

Lecture 7

Inorganic chemistry

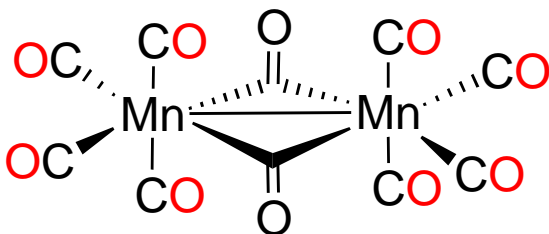
Previous lecture

18 electron rule : How to count electrons

Various models for counting the electrons

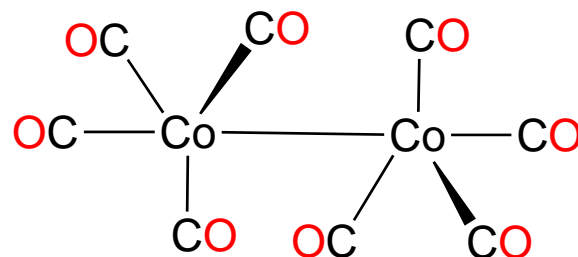
How to determine the total number of metal - metal bonds

Chemistry of carbonyl compounds



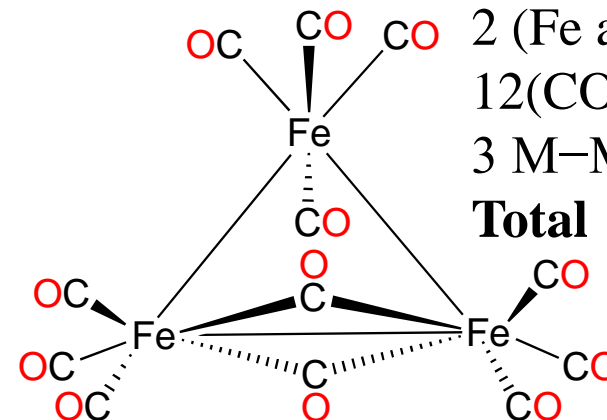
2 (Mn atom) 14 electrons
 10(CO) 20 electrons
 1 M–M 2 electron
Total 36 electrons

18e⁻/Mn atom



2 (Co atom) 18 electrons
 10(CO) 16 electrons
 1 M–M 2 electron
Total 36 electrons

18e⁻/Co atom



2 (Fe atom) 24 electrons
 12(CO) 24 electrons
 3 M–M 6 electron
Total 36 electrons

18e⁻/Fe atom

Compound Name	Total valence electrons	e necessary to follow 18e rule	Number of M–M bond
$\text{Ru}_3(\text{CO})_{12}$	$(3 \times 8) + (2 \times 12) = 48$	$(3 \times 18) - 48 = 6$	3
$\text{Ir}_4(\text{CO})_{12}$	$(4 \times 9) + (12 \times 2) = 60$	$(4 \times 18) - 60 = 12$	6
$\text{Os}_4(\text{CO})_{16}$	$(4 \times 8) + (16 \times 2) = 64$	$(4 \times 18) - 64 = 8$	4
$\text{Rh}_6(\text{CO})_{16}$			Neglect this example as it does not follow 18 election rule

➤ **18-electron rule is very much useful to predict the number of M–M bond in a complex. However, it does not assist us to predict a terminal and bridging ligand.**

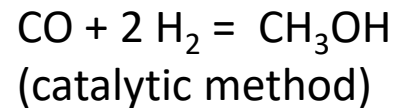
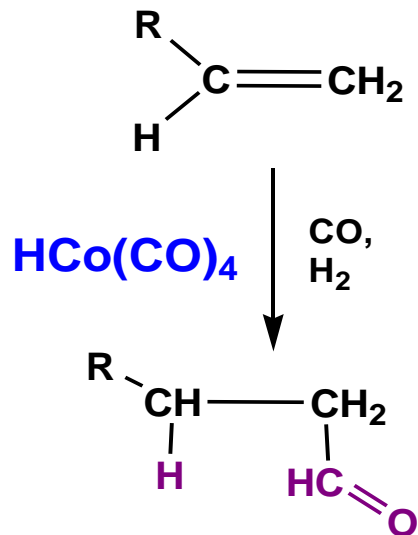
Why study metal carbonyls ?

CO has bond-dissociation energy of 1072 kJ/mol is stronger than that of N₂ (942 kJ/mol) and represents the strongest chemical bond known.

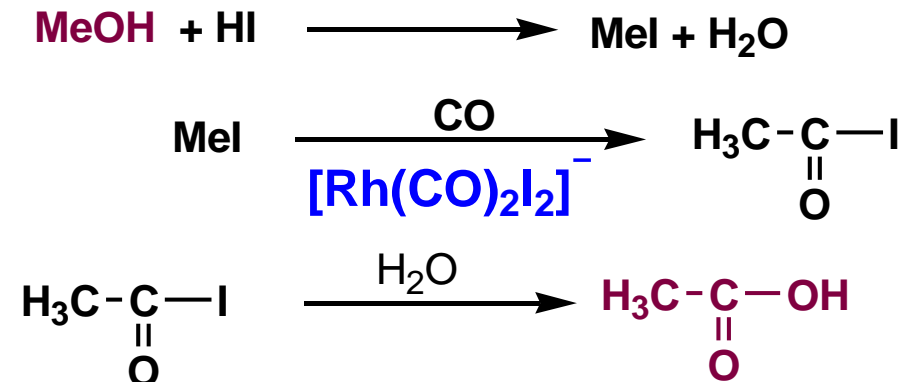
Simplest of organometallic compounds where M-C σ bonding is well understood. CO is one of the strongest π acceptor ligands. Back bonding (π bonding) and variation in electronic properties of CO can be monitored very efficiently by **Infrared spectroscopy**

A range of metal carbonyls are used as catalysts in Chemical Industry

Hydroformylation Alkene to Aldehyde



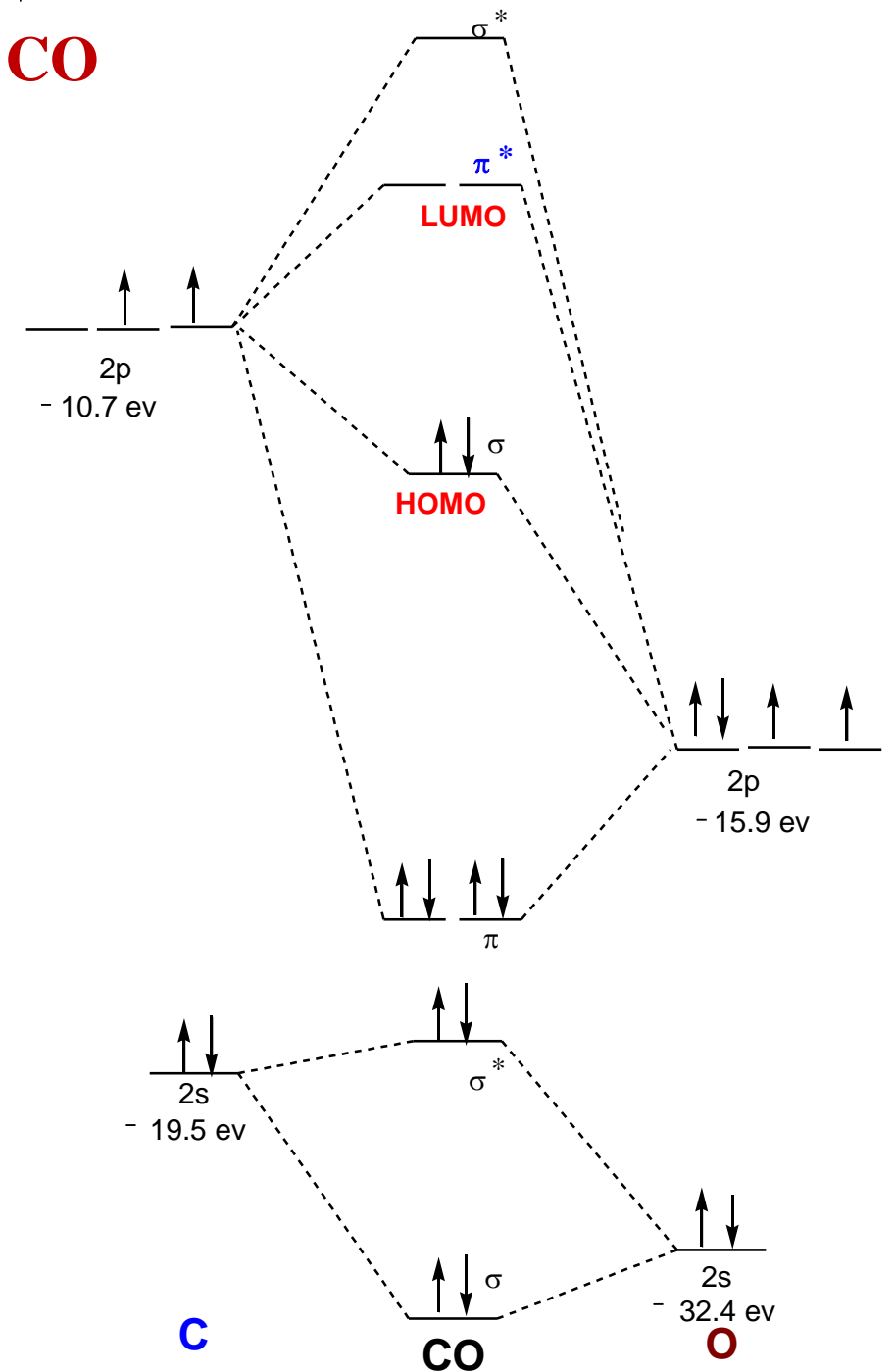
Methanol to Acetic acid Process



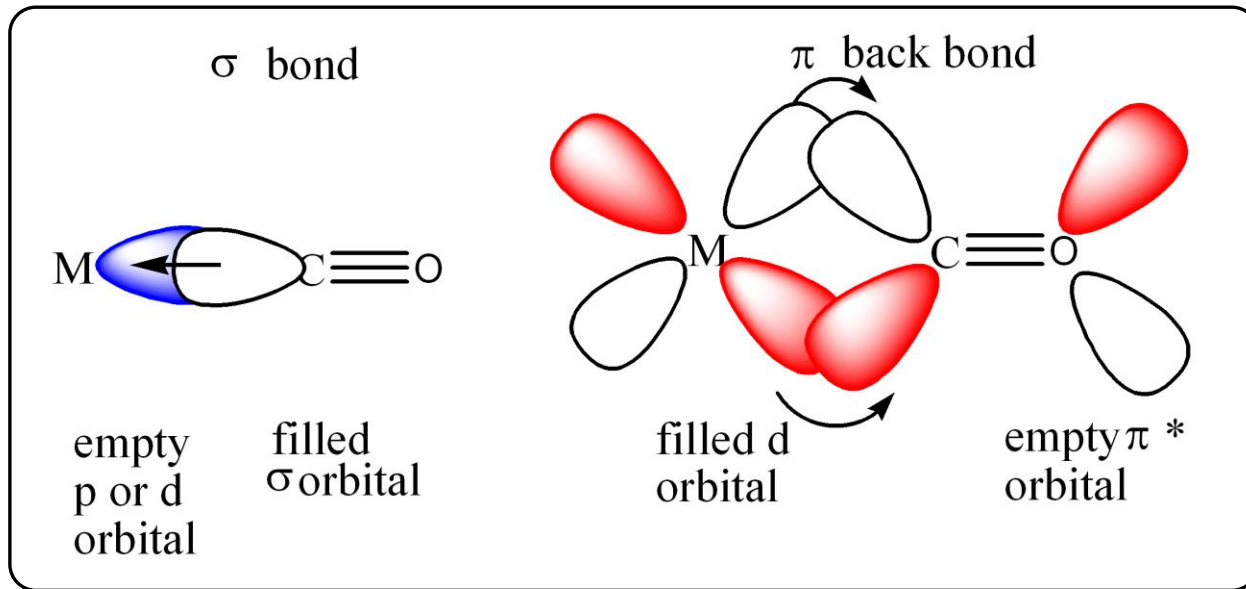
Molecular Orbital diagram of CO

Why does CO bind a metal through its less electronegative carbon atom than its more electronegative oxygen? What makes it a good π acceptor?

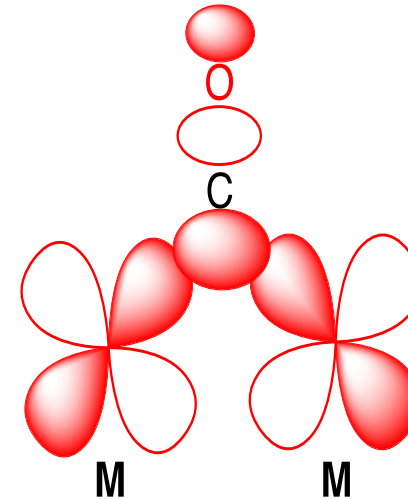
The highest occupied molecular orbital (**HOMO**) of CO is weakly antibonding (compared with the O atomic orbitals) and is an MO which is carbon based. Secondly, the π^* antibonding orbital which is the lowest unoccupied molecular orbital (**LUMO**) is also of comparatively lower energy which makes it possible to interact with metal t_{2g} orbitals for π bonding. There exists a strong back bonding of metal electrons to the π^* antibonding orbitals of CO



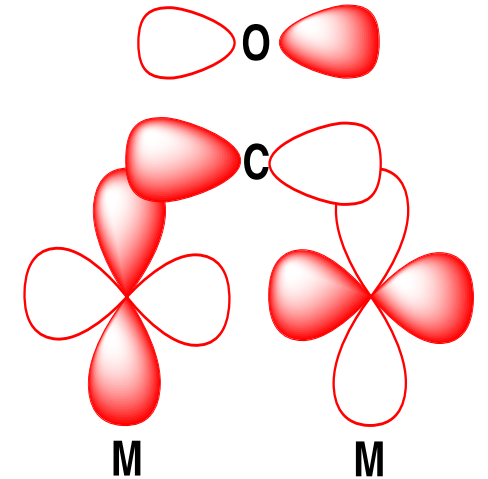
Binding mode of carbon monoxide



σ donation



π acceptance

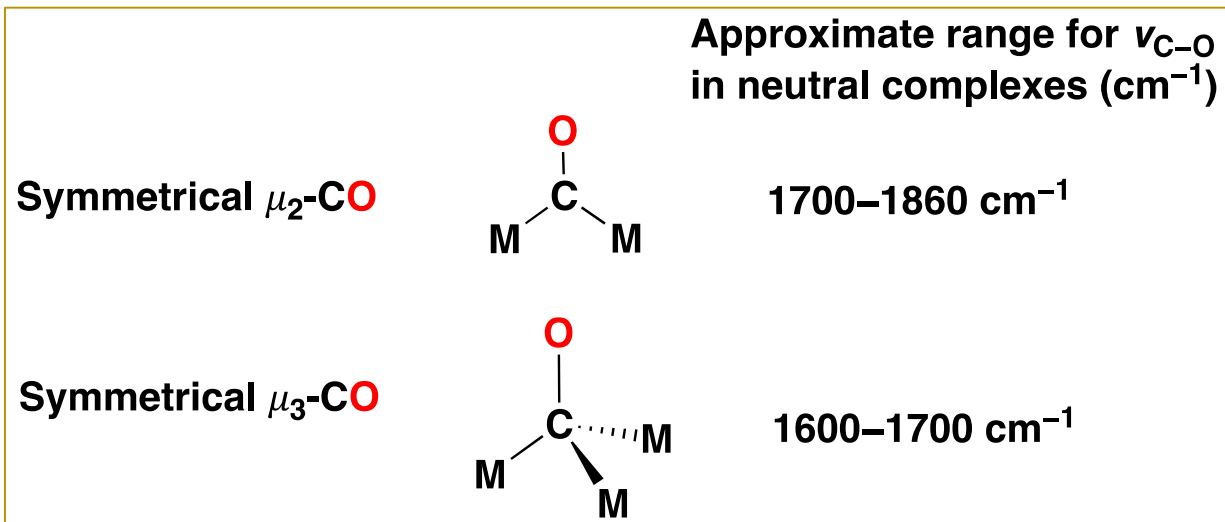


Counting the electrons helps to predict stability of metal carbonyls. But **it will not tell you whether a CO is bridging or terminal**

Bridging modes of CO

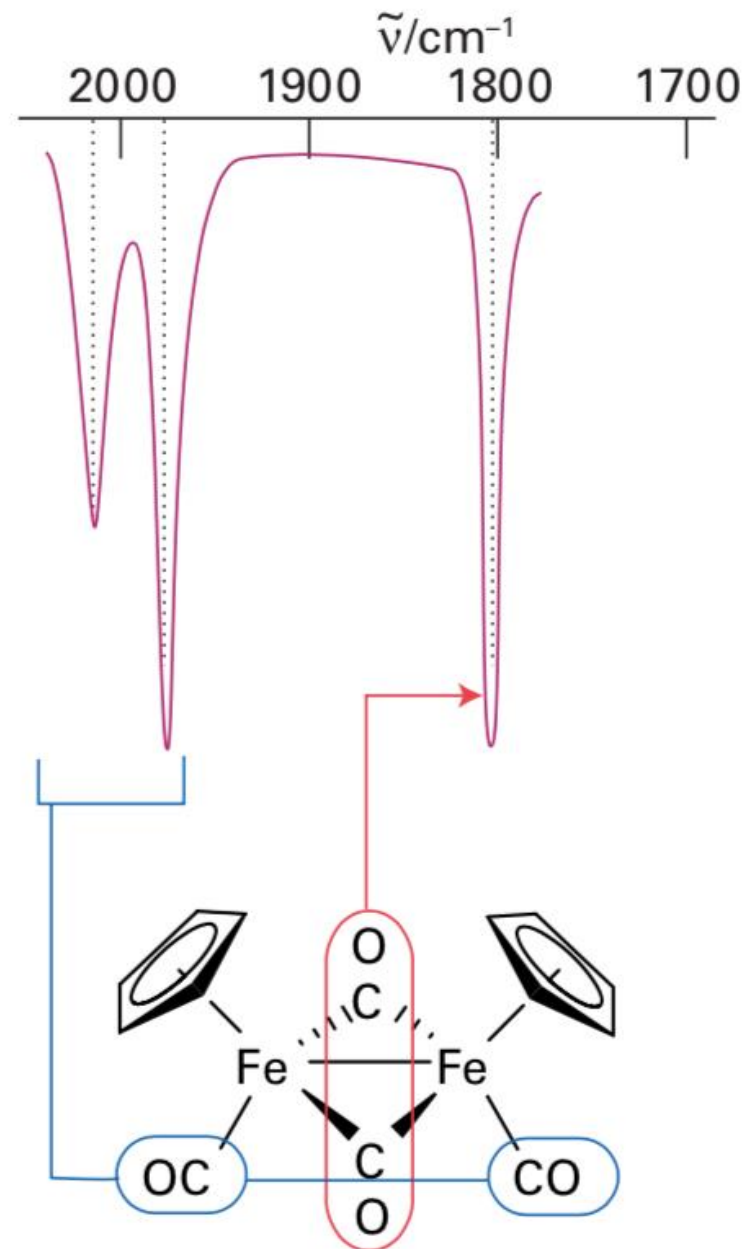
Free CO

2143 cm^{-1}



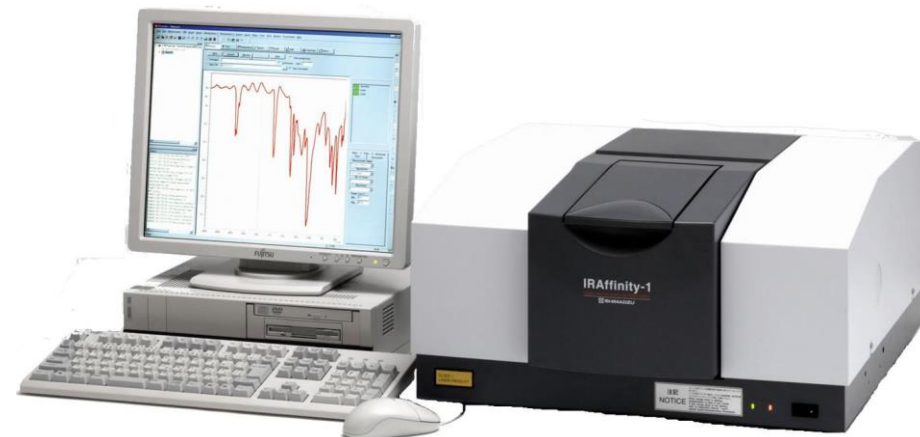
Characterization tools: Infrared spectroscopy and X-ray crystallography.

First, 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), and its energy often provides valuable information about the molecular structure. 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 $\text{Cr}(\text{CO})_6$.



Experimental evidence of M–CO bonding

Infrared spectroscopy (IR). The energy necessary to stretch a bond is proportional to $\sqrt{\frac{k}{\mu}}$, where k = force constant, **a measure of the rigidity of a bond**, μ = reduced mass; for atoms of mass m_1 and m_2 the reduced mass is given by $\mu = \frac{m_1 m_2}{m_1 + m_2}$.



Functional group

Range (cm⁻¹)

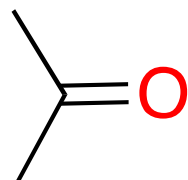
OH 3400–3600 cm⁻¹

NH 3200–3400 cm⁻¹

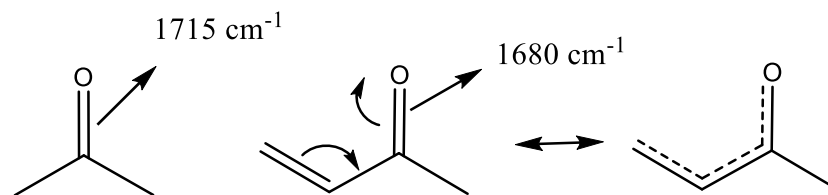
CH 2900–3200 cm⁻¹

C=O (terminal) 1900–2100 cm⁻¹

C=O (bridging) 1800–1900 cm⁻¹

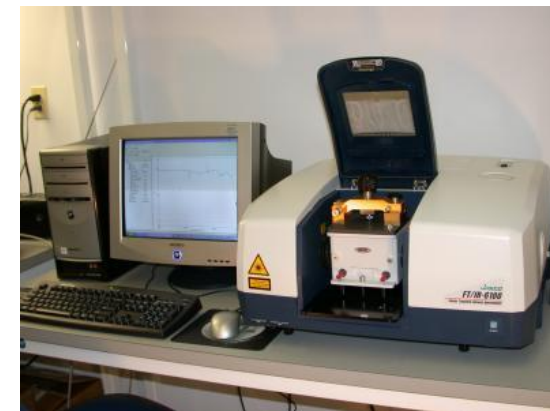
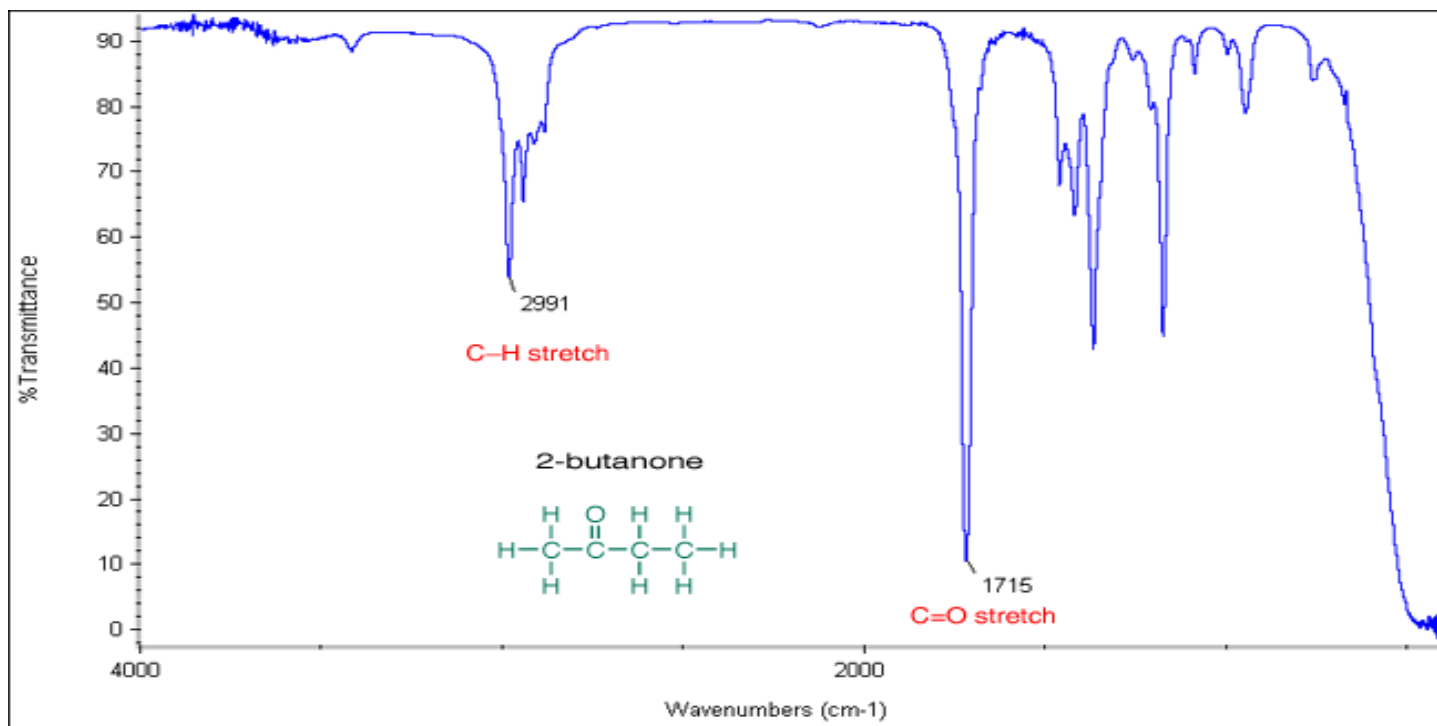


1600–1700 cm⁻¹



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.

Infrared Spectroscopy- A spectro-analytical tool in chemistry

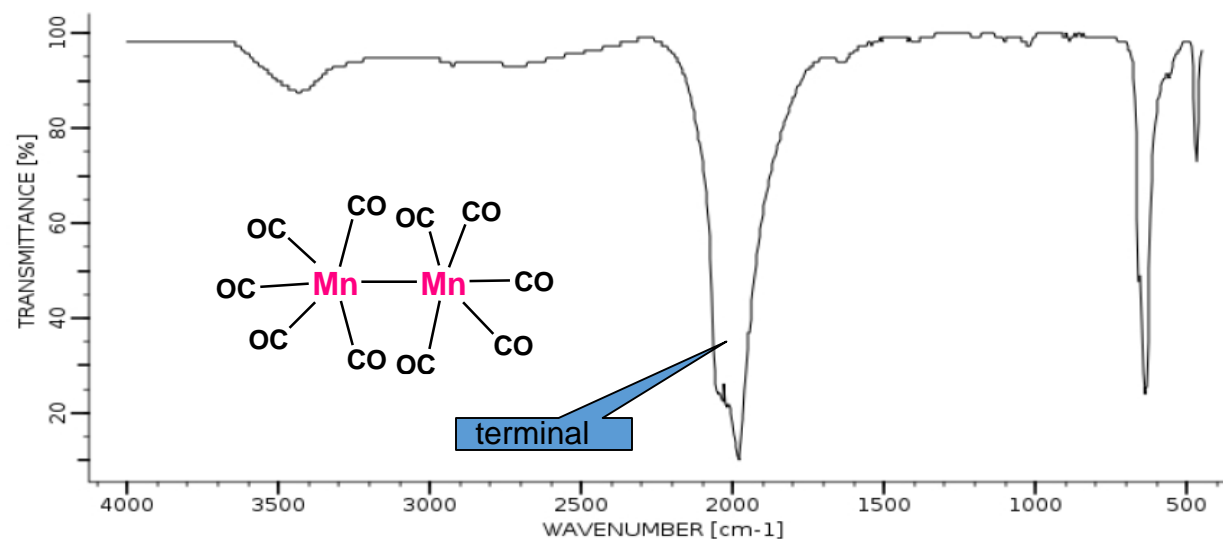


Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply, it is the absorption measurement of different IR frequencies by a compound positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Functional groups are identified based on vibrational modes of the groups such as stretching, bending etc. Different vibrational modes absorb characteristic frequencies of IR radiation. An infrared spectrophotometer is an instrument that passes infrared light through a molecule and produces a spectrum that contains a plot of the amount of light transmitted on the vertical axis against the wavelength of infrared radiation on the horizontal axis. Absorption of radiation lowers the percentage transmittance value.

For more detail (not for this course): https://www.youtube.com/watch?v=0S_bt3JI150&ab_channel=Knowbee

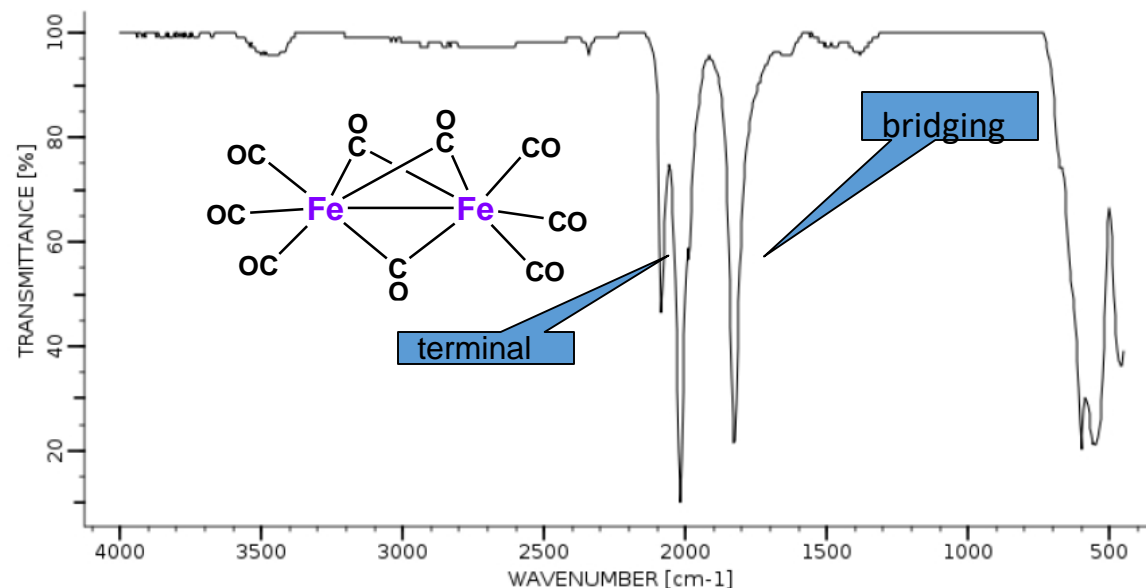
Infrared Spectroscopy- Spectra of Metal Carbonyls

1850-2120 cm^{-1}



The range in which the band appears decides bridging or terminal .

1700-1850 cm^{-1}

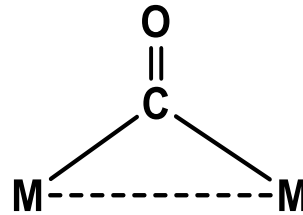


The number of bands is only related to the symmetry of the molecule

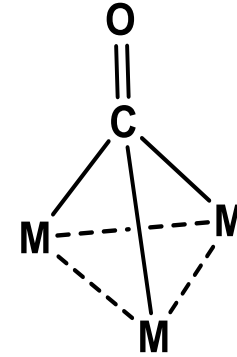
Terminal versus bridging carbonyls



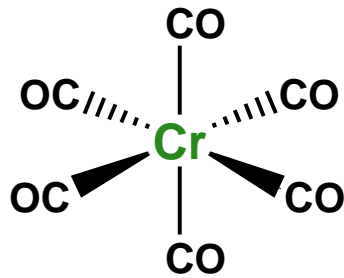
terminal
 ν_{CO} 2120-1850 cm^{-1}



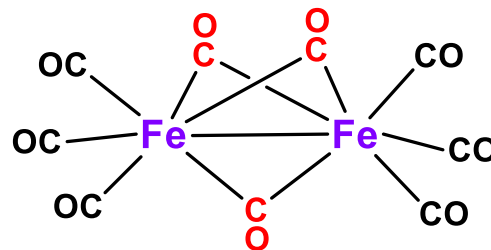
bridging μ_2
1850-1700 cm^{-1}



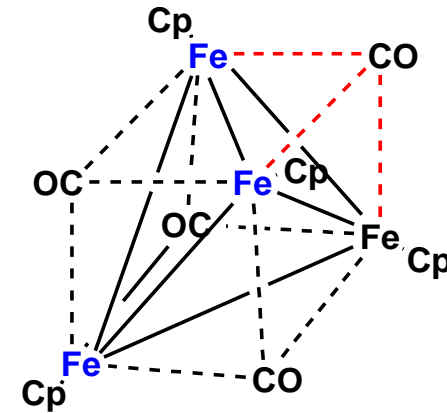
bridging μ_3
1730-1620 cm^{-1}



2000 cm^{-1}



2018, 1826 cm^{-1}



1620 cm^{-1}

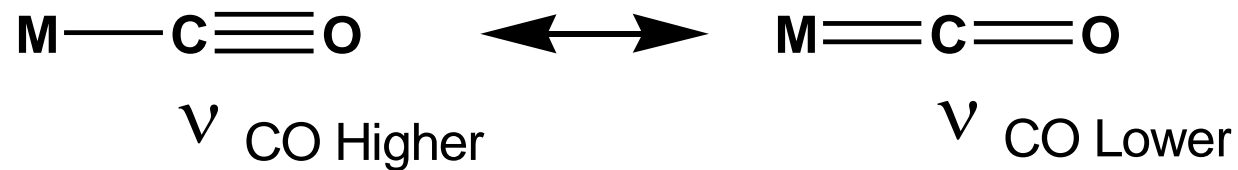
Factors which affect ν_{CO} stretching frequencies

Variation in ν_{CO} (cm^{-1}) of the first row transition metal carbonyls

	free CO 2143	
Ni(CO)_4 2057		
Co(CO)_4^- 1890		$\text{Co}_2(\text{CO})_8$ 2044(av, ter)
$[\text{Fe(CO)}_4]^{2-}$ 1815		Fe(CO)_5 2030
$[\text{Mn(CO)}_4]^{3-}$ 1600,1790	Mn(CO)_6^+ 2098	$\text{Mn}_2(\text{CO})_{10}$ 2013 (av)
$[\text{Cr(CO)}_4]^{4-}$ 1462,1657	Cr(CO)_6 2000	
	V(CO)_6^- 1860	V(CO)_6 1976
	Ti(CO)_6^{2-} 1747	

1. Charge on the metal
2. Effect of other ligands

As the electron density on a metal centre increases, more π -backbonding to the CO ligand(s) takes place. This weakens the C–O bond further as more electron density is pumped into the **empty π^* anti-bonding carbonyl orbital**. This increases the M–C bond order and reduces the C–O bond order. That is, the resonance structure $\text{M}=\text{C}=\text{O}$ becomes more dominant.

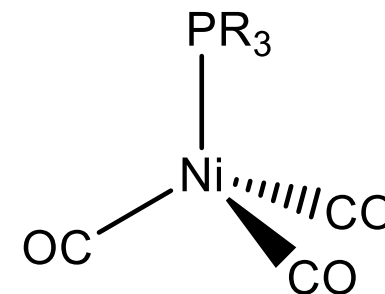


More back bonding

Other spectator ligands: Phosphines

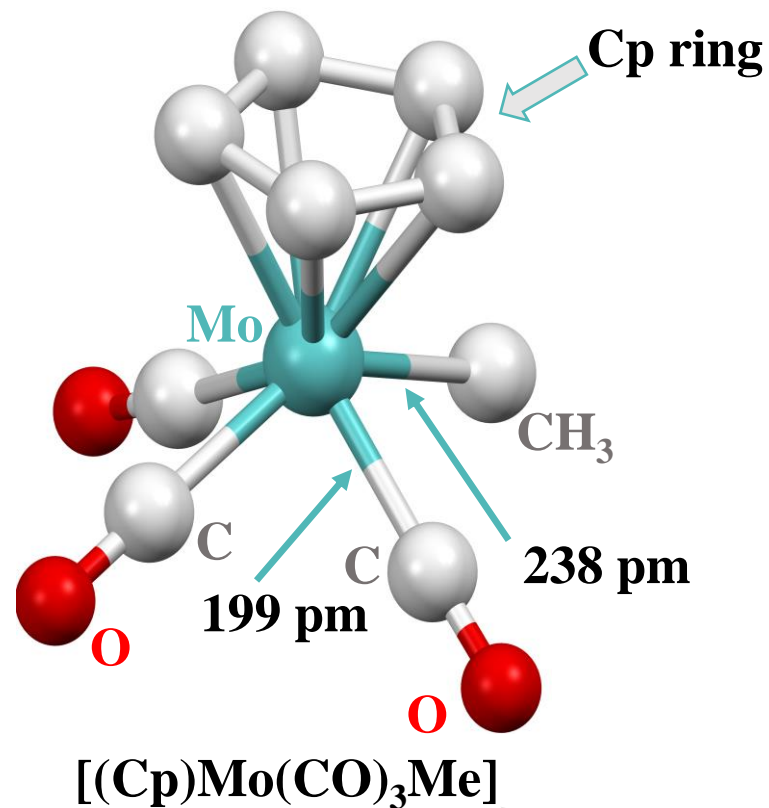
PR_3	$\nu_{\text{CO}}, (\text{cm}^{-1})$	$\chi(\text{cm}^{-1})$ $\Delta \nu_{\text{CO}}$ wrt $\text{P}(\text{t-Bu})_3$	PR_3	$\nu_{\text{CO}}, (\text{cm}^{-1})$	$\chi(\text{cm}^{-1})$ $\Delta \nu_{\text{CO}}$ wrt $\text{P}(\text{t-Bu})_3$
$\text{P}(\text{t-Bu})_3$	2056.1	0.0	$\text{PPh}_2(\text{C}_6\text{F}_5)$	2074.8	18.7
PCy_3	2056.4	0.3	$\text{P}(\text{OEt})_3$	2076.3	20.2
$\text{P}(i\text{-Pr})_3$	2059.2	3.1	$\text{P}(p\text{-C}_6\text{H}_4\text{-CF}_3)_3$	2076.6	20.5
PEt_3	2061.7	5.6	$\text{P}(\text{OMe})_3$	2079.5	23.4
$\text{P}(\text{NMe}_2)_3$	2061.9	5.8	PH_3	2083.2	27.1
PMe_3	2064.1	8.0	$\text{P}(\text{OPh})_3$	2085.3	29.2
PBz_3	2066.4	10.3	$\text{P}(\text{C}_6\text{F}_5)_3$	2090.9	34.8
$\text{P}(o\text{-Tol})_3$	2066.6	10.5	PCl_3	2097.0	40.9
PPh_3	2068.9	12.8	PF_3	2110.8	54.7
PPh_2H	2073.3	17.2	$\text{P}(\text{CF}_3)_3$	2115.0	58.9

Lowest CO stretching frequency
Most donating phosphine
best σ donor



Highest CO stretching frequency
Least donating phosphine
best π acceptor

π back donation is a big contributor to the $M=C$ bond in metal carbonyls, making the $M=C$ bond much shorter than an $M-C$ single bond.



- Back bonding can only happen in d^1 or higher configurations; a d^0 ion such as Ti^{4+} cannot back bond and very seldom forms stable complexes with strong π acceptor ligands, such as CO.

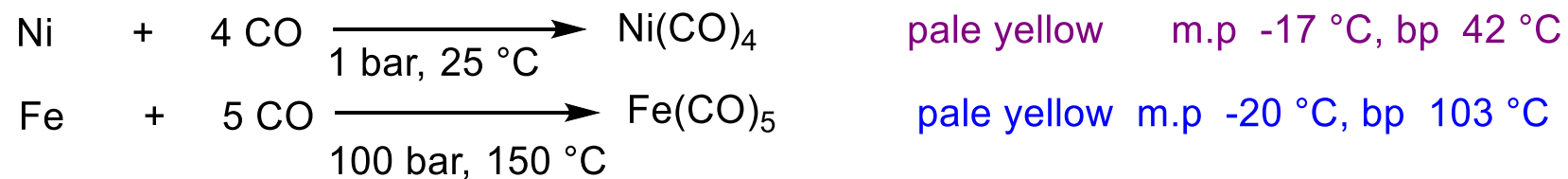
$W(NH_3)_6$ is not known although $W(CO)_6$ is known.

By back bonding, the metal can get rid of some of this excess electron density and delocalize it over the π -acid ligands. In $W(CO)_6$, back bonding is so effective that the compound is air stable and relatively unreactive; the CO groups have so stabilized the metal electrons that they have no tendency to be abstracted by an oxidant such as air.

A true $M-CO$ single bond would be shorter than 2.38 Å by about 7 pm, to allow for the higher s character of sp CO versus sp^3 CH_3 , leaving a substantial shortening of 32 pm that can be ascribed to back bonding.

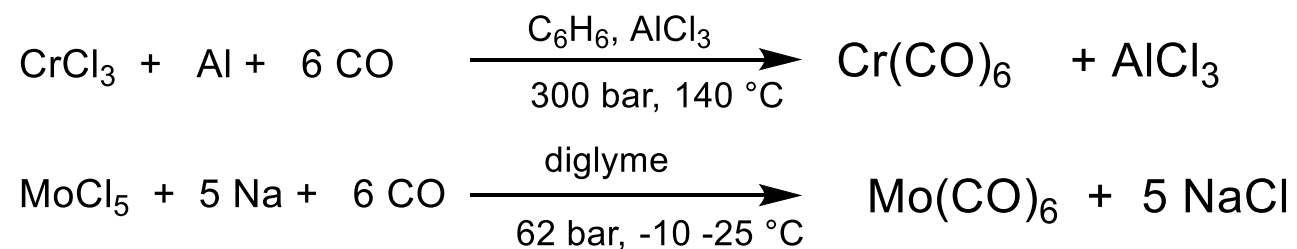
Synthesis of Metal Carbonyls

Direct carbonylation

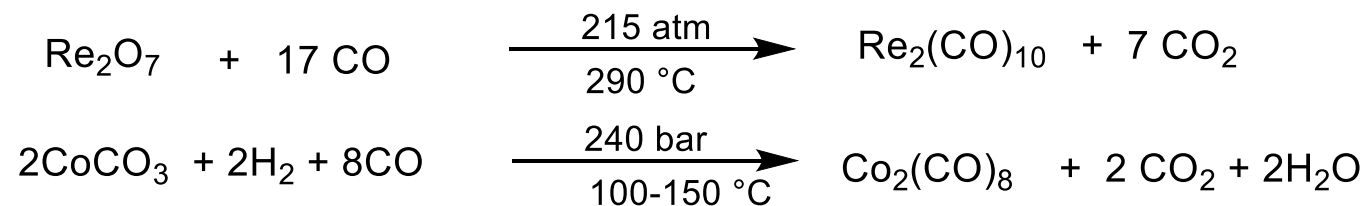


Reductive carbonylation

From Metal Halides

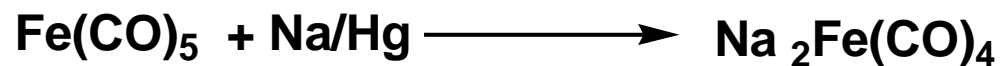
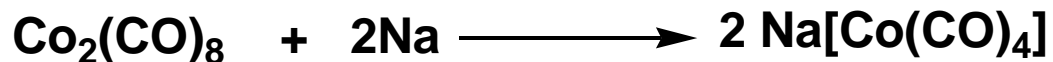
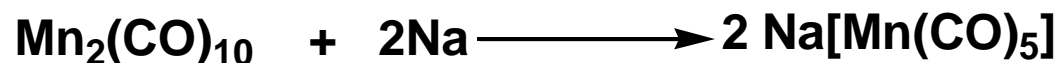
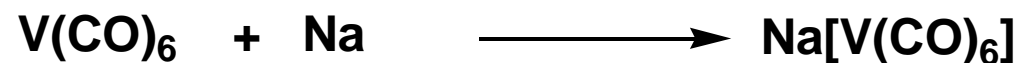


From Metal Oxides and carbonates

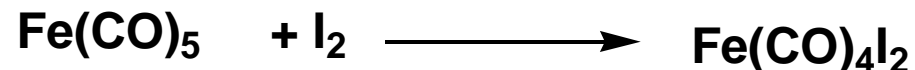


Reactions of Metal Carbonyls

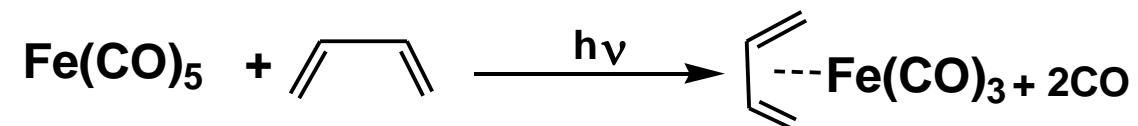
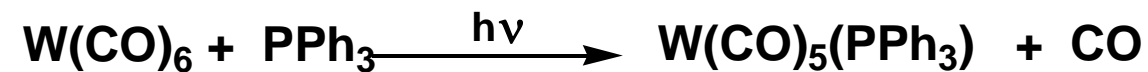
Reduction : Carbonyl anions



Oxidation : Iodocarbonyls



Photochemical substitution



In the presence of UV radiation a monodentate ligand displaces only one CO unit