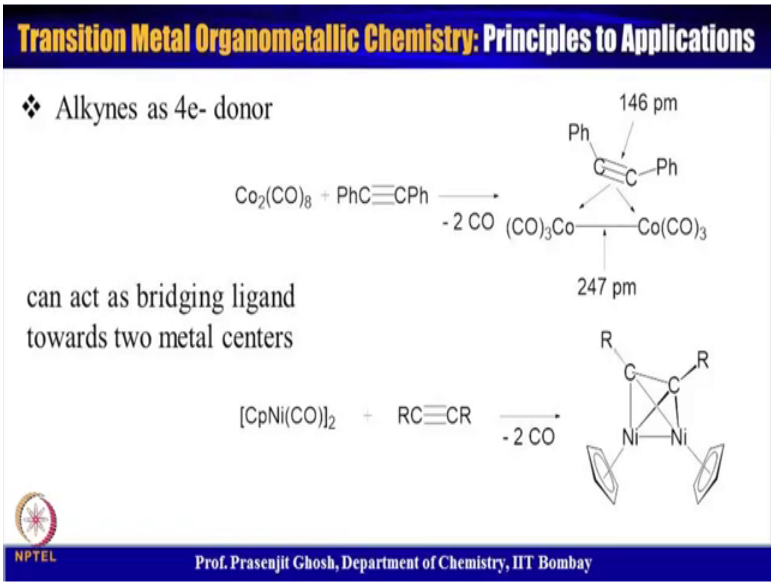

Transition Metal Organometallic Chemistry: Principles to Applications

- Alkynes as 4e- donor

$Co_2(CO)_8 + PhC{\equiv}CPh \xrightarrow[-2\,CO]{}$

can act as bridging ligand towards two metal centers

$[CpNi(CO)]_2 + RC{\equiv}CR \xrightarrow[-2\,CO]{}$

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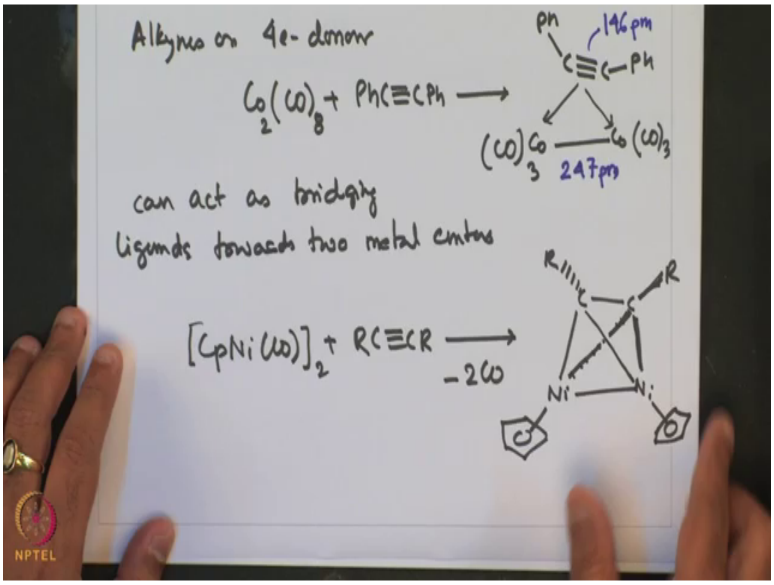

Alkynes as 4e- donor

$Co_2(CO)_8 + PhC{\equiv}CPh \longrightarrow$

can act as bridging ligands towards two metal centres

$[CpNi(CO)]_2 + RC{\equiv}CR \xrightarrow[-2CO]{}$

Alkynes also acts as a 4 electron donors particularly in this reaction with cobalt carbonyl dicobalt C O 8 plus gives this complex where acetylene is acting as a 4 electron donor, cobalt C O 3 C O 3 there is a cobalt cobalt bond and this is 146 picometer, and 247 picometer and alkyne can act as bridging ligand towards 2 metal centres.

An example of this is seen over here as well as in this reaction where reaction of C p N i C O dimer reacts with R C R eliminates 2 molecules of C O to give this compound where alkyne is attached to the 2 metal centre and this eliminates 2 C O. So, these alkynes acting as a between between two centred and with this maybe one more reaction which is of interest is Pauson-Khand reaction Khand reaction.

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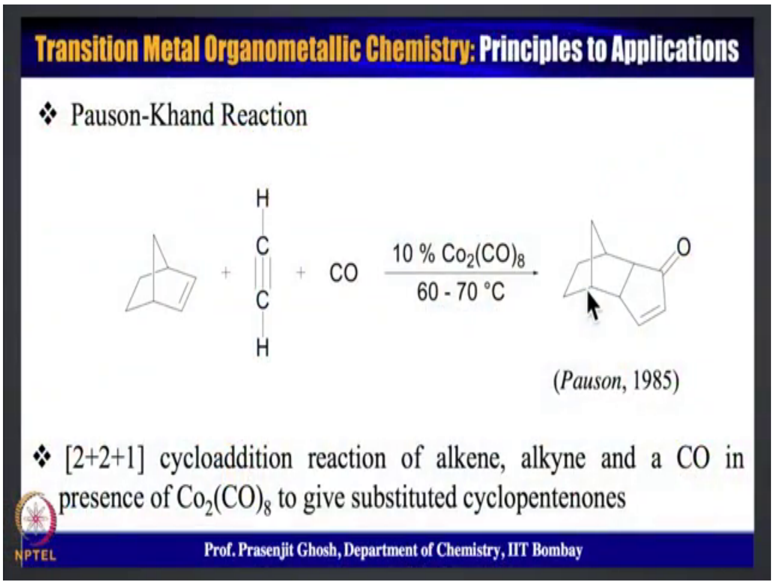

Transition Metal Organometallic Chemistry: Principles to Applications

- Pauson-Khand Reaction

(*Pauson*, 1985)

- [2+2+1] cycloaddition reaction of alkene, alkyne and a CO in presence of $Co_2(CO)_8$ to give substituted cyclopentenones

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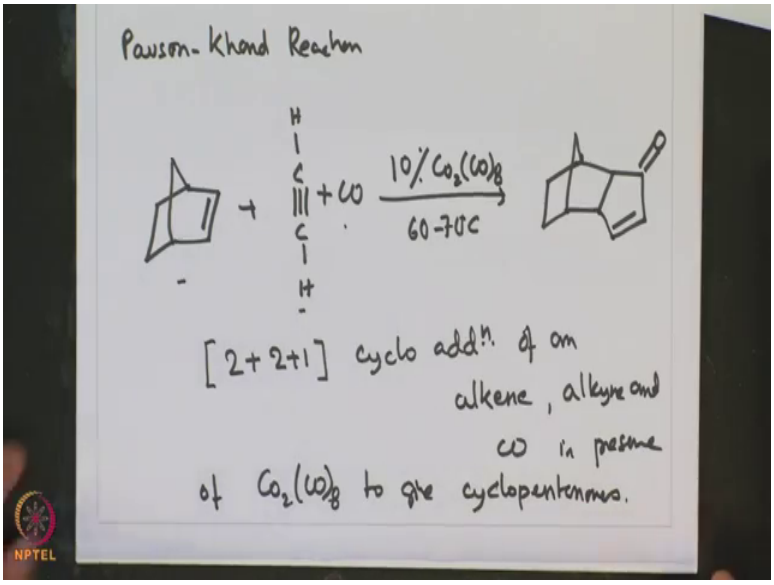

Pauson-Khand Reaction

[2+2+1] cyclo add^n. of an alkene, alkyne and CO in presence of $Co_2(CO)_8$ to give cyclopentenones.

And this reaction is between this no bond in strained olefin plus acetylene plus carbon monoxide in 10 percent of cobalt 2 CO 8 60 to 70 degree centigrade gives these tricyclic compound it has a C O and this is example of 2 plus 2 plus 1 cyclo addition of an alkene, alkyne and C O alkyne, alkene and C O in presence of dicobalt octacarbonyl to give cyclo pentenose.

So, with that let me summarize today’s lecture we began by looking at the reactivity of these transmit metal alkyne complexes and let me summarize this today’s lecture to begin with we started by looking at the reactivity of transmit metal alkyne complexes.

We started by looking at cyclomerization reactions of various kinds of alkynes in presence of nickel and cobalt system whereby we generated 5 6 membered systems. Now, these cyclizition reactions are of different alkyne slightly different from the oligomerization reactions are that we had studied trimerization reactions or tetramerization reactions of same alkyne.

But today what we focused was focused on was cyclisition between two different kinds of alkyne some of the cyclization. So, cyclooligomerization reaction involved insertion of carbon monoxides as well as with that of the nitriles. The one with the nitriles resulted in the formation of heterocycles like pyridines, which is a value added chemical by this and we have also looked at a number of such reactions one could cyclize acetylenes.

We end this discussion with Pauson Khand reaction similar 2 plus 2 plus 1 cyclization addition has been achieved with an alkene, alkyne and carbon monoxide in presence of cobalt catalyst to give this cyclopentanone derivatives.

Now, what is coming out through these discussion is the fact that transition metal alkyne complexes are extremely rich in terms of the reactivity that they show particularly with respect to formations of various kinds of rings which are homocyclic as well as a cyclopentanone or cyclohexanone derivatives.

And in one case with iron carbonyl we saw the reaction of escaline with iron carbonyl gave rise to various kinds of products depending on their substituent on the alkynes moiety. We have also seen that these iron being part of the cyclopentane ring as a metalocycle that can also be formed by reaction with the escaline with iron carbonyl compounds.

So, these sort of further corroborates the fact that transition metal acetylene alkyne complexes are extremely important particularly with regard to the reactivity they show. And this is somewhat different or probably very interesting as compared to other transition metal organometallic compound that we have discussed so far where the extent or depth of reactivity which we had observed for transition metal alkyne complexes are not that much for other classes of compounds.

So, from that standpoint transition metal alkyne complexes are of significant interest. So, with that I would like to conclude this lecture on transition metal alkyne complexes and with that we come to end of this course on transitional organometallic chemistry from principles to applications we have, but one lecture left in the next and the last lecture I am going to summarize all the topics that I have covered so far from the first week to the 59th week on this course.

And we are going to have a walk down the memory lane in terms of the topics covered as well as the important points that I have stressed was while we made this journey through the various facets of transitional organometallic chemistry.

I thank you for patiently being with me and listening to all these talks over these 59 lectures that we have covered so far. And I look forward to being with you in the last the sixtieth lecture which will summarize all the topics that we have covered so far till then good goodbye.

Thank you.