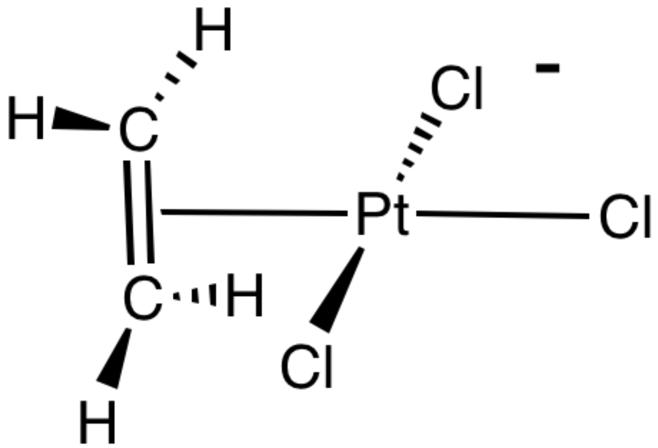
# ORGANOMETALLIC CHEMISTRY

Ch 431

MFT Ch 13

# History of organometallic chemistry: Zeise' salt

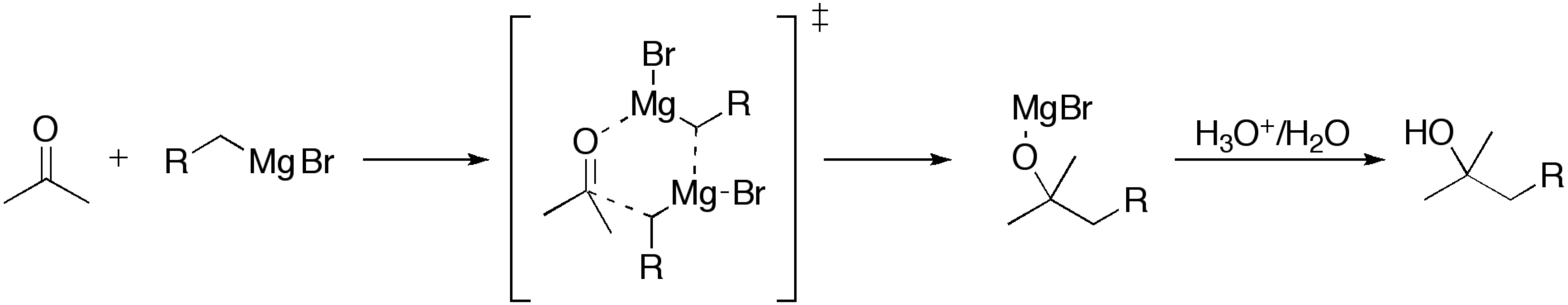
- The first reported organometallic compound: Zeise's salt (1827), structure was not verified until 1868



- This was the first compound identified in which an organic molecule was attached to a metal center through it's pi electrons
- →What do you think the orbital interactions look like in the alkene-metal bond?

# History of organometallic chemistry: Grignard reagents

- Grignard reagents are alkyl-magnesium compounds commonly used in organic synthesis



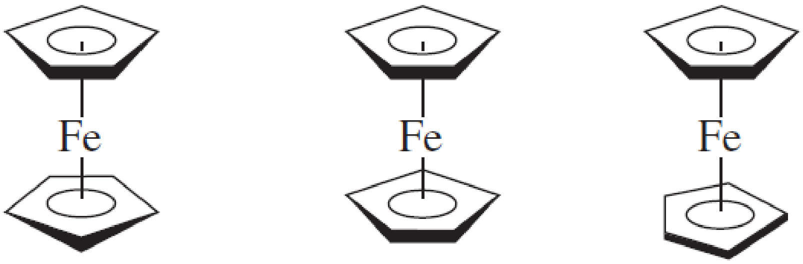
- Grignard reagents contain metal-alkyl sigma bonds
- Similar reagents such as organozinc and organolithium reagents also contain metal-alkyl sigma bonds and are commonly used in organic synthesis

# History of organometallic chemistry: Sandwich complexes

- Ferrocene was synthesized unintentionally during a an attempted synthesis of fulvalene

*cyclo*-$C_5H_5MgBr + FeCl_3 \rightarrow$

ferrocene



$D_{5d}$ Staggered rings

$D_{5h}$ Eclipsed rings

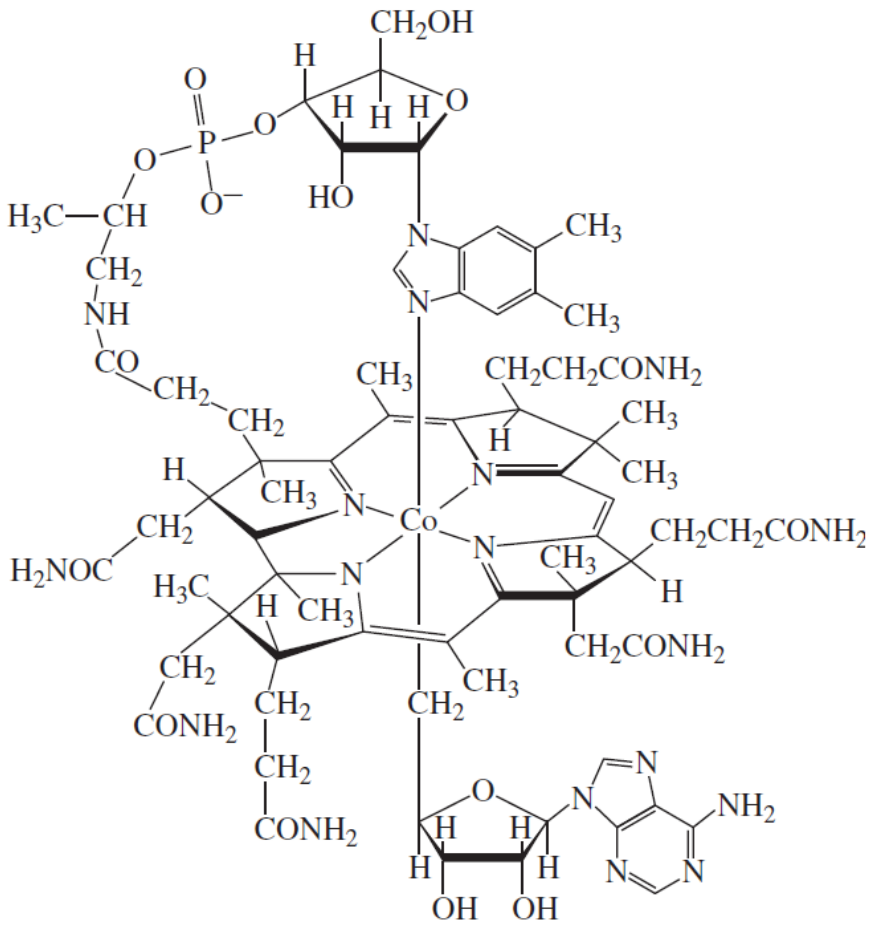
$D_5$ Skew rings

- Now, many other so-called sandwich complexes have been synthesized

# History of organometallic chemistry: Vitamin B12

- Vitamin B12 is the oldest organometallic compound, it is a naturally occurring cobalt-alkyl complex

- This complex is a co-factor in many metalloenzymes and contains a metal-alkyl sigma bond



# Ligands in organometallic chemistry

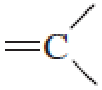
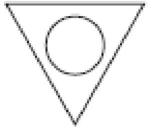
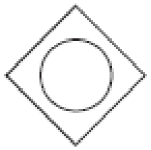
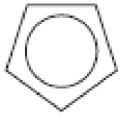
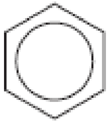
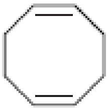
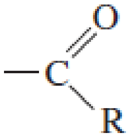
| Ligand | Name |
|---|---|
| CO | Carbonyl |
|  | Carbene (alkylidene) |
| $\equiv C-$ | Carbyne (alkylidyne) |
|  | Cyclopropenyl (*cyclo*-$C_3H_3$) |
|  | Cyclobutadiene (*cyclo*-$C_4H_4$) |
|  | Cyclopentadienyl (*cyclo*-$C_5H_5$) (Cp) |
|  | Benzene |
|  | 1,5-cyclooctadiene (1,5-COD) (1,3-cyclooctadiene complexes are also known) |
| $H_2C{=}CH_2$ | Ethylene |
| $HC{\equiv}CH$ | Acetylene |
|  | $\pi$-Allyl ($C_3H_5$) |
| $-CR_3$ | Alkyl |
|  | Acyl |

**FIGURE 13.7** Classic Organic Ligands.

# The 18 electron rule

- In main group chemistry, we have the octet rule, namely compounds tend to have 8 electrons surrounding each atom to fill their valence shell

- For metal complexes, the valence shell consists of s, p, and d electrons, which gives us 18 total spots for electrons in the valence shell

- Organometallic complexes often follow the 18 electron rule, though just like the octet rule, there are exceptions

# The 18 electron rule: how do we count the electrons?

## **Method A**, donor pair/oxidation state method

1. Determine charges on the ligands (assume all ligands obey octet rule-Lewis structures!, calculate formal charge)
2. Determine charge on the metal center (based on ligand charges and overall charge of complex)
3. Add up electrons from metal ion (d electrons) and ligands (donor pairs)

**TABLE 13.1** Electron Counting Schemes for Common Ligand

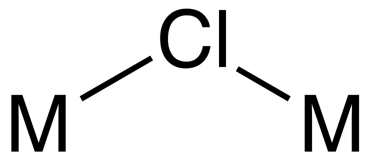
| Ligand | Method A |
|---|---|
| H | 2 ($H^-$) |
| Cl, Br, I | 2 ($X^-$) |
| OH, OR | 2 ($OH^-$, $OR^-$) |
| CN | 2 ($CN^-$) |
| $CH_3$, $CR_3$ | 2 ($CH_3^-$, $CR_3^-$) |
| NO (bent M—N—O) | 2 ($NO^-$) |
| NO (linear M—N—O) | 2 ($NO^+$) |
| CO, $PR_3$ | 2 |
| $NH_3$, $H_2O$ | 2 |
| $=CRR'$ (Carbene) | 2 |
| $H_2C=CH_2$ (Ethylene) | 2 |
| CNR | 2 |
| $=O$, $=S$ | 4 ($O^{2-}$, $S^{2-}$) |
| $\eta^3$-$C_3H_5$ ($\pi$-allyl) | 4 ($C_3H_5^-$) |
| $\equiv CR$ (Carbyne) | 3 |
| $\equiv N$ | 6 ($N^{3-}$) |
| Ethylenediamine (en) | 4 (2 per nitrogen) |
| Bipyridine (bipy) | 4 (2 per nitrogen) |
| Butadiene | 4 |
| $\eta^5$-$C_5H_5$ (Cyclopentadienyl) | 6 ($C_5H_5^-$) |
| $\eta^6$-$C_6H_6$ (Benzene) | 6 |
| $\eta^7$-$C_7H_7$ (Cycloheptatrienyl) | 6 ($C_7H_7^+$) |

# Ligand types

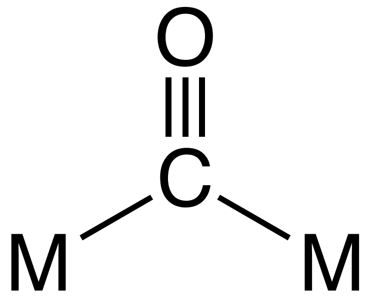
- X-type: monoanionic donors (H-, Cl-, Br-, etc): 2 electron donors
- L-type: neutral donors ($NH_3$, $H_2O$, $PR_3$, etc): 2 electron donors
- For ligands interacting with metal with pi electrons, consider how many pi electrons are interacting with metal (eg, cyclopentadienyl, Cp-)

# Bridging ligands

- For bridging ligands like a Cl- (has multiple lone pairs), Cl- donates 2 electrons to each metal center



- However, for a bridging CO ligand, there is still only one lone pair on the carbon atom, that pair of electrons is shared between the two metals, so CO is a one electron donor to each metal when it is a bridging ligand



# Complexes with M-M bonds

- For counting electrons in complexes containing M-M bonds, split the electrons up evenly between two metal centers

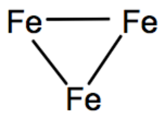
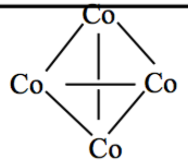
| | |
|---|---|
| M—M | 1 electron goes to each metal |
| M=M | 2 electrons go to each metal |
| M≡M | 3 electrons go to each metal |

- You can also predict the multiplicity of a M-M bond based off of electron counting

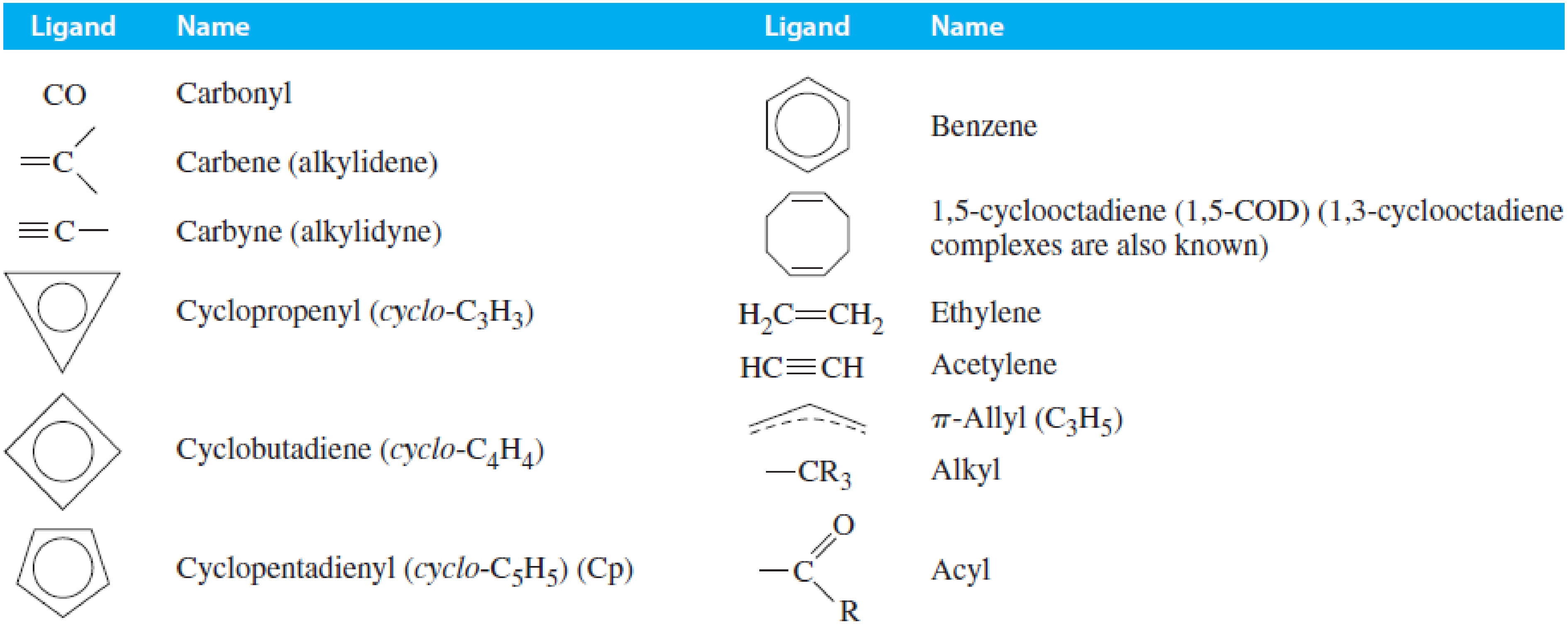
# Using 18 electron rule to predict number of metal-metal bonds

1. Determine total valence electrons (TVE) in entire molecule (number of valence electrons of metal plus the number of electrons from each ligand) say, it is **A**
2. Subtract **A** from ***n*** **× 18** where ***n*** is the number of metals in the complex, that is, **(*n* × 18) – A**; say, it is **B**
3. **B** divided by 2 gives the total number of M–M bonds in the complex
4. **A** divided by **n** gives the number of electrons per metal. If the number of electrons is 18, it indicates that there is no M–M bond; if it is 17 electrons, it indicates that there is 1 M–M bond; if it is 16 electrons, it indicates that there are 2 M–M bonds and so on.

# Examples

| Molecule | TVE (*A*) | (18 × *n*) – *A* (*B*) | Total M–M bonds (*B*/2) | Bonds per metal | Basic geometry of metal atoms |
|---|---|---|---|---|---|
| $Fe_3(CO)_{12}$ | 48 | 54 – 48 = 6 | 6/2 = 3 | 48/3 = 16; 2 |  |
| $Co_4(CO)_{12}$ | 60 | 72 – 60 = 12 | 12/2 = 6 | 60/4 = 15; 3 |  |
| $[\eta^5\text{-}CpMo(CO)_2]_2$ | 30 | 36 – 30 = 6 | 6/2 = 3 | 30/2 = 15; 3 | Mo≡Mo |
| $(\eta^4\text{-}C_4H_4)_2Fe_2(CO)_3$ | 30 | 36 – 30 = 6 | 6/2 = 3 | 30/2 = 15; 3 | Fe≡Fe |
| $Fe_2(CO)_9$ | 34 | 36 – 34 = 2 | 2/2 = 1 | 34/2 = 16; 1 | Fe–Fe |

# Ligands in organometallic chemistry

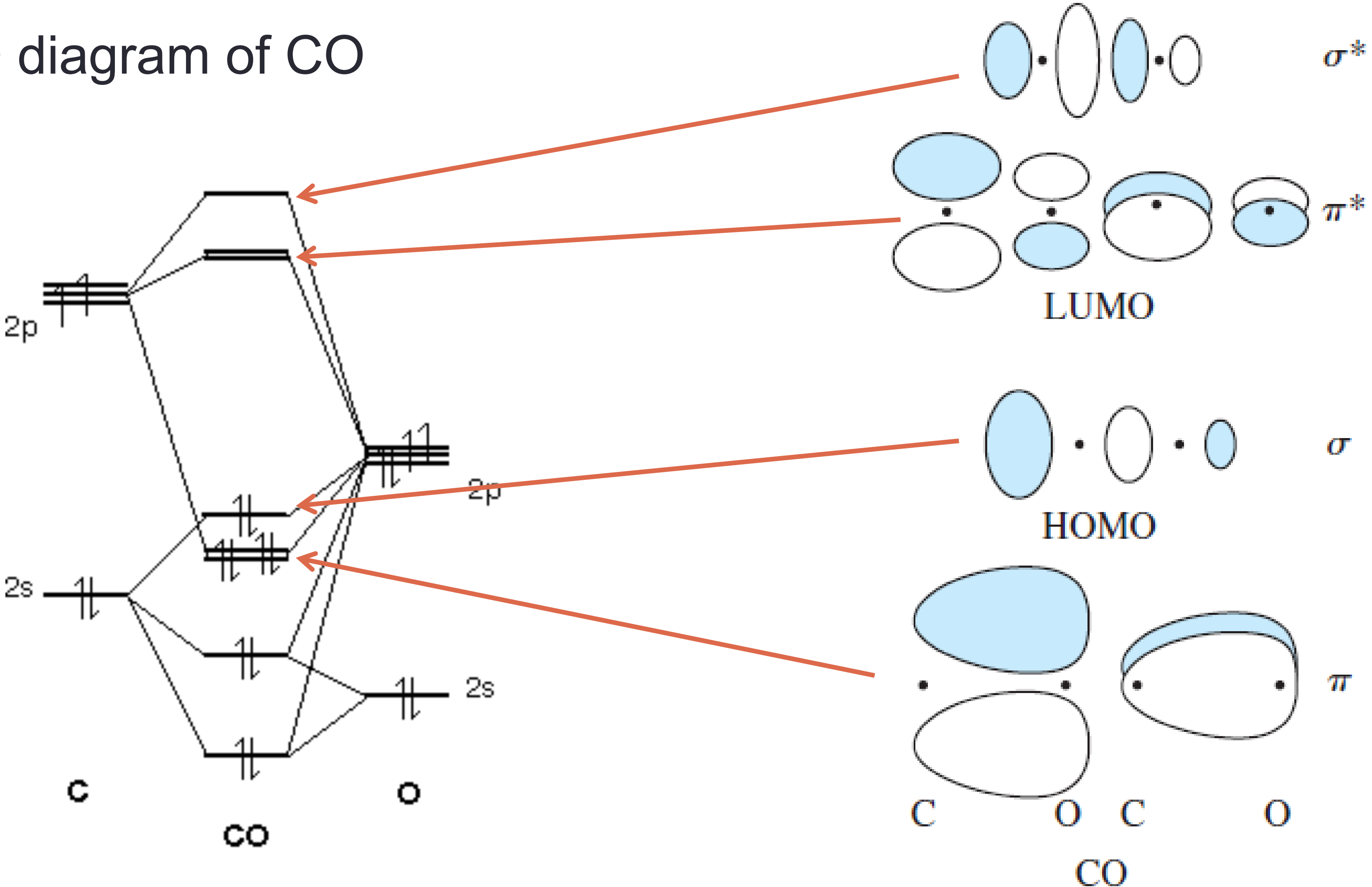


| Ligand | Name | Ligand | Name |
|---|---|---|---|
| CO | Carbonyl |  | Benzene |
|  | Carbene (alkylidene) |  | 1,5-cyclooctadiene (1,5-COD) (1,3-cyclooctadiene complexes are also known) |
| $\equiv C-$ | Carbyne (alkylidyne) | $H_2C=CH_2$ | Ethylene |
|  | Cyclopropenyl (*cyclo*-$C_3H_3$) | $HC\equiv CH$ | Acetylene |
|  | Cyclobutadiene (*cyclo*-$C_4H_4$) |  | $\pi$-Allyl ($C_3H_5$) |
|  | Cyclopentadienyl (*cyclo*-$C_5H_5$) (Cp) | $-CR_3$ | Alkyl |
|  |  |  | Acyl |

**FIGURE 13.7** Classic Organic Ligands.

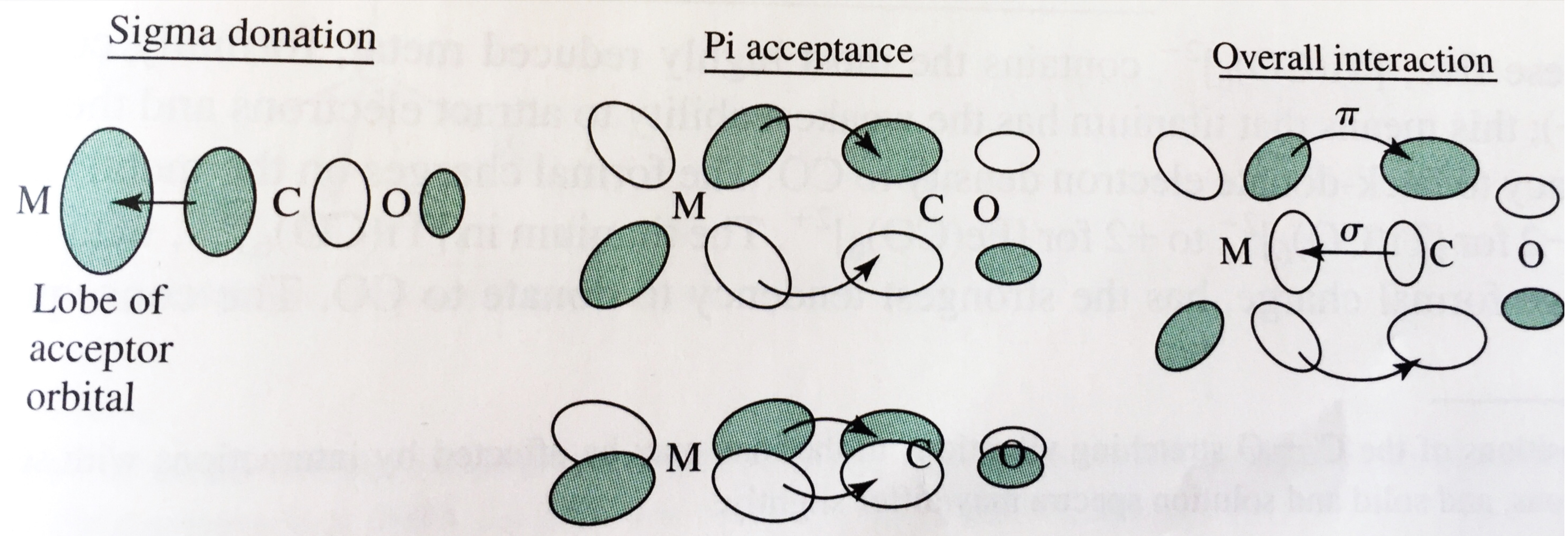
# Carbonyl (CO) complexes (most common organometallic ligand)

MO diagram of CO



See MFT Figure 5.2 and 5.13 for review

# CO interactions with a metal center



Covered previously with crystal field theory and spectrochemical series

# CO interactions with a metal center

- Combination of sigma bonding and pi backbonding between CO and M results in strong bond
- Synergistic effect:
  - CO can donate electron density via a sigma orbital to a metal
  - Metal with more electron density can backbond to a greater extent
- Actual strength of bonding depends on several factors
  - Charge on complex
  - Ligand environment of metal
  - …

# Experimental evidence for differences in M-CO interactions

- Sigma bond between CO and M takes electron density away from CO bond
- $\pi$ backbonding donates electron density into $\pi^*$ anti-bonding orbitals of CO

→Both interactions will weaken the CO bond: this results in lower IR stretching energy and longer CO bond

- Example: free CO vs. $Cr(CO)_6$

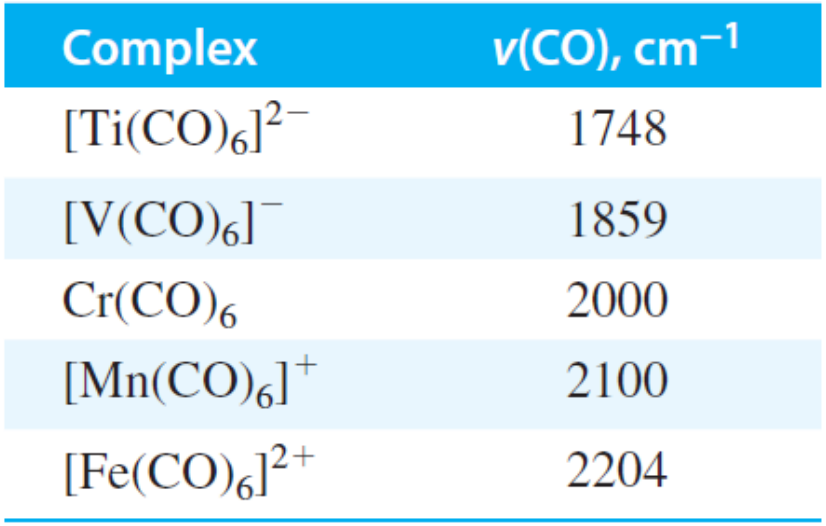
| | **CO stretching frequency (IR)** | **C-O bond distance** |
|---|---|---|
| Free CO | 2143 $cm^{-1}$ | 112.8 pm |
| $Cr(CO)_6$ | 2000 $cm^{-1}$ | ~115 pm |

→Smaller $cm^{-1}$ = lower energy = weaker bond

→Longer bond = lower bond order = weaker bond

# Comparing CO stretching frequencies in different metal complexes

- Free CO: 2143 $cm^{-1}$

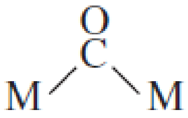
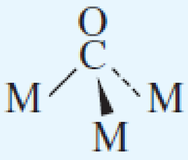
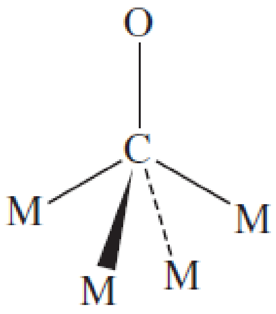


| Complex | ν(CO), $cm^{-1}$ |
|---|---|
| $[Ti(CO)_6]^{2-}$ | 1748 |
| $[V(CO)_6]^{-}$ | 1859 |
| $Cr(CO)_6$ | 2000 |
| $[Mn(CO)_6]^{+}$ | 2100 |
| $[Fe(CO)_6]^{2+}$ | 2204 |

- What is the difference between the metal centers in these complexes?

# CO as a bridging ligand

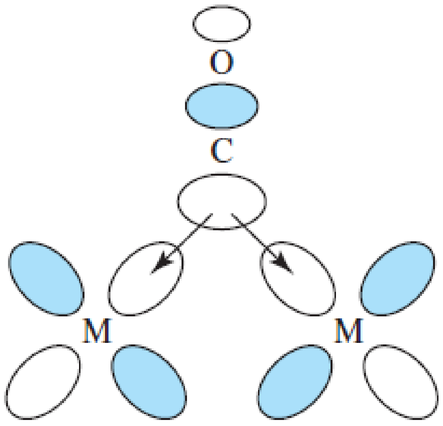
**TABLE 13.2 Bridging Modes of CO**

| Type of CO | Approximate Range for $\nu$(CO) in Neutral Complexes ($cm^{-1}$) |
|---|---|
| Free CO | 2143 |
| Terminal M — CO | 1850–2120 |
| Symmetric[a] $\mu_2$ — CO  | 1700–1860 |
| Symmetric[a] $\mu_3$ — CO  | 1600–1700 |
| $\mu_4$ — CO  | < 1700 (few examples) |

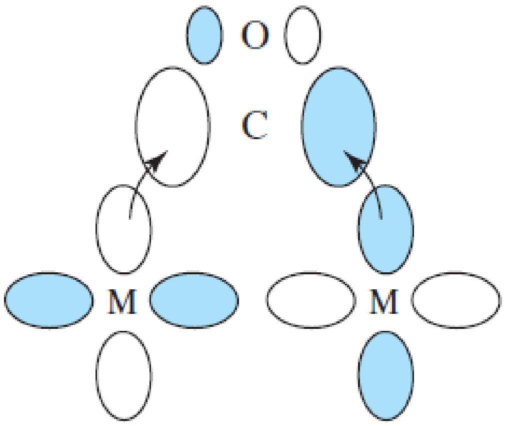
[a] Asymmetrically bridging $\mu_2$- and $\mu_3$-CO are also known.

# CO as a bridging ligand

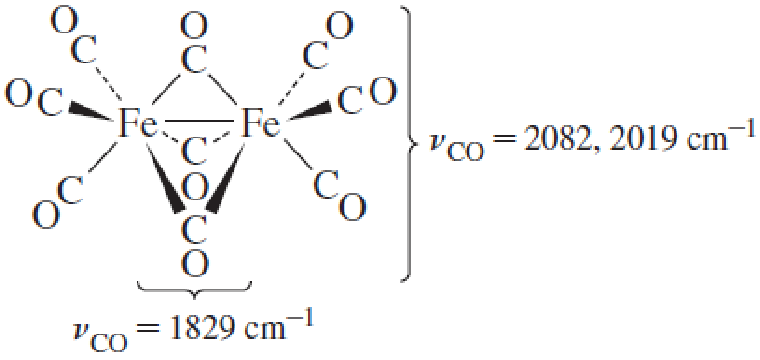
- CO still acts as both a sigma donor and pi acceptor as a bridging ligand



$\sigma$ Donor



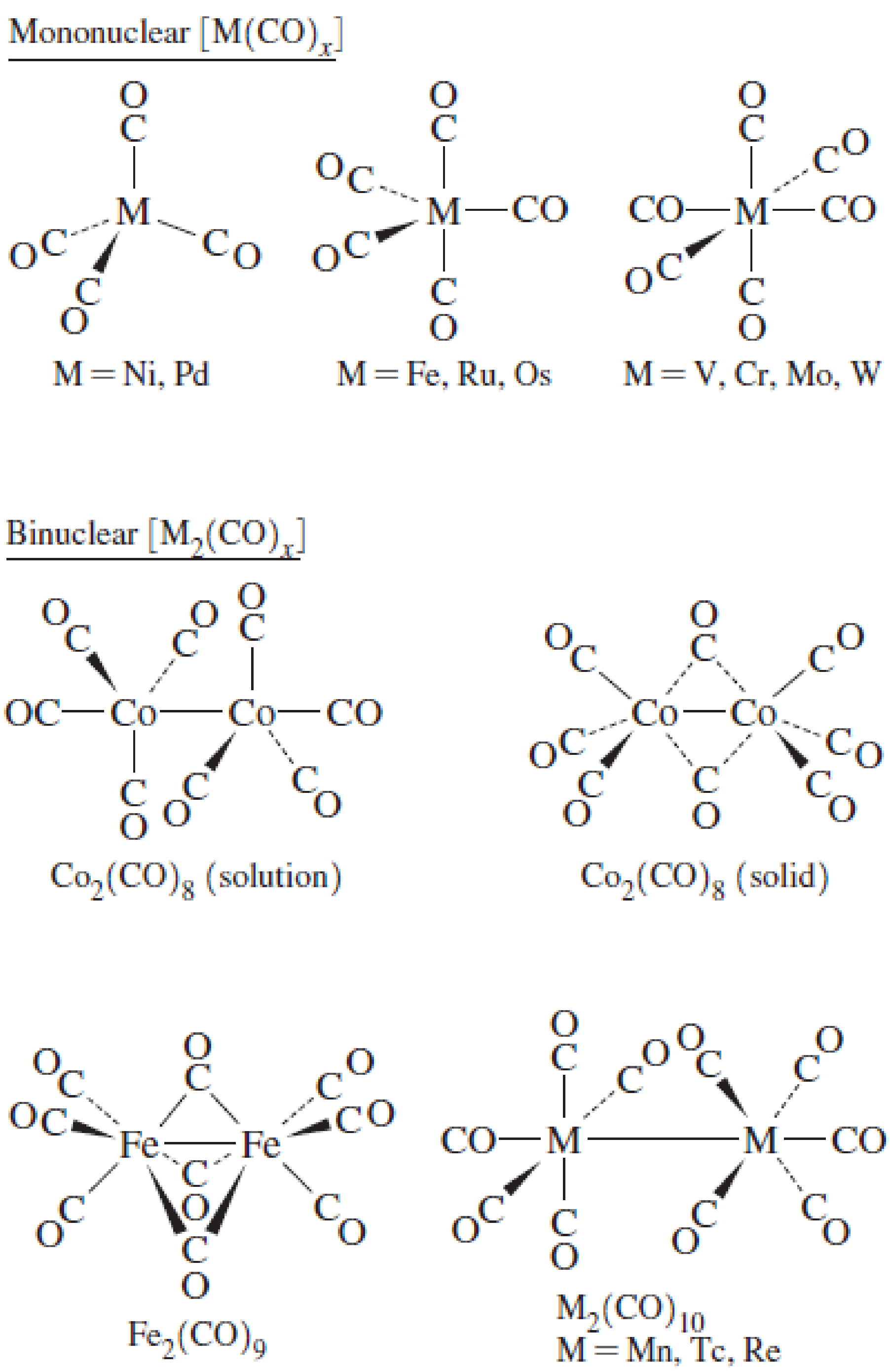
$\pi$ Acceptor



## Take home question:

Metal complexes with pi acceptor ligands such as CO typically follow the 18 electron rule.

In these binary metal carbonyl complexes (they are called this because they are only made up of a metal atom and CO ligands), there are a few examples that do NOT follow 18 electron rule- can you find them?



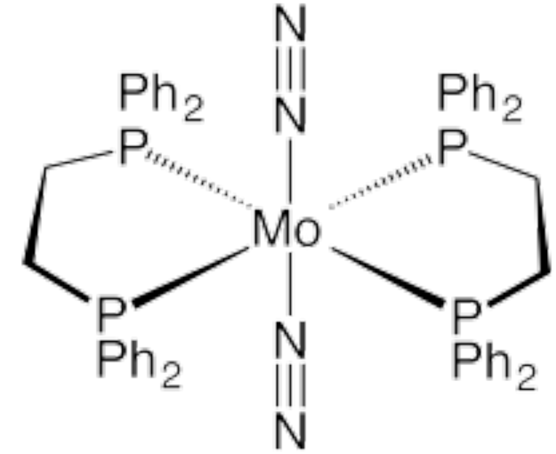
# Ligands similar to CO

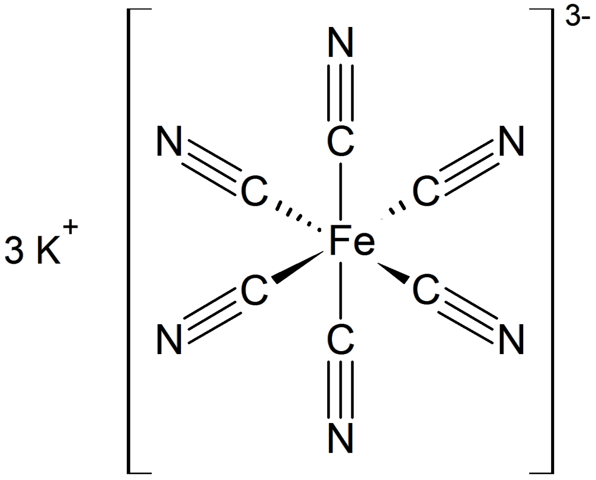
- $CN^-$, $N_2$ are isoelectronic with CO, have similar sigma bonding and pi backbonding interactions

*What are the electron counts of the following metal complexes?

*Draw the orbital interactions between CN-/$N_2$ and the metal centers.

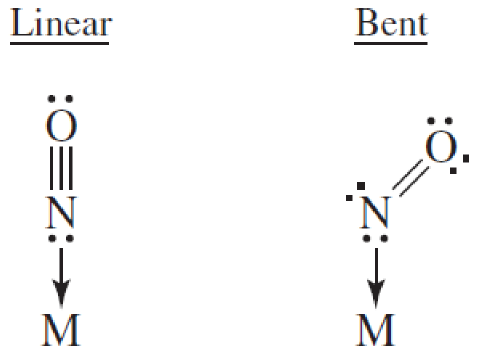
*Compare the $N_2$ bond length and IR stretching frequency between a bridging $N_2$ and a terminal $N_2$





# Ligands similar to CO

- NO: this is a special case. NO has two binding modes, linear and bent:



| | Linear | Bent |
|---|---|---|
| M—N—O angle | 165°–180° | 119°–140° |
| $\nu$ (N-O) in neutral molecules | 1610–1830 $\text{cm}^{-1}$ | 1520–1720 $\text{cm}^{-1}$ |
| Electron donor count | 2 (as $NO^+$)<br>3 (as neutral NO) | 2 (as $NO^-$)<br>1 (as neutral NO) |

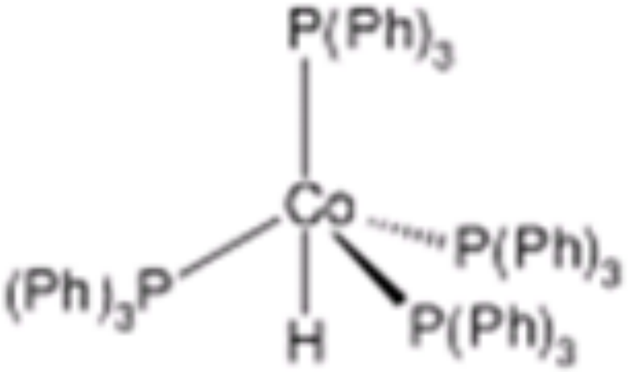
- In linear case, NO behaves like $NO^+$: this is isoelectronic with CO (compare Lewis structures), N is sp hybridized
- In bent case, NO is acting like $NO^-$, in this Lewis structure (draw this to convince yourself!), N is $sp^2$ hybridized, forcing a bent configuration
- For either case, Donor Pair electron counting method counts the ligand as a <u>2 electron donor</u>

# Other common ligands in organometallic complexes

# Hydride ligand, $H^-$

- What orbital(s) does $H^-$ have available for bonding with a metal center?

- What kind of bonding interaction(s) will you observe between a transition metal and a hydride? (sigma? pi bonding? pi backbonding?)



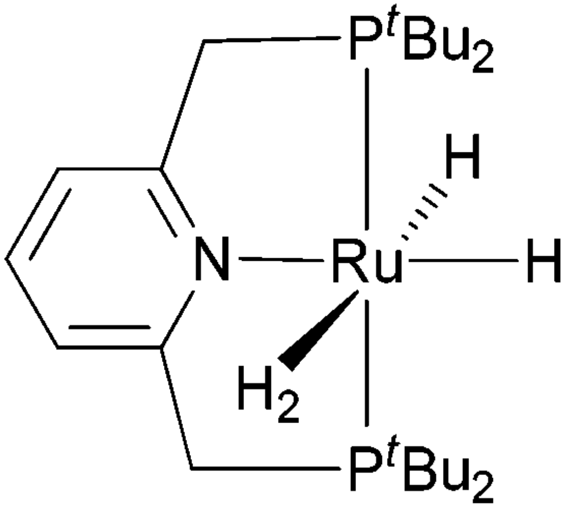
H- is a 2 electron donor

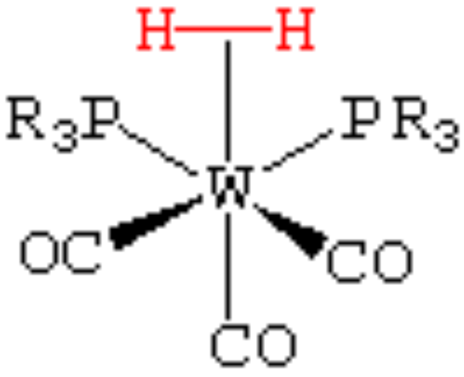
# Dihydrogen ligand, $H_2$

- What orbital(s) does $H_2$ have available for bonding with a metal center?

- What kind of bonding interaction(s) will you observe between a transition metal and $H_2$? (sigma? pi bonding? pi backbonding?)

$H_2$ is a 2 electron donor



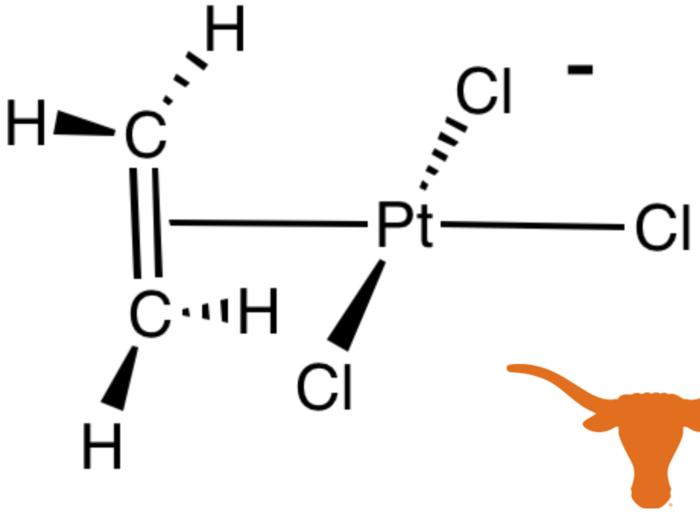


# Ligands with pi systems

- In organometallic chemistry, you will often observe complexes between a metal center and the pi electrons of an alkene, an extended pi system (multiple double bonds), an aromatic system (Cp, benzene)

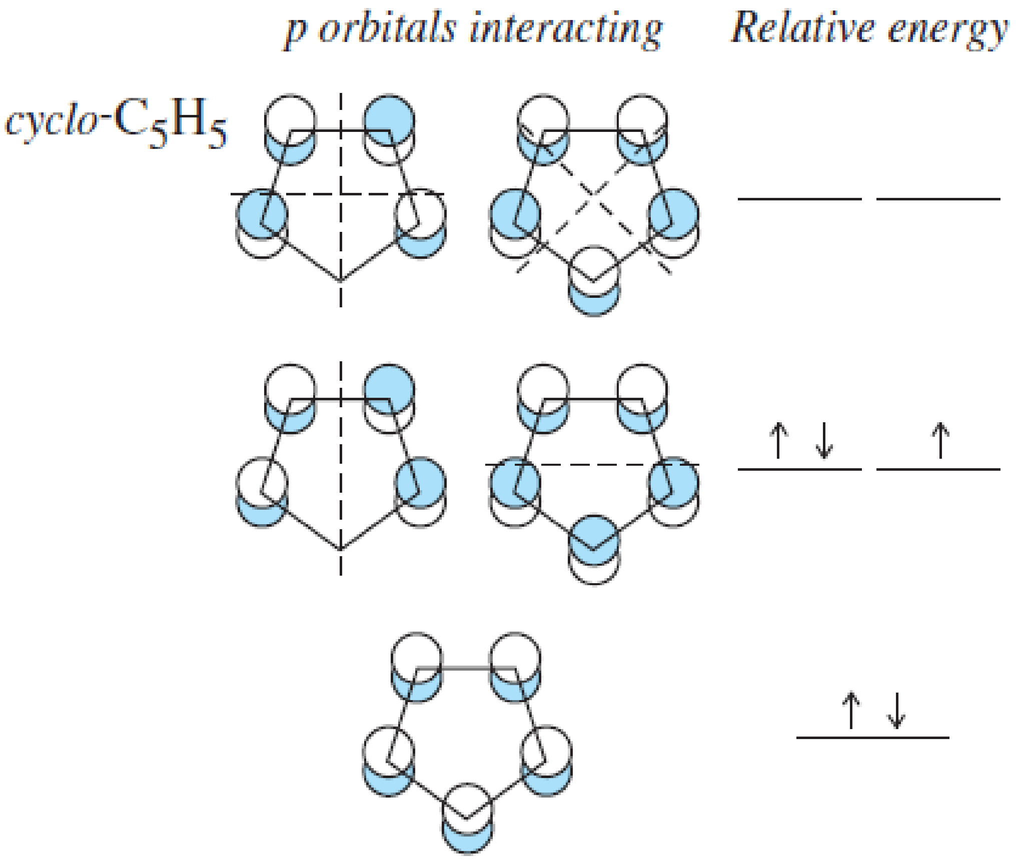
# Ethlyene

- Ethylene typically interacts with metals in a side-on fashion, with the metal-ligand bond forming in between the two carbon atoms.
- This binding mode is a good indication that bond involves the pi electrons of ethylene
- Ethylene uses its pi bonding orbital for sigma interaction with metal and its pi* antibonding orbital for pi backbonding with metal

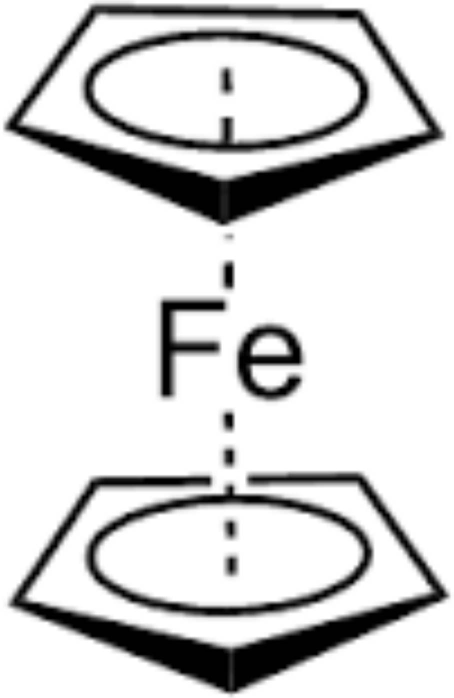


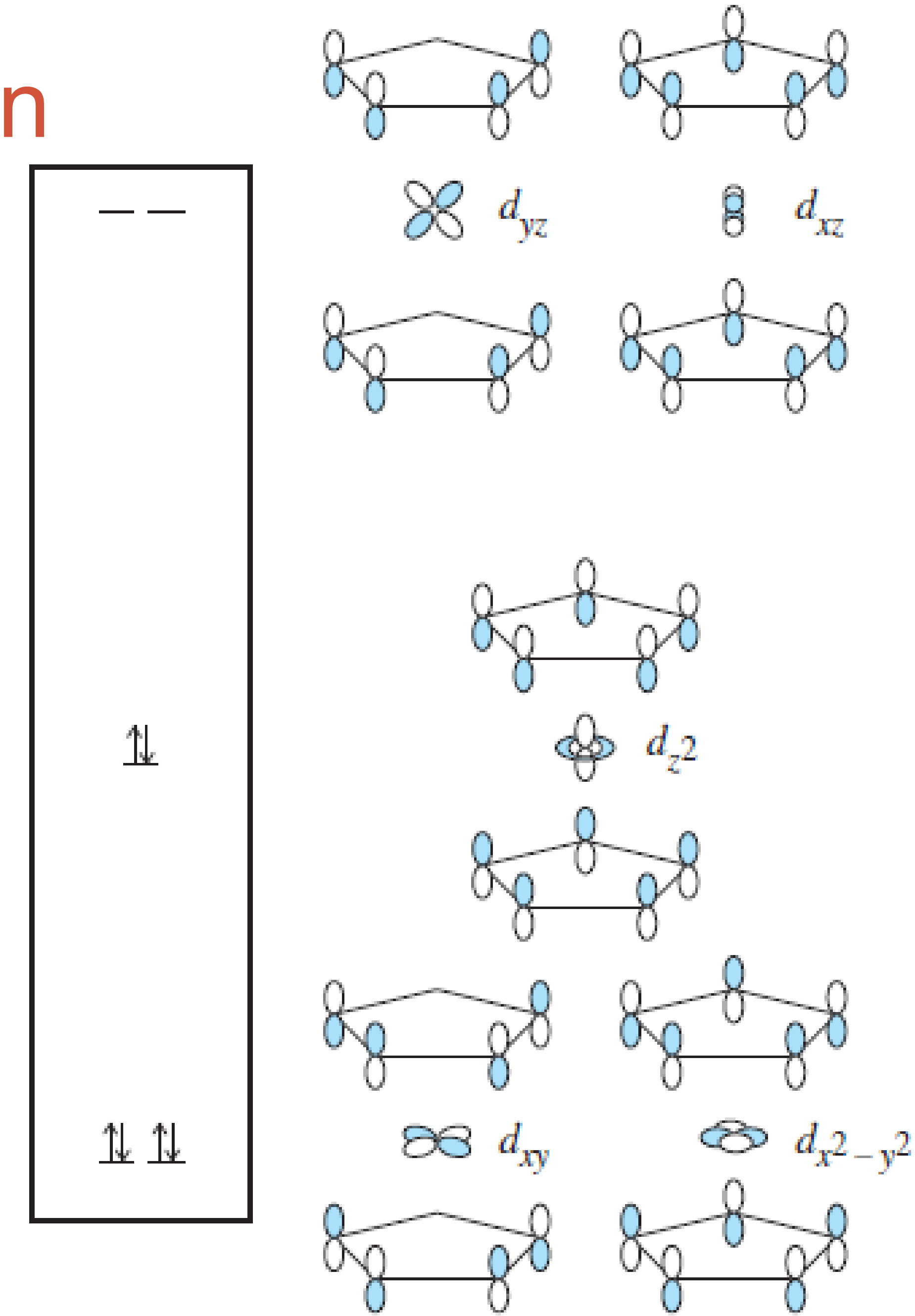
# Cycolpentadienyl (Cp)

- Cp also interacts with metals using its pi system
- Orbitals used for bonding with metal are depicted or right (these will be provided for an exam question if they are needed)
- Based on these orbitals, and the geometry of a complex, can you figure out what metal d orbitals interact with what Cp orbitals?



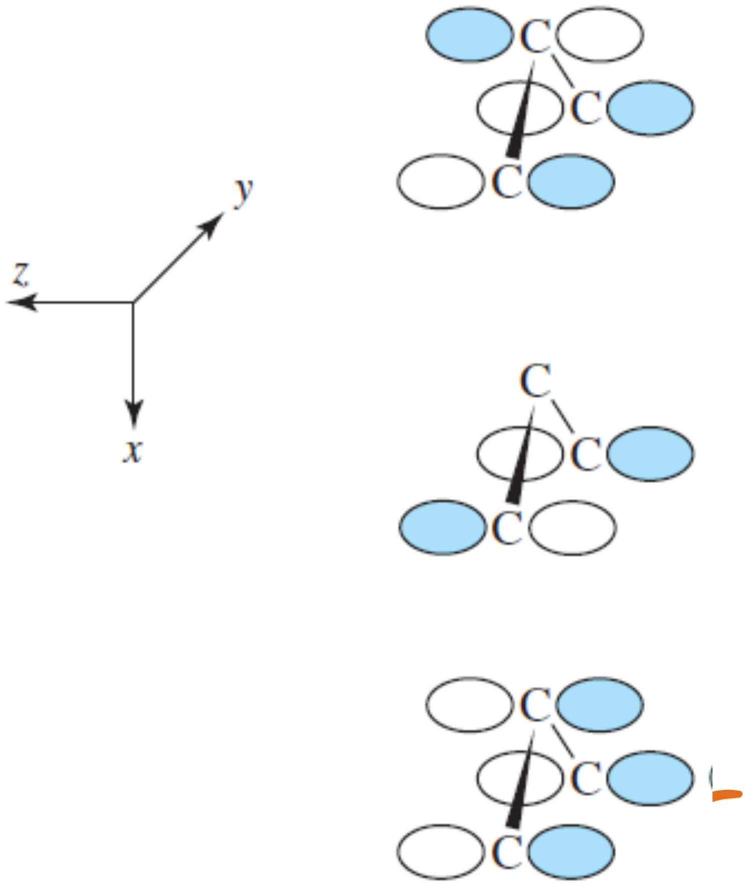
# Orbital interactions in ferrocene: $FeCp_2$





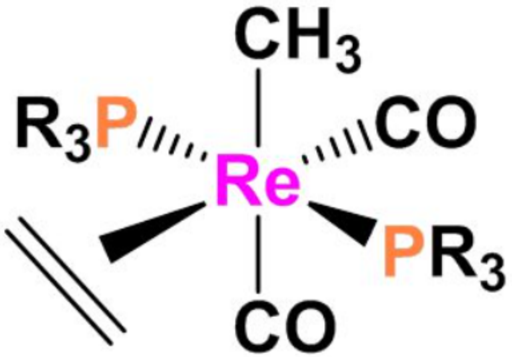
# Example question:

- The picture on the top right depicts the interactions between nickel and an allyl anion ($C_3H_5^-$)
- The allyl orbitals involved in bonding are depicted on the bottom right. Given the depicted coordinate axes, what metal d orbitals have the right symmetry to interact with the allyl orbitals in this complex? What metal s or p orbitals?

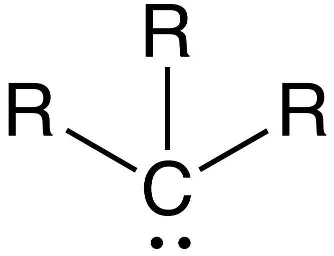


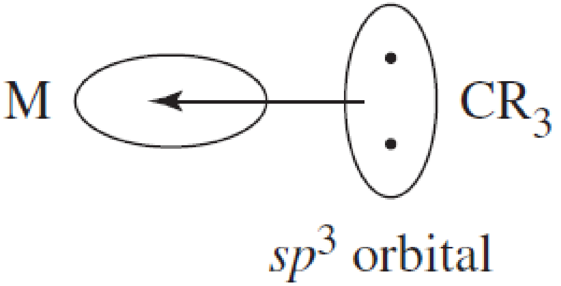
# Metal-alkyls M-$CR_3$

- Metal alkyl complexes contain a metal-carbon single bond
- Alkyl ligand can be thought of as :$CR_3^-$



- Much like $H^-$ (hydride), alkyl ligands are 2-electron donors and interact with metals in a sigma fashion
- This is similar to how $\eta^1$-Cp and $\eta^1$-benzene ligands interact with metal centers



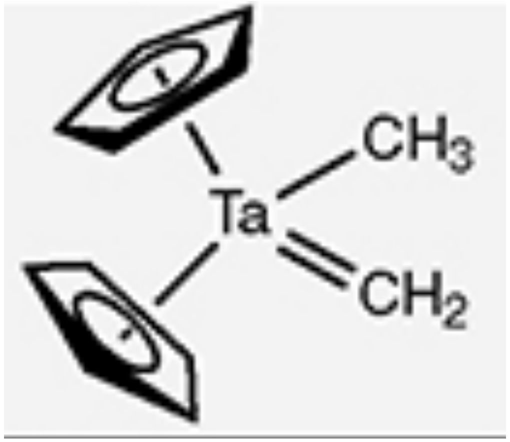


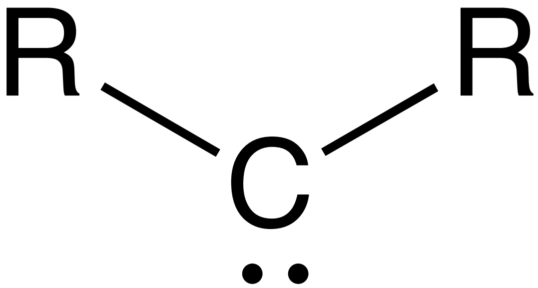
(R=H, alkyl, aryl)

# Metal-carbenes $M{=}CR_2$

- Metal-carbene complexes contain a metal carbon double bond $M{=}CR_2$

- For electron counting purposes, we consider the $CR_2$ ligand to be a two electron donor because carbenes actually have only one lone pair, their structures are $:CR_2$

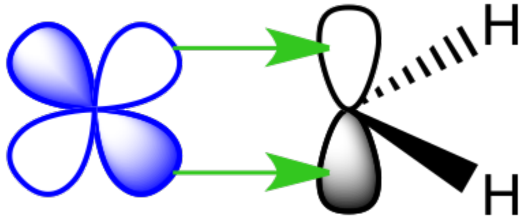




# Metal-carbenes $M{=}CR_2$

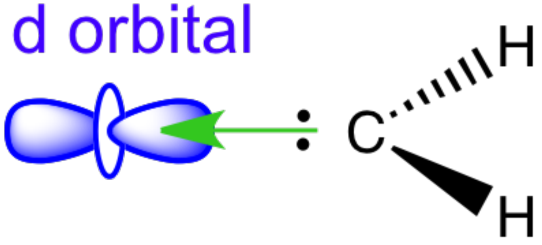
- This lone pair is used for sigma bonding with metal

- The second bond comes from interactions between a metal d orbital and an empty p orbital on the carbene



Metal d orbital

Empty Carbon p orbital

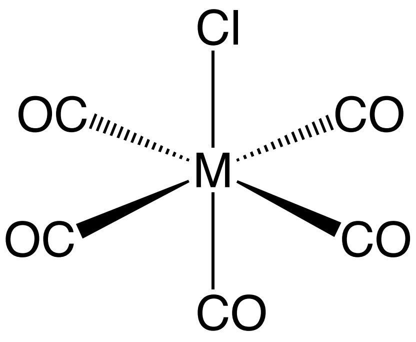


Vacant Metal d orbital

Carbon lone pair

# Throwback to symmetry

- Now that we know more about organometallic complexes, we can look at a complex, understand aspects of its bonding, and predict its spectroscopic properties (i.e. number of IR stretches!)
- We can also use symmetry concepts to predict how many NMR peaks an organometallic complex might have



How many different CO stretches would you expect this complex to have? (Make reducible representation)

How many different $^{13}$C NMR peaks will this complex have? (How many different CO ligands are there?)