

Organometallic Compounds II

(Part I)

B.Sc. (H) Chemistry

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Ligands in Organometallic Chemistry

- ✓ Hundreds of ligands are known to bond to metal atoms through carbon.
- ✓ **Carbon monoxide** forms a very large number of metal complexes and deserves special mention, along with several similar diatomic ligands.
- ✓ Many organic molecules containing linear or cyclic pi systems also form numerous organometallic complexes.

Carbonyl (CO) Complexes

- ✓ Carbon monoxide is the most common ligand in organometallic chemistry.
- ✓ It serves as the only ligand in binary carbonyls such as $\text{Ni}(\text{CO})_4$, $\text{W}(\text{CO})_6$, and $\text{Fe}_2(\text{CO})_9$ or, more commonly, in combination with other ligands, both organic and inorganic.
- ✓ CO may bond to a single metal, or it may serve as a bridge between two or more metals

Bonding in CO

- ✓ It is useful to review the bonding in CO. In MO diagram of CO, two features need to be give attention.
- ✓ The **HOMO** has its largest lobe on carbon. It is through this orbital, occupied by an electron pair, that CO exerts its σ -donor function, donating electron density directly toward an appropriate metal orbital, such as an unfilled d or hybrid orbital.
- ✓ CO also has two empty π^* orbitals (**LUMO**); these also have larger lobes on carbon than on oxygen. A metal atom having electrons in a d orbital of suitable symmetry can donate electron density to these π^* orbitals.

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σ - donor and π -acceptor interactions are illustrated in Fig.1.

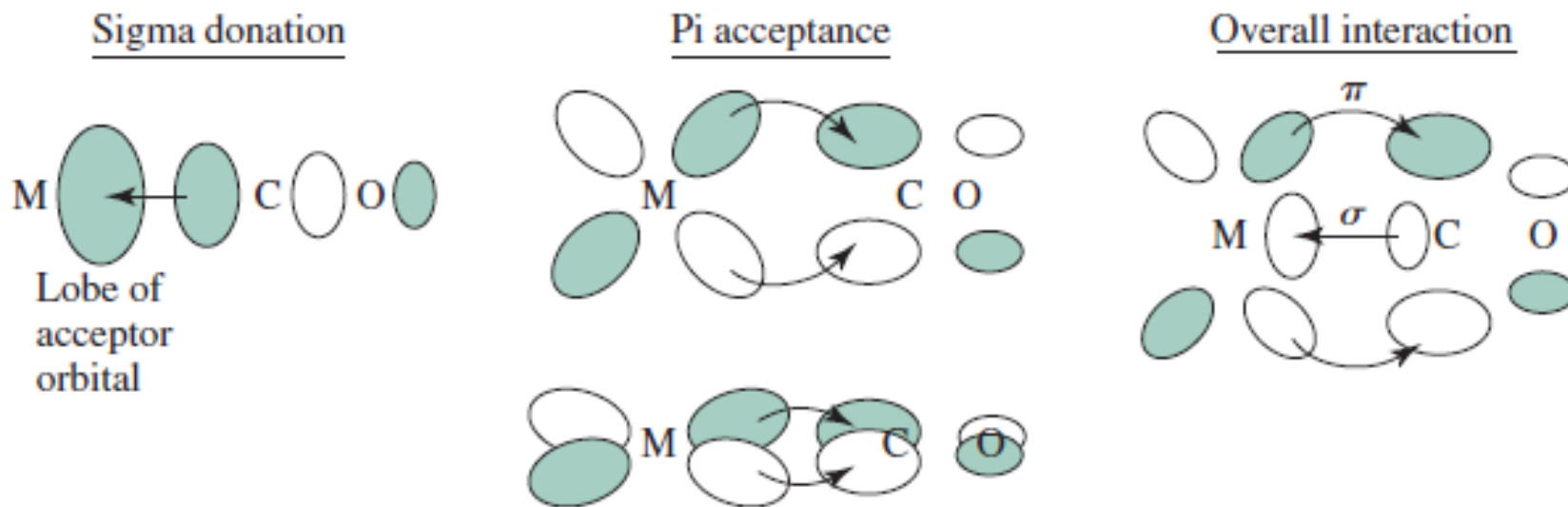


Fig. 1 σ and π interactions between CO and a Metal Atom

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The overall effect is synergistic. CO can donate electron density via a σ -orbital to a metal atom; the greater the electron density on the metal, the more effectively it can return electron density to the π^* orbitals of CO.

The strength of bonding depends on several factors, including the charge on the complex and the ligand environment of the metal.

Analysis of CO by Infrared spectroscopy

- ✓ Infrared spectroscopy is used to study to the bonding between CO and 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 (change in dipole moment), and its energy often provides valuable information about the molecular structure.
- ✓ **Free carbon monoxide has a C-O stretch at 2143 cm^{-1} .** In $\text{Cr}(\text{CO})_6$, C-O stretch at 2000 cm^{-1} . The lower energy for the stretching mode means that the C-O bond is weaker in $\text{Cr}(\text{CO})_6$.

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The energy necessary to stretch a bond is proportional to $\sqrt{\frac{k}{\mu}}$

Where,

$k = \text{force constant}$

$\mu = \text{reduced mass}$

Atoms of mass m_1 and m_2 , the reduced mass is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

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✓ The stronger the bond between two atoms, the larger the force constant; consequently, the greater the energy necessary to stretch the bond and the higher the energy of the corresponding band (the higher the wavenumber, in cm^{-1}) in the infrared spectrum.

✓ Similarly, the more massive the atoms involved in the bond, as reflected in a higher reduced mass, the less energy necessary to stretch the bond, and the lower the energy of the absorption in the infrared spectrum.

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Both σ donation (which donates electron density from a bonding orbital on CO) and π 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.

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The charge on a carbonyl complex is also reflected in its infrared spectrum as shown in table below

Complex	$\nu(\text{CO}), \text{cm}^{-1}$
$[\text{Ti}(\text{CO})_6]^{2-}$	1748
$[\text{V}(\text{CO})_6]^{-}$	1859
$\text{Cr}(\text{CO})_6$	2000
$[\text{Mn}(\text{CO})_6]^{+}$	2100
$[\text{Fe}(\text{CO})_6]^{2+}$	2204

Where, $\nu(\text{CO}) = 2143 \text{ cm}^{-1}$ for free CO

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✓ $[\text{Ti}(\text{CO})_6]^{2-}$ contains the most highly reduced metal, formally containing Ti(2-); this means that titanium has the weakest ability to attract electrons and the greatest tendency to **back-donate electron density** to CO.

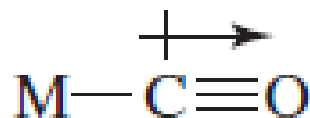
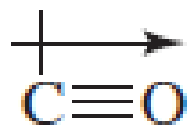
✓ The formal charges on the metals increase from -2 for $[\text{Ti}(\text{CO})_6]^{2-}$ to +2 for $[\text{Fe}(\text{CO})_6]^{2+}$.

✓ The titanium in $[\text{Ti}(\text{CO})_6]^{2-}$, with the most negative formal charge, has the strongest tendency to donate to CO.

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✓ The consequence is strong population of the π^* orbitals of CO in $[\text{Ti}(\text{CO})_6]^{2-}$ and reduction of the strength of the C -O bond.

✓ In general, the more negative the charge on the organometallic species, the greater the tendency of the metal to donate electrons to the π^* orbitals of CO, and the lower the energy of the C -O stretching vibrations.



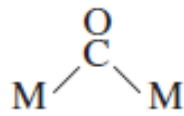
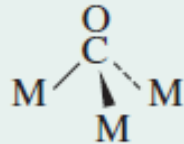
In free CO, the electrons are polarized toward the more electronegative oxygen.

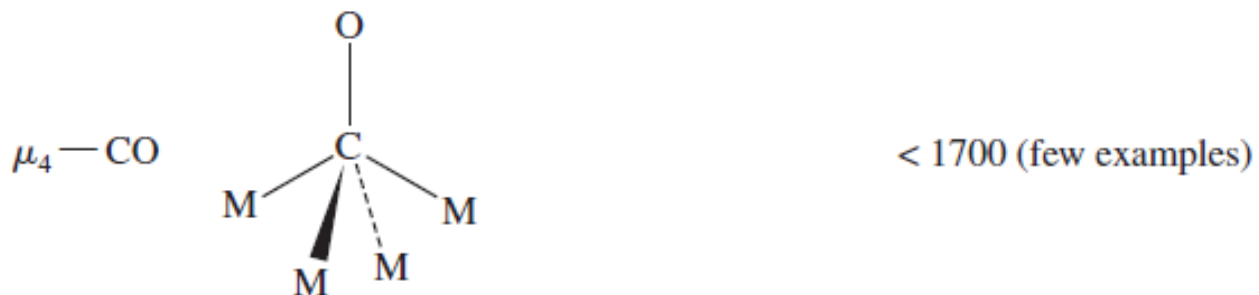
the electrons in the π orbitals are concentrated nearer to the oxygen atom than to the carbon.

The presence of a transition metal cation reduces the polarization in the C-O bond by attracting the bonding electrons.

The consequence is that the electrons in the positively charged complex are more equally shared by the carbon and the oxygen, giving rise to a stronger bond and a higher-energy C-O stretch.

Bridging modes of CO

Type of CO	Approximate Range for $\nu(\text{CO})$ in Neutral Complexes (cm^{-1})
Free CO	2143
Terminal $\text{M}-\text{CO}$	1850–2120
Symmetric ^a $\mu_2-\text{CO}$	 1700–1860
Symmetric ^a $\mu_3-\text{CO}$	 1600–1700



IR ranges of Bridging modes of CO

Assignment

Q 1. How is it possible for cationic carbonyl complexes such as $[\text{Fe}(\text{CO})_6]^{2+}$ to have C-O stretching bands even higher in energy than those in free CO?

Complex	$\nu(\text{CO}), \text{cm}^{-1}$
$[\text{Fe}(\text{CO})_6]^{2+}$	2204

Free CO stretch at 2143 cm^{-1}

Q. 2. How does the strength of the bond increase ?

References:

(1) Miessler, Fischer & Tarr Inorganic Chemistry

(2) Shriver & Atkins Inorganic Chemistry

Thank You