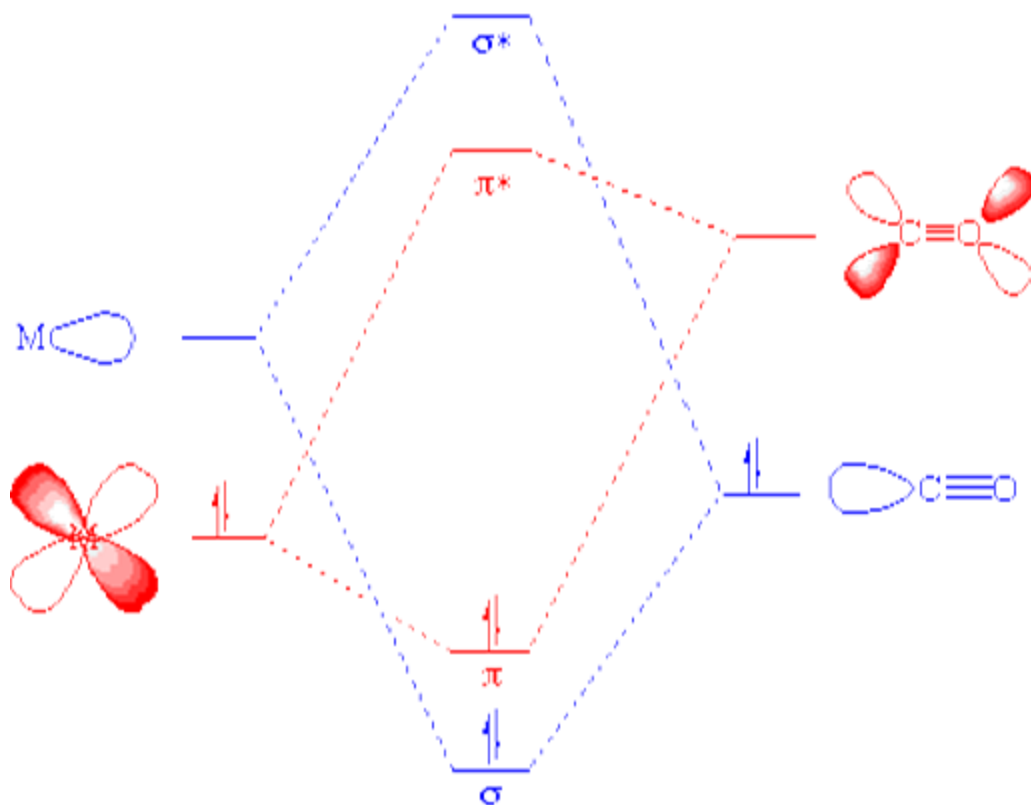


π -Acceptor Ligands

The π -acceptor ligands are a special class of ligands which contain π -bonds. The anti-bonding type π -orbitals in these ligands, if vacant and of comparable energy, may receive electron density from the filled metal orbitals with which the ligand is coordinated.



CO, CNR, R₃P, NO etc. are such ligands which have *filled orbitals* (called *donor orbitals*) as well as *empty π-orbitals* (called *acceptor orbitals*). These ligands are called *π-acid ligands* or *π-acceptor ligands* or *π-bonding ligands*. These ligands combine with transition metals in low oxidation states (*e.g.* -1, 0, +1) and form complexes which are called *π-acid complexes*. Thus *π-acid complexes* are the complexes of transition metals in low oxidation state with *π-acid ligands*. Metallic carbonyls are important examples of *π-acid complexes*. These complexes have ligand → metal σ -bonds as well as metal → ligand π -bonds.

What are metallic carbonyls ?

The compounds formed by the combination of CO molecules with transition metal atoms in low oxidation states are called metallic carbonyls. In these compounds, CO molecule acts as a neutral ligand.

Why is the metallic atom in low oxidation state in metallic carbonyls ?

We have said above that metal atom in metal carbonyls is in low oxidation state. This is because of the fact that there is a higher electron density (electronic charge) on the metal atom in its lower oxidation state than in its higher oxidation state. Thus, since the metal is electropositive in nature, it would feel more comfortable, if some of the excess electronic charge present on the metal atom gets transferred to the vacant π -orbitals of CO (ligand) by forming M→CO π -bond.

Classification of carbonyls

I. Classification based on the number of metallic atoms present in carbonyl

This classification gives the following two types of carbonyls.

(a) **Mononuclear or monomeric carbonyls.** The molecule of these carbonyls contains only one metallic atom. Examples are $\text{Ni}(\text{CO})_4$, $\text{M}(\text{CO})_5$, ($\text{M}=\text{Fe}, \text{Ru}, \text{Os}$) and $\text{M}(\text{CO})_6$ ($\text{M} = \text{V}, \text{Cr}, \text{Mo}, \text{W}$)

(b) **Polynuclear carbonyls.** The molecule of these carbonyls contains two or more metallic atoms. Examples are $\text{Co}_2(\text{CO})_8$, $\text{Fe}_2(\text{CO})_9$, $\text{M}_2(\text{CO})_{10}$, ($\text{M}=\text{Mn}, \text{Tc}, \text{Re}$), $\text{M}_3(\text{CO})_{12}$ ($\text{M}=\text{Fe}, \text{Ru}, \text{Os}$). Polynuclear carbonyls may be *homo-nuclear* [e.g., $\text{Co}_2(\text{CO})_8$, $\text{Fe}_2(\text{CO})_9$, $\text{Fe}_3(\text{CO})_{12}$ etc.] or *hetero-nuclear* [e.g., $\text{MnCo}(\text{CO})_9$, $\text{MnRe}(\text{CO})_{10}$ etc.].

II. Classification based on the structure of carbonyls

(a) **Non-bridged carbonyls.** As the name suggests, these carbonyls do not contain any bridging (ketonic) carbonyl group, $:\ddot{\text{O}}=\text{C}<$. These carbonyls may be of the following types:

- (i) Non-bridged carbonyls which contain only terminal carbonyl groups ($:\text{O} \equiv \text{C}:$). Examples of such carbonyls are $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Ru}(\text{CO})_5$, $\text{Os}(\text{CO})_5$.
- (ii) Non-bridged carbonyls which contain terminal carbonyl groups as well as M---M bonds. Examples are $\text{Co}_2(\text{CO})_8$ (in solution), $\text{Mn}_2(\text{CO})_{10}$, $\text{Te}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$, $\text{Fe}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$.

(b) **Bridged carbonyls.** These contain bridging carbonyl groups along with terminal carbonyl groups and one M---M bond. Examples are $\text{Fe}_2(\text{CO})_9$, $\text{Os}_2(\text{CO})_9$, $\text{Co}_2(\text{CO})_8$ (in solid state). All these are polynuclear carbonyls.

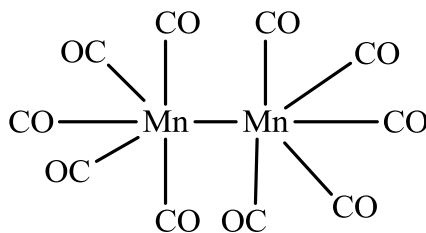
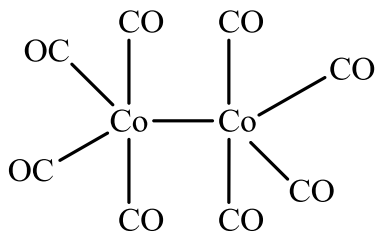
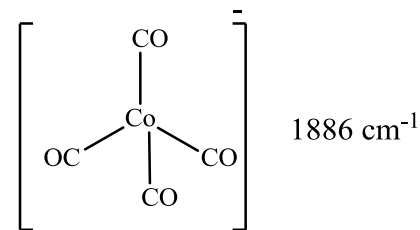
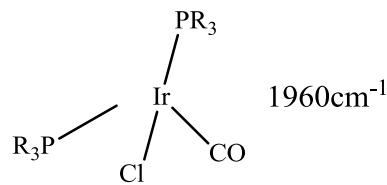
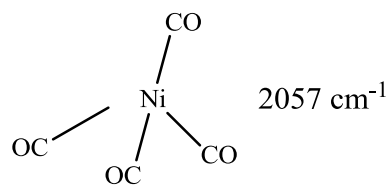
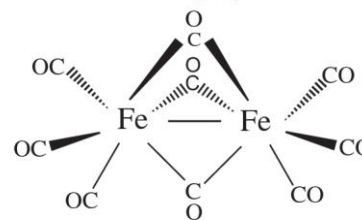
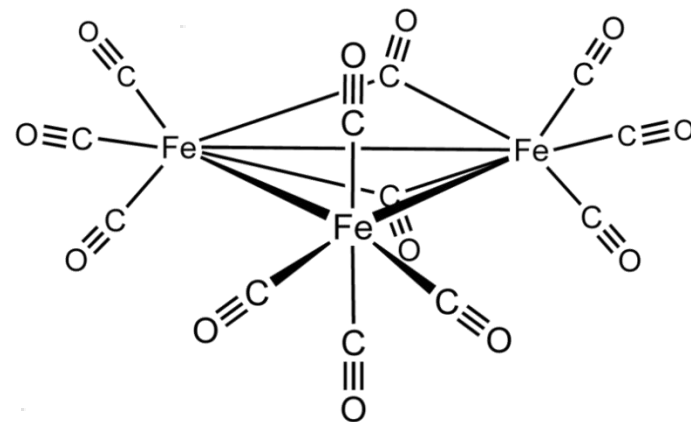
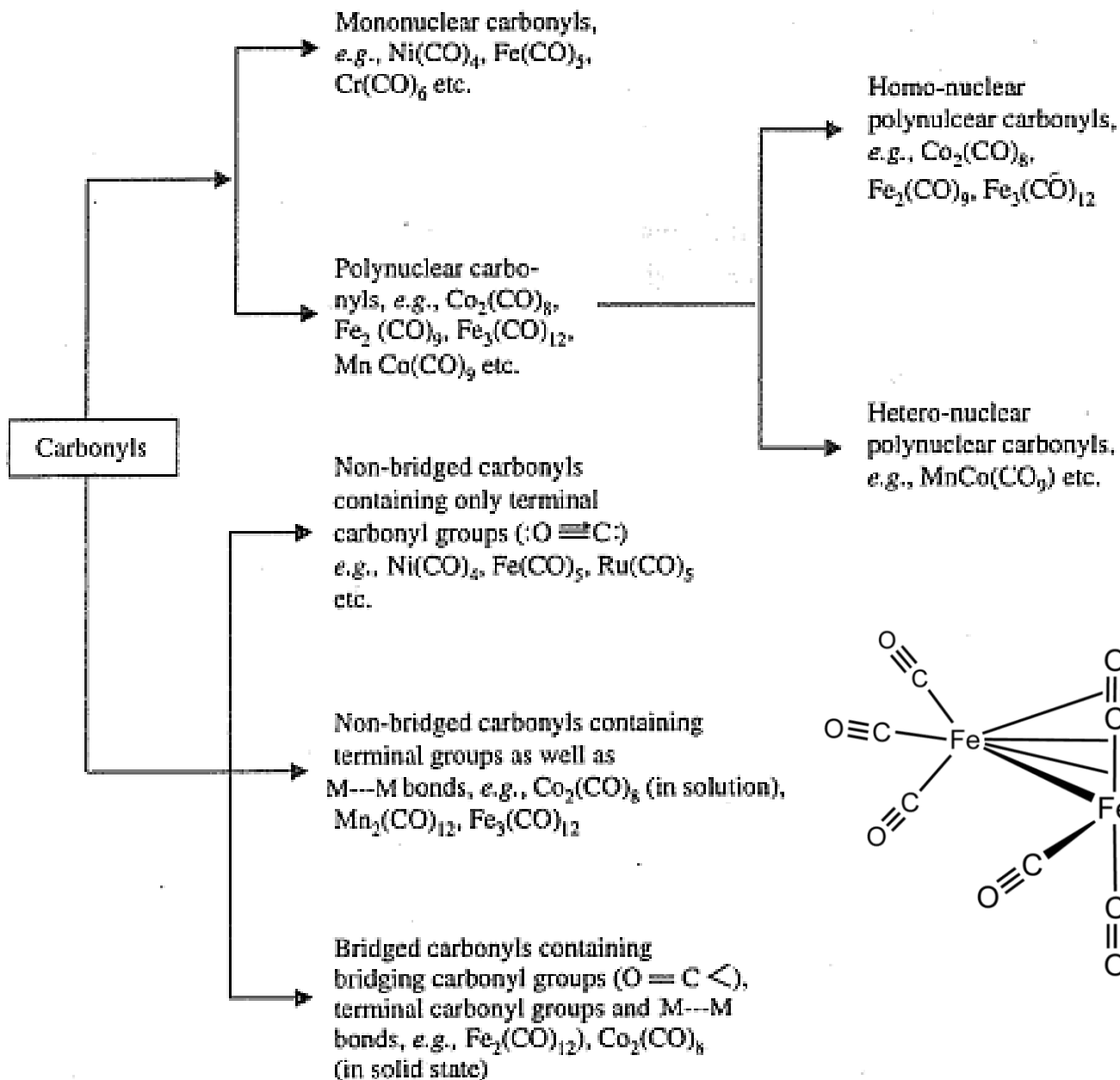


Fig. 1. Molecular structure of $\text{Fe}_2(\text{CO})_9$.



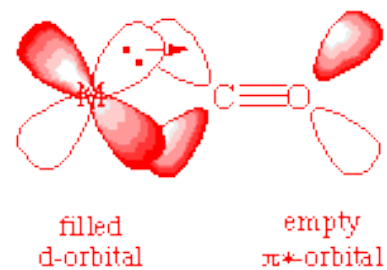
Classification of carbonyls



σ bond:



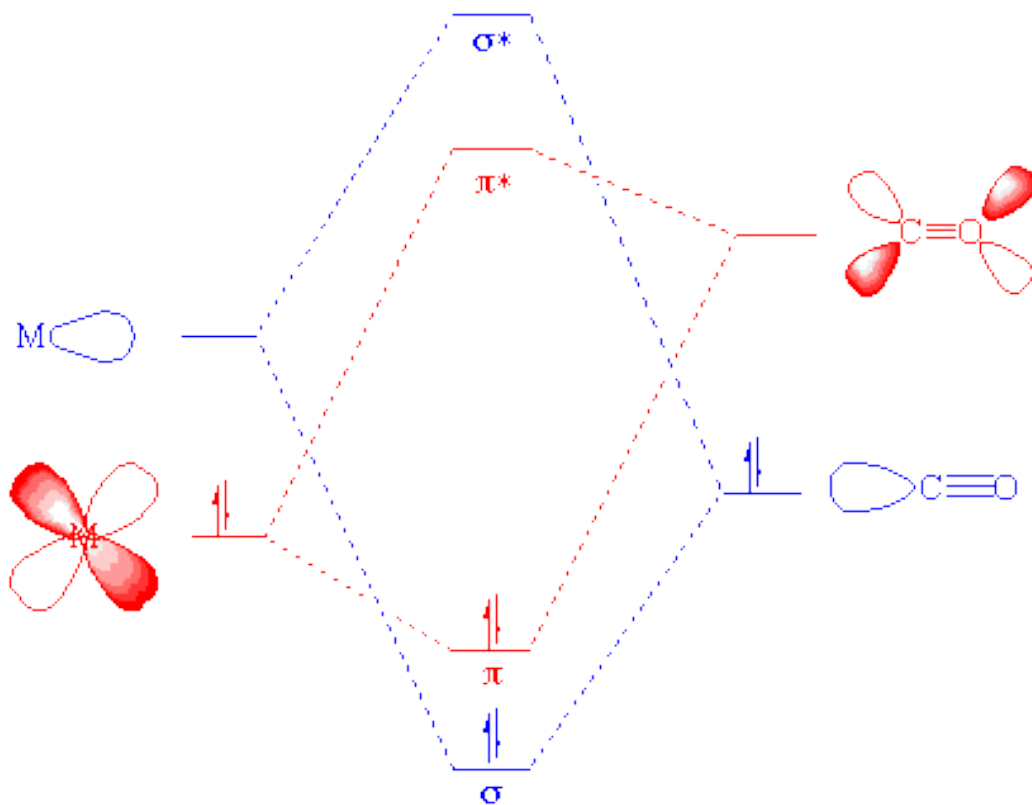
π backbond:



L_nM

$L_nM(CO)$

CO



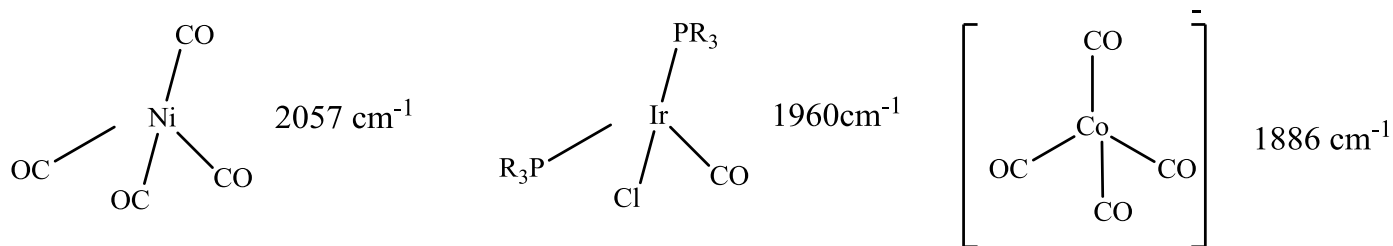
In the IR, typical stretching frequencies are:

Uncoordinated or "free" CO: 2143 cm^{-1}

Terminal M-CO: $2125\text{ to }1850\text{ cm}^{-1}$

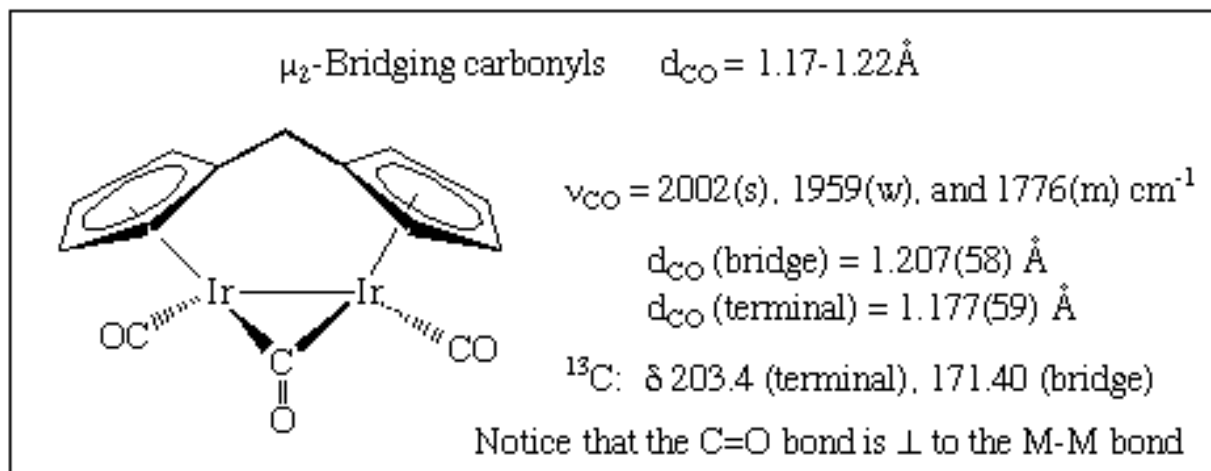
Doubly bridging (μ_2): $1850\text{ to }1750\text{ cm}^{-1}$

Triply bridging (μ_3): $1675\text{ to }1600\text{ cm}^{-1}$

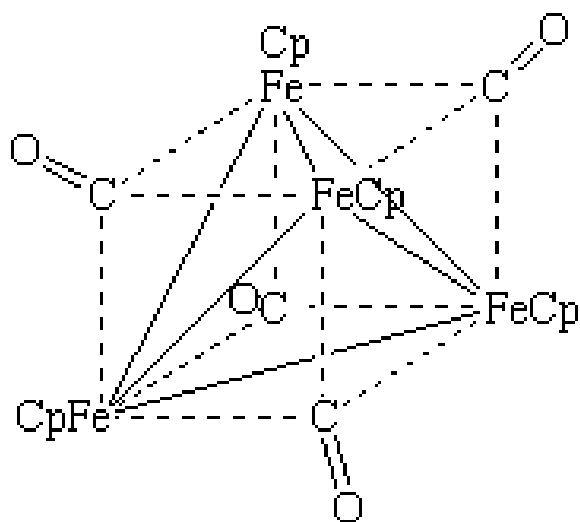


Two convenient trends are observed in the IR spectra of carbonyl complexes:

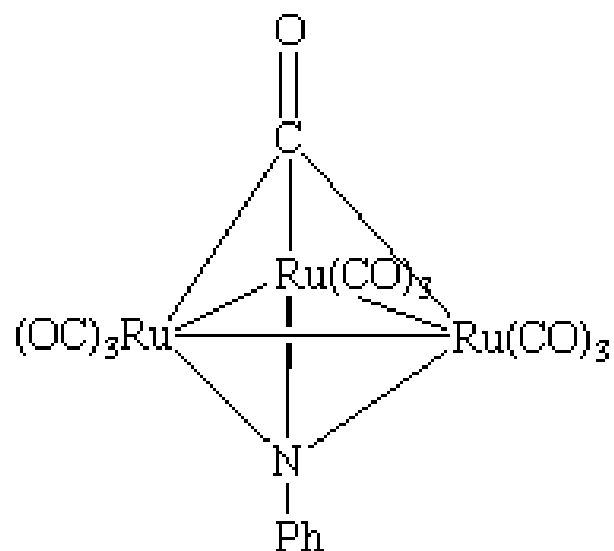
1. With each charge added to the metal center, the CO stretching frequency decreases by approximately 100 cm^{-1} .
2. The better the sigma-donating capability (or worse the pi-acceptor ability) of the other ligands on the metal, the lower the CO stretching frequency.



μ_3 -Bridging carbonyls $d_{\text{CO}} = 1.17\text{-}1.22\text{\AA}$



$\nu_{\text{CO}} = 1620\text{ cm}^{-1}$
 $d_{\text{CO}} = 1.197(7) - 1.209(7)\text{\AA}$



$\nu_{\text{CO}} = 2104(\text{m}), 2070(\text{s}), 2032(\text{vs})$
 $2011(\text{s}), 1978(\text{w}), 1743\text{ cm}^{-1}$