Advanced Transition Metal Organometallic Chemistry
Prof. Prasenjit Ghosh
Department of Chemistry
Indian Institute of Technology-Bombay

Lecture – 19
Transition Metal Cyclopentadienyl Hydride and Halide Complexes

Welcome to today's lecture on advanced transition metal organometallic chemistry we have been discussing transition metal cyclo pentadienyl hydride complexes in the last lecture. As a part of our overall treatment of this topic on half sandwich complexes in that respect we had talked about transition metal cyclo pentadienyl carbonyl complexes followed by transition metal cyclo pentadienyl nitrosyl complexes followed by transition metal cyclo pentadienyl hydride complexes which we would be continuing discussing upon.

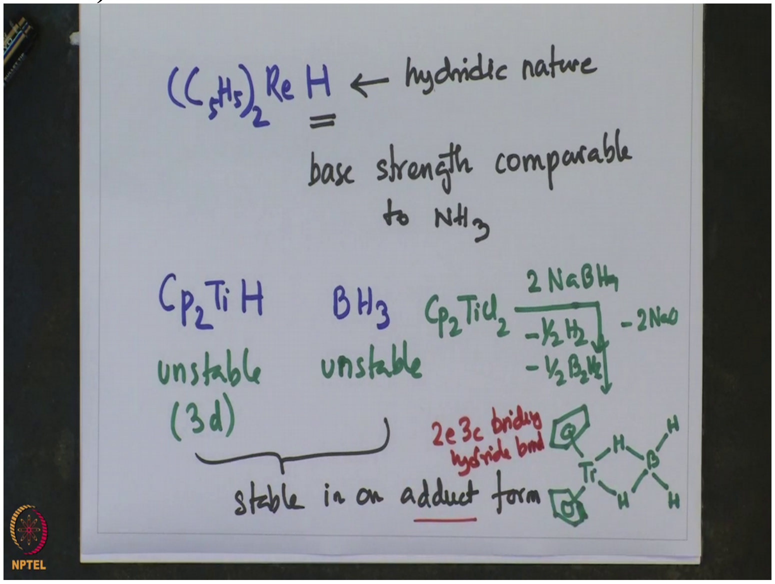
And then we will take up another in this series of half sandwich complexes which is transition metal cyclo pentadienyl halide complexes. Now these are half sandwich complexes they are heterolytic complexes and they offer large reactivity pattern which are kind of unique to them. Now in our continuing with our discussion with transition metal hydride complexes we have in the last class we have looked into their synthesis as well as the reactivity pattern.

And then we have also looked into the characterization of this metal hydride moiety by using NMR as well as IR spectroscopy. Now what we had seen is the that these metal hydride complexes are primarily observed for a 4d and 5d transition metals which are electron rich whereas for 3d transition metals which are electron deficient usually observation of these metal hydride complexes are rare as they are unstable and even if they are formed in situ they eliminate hydrogen to give the dimarize product.

Dimerize product containing two metal center but the hydride moiety eliminates as hydrogen. Now from that perspective the metal hydrides are usually stabilized for more left knowledge 4d and 5d metals where they could be isolated in the monomeric form. Now as a result of this metal hydride moiety being attached to electron rich metals like 4d and 5d the metal hydride moiety is very basic and hydrating in nature and that can be experimental a verified by treatment with acid where these hydrolytic moieties can easily be protonated.

And we had seen reactions to that effect for molybdenum tungsten and rhenium. Now one of the classical metal hydride moiety which have been extensively studied is BCP rhenium hydride.

(Refer Slide Time: 03:42)



$((C_5H_5)_2Re\underline{\underline{H}}$ ← hydridic nature

base strength comparable to NH_3

Cp_2TiH unstable (3d)

BH_3 unstable

$\underbrace{\qquad\qquad}$ stable in an adduct form

$$Cp_2TiCl_2 \xrightarrow[-\frac{1}{2}H_2 \;\; -\frac{1}{2}B_2H_6]{2NaBH_4} -2NaCl$$

2e 3c bridging hydride bond

And we had discussed about the hydrolytic nature of this proton, now this molecule can be easily he protonated it is basic strength is comparable it is highly basic in that say highly hydrolytic in nature and the basic strength is comparable even to a strong base like ammonia. Another interesting thing is the reactivity of these metal hydride and because of the reactivity one can see isolation of very unstable compounds.

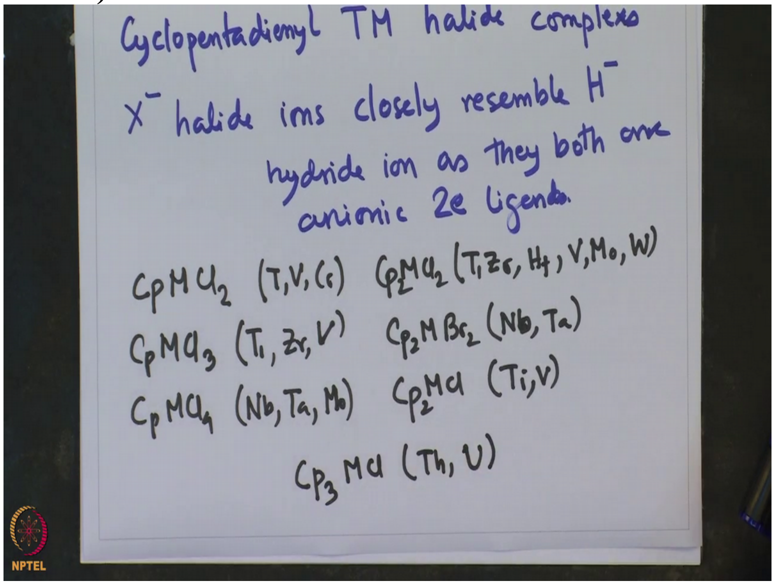
And such an example is for happens is for this 3d metal hydride which of titanium. So, for example CP 2 titanium hydride is unstable and primarily because it is of 3d metal and similarly BH 3 molecule also is unstable however these two molecule combine to make an adduct and they are stable in an adduct form. I am going to illustrate this through the example given over here so CP 2 titanium trichloride in presence of NaBH4 eliminates half hydrogen half B 2 H6 2NaCl to give these titanium PCP hydrogen boron hydrogen hydrogen boron hydrogen which is the titanium boronate.

So, what is remarkable of this reaction is that two entities which is BCB titanium hydride which is the one over here and the BH3 molecules which also is unstable entities get stabilized by this adduct form and when this happens as a result of 3 center 2 electron non-classical bonds electron 3 centered bridging hydride. So, these is an important aspect of transition metal hydride chemistry and what we saw in this nice example that unstable basic cyclopentadienyl titanium hydride which is a hybrid of a 3d metal can even be stabilized in presence of borane BH3 which in its monomeric form is also unstable by formation of an adduct of TI DCP titanium hydride and BH3 through this non-classical to set 3 center 2 electron bridging hydride bond.

So, now this reflects on the beautiful chemistry that can be invoked to stabilize some very unstable species so over here it is as I said that is everything is quite remarkable not only this stabilization of these unstable BCB to titanium hydride but also of this stabilization of this unstable BH 3 and these 2 are stabilized through by a duck formation which again is via a non classical bond which is complete extremely there and something which is not usually observed.

So, the stability is brought about by something which itself is quite rare and remarkable and overall this reaction does weaves an interesting chemistry and demonstration of the fact that some of the very unstable species can be stitched together and stabilized with the help of some remarkable beautiful elegant chemistry a chemical interaction as is found over here. So, with these we are going to finish with our discussion on transition metal cyclopentane hydride complexes and move on to transition cyclopentadienyl transition metal halide complexes.

(Refer Slide Time: 09:56)



Cyclopentadienyl TM halide complexes

X^- halide ions closely resemble H^- hydride ion as they both are anionic 2e ligands.

$CpMCl_2$ (Ti, V, Cr) Cp_2MCl_2 (Ti, Zr, Hf, V, Mo, W)

$CpMCl_3$ (Ti, Zr, V) Cp_2MBr_2 (Nb, Ta)

$CpMCl_4$ (Nb, Ta, Mo) Cp_2MCl (Ti, V)

Cp_3MCl (Th, U)

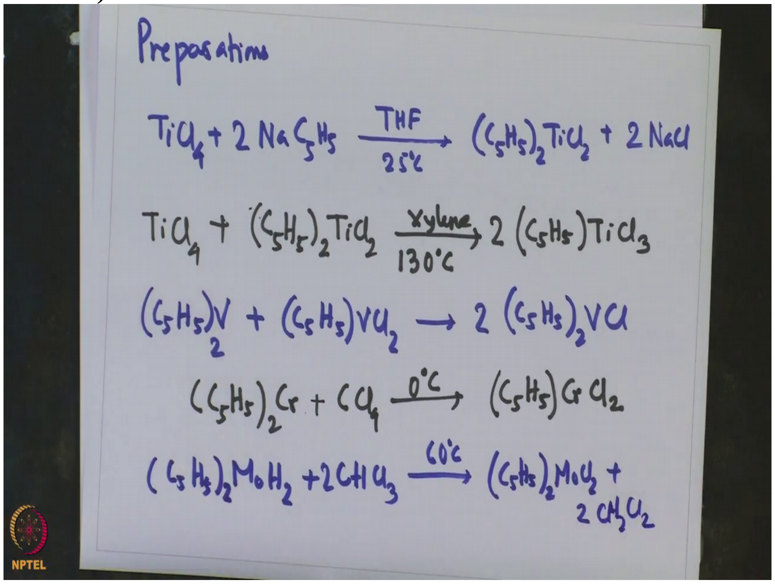
So, this halide as halide ions sort of closely resemble the hydride ions because they are both two anionic 2 electron ligands X - halide ions closely resemble H - hydride ion as they both are an ionic 2 electron ligands. Now these are unlike the transition metal cyclopentadienyl hydride complexes halide complexes are however more common and a large variety of transition metal cyclopentadienyl highlight complexes have been synthesized mainly particularly as a precursor to many other complexes.

So, as a result this halide chemistry has been extensively developed to illustrate this I am going to write out some of the examples of such transition metal cyclopentadiene and halide complexes for example CPM Cl 2 M can be a for titanium, vanadium and chromium okay or CPM Cl 3 again titanium zirconium have vanadium, CPM Cl 4 for niobium tantalum molybdenum then CP 2 MCl 2 for titanium zirconium hafnium vanadium molybdenum tungsten, CP 2 M Br 2 for niobium tantalum and CP 2 M Cl for titanium vanadium also CP 3 M Cl 4 for thorium and uranium.

Now what is evident over here that a large number of transition metal cyclopentadienyl halide complexes can be obtained and they can start of the formula having a single cyclo pentadienyl with different chlorine ligands which can vary from 2, 3, 4 or 4 dicyclopentadiene ligands having 2 or bono or halide ligands as well as for tri cyclopentadienyl transition metal halide complexes where 3 CP's are there and these are usually observed for bulkier or more bigger if block elements.

So, these cyclopentadienyl transition metal halide complexes provide an important foothold for conversion to other type derivatives or transition metal cyclopentadienyl complexes. Now before we look into the reactivity of transition metal cyclopentadienyl halide complexes let me just now briefly go over some of the preparatory methods that are available for preparation of these transition metal cyclopentadienyl halide complexes.

(Refer Slide Time: 14:57)



Preparations

$$TiCl_4 + 2\,NaC_5H_5 \xrightarrow[25^\circ C]{THF} (C_5H_5)_2TiCl_2 + 2\,NaCl$$

$$TiCl_4 + (C_5H_5)_2TiCl_2 \xrightarrow[130^\circ C]{Xylene} 2\,(C_5H_5)TiCl_3$$

$$(C_5H_5)_2V + (C_5H_5)VCl_2 \longrightarrow 2\,(C_5H_5)_2VCl$$

$$((C_5H_5)_2Cr + CCl_4 \xrightarrow{0^\circ C} (C_5H_5)CrCl_2$$

$$(C_5H_5)_2MoH_2 + 2CHCl_3 \xrightarrow{60^\circ C} (C_5H_5)_2MoCl_2 + 2\,CH_2Cl_2$$

Now if one were to look at the strategy used for preparation of this cyclopentadienyl transition metal halide complexes it seems very simple by the fact that these are usually obtained from transition metal halide precursor with cyclopentadienyl reagent. I will illustrate this by the example of TiCl 4 + twice of sodium CP in THF at 25 degree centigrade giving rise to C 5 H 5 whole 2 Ti Cl 2 + twice NaCl. Similarly the reaction of TiCl 4 + B CP C 5 H 5 whole 2 Ti Cl 2 in xylene at 130 degree centigrade will undergo the ligand exchange reaction to give two equivalents to molecules of C 5 H 5 Ti Cl 3.

So, what we would see is that there is a ligand distribution happening from Ti within TiCl 4 and C 5 H 5 whole 2 Ti Cl 2 such that one of the C 5 H 5 and ligand moves over from this molecule on to this and in return one of the chloride ligands move over to this molecule. So, this is a ligand exchange reaction happening over here this there are other examples also of such ligand exchange reaction that occur.

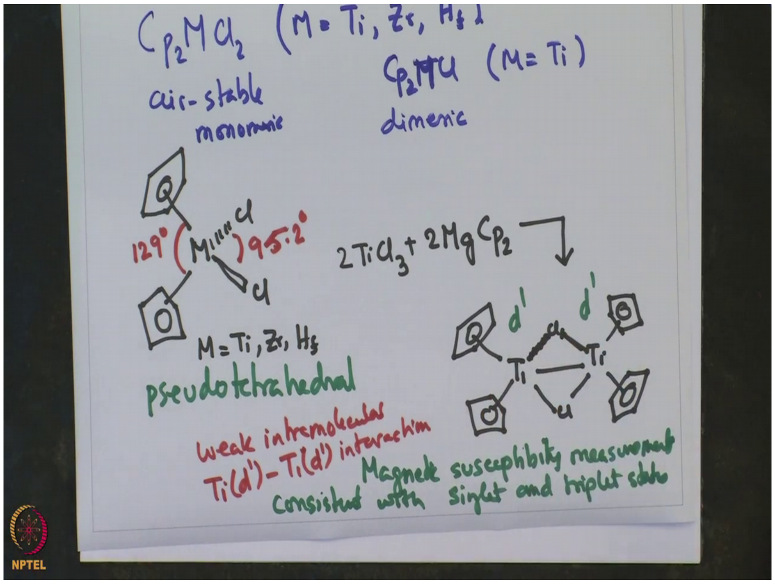
And I am going to give another example of the same for vanadium so here the reaction is between C 5 H 5 whole 2 vanadium + C 5 H 5 VCl 2 vanadium chloride giving to two molecules of C 5 H 5 whole 2 VCl. So, in this case this is vanadium 2 and this is vanadium 4 so not only this is example in which not only this ligand exchange occurred similar to the one over here but also there is a redox chemistry going on over here in which one vanadium two Center reacting with another vanadium 4 center to give rhenium 3 centre vanadium 3 centre in the product.

So, here this is sort of con proportion where vanadium 2 and vanadium 4 giving rise to vanadium 3 along with the corresponding ligand exchange reaction. Another example of this involves reaction of C 5 H 5 whole 2 chromium + CCl 4 at zero degree centigrade give C 5 H 5 chromium chloride. And another example of this preparation is the reaction of C 5 H 5 whole 2 molybdenum hydride + CH 2 CHCl 3 chloroform at 60 degree centigrade giving C 5 H 5 whole 2 M or Cl 2 + 2 molecules of CH dichloromethane CH 2 Cl 2.

So, in the last two source we see that CCl 4 as well as CHCl 3 acting as a chloride source in preparation of these cyclopentadienyl transition metal dihalide complexes. Now with this we sort of see that the relative methods used for preparing this transition metal cyclo pentadienyl halide complexes are also not very many as there are only two or three types of classes of reactions which results in formation of these complexes.

Now we are going to look into the structure and bonding and structure and reactivity of these complexes.

(Refer Slide Time: 20:45)



To begin with we will be looking at complexes of the type this CP CP 2 M Cl 2 M can be titanium, zirconium, hafnium. One of the reasons for starting with these compounds are these are Estoril and also have been structurally characterized. So, these are easy to handle here stable compounds and all of them have been structurally characterized. So, let me just draw the structure of these complexes CP.

So what we see is that this CP are in tilted orientation and the two halides are there the geometry of these complexes are pseudo tetrahedral and the angle at the metal is around 129 degree between the two CP's and 95.2 degree between the two halides and this metal can be a the metal can be a titanium zirconium and hafnium. So, what we see is that even though the dihalide CP M CP M Cl 2 di halide is monomeric CP 2 MC1 3 M = titanium is however dimeric.

Let me just illustrate these and through the synthesis first the; this complex compound is prepared by the reaction of 2Ti Cl 3 + 2 magnesium CP 2 so these a dimeric and that has a bridging a carbonyl. Now the magnet the interesting thing about this compound is that this is paramagnetic with a paramagnetic d1 system. So, there is the magnetic susceptibility measurement shows singlet and triplet states magnetic susceptibility measurements consistent with singlet and triplet states.

So, we suggest and too weak interfering weak interaction so this suggests weak intramolecular titanium t1, titanium d1 interaction so this is kind of a neat example where we saw that when this is halide is a monomeric but in the dimeric when it is mono halide BCP titanium manohalide which is dimeric in nature which will bridging carbonyl and that each of the titanium center is paramagnetic with single electron they can mutually couple and there is interaction going on which can be seen in magnetic susceptibility measurements.

Now with these two I'm going to conclude today's discussion on transition metal cyclopentadienyl halide complexes. Today in particular we have looked into some of the interesting reactivity patterns of transition metal cyclopentadienyl hydride complexes where the unstable at BCP titanium hydride species were stabilized by reacting with BH 3 through another very interesting 3-center 2-electron non-classical bond.

Subsequent to that we have looked into various transition metal cyclopentane halide complexes they are prepared to procedures which are not very many and were mainly a the treatment of metal halide precursors with sodium cyclopentadienyl reagents and ions or some ligand rearrangement or con proportional reactions. We have also looked into the structure of these kind of transition metal halide complexes.

And what we had seen that VCP transition metal dihalide systems are mainly CP tetrahedral whereas when they are three coordinated for example BCP transition metal halide they are demeric in nature we have looked into particular example for titanium and so that they make interesting time Airy compound which has this metal metal d1 and d1 interaction which can be picked up in magnetic susceptibility experiments.

So, with this I would like to conclude today's discussion on transition metal cyclopentadienyl halide complexes we are going to be discussing these half sandwich complexes of transition metal cyclopentane halide in more detail in next lecture and I thank you again for patiently being with me in this talk and I look forward to being with you in the subsequent lecture till then goodbye and thank you