

ORGANOMETALLIC CHEMISTRY

For a complex to be organometallic compound there should be at least one metal-carbon bond.

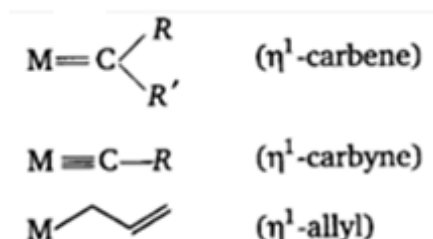
Example: RMgX

There are some complex which do not contain any M-C bond but are consider to be member of organometallics compound.

Example : wilkinson catalyst $\text{Rh}(\text{PPh}_3)_3$ wich is used for hydrogenation of alkene and aklynes.

Hapticity:

- It is the property of ligand. The number of donor atom of a ligand is directly attached with the metal is said to be the hapticity
- A single organic ligand may interact with a central metal atom using one or more of its atoms simultaneously.



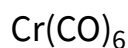
18 Electron Rule:

- The complex which follow 16 and 18 electron rule are stable
- Square planar complex follows 16 electron rule .
- Sixteen-electron square-planar species are most commonly encountered for d8 metals, particularly for metals having formal oxidation states of 2+ (Ni^{2+} , Pd^{2+} , and Pt^{2+}) and 1+ (Rh^{+} , Ir^{+}).
- Complex which follow 17 electron rule and 19 electron rule are paramagnetic.
- Complex which follows 17 electron rule is strong oxidizing agent.
- Complex which follows 19 electron rule is strong reducing agent

Electron counting scheme for common ligand:

Ligand	Method A	Method B
H	2 (H^-)	1
Cl, Br, I	2 (X^-)	1
OH, OR	2 (OH^- , OR^-)	1
CN	2 (CN^-)	1
CH_3 , CR_3	2 (CH_3^- , CR_3^-)	1
NO (bent $\text{M}-\text{N}-\text{O}$)	2 (NO^-)	1
NO (linear $\text{M}-\text{N}-\text{O}$)	2 (NO^+)	3
CO, PR_3	2	2
NH_3 , H_2O	2	2
$=\text{CRR}'$ (Carbene)	2	2
$\text{H}_2\text{C}=\text{CH}_2$ (Ethylene)	2	2
CNR	2	2
$=\text{O}$, $=\text{S}$	4 (O^{2-} , S^{2-})	2
$\eta^3\text{-C}_3\text{H}_5$ (π -allyl)	4 (C_3H_5^-)	3
$\equiv\text{CR}$ (Carbyne)	3	3
$\equiv\text{N}$	6 (N^{3-})	3
Ethylenediamine (en)	4 (2 per nitrogen)	4
Bipyridine (bipy)	4 (2 per nitrogen)	4
Butadiene	4	4
$\eta^5\text{-C}_5\text{H}_5$ (Cyclopentadienyl)	6 (C_5H_5^-)	5
$\eta^6\text{-C}_6\text{H}_6$ (Benzene)	6	6
$\eta^7\text{-C}_7\text{H}_7$ (Cycloheptatrienyl)	6 (C_7H_7^+)	7

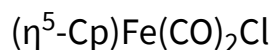
Example:



A Cr atom has 6 electrons outside its noble gas core. Each CO is considered to act as a donor of 2 electrons.

The total electron count is therefore:

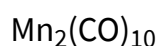
$$\begin{array}{rcl}
 \text{Cr} & & 6 \text{ electrons} \\
 6(\text{CO}) & 6 \times 2 \text{ electrons} = & \underline{12 \text{ electrons}} \\
 \text{Total} = & & 18 \text{ electrons}
 \end{array}$$



Neutral-Ligand Method

$$\begin{array}{rcl}
 \text{Fe atom} & & 8 \text{ electrons} \\
 \eta^5\text{-Cp} & & 5 \text{ electrons} \\
 2(\text{CO}) & & 4 \text{ electrons} \\
 \text{Cl} & & \underline{1 \text{ electron}} \\
 \text{Total} = & & 18 \text{ electrons}
 \end{array}$$

The results of the two methods are equivalent; both give 18 electrons.



Metal-metal single bond counts as one electron per metal, a double bond counts as two electrons per metal, and so forth.

For example, in dimeric $\text{Mn}_2(\text{CO})_{10}$, the electron count per manganese atom is, by either method:

Mn	7 electrons
5 (CO)	10 electrons
Mn - Mn bond	1 electron
<hr/>	
Total	= 18 electrons

Metal Carbonyls

Introduction:

Carbon monoxide is a very common ligand in organometallic chemistry, where it is known as the carbonyl group.

Carbon monoxide is particularly good at stabilizing very low oxidation states, with many compounds such as $\text{Ni}(\text{CO})_4$, $\text{W}(\text{CO})_6$, and $\text{Fe}_2(\text{CO})_9$, $\text{Fe}(\text{CO})_5$ having the metal in its zero oxidation state.

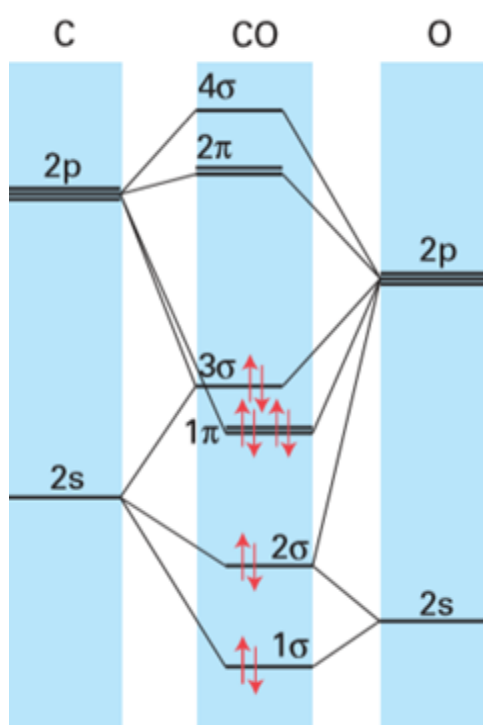


FIGURE: The molecular orbital scheme for CO shows that the HOMO has σ symmetry and is essentially a lobe that projects away from the C atom. The LUMO has π symmetry.

A simple picture of the bonding of CO to a metal atom is to treat the lone pair on the carbon atom as a Lewis σ base (an electron-pair donor) and the empty CO antibonding orbital as a Lewis π acid (an electron-pair acceptor), which accepts π -electron density from the filled d orbitals on the metal atom.

The bonding can be considered to be made up of two parts: a σ bond from the ligand to the metal atom Fig. (1) and a π bond from the metal atom to the ligand Fig.(2) . This type of π bonding is sometimes referred to as backbonding.

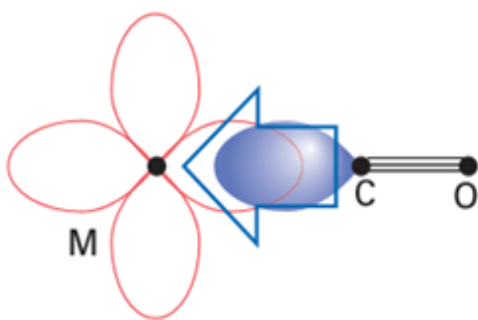


Fig. (1)

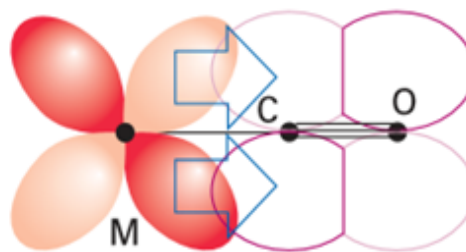


Fig. (2)

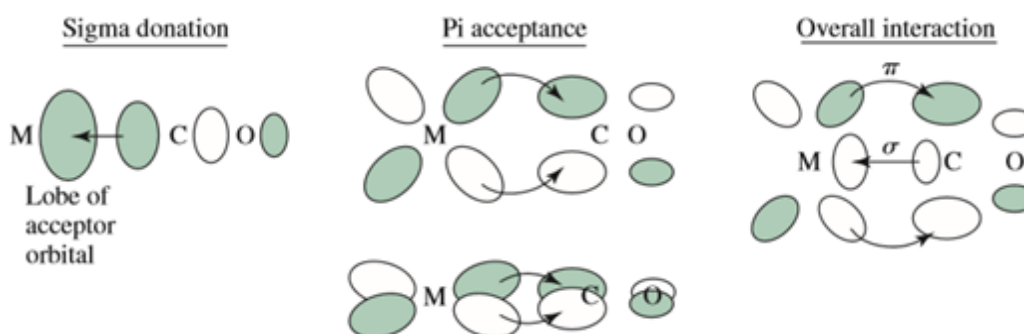
Carbon monoxide is not appreciably nucleophilic, which suggests that σ bonding to a d-metal atom is weak.

As many d-metal carbonyl compounds are very stable, we can also infer that π back bonding is strong and the stability of carbonyl complexes arises mainly from the π -acceptor properties of CO.

Further evidence for this view comes from the observation that stable carbonyl complexes exist only for metals that have filled d orbitals of an energy suitable for donation to the CO antibonding orbital.

However, the bonding of CO to a d metal atom is best regarded as a synergistic (that is, mutually enhancing) outcome of both σ and π bonding: the π backbonding from the metal to the CO increases the electron density on the CO, which in turn increases the ability of the CO to form a σ bond to the metal atom.

Bonding in Metal Carbonyl:



One important consequence of this bonding scheme is the effect on the strength of the CO triple bond: the stronger the metal carbon bond becomes through pushing electron density from the metal atom into the π bond, the weaker the CO bond becomes, as this electron density enters a CO antibonding orbital.

In the extreme case, when two electrons are fully donated by the metal atom, a formal metal carbon double bond is formed; because the two electrons occupy a CO antibonding orbital, this donation results in a decrease in the bond order of the CO to 2.

The metal to ligand pi back bonding increase the M-C bond strength and decrease the C-O bond strength.

The bonding is somewhere between $M-C\equiv O$ with no back bonding, and $M=C=O$ With back bonding

If the metal in its high oxidation state (e-poor) then there will be poor back bonding and bond order of M-C closed to 1 and that of C-O close to 3.

If the metal in its low oxidation state (e- rich) then there will be strong back bonding and bond order of M-C closed to 2 and that of C-O close to 2.

Evidence for Back Bonding:

Infrared spectroscopy is extensively used to characterize metal carbonyls since the C-O stretching frequencies give very strong sharp bands in a very uncrowded region of the spectrum (i.e., these bands are well separated from stretching frequencies of any other ligands coordinated to metal).

Any change in the bonding between carbon and oxygen should be reflected in the C-O stretching vibration as observed by IR.

The C-O stretch in organometallic complexes is often very intense (stretching the C-O bond results in a substantial change in dipole moment).

Free carbon monoxide has a C-O stretch at 2143 cm^{-1} . $\text{Cr}(\text{CO})_6$, on the other hand, has its C-O stretch at 2000 cm^{-1} .

The lower energy for the stretching mode means that the C-O bond is weaker in $\text{Cr}(\text{CO})_6$.

The vibrational frequency of a bond depends on the strength of bond which is measured by the force constant

$$\nu \text{ (in cm}^{-1}\text{)} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

k = force constant

μ = reduced mass, for atoms of mass m_1 and m_2

Both the sigma donation (which donates electron density from a bonding orbital on CO) and pi acceptance (which places electron density in C-O antibonding orbitals) would be expected to weaken the C-O bond and to decrease the energy necessary to stretch that bond.

2.3(A) Factors Affecting the Magnitude of Stretching Frequency

Various factors affecting the stretching frequency are given below:

IR stretching frequency \propto Bond strength and bond order

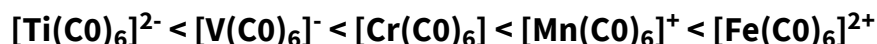
(a) Charge on Metal :

Greater the -ve charge on the metal (i.e. more electron density on metal) stronger will be the back bonding, hence lower will be the C-O stretching frequency.

Since the increased extent of back bonding increases the M-C double-bond character and therefore, the stretching frequency of M-C bond increases.

A formal positive charge on a metal carbonyl causes the great ability of metal to attract electrons and lower will be the tendency of metal to back donate electron density to π^* on CO. therefore the C-O bond order and stretching frequency increases.

For isoelectronic species C-O stretching frequency increase in the order:



(b) Number of CO Ligand:

As the number of CO ligands attached to a metal increases, the formal negative charge on metal increases.

Therefore, the extent of back donation increases and hence stretching frequency decreases as shown in table;

Compound	frequency
$\text{Ni}(\text{CO})_4$	2057
$\text{Fe}(\text{CO})_5$	2034
$\text{Cr}(\text{CO})_6$	1981

(c) Presence of Other Ligand on Metal:

sigma- donor:

Presence of sigma bonded ligand (i.e. electron donating) on a metal like NH_3 , Pyridine.

Increase electron density on the metal, so π -back bonding increases and C-O frequency decreases.

pi- acceptor Ligands:

Presence of pi-bonded ligand (i.e. electron withdrawing) on a metal like PF_3 , CS, NO.

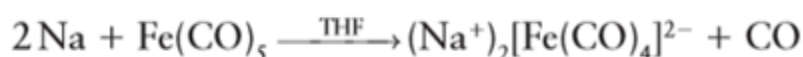
The pi-acceptor ligands decreases the electron density on metal. So, π -back bonding decrease and hence C-O frequency increase.

The effect of other ligands present on CO frequency:

Complex	$\nu(\text{CO}), \text{cm}^{-1}$
CO	2143
$\text{Ni}(\text{CO})_4$	2131
$\text{Ni}(\text{CO})_3(\text{PF}_3)$	2111
$\text{Ni}(\text{CO})_3[\text{P}(\text{OPh})_3]$	2085
$\text{Ni}(\text{CO})_3(\text{PMe}_3)$	2064

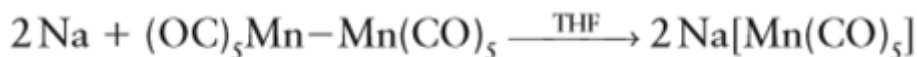
Metal Carbonyl Basicity:

Most neutral metal carbonyl complexes can be reduced to an anionic form known as a metal carbonylate.



Polynuclear carbonyls, which obey the 18-electron rule through the formation of M-M bonds, are generally cleaved by strong reducing agents.

The 18-electron rule is obeyed in the product and a mononegative mononuclear carbonylate results:



The basicity increases on descending the group because on descending the group, electrons become less tightly bound and the carbonylate ions donate electrons readily.

Higher the negative charge on the carbonylate ion, more will be its basicity

Metal Carbonyl Hydride:

Carbonyl hydrides are hydrogen derivatives of carbonyl complexes. These are conjugate acids of carbonylate ions.

A hydrogen atom directly bonded to a metal is commonly found in organometallic complexes and is referred to as a hydride ligand.

The carbonyl hydrides of transition metals behave as both acid as well as base

Thermal stability of carbonyl hydrides of transition metals increases on descending the group.

Order of thermal stability.



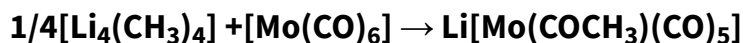
Hydrides are readily identified by NMR spectroscopy as their chemical shift is rather unusual, typically occurring in the range $-50 < \delta < 0$.

Infrared spectroscopy can also be useful in identifying metal hydrides as they normally have a stretching band in the range $2850 - 2250 \text{ cm}^{-1}$.

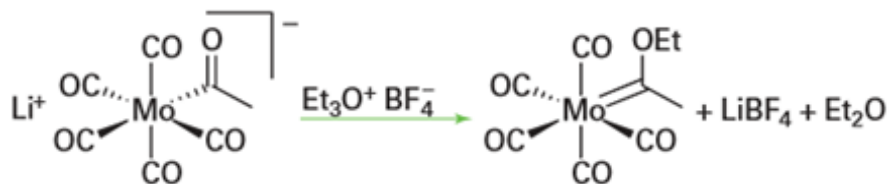
Reactions of the Metal Carbonyl :

The C atom of CO is susceptible to attack by nucleophiles if it is attached to a metal atom that is electron poor; the O atom of CO is susceptible to attack by electrophiles in electron-rich carbonyls.

Strong nucleophiles (such as methyllithium,) attack the CO in many neutral metal carbonyl compounds:



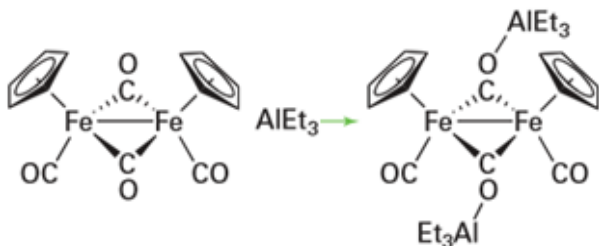
The resulting anionic acyl compound reacts with carbocation reagents to produce a stable and easily handled neutral product:



In electron-rich metal carbonyls, considerable electron density is delocalized on the CO ligand.

As a result, in some cases the O atom of a CO ligand is susceptible to attack by electrophiles.

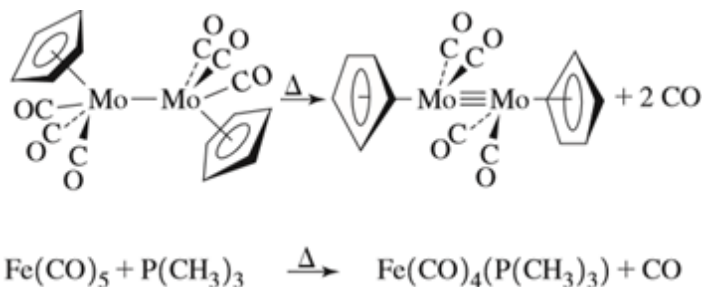
A bridging carbonyl is particularly susceptible to attack at the O atom:



CO Dissociation

carbonyl dissociation reactions, in which CO may be lost thermally or photochemically.

Such a reaction may result in rearrangement of the remaining molecule or replacement of CO by another ligand:



Dissociative Mechanism:

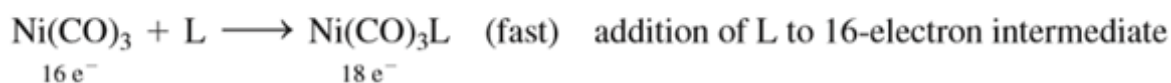
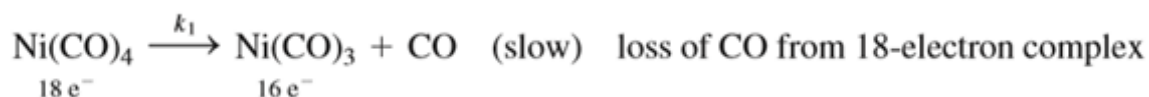
reactions involving replacement of CO by another ligand, L.

rates are independent of the concentration of L;

they are first order with respect to the metal complex.

mechanism involving slow loss of CO, followed by rapid reaction with L.

the complex which obeys 18 electron rule undergo substitution reaction by dissociative mechanism.



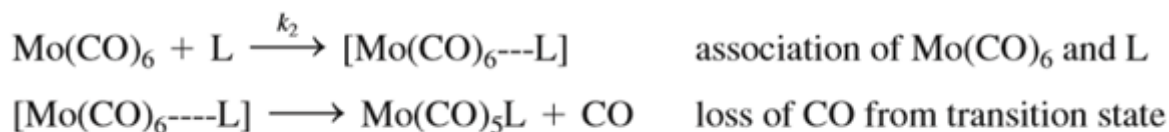
Associative Mechanism:

reactions involving replacement of CO by another ligand, L.

rates are dependent of the concentration of L and on the metal complex.

overall it is second order reaction. they are first order with respect to the metal complex and first with respect to ligand .

involving a bimolecular reaction of Mo(CO)_6 and L to form a transition state that loses CO.



the complex which contain 16 or 17 electrons undergo substitution reaction by associative mechanism.

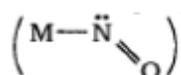
Odd electron complexes (17/19 e-) react faster than even electron complex.

Metal Nitrosyls :

When an electron is removed from π^* of NO the bond order increases from 2.5 to 3. Because NO^+ is nitrosyl ion, the compound containing both NO and CO are called carbonyl nitrosyls. The NO can act as 1- or 3-electron donor on the neutral ligand or covalent model.

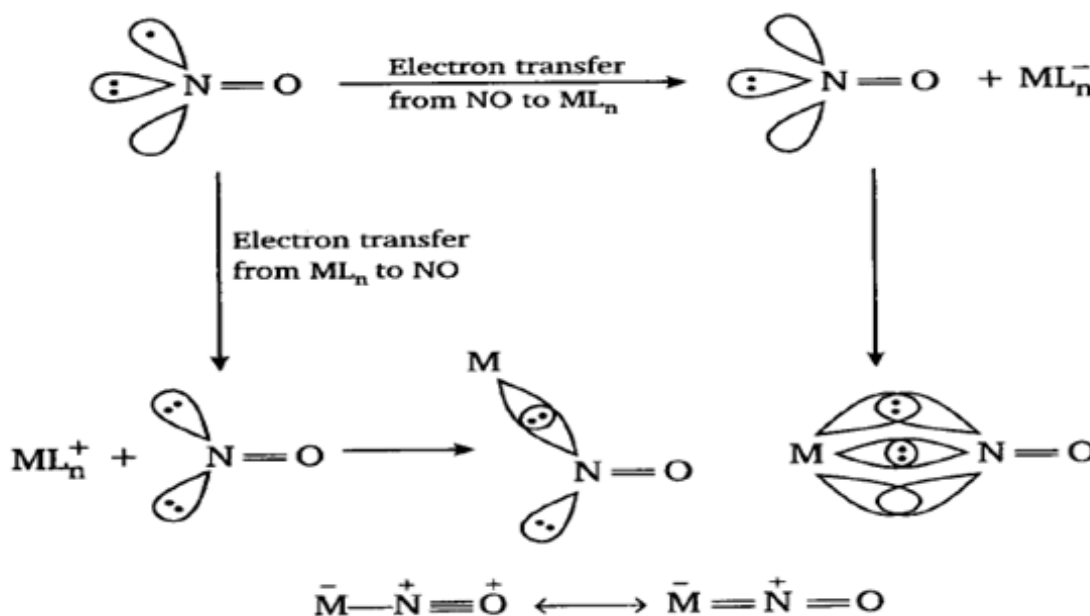
When NO acts as 3e- donor, the M-NO unit is linear [Fig (a)]. In majority of nitrosyl complexes the MNO unit is linear, consistent with sp -hybridization on nitrogen.

When NO acts as a one electron donor, the M-NO unit is bent.


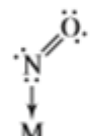


The bent geometry is due to the presence of a lone pair of O electrons on nitrogen.

(a) Linear Structure (b) Bent Structure of M-NO unit on the basis of covalent model



Useful information about the linear and bent bonding modes of NO is summarized in below figure :

	<u>Linear</u>	<u>Bent</u>
		
M—N—O angle	165°–180°	119°–140°
ν (N-O) in neutral molecules	1610–1830 cm ⁻¹	1520–1720 cm ⁻¹
Electron donor count	2 (as NO ⁺)	2 (as NO ⁻)
	3 (as neutral NO)	1 (as neutral NO)

NEXT (Reaction in Organometallic Chemistry) >

(chemicalScience_topic52a.jsp)