metal to form a σ-bond (Figure 7b). The π-back donation (Figure 7c) is from two *dπ*-orbitals of the metal into the two-perpendicular *p*-orbitals of the carbon which results in a metal-carbon triple bond. The carbyne ligand can act as a 3e-donor.

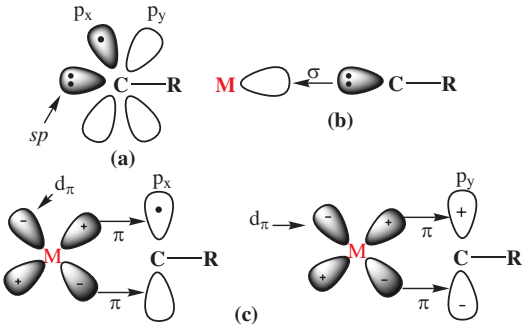

Figure 7. (i) Orbitals of the free carbyne ligand; (ii) σ- and π-orbital overlap between a metal (M) and a carbyne ligand.

Other *monohapto*-ligands with M-C bonds

Thiocarbonyl (:C≡S)	• A better σ-donor and a better π-acceptor than C≡O. • Like C≡O, it can show bridging coordination modes such as $M_2(\mu_2\text{-}C{\equiv}S)$ and $M_3(\mu_3\text{-}C{\equiv}S)$
Isocyanide or isonitrile (RN≡C:)	• Isoelectronic with C≡O • Stronger σ-donor and weaker π-acceptor than C≡O • Capable of forming stable complexes with d^0 metals and metals in higher oxidation states
Cyanide ($^-$C≡N)	• Isoelectronic with C≡O • A good σ-donor and a weaker π-acceptor. • Forms stable complexes with more electropositive transition metals in higher oxidation states

Student Corner

Dihydrogen Complexes

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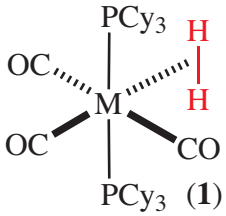
We know that neutral ligands such as H_2O, NMe_3 and PPh_3 donate a pair of electrons on the heteroatom to a metal center when coordinate bond is formed. Transition metal hydrides contain at least one M-H bond where a pair of electrons is shared between hydrogen and the metal center. In this article, syntheses and properties of complexes with **molecular hydrogen** (H_2) are presented.

Can a simple molecule such as H_2 form a bond with a metal center?

Molecular hydrogen or dihydrogen does not contain a lone pair of electrons and it has only **a pair of σ-bonding electrons** shared between both hydrogen atoms. H_2 can use these two electrons to ligate to a metal forming a **dihapto** dihydrogen (η^2-H_2) ligand. Formation of metal-dihydrogen complexes, $[L_nM(\eta^2\text{-}H_2)]$ was recognized by Kubas in 1984, *e.g.*, $[M(\eta^2\text{-}H_2)(CO)_3(PR_3)_2]$ (**1**) where M = W or Mo, R = Pr^i and Cy.



(**1**)

Figure 1. *mer,trans*-$[M(\eta^2\text{-}H_2)(CO)_3(PCy_3)_2]$, Cy = chyclohexyl

These are zerovalent octahedral complexes and not seven coordinated divalent complexes (or dihydrides). These are called non-classical hydrides. The coordinated H–H bond can be cleaved to form classical dihydrides. Thus, a dihydrogen complex can be considered as an intermediate in the oxidative addition process of H_2 to a metal centre.

Formation of H_3^+ ion

Donation of σ-bonding electrons of H_2 to the H^+ ion produces a triangular H_3^+ ion (**2**) in the gas phase

which can be considered as the dihydrogen complex of the proton (H^+).

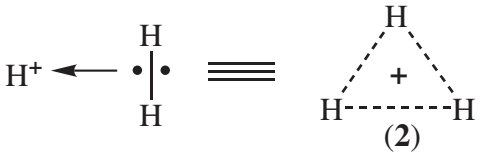


Figure 2. Formation of H_3^+ ion

Formation of CH_5^+ ion

The methyl cation (CH_3^+) combines with H_2 to form the CH_5^+ ion (**3**) or the dihydrogen complex of the methyl carbonium ion as shown in Figure 3.

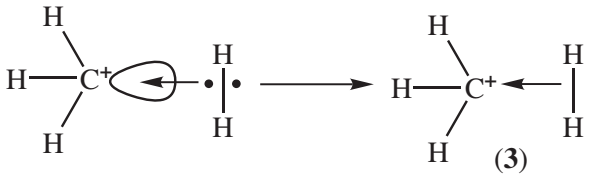


Figure 3. Formation of CH_5^+ ion (**3**)

Formation of dihydrogen complexes

Molecular H_2 can form a complex with a suitable metal fragment L_nM to produce $[L_nM(\eta^2\text{-}H_2)]$ (**4**) as shown in Figure 4.

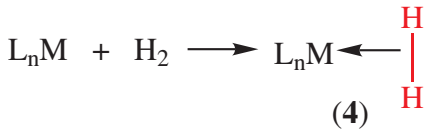


Figure 4. Formation of $[L_nM(\eta^2\text{-}H_2)]$ (**4**)

Here, the H-H bond acts as a ligand. The coordination of dihydrogen weakens the H-H bond but does not break it as found in oxidative addition (O.A.) reactions of H_2. It is quite possible to have back bonding due to donation of metal *dπ* electrons to the H-H σ*-orbital. Sometimes, this back donation component is strong enough to break the H-H bond resulting in the dihydride $[L_nMH_2]$ (**5**) as shown in Figure 5.

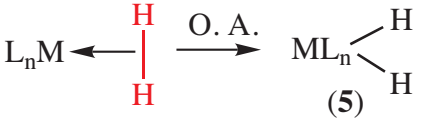


Figure 5. Formation of $[L_nMH_2]$ (**5**)

Note: Since H_2 is a weak donor ligand some degree of back bonding is essential to form an isolable η^2-dihydrogen complex.

Properties of dihydrogen complexes

IR and NMR spectroscopies can be used to study the behaviour of dihydrogen complexes.

a) The IR absorption frequency, υ(HH), of the coordinated H–H should appear at 2300-2900 cm^{-1}, but it is not always seen. Free H_2 is IR inactive.

b) In the ^{1}H-NMR spectrum, the hydrogen resonance is often broad and appears between 0 to –12 ppm. The presence of a coordinated H–H bond can be confirmed by preparing the H–D analogue where there is a ^{1}J(HD) coupling of about 20–34 Hz. Free HD has a ^{1}J(HD) value of 43 Hz. In classical hydrides ^{2}J(HD) is less than 1 Hz.

c) Free dihydrogen has a H–H bond distance of 0.74 Å. In dihydrogen complexes, the H–H bond distance varies between 0.82-1.0 Å.

d) The bound H_2 ($pK_a \approx 0$ to 15) is much more acidic than the free H_2 ($pK_a = 35$).

Synthesis of dihydrogen complexes

Some classical hydrides can be protonated to synthesize dihydrogen complexes. Some coordinatively unsaturated complexes tend to accommodate H_2 into the vacant site, thereby satisfying the 18e rule. Some examples are given below.

By protonating metal hydrides

(a) Protonation of *trans*-$[FeH_2(dppe)_2]$ (**6**) with HBF_4 gives the dihydrogen complex $[FeH(\eta^2\text{-}H_2)(dppe)_2]$ BF_4 (**7**) as a pale yellow solid.

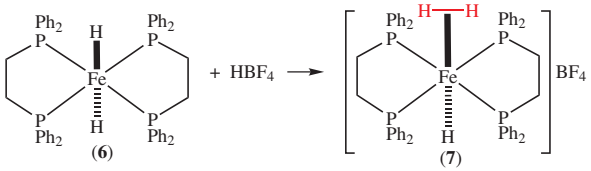


Figure 6. Formation of (**7**) from (**6**)

(b) HBF_4 can reversibly protonate the multihydride $[IrH_5(PCy_3)_2]$ (**8**) to generate the complex $[IrH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]BF_4$ (**9**) with two dihydrogen ligands.

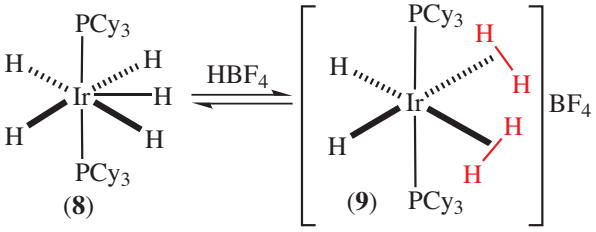


Figure 7. Formation of (**9**) from (**8**)

At room temperature, the ^{1}H-NMR spectrum of the complex (**9**) is fluxional and gives a broad peak at –8 ppm for both hydrides and dihydrogen ligands. At –85^{O}C, it gives two resonance with intensity ratio of 2:1; one at –5.05 ppm the half-width $W_{1/2}$ = 175 Hz for two dihydrogen and the other at –15.3 ppm with $W_{1/2}$ = 154 Hz for the two hydrides.

By filling a vacant site

The zerovalent complex $[M(CO)_3(PCy_3)_2]$ (**10**) where M = Mo, W, takes up H_2 to give a six-coordinate dihydrogen complex *mer,trans*-$[M(\eta^2\text{-}H_2)(CO)_3(PCy_3)_2]$ (**1**). In this case, H_2 binds reversibly and H_2 can be removed by bubbling argon through the solution.

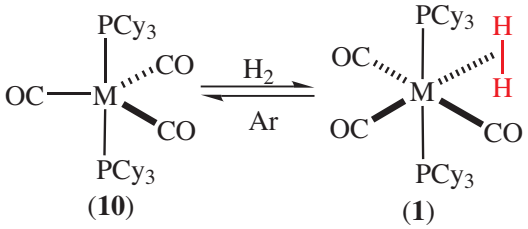


Figure 8. Formation of (**1**) from (**10**)

According to X-ray crystal structure of the tungsten analogue of (**1**), the H–H vector is parallel to the P-W-P axis rather than the OC–W–CO axis. d(H-H) = 0.82 Å, d(W-H) = 1.89 Å.

In the proton NMR spectrum, the resonance due to (η^2-H_2) is broad in the region -3 to -4.5 ppm. H_2 ligand rotates readily about the M–(H_2) axis. The IR absorption frequency of H-H bond is 2690 cm^{-1}.

SO_2 can displace dihydrogen ligand from $[Mo(\eta^2\text{-}H_2)(CO)_3(PCy_3)_2]$ to produce the red orange complex $[Mo(SO_2)(CO)_3(PCy_3)_2]$.

$[W(\eta^2\text{-}H_2)(CO)_3(PPr^i_3)_2]$ reacts with N_2 to give the N_2-bridged binuclear complex $[(OC)_3(Pr^i_3P)_2W(\mu\text{-}N_2)W(PPr^i_3)_2(CO)_3]$(**11**).

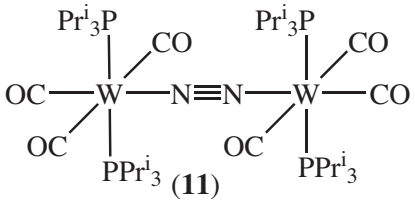


Figure 9. Structure of N_2-bridged complex (**11**)

Problems

1. Explain the formation of CH_5^+ cation.
2. Draw the structures of the following dihydrogen complexes.
   a) *mer,trans*-$[W(\eta^2\text{-}H_2)(CO)_3(PPr^i_3)_2]$
   b) *trans*-$[Fe(\eta^2\text{-}H_2)H(dppe)_2]BF_4$
   c) $[CpRu(\eta^2\text{-}H_2)(PPh_3)(NCBu^t)]^+$
   d) $[CpRe(NO)(CO)(\eta^2\text{-}H_2)]^+$
   e) *trans*-$[IrH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]^+$
   f) *mer,cis*-$[FeH_2(\eta^2\text{-}H_2)(PPh_3)_3]$
   g) $[ReH_5(\eta^2\text{-}H_2)(PPh_3)_2]$