Transition Metal Organometallic Chemistry: Principles to Applications

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Lecture – 29
Transition Metal Aryl/Alkyne Complexes

Welcome to this lecture on Transition Metal Organometallic Chemistry from Principles to Applications. In our last lecture we discussed about transition metal sigma aryl complexes, particularly with respect to their stability which arise due to the interaction of transition metal with aryl ligand. And what we had observed that the two interactions which are crucial to transition metal organometallic complexes which are these.

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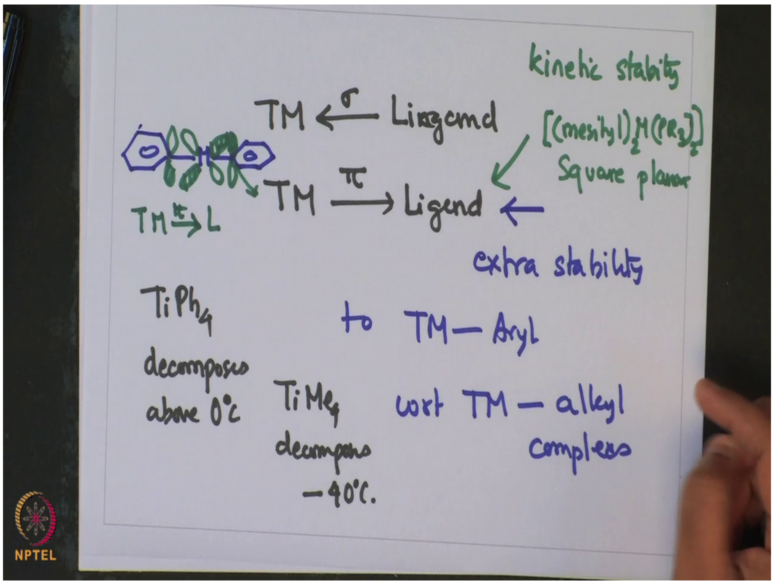

So, ligand to transition metal sigma interaction and transition metal to ligand pi back to donation is very crucial to bring about the stability of transition metal aryl complexes. And what we had seen that the influence of transition metal to ligand sigma pi back donation causes extra stability to transition metal aryl complexes with regard to transition metal sigma alkyl complexes. So, this extra stability results in higher bond energy of transition metal aryl bond and also subsequently higher decomposition temperatures and we had seen that with respect to titanium tetraphenyl that decomposes above 0 degree centigrade whereas, titanium tetra methyl decomposes at minus 40 degree centigrade.

In our discussion we had also seen how this transition metal to ligand pi interaction brings kinetic stability to this mesityl metal PR 3 whole 2 type square planar complexes and that was explained by this transition metal to ligand pi interaction occurring between this ligand pi star orbital. So, this is transition metal to ligand pi star orbital that brings about stability to transition metal aryl complexes. So, with that we saw that these transition metal aryl complexes are somewhat more stable than transition metal sigma alkyl complexes.

Now, today we are going to see another very interesting application of transition metal aryl complexes with regard to the formation of metallabenzenes.

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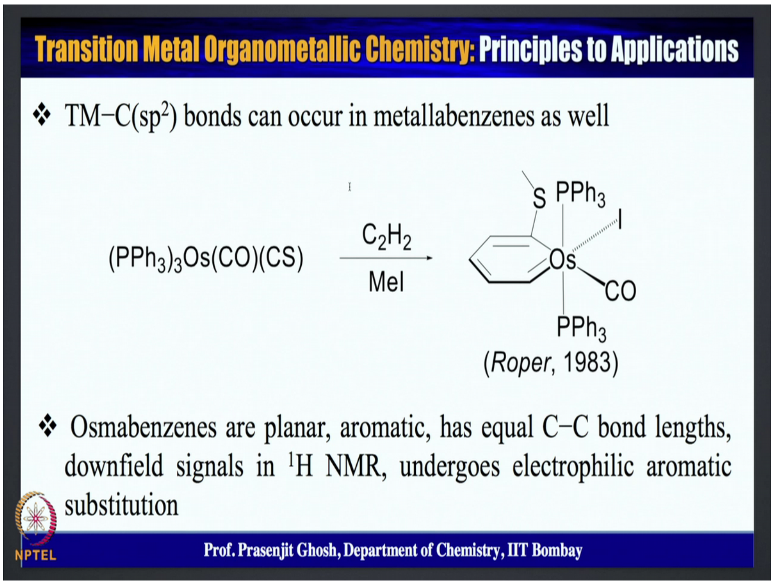

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- TM–C(sp^2) bonds can occur in metallabenzenes as well

$$(PPh_3)_3Os(CO)(CS) \xrightarrow[MeI]{C_2H_2}$$

(*Roper*, 1983)

- Osmabenzenes are planar, aromatic, has equal C–C bond lengths, downfield signals in ^1H NMR, undergoes electrophilic aromatic substitution

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And metallabenzenes are an important class of molecules in which the metal itself is a part of the benzenes frameworks.

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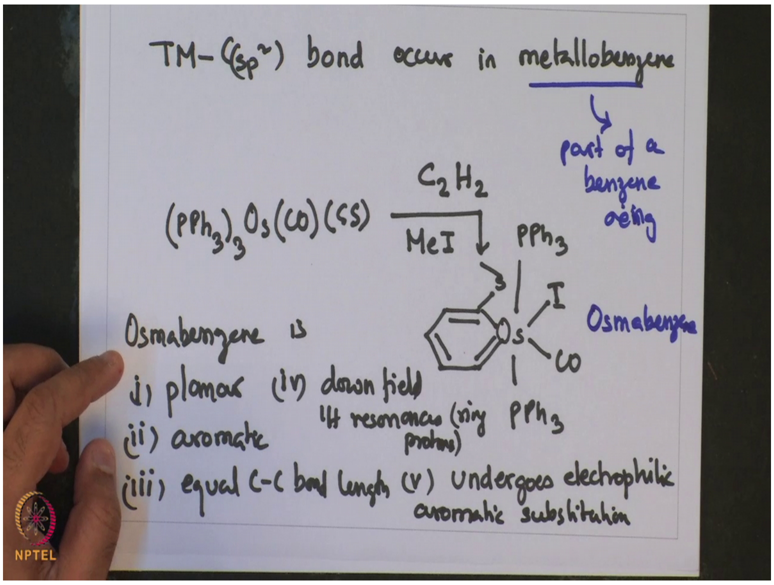

TM–C(sp^2) bond occurs in metallobenzene

↳ part of a benzene ring

$(PPh_3)_3Os(CO)(CS) \xrightarrow[MeI]{C_2H_2}$

Osmabenzene is

i) planar

ii) aromatic

iii) equal C–C bond length

(iv) down field ^1H resonance (ring protons)

(v) undergoes electrophilic aromatic substitution

And this is a very interesting applications of transition metal aryl complexes. In metallabenzenes where the metal is part of a benzene ring and the metallabenzen has been prepared for osmium in the reaction PPh 3 whole 3 osmium CO CS in presence of C 2 H 2 aslain methyl iodide giving this metallabenzene complexes of osmium having a S Me substituent with 2 PPh 3 and 1 CO and iodide ligands. So, this benzene with a metal which is osmium occupying vertices of the benzene ring is called osmabenzene. So, these metallabenzenes are similar to organic benzene in with regard to they being planar aromatic displaying equal bond lengths and also showing downfield enamel shapes.

So, osmabenzene is planar, aromatic, exhibit equal carbon carbon bond length, downfield signal in proton NMR 1 H resonance, for benzene it comes at around 7. So, similar downfield resonance of these protons, ring protons and undergoes electrophilic aromatic substitution. So, this is an important application or of metal aryl compounds whereby inorganic analog of the very famous organic molecule benzene can be prepared and these metallabenzenes can also exhibit parallel activity similar to that the real organic benzene in terms of being planar aromatic displaying equal bond links carbon carbon bond links also showing downfield shapes for the ring proton and finally, a exhibit similar europtophilic aromatic substitution reaction as shown by real benzene.

So, with that we conclude our discussion on transition metal aryl complexes which has been going on in the last two lectures and now we are going to move on to another very exciting class of transition metal sigma complexes and these are transition metal sigma alkyne complexes.

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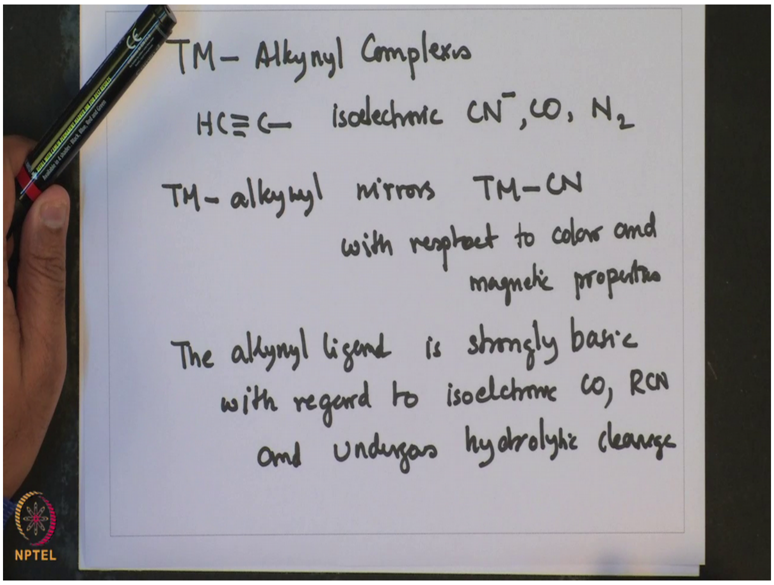

TM– Alkynyl Complexes

$HC\equiv C-$ isoelectronic CN^-, CO, N_2

TM– alkynyl mirrors TM–CN
with respect to color and
magnetic properties

The alkynyl ligand is strongly basic
with regard to isoelectronic CO, RCN
and undergoes hydrolytic cleavage

These transition metal alkynyl complexes are complexes with ligands of the type, these there is alkyne bond triple bond and these ligands are isoelectronic with cyanide, carbon monoxide, nitrogen and even and these transition metal alkynyl complexes mirrors transition metal cyanide complexes with respect to color and magnetic properties. And the alkynyl ligand is strongly basic with regard to the isoelectronic ligand carbon monoxide as well as RCN and undergoes hydrolytic cleavage.

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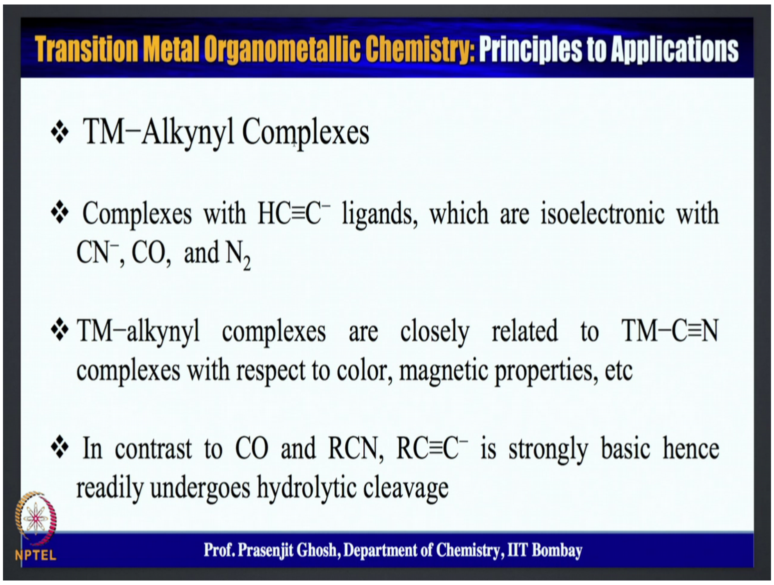

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- ❖ TM−Alkynyl Complexes
- ❖ Complexes with $HC{\equiv}C^-$ ligands, which are isoelectronic with CN^-, CO, and N_2
- ❖ TM−alkynyl complexes are closely related to TM−C≡N complexes with respect to color, magnetic properties, etc
- ❖ In contrast to CO and RCN, $RC{\equiv}C^-$ is strongly basic hence readily undergoes hydrolytic cleavage

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So, these transition metal alkynyl complexes undergo ready hydrolysis. So, one has to be extremely careful while preparing these complexes to protect it from water and subsequent the hydrolysis (Refer Time: 12:40) may undergo in water.

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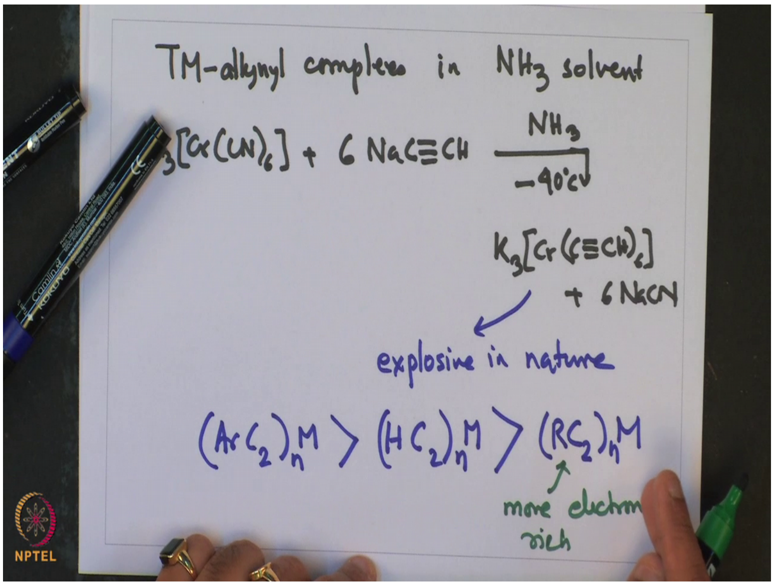

TM-alkynyl complexes in NH_3 solvent

$$_3[Cr(CN)_6] + 6\,NaC{\equiv}CH \xrightarrow[-40^\circ C]{NH_3} K_3[Cr(C{\equiv}CH)_6] + 6\,NaCN$$

explosive in nature

$$(ArC_2)_nM > (HC_2)_nM > (RC_2)_nM$$

more electron rich

These transition metal alkynyl complexes are prepared in ammonia, in ammonia solvent by following the following reaction K 3 Cr CN 6 plus 6 sodium acetylide in liquid ammonia minus 40 degree centigrade giving K 3 Cr C CH whole 6 plus 6 Na CN.

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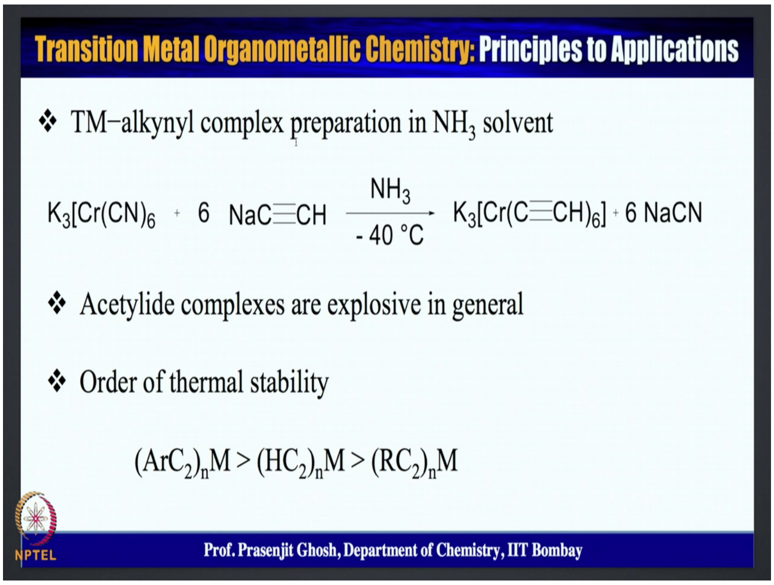

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- TM−alkynyl complex preparation in NH_3 solvent

$$K_3[Cr(CN)_6] + 6\ NaC{\equiv}CH \xrightarrow[-40\ °C]{NH_3} K_3[Cr(C{\equiv}CH)_6] + 6\ NaCN$$

- Acetylide complexes are explosive in general
- Order of thermal stability

$$(ArC_2)_nM > (HC_2)_nM > (RC_2)_nM$$

NPTEL

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So care must be taken in handling these compounds because these are acetylide compounds are explosive in nature and their order of thermal stability depends on aryl acetylide being more stable than HC acetylide which in turn is more stable than RC 2 N alkyl acetylide.

Now, if one looks at this series its very obvious that this is more electron rich going to the alkyl substituent as a result these compounds are more reactive and less stable. Whereas, the aryl groups being sp 2 hybridized can siphon off some of the electron density from the acetylide moiety onto the aryl ring and therefore, these compounds are relatively less electron rich and hence they more stable.

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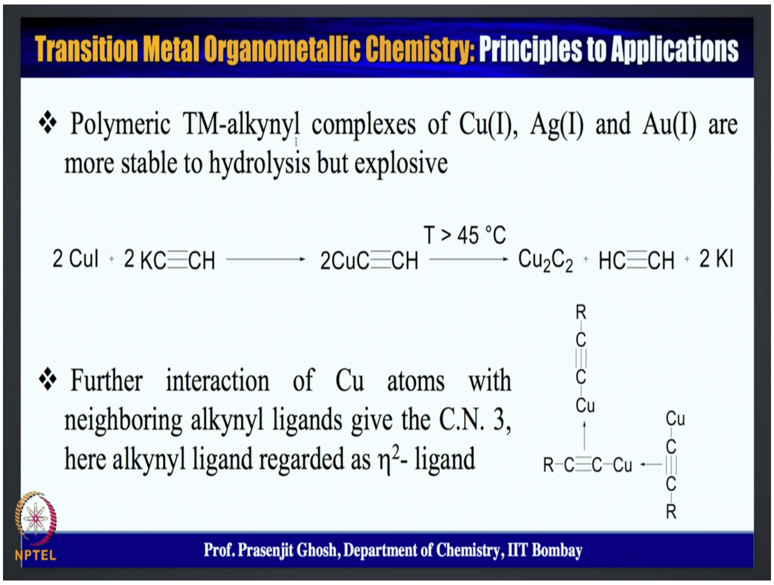

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- Polymeric TM-alkynyl complexes of Cu(I), Ag(I) and Au(I) are more stable to hydrolysis but explosive

$$2\,CuI + 2\,KC\equiv CH \longrightarrow 2CuC\equiv CH \xrightarrow{T > 45\,°C} Cu_2C_2 + HC\equiv CH + 2\,KI$$

- Further interaction of Cu atoms with neighboring alkynyl ligands give the C.N. 3, here alkynyl ligand regarded as η^2- ligand

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Now, because of this exceptional lateral richness of this alkynyl ligands with so many pi electrons, pi bonds being around it transition metal alkynyl complexes tend to be polymeric in nature interacting with the transition metal where these pi clouds interact directly with transition metal.

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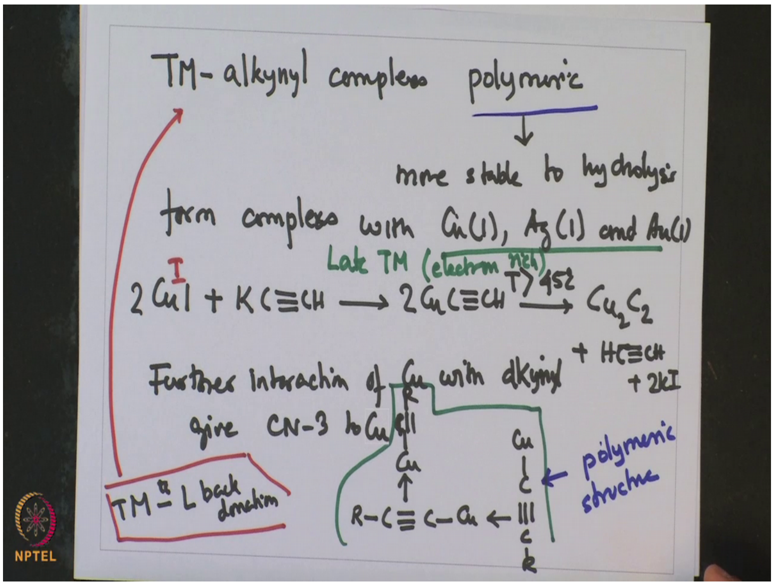

TM- alkynyl complexes polymeric

↓

more stable to hydrolysis

form complexes with Cu(I), Ag(I) and Au(I)

Late TM (electron rich)

$2\,CuI + KC\equiv CH \longrightarrow 2CuC\equiv CH \xrightarrow{T > 45°C} Cu_2C_2 + HC\equiv CH + 2KI$

Further Interaction of Cu with alkynyl give CN-3 to Cu

$TM \overset{\pi}{\rightleftharpoons} L$ back donation

So, transition metal alkynyl complexes are polymeric, are polymeric and this is primarily because of the electron rich nature. So, that they tend to bind more to metal ions through polymerization and in their polymeric form they are more stable to hydrolysis a, but still are exclusive.

So, they usually form complexes with copper 1, silver 1 and gold 1. These metals are also called carbophilic because they have special preference for forming complexes with this acetylide type of moiety. Here is an example of the formation of a copper acetylide complex which starts with copper iodide, where copper is in plus one oxidation state that reacts with potassium acetylide to give copper acetylide which above 45 degree centigrade gives Cu 2 C 2 plus acetylene plus 2 KI. Now, interaction further interaction of copper with alkynyl ligand give coordination number 3, coordination number 3 to copper and that is illustrated by example over here.

For example, here is a copper acetylide now this copper interacts with the pi bond of another acetylide moiety and this pi bond now interacts with another proper acetylide moiety. So, what is seen over here that such kind of interaction leads to polymeric structure of this compound as was discussed over here and another important aspect to note that these isolated complexes are mainly formed of gold 1, copper 1, silver 1 which are late transition metal and also are electron rich.

As a result they can form this acetylide complexes and the stabilized acetylide complexes by a transition metal to ligand pi back donation which is required for stabilizing these transition metal alkynyl kind of complexes. And because of their extreme basicity of these acetylide moieties they stabilize themselves by polymerizing and binding to several metal centers as shown over here and thereby gaining some stability arising out of this reactivity of the acid moiety.

Similar to copper, gold also forms gold acetylide complexes and an example of the preparation of gold alkynyl complexes in provided below.

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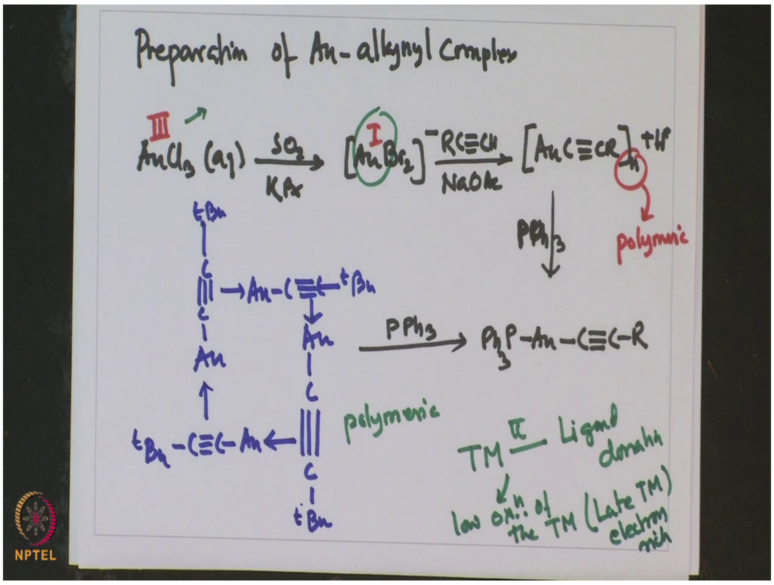

Au Cl 3 in aqueous medium reacts with SO 2 K Br giving Au Br 2 minus where gold is in got reduced from plus 3 to plus 1 and then its reacts with acetylene in presence of sodium acetate to give this polymeric gold acetylide complex.

Now, this gold acetylidical complex is polymeric in nature and the polymeric structure can be broken by addition of dative ligand like PPh 3 to give this monomeric gold triphenyl phosphene C-R acetylide complex, and these can be shown over here that this becomes monomeric and the structure of the polymeric gold acetylide is shown over here for a particular example t butyl C, C gold interacting with C t butyl gold. Now, each of these triple bond interacts with gold C t butyl and that interacts with another C t butyl and this interacts with this.

So, what one gets is polymeric structure as mentioned here and which the polymeric framework can be broken by fitment with PPh 3 as shown over here. Now, what is obvious over here that these polymeric framework stabilizes the exceptional wave reactivity of extremely basic acetylide moiety which become very susceptible to hydrolysis and this stabilization is gained through polymerization.

Another aspect which come to the fore is that the metal has to be in low oxidation state as in gold 1 over here as opposed to gold 3 over here for stabilizing these acetylide moiety. And this stabilization thus arises from the transition metal to ligand pi back donation and these back donation arises because of low oxygen state of the transition metal, but preferably late transition metal which are electron rich.

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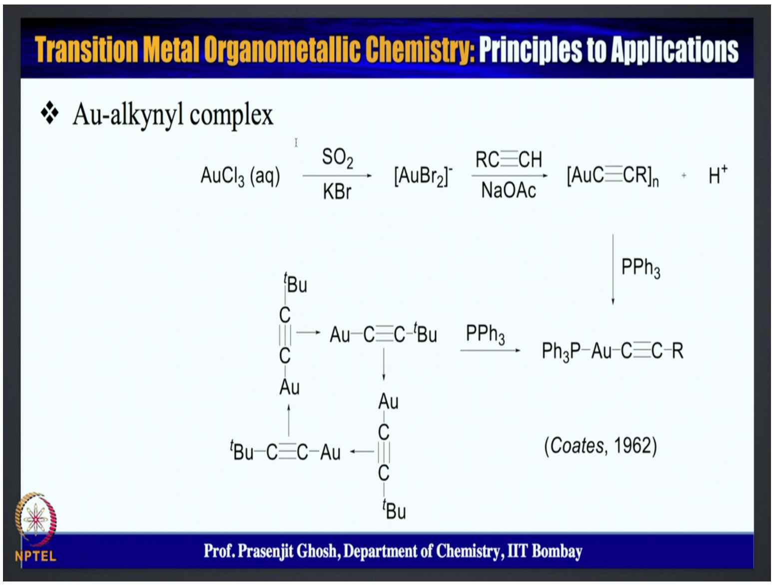

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- ❖ Au-alkynyl complex

$$AuCl_3\,(aq) \xrightarrow[KBr]{SO_2} [AuBr_2]^- \xrightarrow[NaOAc]{RC\equiv CH} [AuC\equiv CR]_n + H^+$$

$$[AuC\equiv CR]_n \xrightarrow{PPh_3} Ph_3P{-}Au{-}C\equiv C{-}R$$

(*Coates*, 1962)

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Now, let me summarize the topics that has been discussed in this lecture. We have looked into an interesting transition metal sigma aryl complex in terms of the osmabenzene or metallabenzen, where metal is part of the benzene ring. This metal of benzene display parallel activity similar to that of benzene in many respects and mirror the organic molecule benzene in many respects particularly with respect to their penalty their aromaticity, the downfield shift of the proton resonance, their aromatic electrophilic substitution reaction so on and so forth.

We have also looked into these transition metal alkynyl complexes particularly with regard to their stability and synthetic protocols. And what we have seen is that transition metal alkynyl complexes are mainly formed for of late transition metals mainly gold, copper, silver that in their low oxygen state of plus 1. And these complexes are polymeric in nature and they are problematic framework can be broken by addition of dative ligands like PPh 3 as we have observed in case of this gold, as well as in case of the copper example that we had discussed in the previous slide.

So, with that let me conclude today’s lecture on metal alkynyl complexes we are going to discuss some more examples of metal alkynyl complexes from the perspective of their utility, synthesis, stability and their applications. And I look forward to being with you in the next lecture.

Thank you.