Advanced Transition Metal Organometallic Chemistry

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Lecture – 18
Transition Metal Cyclopentadienyl Hydride Complexes

Welcome to today's lecture on advanced transition metal organometallic chemistry we have been discussing half sandwich complexes of cyclopentadienyl ligand in the last few lectures and in the past the last lecture we have exclusively looked into transition metal cyclo pentadienyl nitrosyl complexes. We have looked into the structure reactivity and the preparation of these complexes and today we are going to finish the little bit of discussion which is left on transition metal cyclo pentadienyl nitrosyl complexes before I take up today's topic which is on transition metal cyclo pentadienyl hydride complexes.

Now if I recapitulate in our past or discussion this transition metal cyclo pentadienyl nitrosyl complexes can exhibit two kinds of binding one can be linear another can be bent this type of bond binding can be easily characterized using x-ray as well as infrared spectroscopy. Now we have looked into several examples in our last lecture where these metal nitrosyl binding have been characterized using x-ray that looked into the metal nitrogen in nitrosyl bond distances as well as metal nitrogen bond angles depending on the binding.

And correspondingly that was also verified or supported by infrared spectroscopic data. Now we have also seen that the nitrosyl when they bind as a 3 up to donor they bind in a linear fashion which results in a very short or metal nitrogen bond and that means that it is a stronger metal hydrogen bond and hence at the infrared new stretching frequency appear at higher wave numbers.

And when the nitrosyl is bound in a bent fashion it uses a single electron hence it is a weaker binding and hence metal nitrogen bond now is longer and as a result the frequency of the new NO is also appear at a lower frequency. Now having said that the next we are going to discuss about a particular interesting example in which people make a chiral compound of half-sandwich transition metal cyclo pentadienyl nitrosyl complexes.

And then they study their configuration retentions are various reactivity under optically active environment.

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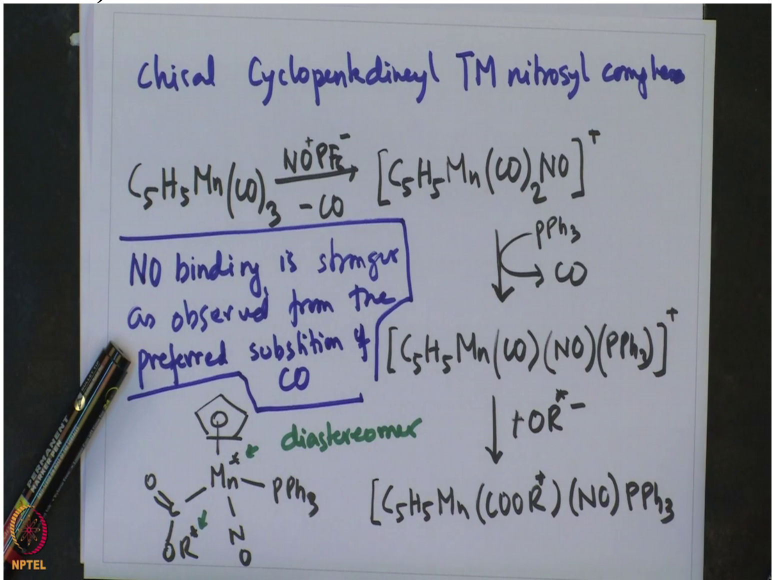

Chiral Cyclopentadienyl TM nitrosyl complexes

$C_5H_5Mn(CO)_3 \xrightarrow[-CO]{\overset{+}{NO}\overset{-}{PF_6}} [C_5H_5Mn(CO)_2NO]^+$

$\downarrow$ PPh$_3$ $\rightarrow$ CO

$[C_5H_5Mn(CO)(NO)(PPh_3)]^+$

$\downarrow$ $+O\overset{*}{R}^-$

$[C_5H_5Mn(CO O\overset{*}{R})(NO)PPh_3$

NO binding is stronger as observed from the preferred substitution of CO

So, we are going to talk about chiral cyclo pentadienyl transition metal nitrosyl complexes, so one can sort of envision that this transition metal is bound to CP and 3 other ligands that secondly again being nitrosyl and the 3rd and the 4th has to be two different ligands one can be carbon monoxide and the other can be phosphine. So, let us take a look at the preparations of these interesting compounds and procedure starts with a sequence of reactions the first obviously a of that sequence is simple preparation for transition metal nitrosyl complexes starting from transition metal carbonyl complexes.

So, the reaction is as follows C5 H5 MN CO3 reacting with NO+ PF6- eliminating a CO to give C5 H5 MN CO2 NO+ now one thing that one needs to see over here is that one of the CO is getting replaced by NO and we had discussed about replacing the CO's by NO’s and in our earlier discussion we had said that if a single CO is replaced by NO then a positive charge is introduced and that is exactly a what this reaction turns out to be.

Another important thing of this particular reaction is that even though we have this notion of carbonyl being very tightly bound to the transition metal because we had ligand metal for donation and metal to ligand powered backward donation but it turns out that the NO can replace a tightly bound CO and make metal nitrosyl complexes. So, well now still C5 H5 MN dicarbonyl nitrosyl is still not a optically active compound.

So, one then further needs to replace one of the CO’s with another ligand and the reaction is done with phosphine with the elimination of another CO. So, in this case the phosphine replaces CO to give this C5 H5 MN CO NO PPh3+ compound now this is optically active compound in a cationic form. Now one also sees an important trend which is emerging over here that in both of the reactions the carbon monoxide carbon monoxides get replaced first by NO.

And when this dicarbonyl nitrosyl is treated with phosphine the nitrosyl does not get replaced but instead another carbon will get replaced to give carbolyn nitrosyl phosphine in compound. So, this is the interesting observation is that that these CO gets replaced by NO first and then by phosphine second to give this optically active cation. So, that then reacts with any chiral nucleophile like our O star -, produces the corresponding acid okay.

So, this sort of is the optically active compound which is some somewhere like Mn star and these this right now is a diastereomer because of two chiral centers this is a diastereomer because of two chiral centers and can be separated using the particular enhanced solubility of one particular diastereomer over other resulting in isolation of chiral compound. So, this is a very interesting technique whereby chiral cyclopentadienyl transition metal nitrosyl complex has been synthesized and then the subsequent isolation of a particular obtain in its optically active form is achieved by making the ester with a chiral ancillary.

And then exploiting the fact that one of the diastereomer is more soluble over the other and like taking advantage of the differential solubility one can then separate this optically active compound, now what this reaction underlines though is the that the stronger binding of NO binding is stronger as observed from the preferred substitution of CO. So, what is important over here is that the phosphine knocks off another carbonyl and not a nitrosyl thereby indicating that NO binds strongly to the metal center.

So, with this we will sort of close our discussion on transition metal nitrosyl complexes and then move on to transition metal cyclo pentadienyl hydride complexes.

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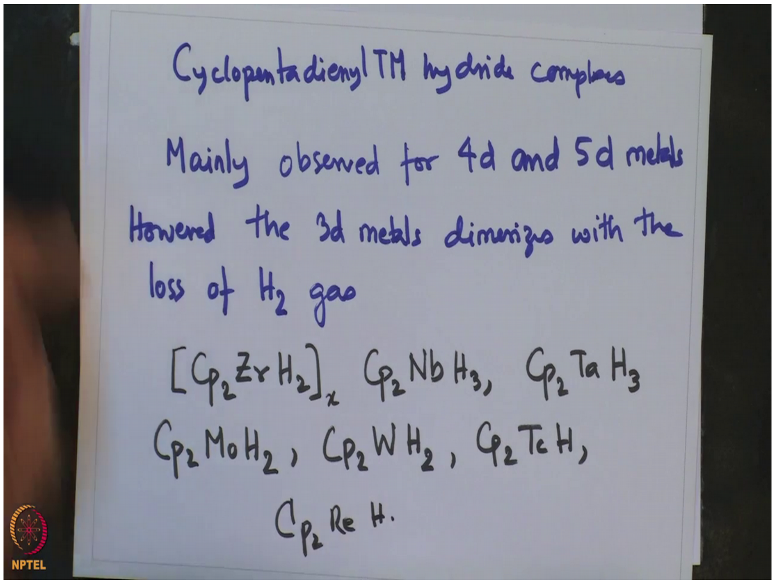

Cyclopentadienyl TM hydride complexes

Mainly observed for 4d and 5d metals

Howered the 3d metals dimerizes with the loss of H_2 gas

$[Cp_2ZrH_2]_x$ Cp_2NbH_3, Cp_2TaH_3

Cp_2MoH_2, Cp_2WH_2, Cp_2TcH,

Cp_2ReH.

So, these are important complexes cyclopentadienyl transition metal hydride complexes these these mainly are observed for 4d and 5d metals and for 3d these are usually a not observed because 3d hydrides are extremely reactive and 3d metals dimerizes with the loss of hydrogen gas. However however the 3d metals dimerizes with the loss of hydrogen gas. So, some of the examples of these complexes are as CP to zirconium ti hydride which sometimes can be in navigated from CP to niobium tri hydride, CP to tantalum tri hydride, CP to molybdenum dihydride, CP to tungsten di hydride, CP to technetium hydride or CP to rhenium hydride.

Now these are transient metal cyclo pentadienyl hydride complexes so many variants of these are known and one of their important services from the fact that they are important catalytic intermediates in many organic catalytic transformations and hence arises interest and have also been extensively studied. So, we are going to look at some of the preparation repetitive methods available for preparing these transition metal hydride complexes.

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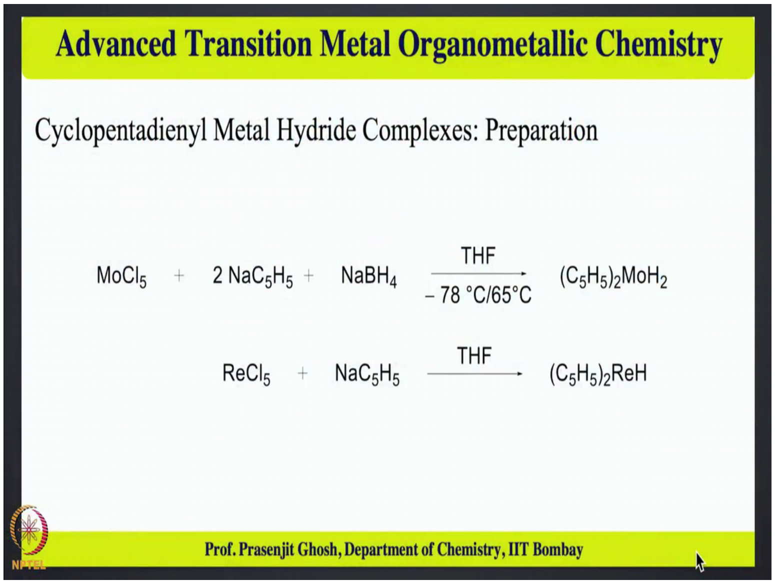

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Cyclopentadienyl Metal Hydride Complexes: Preparation

$$MoCl_5 + 2\,NaC_5H_5 + NaBH_4 \xrightarrow[-78\,°C/65°C]{THF} (C_5H_5)_2MoH_2$$

$$ReCl_5 + NaC_5H_5 \xrightarrow{THF} (C_5H_5)_2ReH$$

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And the simplest of all and the simplest of all involved the reaction of metal halides with some kind of hydride source which are usually Ibero hydrides and also a cyclo pentadienyl source resulting in the formation of this transition metal cyclo pentadienyl hydride compounds.

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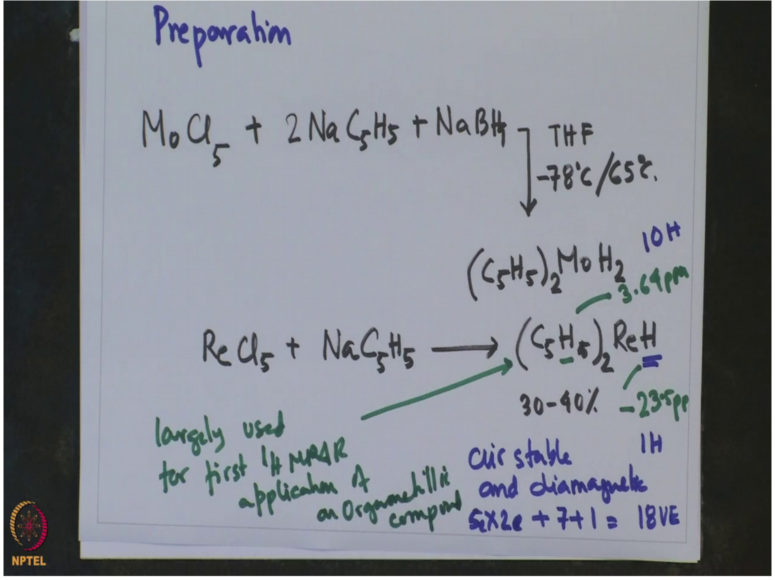

Preparation

$$MoCl_5 + 2\,NaC_5H_5 + NaBH_4 \xrightarrow[-78°C/65°C]{THF} (C_5H_5)_2MoH_2$$

$$ReCl_5 + NaC_5H_5 \longrightarrow (C_5H_5)_2ReH$$

10H

3.64ppm

30-40%

-23.5ppm

1H

largely used for first ¹H NMR application of an Organometallic compound

air stable and diamagnetic

$5\times 2e + 7 + 1 = 18\,VE$

So, for example the reaction of Mo CL5 + 2NaC5H5+ Na BH4 in THF - 78 degree centigrade the reaction the low temperature and then warm up to 65 degree centigrade giving C5 H5 whole 2 Mo H2, similarly the reaction of Re Cl5 + Na C5 H5 giving C5 H5 whole 2 Re H, now this yield is kind of an issue 30 to 40% and the moiety has been characterized in proton NMR where the rhenium hydride appears at -23.5 ppm.

So, it is this metal hydride appearing at highly up filled region which is at -23.5 ppm whereas the this 5 proton of the C5 H5 appearing at 3.64 ppm so the proton the proton NMR are is kind of extremely a informated and it is very simple because it has two peaks the peak at 3.64 which belongs to this C5 H5 appearing as 10 integration ratio 10H whereas the hydride appearing as 1H and another important thing is that CP rhenium hydride however is a stable compound and diamagnetic they are stable and diamagnetic.

As a result these can be very extensively used in applications of ergonomic chemistry in proton NMR spectroscopy. So, technician so the diamagnetic it is from a hitting valence electron rule so 2CP is 5 * 2, 5 electron into 2 + manganese technician rhenium is in the same group 7 + 1 equals 18 valence electron diamagnetic compound and because of this additional stability this compound was largely used for first applique forced proton NMR applications of an organometallic compound.

So, this was studied from that perspective the structural characterization of this compound showed that the CP rings are tilted and they are not parallel to each other unlike what was it observed in case of the metallocene chemistry.

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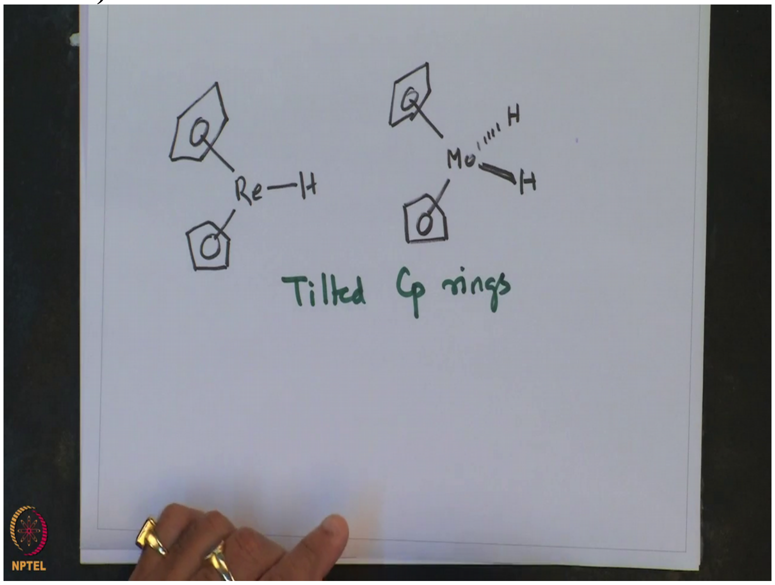

So, let me illustrate that with this diagram so CP rhenium hydride has are CP ring similar to that of the molybdenum complex. Similar to so these have tilted CP rings now another interesting thing about rhenium complexes is the fact that at higher oxidation state they can accommodate a large number of hydrides.

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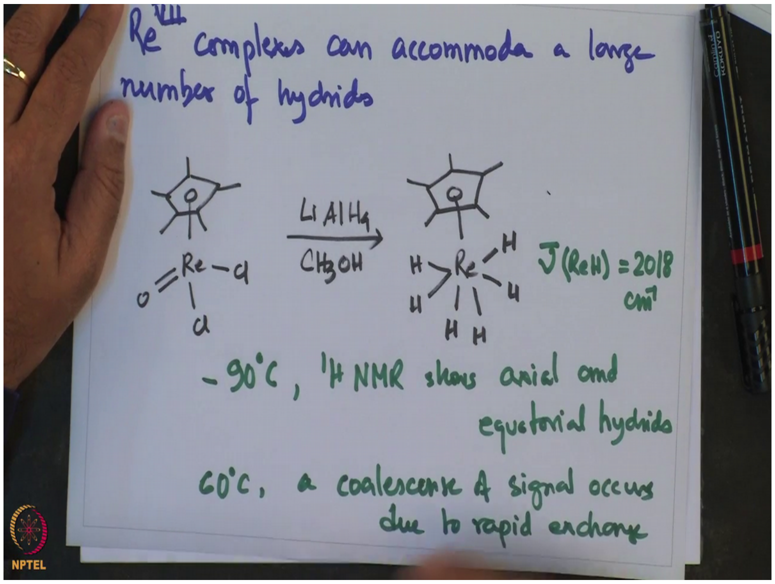

Re^{VII} complexes can accommoda a large number of hydrids

$\xrightarrow[CH_3OH]{LiAlH_4}$

J(ReH) = 2018 cm^{-1}

-90°C, ^1H NMR shows axial and equatorial hydrids

60°C, a coalescence of signal occurs due to rapid exchange

For example rhenium 7 complexes can accommodate number of hydrides, for example this CP star rhenium chloride in presence of lithium aluminum hydride Li AlH4 and methanol produces this rhenium hexahydrate peak and the stretching frequency of this rhenium hydride is 20/18 centimeter inverse. Now these are fluxional molecules so you can see the dynamic exchange between the axial and equatorial hydrogen's.

As a result at a very low temperature 90 degree centigrade rutten NMR shows axial axial and equatorial hydrides whereas at much elevated temperature 60 degree centigrade coalescence of signal occurs due to rapid exchange. Now these shows that NO these hydride exchanges are sort of becomes very rapid at higher temperature and as a result single coalescence happen at higher temperature.

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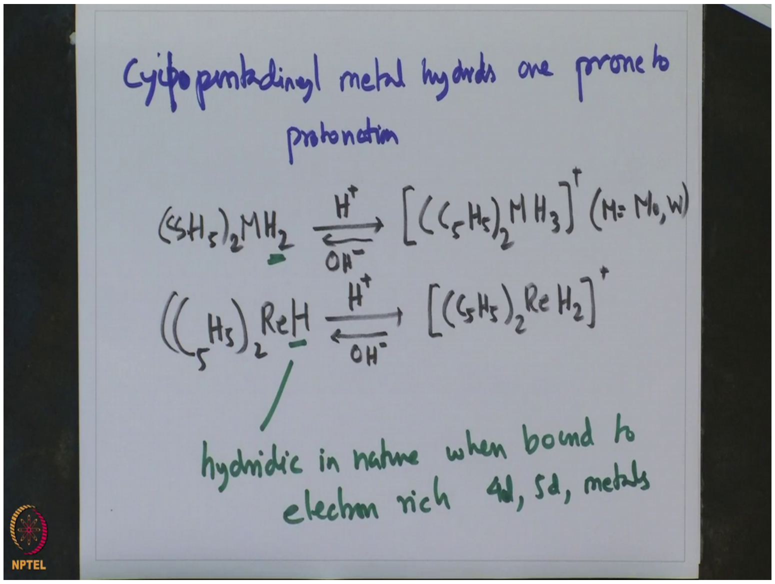

Cyclopentadienyl metal hydrids are prone to protonation

$$(C_5H_5)_2M\underline{H_2} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [(C_5H_5)_2MH_3]^+ \quad (M = Mo, W)$$

$$(C_5H_5)_2Re\underline{H} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [(C_5H_5)_2ReH_2]^+$$

hydridic in nature when bound to electron rich 4d, 5d, metals

Another interesting property of these transition metal rhenium hydrides are their reactivity and these hydrides are generally prone to protonation cyclo penta dienyl metal hydrides are prone to protonation for example these I am illustrating using this C5 H5 whole 2 and H2 in presence of H+ giving C5 H5 whole 2 MH3+ M can be molybdenum tungsten. Similarly C5 H5 whole 2 rhenium hydride can protonate to give C5 H5 whole 2 Re H2+.

Now once protonated they can also be deprotonated by using a base like OH- and the same applies over here. So, what is interesting to see that these hydrides hydrides are very hydrating in nature in nature when bound to electron rich 4d and 5d metals so the electron rich metals make them very hydrating as a result they get protonated easily and these can be observed over here and once protonated they form cations which can be deprotonated using nucleophiles such as hydroxide.

And now with this I would like to conclude my today's lecture on transition metal cyclo pentadienyl hydride complexes. Today in particular we have looked into two as two things we finished up with our little bit of discussion left on the chiral transition metal cyclo pentadienyl nitrous in complexes the formation of the chiral complexes and then took up this topic of transition metal cyclo pentadienyl hydride complexes.

In particular we looked into the various propriety methods which are available for synthesizing these complexes and the method sort of involved direct reaction of metal halides with hydride source and the cyclopentadienyl source to be to form these complexes. Also we have seen that these metal hydride moieties have been can be characterized easily by proton NMR spectroscopy where they apply appear very high filled at -28, 25 ppm.

And we have also looked into the formation of poly hydrides for higher oxidation states of rhenium and lastly we have also looked into the hydrolytic nature of this metal hydrides when bound to 4d or 5d metals and that can be ascertained by simple protonation reactions which protonates this metal hydride complexes. Now with this I conclude today's lecture I thank you again listening to this lecture and we are going to be talking more about transition metal cyclo pentadienyl hydride complexes in the next lecture, till then good bye.