Advanced Transition Metal Organometallic Chemistry
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Lecture – 21
Transition Metal Cyclopentadienyl Halide and Transition Metal Arene Complexes

Welcome to this lecture on advanced transition metal organometallic chemistry we have been discussing transition metal cyclopentadienyl halide complexes. In the last lecture we had seen how these halide complexes are important organometallic compounds which can give rise to many other very useful reagents and these are obtained by conversion of these transition metal cyclopentane halide complexes to these particular reagents.

To begin with we saw that these compounds can be converted to simple aqua complexes just by abstraction of the halide using silver salts and these aqua complexes are useful examples for that depicts two aspects of chemistry which is the organometallic aspect by virtue of having transition metal cyclopentadienyl bond as well as the coordination aspect by virtue of having the aqua transition metal bond so transition metal cyclopentadienyl halide complexes can be converted to the aqua complexes by simple abstraction method.

Now we have also seen how these transition metal cyclopentadienyl halide complexes can give rise to another useful reagent in the form of getting converted to transition metal cyclo pentadienyl mixed halide hydride complexes which is just called Schwartz reagent and that is useful for converting olefins via hydrogenation to various useful organic as intermediates and products.

We have also seen in the last class the versatility of Jordan's cation which is nothing but a be cyclo pentadienyl zirconium methyl THF cation and these compound primarily is about versatile active catus for many kinds of transformations like CH activations CC coupling as well as polymerization reactions. And we are taking up examples in which we could see that these Jordan’s cation reacts with alkyne olefin carbon monoxide by via coordination insertion pathway.

As well as it reacts with alkenes by a sigma the metathesis pathway by generating the corresponding alkyl derivative along with formation of the methane. So, continuing further on these transition metal halide complexes we are going to look at another interesting family of compound which are derived from these transition metal cyclo butane halide complexes and these are called transition metal cyclo pentadienyl halide carbonyl complexes okay.

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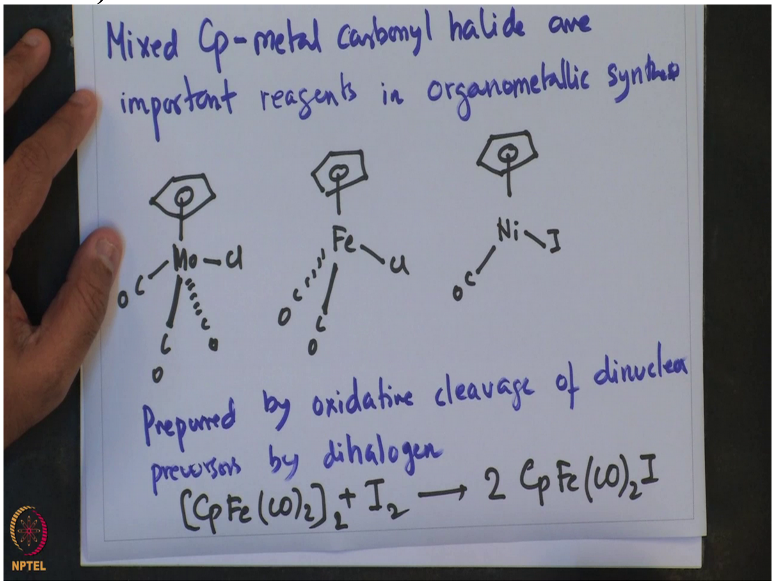

Mixed Cp-metal carbonyl halide are important reagents in organometallic synthes

Prepared by oxidative cleavage of dinuclea precursors by dihalogen

$[CpFe(CO)_2]_2 + I_2 \longrightarrow 2\ CpFe(CO)_2I$

And these are also important or agent in organic synthesis, so, mixed cyclopean CP metal carbonyl halide are important reagents in organometallic synthesis and some of the examples of these compounds molybdenum tricarbonal chloride or CP iron chloride dicarbonyl or CP nickel iodide and the propriety method involves oxidative cleavage of the dimers using die halogen compounds.

So, these methods they are prepared by oxidative cleveite of di nuclear precursors by di halogens an example of this is shown over here. So, CP Fe dicarbonyl dimer + iodine giving 2 molecules of CP Fe dicarbonyl iodide, so this method is kind of a general method and involves the oxidative cleavage of dinuclear compound by reacting with the halogens. Now these di CP iron like carbonyl halide complexes are important starting points for creating other kinds of complexes and here is the nice demonstrations in which this mixed carbonyl halide complexes can be converted to another interesting compound which contained both CP bound in eta 5 as well as eta 1 bound fashion.

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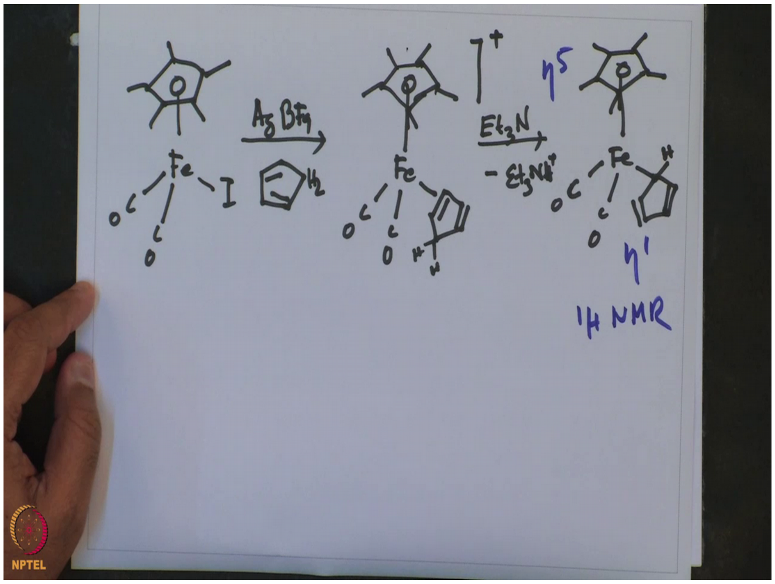

So, I will illustrate this with an example shown over here so CP star violent the carbonyl iodide when treated with Ag BF 4 in presence of cyclo penta dyne gives first the abstraction of decided happened resulting in the formation of silver iodide along with this olefin bound complex to iron results giving CP star Fe they are in complex of this and its cation because this halide had been abstracted.

Now in presence of a base one of the protons get deprotonated the base can be tri ethylamine resulting in Et 3 NH+ which eliminates to give this CP star if we CO CO olivine compound so this is an interesting compound where we see that it contains eta 5 bound CP as well as eta 1 by n cyclopentadienyl ring and the binding of these the differential binding of these two cyclopentadienyl ring is easily a picked up in proton NMR spectroscopy where the flux immunity of these protons is greatly visible.

So, what we see is that there are several types of new compounds or new two subclasses that can be obtained from cyclopentadienyl transition metal halide complexes and this being its aqua complexes is mixed halide hydride complexes it's a alkyl base cationic complexes which are jordan reagent. And then it is mixed halide carbonyl complexes so and all of these offers different perspective or different new chemistry a and that is why it over all this makes these transition metal cyclo pentadiene halide complexes so interesting.

Now we have covered most of the topic for this half-sandwich class of compound and we are going to now move on to another interesting class of compounds and these are transition metal arene complexes. So, with these we make a transition from 5 membered ring see cyclopentadienyl ring to the 6 membered arene complexes. So, from now on in that in this lecture we are going to be discussing on arene complexes and to start off we are going to look at the simplest look at the most simplest of all that is the benzene complexes of these transition metals.

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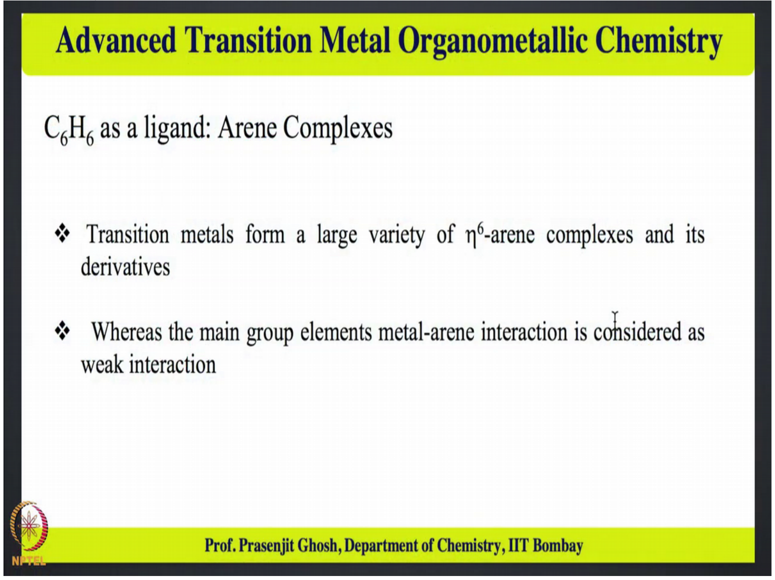

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C_6H_6 as a ligand: Arene Complexes

- Transition metals form a large variety of η^6-arene complexes and its derivatives
- Whereas the main group elements metal-arene interaction is considered as weak interaction

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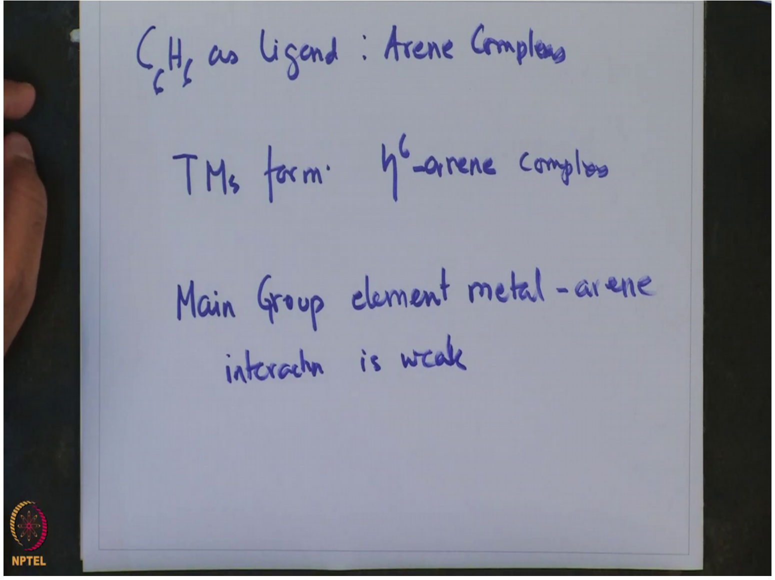

C_6H_6 as ligand : Arene Complexes

TMs form: η^6-arene complexes

Main Group element metal-arene interachn is weak

So, today we are going to be discussing C 6 H 6 as ligands and these are called arene complexes. Now these brands like the cyclopentadienyl complexes where C 5 H 5 binds through the PI electron in eta 5 fashion similarly the transition metal forms eta 6 arene complexes metals form arene complexes. And now with respect to the main group such main group transition metal arene complexes are considered to have weaker interactions and they are not as common as that of the transition metals.

So, this is an important observation that main group elements metal arene interaction is weak and hence they do not occur that open as compared to its transition metal complexes. Now transition metal arene complexes these binary Bis arene metal complexes similar to that of the metaloscene are quite common.

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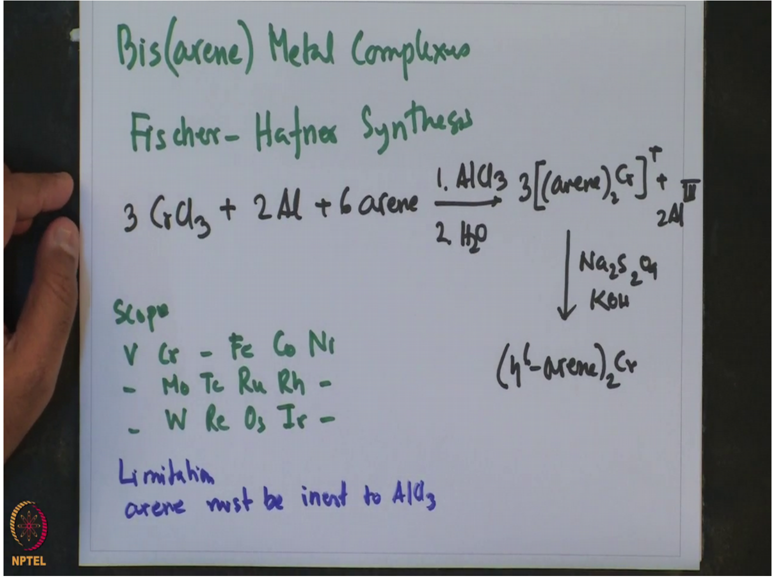

Bis(arene) Metal Complexes

Fischer- Hafner Synthesis

$$3\,CrCl_3 + 2\,Al + 6\,arene \xrightarrow[2.\ H_2O]{1.\ AlCl_3} 3[(arene)_2Cr]^+ + 2Al^{III}$$

$$\downarrow Na_2S_2O_4,\ KOH$$

$$(\eta^6\text{-arene})_2Cr$$

Scope

V Cr - Fe Co Ni
- Mo Tc Ru Rh -
- W Re Os Ir -

Limitation
arene must be inert to $AlCl_3$

And they are particularly a called as these Bis arene metal complexes so these are binary arene complexes which are quite common in which they are in binds in this expression. The synthesis is commonly referred to as Fisher Hafner synthesis this is quite a general route for making these compounds and the first synthesis was reported with chromium 3 Cr Cl 3 + 2Al + 6 arene giving 6 arene in presence of AlCl 3 and water giving 3 arene to chromium ++ 2Al 3.

This in presence of Na 2 S 2 O 4 and KOH gives this eta 6 arene chromium, now this is quite a versatile synthesis and the scope is for vanadium, chromium, iron, cobalt, nickel then molybdenum, technetium, ruthenium, rhodium, tungsten, rhenium, osmium, iridium so it seems that this is quite a interesting bit of reaction because it is quite general for so many different metals they but the only limitations that it offers is that arene must be inert towards AlCl 3.

The only limitation is arene must be inert to AlCl 3 because sometimes this alkylated arene's are isomerised by AlCl 3and so on and so forth. So, these like you these does have a limitation that this arene should not be attacked by AlCl 3 otherwise if that is not the case then this Fisher-Hafner synthesis is quite unusual synthesis for preparing these bis arene transition metal complexes.

So, we are going to dwell upon some other interesting reactions which are useful for preparing these p7 complexes.

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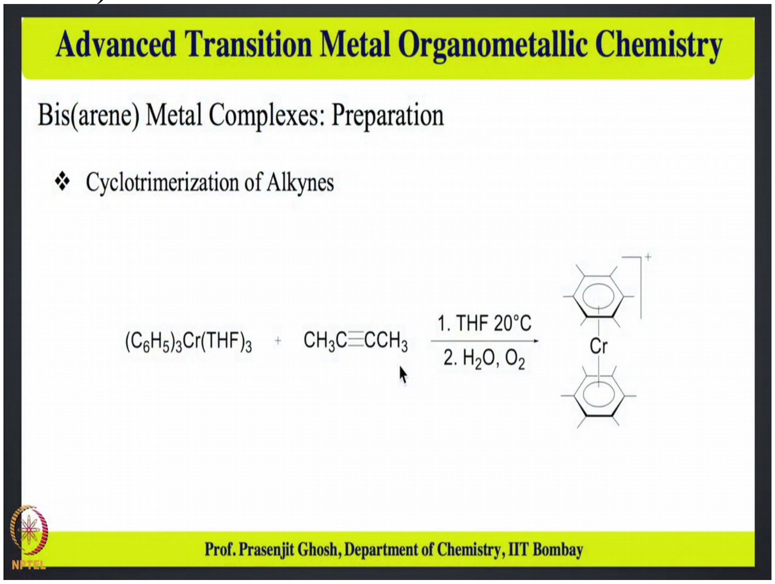

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Bis(arene) Metal Complexes: Preparation

- Cyclotrimerization of Alkynes

$(C_6H_5)_3Cr(THF)_3$ + $CH_3C{\equiv}CCH_3$ $\xrightarrow[2.\ H_2O,\ O_2]{1.\ THF\ 20°C}$

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And the next one is by cyclotrimerisation of arena the next reaction is so to illustrate this:

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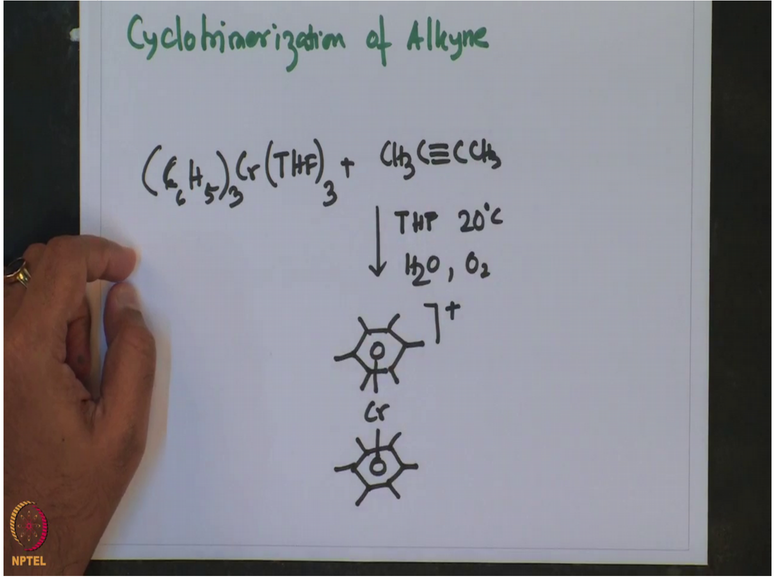

Cyclotrimerization of Alkyne

$(C_6H_5)_3Cr(THF)_3$ + $CH_3C{\equiv}CCH_3$

$\downarrow$ THF 20°C, H_2O, O_2

Let us take a look at this example C 6 H 5 whole 3 chromium THF whole 3 plus CH 3 C CH 3 in presence of THF 20 degree centigrade water oxygen giving the seismic arene complex of hexa ethyl benzene. So, this is a interesting reaction which sees that the metal sort of primerises alkyne this methyl C triple bond methyl to give this hexa methylene benzene and then subsequently forming a sandwich complex of that.

So, this is a very elegant way of making this this arene complex in which this example two of the hexa methyl rings are bound in eta 6 fashion parallel to each other similar to what has one seen in metalloscene type of complexes.

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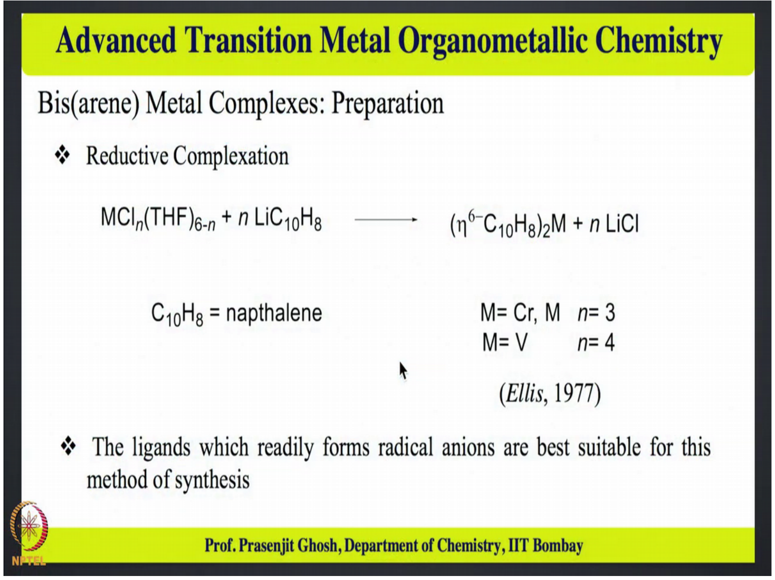

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Bis(arene) Metal Complexes: Preparation

- Reductive Complexation

$MCl_n(THF)_{6-n} + n\,LiC_{10}H_8 \longrightarrow (\eta^{6}\text{-}C_{10}H_8)_2M + n\,LiCl$

$C_{10}H_8$ = napthalene

M= Cr, M n= 3
M= V n= 4

(*Ellis*, 1977)

- The ligands which readily forms radical anions are best suitable for this method of synthesis

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So, the next reactions is also a very interesting one and that involves reductive complexation. So, the reductive complexation involves the reaction of metal halides with radical anions and so this reaction is useful for ligands which can be easily led to the formation of its radical anions.

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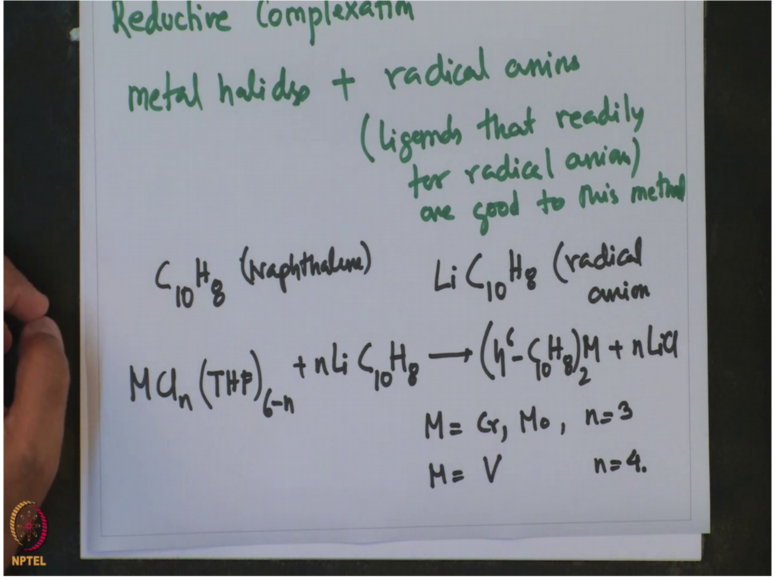

Reductive Complexation

metal halides + radical anions
(ligands that readily for radical anion) are good to this method

$C_{10}H_8$ (naphthalene) $Li\,C_{10}H_8$ (radical anion

$MCl_n(THF)_{6-n} + n\,Li\,C_{10}H_8 \longrightarrow (\eta^6\text{-}C_{10}H_8)_2M + nLiCl$

M = Cr, Mo , n=3
M = V n=4.

So, this reaction sort of proceeds for metal halides plus radical anions and hence ligands which hence ligands that readily form radical anions are good for this method of synthesis are good for this method. Now example of such ligand is this naphthalene and in its the naphthalene for critical readily radical anion for example with lithium it forms a Li C10 H 8 this is a radical anion and then the reaction MCl n THF 6 - n + n Li C10 H8 giving eta 6 bound C10 H 8 whole 2 M + n LiCl.

Now this is quite a common method for chromium molybdenum and n = 3 and for vanadium for n = 4 so this reductive coupling is used is a unique reaction so for that we have been saying that involves converting the ligands to their radical anions and then treatment of the radical anions to the metal halides and nice demonstration of this have been used in case of various metals like chromium molybdenum vanadium that produces this anion.

We are going to look at another such example that involves this radical anion and this one is with biphenyl or C12 H 10 ring.

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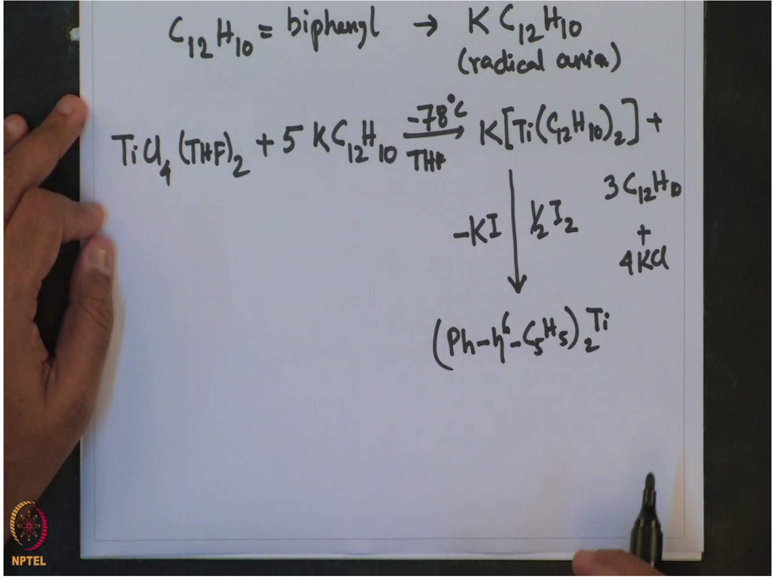

So, C 12 H 10 is biphenyl and it is radical anion is potassium C 12 H 10 radical anion so the reaction is TiCl 4 THF whole twice +5K C 12 H 10 very low temperature -78 degree centigrade giving K TI C12 H 10 whole 2 + 3 C 12 H 10 + 4 K Cl - KI and presence of iodine gives this Ph eta 6 bound C 5 H 5 whole 2 titanium. Now so here we see that two of the of the two bi phenyl ring one of the bi phenyl ring is bound in an eta 6 fashion to titanium.

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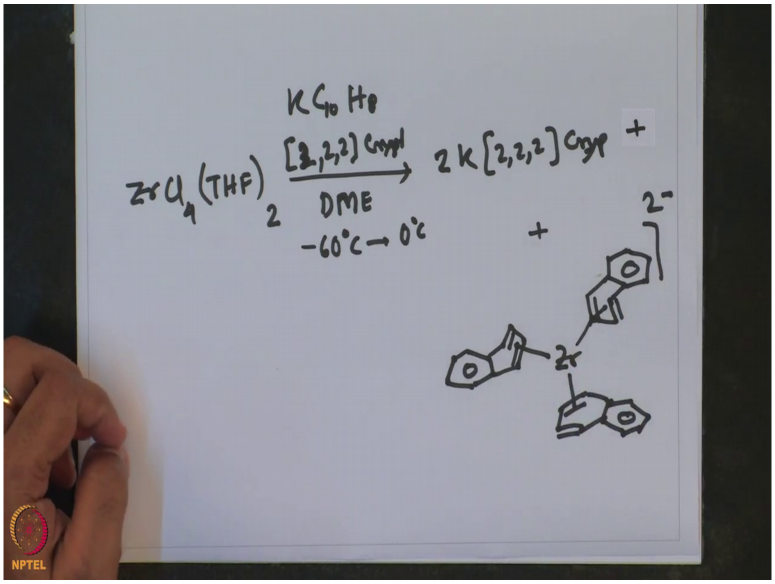

Now another example of this reaction is reactive coupling is shown over here that involves this zirconium tetrachloride THF whole 2 in presence of K C10 H 8 and crypton and 3 2 2 crypton in DME and the temperature is from -60 degree C to 0 degree C then one gets 2 potassium 2,2,2 crypton + this very interesting compound bound to the zirconium this 2 O- okay. So, here this is an interesting example of this reductive coupling where it reacts with naphthalene but with only the naphthalene only with the two of the olefinic bonds of the naphthalene.

And as a result naphthalene ring is sort of no longer planar and is found bound to zirconium in a metalic dynamic form, so, with that I conclude today's discussion on this transition metal cyclo pentadienyl halide complexes as well as the corresponding Bis arene complexes and to summarize we had looked into these various methods of preparation of this transition metal bis arene complexes and some of them involved using the reaction of halides metal halide precursors with arene in presence of reducing agents like aluminum this was we Fisher-Hafner synthesis.

One has to this is quite a general reaction but one has to be careful that the arene does not react with AlCl 3. The other method involved was these the reaction of metal halides with the ligands which can form radical anion and these are called reductive coupling we have seen some useful interesting examples which are successfully used in producing for the these transition metal adding complexes using this method.

So, with these I would like to draw a conclusion on today's lecture in which we have looked in to be serene as well as and metal cyclopentadienyl halide complexes. In particular in that front we are looked into the mixed transition metal cyclo pentadienyl halide carbonyl complexes and how they are also used in making interesting compounds in which we had one eta 5 bound CP and another eta 1 bound CP rings.

So, now we are going to continue more on this discussion on transition metal bis arene complexes in the next lecture until then I goodbye and I thank you for patiently listening to this lecture today.