Bonding in Organometallic Complexes

K. Sarath D. Perera

Senior Professor in Chemistry, Department of Chemistry, The Open University of Sri Lanka

Neutral ligands (:L) and monoanionic ligands (X^-) donate *a pair of electrons or a lone-pair* to a vacant orbital in a transition metal centre (M) to form a covalent **σ-bond** between them. Ligands such as :C≡O, :C≡NR (isonitrile or isocyanide) and :PR_3 (tertiary phosphine or phosphite) can donate a pair of electrons to a metal centre to form a σ-bond. These ligands are considered as **σ-donors**. During this process the electron density of the metal centre increases. Some of the ligands can accept *dπ*-**electrons** from the metal centre, *i.e.* these ligands can act as **π-acceptors** or **π-acid ligands**. This process of donating *dπ*-electrons in a filled *d* orbitals of a metal is known as **back donation** or **back bonding**. Thus, back donation introduces the π character into the M-L bond and makes the M-L bond stronger.

$$M \underset{\pi}{\overset{\sigma}{\rightleftharpoons}} L \qquad L = CO, CNR \text{ and } PR$$

Hard and soft metals

Metals can be broadly classified into **hard** and **soft** metals. Early transition metals in higher oxidation states are positively charged and classified as **hard metals**. They are more likely to form strong bonds with **electron rich σ-donors**. These hard metal centres are **electrophilic**, *i.e.* they are electron loving. Late transition metal centres in lower or zero oxidation states are electron rich (or more π-basic) and are classified as soft metals. They are more likely to form strong bonds with **electron withdrawing π acceptors**. These π-basic metal centres are **nucleophilic**.

Organometallic complexes have at least one M-C bond. In this article, bonding between a metal centre and ligands such as C≡O, alkyl, carbene and carbyne ligands are presented.

Metal carbonyls

Coordination chemistry of carbon monoxide C≡O is well studied. Transition metals, particularly in zero or lower oxidation states, form stable metal carbonyls with carbon monoxide, *e.g.*, $[Cr(CO)_6]$, $[Mn(CO)_5Br]$, $[Fe(CO)_5]$, $Na[Co(CO)_4]$ and $[Ni(CO)_4]$. The ligand C≡O is a weak σ-donor but a good π-acceptor. Its primary mode of attachment to metal centre is through carbon atom.

Consider the bonding in carbon monoxide (Figure 1a), both carbon and oxygen atoms are *sp*-hybridised; these *sp* hybridised orbitals are directional. They overlap along the internuclear axis to form a **σ-bond** (Figure 1a). The unhybridised $2p_z$ and $2p_y$ orbitals of each atom overlap collaterally (Figure 1b) to form **two π bonds**. The result is a triple bond (Figure 1c).

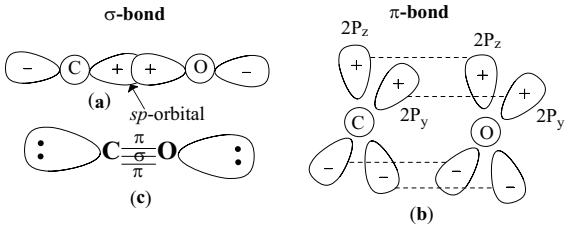


Figure 1. Orbitals involved in bonding in C≡O

The schematic representation of the orbital overlap in the formation of the M-CO bond is given in Figure 2.

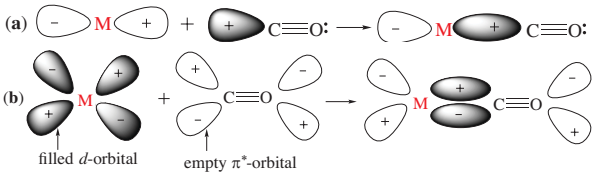


Figure 2. Orbital overlaps in the M-CO bond

The bonding between CO and a metal in a metal carbonyl can have the following contributions.

a) σ-overlap: a σ-bond is formed because of the overlap of the directional *sp*-hybrid orbital containing the lone pair on carbon with a vacant hybrid orbital with the proper symmetry of the transition metal as in Figure 2a.

b) π-overlap: a π-bond is formed because of the overlap of filled metal *d* orbitals with low-lying vacant π*antibonding orbitals of C≡O as in Figure 2b. This overlap is generally referred to as **back-bonding** or **back-donation**.

Metal carbon bond in metal carbonyls has multiple bond

character, due to these two contributions.

Metal alkyls

Alkyl metal complexes are formed during many catalytic cycles. They contain M-C bonds. Some binary examples include $[Cr(Bu^t)_4]$, $[WMe_6]$, $[ReMe_8]$ and $HgMe_2$.

The M-C σ-bond is formed due to the interaction between an empty d-orbital of the metal and a filled orbital of the carbon of the organic group as shown below.

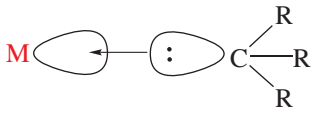


Figure 3. M-C σ-bond formation (R = alkyl)

The carbon in metal alkyls is *sp*, sp^2 or sp^3 hybridised. The M-C bond strength varies in the following order.

$$M\text{-}CR_3 < M\text{-aryl}, M\text{-}CH{=}CRR' < M\text{-}C{\equiv}CR$$

$$sp^3\text{-carbon} < sp^2\text{-carbon} < sp\text{-carbon}$$

The electron withdrawing ability of the carbon increases from sp^3 to *sp*. The alkynyl (-C≡CR), olefinic (-CH=CRR′) and aryl (Ar) groups can accept *d*-electrons from the metal centre forming stronger M-C bonds. Common metal-alkyl bonding modes are given in Figure 4 (R = H, organic group).

Terminal alkyls/aryls

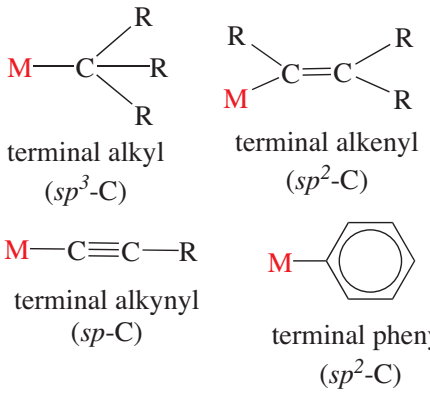


Figure 4. M-C σ-bond formation with *sp*, sp^2 or sp^3 -hybridised carbon atom

Some metal alkyls contain stabilizing ligands, *e.g.*, Cp^- ($C_5H_5^-$), C≡O, and PR_3. Some examples include $[Cp^*_2ScMe]$, $[Cp_2TiMe_2]$, $[MnMe(CO)_5]$, $[Cp^*_2IrMe_4]$, $[NiPh_2(PPh_3)_2]$ and $[CpMo(CO)_3Me]$.

Bridging alkyls/aryls

Alkyl or aryl group can act as a bridging ligand as shown in Figure 5.

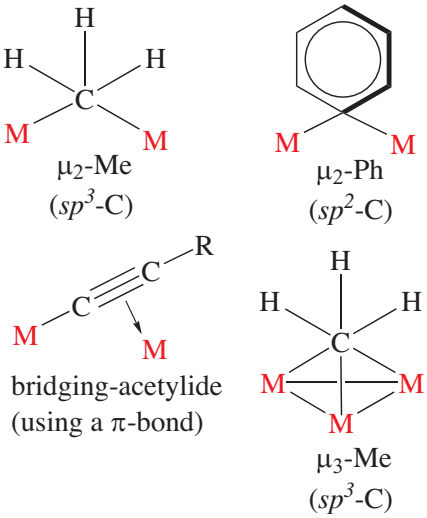


Figure 5. Organic groups bridge 2 or 3 metals

Metal carbenes

The bonding of a carbene ligand (:CRR') to a metal is similar to those in metal carbonyls. The M=CRR' skeleton has a planar arrangement. Carbene ligand (Figure 6a) is a 2e-donor, and the carbon is sp^2-hybridised. The lone pair in the low-lying sp^2-orbital is donated to a vacant orbital on the metal forming a σ-bond (Figure 6b). The π-back donation forms a π-bond as shown in Figure 6b.

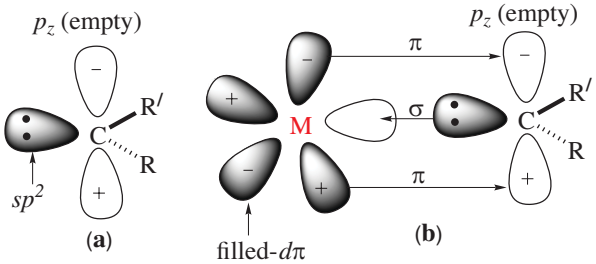


Figure 6. (a) Orbitals of a free carbene ligand; (b) σ- and π-orbital overlaps between a metal (M) and a carbene ligand.

Metal carbynes

The carbon of a carbyne ligand (≡C-R) (Figure 7a) is *sp*-hybridised and it contains 2e in the *sp* orbital and 1e in the π-orbital. Carbyne complexes contain a M≡C-R unit and the M-C-R group is linear or near linear. The lone-pair in the *sp*-orbital on the carbon is donated to the

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.

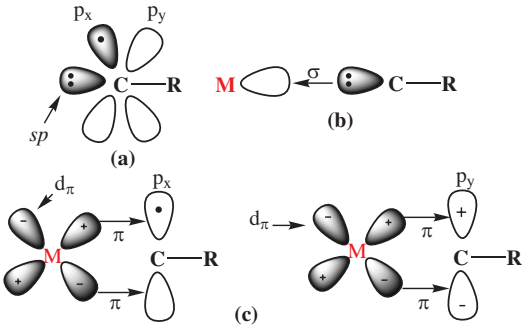


Figure 7. (i) Orbitals of the free carbyne ligand; (ii) σ- and π-orbital overlap between a metal (M) and a carbyne ligand.

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

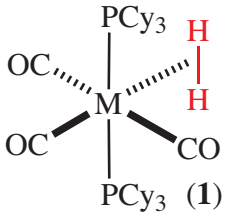
K. Sarath D. Perera

Senior Professor in Chemistry, Department of Chemistry, The Open University of Sri Lanka

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^+).

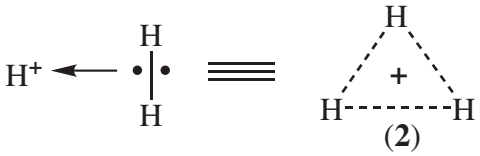


Figure 2. Formation of H_3^+ ion

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.

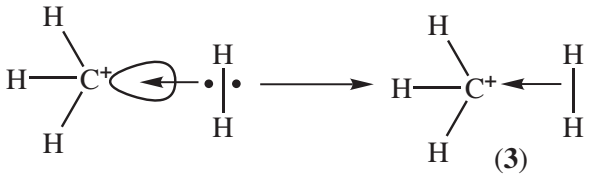


Figure 3. Formation of CH_5^+ ion (**3**)

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.

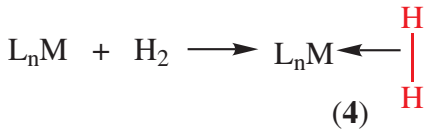


Figure 4. Formation of $[L_nM(\eta^2\text{-}H_2)]$ (**4**)

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.

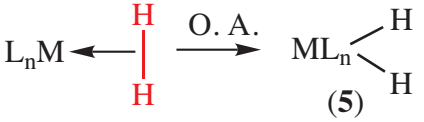


Figure 5. Formation of $[L_nMH_2]$ (**5**)

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.

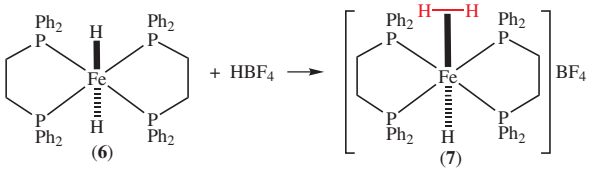


Figure 6. Formation of (**7**) from (**6**)

(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.

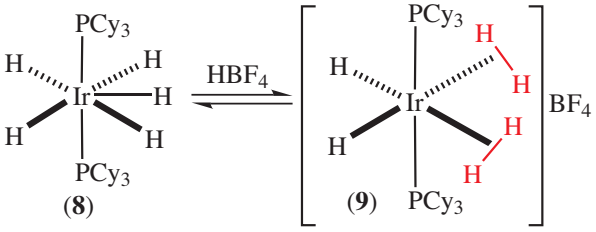


Figure 7. Formation of (**9**) from (**8**)

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.

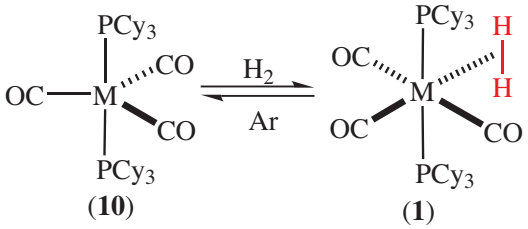


Figure 8. Formation of (**1**) from (**10**)

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**).

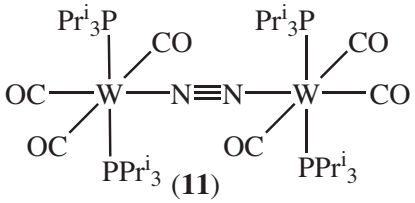


Figure 9. Structure of N_2-bridged complex (**11**)

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) $[ReH_5(\eta^2\text{-}H_2)(PPh_3)_2]$