Advanced Transition Metal Organometallic Chemistry
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Lecture – 20
Transition Metal Cyclopentadienyl Halide Complexes

Welcome to today's lecture on advanced transition metal organometallic chemistry we have been discussing about transition metal cyclopentadienyl halide complexes. These complexes are part of sandwich complexes which we have been discussing in the last few lectures. We started off by talking about transition metal cyclo pentadienyl carbonyl complexes then went on to talk about cyclopentadienyl transition metal nitrosyl complexes then we went to went on to speak further about cyclopentadienyl transition metal hydride complexes and now we are talking about transition metal cyclopentadienyl halide complexes.

These all belong to the category of half sandwich complexes and with regard to transition metal cyclopentadienyl halide complexes in our previous lecture we had looked into various preparatory methods that are available for synthesizing these complexes it is worth mentioning that these transition metal cyclopentadienyl halide complexes are important precursor to many other cyclopentadienyl transition metal complexes and hence these complexes have been synthesized to a great extent and their reactivity also explored to a great extent.

So, from that perspective we looked into various synthetic methods which were available for preparing these complexes and also we have looked into the structure of cyclopentadienyl transition metal halide complexes. So, today a continuing further on this discussion we are going to be talking about something which are important derivatives are compounds which are derived from this transition metal cyclo pentadienyl halide complexes.

And in particular I would be talking about the transition metal cyclo pentadienyl aqua complexes which are indeed derived from these transition metal cyclo pentadienyl halide complexes.
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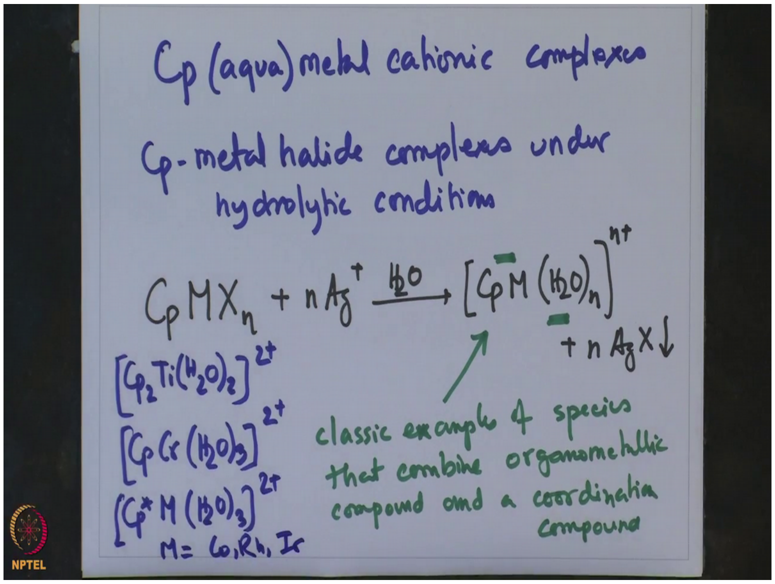

Cp (aqua) metal cationic complexes

Cp-metal halide complexes under hydrolytic conditions

$$CpMX_n + nAg^+ \xrightarrow{H_2O} [CpM(H_2O)_n]^{n+} + nAgX\downarrow$$

$[Cp_2Ti(H_2O)_2]^{2+}$

$[CpCr(H_2O)_3]^{2+}$

$[Cp^*M(H_2O)_3]^{2+}$

M = Co, Rh, Ir

classic example 4 species that combine organometallic compound and a coordination compound

So, today as a part of this discussion we are going to be talking about CP aqua metal cation cationic complexes and these are formed from CP metal halide complexes under hydrolytic conditions. Let me illustrate this by the simple example of the reaction of cyclopentane metal halide complexes of the type CP MX n that reacting with in Ag+ no silver cation is used for precipitating where this halide abstracting this halide as a part of AgCl along with the formation of this aqua complex the reaction that is why to be done in water would give this CP M H2O + n + + nAgX as a precipitate.

So, this is a nice reaction which involves the low solubility product of silver chloride or silver halide utilizes that which is used to abstract this halides from this CP metal X kind of compounds freeing up a vacant coordinates coordination site at the metal and that to be readily occupied by these water. Now these are important organometallic compounds and actually these compounds are both in nature they are organometallic compound as well as coordination compounds.

So, these are classic examples of species that combine organometallic compound and a coordination compound. So, the organometallic component arises from this CP metal bond and the coordination component arises from the aqua metal bond. So, these are three nice neat examples which combines both the aspects of organometallic chemistry and coordinates in chemistry and all of them being present in the same metal species okay.

So, now coming back to it then there are many complexes of these have been reported and some of the examples that include are shown over here are VCP 2 titanium di echo whole 2 + CP chromium di echo 2 + CP star M tri echo 2+ M can be cobalt rhodium and iridium. So, one important thing is that in this aqua reaction that the halides are abstracted and then a vacant coordination site is formed and that vacant coordination site is occupied by a donor ligand like water resulting in the formation of these complexes.

Now if you look at the geometry of these complexes the as we had mentioned earlier that CP or CP star sort of enforces pseudo tetrahedral geometry that a metal center and that can be seen over here in all of the examples that we have been talking about. For example in the first one there are 2 CP and 2, water so there is there are 4 ligands around titanium in a pseudo tetrahedral geometry. Whereas for the chromium there is 1 CP and 3 water again 4 ligands around the metal center in a pseudo tetrahedral geometry.

As well as 4 in the last complex cobalt iridium or rhodium and indium there also is 1 CP star and 3 water resulting in 4 ligands around the metal in a pseudo so tetrahedral geometry. So, what we see is that, this aqua cationic complexes are important class of compound by themselves and which can be accessible from the half-sandwich CP transition metal halide complexes by simple abstraction of the halide using silver ions in aqueous medium.

And these complexes are also classic examples of organometallic compound by virtue of having a CP metal bond and also simultaneously a classic example of coordination compounds by virtue of having water metal bond and are quite elegant examples by themselves. Now along this line we are going to see another very interesting compound which are also formed from this transition metal cyclo pentadienyl halide complexes.

And these are just transition metal cyclopentadienyl halide hydride complexes these are kind of interesting and these are popularly known as Schwartz reagent.

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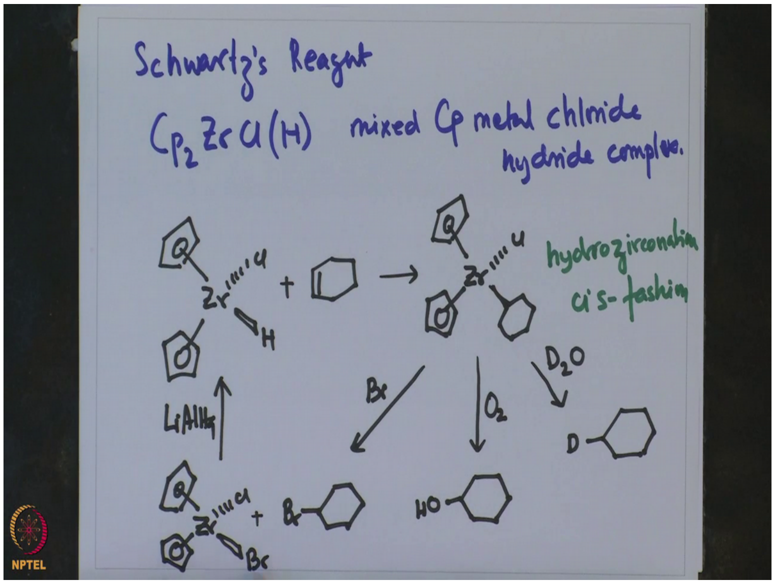

And they are of the formula CP 2 zirconium chloride and hydride and these are called mixed CP metal hydride chloride hydride complex. Now these the structure of this compound is again in pseudo tetrahedral geometry as it is supposed to be and it has tilted CP the way it should be the while we had discussed the other compounds so that now this BCP zirconium chloride hydride complex which is called source region can be used for converting olefin to many other derivatives which we will be seeing this.

So, the first reaction of this source region with olefin like cyclohexane gives this cyclohexyl derivative by method called hydros zirconation this is popularly referred to as hydro zirconation and this is kind of evident from the fact that the zirconium and hydrogen adding against this olefinic bond. Now this hydrogenation like is sort of proceeds in a Cis fashion as would be expected from this zirconium hydrogen bond adding against this olefin from the same side.

And similar to that of hydroboration or other C's additions that one is familiar with. Now this is zirconium cyclohexyl derivative obtained by hydrogenation using Schwartz reagent can further be converted to many important organic compounds for example by treatment with D 2O gives deuterated cyclohexane with the deuterium residing at place of zirconium with oxygen it gives the corresponding alcohol and with bromine it gives the corresponding bromide cycoexyl bromide along with the formation of BCP zirconium chloride bromide.

And subsequently this zirconium BCP zirconium chloride bromide when treated with lithium aluminum hydride gives back this Schwartz reagent. Now thing which is to be noted over here that where this mixed halide compound BCP zirconium chloride bromide treated with hydrogen the hydride formation does not happen at the chloride but it happens at the bromide which sort of reflects the fact that zirconium chloride bond is even more, stronger than the zirconium bromide bond.

And as a result the zirconium bromide, undergo a replacement giving back to this Schwartz reagent. Now we have been looking at some very interesting chemistry which are being derived from transition metal cyclohexyl transition metal cyclo pentadienyl halide complexes one such example are cyclopentadienyl metal aqua complexes then we saw these cyclo pentadienyl mixed halide hydride complexes which is sort of Schwartz reagent which can convert olefin to so useful so many useful organic products.

Now we are going to look at another useful application of these halide complexes which is just this Cis acidic cationic complexes formed from the abstraction of the halides similar to the aqua's complexes that we had earlier observed about.

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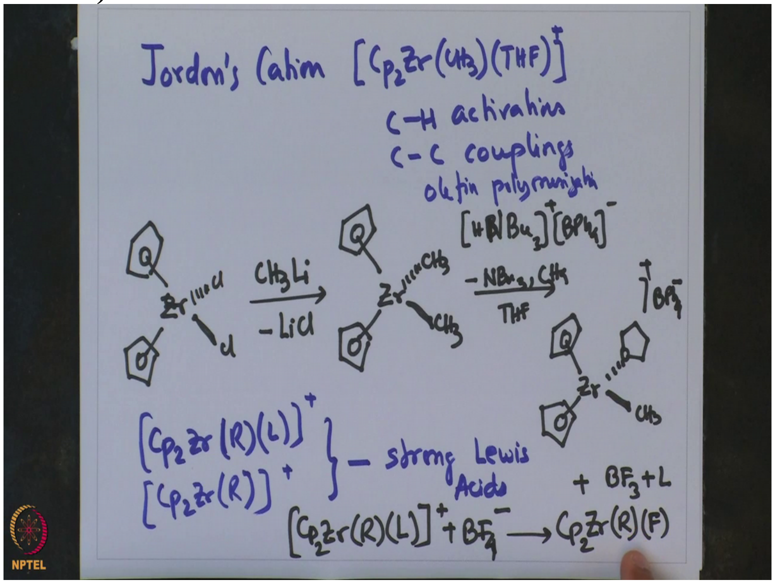

Jordan's Cation $[Cp_2Zr(CH_3)(THF)]^+$

C–H activations

C–C couplings

olefin polymerization

$[Cp_2Zr(R)(L)]^+$, $[Cp_2Zr(R)]^+$ } – strong Lewis Acids

$$[Cp_2Zr(R)(L)]^+ + BF_4^- \longrightarrow Cp_2Zr(R)(F) + BF_3 + L$$

So, these are kind of strong highly electron deficient molecules which are highly acidic and in this context one has to mention about Jordan's cation which is nothing but have the formula CP 2 zirconium methyl THF cutta positive and these is highly lewd acidic cationic species which can carry out various kind of CH activations and CH CC couplings and CC couplings. So, what we see is this Jordan's cations is the electron deficient lewd acidic compound which can be formed from transition metal cyclo pentadiene halide complexes.

And they are extremely good in various kinds of types of catalytic transformations for example CH and CC coupling reactions. So, before we talk about the reactivity of these let me just first leave the synthesis of these Jordans cation as well Jordans cation of the type these BCP zirconium dichloride with methyl lithium and that results in lithium chloride giving BCP zirconium dimethyl.

Now this is these di methyl complexes can be generated from the halide complexes by simple treatment with miguel lithium. And then comes this methyl abstraction reaction in THF and usually this is done by using some kind of proton source like HB HBu whole 3 + + BF4 BPH 4 - which eliminates NBu 3 and methane and the reaction done in THF now giving CP zirconium CH 3 THF + BPH 4 - so these complexes are cationic in nature and also acidic in nature and have the general formula as CP 2 Zr RL okay.

As well as it is basically from is CP 2 Zr there are these are strong lewis acids and can can carry out many kinds of catalyst catalytic reactions for example create activations is a coupling even olefin polymerization and so an example of its ability for abstracting the base is given in the reaction CP to zirconium Rl + BF 4 - giving CP to zirconium RF+ BF 3 + L. So, here is a demonstration of the lewis acidic nature of this BCP zirconium Rl where this l gets replaced by the obstruction of a fluoride from BF4 giving this mixed fluoro alkyl zirconium BCP halide complex along with BF3 and ligand.

So, now this Jordan cation is useful species which has actors about still active species for many catalytic transformations and we are going to look at some of the examples on the same.

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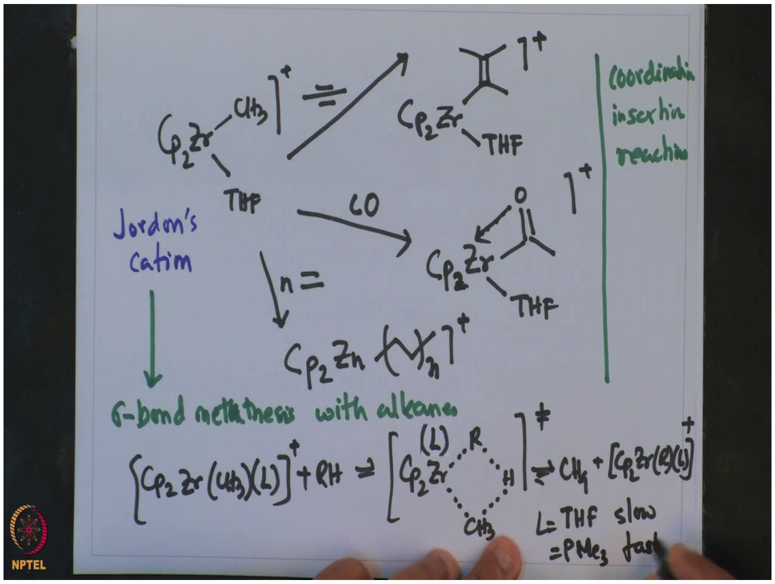

So, for example BCP zirconium methyl THF cation reacts with alkyne where it undergoes this methyl zirconium addition giving this olefin zirconium THF it also reacts with CO where the carbonyl insights into the zirconium metal bond giving a zirconium allyl moiety CP to zirconium CO THF and this oxygen is loosely a the lone pair of oxygen is loosely coordinated to zirconium, zirconium being highly electron deficient species.

And also reacts with olefin in form of olefin polymerization to give VCP 2 zirconium alkyl species where the long polymer chain is attached to the metal center. So, one can see the versatility of this Jordan cotton cation which can carry out so many different reactions. Now apart from all the these reactions are called are called coordination insertion reactions these are called coordination these are called coordination insertion reactions which means that each of these alkene force coordinates and then inserts onto the species.

Whereas the these Jordan's cation can also undergo sigma metathesis reactions sigma bond metathesis with alkanes and this is illustrated in the following a beautiful example + RH goes through this transition state eliminating methane + BCP to zirconium Rl cation so l can be THF then it is slow or PMe 3 then it is fast okay. So, with this I would like to conclude upon today's discussion on transition metal cyclopentadienyl halide complexes.

These are part of a half sandwich complexes that we have discussed we are discussing and what we saw that these transition metal cyclopentadiene and halide complexes are important precursors to many other interesting compounds to start with we looked into the conversion of cyclopentane time transition metal halide complexes to the corresponding aqua complexes by simple abstraction with silver reagents the abstractions of the halide in water.

Now this transition metal aqua complexes are interesting examples depending simultaneous aspects of code organametallic chemistry by virtue of the presence of metal cyclo pentadienyl bond as well as coordination chemistry the virtue of the presence of water coordinating to the transition metal. We have also seen how these halide complexes could be a transform to mix two halide hydride complexes and giving rise to this important reagent called Schwarz reagent is a useful reagent for organic transformations in which it can convert olefins to various derivatives upon reaction with this mixed halide hydrate complex by hydrogenation.

We have also come across another very versatile catalytically active species called Jordan's cation which is nothing but B cyclopentadienyl zirconium methyl THF cation and these is a useful cation for many catalytic processes involving CH activation CC couplings as well as olefin polymerization. We have looked how these reaction proceeds and primarily with various substrates like alkanes carbon monoxide alkenes.

This cation precedes by this coordination insertion mechanism in which it first coordinates and then gets inserted into zirconium methyl bond. We have also seen that this Jordan's cation and can is capable of exhibiting sigma bond metathesis and this occurs when these are treated with alkanes via a 4 member transition state. So, all of these chemistry the further highlights are testifies the important versatility of Jordans cation.

And the so much of different reactivity of cation can be traced down to their highly Lewis acidic nature which allows for radius activation of substrates first by coordination insertion pathway as well as by Sigma method metathesis per se. So, this highly possibility of Jordans cation can be picked to the newest acidity of these species. So, with this I would like to conclude today's discussion which had been primarily on transition metal halide complexes and the reactivity still some of the topics are to be discussed which will be taken up in the next lecture.

And I thank you again for being with me in this lecture and I look forward to being with you in the next lecture when we take up this topic and many more in more details, till then good bye.