Introduction to Organometallic Chemistry

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Lecture - 14
Metal dihydrogen and hydrides

Although the metal hydride implies that there is only a metal hydrogen bond and not a metal carbon bond, metal hydride chemistry is extremely important in organometallic chemistry. That is because in several organometallic complexes, where there is a metal carbon bond, you might end up with some chemistry that generates a metal hydrogen bond. We will see how this can happen as time go along.

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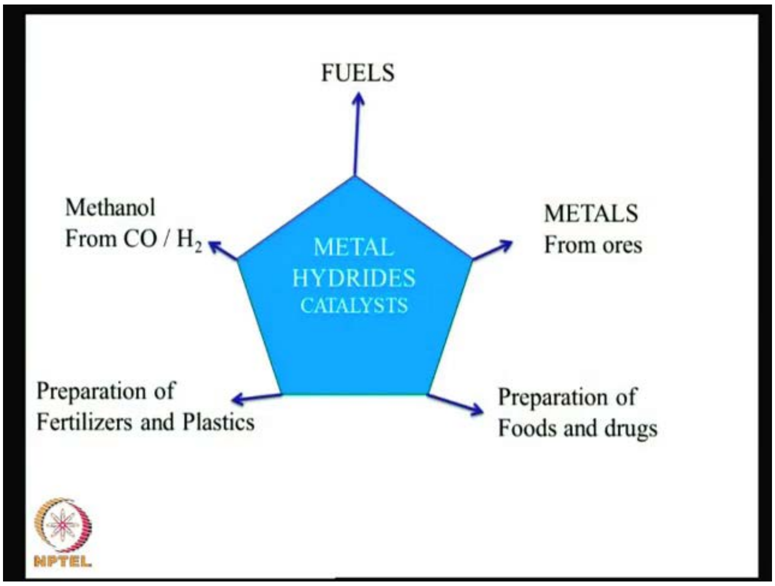

FUELS

Methanol
From CO / H_2

METAL
HYDRIDES
CATALYSTS

METALS
From ores

Preparation of
Fertilizers and Plastics

Preparation of
Foods and drugs

Let us first start with why they are so important, why metal hydrogen complexes are so important. If we look at the industrial chemistry that is going on, you will notice that much of it is oriented towards fuels and metal hydrides. Catalysts containing metal hydrogen bond are in fact key component of the fuel industry. It is possible to make methanol from carbon monoxide and hydrogen. This also requires a use of a metal catalyst that contains a metal hydrogen bond.

So, metal hydrides are important in the fuel industry. Secondly, we notice that in the case of manufacturing fine chemicals, one often uses metal hydrides as catalysts. This is true of bulk chemicals like fertilisers and plastics also. All of them end up using metal hydrides. Another important place where metal hydrides might be involved is in the generation of metals from metal ores. During the reduction of a metal ore from the oxide or the sulphide, it is possible that metal hydrides are intermediates. So, let us take a look at the chemistry and the synthesis of metal hydrides.

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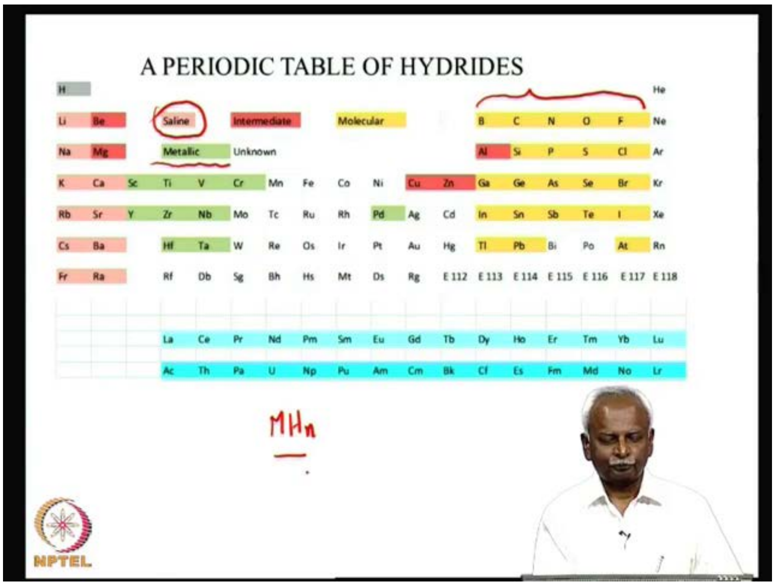

A PERIODIC TABLE OF HYDRIDES

H																	He
Li	Be		Saline		Intermediate			Molecular				B	C	N	O	F	Ne
Na	Mg		Metallic		Unknown							Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	E 112	E 113	E 114	E 115	E 116	E 117	E 118
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

MH_n

If you look at the periodic table and look at all the metal hydride complexes, you will notice that there is a distinct gradation in the properties of metal hydrides that are formed. There are some metal hydrides, which are formed by alkali and alkaline earth metals, which are on the left side of the periodic table. These are marked in pink. You will notice that they are marked as saline. They are marked as salt like metal hydrides. These are salt like metal hydrides. These salts like metal hydrides imply that they will react with water and generate hydrogen. So, the type of chemistry that you have here is that of H minus and M plus.

There are other metal hydrides or hydride compounds, which are completely molecular. These are on the extreme right side of the periodic table. These are marked in yellow. So, these are molecular metal hydrides with an exception of aluminium, which we can understand readily as being an intermediate metal hydride. This is because you have both covalent character and also a little bit of ionic character. But, other than that, most of the hydrides on the right side of the periodic table are covalent metal hydrides, hydrogen compounds such as methane ammonia water phosphine and so on. So, these are extremely covalent. They will not ionize in water as H minus or H plus.

On the other hand, the group of transition metals, which lie in the in between these two extremes are compounds, which may not form sometimes only metal hydrogen compounds. There are some which form metallic hydrides, which means that after the hydrogen compound is formed with just M H n. So, we are talking about species, which form only M H n. These species are completely metallic. So, they are marked in green. That is what we have here on my left, on the left side of the periodic table. These are marked as metallic.

Now, what is left in white corresponding to ruthenium iron cobalt etcetera? They are either complexes, which form alloys or species, which are not definite compositions. So, they are left as unknown hydrides. So, practically the whole periodic table, all the elements in the periodic table can be converted into hydrides or hydrogen containing compounds. Their chemistry has been extremely well studied.

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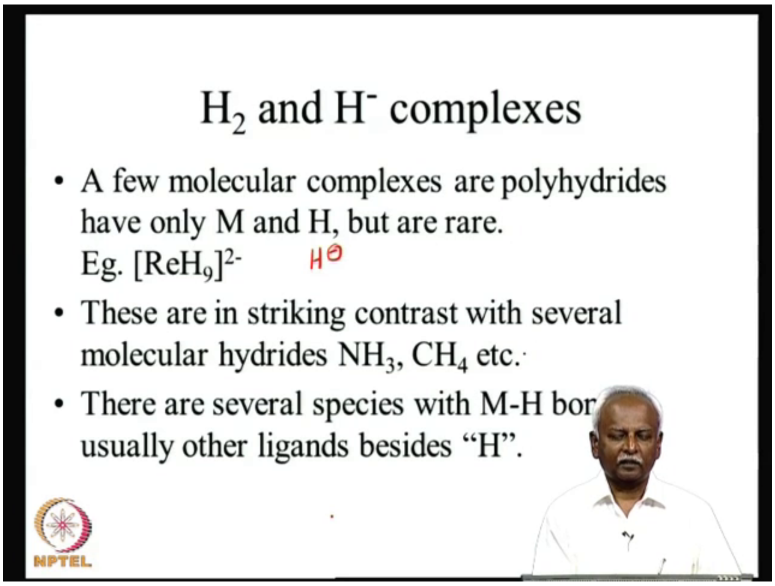

H_2 and H^- complexes

- A few molecular complexes are polyhydrides have only M and H, but are rare.
  Eg. $[ReH_9]^{2-}$ $H^{\ominus}$
- These are in striking contrast with several molecular hydrides NH_3, CH_4 etc.
- There are several species with M-H bor
  usually other ligands besides "H".

So, these are as I mentioned hydride complexes, they are usually called hydrides. They are in striking contrast with several molecular hydrides like covalent hydrides like ammonia methane etcetera. Metal hydrides are usually those compounds which have other ligands as well apart from hydrogen. The few complexes of transition metals with hydrogen and hydrogen only where there is only hydrogen as a ligand are few and rare.

But, nevertheless, they are present. One example, one very interesting example is that of Re H 9, 2 minus. You will notice that rhenium is; if hydrogen is acting as H minus, then rhenium is in the plus 7 oxidation state that is a maximum oxidation state. That one can think of for a group 7 or a rhenium metal. It is interesting that it forms a poly hydride like that.

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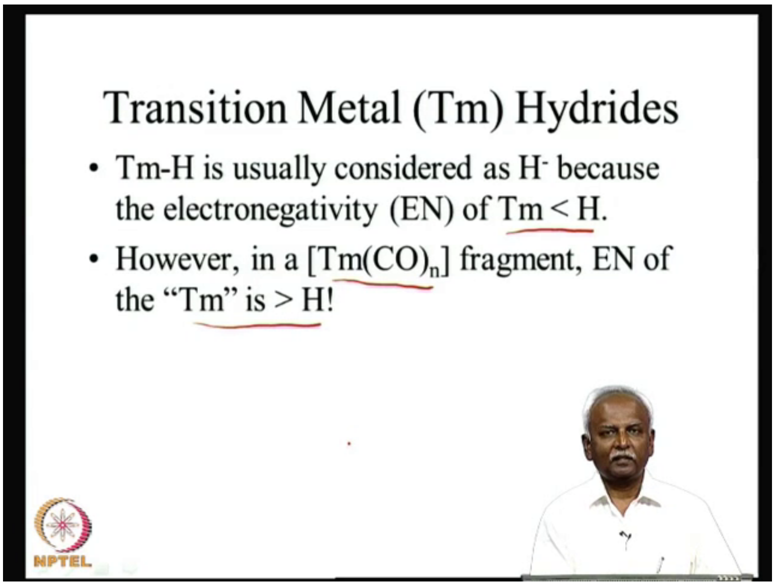

Transition Metal (Tm) Hydrides

- Tm-H is usually considered as H^- because the electronegativity (EN) of Tm < H.
- However, in a $[Tm(CO)_n]$ fragment, EN of the "Tm" is > H!

Usually transition metal hydrides are considered hydrides because the electro negativity of the transition metal is less than that of the hydrogen. Now, it is difficult to assign electro negativity to complexes because once you have a complex and you have several other ligands, the electro negativity of the fragment has to be considered. In this particular instance, if I write a metal carbonyl, the metal carbonyl fragment might have an electro negativity that is different from that of the transition metal itself.

So, we are talking about the ability of the fragment to pull electrons to it when it is bonded to another element. So, if you look at T m CO n, which is the species, which is pictured here, then the ability of the transition metal in this fragment to pull electrons to itself might be greater than that of hydrogen. So, if this is the case, then we have a problem. In the free state as a transition metal, its electro negativity was less than that of hydrogen. So, we called it a hydride meaning hydrogen will pull electrons to itself.

In a complex containing T m H, the hydrogen will behave as a hydride. When it is in this situation where you have a carbon monoxide, which has increased the electro negativity of the transition metal, transition metal hydride might not be real hydride.

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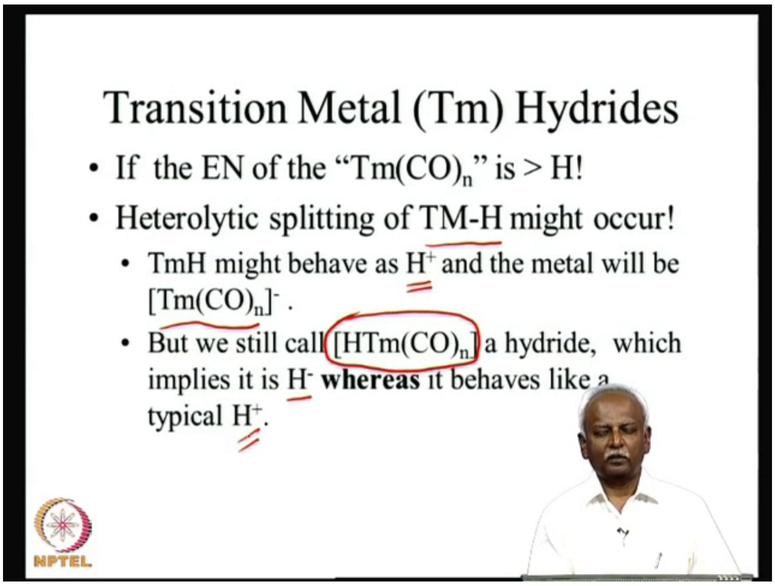

Transition Metal (Tm) Hydrides

- If the EN of the "$Tm(CO)_n$" is > H!
- Heterolytic splitting of TM-H might occur!
  - TmH might behave as H^+ and the metal will be $[Tm(CO)_n]^-$.
  - But we still call $[HTm(CO)_n]$ a hydride, which implies it is H^- **whereas** it behaves like a typical H^+.

So, if T m CO n has got an electro negativity greater than hydrogen, heterolytic splitting of T M H might occur, by which we mean that T m H might now behave as H plus and T m CO n minus. The negative charge would be stabilised by the transition metal CO fragment, the carbonyl fragment. So, H might behave more like a proton.

So, this will create some confusion because we call all metal hydrogen containing compounds metal hydrides. It implies that it is an H minus, whereas in the complex that we have synthesized which is H T m CO n, H T m CO n, the hydrogen is behaving as a typical proton. So, this is something that can lead to a confusion because the chemistry implies that hydrogen is H plus in the complex, whereas in the nomenclature we refer to it as a hydride.

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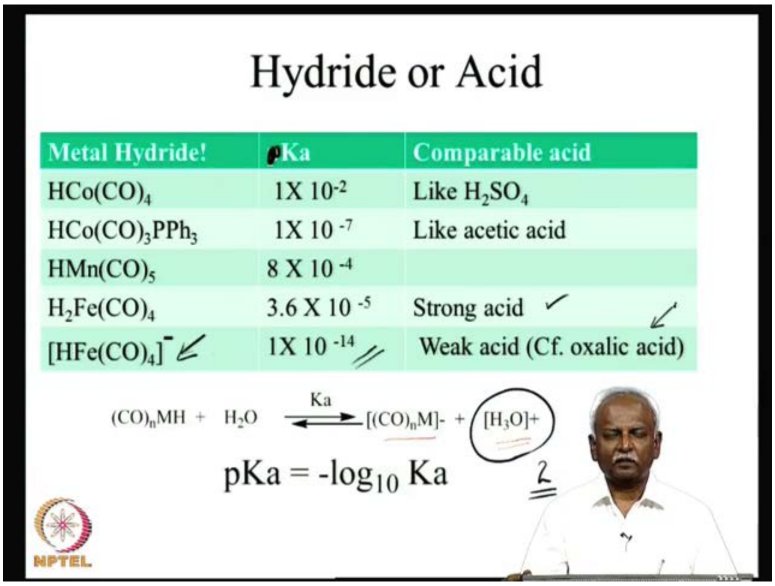

Hydride or Acid

Metal Hydride!	~~p~~Ka	Comparable acid
$HCo(CO)_4$	1X 10^{-2}	Like H_2SO_4
$HCo(CO)_3PPh_3$	1X 10^{-7}	Like acetic acid
$HMn(CO)_5$	8 X 10^{-4}	
$H_2Fe(CO)_4$	3.6 X 10^{-5}	Strong acid ✓
$[HFe(CO)_4]^-$	1X 10^{-14}	Weak acid (Cf. oxalic acid)

$$(CO)_nMH + H_2O \overset{Ka}{\rightleftharpoons} [(CO)_nM]^- + [H_3O]^+$$

$$pKa = -\log_{10} Ka$$

2

So, here is an example of a few compounds, which are formed by hydrogen. These are all metal carbonyl containing complexes. The situation that I have just described to you is very easy to follow. HCOCO4 is a hydrido complex of a cobalt carbonyl complex. Cobalt has got 4 carbon monoxides. It can stabilise the negative charge. As a result, if you dissolve HCOCO4 in water, you will end up with COCO4 minus which is there on the right side. A proton would be generated in the aqueous medium, which means that it is really an acid.

Here, I have listed for you the equilibrium constants. This is not p Ka. So, we will strike off. This is the Ka which is listed here. You will notice that the Ka of HCOCO4 is 10 to the power of minus 2, which is almost like that of sulphuric acid. So, you will have a large amount of protons in solution when you dissolve HCOCO4 in water. So, p Ka is actually the minus log 10 Ka. So, p Ka of HCOCO4 would be equivalent to 2. So, the first compound would have a p Ka of 2. So, it is a very strong acid. You will notice that when we replace one of the carbon monoxides with a triphenyl phosphine.

What we have done is we have reduced the capacity of the transition metal cobalt in this case to accept electron density. That in turn reduces the effectiveness of cobalt in pulling electrons towards itself and in turn the effectiveness with which it will release H plus in solution. So, what happens is the equilibrium constant has a smaller value, 10 power minus 7. It behaves as a weak acid. So, just by replacing carbon monoxide with triphenyl phosphine, we have reduced the acetic nature of this metal hydride species. It behaves like acetic acid, whereas the HCOCO4 was a strong acid.

Now, this is a common phenomenon. You can experience this with many metal carbonyl complexes, which have hydrides. The hydrogen will behave as an acid when you have only carbon monoxide. When you replace carbon monoxide with poorer pi acceptors, then it will behave as a weaker acid.

Now, let us proceed. Let us take another example H 2 F e CO4. This is an extremely strong acid. There are 2hydrogens attached to the iron. It will ionise to give you H3O plus in solution, but when it ionises, it leaves behind H F e CO4 minus the species, which we have listed as a second compound here as the last compound in this table. So, H 2 F e CO4 will ionise like a strong acid. The second ionisation constant just as in the case of oxalic acid; the second ionisation constant turns out to be a very small number.

In other words, it does not dissociate very readily. You have a small Ka. In turn, the p Ka would be close to 14. So, the p Ka of this compound, which is listed last in this table, is going to be something like 14. This means it is a very weak acid. This is exactly what happens in organic acids also. I have written here confer oxalic acid because that is this acid where the second ionisation constant is much lower. It ionises to lower extent compared to the first ionisation.

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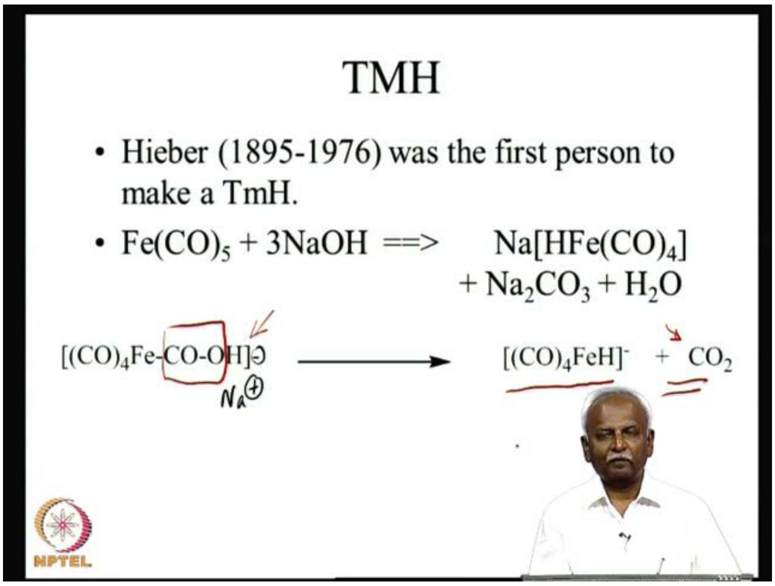

TMH

- Hieber (1895-1976) was the first person to make a TmH.
- $Fe(CO)_5 + 3NaOH \Longrightarrow Na[HFe(CO)_4] + Na_2CO_3 + H_2O$

$$[(CO)_4Fe\text{-}\boxed{CO\text{-}O}H]^{\ominus} \; Na^{\oplus} \longrightarrow \underline{[(CO)_4FeH]^-} + \underline{\underline{CO_2}}$$

So, the chemistry of transmission metal hydride is a bit confusing because it is something that we call as a hydride. It behaves like an acid in solution. So, Hieber was the first person. In fact, he discovered it way back in the early 1900s and he made transition metal hydrides and metal hydrogen complexes. He in fact was studying the reaction of sodium hydroxide with iron penta carbonyl. During the course of this reaction, he made a compound which is Na H F e CO4.

Now, you will notice that the essential reaction in this particular case is that sodium hydroxide. The OH minus has reacted with carbon monoxide. It has formed an anionic compound. You have this anion and N a plus. So, this sodium salt is formed by Na OH reacting with F e CO5. OH minus attacks one of the carbon monoxides and generates the sodium salt, which can now decompose. This is because you have the elements of carbon dioxide in this compound.

If you eliminate carbon dioxide, what you end up with is a hydrido complex H F e CO4 minus. Notice that OH minus attacked the carbon monoxide. So, the net charge on this compound would be minus 1. After you eliminate a neutral carbon dioxide molecule, you will be left with a hydrido complex, which will be negatively charged.

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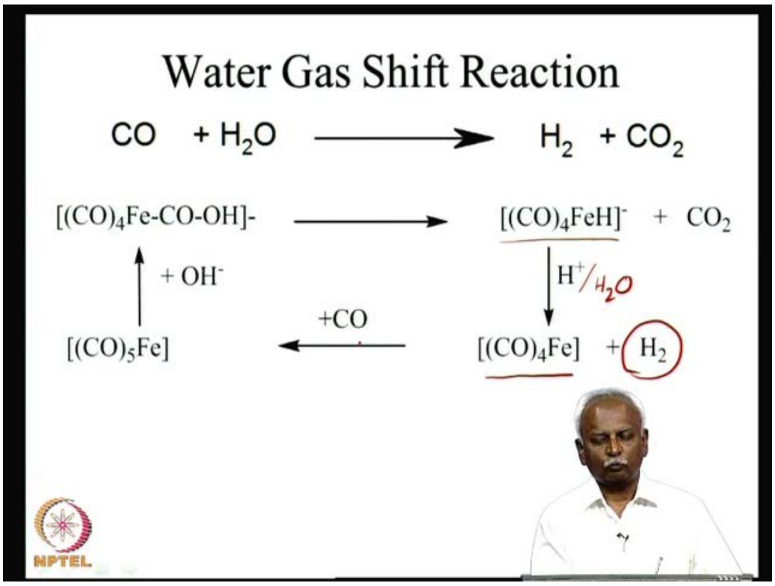

Water Gas Shift Reaction

$CO + H_2O \longrightarrow H_2 + CO_2$

$[(CO)_4Fe\text{-}CO\text{-}OH]^- \longrightarrow [(CO)_4FeH]^- + CO_2$

$+ OH^-$

H^+/H_2O

$+CO$

$[(CO)_5Fe]$

$[(CO)_4Fe] + H_2$

So, this chemistry is in fact reminiscent of what happens in the water gas shift reaction. The water gas shift reaction, which is an extremely industrial process, is used to generate hydrogen from water using carbon monoxide as a reductant. It is something that can be written in this fashion CO plus H2O to give H2 and CO2.

If you recollect the reaction of OH minus in water results in the conversion of the net conversion of carbon monoxide to CO2 F e COOH minus. It was he species that we generated by reacting a carbon monoxide on the iron coordination sphere with OH minus. In fact, this is F e CO5 reacting with OH minus to give the anionic salt. The anionic salt now decomposes to give you the hydride. If this hydride reacts with proton in water, this is H plus in water. Then, what would happen is it would lead to the generation of dihydrogen or hydrogen molecule and F e CO4 as a neutral species.

This is because we react an anionic species with a cation proton. As a result, we will eliminate a neutral water molecule. This results in the formation of F e CO4. F e CO4 is a 16 electron species. It will grab carbon monoxide from the atmosphere in the reaction medium and form F e CO5 again. So, you can write a catalytic cycle, which involves F e CO5, water and carbon monoxide. F e CO5 is a catalyst. It converts carbon monoxide and water to carbon dioxide and di hydrogen. So, this is basically how the water gas shift reaction might be happening.

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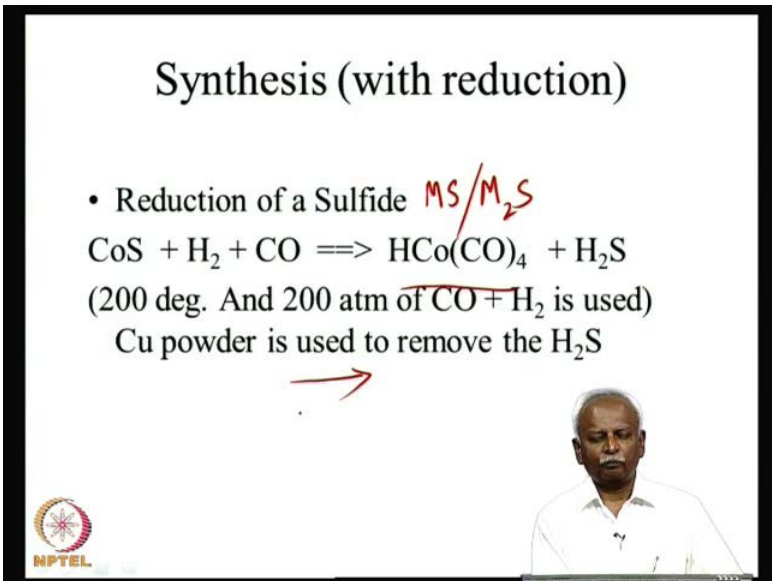

Synthesis (with reduction)

- Reduction of a Sulfide MS/M_2S

$CoS + H_2 + CO$ ==> $HCo(CO)_4 + H_2S$

(200 deg. And 200 atm of CO + H_2 is used)

Cu powder is used to remove the H_2S

So, let us take a look at some of the general methods by which we can synthesise transition metal hydrides. The synthesis of metal carbonyl complexes involves taking metal in its higher oxidation state and reducing it with some reductant. In the case of metal hydrides, you often encounter very similar chemistry. You can start with a metal sulphide. So, you can start with MS or M2S depending on the oxidation state of the metal. You can reduce it with hydrogen in the presence of carbon monoxide. Then, you form very nice hydrido carbonyl complexes.

In this particular instance, you liberate a molecule of H2S hydrogen sulphide. The reaction has to be carried out at a higher temperature 200 degrees Celsius and 200 atmospheres of pressure of hydrogen and carbon monoxide. You liberate hydrogen sulphide. It is convenient to push the reaction to the right hand side of this equilibrium. You have to add copper powder, so that the hydrogen sulphide is completely absorbed the copper to form copper sulphide. So, this is a convenient way of making hydrido carbonyl complexes.

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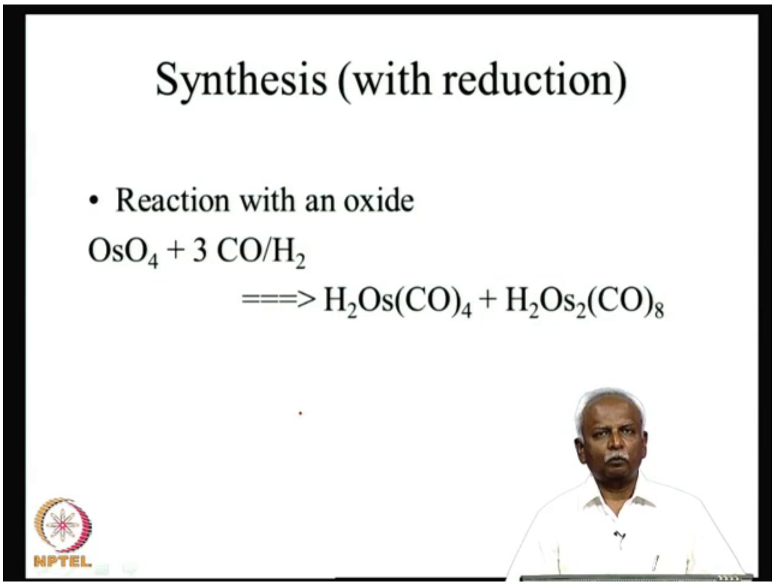

Synthesis (with reduction)

- Reaction with an oxide

$OsO_4 + 3\ CO/H_2$

$\Longrightarrow H_2Os(CO)_4 + H_2Os_2(CO)_8$

Hydrogen can also reduce oxides. This is what we refer to in the beginning of this lecture when we said that to form pure metals from ores. One very often uses hydrogen gas. So, if you can take osmium tetroxide and reduce it with carbon monoxide and hydrogen, one can generate a hydrido osmium carbonyl complex. Here, I have pictured 2 complexes that are formed as a result of this reduction reaction. You can form hydrido osmium complexes, both di nuclear and mono nuclear species.

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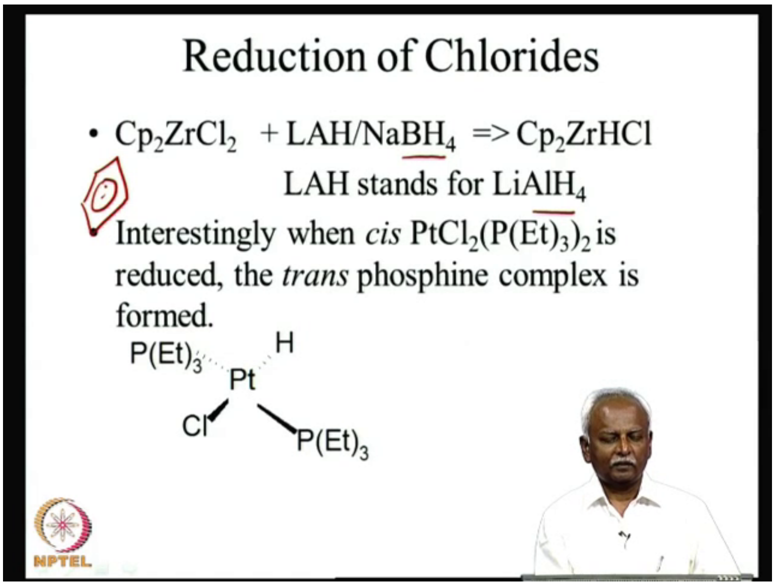

Reduction of Chlorides

- Cp_2ZrCl_2 + LAH/NaBH$_4$ => Cp_2ZrHCl

  LAH stands for LiAlH$_4$
- Interestingly when *cis* $PtCl_2(P(Et)_3)_2$ is reduced, the *trans* phosphine complex is formed.

Apart from oxides and sulphides, one can also start with chlorides. In the case of chlorides, very often early transition metal hydrides or saline hydrides can be used. I have shown for you 2 possibilities; either the use of lithium aluminium hydride. Lithium aluminium hydride is Li Al H 4. So, this is essentially an aluminium hydride or sodium borohydride. That is BH4 minus is a reductant. So, either BH4 minus or AlH4 minus are used as reductants to reduce Cp2 Z r Cl2.

In this instance, what we have here is cyclopentadienyl compound where C p in fact stands for cyclopentadienyl anion. 2 of them are there in the zirconium. The chlorides are reduced to hydrogen. So, this can be carried out with fairly easy laboratory methods. You can convert the chloro compounds into the hydride. Interestingly, if you take cis platinum complex, cis chloro platinum complex and reduce it, you end up with Trans platinum compound during the reduction.

Now, we will talk about what happens with hydrogen and its bonding in a few minutes. This is one of the few instances where a ligand has only sigma bonding interactions, whereas most other ligands that we encounter in coordination chemistry and in organometallic chemistry, there are pi interactions which are present. They are either very strong pi interactions or weak pi interactions. But, nevertheless, they are there. In the case of hydride of course, you do not have the possibility of having a pi type orbital on hydrogen. So, only sigma interactions are present.

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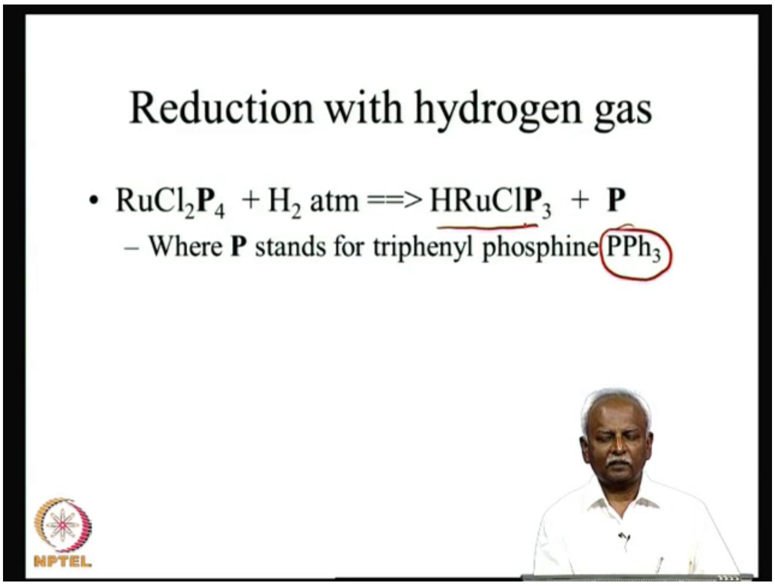

Reduction with hydrogen gas

- $RuCl_2\mathbf{P}_4$ + H_2 atm ==> $HRuCl\mathbf{P}_3$ + **P**
  - Where **P** stands for triphenyl phosphine PPh_3

Reduction with hydrogen gas of chloro compounds can be carried out in group 8 metals especially the ruthenium group. They are readily reduced with dihydrogen. We know this chemistry from Wilkinson. Here, we have generated H R u C l P tris triphenyl phosphine. Complex P actually stands for triphenyl phosphine. So, if you can reduce the tetra case triphenyl phosphine complex with hydrogen, you end up with this very interesting very valuable ruthenium complex, which is something that we will encounter later on when we study the chemistry of hydrides.

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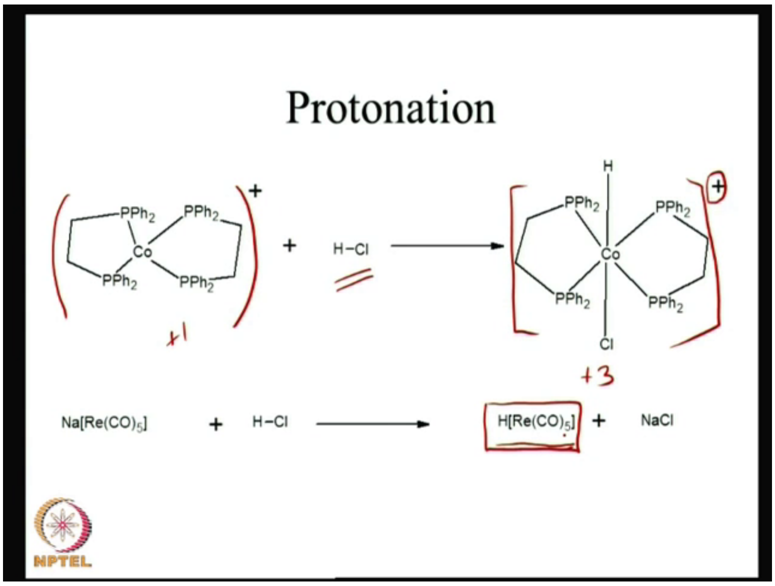

Protonation

Na[Re(CO)$_5$] + H–Cl ⟶ H[Re(CO)$_5$] + NaCl

So, interestingly up to this point, I have talked to you about the use of hydrides and the use of di hydrogen for reducing. There is also this possibility of adding a proton. This should not surprise us because when we talked about metal carbonyls metal hydrides, what are so called metal hydrides carbonyl compounds, released protons h plus.

So, if you take a cobalt complex, which I have written for you here and net charge on this cobalt complex is there is a plus charge on this cobalt complex. This tetra coordinated phosphine complex of cobalt 1, we can protonate it with H plus. It generates a 5 coordinate species, which grabs the C l minus. It now forms an octahedral complex of cobalt with a net charge of plus 1.

So, if you consider the hydrogen as a hydridic species, then you will realise that we have changed the oxidation state of cobalt from plus 1 in this instance to plus 3 in this on the left hand side. These are reactions, which are easy to carry out in the laboratory and have been extensively studied in the recent past. I will come to that towards the end of this lecture. Now, it is also possible to take the sodium salt of carbonyl compounds. In this particular instance, I have pictured for you a sodium pent carbonyl rhenium compound. So, this is actually R e CO5 minus. It can be reacted with hydrochloric acid to generate H R e CO5.

So, if you remember your manganese chemistry, rhenium is in the same group as manganese. You can recollect that H M n CO5 was behaving as an acid. It will liberate H plus. Here is a reaction where we have used sodium salt of the carbonyl anion and protonated it in order to generate H R e CO5. So, this chemistry should not surprise us that we are using an acid to generate a hydridic. So, it is called hydridic complex. The hydridic complex in fact is formed in the reaction, which requires an acid H plus.

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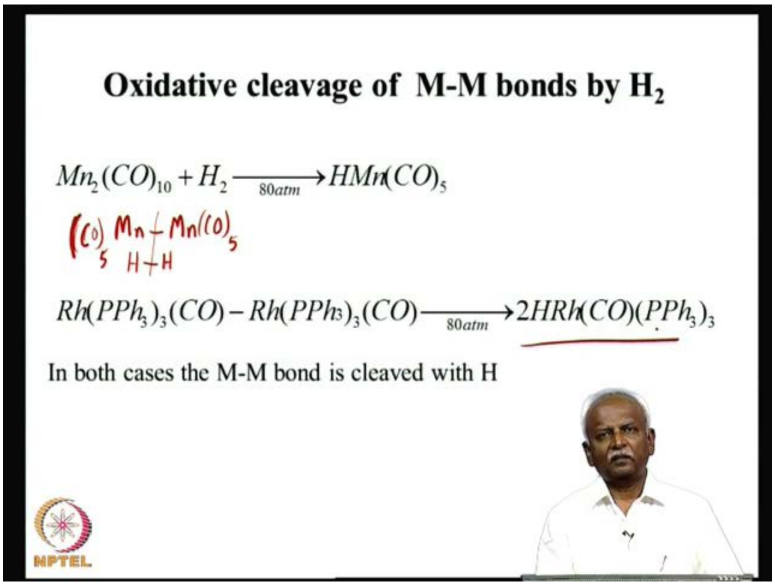

Oxidative cleavage of M-M bonds by H_2

$Mn_2(CO)_{10} + H_2 \xrightarrow[80atm]{} HMn(CO)_5$

$(CO)_5 Mn + Mn(CO)_5$
$H + H$

$Rh(PPh_3)_3(CO) - Rh(PPh_3)_3(CO) \xrightarrow[80atm]{} 2HRh(CO)(PPh_3)_3$

In both cases the M-M bond is cleaved with H

So, it is also possible for us to cleave metal metal bonds. As I had mentioned metal metal bonds in carbonyl chemistry can be cleaved very easily with hydrogen. In this example, M n 2 CO10, which is a decacarbonyl complex of dimanaganese, is reduced with H2 that is dihydrogen to generate H M n CO5. If you remember, we made H R e CO5, which is the analogue.

Now, we are making H M n CO5 by cleaving the manganese manganese bond. Manganese 2, 2 CO10 is actually a combination of 2 CO 5 M n species. So, there are 5 carbon monoxides on each manganese. There is M n single bond. So, this a single bond between 2 manganese atoms. If you wish, you can write H2 below that and see how heterolysis splitting or homolytic splitting of these 2 bonds can generate H M n CO5 very easily.

A similar reaction is pictured here with a cobalt analogue of carbon monoxide complex. Here also the rhodium rhodium bond is broken. H R h CO complex is formed. So, the metal metal bond is easy to cleave. The formation of a metal hydride, which is also forming a strong bond leads to the synthesis of these complexes.

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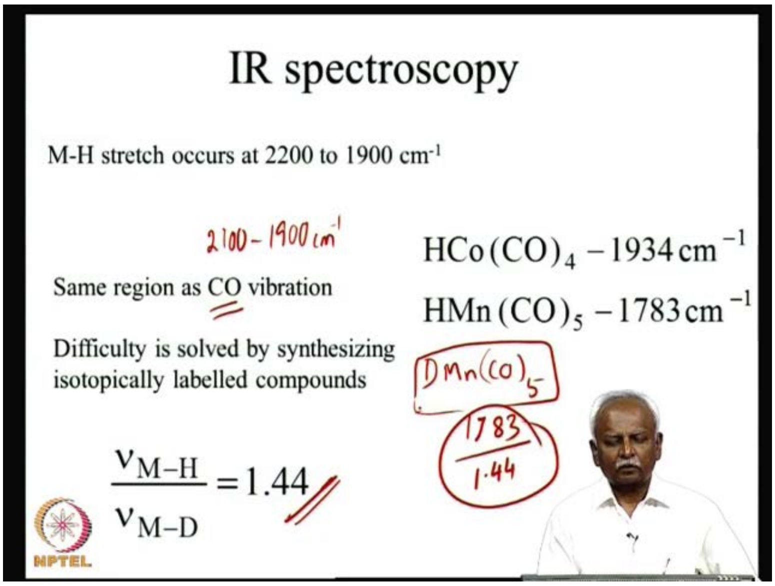

IR spectroscopy

M-H stretch occurs at 2200 to 1900 cm^{-1}

$2100 - 1900\ cm^{-1}$

Same region as CO vibration

Difficulty is solved by synthesizing isotopically labelled compounds

$$\frac{\nu_{M-H}}{\nu_{M-D}} = 1.44$$

$HCo(CO)_4 - 1934\ cm^{-1}$

$HMn(CO)_5 - 1783\ cm^{-1}$

$DMn(CO)_5$

$\frac{1783}{1.44}$

Having considered the synthesis of these complexes, let us talk a little about how one can characterise these species. Metal hydrides are often characterised by carrying out infrared spectra on these species. They have characteristic stretches. MH stretch occurs around 2200 to 1900 centimetres minus 1. So, the CH stretch usually comes around 3000 centimetre minus 1. This is because the metal is heavier. Now, you have a shift to the lower wave numbers. You are going to 2200 centimetre minus 1.

So, this stretching frequency is very diagnostic of the formation of a carbonyl species. It is dependent on the other ligand, which are present on the metal species. Unfortunately, this stretching frequency is occurring at a region where the carbon monoxide itself absorbs. If you remember free carbon monoxide is 2143 centimetre minus 1, metal carbonyls range all the way from 2100 to 1900 centimetre minus 1. So, you have a conflict between the metal carbonyl metal hydride stretch and the CO stretch in a metal hydrido carbonyl complex.

But, nevertheless, it is easy to distinguish the 2 by a simple substitution of the hydrogen with a deuterium. If one does that because deuterium is heavier, the reduced mass of the species changes. You have approximately a change of stretching frequency, which is in the ball park of 1.44. The ratio between new MH and new MD is 1.44. So, as a result if you substitute H M n CO5 with a deuterium D M n CO5, we will have a stretching frequency. It is 1783 divided by 1.44. So, this would be the range at which the stretching frequency occurs if we make the D M n CO5 complex.

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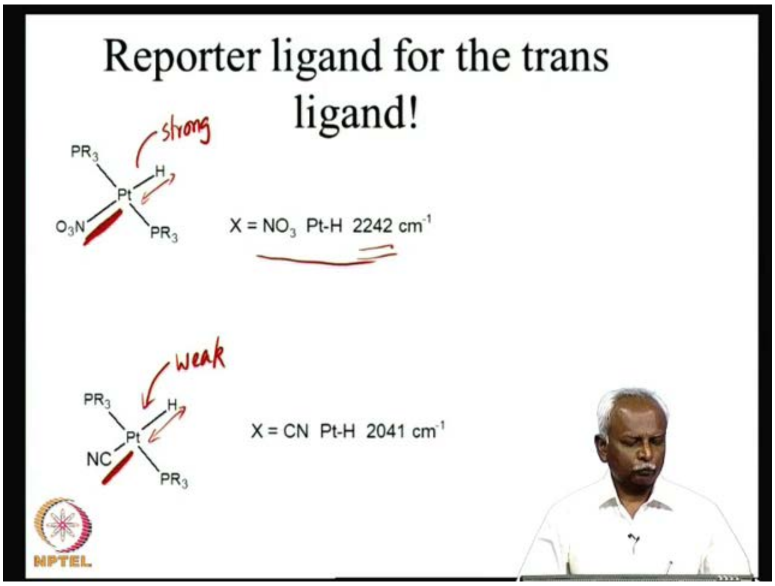

Reporter ligand for the trans ligand!

X = NO_3 Pt-H 2242 cm^{-1}

X = CN Pt-H 2041 cm^{-1}

So, it is easy to use infrared spectra as a diagnostic tool and very often metal hydrogen spectra, metal hydrogen frequencies are readily observed. This is because it is in a region where other species do not vibrate and except in the case of metal carbonyls. Then, you would have to use some another diagnostic tool. So, here I have shown you 2 metal hydrides. In one case, it is a cyano group, which is Trans to the hydride. Here is the metal hydrogen, which would have a stretch of 2041 centimetre minus 1

If you have a nitro group, then the metal hydrogen stretch goes up to 2242 centimetre minus 1. Now, what is going on here? Why is the frequency changing drastically? When you replace a nitro group with a cyano group, we know very well that cyanide is a great pi acceptor. So, the bonding between platinum and CN group here is extremely strong, whereas the nitro group is only a pi donor. It is a weak ligand. So, the strong ligand in fact weakens the Trans bond.

So, this bond is weak. This bond is much stronger. So, the metal hydrogen when it is strong will have a frequency; will require greater energy obviously to stretch that bond. You have a stretching frequency, which is close to 200 centimetres minus 1 greater in the nitro complex. So, the metal hydrogen stretch can in fact be used as a tool to find out how is the ligand in the Trans position interacting with the metal. So, the metal hydrogen stretch is a great useful tool for understanding the bonding.

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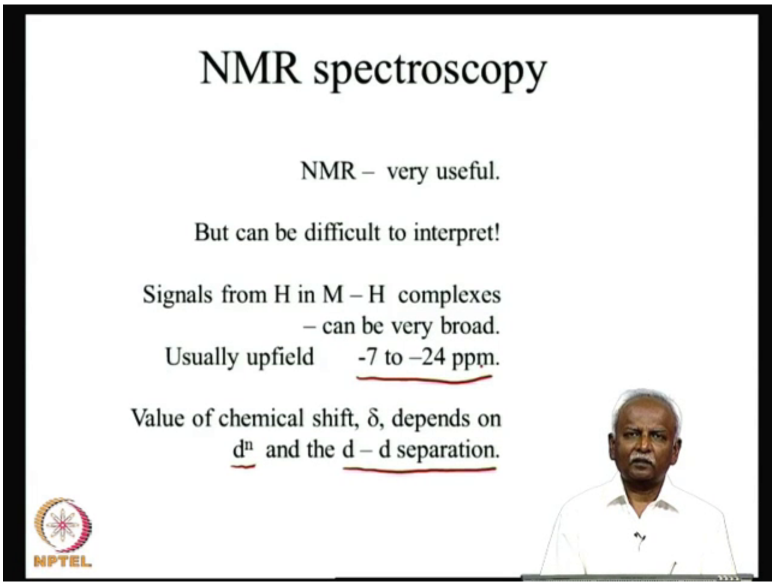

NMR spectroscopy

NMR – very useful.

But can be difficult to interpret!

Signals from H in M – H complexes
– can be very broad.
Usually upfield -7 to –24 ppm.

Value of chemical shift, δ, depends on d^n and the d – d separation.

So, I will call it the reporter ligand for the Trans ligand. So, one can imagine that you can use NMR spectra very readily for understanding the chemistry. In these cases, NMR is indeed very useful, but it can be difficult to interpret the NMR spectra that we get for several reasons. One of them is the fact that signals from hydrogen in MH complexes can be very broad. These hydrogen atoms are fluxional, which means they do not stay in one position in the metal complex. When they are moving about the electronic environment changes; that makes the resonance very broad.

So, you have a range of chemical shifts for this hydrogen, which leads to a broad spectrum. You do not might even miss the metal hydrogen resonance. Usually, if you have a complex, which is not so fluxional, you can observe it readily. Then, the stretching frequency ranges from minus 7 to minus 24 p p m. This means that they do not interfere with normal organic compounds. To look at metal hydrides, one in fact has to look at the negative region in the NMR spectra. Now, the value of the chemical shift depends very much on 2 factors, which is the d electron count on the transition metal.

So, the d electron count on the transition metal can make a difference and the separation between the lowest energy level and the next highest energy level or the d d separation usually makes a difference in the chemical shift. So, it is difficult to predict exactly where you would get a resonance for metal hydrides and the arid complication is the fact that it can be broad.

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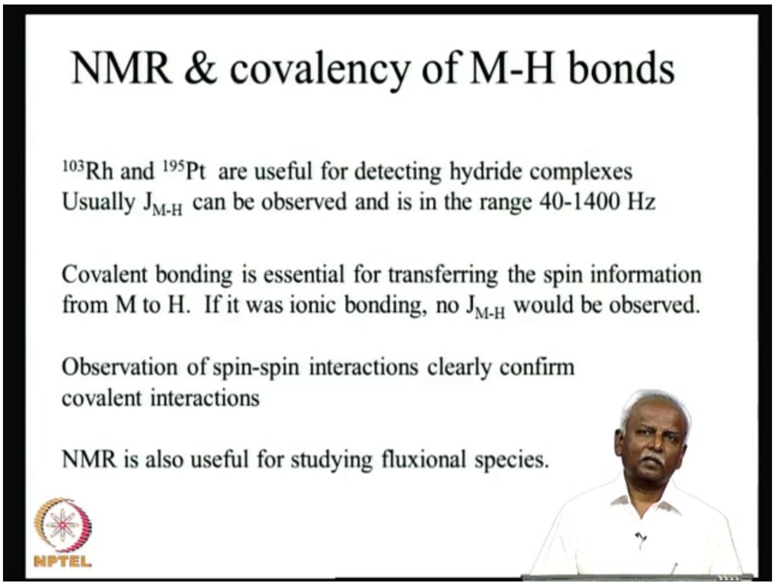

NMR & covalency of M-H bonds

^{103}Rh and ^{195}Pt are useful for detecting hydride complexes
Usually $J_{M\text{-}H}$ can be observed and is in the range 40-1400 Hz

Covalent bonding is essential for transferring the spin information from M to H. If it was ionic bonding, no $J_{M\text{-}H}$ would be observed.

Observation of spin-spin interactions clearly confirm covalent interactions

NMR is also useful for studying fluxional species.

But, nevertheless, there are several instances where it has been possible to use NMR spectra very effectively. That is because the coupling between a nucleus of the metal and the hydrogen can be observed. This when it is observed; it is a great indicator of covalency in the metal hydrogen bond. So, it is impossible for an ionic species where there is no overlap of electrons between in the hydride and the metal to show any coupling interaction.

So, once we observe that there is coupling between the metal and the hydrogen, then we are quite sure that there is covalent interaction for transferring the spin information from the metal to the hydrogen. So, take rhodium for example, at 103 and platinum 195, these are atoms, which have hydrides being formed. These hydrides have a very strong coupling with the metal atom.

So, observation of spin-spin interaction clearly implies covalency in these compounds. I mentioned that there can be fluxional properties. This can be a boon and a bane. It is a boon when you can in fact observe them at say low temperature, you observe the chemical shift. Then, it is useful for identifying such fluxional properties occurring in solution.

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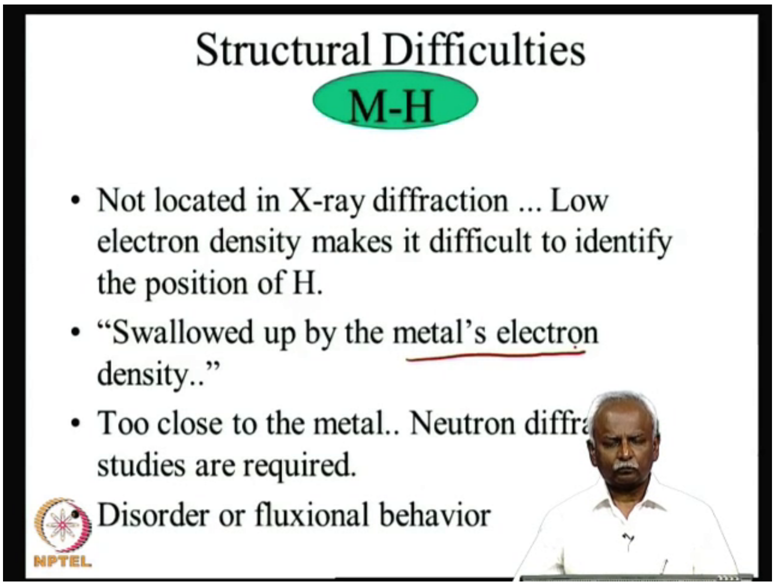

Structural Difficulties

M-H

- Not located in X-ray diffraction ... Low electron density makes it difficult to identify the position of H.
- "Swallowed up by the metal's electron density.."
- Too close to the metal.. Neutron diffra studies are required.
- Disorder or fluxional behavior

Structural difficulties for metal hydrides are significant. When you look at the solid state structure of metal complexes very often, they are not located in the X ray diffraction pattern. This is because the low electron density on the hydrogen has got only 1 s shell. It can at most accommodate 2 electrons. So, when it has a maximum of 2 electrons, you would be able to locate it in the diffraction pattern. It would give rise to a peak.

If the hydride behaves less like H minus and it behaves more like H plus, the position of the hydrogen atom is difficult to identify. This is because there is very little electron density around the nucleus, the hydrogen nucleus. To add to this complication, you can have a large electron density on the metal. The metal's electron density can be very large. The hydrogen electron density is relatively small. So, one can say that the electron density at the hydrogen is literally swallowed up by the metal's electron density.

So, one way people have solved this problem to understand the bonding between hydrogen and a metal is to use neutron diffraction. Only problem with neutron diffraction is the fact that you need very large crystals in order to get this. This problem has been solved by better embedded technology. It is now possible to do neutron diffraction fairly easily. One is able to locate the position of the nucleus without difficulty. This leads to accurate structures for metal hydrides. The problems of disorder and fluxional behaviour are solved to a greater and greater extent.

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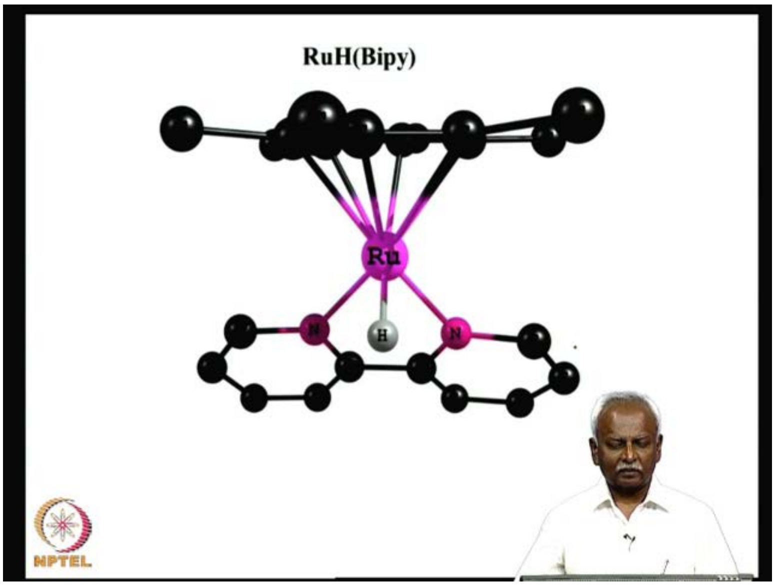

RuH(Bipy)

Let us move on. Let us take a look at a typical metal hydrido complex. Here, I have pictured for you a metal hydrido complex, which is in fact the ruthenium complex.

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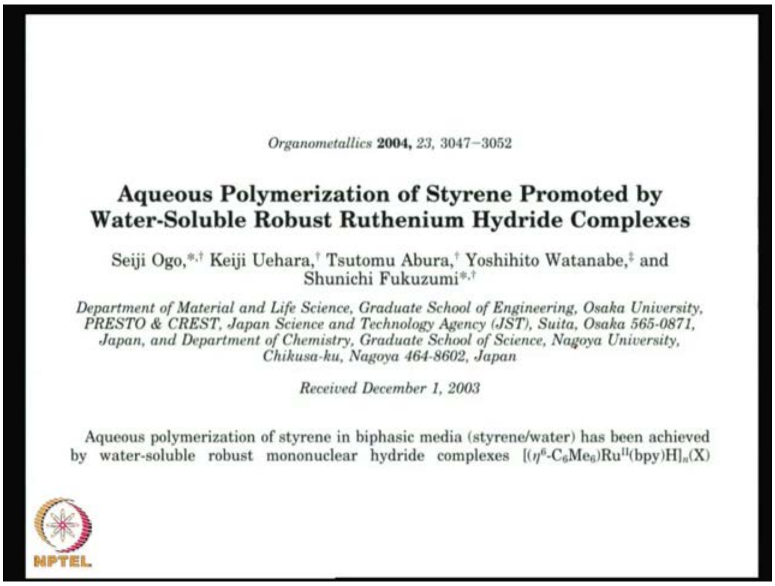

Organometallics **2004,** *23,* 3047–3052

Aqueous Polymerization of Styrene Promoted by Water-Soluble Robust Ruthenium Hydride Complexes

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Received December 1, 2003

Aqueous polymerization of styrene in biphasic media (styrene/water) has been achieved by water-soluble robust mononuclear hydride complexes $[(\eta^6\text{-}C_6Me_6)Ru^{II}(bpy)H]_n(X)$

It has been studied recently for water soluble polymerization. This is very interesting because people have been looking at how one can use green solvents for various reactions. If you want to do a polymerization of styrene, it is usually done in organic solvents. If you can do it in water with the help of a metal complex, it would be a great advantage. This is a recent paper which has been published, which suggests that ruthenium hydride complex can be an excellent catalyst for water soluble or aqueous polymerization of styrene.

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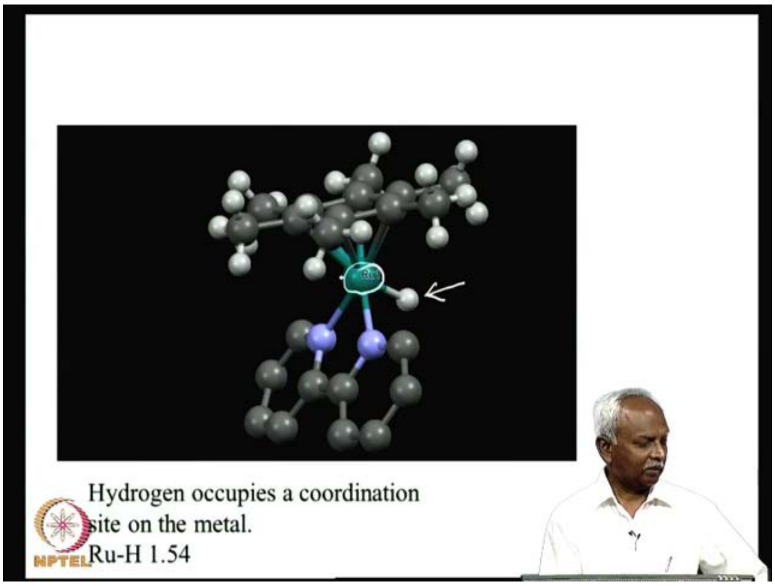

Hydrogen occupies a coordination site on the metal.
Ru-H 1.54

So, here is a complex. I will show you the structure in three dimensions. Now, this picture shows you how hydrogen is present right on the ruthenium. The hydrogen is present on the ruthenium. Let me show this to you. Right here is the hydrogen and that hydrogen is connected to the ruthenium, which is the metal centre right here. That has got a bipyridyl, which is complex to it and also a benzene ring, which is coordinated to it. So, we will talk about the chemistry of these compounds a little later. Let us take a look at the three dimensional structure in order to appreciate this system little better.

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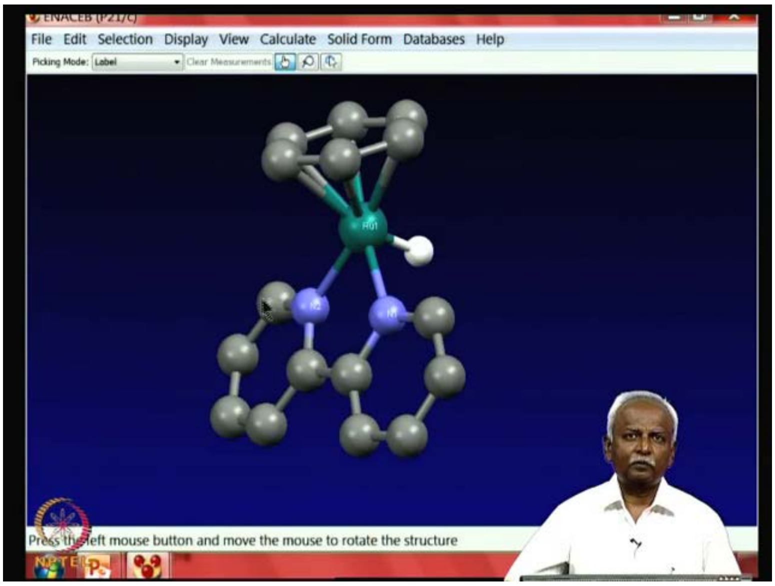

Press the left mouse button and move the mouse to rotate the structure

So, this is the complex in 3 d. In order to simplify the orientation, I have removed the carbon atoms, which were attached to the benzene ring. Here, the benzene ring which is pictured here had other carbon monoxide, carbon other methyl groups. This benzene ring had methyl groups. I have removed it. So, you can see how the hydrogen is linked to the ruthenium and a simple bipyridyl ligand.

So, there are 2 nitrogens, which are marked in blue here. These are interacting with a ruthenium. You have this hydrogen. You can see that this is just as good as any other simple ligand like chlorine or bromine or a triphenyl phosphine interacting with a metal centre. So, this is a hydrido complex, which has been characterised quite well.

So, let us get back to our presentation here. We have the distance between the ruthenium and hydrogen is around 1.54 angstroms. It is exactly what you expect for a single bond. As I mentioned, hydrogen is the only element, which will interact through only a sigma bonded interaction because there is only s orbital and no pi interactions are possible.

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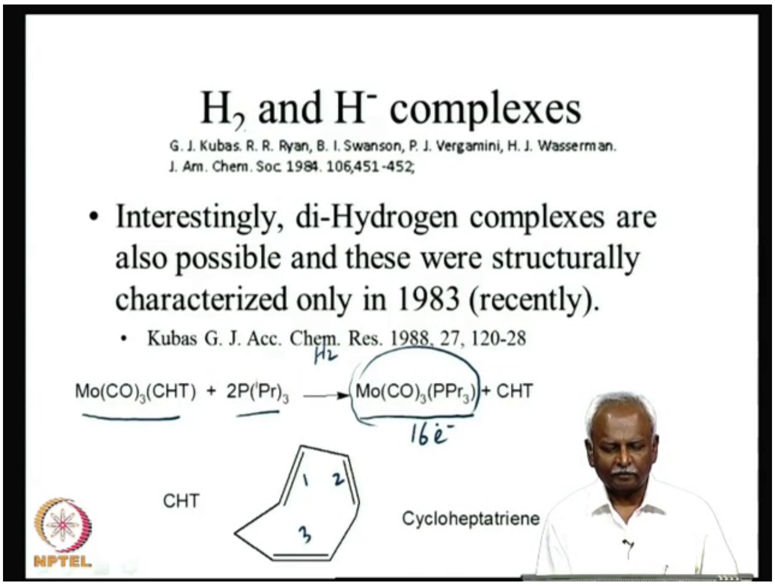

H_2 and H^- complexes

G. J. Kubas. R. R. Ryan, B. I. Swanson, P. J. Vergamini, H. J. Wasserman. J. Am. Chem. Soc 1984. 106,451-452;

- Interestingly, di-Hydrogen complexes are also possible and these were structurally characterized only in 1983 (recently).
  - Kubas G. J. Acc. Chem. Res. 1988, 27, 120-28

$$\mathrm{Mo(CO)_3(CHT)} + 2\mathrm{P(^iPr)_3} \xrightarrow{H_2} \underbrace{\mathrm{Mo(CO)_3(PPr_3)}}_{16e^-} + \mathrm{CHT}$$

CHT

Cycloheptatriene

So, let us now move on to some other complications, which occur with hydrogen. It was discovered fairly recently about 20 or 30 years ago; close to 25, 30 years. It is possible to form not just hydride complexes, but one can also form dihydrogen complexes. So, these are compounds, in which the metal is interacting with H2. So, it is done instead of simple hydrogen as H minus. Now, you have a whole molecule of dihydrogen interacting with the metal. So, this was discovered when a substitution reaction was carried out between cycloheptatriene.

So, this is a ligand cycloheptatriene I have listed for you here. This is cycloheptatriene. It has got 3 double bonds. These 3 double bonds can interact with molybdenum. As a result, you would have an 18 electron complex formed between 3 carbonyls and cycloheptatriene. It is possible to do a simple substitution reaction by replacing the cycloheptatriene with triphenyl phosphine. During this displacement or substitution, what happens is you are left with a vacant coordination site.

This is because this is now a 16 electron species. Only 16 valence electrons are present around the coordination sphere. You have 1 vacant coordination sphere. If this reaction is carried out in the presence of di hydrogen or H2, it was found that dihydrogen complexes are formed in this reaction. So, dihydrogen complexes are formed when you do the substitution reaction.

So, this was reported recently by Kubas. One can read about it in the accounts of chemical research paper in 1988.

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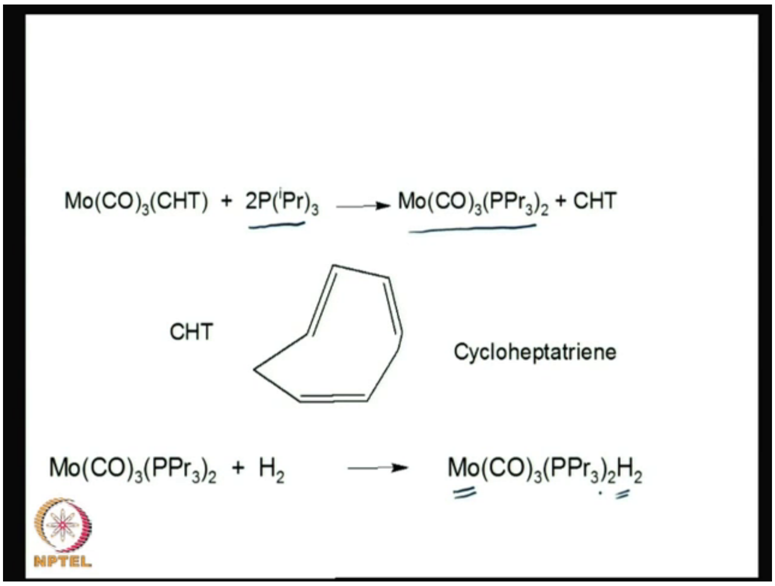

$$Mo(CO)_3(CHT) + \underline{2P(^iPr)_3} \longrightarrow \underline{Mo(CO)_3(PPr_3)_2} + CHT$$

CHT

Cycloheptatriene

$$Mo(CO)_3(PPr_3)_2 + H_2 \longrightarrow \underline{\underline{Mo}}(CO)_3(PPr_3)_2\underline{\underline{H_2}}$$

Now, what is exactly going on is that a bis triphenyl, tri isopropyl complex of this molybdenum has got a vacant coordination site. It cannot accommodate an extra phosphine. Instead, a small molecule like di hydrogen can form a complex. So, because of the bulky nature of this tris isopropyl phosphine, it results in a situation where the molybdenum would rather interact with dihydrogen, then another molecule of tris isopropyl phosphine.

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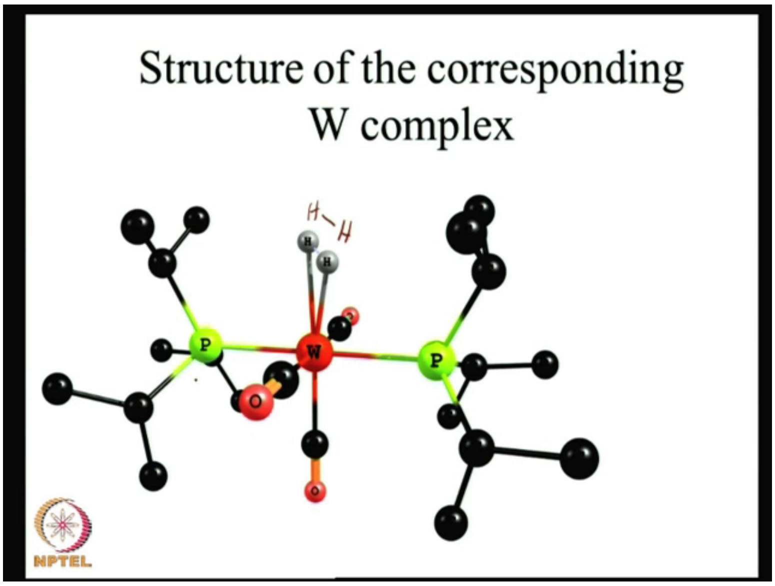

Structure of the corresponding W complex

Now, let us take a look at the metal complex. The molybdenum complex could not be isolated and characterised, but the corresponding tungsten compound was characterised crystallographically. These are compounds, which have to be carried out. They have to be studied using neutron diffraction. I have pictured for you the complex that was formed with the tungsten.

I will show you a three dimensional version of the same molecule. Here is a nice drawing of the same molecule. You will notice that instead of a single atom, you have a dihydrogen or H2, which is pictured here. You have a dihydrogen, 2hydrogens here. So, it is this di hydrogen, which is sitting in the vacant site, which is formed when you have 3 carbon monoxides and 2 tris isopropyl phenyl isopropyl phosphine complexes. So, let us take a look at the three dimensional structure in order to appreciate this system a little better.

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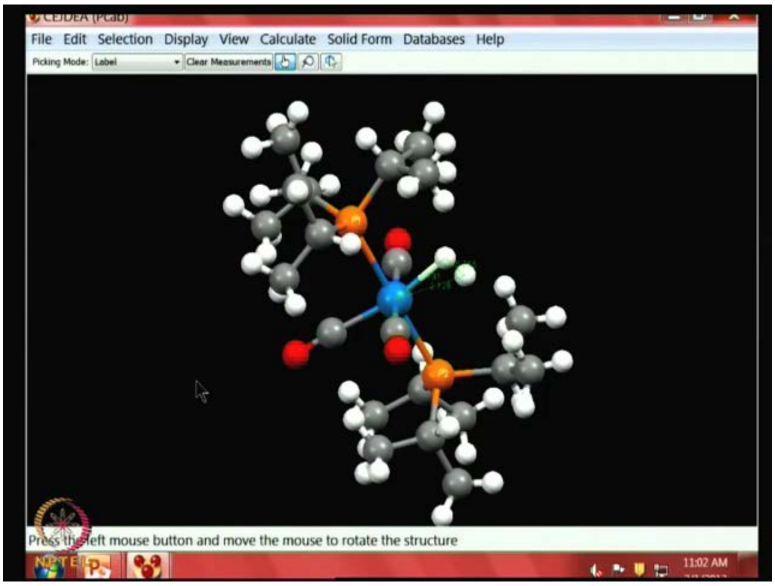

Press the left mouse button and move the mouse to rotate the structure

I have it pictured here. You can see 2 hydrogen atoms. Once again, the hydrogen atom is shown for you in white colour. You can see the 2hydrogens, which are marked here. One of them is at a distance of 2.126 angstroms. That is the one on the right side. The 2hydrogens are pictured here. The one on the right side is at 2.126 angstroms the one on the left side, which is slightly higher in level. That is at 1.71, 0.898. So, there is a slight asymmetry in the way in which the di hydrogen is interacting with the tungsten. But, nevertheless, it is a full molecule of hydrogen, which is interacting with tungsten.

How do we know that this is not 2 atoms of hydrogen interacting independently? First of all, we realise that the distance is not symmetric. It is not a di hydride, but we also notice that the distance between the 2hydrogens is in fact 0.755 angstroms. This means they are much closer than what you would expect for a dihydrogen species. So, here is an instance where the distance between the 2 nuclei are so close that you have to think of it as a dihydrogen interacting with metal complex and not 2 hydrogen atoms.

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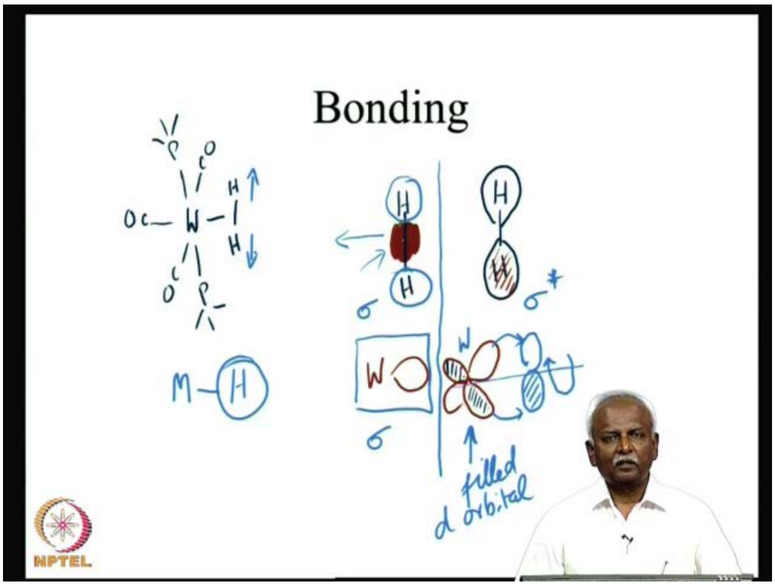
Bonding

So, let us take a look back to the presentation. So, how do we understand the bonding in these systems? When you have simple hydrogen interacting with a metal atom, you can think of it as you can think of it as M interacting with the 1 s orbital on the hydrogen. If you have di hydrogen, then you have 2 hydrogen atoms. Here, you have 2 hydrogen atoms here. In between the 2 hydrogen atoms is a little bit of extra electron density that is collected because of the formation of a molecular orbital.

In this molecular orbital, this extra electron density is stored. This can now donate this electron density to a vacant orbital on the tungsten. So, the vacant orbital on tungsten is pictured here. Into this vacant orbital, you can donate this electron density on the di hydrogen. On the other hand, you can also think of a situation where there is a sigma star orbital on the dihydrogen. This is your sigma orbital.

The sigma star orbital on the dihydrogen will have 2 lobes of opposite sign. This can now interact very easily with the empty, with the filled d orbital. This is a filled d orbital on filled d orbital on tungsten. This can now pump in electron density into the dihydrogen. So, dihydrogen chemistry is significantly different from hydrogen complexes where you have MH bonds hydride compounds. In these cases, you do have this is a pi type interaction.

Now, that is happening between the filled d orbital on tungsten and the pi star or the sigma star orbital on the hydrogen on the dihydrogen. So, here is the pumping in of electron density into the sigma star. This is a pi type interaction because if you rotate it around this axis, you will break the bond. So, this is a pi type interaction. This is a sigma type interaction. You have weakening of the hydrogen. The 2hydrogens and that bond would be elongated. This bond would now be elongated by hydrogen bond from what you would expect for free dihydrogen. So, dihydrogen chemistry is slightly different from hydride chemistry.

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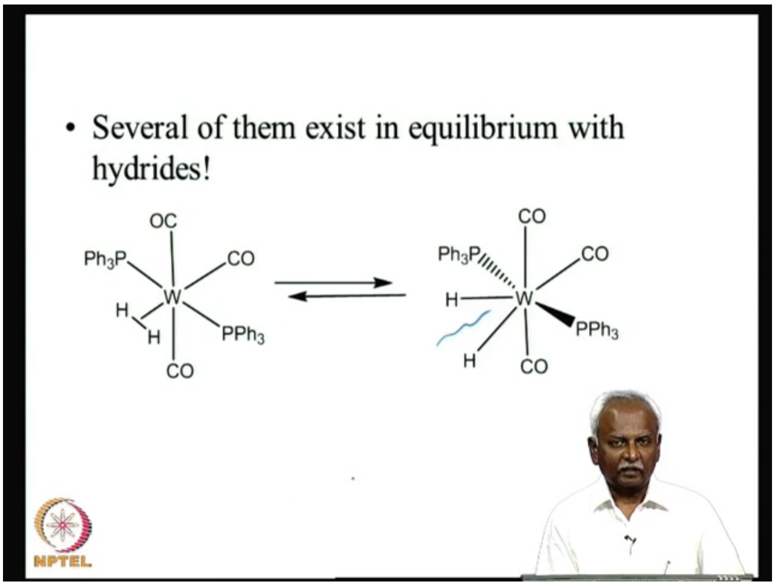

- Several of them exist in equilibrium with hydrides!

What is interesting is that in several of these complexes, it has been shown to be in equilibrium with dihydrides. This means di hydride can convert to a dihydrogen complex. So, this means that you have this H2 going to MH2. So, this is the equilibrium that we are talking about, which is pictured here. You have 2 distinct bonds. This bond is now been broken.

There is no bond here between the 2hydrogens. You can have this equilibrium very readily, which means that on the right hand side, I have 2H minuses interacting with the tungsten. On my left side, I have the di hydrogen molecule interacting with the tungsten.

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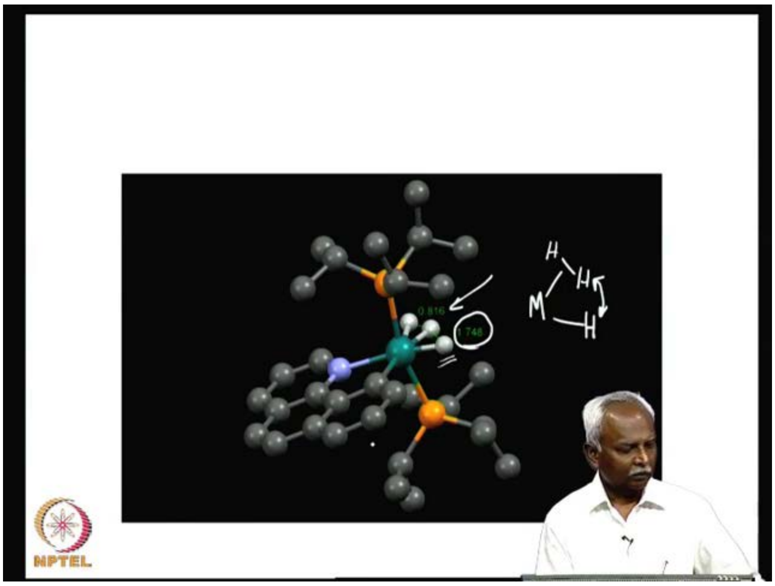

Now, to complicate matters, there are species where 3hydrogen are present. From the neutron diffraction data, it has been shown that 2hydrogens are close to each other. Let me illustrate this with this particular structure, which is shown. Here, the 2hydrogens, which are close to each other are the ones on the top part of this metal hydride system. The one on the lower side is a hydrido complex MH. So, it is as if you have M interacting with 2hydrogens, then it is also interacting with a hydride.

So, that is what is happening here. Surprisingly, the distance between these 2 is much longer at 1.748 angstroms. The distance between the dihydrogen compounds the dihydrogen ligand is much closer. It is reminiscent of what would you have if H2 is interacting with the metal.

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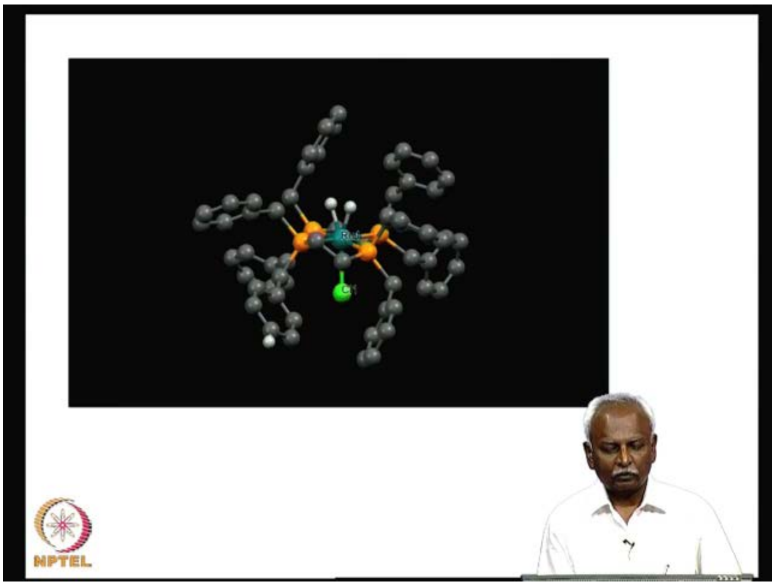

So, here is another instance, another complex of ruthenium. It also has dihydrogen interacting with the metal. You can see how you can have only dihydrogen or dihydrogen and hydrogen or the species in equilibrium.

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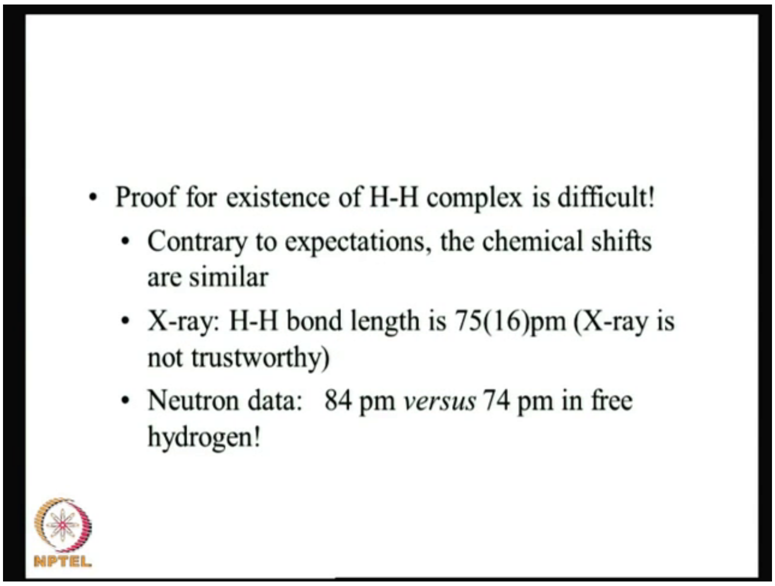

- Proof for existence of H-H complex is difficult!
  - Contrary to expectations, the chemical shifts are similar
  - X-ray: H-H bond length is 75(16)pm (X-ray is not trustworthy)
  - Neutron data: 84 pm *versus* 74 pm in free hydrogen!

So, the proof for existence of a dihydrogen complex is quite difficult because it is difficult to distinguish between the 2 species on the basis of n m r spectra. Surprisingly, x ray evidence and neutron data needs to be used. Neutron data is more reliable. It has been shown that the distance between 2 hydrogen atoms can be little bit longer than what you have in the free hydrogen. That is 74 picometers in free hydrogen and 84 picometers in the complex species. So, this has allowed the study of some very complicated chemistry with metal complexes and di hydrogen and hydrides.

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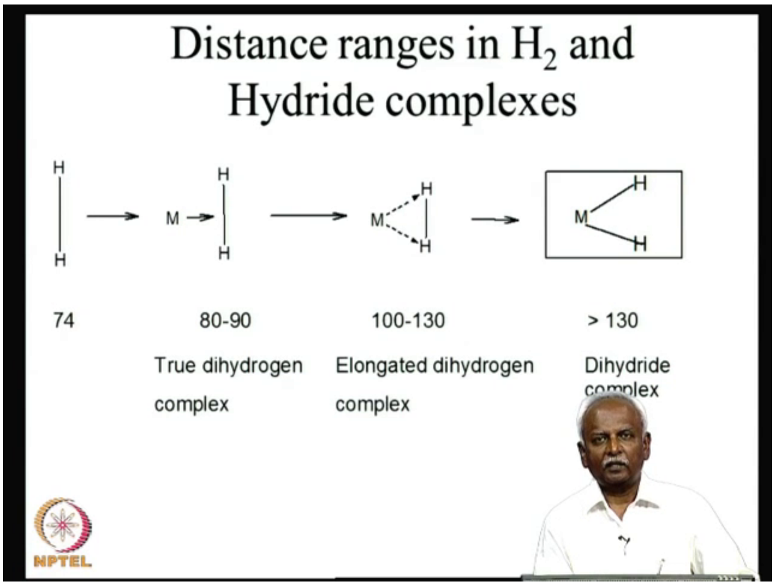

Distance ranges in H_2 and Hydride complexes

74	80-90	100-130	> 130
	True dihydrogen complex	Elongated dihydrogen complex	Dihydride complex

As I mentioned earlier, the systems are in equilibrium sometimes which complicates matters, but in many instances, there is a range of hydrogen hydrogen distances that are observed. So, these are in picometers. These distances are in picometers. You go from 74 picometers for H2 species all the way to 100 and 130 picometers for a di hydride complex. So, you have elongation of the hydrogen hydrogen bond as you pump in more and more electron density into the anti bonding orbital of the di hydrogen.

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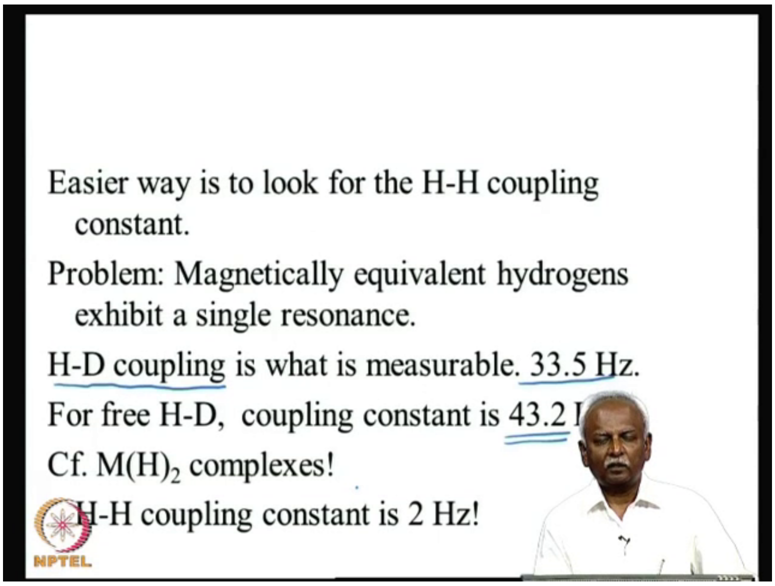

Easier way is to look for the H-H coupling constant.

Problem: Magnetically equivalent hydrogens exhibit a single resonance.

H-D coupling is what is measurable. 33.5 Hz.

For free H-D, coupling constant is 43.2

Cf. $M(H)_2$ complexes!

H-H coupling constant is 2 Hz!

One way is to look for the hydrogen hydrogen coupling, but unfortunately that would not be visible. So, HD coupling is what one usually looks for. It turns out that if you have a dihydrogen compound, you should be able to observe HD coupling. This is in the range of 33 hertz for free dihydrogen. If you substitute 1hydrogen with a deuterium, then the coupling constant is around 43 hertz.

So, the reduction in the coupling constant is indicative of the fact that you have reduction in the bonding between the 2 hydrogen atoms. So, you have a lower coupling constant and a lower covalency. This is because of the bonding description that we just went through, which suggests that the anti bonding orbitals in dihydrogen are populated.

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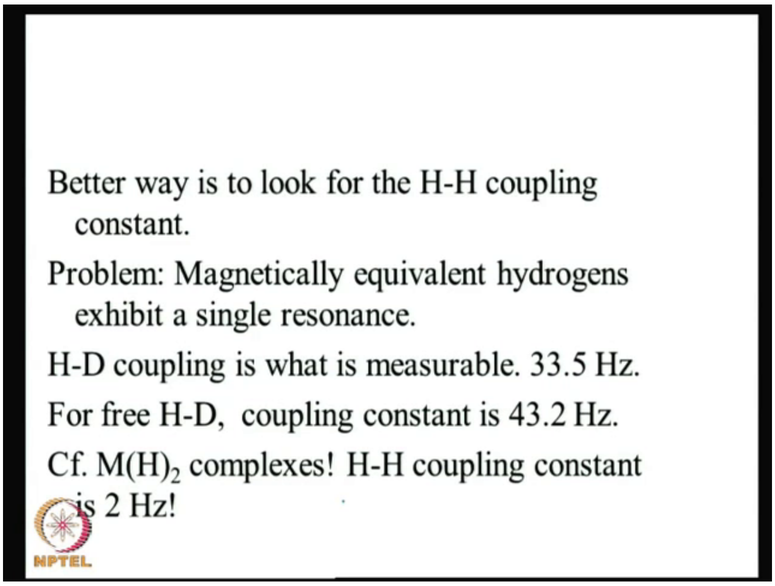

Better way is to look for the H-H coupling constant.

Problem: Magnetically equivalent hydrogens exhibit a single resonance.

H-D coupling is what is measurable. 33.5 Hz.

For free H-D, coupling constant is 43.2 Hz.

Cf. $M(H)_2$ complexes! H-H coupling constant is 2 Hz!

So, MH 2 two complexes and MH 2 complexes are interesting species, which can be studied. You can use HD coupling to study them.

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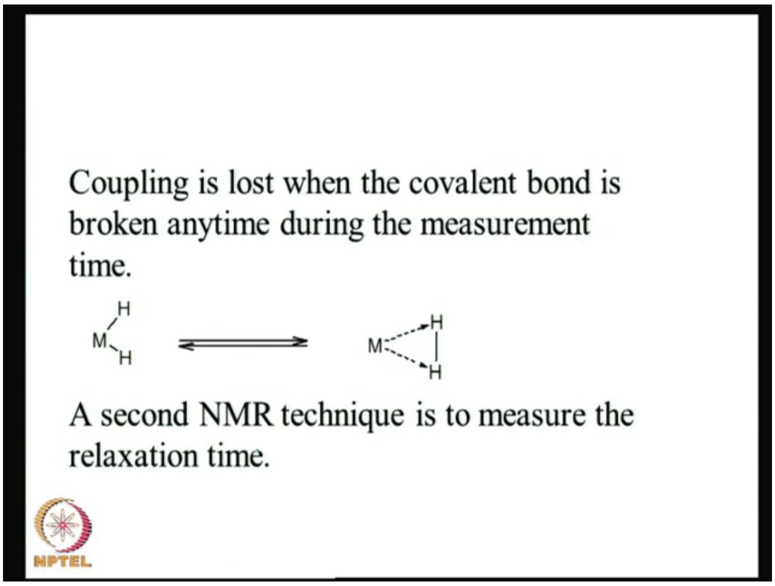

Coupling is lost when the covalent bond is broken anytime during the measurement time.

A second NMR technique is to measure the relaxation time.

You can also use what is called a relaxation time measurement in order to study them. This is beyond the scope of today’s lecture, but it is easy to measure relaxation times and distinguish between when a species is present as you can find out when a species is present as a dihydride and when a species is present as an MH 2 complex.

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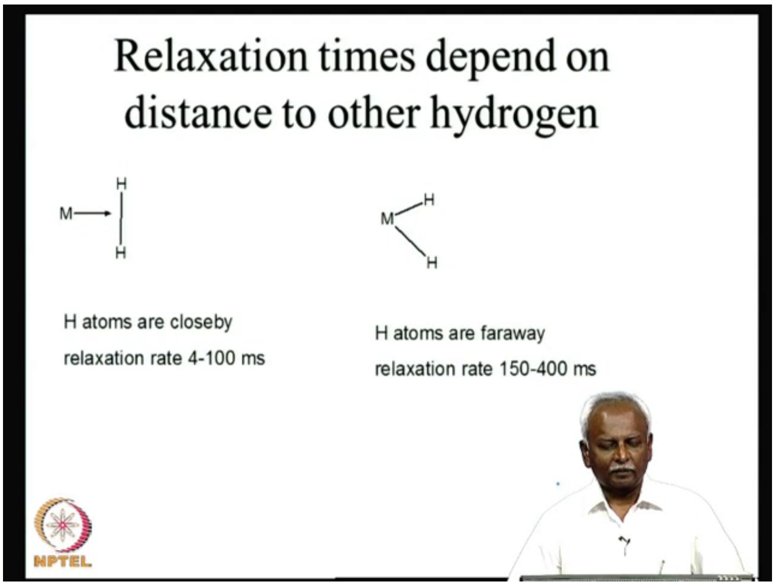

Relaxation times depend on distance to other hydrogen

H atoms are closeby
relaxation rate 4-100 ms

H atoms are faraway
relaxation rate 150-400 ms

So, when the hydrogen atoms are close by, the relaxation rate is around 4 to 100 milliseconds. If they are far away, the relaxation rate is between 150 and 400 milliseconds, but these measurements are more time consuming. They can be quite complicated.

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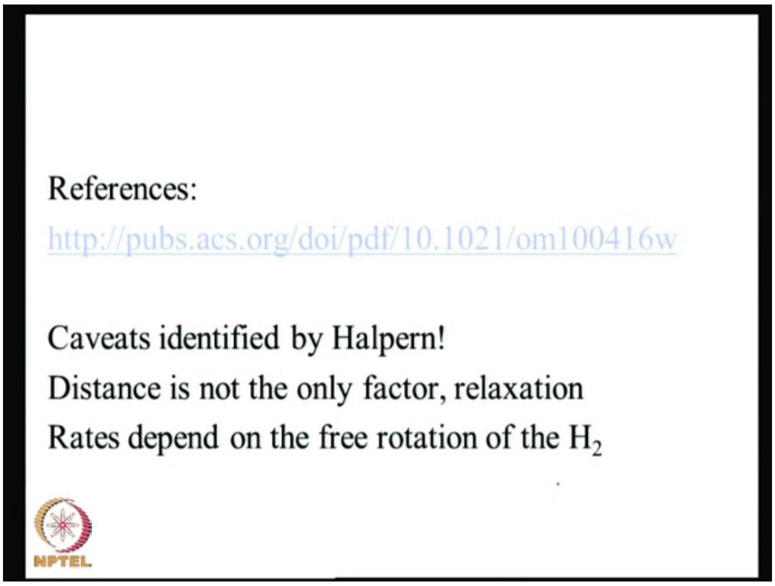

References:
http://pubs.acs.org/doi/pdf/10.1021/om100416w

Caveats identified by Halpern!
Distance is not the only factor, relaxation
Rates depend on the free rotation of the H_2

So, the relaxation time measurements have also been studied by Halpern. He has pointed out that there are problems with even that technique. Distance is not the only factor. Relaxation rates also depend on how freely the dihydrogen rotates.

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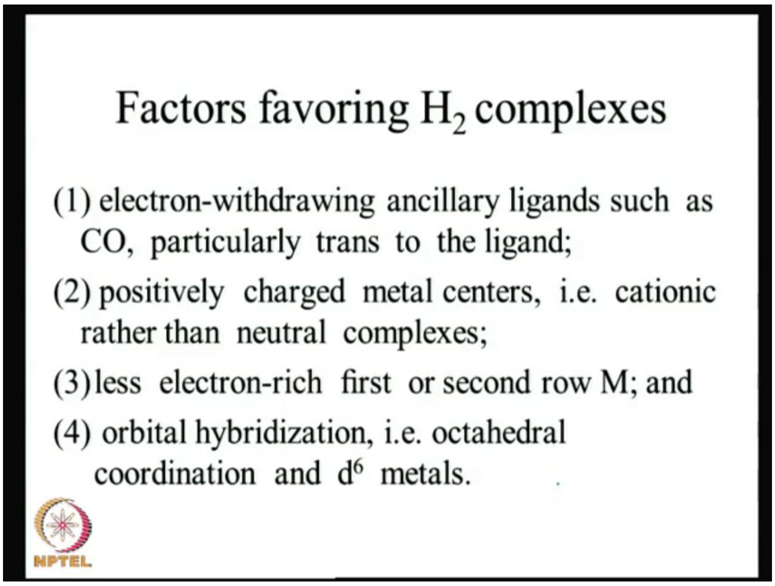

Factors favoring H_2 complexes

(1) electron-withdrawing ancillary ligands such as CO, particularly trans to the ligand;

(2) positively charged metal centers, i.e. cationic rather than neutral complexes;

(3) less electron-rich first or second row M; and

(4) orbital hybridization, i.e. octahedral coordination and d^6 metals.

So, let us take a look at what factors favour H 2 complexes and what factors will favour the dihydride complex. If you have electron withdrawing ancillary ligands like carbon monoxide Trans to the ligand, then you would favour a H2 complex. If you have positively charged system, then once again, you would form the hydrogen complex. If you have a lot of electron density on the metal, you can pump it in and form breaks it and form dihydrides. Usually, this is formed for the second row elements.

If you have less electron rich first transition metal series metal, then you can form the dihydrogen complex more easily. If you have a 4 d and 5 d transition elements, it becomes easier to do oxidative reaction and transfer electron density into the pi star orbital. So, let us stop at this particular stage where we discussed dihydrogen and hydrogen chemistry. We will try to summarise what we have just learnt.

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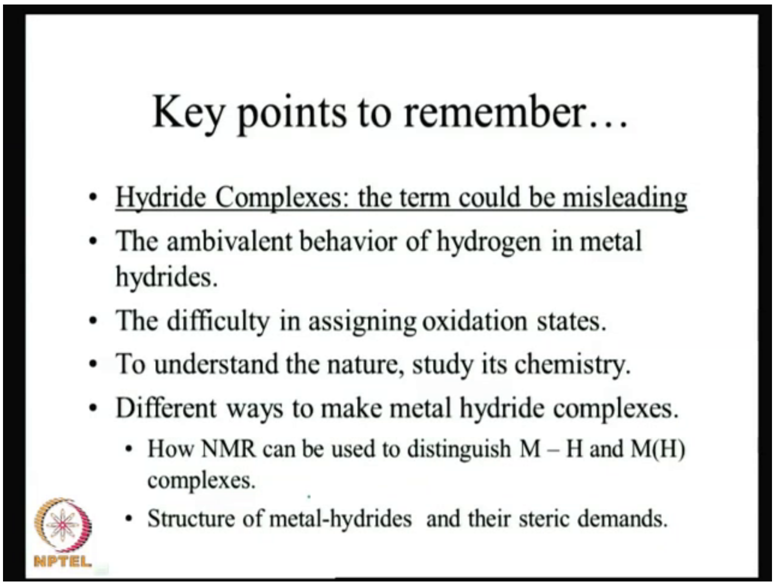

Key points to remember…

- Hydride Complexes: the term could be misleading
- The ambivalent behavior of hydrogen in metal hydrides.
- The difficulty in assigning oxidation states.
- To understand the nature, study its chemistry.
- Different ways to make metal hydride complexes.
  - How NMR can be used to distinguish M – H and M(H) complexes.
  - Structure of metal-hydrides and their steric demands.

So, the key points to remember in this section are that hydride complexes are in fact species where an MH bond is there. But, this term itself that it is a hydride is misleading because you have the ionisation of an MH complex; many times as H plus and M minus. The difficulty in assigning oxidation states arises from this particular problem. The ambivalent nature of hydrogen in hydrides is something that we have covered. Later on, in our future lecture, we will look at some of the chemistry that is behind the metal dihydrogen and metal hydrides. So, with this, we conclude today’s discussion on metal hydrides.