Transition Metal Organometallic Chemistry: Principles to Applications

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Week - 06
Lecture – 28
Transition Metal Aryl Complexes

Welcome to this lecture on transition metal organometallic chemistry from principles to applications. We have been discussing about a very important class of organometallic compounds namely the transition metal sigma alkyl complexes.

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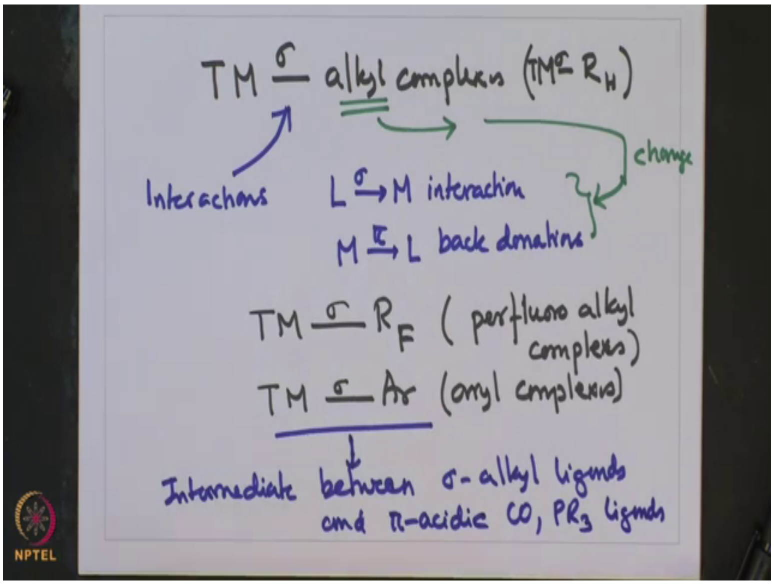

$TM \overset{\sigma}{—}$ alkyl complexes $(TM \overset{\sigma}{—} R_H)$

Interactions

$L \xrightarrow{\sigma} M$ interaction

$M \xrightarrow{\pi} L$ back donations

change

$TM \overset{\sigma}{—} R_F$ (perfluoro alkyl complexes)

$TM \overset{\sigma}{—} Ar$ (aryl complexes)

Intermediate between σ-alkyl ligands and π-acidic CO, PR_3 ligands

Now, we have looked into kind of interaction that occurs in these type of complexes and interaction wise there are 2 types usually privileged for transition metal organometallic complexes and these are ligand to metal sigma interaction or metal to ligand pi back donation. Now, what we have come across is that depending on this ligand or variation of this ligand, the extent of this interaction change.

In this perspective, we have looked into several kinds of transition metal sigma alkyl complexes, right from the ones that we have I am talking about is TM sigma RH or sigma alkyl complexes, we have also looked at TM sigma R F which are perfluoro alkyl complexes and in the last lecture we have been talking about arryl complexes and what we have seen that the extent of metal ligand, sigma donation, ligand metal sigma donation or metal to ligand pi back donation, the interaction in all of these type organometallic complex is very. Now, with that being in mind we have also discussed that these transition metal sigma arryl complexes they are intermediate between sigma alkyl ligands and pi acidic CO PR3 ligands.

Now, what does this mean? This means that in sigma alkyl ligands the extent of metal to ligand back donation is minimal, whereas in pi acidic legand the extent of back donation is significant. As a result this arryl ligand has back donation, which is more than that of the sigma alkyl complexes, but they are back donation is much less than that of these pi acidic ligands. So, that is why this transition metal sigma arryl complexes lie in between sigma alkyl and pi acidic ligand complexes and illustrate this with example on their stability.

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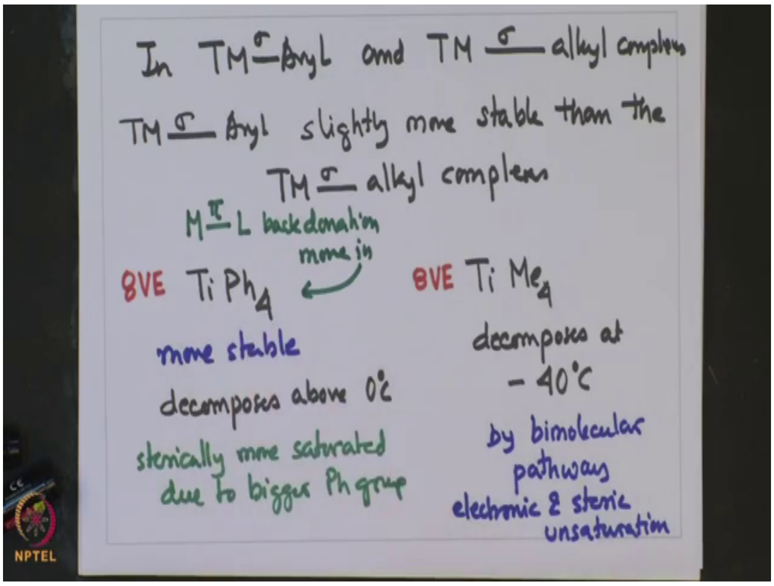

In $TM \overset{\sigma}{—} Aryl$ and $TM \overset{\sigma}{—}$ alkyl complex

$TM \overset{\sigma}{—} Aryl$ slightly more stable than the $TM \overset{\sigma}{—}$ alkyl complex

$M \overset{\pi}{—} L$ backdonation more in

8VE $TiPh_4$ ← 8VE $TiMe_4$

more stable

decomposes above 0°C

sterically more saturated due to bigger Ph group

decomposes at −40°C

by bimolecular pathway

electronic & steric unsaturation

So, transition metal incompletion to transition metal aryl and transition metal sigma alkyl complexes, transition metal sigma aryl as they have more metal to ligand pi back donation, then the sigma alkyl ones these are slightly more stable, then the transition metal alkyl complexes.

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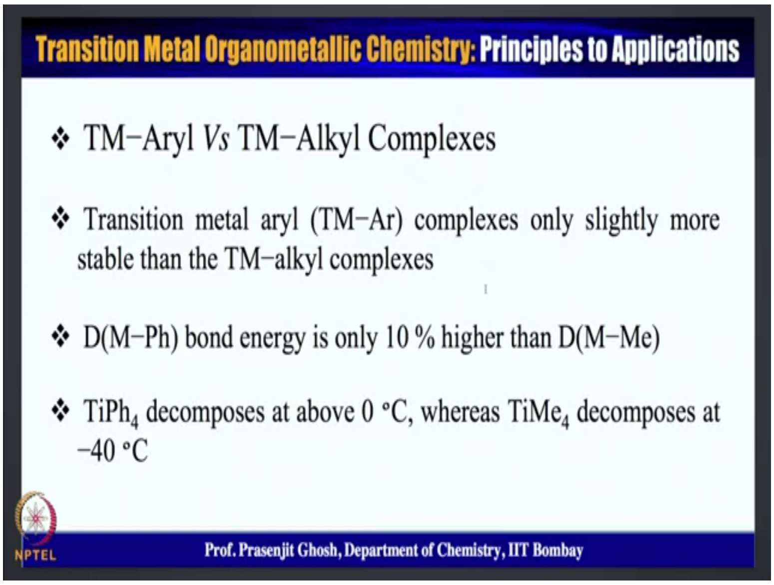

Transition Metal Organometallic Chemistry: Principles to Applications

- TM–Aryl *Vs* TM–Alkyl Complexes
- Transition metal aryl (TM–Ar) complexes only slightly more stable than the TM–alkyl complexes
- D(M–Ph) bond energy is only 10 % higher than D(M–Me)
- $TiPh_4$ decomposes at above 0 °C, whereas $TiMe_4$ decomposes at −40 °C

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Illustrated these let us take a look at the 2 compounds, one is titanium tetraphenyl containing a continuum aryl bond and titanium tetramethyl. Now, titanium between these 2 titanium tetraphenyl is more stable, as this one decomposes as the compound decomposes above 0 degree centigrade, whereas titanium tetramethyl is so unstable, that it decomposes at minus 40 degree centigrade. In our earlier discussion, we have referred to the reason for this high instability of this titanium tetramethyl as it decomposes by a bimolecular pathway and also, that it leads to decomposition going to it is electronic as well as steric unsaturation.

Now, in titanium tetraphenyl, the steric electronic unsaturation is same as that in titanium tetramethyl because both of these are 8 valence electron compounds. So, electronically they are equally unsaturated. However, as phenyl groups are more bulkier than the methyl groups, sterically titanium tetraphenyl is more saturated, bigger phenyl group then the methyl ones. As a result titanium tetraphenyl is more stable, but then the titanium tetramethyl. The second reason for extra stability apart from the steric can also be metal to ligand pi back donation, which is more in titanium tetraphenyl than in titanium tetramethyl.

So, metal to ligand pi back donation is more in this which leads to this extra stability of titanium tetra phenyl complex. As a result between this extra statics that the aryl brings and also because of the extra interaction of transition metal with the empty ligand orbital or metal to ligand pi back donation, the transition metal aryl complexes are more stable than transition metal alkyl complexes and the transition metal aryl bonds are more stronger than the transition metal alkyl bonds.

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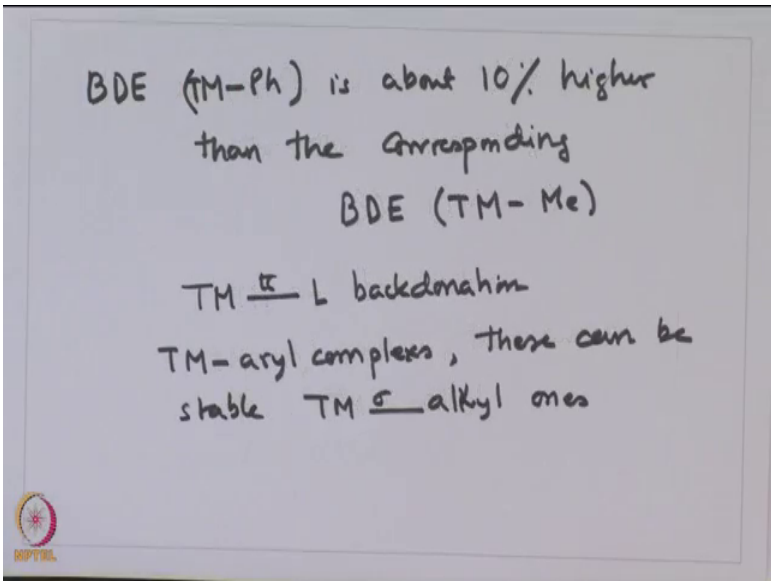

BDE (TM-Ph) is about 10% higher than the corresponding BDE (TM-Me)

TM $\overset{\pi}{\text{—}}$ L backdonation

TM-aryl complexes, these can be stable TM $\overset{\sigma}{\text{—}}$ alkyl ones

For example, the bond energy of metal; mention metal phenyl is about 10 percent higher than the corresponding bond dissociation energy of transition metal methyl bonds. So, what we see is that because of transition metal to ligand back donation that occurs in transition metal aryl complexes, these can be more stable than transition metal sigma alkyl ones.

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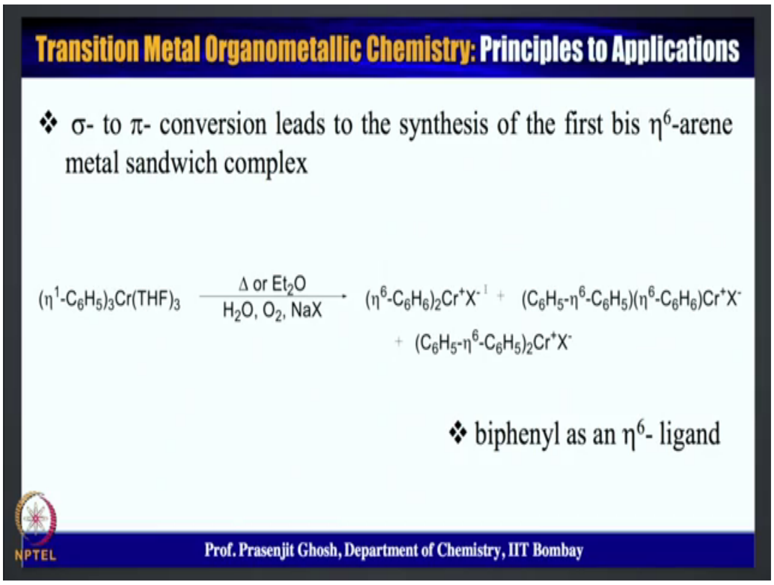

Transition Metal Organometallic Chemistry: Principles to Applications

- σ- to π- conversion leads to the synthesis of the first bis η^6-arene metal sandwich complex

$(\eta^1\text{-}C_6H_5)_3Cr(THF)_3 \xrightarrow[H_2O,\ O_2,\ NaX]{\Delta \text{ or } Et_2O} (\eta^6\text{-}C_6H_6)_2Cr^+X^- + (C_6H_5\text{-}\eta^6\text{-}C_6H_5)(\eta^6\text{-}C_6H_6)Cr^+X^- + (C_6H_5\text{-}\eta^6\text{-}C_6H_5)_2Cr^+X^-$

- biphenyl as an η^6- ligand

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Let me illustrate this with few more examples in the subsequent slides, also another interesting observation unique to this transition metal sigma aryl complexes is sigma to pi conversion.

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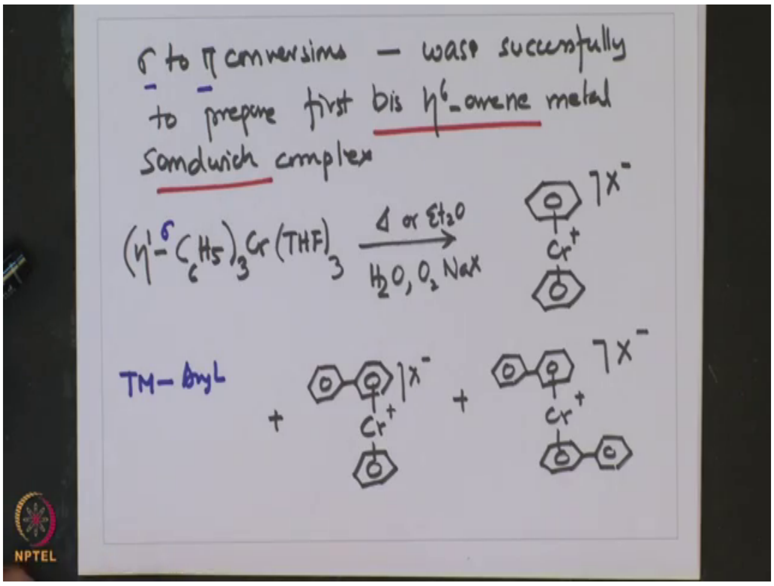

σ to π conversions – was successfully to prepare first bis η^6-arene metal sandwich complex

$(\eta^1\text{-}C_6H_5)_3Cr(THF)_3 \xrightarrow[H_2O,\ O_2\ NaX]{\Delta \text{ or } Et_2O}$

TM-Aryl

And, this is an interesting way in which a metal aryl sigma bond gets converted to a pi bond and was successfully used. To prepare first these arene metal sandwich complexes, would illustrated this with an example for example, this is eta1 C6 H5 whole 3 chromium THF whole 3 complex, when heated or in ether in presence of H2O oxygen and sodium salt, gave a mixture of the sandwich chromium of C6 H6 ether 6 5 plus by phenyl C6 H5 eta 6 C6 H5 chromium C6 8 6 plus X minus plus bis by phenyl type plus X minus.

So, this is an interesting example and unique to transition metal sigma aryl complexes that they can go or they can undergo a shift from sigma 2 pi bond, this was example where they are bound in a sigma fashion to the metal center and then it binds to the binds with these pi cloud and there are 3 C6 H5 moieties bound to frame chromium in a eta1 fashion, when heated under this condition gives the sandwich complex whereby there are 2 benzene C6 H6 bound eta6 using the pi cloud to chromium or it was 1 C 6 H 5 ligand.

And resulting in this by phenyl legand, which is bound using the pi cloud eta using a eta6 to chromium the other ring is a benzene C6 H6 ring, again bound to chromium with pi cloud and last third mixture is about 2 by phenyl rings bound to chromium using it is pi cloud and this method was successfully used for preparing the first bis arene metal sandwich complex of chromium as shown here.

Now, going back on the discussion elegant to metal sigma donation and metal to ligand pi back donation, we would see that how this or interplay between these 2 interactions affect the stability of transition metal aryl complexes.

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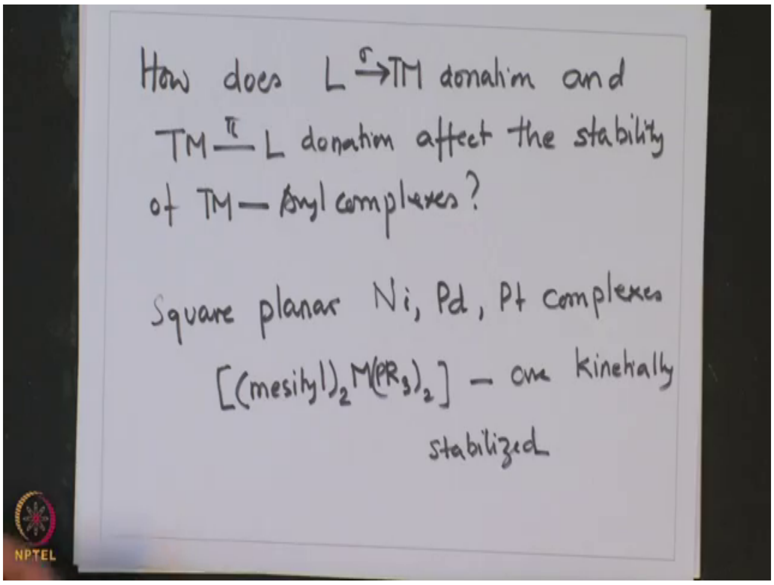

How does L $\xrightarrow{\sigma}$ TM donation and TM $\xrightarrow{\pi}$ L donation affect the stability of TM — Aryl complexes?

Square planar Ni, Pd, Pt complexes

$[(\text{mesityl})_2M(PR_3)_2]$ — are kinetically stabilized

So, how does ligand to metal sigma donation and metal to ligand pi back donation affect the stability of transition metal aryl complexes and these can be explained by square planar complexes of transition metal aryl square planar complexes, which have been rendered kinetically stable.

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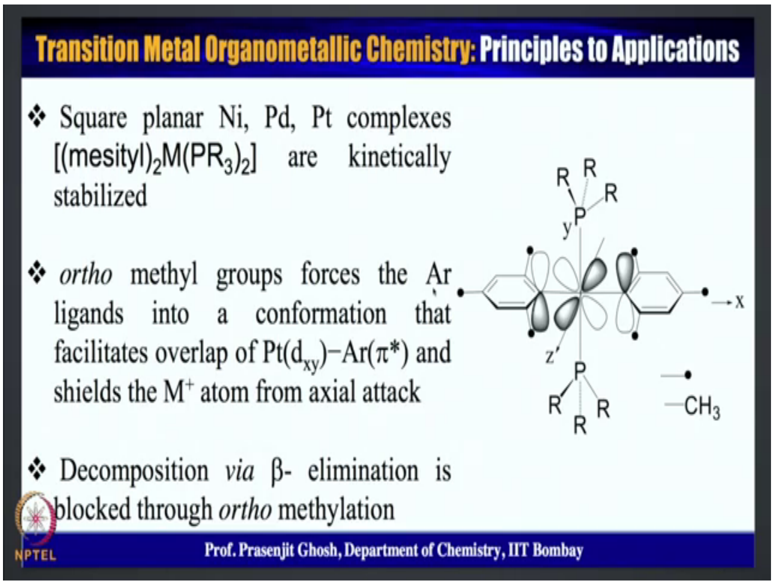

Transition Metal Organometallic Chemistry: Principles to Applications

- Square planar Ni, Pd, Pt complexes $[(\text{mesityl})_2\text{M}(\text{PR}_3)_2]$ are kinetically stabilized
- *ortho* methyl groups forces the Ar ligands into a conformation that facilitates overlap of Pt(d_{xy})–Ar(π^*) and shields the M^+ atom from axial attack
- Decomposition *via* β- elimination is blocked through *ortho* methylation

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Because of the interplay between these 2 types of forward donation and backward donation and the best examples of these are square planar nickel, palladium, platinum complexes of formula mesityl M PR kinetically stabilized.

Let us illustrate this with the molecular orbital that diagram for this kind of complexes.

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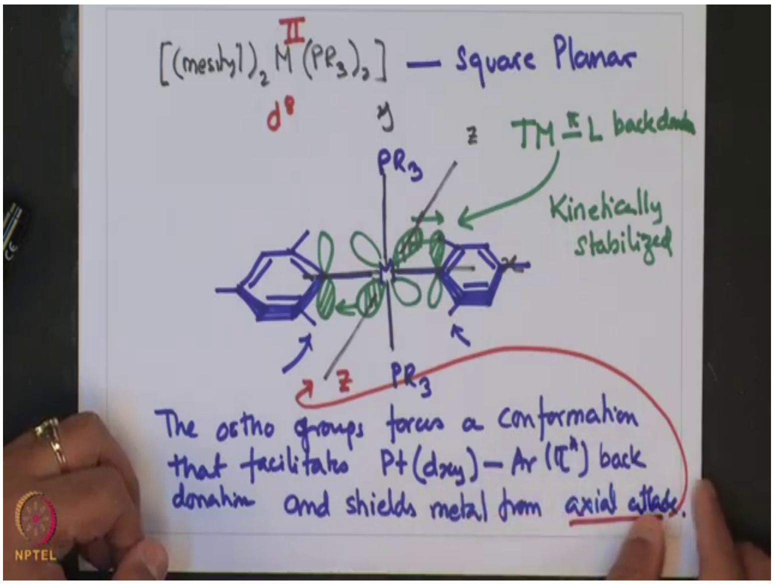

$[(\text{mesityl})_2\overset{\text{II}}{\text{M}}(\text{PR}_3)_2]$ — Square Planar

The ortho groups forces a conformation that facilitates $Pt(d_{xy}) - Ar(\pi^*)$ back donation and shields metal from axial attack.

So, for example, for this mesityl this is a square planar complex and here the metal center is in plus 2. So, this is d 8 square planar system. Now, let us look at it how the interaction occurs. So, let us say this is the x y plane and the metal is sitting over here, it has 2 tier ligands which are trans to each other, as given by and this bond is along the axis and it has 2 aryl groups of the mesityl moiety along this bond. Now, this misityl moiety is in a plane perpendicular to the plane of the paper and this is designated by the wedge bond shown over here. So, it has along z x is empty space, where it can undergo some kind of attack nucleophilic or nucleophilic attack.

But, because of the kinetic stabilization such attack does not occur and these can be seen with respect to the orbital interaction or that occur between the metal to ligand pi back donation and that takes place between a ligand metal orbital of appropriate symmetry interacting with ligand orbital and as a result of this transition metal to ligand pi back donation, these compounds are kinetically stabilized and this interaction is very strong and that occurs because the ortho methyl groups, these ortho methyl groups forces are conformation that facilitates platinum or metal dxy to aryl pi star back donation and shields metal from axial attack.

The axial attack can happen from the z axis and what is seen over here that kinetic stabilization between the transition metal to ligand pi back donation sort of inhibits this kind of axial attack thereby stabilizing transition metal aryl kind of complexes. So, let me summarize in this lecture we have looked into the orbital interaction leading to extra stability of transition metal aryl complexes and what we had observed is that the interplay between the ligand to metal sigma donation and metal to ligand pi back donation play a vital role in bringing about extra stability to these complexes and with regard to the stability the transition metal aryl complexes lie between that of transition metal sigma alkyl complexes and that of the other pi acidic ligands, like carbon monoxide, PRPP, PR3 where the extent of transition metal to ligand pi back donation is at the maximum.

So, these interaction particularly the transition metal to the ligand pi back donation also brings about extra stability to these transition metal aryl complexes. We have also looked into another interesting feature of these transition metal aryl complexes in the fact that they can undergo sigma pi conversion as a result it gives various kinds of transition metal sandwich complexes which are also of very interest.

So, with that let me conclude today’s lecture and I look forward to a next lecture in which we will discuss some more applications of this transition aryl complexes and also take up transition alkyne complexes, which is a subject by itself.

So, till then, thank you for being with me in this lecture and I look forward to being with you in the subsequent lecture, good bye.