Advanced Transition Metal Chemistry – Classification of Ligands
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Lecture – 28
Classification of Ligands - Hydrogen

Hello everyone. It is with pleasure I welcome you again to MSB lecture series on transition metal chemistry. In my previous lecture, I started discussion on classification of ligands by donor atoms. And after giving little bit of introduction, I started discussing about metal hydride compounds, that means using hydrogen as a donor atom. So, let me continue from where I had stopped.

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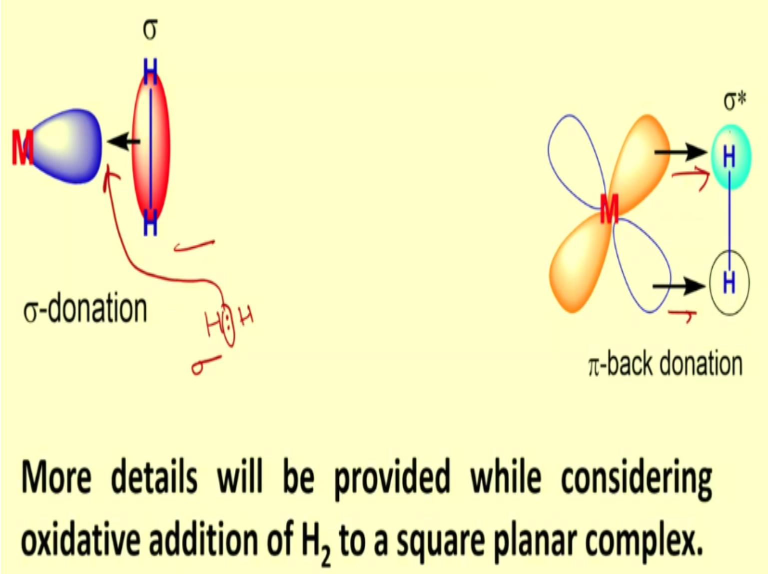

More details will be provided while considering oxidative addition of H_2 to a square planar complex.

So, when I mentioned that hydrogen molecule or hydrogen is a sigma donor as well as a pi acceptor. So, how that happens, I have shown here. You can see here in this diagram, I have shown how H_2 molecule acts as a sigma donor. For example, if you recall writing Lewis dot structure, we put a pair of electron between two hydrogen atoms that is responsible for making H_2 and this is what I am referring to.

This is going to suitable empty orbital on metal to establish metal to hydrogen bond, so this is called sigma. And then if you see the molecular orbital diagram that I am going to show in a couple of minutes, we have filled sigma orbital with pair of electrons that is responsible for making H_2 molecule and also you have high energy empty sigma star. The energy of sigma star is more or less comparable to the energy of nonbonding electrons present in a given metal complex, whether it is tetrahedral square planar or octahedral.

So, in that case what happens? The electrons from metal orbitals can be promoted to sigma star that is called back bonding. So, this is how it acts as a back bonding, you can see here, this is the sigma star, so this will be like back bonding. So, it will become more clear in my next slide. So, more details I am going to provide, once again when I consider oxidative addition of H_2 to a typical square planar complex.

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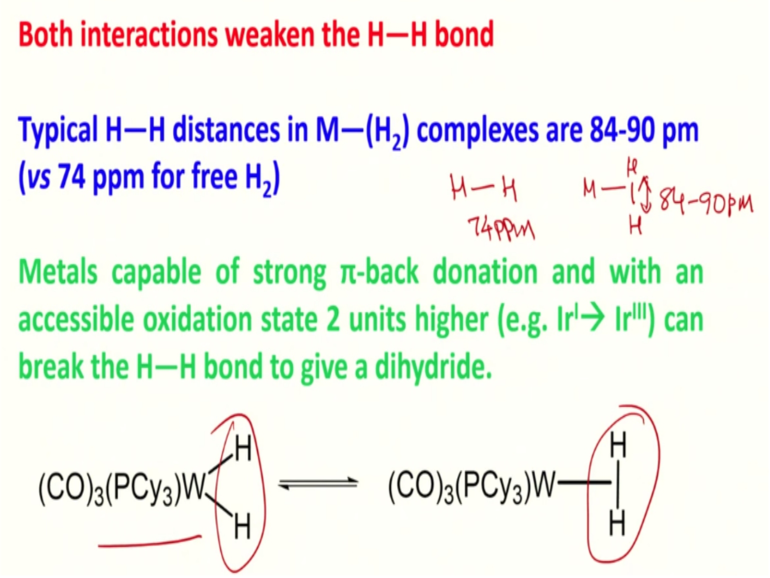

Both interactions weaken the H—H bond

Typical H—H distances in M—(H_2) complexes are 84-90 pm (*vs* 74 ppm for free H_2)

Metals capable of strong π-back donation and with an accessible oxidation state 2 units higher (e.g. $Ir^{I} \rightarrow Ir^{III}$) can break the H—H bond to give a dihydride.

Let us look into how these interactions: sigma donation as well as pi acceptor nature of H_2 would weaken the H-H bond. If you consider an isolated H_2 molecule, a typical H-H distance is about 84 to 90 picometre. It is about 74 picometre for free H_2. When it forms a complex with H_2 as a neutral donor in that case bond distance increases to 84 to 90, the H-H distance I am talking about.

So, that means H-H distance in free molecule in 74 pm. When it is binding to metal, so this distance I am referring to, this will be in the range of 84 to 90 pm depending upon to what extent these electron pairs are drifted more towards the metal atom. So, metals capable of strong back donation and with an accessible oxidation state 2 units higher, can break the H-H bond to give a dihydride.

That means you should recall whenever we want to perform oxidative addition on a metal, metal should have two stable oxidation states with a difference of 2 electrons. That means for example, if you consider a d^0 system, it should be readily oxidized to d^2 system. For example, if you consider and metal in 0 valence state, it should be readily oxidized to +2 state or if you consider M in +1 state then it should be readily oxidized to +3 state.

So, for example if you consider a d^{10} system palladium 0, palladium 0 can be readily oxidized to palladium(II). In the same way if you consider rhodium or iridium, d^8 system is +1, so +1 can be readily converted into +3. That means whenever you want to perform oxidative addition, you should consider a metal having two stable oxidation states with a difference of 2 electrons because, this oxidative addition as well as the reductive elimination process are 2 electron process.

In that context, if the metals are capable of strong back donation with an accessible oxidation state two higher than the original oxidation state, that means iridium(I) to iridium(III) or palladium(0) to palladium(II) something like that or palladium(II) to palladium(VI), in that case if H_2 comes one can break H-H bond to form two metal to hydrogen bonds or metal hydride bonds that is what it means. You can see one such example is given here.

You consider this molecule here, tungsten complex here. So, this one is in equilibrium with neutral as well as anionic bond. So, of course one can always tilt that equilibrium either towards the right side or towards the left side, by choosing appropriate ligands having the right kind of donor and acceptor properties.

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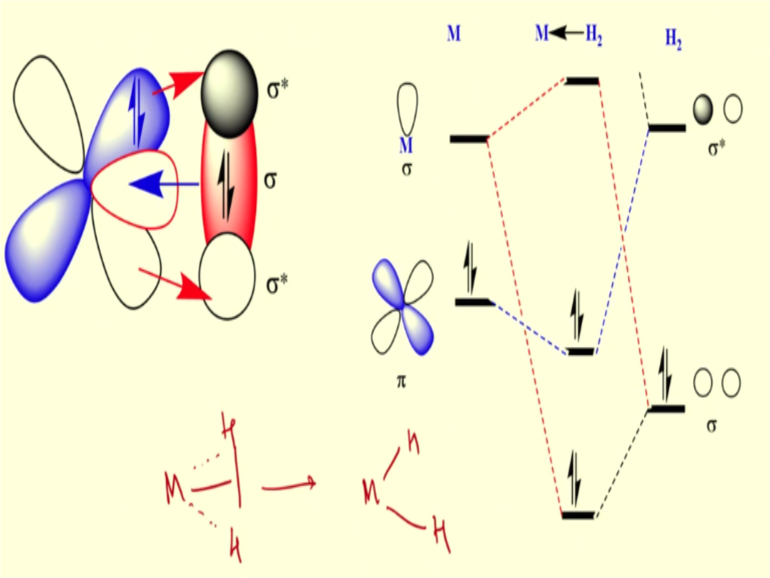

Once again, to make it clear I have shown here. You can see clearly here a pair of electrons are there and this is going to metal through sigma donation and then the electrons present in its nonbonding are pi orbitals that can be promoted to sigma star. So, in this MO diagram, it is very clear that these two electrons are coming from H_2 molecule and to the metal through sigma donation, this is the sigma bond.

And then these electrons with pi symmetry would be going to sigma star, this is back bonding. Now, what happens? The bonded electrons you are drifting away, one thing so, that essentially loosens or weakens H-H bond. Once again, besides this, you are also adding electrons to the sigma star. So that means there is a two way weakening effect one can envisage here. One is taking the bonded electrons and then adding electrons to the antibonding, both would result in weakening of H-H bond.

If the back donation is extensive and pi acceptor nature is also extensive that eventually leads to the breakage of H-H bond to form two M-H bonds, that means whatever we have something like this, and you can see some sort of intermediate coming like this and then that would become something like this. So, this is what a metal complex is capable of doing for H_2 molecule when we use these kinds of complexes in hydrogenation of olefins and other molecules in organic transformations.

And for example, if you take an olefin such as ethylene and add H_2 under high pressure and high temperature and even leave it for days, probably at the end, you can see only about 10% or a maximum of 10 to 15% conversion of olefine to corresponding hydrocarbon, but in contrast using an appropriate metal complex and interact that with hydrogen molecule in presence of olefine you should be able to do it even at room temperature, hydrogenation of olefin.

How it does? This is how it does. First what it does is through a sigma bond establishment, this electron pair is taken away from H_2 to weaken H-H bond and then more electrons from metal are added to the sigma star and then your bond order is totally destabilized and eventually this bond breaks. And once this bond is broken and olefin comes and sits here and then it is what opposite to beta-hydride elimination happens, and then hydrogenation process proceeds. So, we will discuss those things once again later.

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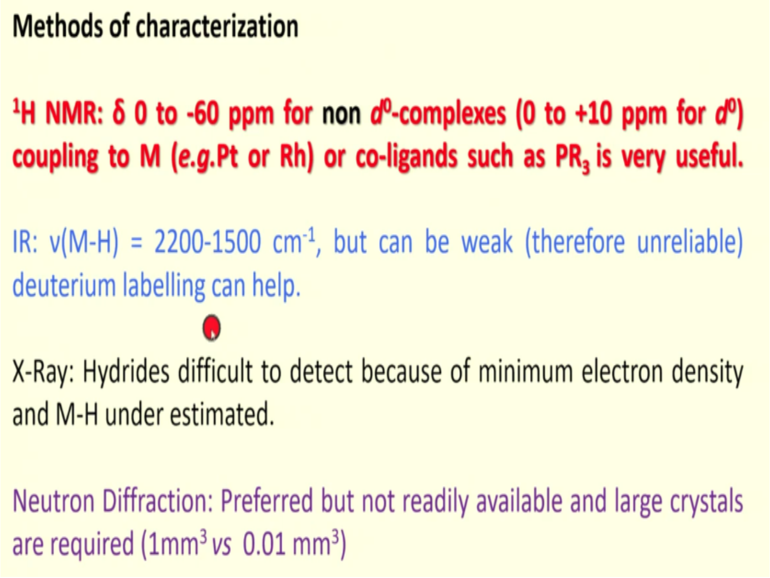

Methods of characterization

^{1}H NMR: δ 0 to -60 ppm for non *d*^{0}-complexes (0 to +10 ppm for *d*^{0}) coupling to M (*e.g.*Pt or Rh) or co-ligands such as PR_3 is very useful.

IR: ν(M-H) = 2200-1500 cm^{-1}, but can be weak (therefore unreliable) deuterium labelling can help.

X-Ray: Hydrides difficult to detect because of minimum electron density and M-H under estimated.

Neutron Diffraction: Preferred but not readily available and large crystals are required (1mm^3 *vs* 0.01 mm^3)

What are the methods we have at our disposal to characterize a metal complex when we have M-H bond? ^{1}H NMR spectroscopy comes very handy and you should remember in ^{1}H NMR we can see anywhere from 0 to –60 ppm for non d^0 complexes. That means if you make metal-hydrogen bond for a metal having non d^0 electronic configuration, that means if you have more than 1, 2 up to 8 or 9 electrons, then in that case for non-hydrogen complexes, then 0 to +10 for d^0 complex.

You should remember ^{1}H NMR signal for M-H bond would appear between 0 to +10 for d^0 system whereas for non d^0 complexes, it can come anywhere from 0 to –60 because of paramagnetic effect and also shielding effect. And once again if you have NMR active nuclear such as platinum or rhodium, this coupling also comes very handy in characterizing these compounds.

And also, sometimes if you have co-ligands which are also NMR active, for example you have fluorine or even phosphorus, ^{31}P phosphorus nucleus with nuclear spin I = ½ is also 100% abundant. So, this also comes very handy in observing phosphorus to hydrogen coupling. And when you look into IR spectroscopy, M-H stretching frequency for a typical terminal hydrogen appears around 2200 To 1500 cm^{-1}, but can be weak therefore unreliable of course.

This is always a weak absorption, as a result what happens, it is unreliable, you cannot really depend on IR data to know whether M-H bond is formed or not or it is broken or not or it is disappeared or not. And sometimes deuterium labelling can also help because in that case what happens when ^1H NMR does not show any signal. And once again, if you have single crystals of molecules containing M-H bond, one can go for a single X-ray diffraction.

But hydrides, difficult to detect because of minimum electron density we have and M-H bond may be underestimated. And if you want to really get precise bonding parameters, one has to go for neutron diffraction, it is most preferred one, but not readily available and large crystals are required here, unlike x-ray diffraction.

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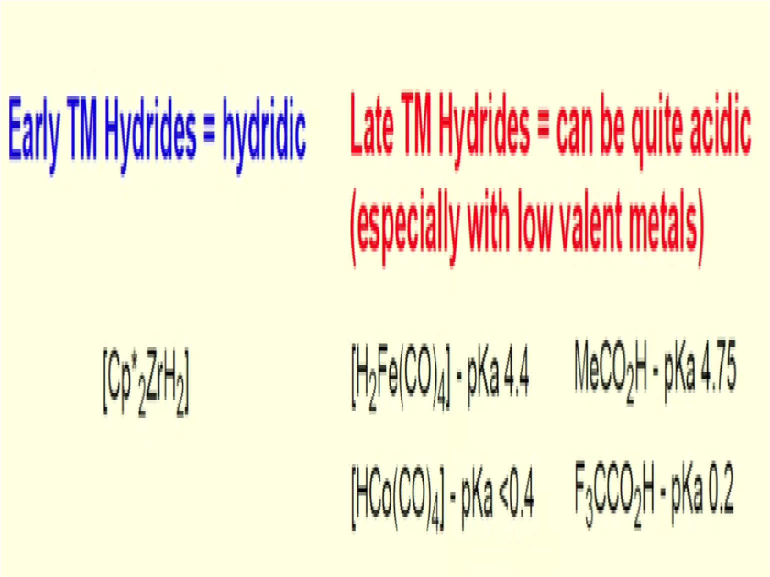

Early TM Hydrides = hydridic

Late TM Hydrides = can be quite acidic (especially with low valent metals)

$[Cp^*_2ZrH_2]$

$[H_2Fe(CO)_4]$ - pKa 4.4 $MeCO_2H$ - pKa 4.75

$[HCo(CO)_4]$ - pKa <0.4 F_3CCO_2H - pKa 0.2

So, early transition metal hydrides are acidic in nature. For example, you can see the pKa value will tell you. Late transition metals can be quite acidic especially with low valent metals. If the metals are in low valent state, they can be quite acidic. If you can see here $[H_2Fe(CO)_4]$ is there, pKa is 4.4 and here iron is in, +2 state. And when you look into this one pKa of acetic acid is 4.75, it is somewhat comparable.

And then if you go for this one where we have $[HCo(CO)_4]$ pKa is 0.4, that means it is quite acidic. And see here very similar to we have in trifluoroacetic acid like that. So, that means pKa values will give you some idea about to what extent metal bound hydrogen is acidic or not. That also helps in using such compounds in catalytic transformations.

Now, let us look into various methods that we have at our disposal to make some of these compounds having M-H bond, whether we can use directly H_2 or whether we can use some reagents so that we can perform reaction under mild conditions. One such method is protonation.

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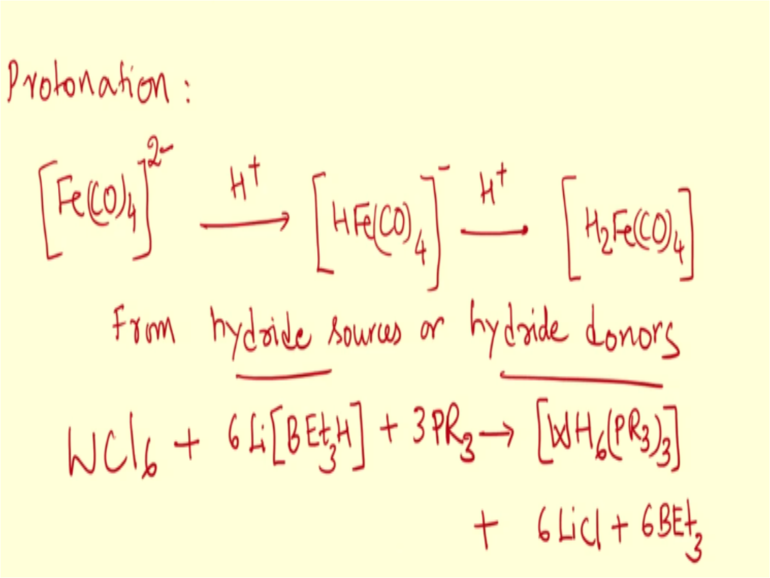

Protonation :

$$[Fe(CO)_4]^{2-} \xrightarrow{H^+} [HFe(CO)_4]^- \xrightarrow{H^+} [H_2Fe(CO)_4]$$

from hydride sources or hydride donors

$$WCl_6 + 6Li[BEt_3H] + 3PR_3 \rightarrow [WH_6(PR_3)_3] + 6LiCl + 6BEt_3$$

Let us take $[Fe(CO)_4]^{2-}$ and add H^+ here, we can make anionic and then if we add one more, we can make neutral complex here. So, this is from hydride sources or hydride donors. So, this is through protonation. Now let us look into, if we have some hydride sources or hydride donors, how we can perform reaction to make metal to hydrogen bond? Let us take WCl_6.

Tungsten is in +6 state and treat this one with this lithium boride in presence of a tertiary phosphine such as, it is a mixed hydride phosphine complex. So, this typical reaction involves hydride sources or hydride donors. And if you look into synthetic method one can use in laboratory for small scale preparation, we can go for alcoholic KOH.

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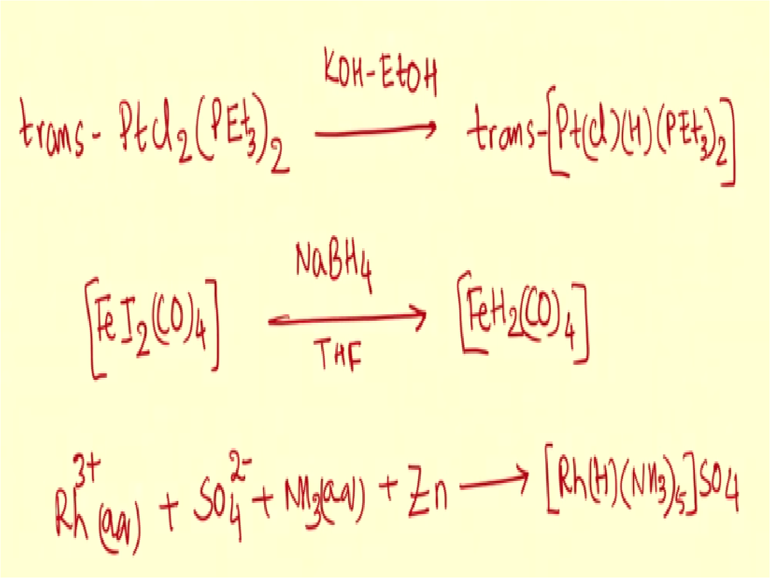

$$trans\text{-}PtCl_2(PEt_3)_2 \xrightarrow{KOH\text{-}EtOH} trans\text{-}[Pt(Cl)(H)(PEt_3)_2]$$

$$[FeI_2(CO)_4] \xrightarrow[THF]{NaBH_4} [FeH_2(CO)_4]$$

$$Rh^{3+}(aq) + SO_4^{2-} + NH_3(aq) + Zn \rightarrow [Rh(H)(NH_3)_5]SO_4$$

For example, let us consider platinum complex such as bis(triethyl phosphine) dichloroplatinum, a trans compound and treat this one with KOH in EtOH, this is also called alcoholic-KOH, this gives selectively monohydride. Another example is, let us consider this complex. When you treat this one with sodium borohydride in THF. Similarly, one can also perform a reaction in aqueous medium using a reducing agent such as zinc.

Consider rhodium(III) in aqueous solution, it can give rhodium hydride of this type. Of course, just by looking into it and type of anionic ligand we have and also the counter anion we have here you should be able to tell the oxidation state of rhodium. I leave it to you to guess the oxidation state of rhodium in this case.

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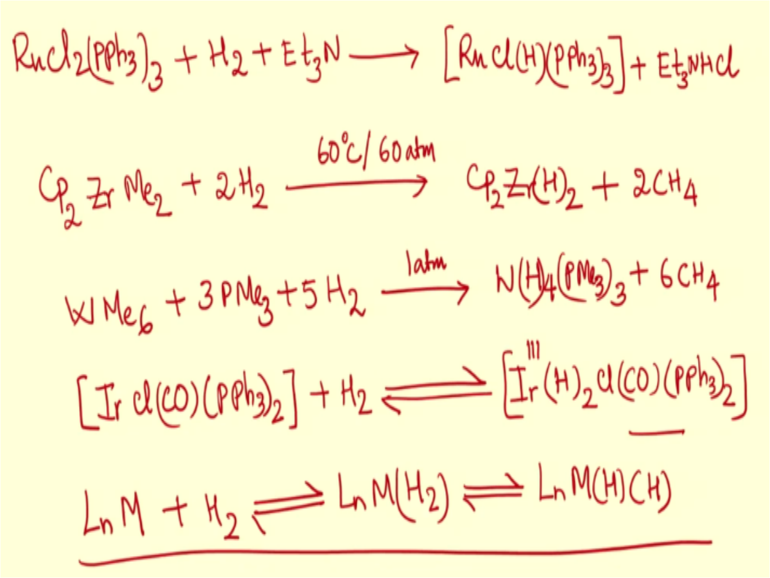

$$RuCl_2(PPh_3)_3 + H_2 + Et_3N \longrightarrow [RuCl(H)(PPh_3)_3] + Et_3NHCl$$

$$Cp_2ZrMe_2 + 2H_2 \xrightarrow{60^\circ C/\ 60\ atm} Cp_2Zr(H)_2 + 2CH_4$$

$$WMe_6 + 3PMe_3 + 5H_2 \xrightarrow{1atm} W(H)_4(PMe_3)_3 + 6CH_4$$

$$[IrCl(CO)(PPh_3)_2] + H_2 \rightleftharpoons [\overset{III}{Ir}(H)_2Cl(CO)(PPh_3)_2]$$

$$L_nM + H_2 \rightleftharpoons L_nM(H_2) \rightleftharpoons L_nM(H)(H)$$

Let me give you some methods of preparation involving H_2 gas. Take $[RuCl_2(PPh_3)_3]$. I gave you the preparation of this one in my previous lecture. Treat this one with H_2 in presence of a base such as triethylamine. So, it leads to the formation of a very useful hydride chlorohydride complex plus triethylammonium chloride is formed. One can also start from dimethyl zirconocene, of course zirconium is in +4 state in this case.

When you treat this one with H_2 at 60 °C and 60 atmosphere pressure, it forms the corresponding dihydride. We should be careful here when something like this is written like this, we have two zirconium to hydrogen bonds, that means hydride. So, if you simply put H_2 then it indicates H_2 is acting as a neutral ligand. And now of course, you can anticipate the product that comes out here 2 equivalents of methane would come out.

Similarly, if you take hexamethyltungsten and treat this one with hydrogen in presence of a phosphine such as trimethyl phosphine, here 1 atmospheric pressure of hydrogen is sufficient, it can give you. So, here all methyl groups are coming out as methane. So how it would be with rhodium or iridium, let us consider one such example. Let us consider Vaska's compound that you are all familiar with. Of course, in this one iridium is in +1 state, add hydrogen, it is a reversible reaction.

Now oxidative addition takes place and we get dihydride complex. So, I will be elaborating this particular reaction in more detail later when I take up oxidative addition, reductive elimination reactions of coordination components. These are the few representative examples in which one can see how some metal complexes with appropriate ligands can be treated with directly hydrogen gas under various pressures and temperatures suitable for that particular transformation to get metal hydride bonds.

A typical reaction is something like this. A general reaction I would write here, a general reversible reaction will be something like this initially and then it changes to hydride complex or oxidative addition process is completed. So, this is very important when it comes to the hydrogenation process in homogeneous catalysis.

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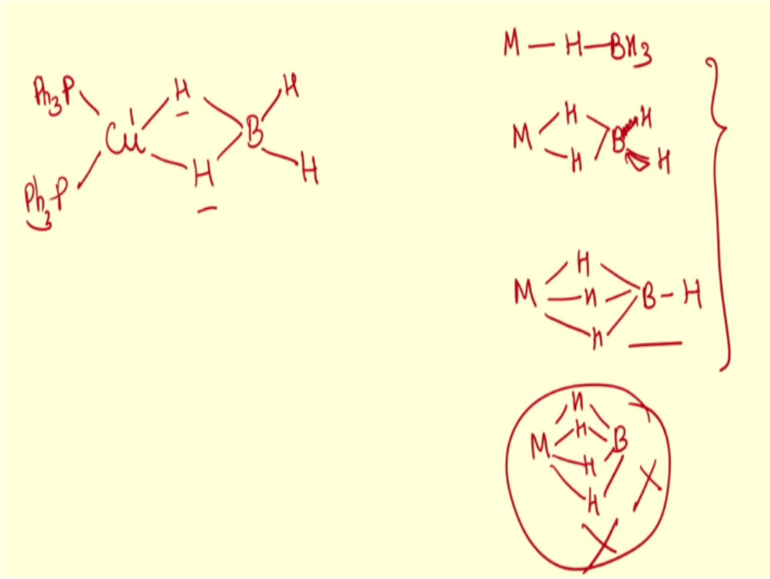

Besides this, we also use some of hydrogen species such as $NaBH_4$ also to make metal hydride complexes, let me write couple of examples here. You can see here copper is in +1 state and then BH_4^- is bridging and making two bridged hydrogen bonds here. So, that means borohydride you can establish either single bond or triple bond or even double bond, I mean you can have two bridging units or one bridging unit or even three bridging units.

That means if you take a typical, one can have something like this or one can also have something like this or, so all these three types of examples are known. If you ask me whether this is possible, certainly this is not possible because you should remember in BH_4^-, B is utilizing its *sp*^{3} hybrid orbitals which are disposed in this fashion, in that case what happens? So, visualizing this one is something very difficult.

On the other hand, in this case, it can have some sort of pyramidal, still it can retain distorted tetrahedral geometry, whereas in this case it is not possible, as a result this kind of utilizing all four hydrogen atoms for establishing bridging something like this cannot be seen or it is not possible, whereas these things are quite possible here. So, let me continue discussing more chemistry and also why we have to make these complexes.

Of course, we have seen in case of oxidative addition of H_2 to iridium(I) to form iridium hydride complex and that can very efficiently do hydrogenation of unsaturated organic molecules, but can we go beyond this one, utilizing further for organic transformation? Let us see in my next lecture. Until then have an excellent time reading chemistry.