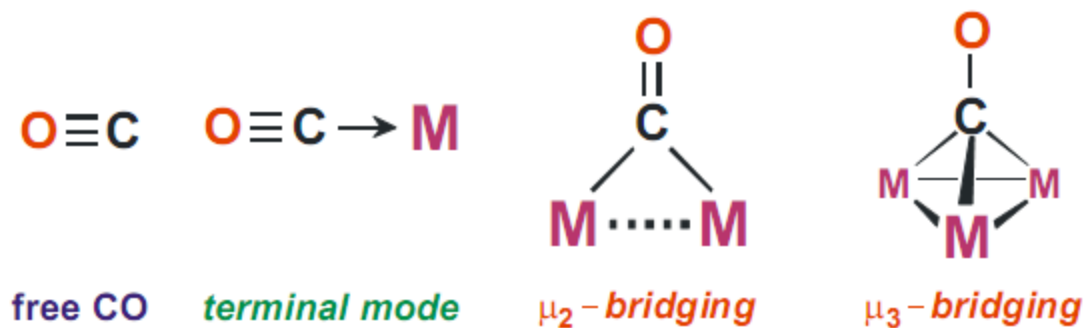


IR Evaluation of Bonding in Metal Carbonyls

Stretching Frequencies

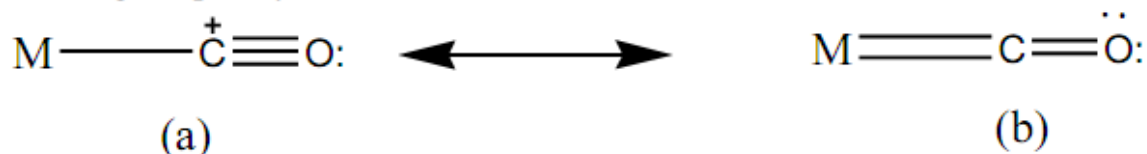
- The **position** of the carbonyl bands in the IR spectra depends mainly on the bonding mode of the CO (terminal, bridging) and the amount of electron density on the metal being π -back bonded to the CO.
- The **number** (and intensity) of the carbonyl bands depends on the number of CO ligands present and the symmetry of the metal complex. There are also secondary effects such as Fermi resonance and overtone interactions that can complicate carbonyl IR spectra.
- **Bonding Modes:**
 - As one goes from a terminal CO-bonding mode to μ_2 -bridging and finally μ_3 -bridging, there is a relatively dramatic drop in the CO stretching frequency seen in the IR.



- These ranges are typical for “**neutral**” transition metal complexes with an average amount of electron density on the metal center.
- Bridging carbonyls tend to have weaker and broader IR bands.

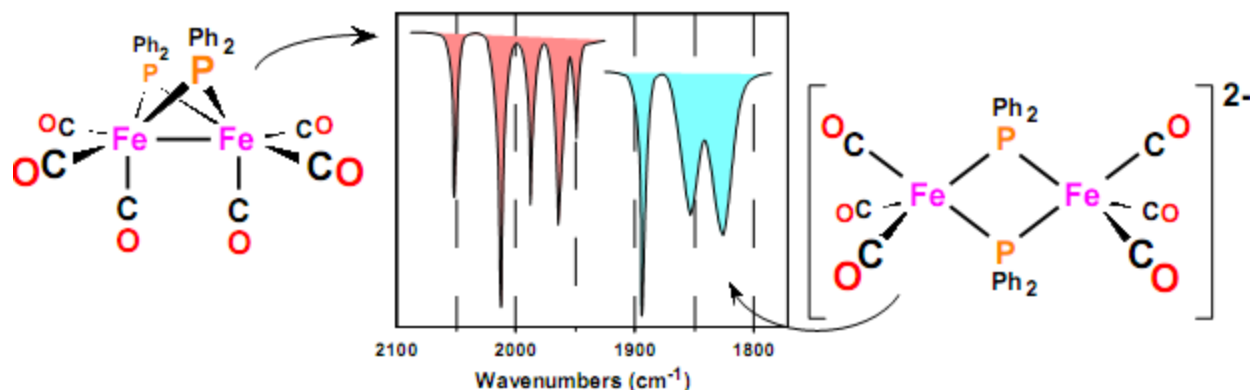
• Effect of Electron Density on Metal:

- As the electron density on a metal center increases, more π -backbonding to the CO ligand(s) takes place. This further weakens the C-O bond by pumping more electron density into the formally empty carbonyl π^* orbital. This increases the M-CO bond strength making it more double-bond-like, i.e., the resonance structure $\text{M}=\text{C}=\ddot{\text{O}}$ assumes more importance.
- This can clearly be seen on the table below that illustrates the effect of charge on metal on CO π -backbonding and the CO IR stretching frequency.



ν_{CO} Cm^{-1}	$\text{Mn}(\text{CO})_6^+$	$\text{Cr}(\text{CO})_6$	$\text{V}(\text{CO})_6^{-1}$
	2096	2000	1859
ν_{CO} Cm^{-1}	$\text{Ni}(\text{CO})_4$	$\text{Co}(\text{CO})_4^{-1}$	$\text{Fe}(\text{CO})_4^{-2}$
	2046	1883	1788

- Shown below is another example of the dramatic effect on the ν_{CO} IR stretching frequencies on reducing $\text{Fe}_2(\mu\text{-PPh}_2)_2(\text{CO})_6$ by 2 electrons to form the dianionic complex $[\text{Fe}_2(\mu\text{-PPh}_2)_2(\text{CO})_6]^{2-}$. The average ν_{CO} frequency shifts almost 150 cm^{-1} to lower energy on reduction.



Ligand Donation Effects on $\bar{\nu}_{\text{CO}}$ Cm^{-1}

The ability of the ligands on a metal to donate electron density to the metal center certainly has considerable effect on the absolute amount of electron density on that metal. This, in turn, naturally affects the ν_{CO} IR stretching frequencies in metal carbonyl complexes. As CO groups in metal carbonyls are replaced by other ligands which are stronger σ -donors but weaker π -acceptors ν_{CO} will decrease. The π -charge density from metal to stronger σ -donor ligands other will be drifted more toward CO and bond order of CO group will further decrease. Consequently ν_{CO} will shift to still lower wave number. This is illustrated by comparing the IR spectra of $\text{Ni}(\text{CO})_4$ derivatives with trimethylphosphine

	$\text{Ni}(\text{CO})_4$	$\text{Me}_3\text{PNi}(\text{CO})_3$	$(\text{Me}_3\text{P})_2\text{Ni}(\text{CO})_2$
$\bar{\nu}_{\text{CO}}$ Cm^{-1}	2046	1943	1934

On the other hand the ligands which have the tendency to inhibit transfer of electron density from metal to the π^* -CO orbital by creating positive charge on the metal, due to electron with drawing effect, will cause increase in $\bar{\nu}_{\text{CO}}$ values. For example halogens being electronegative will create electropositive center on the metal atom and shift the $\bar{\nu}_{\text{CO}}$ to higher values. This effect is shown below:

	$\text{ClMn}(\text{CO})_5$	$\text{BrMn}(\text{CO})_5$	$\text{IMn}(\text{CO})_5$
ν_{CO} Cm^{-1}	2138, 2054	2133, 2050	2125, 2044

Effect of bridging CO on the $\bar{\nu}_{\text{CO}}$ cm^{-1}

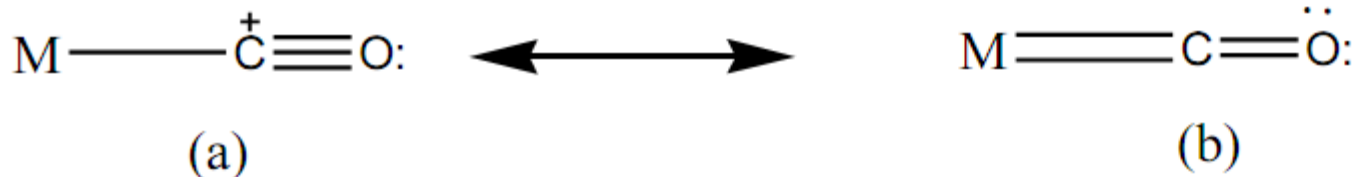
Low ν_{CO} values in neutral carbonyls may be due to bridging CO groups. In IR spectra bands at about 1800 cm^{-1} may due bridged CO group. IR spectra of $\text{Fe}_2(\text{CO})_9$ and $\text{Ru}_3(\text{CO})_{12}$ shows that $\text{Fe}_2(\text{CO})_9$ has a peak at about 1800 cm^{-1} which correspond to bridged CO where as there is no such IR signal seen in the IR spectrum of $\text{Ru}_3(\text{CO})_{12}$

Effect of groups attached to ligands bonded to metal atoms on $\bar{\nu}_{\text{CO}}$ Cm^{-1}

Changes in CO stretching frequencies are also observed as groups bonded to ligands are changed. For example:

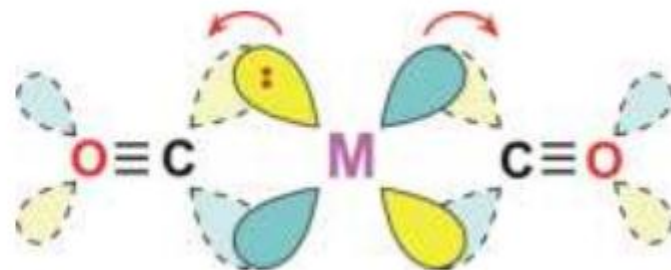
ν_{CO} Cm^{-1}	$(\text{F}_3\text{P})_3\text{Mo}(\text{CO})_3$ 2074, 2026	$(\text{Cl}_3\text{P})_3\text{Mo}(\text{CO})_3$ 2041, 1989	$(\text{C}_6\text{H}_5\text{PCl}_2)_3\text{Mo}(\text{CO})_3$ 2016, 1943
ν_{CO} Cm^{-1}	$[(\text{C}_6\text{H}_5)\text{PCl}]_3\text{Mo}(\text{CO})_3$ 1977, 1885		$[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Mo}(\text{CO})_3$ 1949, 1835

Phosphines are similar to CO as regards their π -acceptor capacity. In phosphines the 3d orbitals of phosphorous atoms are vacant, but the extent of their overlap with a filled d-orbital depends on the nature of groups attached to the ligands atoms. Highly electronegative fluorine effectively contracts the phosphorous 3d orbital making π -bonding between P and the metal atom more effective. More charge density drifts towards phosphines groups and less toward the CO groups. The structure (a) becomes more predominant and ν_{CO} Cm^{-1} value shift to slightly higher wave number. Chlorine and phenyl groups are less electronegative and less effective in this respect.



. Therefore there is an increased flow of charge to the metal during σ -bond formation.

Ligands that are *trans* to a carbonyl can have a particularly large effect on the ability of the CO ligand to effectively π -backbond to the metal. For example 2 *trans* π -backbonding ligands will partially compete for the same *d*-orbital electron density, weakening each others net M-L π -backbonding.



When the *trans* ligand is a π -donating ligand, this can increase the M-CO bond strength (more M=C=O character) by allowing unimpeded metal to CO π -backbonding. Pyridine and amines are not that strong π -donors, but they are even worse π -backbonding ligands. So the CO has virtually no competition for π -backdonation.

Based on CO IR stretching frequencies, the following ligands can be ranked from **best** π -acceptor to **worst**:

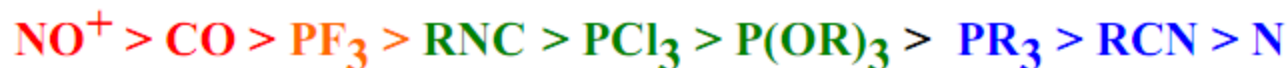
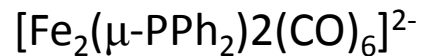
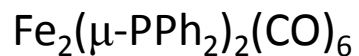
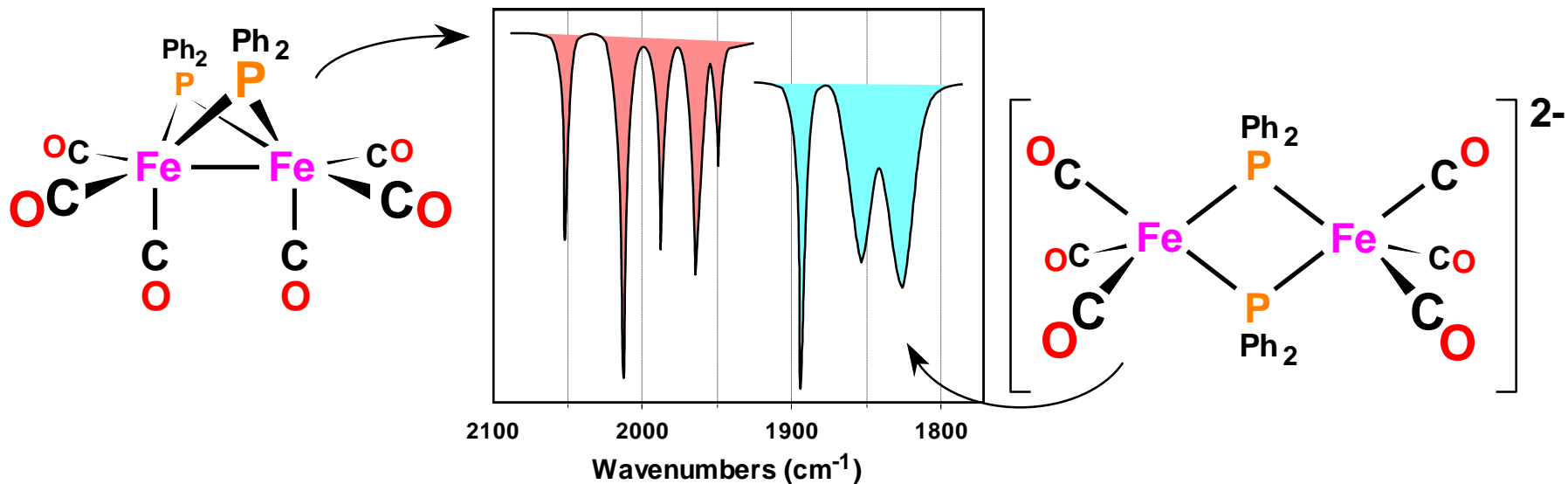


Table 1. IR Data for Selected Metal Carbonyls

Complex	IR ν_{CO} cm^{-1}	Complex	IR ν_{CO} cm^{-1}
V(CO)_6	1976	$\text{Co}_2(\text{CO})_8$	2107, 2069, 2042, 2031, 2023, 1991
Cr(CO)_6	2000	Ru(CO)_5	2035, 1999
Mo(CO)_6	2004	Os(CO)_5	2034, 1991
W(CO)_6	1998	Ni(CO)_4	2057
$\text{Mn}_2(\text{CO})_{10}$	2044, 2013, 1983	$\text{Fe}_2(\text{CO})_9$	2082, 2019, 1829
$\text{Tc}_2(\text{CO})_{10}$	2065, 2017, 1984	$\text{Fe}_2(\text{CO})_9$	2082, 2019, 1829
$\text{Re}_2(\text{CO})_{10}$	2070, 2014, 1976	Ru(CO)_5	2035, 1999
Fe(CO)_5	2034, 2013	Os(CO)_5	2034, 1991

EFFECT OF CHARGE ON THE METAL ATOM ON IR STRETCHING FREQUENCIES



Ligand Donation Effects:

	$\text{Ni}(\text{CO})_4$	$\text{Me}_3\text{PNi}(\text{CO})_3$	$(\text{Me}_3\text{P})_2\text{Ni}(\text{CO})_2$
$\nu_{\text{CO}} \text{ cm}^{-1}$	2046	1943	1934
	$\text{ClMn}(\text{CO})_5$	$\text{BrMn}(\text{CO})_5$	$\text{IMn}(\text{CO})_5$
$\nu_{\text{CO}} \text{ cm}^{-1}$	2138, 2054	2133, 2050	2125, 2044
	$(\text{F}_3\text{P})_3\text{Mo}(\text{CO})_3$	$(\text{Cl}_3\text{P})_3\text{Mo}(\text{CO})_3$	$(\text{C}_6\text{H}_5\text{PCl}_2)_3\text{Mo}(\text{CO})_3$
$\nu_{\text{CO}} \text{ cm}^{-1}$	2074, 2026	2041, 1989	2016, 1943
	$[(\text{C}_6\text{H}_5)\text{PCl}]_3\text{Mo}(\text{CO})_3$	$[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{Mo}(\text{CO})_3$	
$\nu_{\text{CO}} \text{ cm}^{-1}$	1977, 1885		1949, 1835

Uses of infra-red (IR) absorption spectra of metallic carbonyls

The IR absorption spectra of metallic carbonyls have been put to the following uses:

1. **To determine the geometry of metallic carbonyls.** If theoretically, a metallic carbonyl can have more than one geometry, we can decide which geometry is the most stable. This can be done as follows. We calculate the number of I.R. active together with Raman-active vibrational bands for each geometry and then run the I.R. and Raman spectra and finally tally the number of bands observed with the number of bands predicted theoretically (*i.e.* by calculations) for each geometry.

Example. Although, theoretically, $\text{Fe}(\text{CO})_5$ molecule can have trigonal bipyramidal as well as square pyramidal geometry, the I.R. bands actually observed tally the number of such bands calculated for trigonal bipyramidal geometry. Thus $\text{Fe}(\text{CO})_5$ has trigonal bipyramidal geometry.

2. **To determine the bond order (B.O.) of ligated CO.** It has been seen that I.R. absorption frequency of ligated CO is directly proportional to its B.O. In other words the I.R. absorption band due to the stretching vibration of ligated CO with a higher B.O. would occur at a higher frequency and the I.R. absorption band of ligated CO with a lower B.O. would occur at a lower frequency. Since the absorption frequency for free CO is equal to 2250 cm^{-1} while that for ligated CO lies between $2220\text{--}1700 \text{ cm}^{-1}$, ligated CO has lower B.O. The lower B.O. is due to the transfer of metal $d\pi$ electrons into the π^* orbitals of ligated CO. Let us study the following examples.

<i>Metal carbonyl :</i>	$[\text{V}(\text{CO})_6]^-$	$\text{Cr}(\text{CO})_6$	$[\text{Mn}(\text{CO})_6]^+$
<i>Charge on metal carbonyl :</i>	—	0	+
<i>Absorption frequency for CO (cm^{-1}) :</i>	1860	1980	2090

Since the presence of positive charge on $[\text{Mn}(\text{CO})_6]^+$ resists the flow of metal $d\pi$ electrons into the π^* orbitals of CO, the B.O. of CO increases. Due to the increase in B.O., the absorption band of ligated CO occurs at higher frequency ($=2090 \text{ cm}^{-1}$).