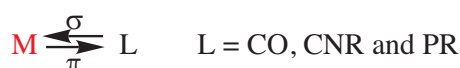


## Bonding in Organometallic Complexes

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



### 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  $\sigma$ -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  $\pi$ -basic) and are classified as soft metals. They are more likely to form strong bonds with **electron withdrawing  $\pi$  acceptors**. These  $\pi$ -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  $C\equiv O$ , alkyl, carbene and carbyne ligands are presented.

### Metal carbonyls

Coordination chemistry of carbon monoxide  $C\equiv O$  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  $C\equiv O$

is a weak  $\sigma$ -donor but a good  $\pi$ -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  $\sigma$ -bond (Figure 1a). The unhybridised  $2p_z$  and  $2p_y$  orbitals of each atom overlap collaterally (Figure 1b) to form **two  $\pi$  bonds**. The result is a triple bond (Figure 1c).

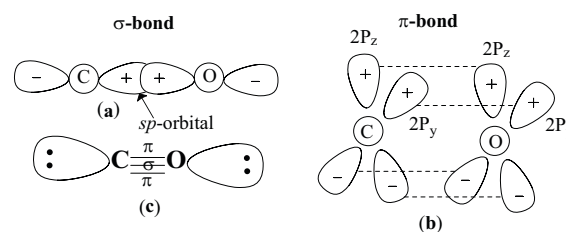


Figure 1. Orbitals involved in bonding in  $C\equiv O$

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

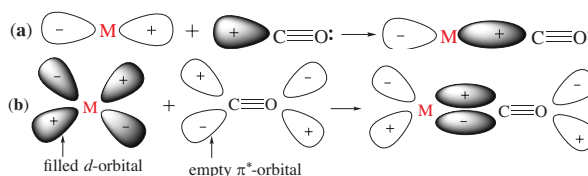


Figure 2. Orbital overlaps in the M-CO bond

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

**a)  $\sigma$ -overlap:** a  $\sigma$ -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)  $\pi$ -overlap:** a  $\pi$ -bond is formed because of the overlap of filled metal  $d$  orbitals with low-lying vacant  $\pi^*$  antibonding orbitals of  $C\equiv O$  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.

$[\text{NiPh}_2(\text{PPh}_3)_2]$  and  $[\text{CpMo}(\text{CO})_3\text{Me}]$ .

### Metal alkyls

Alkyl metal complexes are formed during many catalytic cycles. They contain M-C bonds. Some binary examples include  $[\text{Cr}(\text{Bu}^t)_4]$ ,  $[\text{WMe}_6]$ ,  $[\text{ReMe}_8]$  and  $\text{HgMe}_2$ .

The M-C  $\sigma$ -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.

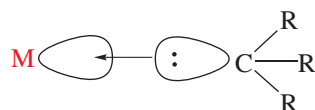


Figure 3. M-C  $\sigma$ -bond formation (R = alkyl)

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



The electron withdrawing ability of the carbon increases from  $sp^3$  to  $sp$ . The alkynyl ( $-\text{C}\equiv\text{CR}$ ), olefinic ( $-\text{CH}=\text{CRR}'$ ) 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

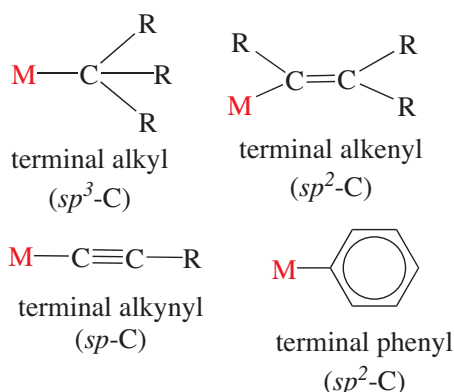


Figure 4. M-C  $\sigma$ -bond formation with  $sp$ ,  $sp^2$  or  $sp^3$ -hybridised carbon atom

Some metal alkyls contain stabilizing ligands, e.g.,  $\text{Cp}^-$  ( $\text{C}_5\text{H}_5^-$ ),  $\text{C}\equiv\text{O}$ , and  $\text{PR}_3$ . Some examples include  $[\text{Cp}^*_2\text{ScMe}]$ ,  $[\text{Cp}_2\text{TiMe}_2]$ ,  $[\text{MnMe}(\text{CO})_5]$ ,  $[\text{Cp}^*_2\text{IrMe}_4]$ ,

### Bridging alkyls/aryls

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

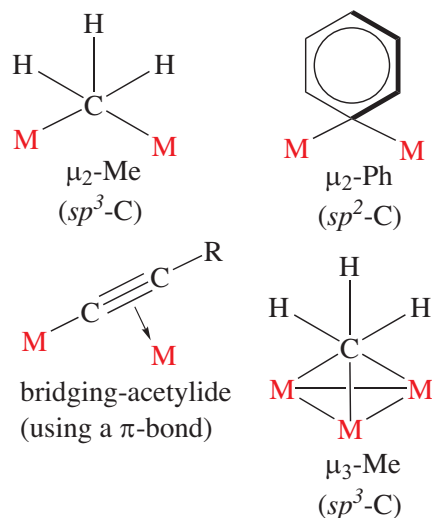


Figure 5. Organic groups bridge 2 or 3 metals

### Metal carbenes

The bonding of a carbene ligand ( $:\text{CRR}'$ ) to a metal is similar to those in metal carbonyls. The  $\text{M}=\text{CRR}'$  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  $\sigma$ -bond (Figure 6b). The  $\pi$ -back donation forms a  $\pi$ -bond as shown in Figure 6b.

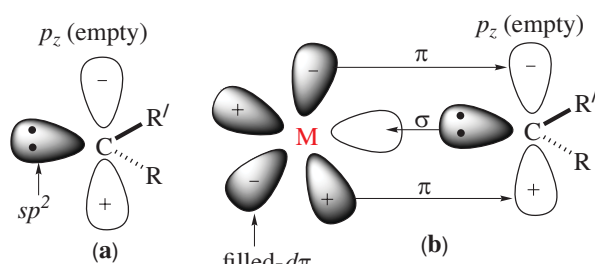
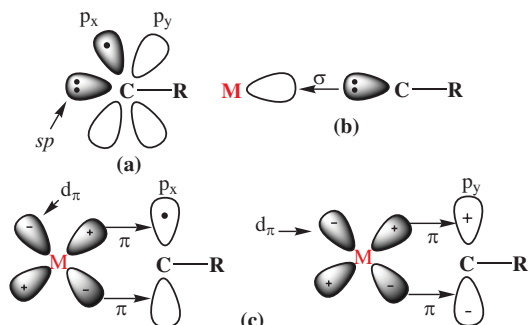


Figure 6. (a) Orbitals of a free carbene ligand; (b)  $\sigma$ - and  $\pi$ -orbital overlaps between a metal (M) and a carbene ligand.

### Metal carbynes

The carbon of a carbyne ligand ( $\equiv\text{C-R}$ ) (Figure 7a) is  $sp$ -hybridised and it contains 2e in the  $sp$  orbital and 1e in the  $\pi$ -orbital. Carbyne complexes contain a  $\text{M}\equiv\text{C-R}$  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  $\sigma$ -bond (Figure 7b). The  $\pi$ -back donation (Figure 7c) is from two  $d\pi$ -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)  $\sigma$ - and  $\pi$ -orbital overlap between a metal (M) and a carbyne ligand.

#### Other monohapto-ligands with M-C bonds

Thiocarbonyl ( $\text{:C}\equiv\text{S}$ )	<ul style="list-style-type: none"> <li>• A better <math>\sigma</math>-donor and a better <math>\pi</math>-acceptor than <math>\text{C}\equiv\text{O}</math>.</li> <li>• Like <math>\text{C}\equiv\text{O}</math>, it can show bridging coordination modes such as <math>\text{M}_2(\mu_2\text{-C}\equiv\text{S})</math> and <math>\text{M}_3(\mu_3\text{-C}\equiv\text{S})</math></li> </ul>
Isocyanide or isonitrile ( $\text{RN}\equiv\text{C:}$ )	<ul style="list-style-type: none"> <li>• Isoelectronic with <math>\text{C}\equiv\text{O}</math></li> <li>• Stronger <math>\sigma</math>-donor and weaker <math>\pi</math>-acceptor than <math>\text{C}\equiv\text{O}</math></li> <li>• Capable of forming stable complexes with <math>d^0</math> metals and metals in higher oxidation states</li> </ul>
Cyanide ( $\text{:C}\equiv\text{N}$ )	<ul style="list-style-type: none"> <li>• Isoelectronic with <math>\text{C}\equiv\text{O}</math></li> <li>• A good <math>\sigma</math>-donor and a weaker <math>\pi</math>-acceptor.</li> <li>• Forms stable complexes with more electropositive transition metals in higher oxidation states</li> </ul>