

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 ($\eta^2\text{-H}_2$) ligand. Formation of metal-dihydrogen complexes, $[\text{L}_n\text{M}(\eta^2\text{-H}_2)]$ was recognized by Kubas in 1984, e.g., $[\text{M}(\eta^2\text{-H}_2)(\text{CO})_3(\text{PR}_3)_2]$ (1) where M = W or Mo, R = Pr^i and Cy.

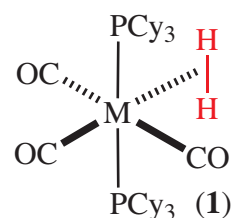


Figure 1. *mer,trans*- $[\text{M}(\eta^2\text{-H}_2)(\text{CO})_3(\text{PCy}_3)_2]$,

Cy = cyclohexyl

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^+).

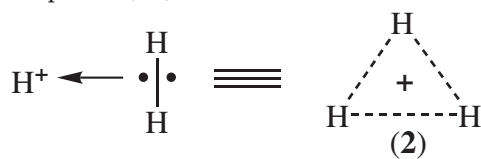


Figure 2. Formation of H_3^+ ion

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.

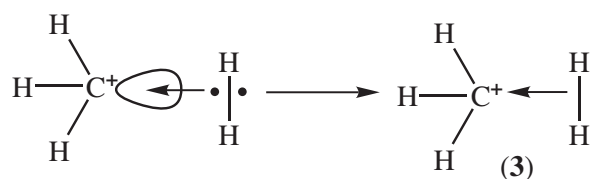


Figure 3. Formation of CH_5^+ ion (3)

Formation of dihydrogen complexes

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

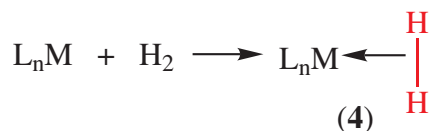


Figure 4. Formation of $[L_nM(\eta^2-H_2)]$ (4)

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 $d\pi$ 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.

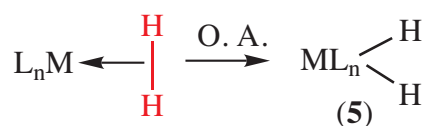


Figure 5. Formation of $[L_nMH_2]$ (5)

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.

- The IR absorption frequency, $\nu(HH)$, of the coordinated H-H should appear at $2300-2900\text{ cm}^{-1}$, but it is not always seen. Free H_2 is IR inactive.
- In the 1H -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 $^1J(HD)$ coupling of about $20-34\text{ Hz}$. Free HD has a $^1J(HD)$ value of 43 Hz . In classical hydrides $^2J(HD)$ is less than 1 Hz .
- Free dihydrogen has a H-H bond distance of 0.74 \AA . In dihydrogen complexes, the H-H bond distance varies between $0.82-1.0\text{ \AA}$.
- 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 $[FeH(\eta^2-H_2)(dppe)_2]BF_4$ (7) as a pale yellow solid.

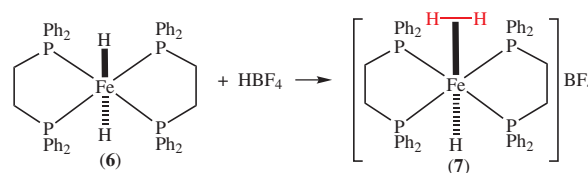


Figure 6. Formation of (7) from (6)

(b) HBf_4 can reversibly protonate the multihydride $[IrH_5(PCy_3)_2]$ (8) to generate the complex $[IrH_2(\eta^2-H_2)_2(PCy_3)_2]BF_4$ (9) with two dihydrogen ligands.

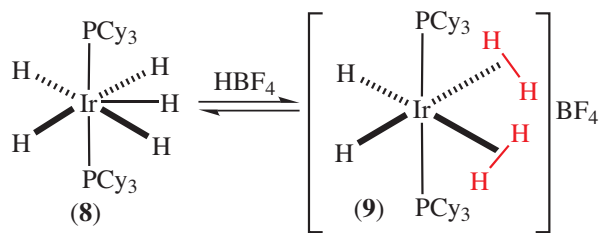


Figure 7. Formation of (9) from (8)

At room temperature, the $^1\text{H-NMR}$ spectrum of the complex (9) is fluxional and gives a broad peak at -8 ppm for both hydrides and dihydrogen ligands. At -85°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 $[\text{M}(\text{CO})_3(\text{PCy}_3)_2]$ (10) where $\text{M} = \text{Mo}, \text{W}$, takes up H_2 to give a six-coordinate dihydrogen complex $\text{mer,trans-}[\text{M}(\eta^2\text{-H}_2)(\text{CO})_3(\text{PCy}_3)_2]$ (1). In this case, H_2 binds reversibly and H_2 can be removed by bubbling argon through the solution.

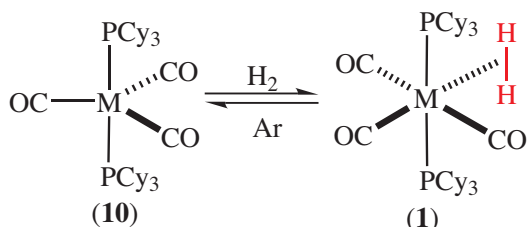


Figure 8. Formation of (1) from (10)

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. $d(\text{H-H}) = 0.82 \text{ \AA}$, $d(\text{W-H}) = 1.89 \text{ \AA}$.

In the proton NMR spectrum, the resonance due to $(\eta^2\text{-H}_2)$ is broad in the region -3 to -4.5 ppm. H_2 ligand rotates readily about the $\text{M-(H}_2)$ axis. The IR absorption frequency of H-H bond is 2690 cm^{-1} .

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

$[\text{W}(\eta^2\text{-H}_2)(\text{CO})_3(\text{PPr}^i_3)_2]$ reacts with N_2 to give the N_2 -bridged binuclear complex $[(\text{OC})_3(\text{Pr}^i_3\text{P})_2\text{W}(\mu\text{-N}_2)]$

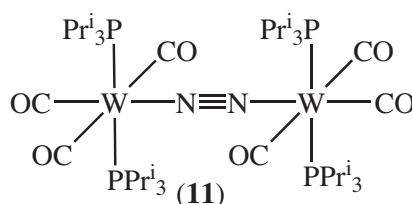
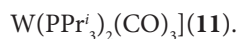


Figure 9. Structure of N_2 -bridged complex (11)

Problems

1. Explain the formation of CH_5^+ cation.
2. Draw the structures of the following dihydrogen complexes.
 - a) $\text{mer,trans-}[\text{W}(\eta^2\text{-H}_2)(\text{CO})_3(\text{PPr}^i_3)_2]$
 - b) $\text{trans-}[\text{Fe}(\eta^2\text{-H}_2)\text{H}(\text{dppe})_2]\text{BF}_4$
 - c) $[\text{CpRu}(\eta^2\text{-H}_2)(\text{PPh}_3)(\text{NCBu}^t)^+]$
 - d) $[\text{CpRe}(\text{NO})(\text{CO})(\eta^2\text{-H}_2)]^+$
 - e) $\text{trans-}[\text{IrH}_2(\eta^2\text{-H}_2)_2(\text{PCy}_3)_2]^+$
 - f) $\text{mer,cis-}[\text{FeH}_2(\eta^2\text{-H}_2)(\text{PPh}_3)_3]$
 - g) $[\text{ReH}_5(\eta^2\text{-H}_2)(\text{PPh}_3)_2]$