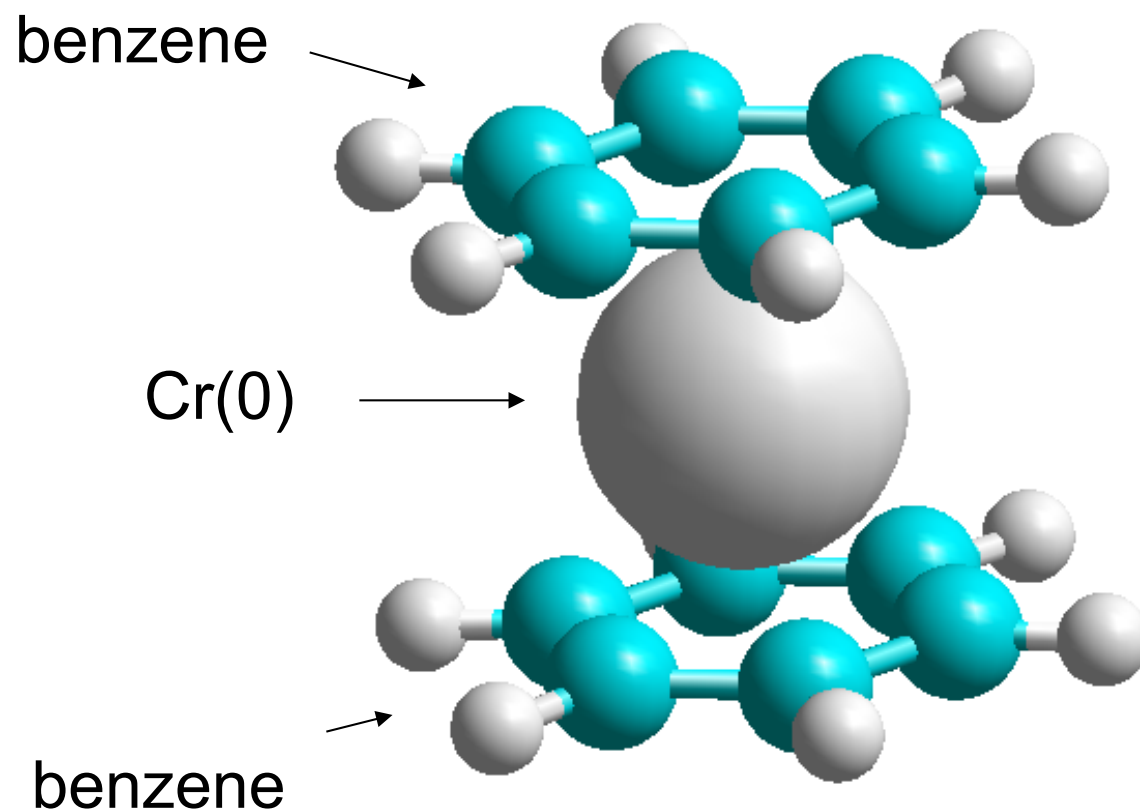


An introduction to organometallic chemistry



The 'sandwich' complex of Cr(0), which is $[\text{Cr}(\text{benzene})_2]$

Organometallic complexes.

Organometallic complexes are strictly those that contain a metal to carbon bond, but also include a large number where the donor atoms are only such soft donor atoms as P or S. Typically, such complexes involve very soft ligands, and very soft metal ions in low oxidation states. We thus saw on the slide above the complex of Cr(0) with two benzene ligands. Important ligands for organometallic complexes in this course are:

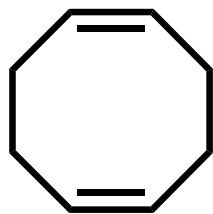
$\text{C}\equiv\text{O}$ The carbonyl ligand

PR_3 The phosphines, where R is, for example $-\text{CH}_3$ or $-\text{C}_6\text{H}_5$ (trimethyl phosphine and triphenylphosphine).

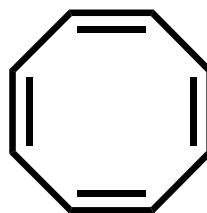
ethylenes, butadiene, cyclooctadiene, cyclooctatetraene, cyclopentadienyl anion:



butadiene



cyclooctadiene (COT)



cyclooctatetraene (COD)

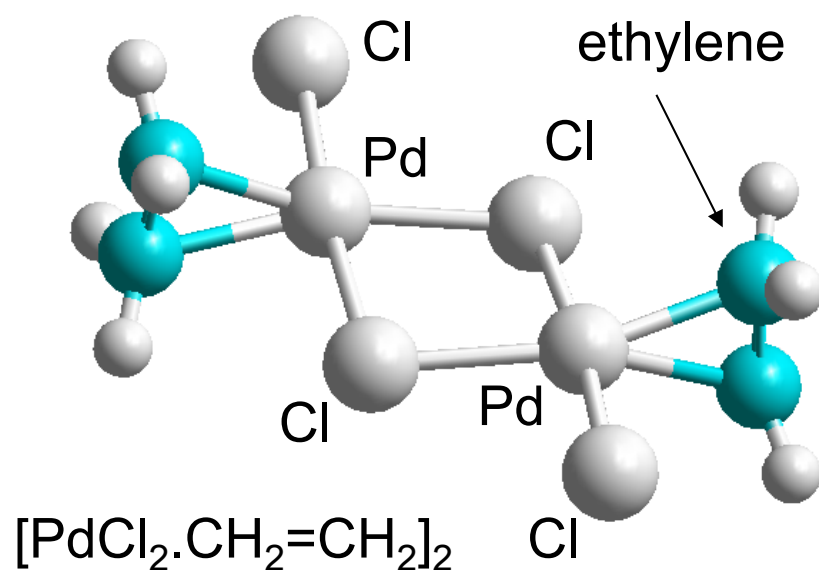


cyclopentadienyl
anion

Early organometallics:

Until fifty years ago, organometallic chemistry was restricted to a few oddities that were hard to understand.

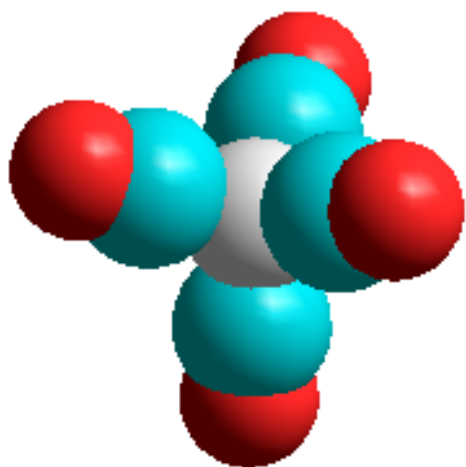
For example, $[\text{Ni}(\text{CO})_4]$ has been known since at least 1889, when it was used in the **Mond process** for production of ultrapure Ni. Ni is the only metal that will react directly with CO to produce a carbonyl, which is actually volatile, aiding separation of Ni from other metals.



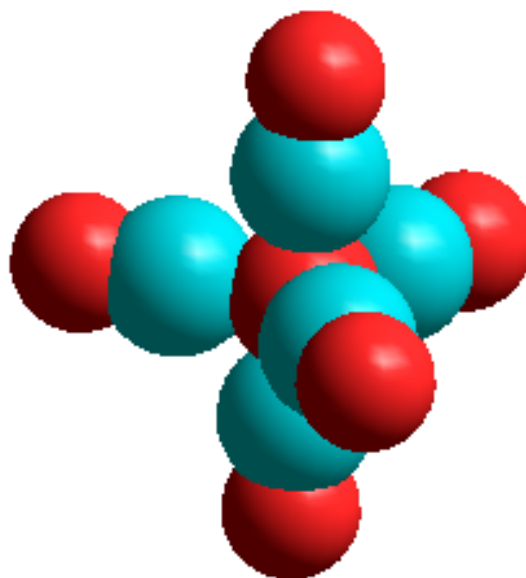
It was known that PdCl_2 would react with ethylene to give a compound that analyzed as $\text{PdCl}_2 \cdot \text{CH}_2=\text{CH}_2$. But why? We now know that the structure is as at left, but why does the $\text{CH}_2=\text{CH}_2$ bind to the Pd? We will look at some of this chemistry

Carbonyl complexes

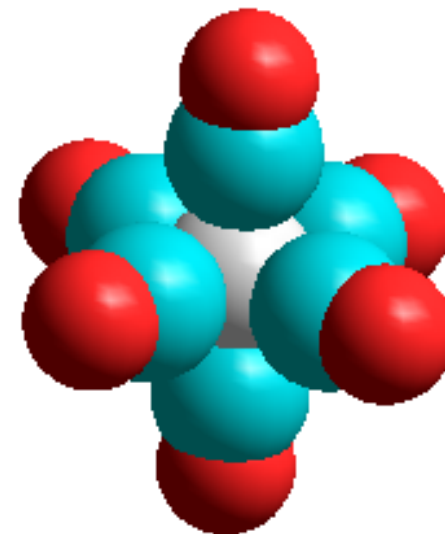
The carbonyl ligand forms a huge number of complexes with metal ions, most commonly in low oxidation states, where it binds to the metal through its C-donor, as in the complexes below, where all the metal ions are zero-valent:



$[\text{Ni}(\text{CO})_4]$
 T_d



$[\text{Fe}(\text{CO})_5]$
TBP (D_{3h})



$[\text{Cr}(\text{CO})_6]$
 O_h

Carbonyl complexes and the 18-electron rule

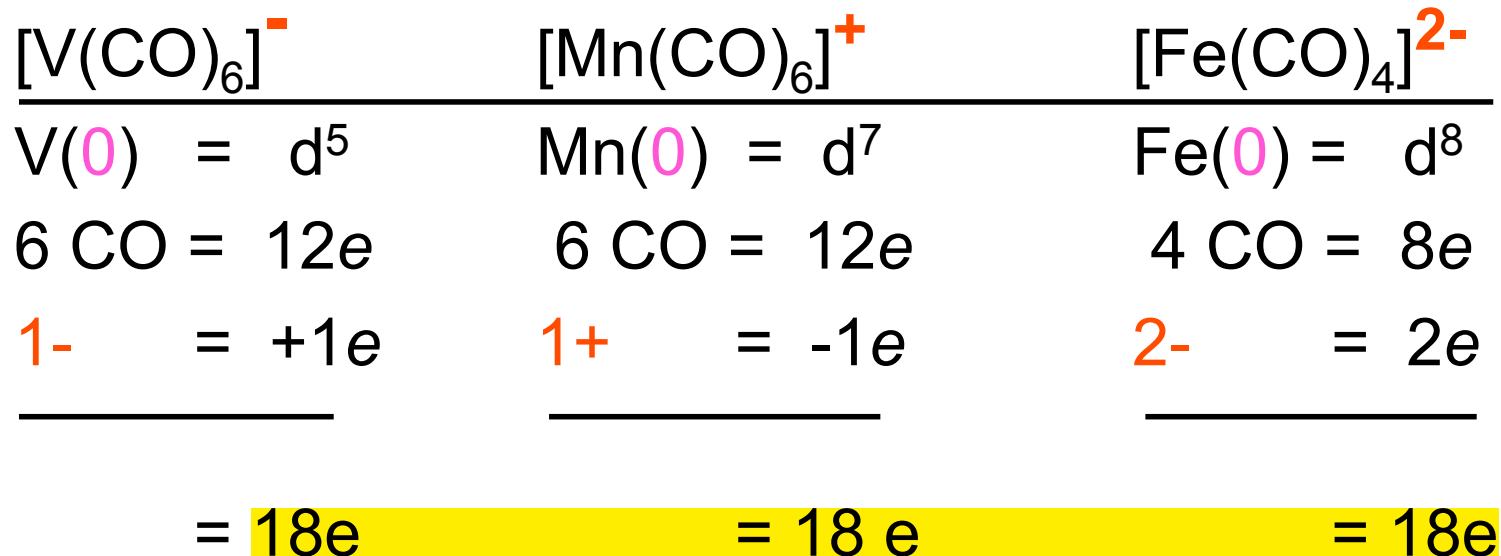
One might wonder why in the above complexes Ni(0) has four C≡O groups attached to it, Fe(0) five C≡O, and Cr(0) six C≡O. A very simple rule allows us to predict the numbers of donor groups attached to metal ions in organometallic complexes, called the **eighteen electron rule**. The latter rule states that the sum of the d-electrons possessed by the metal plus those donated by the ligands (2 per C≡O) must total eighteen:

[Ni(CO) ₄]	[Fe(CO) ₅]	[Cr(CO) ₆]
Ni(0) = d ¹⁰	Fe(0) = d ⁸	Cr(0) = d ⁶
4 x CO = 8	5 x CO = 10	6 x CO = 12
<hr/>	<hr/>	<hr/>
18 e	18e	18e

Formal oxidation states are all zero.

Carbonyl complexes and the 18-electron rule

To obey the 18-electron rule, many carbonyl complexes are anions or cations, as in:



Formal oxidation
state = V(-I)

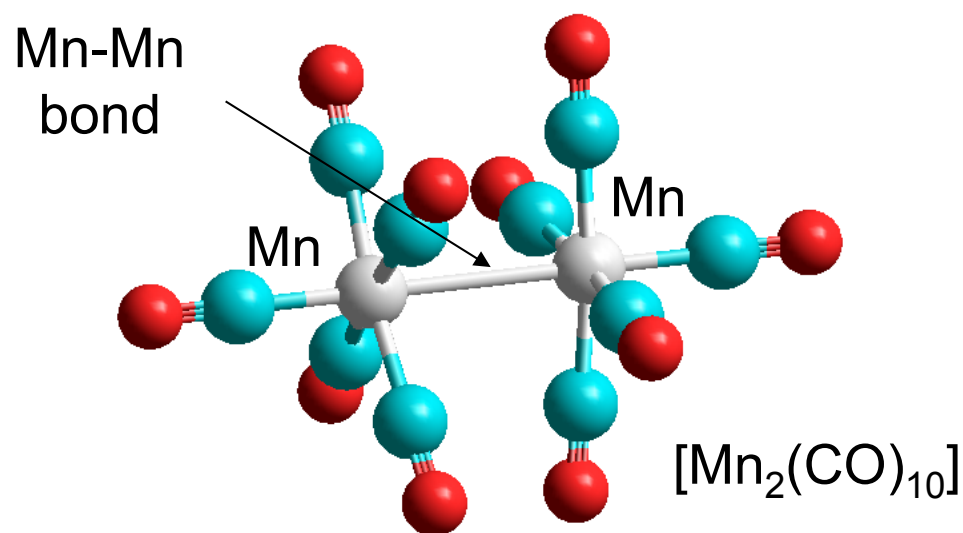
Formal oxidation
state = Mn(I)

Formal oxidation
state = Fe(-II)

[NOTE: In applying the 18-electron rule, metal ions are always considered to be zero-valent, not the formal oxidn. state]

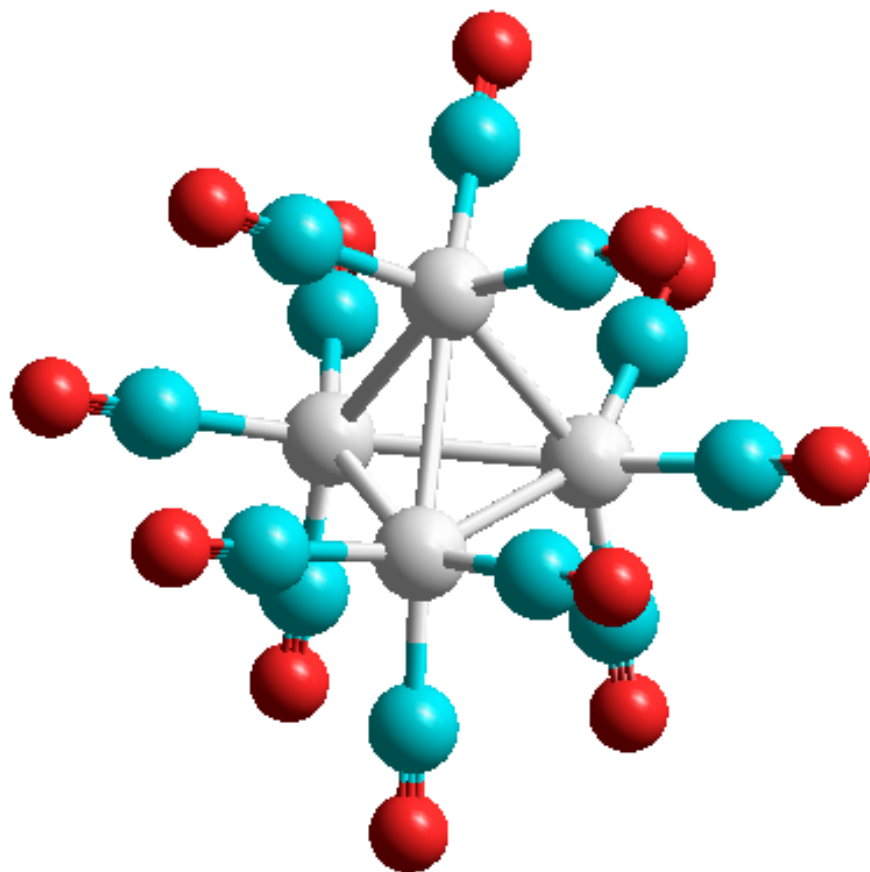
Metal-Metal bonding in Carbonyl complexes

A species such as $[\text{Mn}(\text{CO})_5]$ would have only 17 e. The 18e rule can be obeyed by two such entities forming a Mn-Mn bond, where each Mn contributes one electron to the valence shell of the other Mn, giving the metal-metal bonded species $[(\text{CO})_5\text{Mn}-\text{Mn}(\text{CO})_5]$. To check on the 18e rule, we look at one metal at a time:



Mn(0)	=	d^7
5 C≡O	=	10
Mn-Mn	=	1
<hr/>		
		18 e

Metal carbonyl metal-metal bonded clusters:



Here we see a Rhodium trimer where each Rh forms three Rh-Rh bonds to the other Rh atoms.
18-electron rule: Focus on one Rh atom:

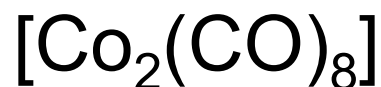
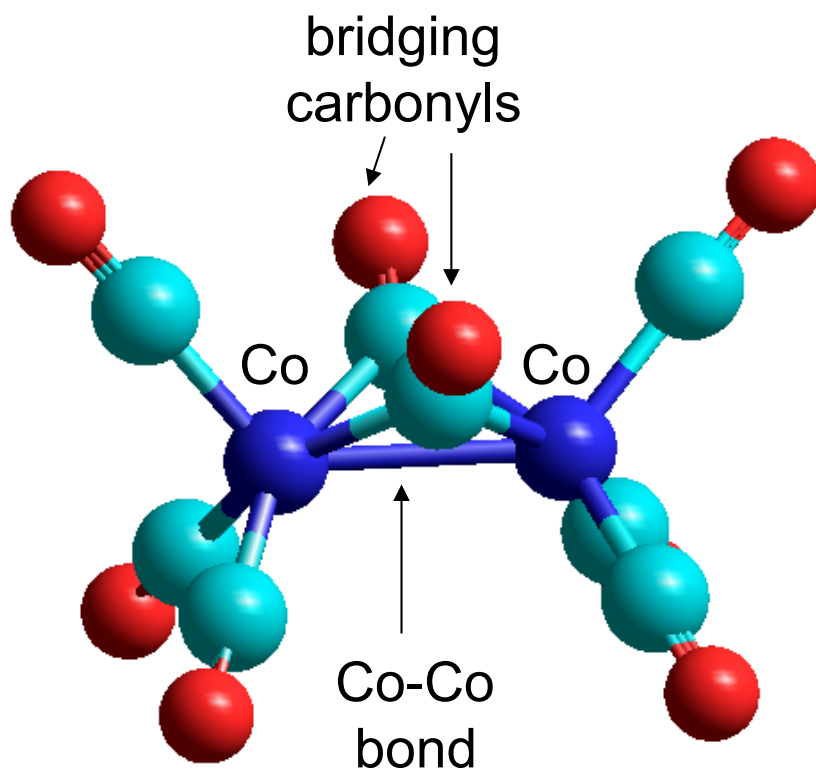
$$\text{Rh}(0) = d^9$$

$$3 \text{ CO per Rh} = 6$$

$$3 \text{ Rh-Rh bonds:} = 3$$

18e

Bridging Carbonyls in carbonyl complexes



Carbonyls may form bridges between two metals, where they donate one electron to each metal in working out the 18 electron rule. In [Co₂(CO)₈] at left each Co has three terminal CO's, two bridging CO's, and a Co-Co bond:

$$\text{Co}(0) = d^9$$

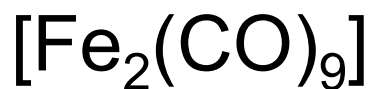
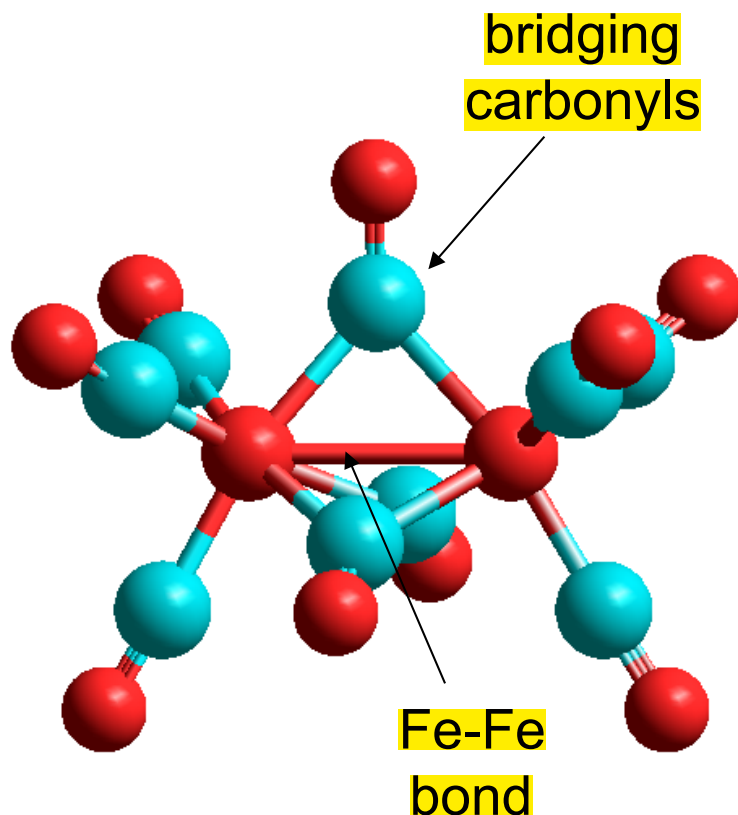
$$3 \text{ CO's} = 6$$

$$2 \text{ bridge CO's} = 2$$

$$\text{Co-Co bond} = 1$$

$$18 e$$

Bridging Carbonyls in $\text{Fe}_2(\text{CO})_9$



$\text{Fe}_2(\text{CO})_9$ has each Fe with three terminal CO's, three bridging CO's, and an Fe-Fe bond. The 18 electron rule holds for each Fe atom as:

Fe(0)	=	d^8
3 CO's	=	6
3 bridge CO's	=	3
Fe-Fe bond	=	1

18 e

Charged ligands and the eighteen-electron rule

The formally charged ligands that are important in organometallic chemistry are mainly soft ligands such as Cl^- , Br^- , and I^- , with CN^- also occurring. Hydride (H^-) is also very important. These mono-anionic ligands all contribute one electron for the 18-electron rule, as in the following examples:



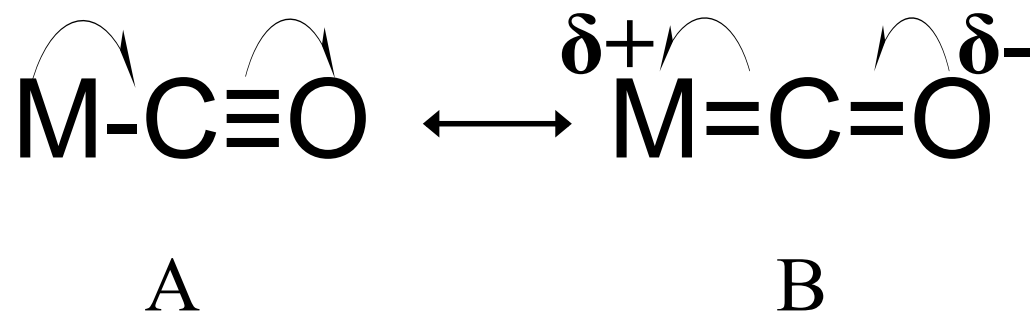
18 e

18 e

18 e

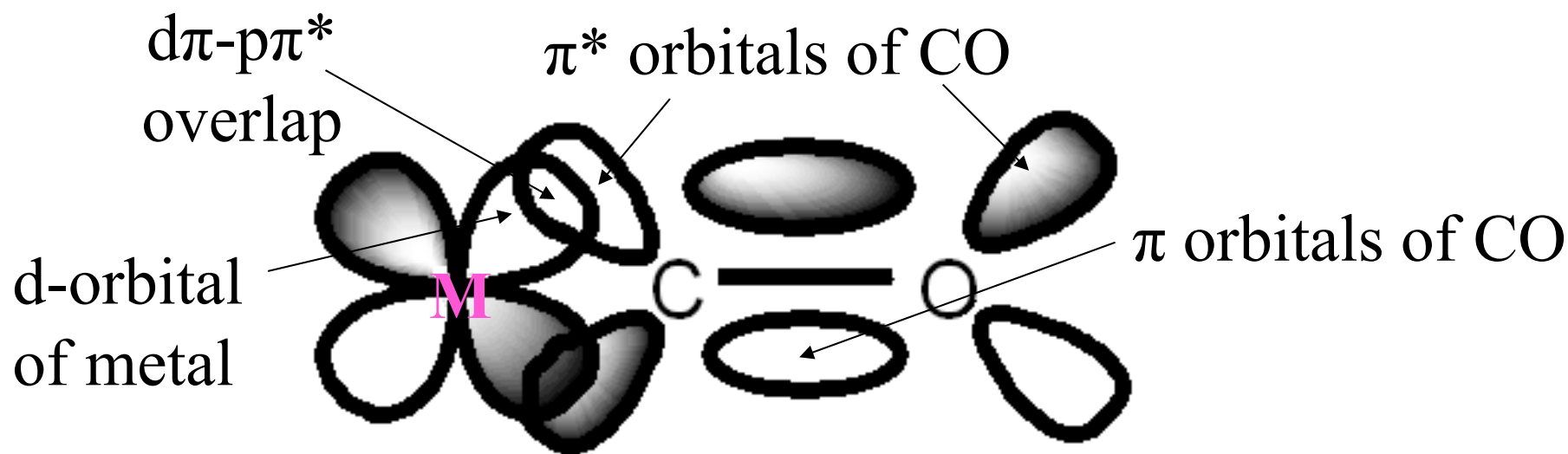
Metal-Carbon bonding in carbonyl complexes

The carbonyl ligand is a π -acid. This is an acid in the Lewis sense, where it receives electrons from the metal ion, and it is a π -acid because this involves π -bonding. The π -bonding involves overlap of the π^* orbitals of the CO with d orbitals from the t_{2g} set of the metal, and so is $d\pi$ - $p\pi$ bonding. The canonical structures involved in the π -acid nature of CO are:



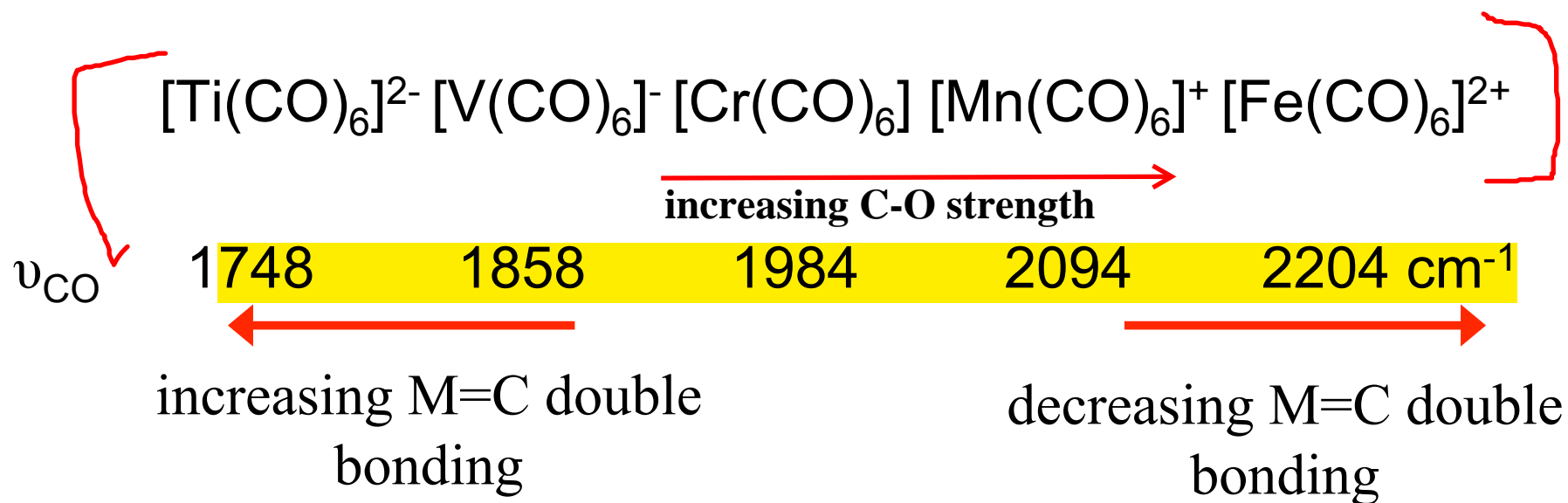
Metal-Carbon bonding in carbonyl complexes

What stabilizes CO complexes is $M \rightarrow C$ π -bonding. The lower the formal charge on the metal ion, the more willing it is to donate electrons to the π -orbitals of the CO. Thus, metal ions with higher formal charges, e.g. Fe(II) form CO complexes with much greater difficulty than do zero-valent metal ions such as Cr(0) and Ni(0), or negatively charged metal ions such as V(-I). The π -overlap is envisaged as involving d-orbitals of the metal and the π^* -orbitals of the CO:



IR spectra and Metal-Carbon bonding in carbonyl complexes

The ν_{CO} stretching frequency of the coordinated CO is very informative as to the nature of the bonding. Recall that the stronger a bond gets, the higher its stretching frequency. Thus, the more important the $\text{M}=\text{C}=\text{O}$ ($\text{C}=\text{O}$ is a double bond) canonical structure, the lower the ν_{CO} stretching frequency as compared to the $\text{M}-\text{C}\equiv\text{O}$ structure ($\text{C}\equiv\text{O}$ is a triple bond): (Note: ν_{CO} for free CO is 2041 cm^{-1})



IR spectra and bridging versus terminal carbonyls

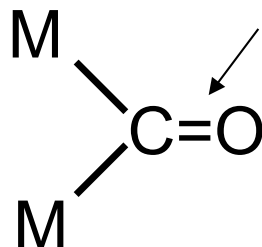
Bridging CO groups can be regarded as having a double bond C=O group, as compared to a terminal C≡O, which is more like a triple bond:

~ triple bond



terminal carbonyl
(~ 1850-2125 cm⁻¹)

~ double bond



bridging carbonyl
(~1700-1860 cm⁻¹)

the C=O group in a bridging carbonyl is more like the C=O in a ketone, which typically has $\nu_{\text{C}=\text{O}} = 1750 \text{ cm}^{-1}$

One can thus use the CO stretching frequencies around 1700-2200 cm⁻¹ to detect the presence of bridging CO groups.

IR spectrum and bridging versus terminal carbonyls in $[\text{Fe}_2(\text{CO})_9]$

