

CH 101

Lecture 9

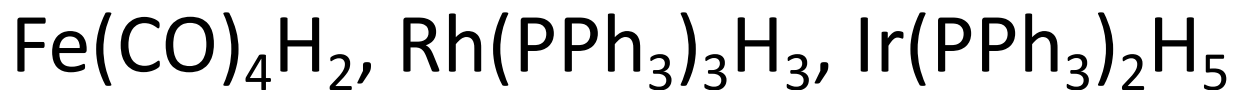
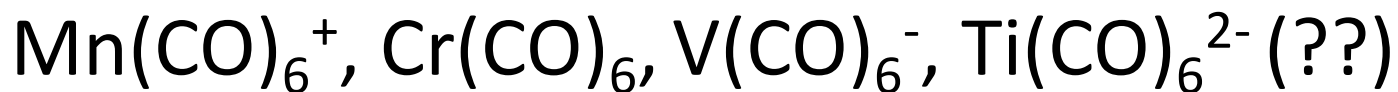
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Metal complexes that obey 18-Electron Rule;

- ✧ Works well with small ligands (particularly with π -acceptors and also with H)
- ✧ Both CO and H result in a large Δ (CO strongly “pulls down” the d_{π} orbitals & H^- “pushes up” the d_{σ} orbitals to a great extent)



Exceptions to the 18e rule

✧ Paramagnetic complexes $V(CO)_6$, Cp_2Fe^+ , Cp_2Ni

✧ $CpFe(\eta^6\text{-arene})$ – powerful 1e reductant

✧ Lanthanides and actinides ($U(cot)_2$, Cp_2LuMe)

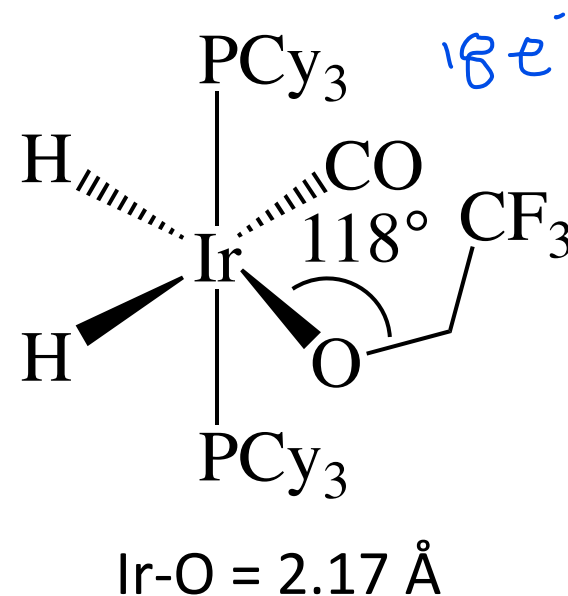
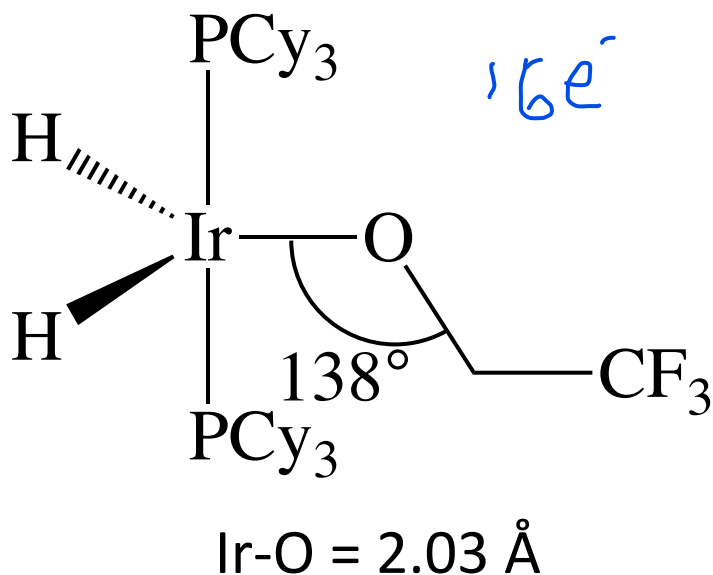
✧ Early metals and d0 { $W(OMe)_6$ 12e or 24e? }

Cp_2TiCl_2 ?

18e rule less useful

Exceptions to the 18e rule

✧ π donating ligands $(\text{PR}_3)_2\text{Ir}(\text{H})_2\text{Cl}$ – 16e or 18e??



✧ Bulky Ligands $\text{Pt}(\text{PPh}_3)_3$ Vs $\text{Pt}(\text{PMe}_3)_4$

Square-planar Complex

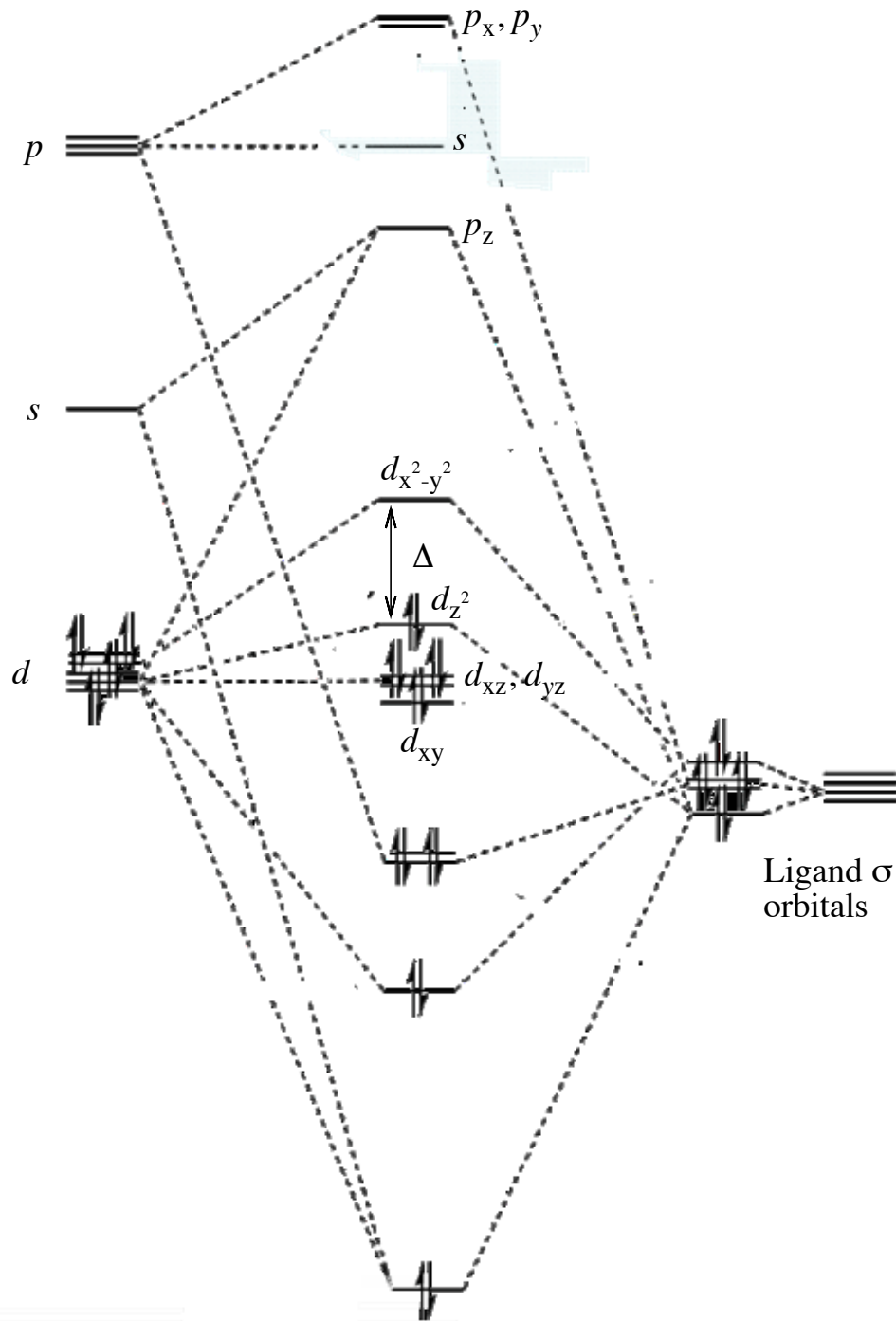
16e rule prevails; d^8 metals

Group			
8	9	10	11
Fe(0) ^a	Co(I) ^b	Ni(II)	Cu(III) ^c
Ru(0) ^a	Rh(I) ^b	Pd(II)	—
Os(0) ^a	Ir(I) ^b	Pt(II)	Au(III)

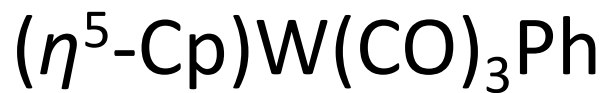
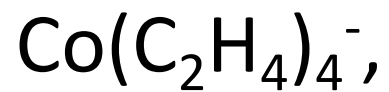
^aThese metals prefer 18e to 16e.

^bThe 16e configuration is more often seen, but 18e complexes are common.

^cA rare oxidation state.



Ligand	Type	Covalent Model	Ionic Model
Me, Cl, Ph, Cl, η^1 -allyl, NO (bent) ^a	X	1e	2e
Lone-pair donors: CO, NH ₃	L	2e	2e
π -Bond donors: C ₂ H ₄	L	2e	2e
σ -Bond donors: (H ₂)	L	2e	2e
M–Cl (bridging)	L	2e	2e
η^3 -Allyl, κ^2 -acetate	LX	3e	4e
NO (linear) ^a		3e	2e ^a
η^4 -Butadiene	L ₂ ^b	4e	4e
=O (oxo)	X ₂	4e	2e
η^5 -Cp	L ₂ X	5e	6e
η^6 -Benzene	L ₃	6e	6e

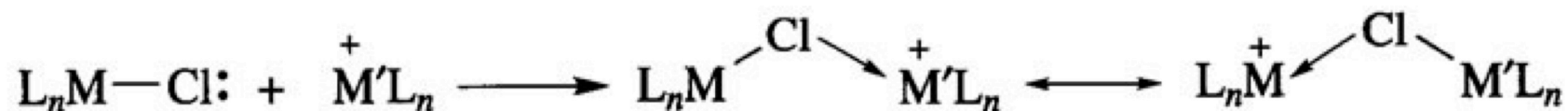


Bridging ligands (denoted as μ)

Bridging ligands (Cl^- , RS^- , RO^- , R_2P)

Covalent Model; 1e donor to M and 2e donor to M'

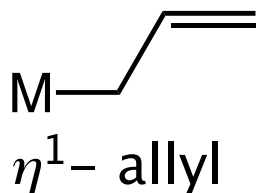
Ionic model; 2e donor to both Metals



Bridging ligands (CO, Methylene and oxo)

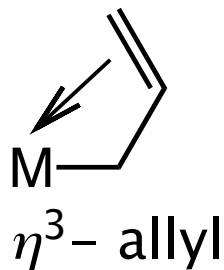
Covalent Model; 1e donor to each Metal

Ionic model; 1e donor to both Metals



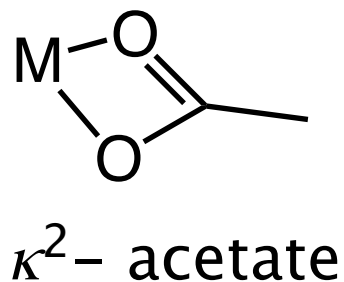
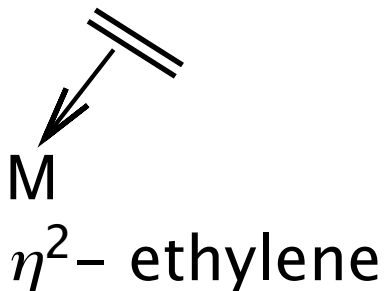
X

Covalent Model; 1e donor
 ionic model; 2e donor
 No. of ligating atoms = 1



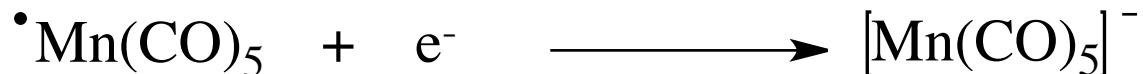
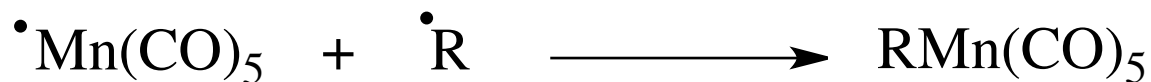
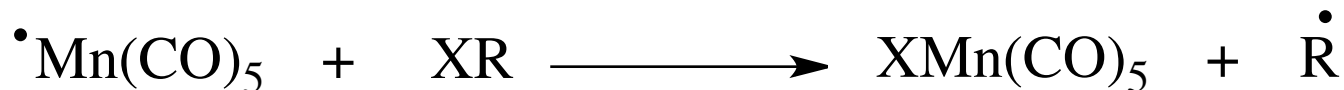
LX

Covalent Model; 3e donor
 ionic model; 4e donor
 No. of ligating atoms = 3

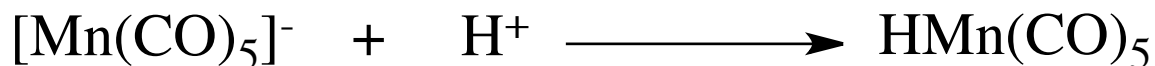
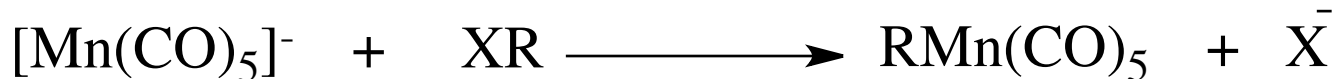


Can one predict the reactivity pattern based on 18e rule?

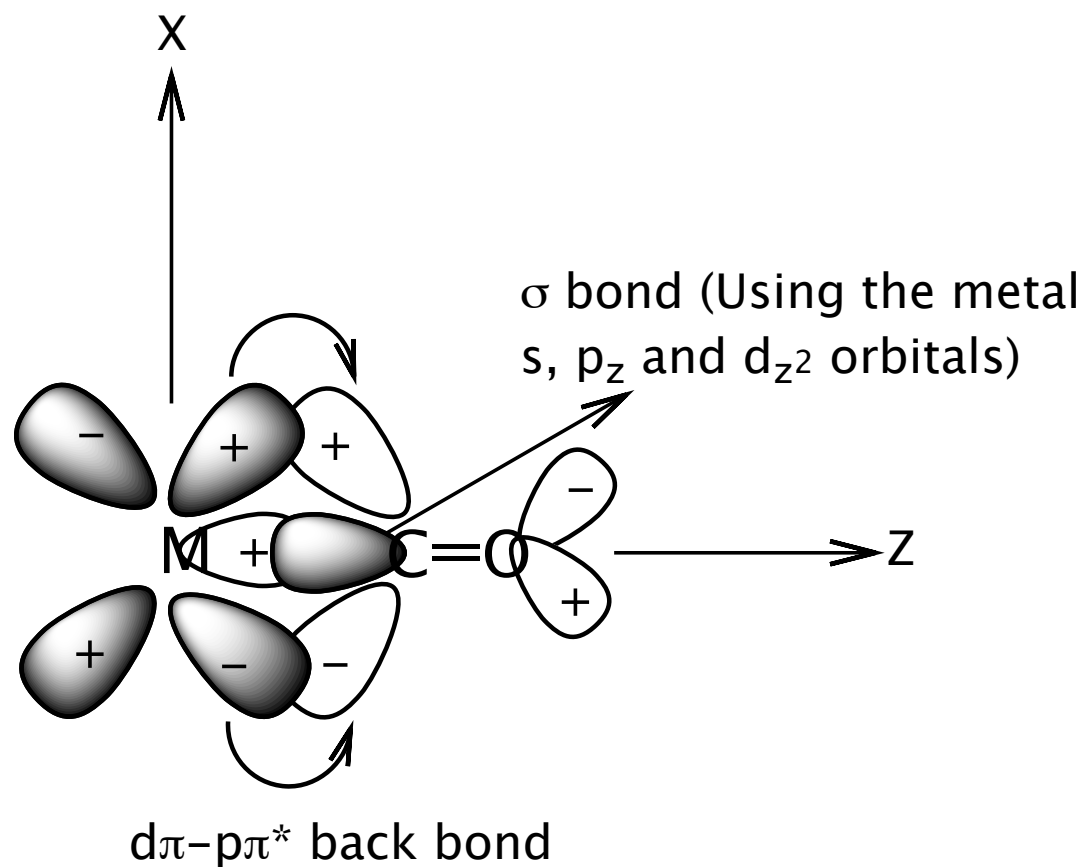
$\bullet\text{Mn}(\text{CO})_5$ is like $\bullet\text{CH}_3$



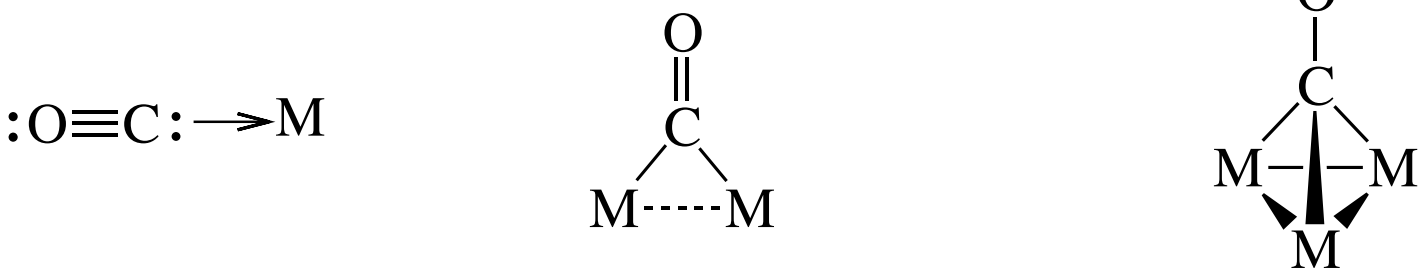
Is $[\text{Mn}(\text{CO})_5]^-$ like CH_3^-



Bonding in Metal Carbonyls



Metal-carbonyls: Bonding Modes



Terminal Mode 2e neutral donor			μ_2 -bridging mode 2e neutral donor		μ_3 -bridging mode 3e neutral donor		
4	5	6	7	8	9	10	11
Ti	V(CO) ₆	Cr(CO) ₆	Mn ₂ (CO) ₁₀	Fe(CO) ₅ Fe ₂ (CO) ₉ Fe ₃ (CO) ₁₂	Co ₂ (CO) ₈ Co ₄ (CO) ₁₂	Ni(CO) ₄	Cu
Zr	Nb	Mo(CO) ₆	Te ₂ (CO) ₁₀	Ru(CO) ₅ Ru ₃ (CO) ₁₂	Rh ₄ (CO) ₁₂ Rh ₆ (CO) ₁₆	Pd	Ag
Hf	Ta	W(CO) ₆	Re ₂ (CO) ₁₀	Os(CO) ₅ Os ₃ (CO) ₁₂	Ir ₄ (CO) ₁₂	Pt	Au

Metal-carbonyls: Evidence for Bonding

General observation is in line with model

Weakened C-O bond

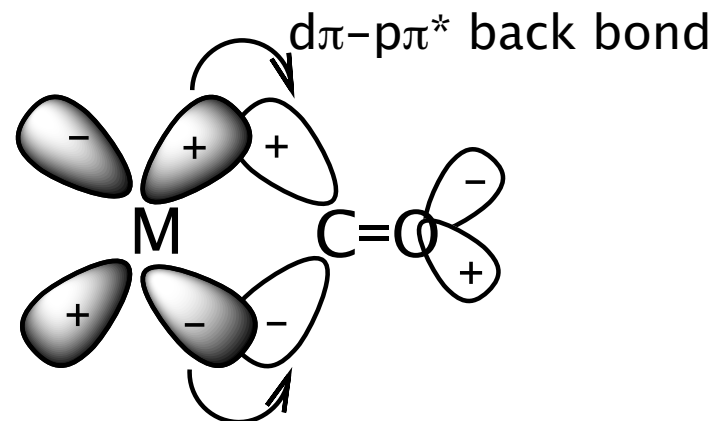
Lower carbonyl stretching frequency
(compared to free CO)

Point to decrease in C-O bond order

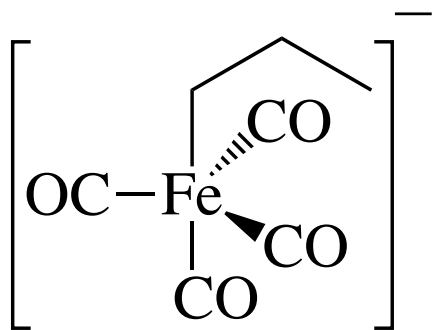
C-O bond $\text{C}\equiv\text{O}$ 1.13 Å

$\text{H}_2\text{C}=\text{C}=\text{O}$ 1.17 Å

$\text{M}\equiv\text{C}\equiv\text{O}$ 1.13 – 1.16 Å



Metal-carbonyls: Evidence for Bonding



Fe-propyl = 2.20 Å

Fe-CO = 1.75 Å

Covalent bond radius; $C(sp^3) = 0.77 \text{ Å}$ and $C(sp) = 0.70 \text{ Å}$

Confirms the formation of M-C multiple bond

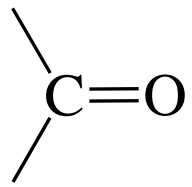
Chemische Berichte **1975**, 108, 1373-83.

Carbonyl IR Stretching Frequencies

1. The **position** of the carbonyl bands in the IR depends mainly on the **bonding mode** of the CO (terminal, bridging) and the **amount of electron density on the metal being pi-backbonded to the CO**.
2. The **number** (and intensity) of the carbonyl bands one observes depends on the **number of CO ligands present** and the **symmetry** of the metal complex.

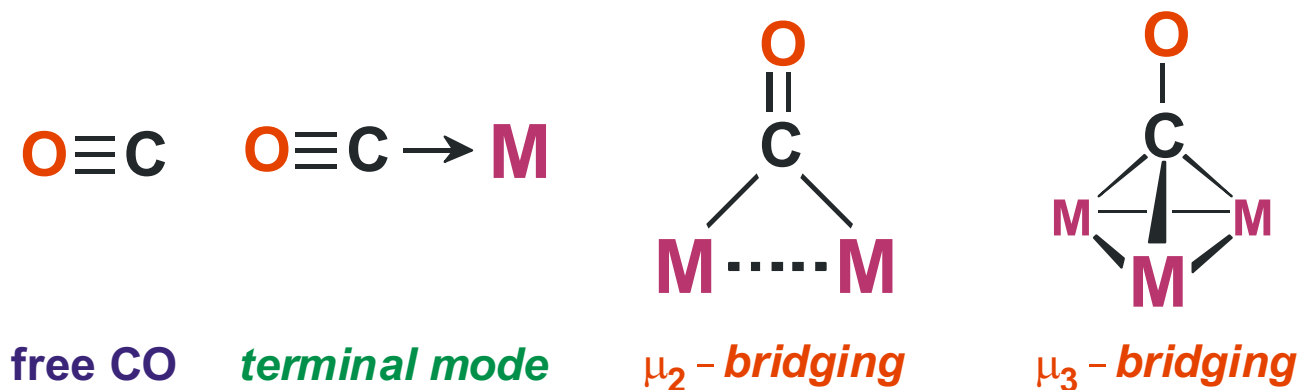
Metal-carbonyls: Evidence for Bonding

IR Data $\nu_{\text{CO}} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu_{\text{co}}}}$ k and hence ν is a measure of bond strength

Molecule	ν_{CO}
$\text{H}_3\text{C}-\text{O}-\text{CH}_3$	1000 cm^{-1}
	1720 cm^{-1}
$\text{C}\equiv\text{O}$	2143 cm^{-1}
$\text{H}_3\text{B}\leftarrow\text{C}\equiv\text{O}$	2165 cm^{-1}

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.



ν_{CO} IR (cm^{-1})	2143	2120 - 1850	1850 - 1720	1730 - 1500
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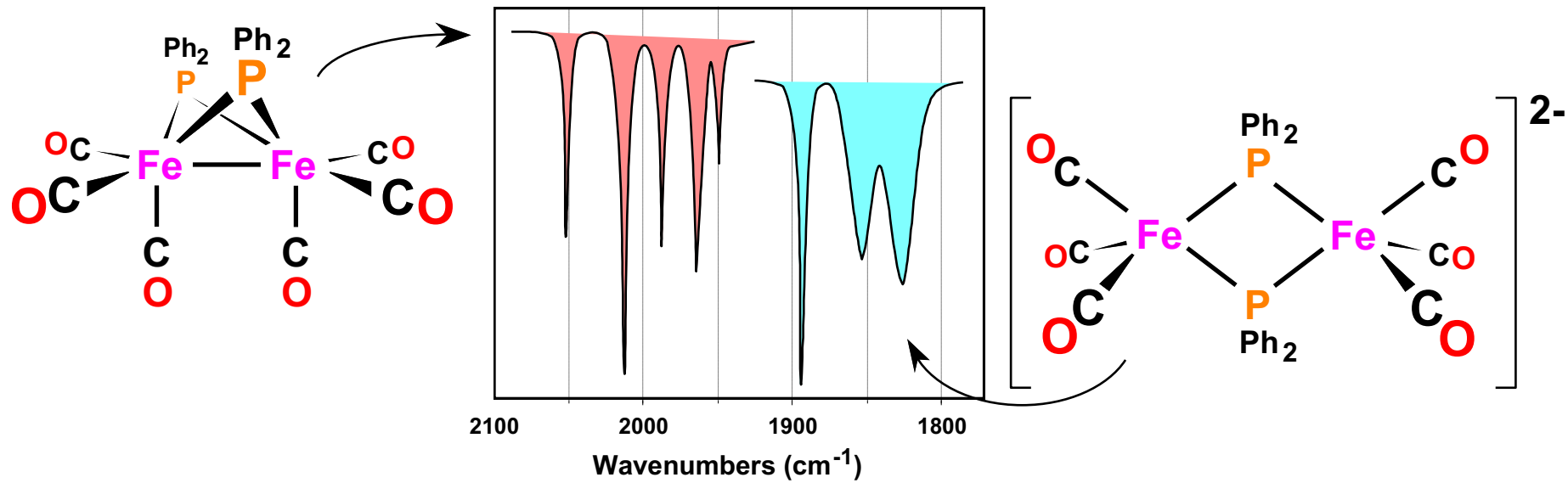
(for neutral metal complexes)

Bridging carbonyls tend to have weaker and broader IR bands.

Effect of Electron Density on Metal in Homoleptic Complexes

Weakening of the CO bond can be correlated to the back-donation of metal e density to CO

Molecule	ν_{CO}	Molecule	ν_{CO}
Mn(CO)_6^+	2090 cm^{-1}	free CO	2143
Cr(CO)_6	2000 cm^{-1}	$[\text{Ag(CO)}]^+$	2204
V(CO)_6^-	1860 cm^{-1}	Ni(CO)_4	2060
Ti(CO)_6^{2-}	1750 cm^{-1}		
Ni(CO)_4	2046 cm^{-1}		
Co(CO)_4^-	1883 cm^{-1}		
Fe(CO)_4^{2-}	1788 cm^{-1}		

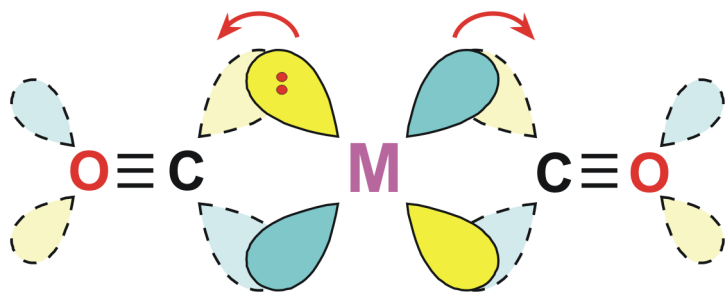


Ligand Donation Effects:

Ligands that are *trans* to a carbonyl can have a particularly large effect on the ability of the CO to effectively π -backbond to metal.

Two *trans* π -backbonding ligands will partially compete for same d -orbital electron density and weakens each others net M-L bond

Trans σ -backbonding ligands strengthens the M-CO bond



Pyridines and amines –
Weak σ -donors and

worse π -acceptors. CO has no competition for π -acceptance

Complex	ν_{CO} cm^{-1}
$\text{Mo}(\text{CO})_3(\text{PF}_3)_3$	2090, 2055
$\text{Mo}(\text{CO})_3(\text{PCl}_3)_3$	2040, 1991
$\text{Mo}(\text{CO})_3[\text{P}(\text{OMe})_3]_3$	1977, 1888
$\text{Mo}(\text{CO})_3(\text{PPh}_3)_3$	1934, 1835
$\text{Mo}(\text{CO})_3(\text{NCCH}_3)_3$	1915, 1783
$\text{Mo}(\text{CO})_3(\text{triamine})_3$	1898, 1758
$\text{Mo}(\text{CO})_3(\text{pyridine})_3$	1888, 1746

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

