18- Electron Rule.

Recall that for MAIN GROUP elements the **octet rule** is used to predict the formulae of covalent compounds.

This rule assumes that the central atom in a compound will make bonds such that the total number of electrons around the central atom is **8**. **THIS IS THE MAXIMUM CAPACITY OF THE s and p orbitals.**

This rule is only valid for Period 2 nonmetallic elements.

The **18-electron Rule** is based on a similar concept.

The central TM can accommodate electrons in the s, p, and d orbitals.

s (2) , p (6) , and d (10) = maximum of 18

This means that a TM can add electrons from Lewis Bases (or ligands) in addition to its valence electrons to a total of 18.

This is also known Effective Atomic Number (EAN) Rule

Note that it only applies to metals with low oxidation states.

18 Electron Rule cont'd

Example 1.

$[Co(NH_3)_6]^{+3}$

Oxidation state of Co?
Electron configuration of Co?
Electrons from Ligands?
Electrons from Co?
Total electrons?

Example 2.

$[Fe(CO)_5]$

Oxidation state of Fe?
Electron configuration of Fe?
Electrons from Ligands?
Electrons from Fe?
Total electrons?

What can the EAN rule tell us about **$[Fe(CO)_5]$**?

It can't occur…… 20-electron complex.

EAN Summary

1. Works well only for d-block metals. It does not apply to f-block metals.

2. Works best for compounds with TMs of low ox. state.

3. Ligands which are good σ-donors and π-acceptors utilize all the valence orbitals and thus such compounds obey this rule.

4. Complexes which contain a combination of σ-donors and π-acceptors conform to this rule. (e.g. $Cr(NH_3)_3(CO)_3$, $Cr(\eta^6\text{-}C_6H_6)(CO)_3$).

5. Compounds which obey this rule are kinetically inert to substitution reactions.

6. Exceptions to the rule occur at the two ends of the transition series where *nd, (n+1)s, and (n+1)p* valence orbitals are less well matched in energy.

Let's talk about electron counting briefly.

Sandwich Compounds Obeying EAN

Let's draw some structures and see some new ligands.

Each of these ligands is π-bonded above and below the metal center.

Ferrocene is an interesting example.

Half-Sandwich Compounds Obeying EAN

Let's draw some more structures.

CO, NO, H, and PR_3 can be brought together in combination to give 18 electrons.

Some other cool ligands.

These cyclic ligands need not be planar.

Here are some examples of compounds of cyclooctatetraene.

Can a reaction involve only compounds which obey the 18 electron rule?

YES.

Compounds and the EAN Rule

We can divide compounds into three groups.

1. Electronic configurations are completely unrelated to the EAN rule. The central metal may have >, <, = 18 electrons.

2. Electron configurations follow the EAN rule and never have >18 electrons, but may have less.

3. A group that follows EAN rule rigorously.

How can we understand this?

Chemistry and "Magic Numbers"

The Octet Rule: **Period 2 nonmetallic elements tend to form compounds resulting in eight electrons around the central atom. You have been told this is because elements desire a pseudo-noble gas configuration.**

This is a VAST simplification.

Stable Fullerenes: **The allotrope of Carbon known as fullerenes (C_{60} or "Bucky-ball" is the most famous) take on a cage structure and it has been observed that particular numbers of C atoms yield more stable compounds.**

$$C_{60}, C_{70}, C_{76}, C_{84}, C_{90}, C_{94}$$

Nanoparticles: **Metal Nanoparticle are really COOL! It has been observed that "magic numbers" of atoms preferentially come together to form stable structures.**

Bonding in TM Complexes: **Many TM complexes will form with 18 electrons around the central metal atom. It was first observed by Sedgwick in 1927.**

18- Electron Rule.

Recall that for MAIN GROUP elements the **octet rule** is used to predict the formulae of covalent compounds.

Think about Na^+ and Cl^-

This rule assumes that the central atom in a compound will make bonds such that the total number of electrons around the central atom is **8**.

THIS IS THE MAXIMUM CAPACITY OF THE s and p orbitals.

This rule is only valid for Period 2 nonmetallic elements.

The **18-electron Rule** is based on a similar concept.

The central TM can accommodate electrons in the s, p, and d orbitals.

s (2) , p (6) , and d (10) = maximum of 18

This means that a TM can add electrons from Lewis Bases (or ligands) in addition to its valence electrons to a total of 18.

This is also known Effective Atomic Number (EAN) Rule

Simple Examples of the 18 Electron Rule

Example 1.

$[Co(NH_3)_6]^{+3}$

Oxidation state of Co?
Electron configuration of Co?
Electrons from Ligands?
Electrons from Co?
Total electrons?

Example 2.

$[Fe(CO)_5]$

Oxidation state of Fe?
Electron configuration of Fe?
Electrons from Ligands?
Electrons from Fe?
Total electrons?

What can the EAN rule tell us about **$[Fe(CO)_5]$**?

It can't occur…… 20-electron complex.

Approach 1 to counting

Oxidation State Electron Count. Ligands are viewed as "close-shelled" entities. (No radicals). **This is what we did in the earlier examples.**

We dissect the structure

When neutral Lewis base ligands (like NH_3) are considered they are viewed as neutral molecules with 2 electrons for donation to the metal.

Ligands like methyl (CH_3 and Cl) are viewed as anions….**NOT AS NEUTRAL RADICALS. (By definition H is viewed as H^-)**

After removal of the ligands the metal is assigned a formal charge.

$[Ni(CO)_4]$	**Ni^0 10 e^-, CO 2 e^- each (8) = 18**
$[PtCl_2(PMe_3)_2]$	**Pt^{2+} 8 e^-, Cl^- 2 e^- each (4), PMe_3 2 e^- each (4) = 16**
$[Ta(Me)_5]$	**Ta^{5+} 0 e^-, Me^- 2 e^- each (10) = 10**
$Fe(\eta^{5}\text{-}C_5H_5)_2$	**Fe^2 6 e^-, $\eta^{5}\text{-}C_5H_5$ 6e^- each (12) = 18 Ferrocene**

Approach 2 to counting

Neutral Atom Counting.

The general premise to this approach is:

REMOVE ALL THE LIGANDS FROM THE METAL AS NEUTRAL SPECIES.

This approach results in no difference for neutral ligands like NH_3 or CO.

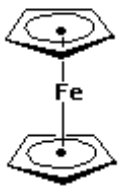
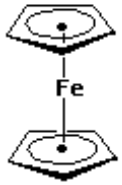
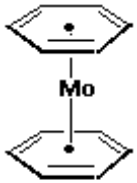
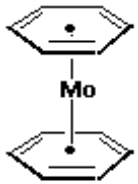
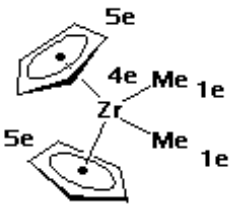
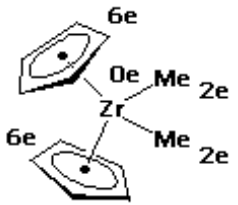
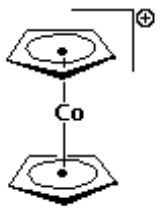
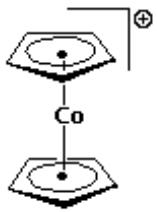
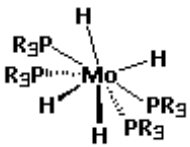
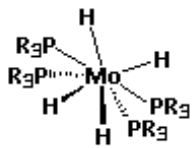
BUT

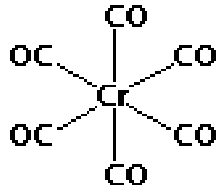
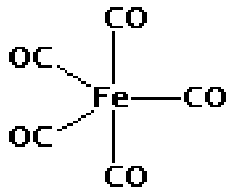
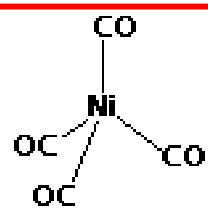
For ligands such as methyl we remove the ligand as a radical. It is therefore a single electron donor in this model.

Furthermore, in this model both the ligand and the metal must donate an electron to the bond.

This method provides NO information about the metal oxidation state.

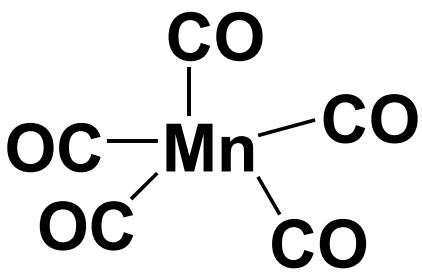
Electron Counting Examples

Covalent Counting Rules		Ionic Counting Rules	
	5e 8e 5e 18e		6e ($Cp^{\ominus}$) 6e (Fe^{2+}) 6e ($Cp^{\ominus}$) 18e
	6e 6e 6e 18e		6e 6e 6e 18e
	5e 4e Me 1e 5e Me 1e 16e		6e 0e Me 2e 6e Me 2e 16e
	-1e 5e 9e 5e 18e		6e ($Cp^{\ominus}$) 6e (Co^{3+}) 6e ($Cp^{\ominus}$) 18e
	Mo 6e 4 H 4e 4 PR_3 8e 18		Mo $^{4+}$ 2e 4 H - 8e 4 PR_3 8e 18

d Group	Formula	Valence electrons		Structure
6	$Cr(CO)_6$	Cr 6 CO	6 12 18	
7	Mn			
8	$Fe(CO)_5$	Fe 5 CO	8 10 18	
9	Co			
10	$Ni(CO)_4$	Ni 4 CO	10 8 18	

Look at CO complexes of Mn

You may expect to have the following structure for a CO complex of Mn.

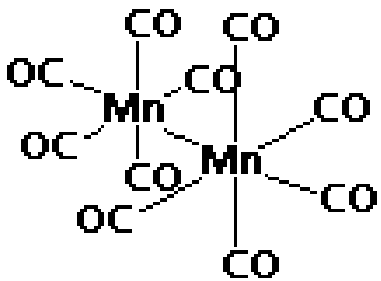


Mn 7
3 CO Terminal 10

Total 17 electrons

7

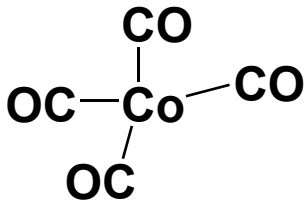
$Mn_2(CO)_{10}$	Mn	7
	5 CO	10
	M-M	1
		18



Prediction of Structure.

(metal carbonyls)

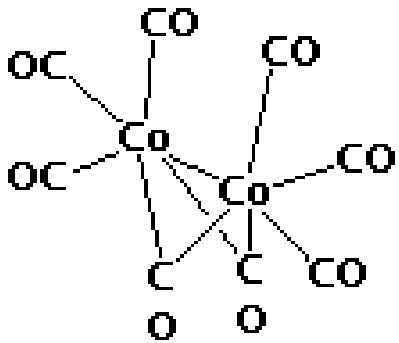
You may expect to have the following structure for a CO complex of Mn.

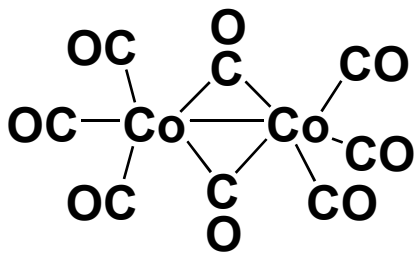


What about ?

$Co_2(CO)_5$

Co 9
3 CO Terminal 6
2 CO Bridging 2
1 Co-Co 1





Is this the only possible structure for bis[tetracarbonylcobalt]?

The EAN Rule cannot differentiate structures of compounds but it CAN provide possibilities for investigation.

Compounds and the EAN Rule

We can divide compounds into three groups.

1. Electronic configurations are completely unrelated to the EAN rule. The central metal may have >, <, = 18 electrons.

2. Electron configurations follow the EAN rule and never have >18 electrons, but may have less.

3. A group that follows EAN rule rigorously.
   (This is what I have shown you so far)

How can we understand this?

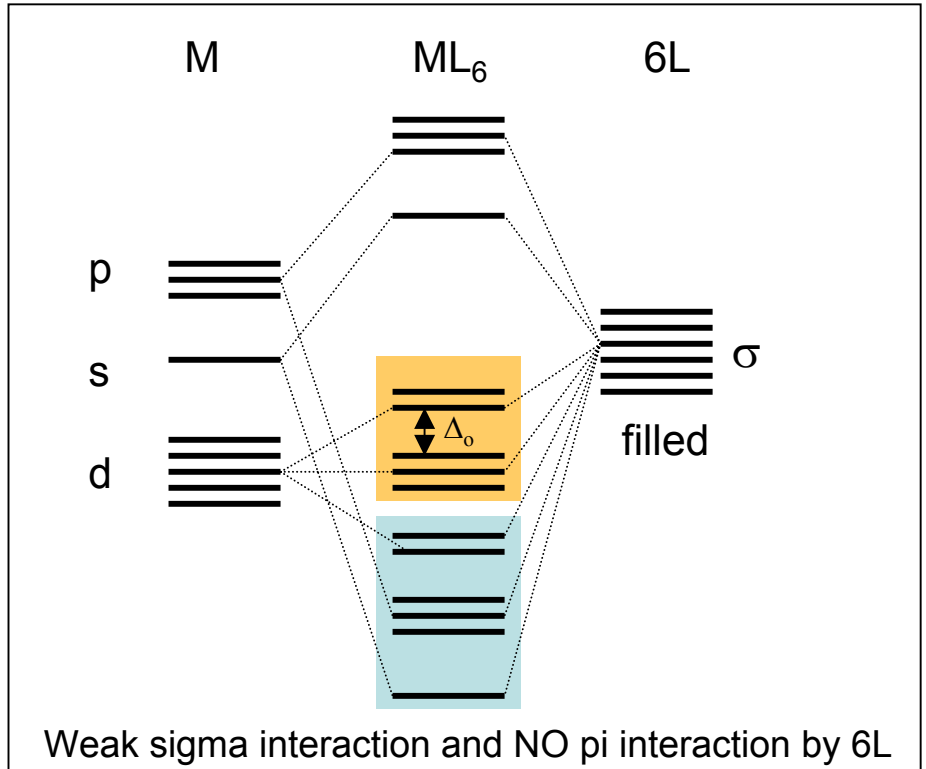
Group I

	(d-electrons, valence)
$TiCl_4(THF)_2$	(O,12)
$Ti(H_2O)_6^{3-}$	(1 ,13)
$V(urea)_6^{3-}$	(2 ,14)
$CrCl_6^{3-}$	(3 ,15)
$CrI_2(DMSO)_4$	
$Mn(H_2O)_6^{2+}$	
CoF_6^{3-}	
$CuCl_5^{3-}$	
$Ni(H_20)_6^{2+}$	
$Cu(H_20)_6^{2+}$	
$ZnCl_2(biuret)_2$	

You figure out.

Valence electrons from 12 to 22.

Ligands are weak field, Δ_o is small.



Weak sigma interaction and NO pi interaction by 6L

Little or no pi interaction between metals and ligands. Energy of the t_{2g} orbitals is the same as the free metal.

There are 6 low energy bonding MO's, 5 medium energy MO's and and 4 strongly antibonding MO's (too high energy to be occupied).

12 electrons from the ligands fill the lowest energy orbitals (blue). Up to 6 metal electrons reside in the t_{2g} set (nonbonding) without any destabilization of bonding.

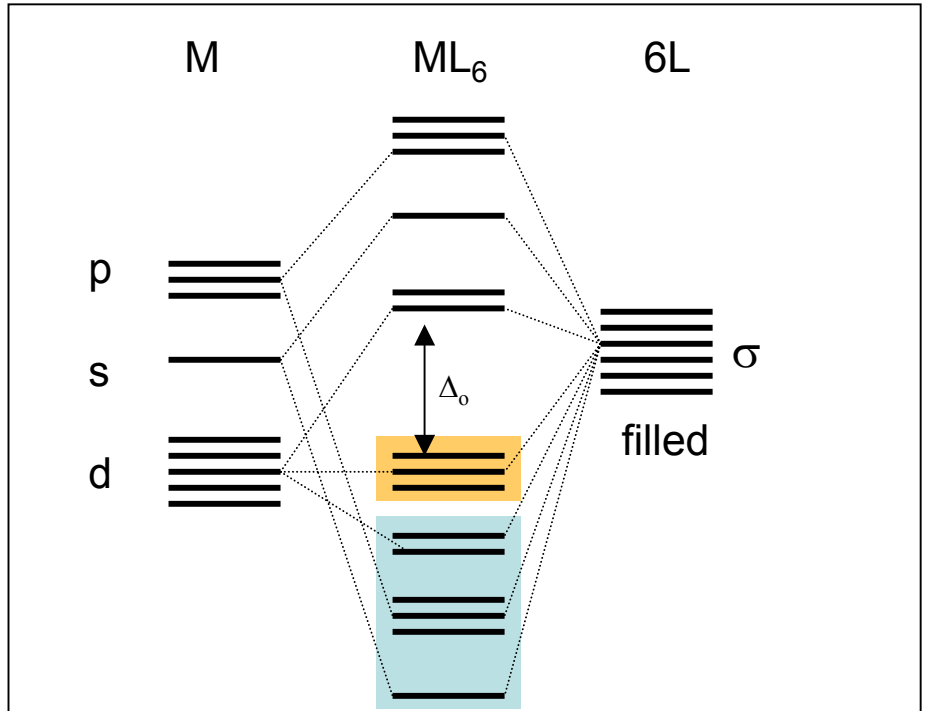
Δ_o is so small that up to 4 electrons can be put into the e_g set with only a small penalty.

Group II

	(d-electrons, valence)
$Zr(CH_3)_2^{2-}$	(O,12)
$Ti(en)_3^{3--}$	(1 ,13)
$Re(NCS)_6^{-}$	(2 ,14)
$Mo(NCS)_6^{3-}$	(3 ,15)
$Os(SO_3)_6^{8-}$	
$Ir(NH_3)_4Cl_2^{2+}$	
ReH_9^{2-}	

You figure out.

Valence electrons equal to 12 to 18.



Strong sigma interaction and NO pi interaction by 6L

Strong sigma donation increases e_g energy and increases Δ_o .

Little or no pi interaction between metals and ligands. Energy of the t_{2g} orbitals is the same as the free metal. Their occupation has no impact on the stability of the complex.

There are 6 low energy bonding MO's, 3 medium energy MO's and and 6 strongly antibonding MO's (too high energy to be occupied).

12 electrons from the ligands fill the lowest energy orbitals (blue). Up to 6 metal electrons reside in the t_{2g} set (nonbonding) without any destabilization of bonding.

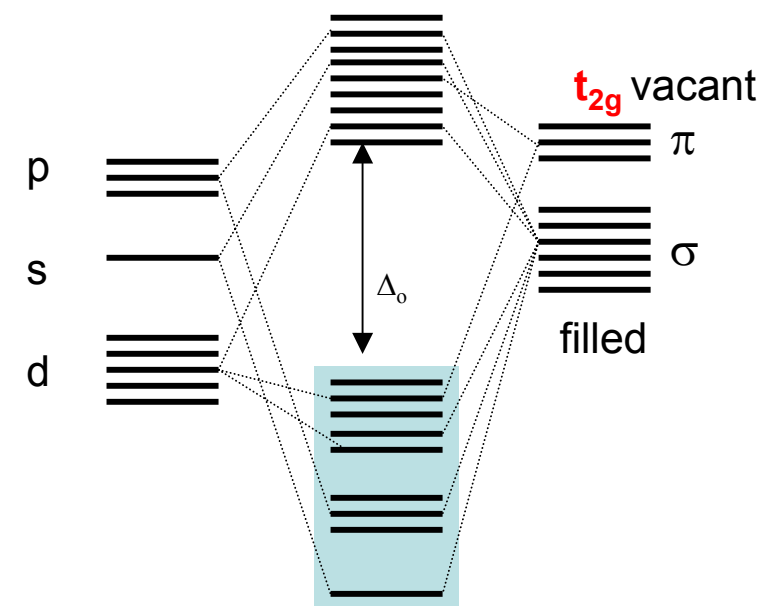
Δ_o is so large that electrons cannot be put into the e_g set without large penalty.

Group III

	(d-electrons, valence)
$Ti(cp)_2(CO)_2$	(4, 18)
$V(CO)_5NO$	(5 ,18)
$Cr(C_6H_6)_2$	(6 ,18)
$MnH(CO)_5$	(7 ,18)
$Fe(NO)_2(CO)_2$	
$Co(NO)(CO)_3$	
$Ni(CO)_4$	

You figure out.

Valence electrons always equal to 18.



Strong sigma interaction and strong pi acceptor interaction by 6L.

Strong sigma donation increases e_g energy
Pi accepting ligands lower t_{2g} energy. BOTH increase Δ_o .

There are 9 low energy bonding MO's,
9 strongly antibonding MO's (too high energy to be occupied).

12 electrons from the ligands and 6 metal electrons in the t_{2g} orbitals fill the lowest energy orbitals (blue). **Removal of the d electrons from the t_{2g} set would destabilize the bonding.**

Δ_o is so large that electrons cannot be put into the e_g set without large penalty.

Examples include CO and NO ligands which are at the top of the **SCS**.

EAN Summary

1. Works well only for d-block metals. It does not apply to f-block metals.

2. Works best for compounds with TMs of low ox. state.

3. Ligands which are good σ-donors and π-acceptors utilize all the valence orbitals and thus such compounds obey this rule.

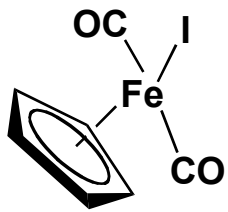
4. Complexes which contain a combination of σ-donors and π-acceptors conform to this rule. (e.g. $Cr(NH_3)_3(CO)_3$, $Cr(\eta^6\text{-}C_6H_6)(CO)_3$).

5. Compounds which obey this rule are kinetically inert to substitution reactions.

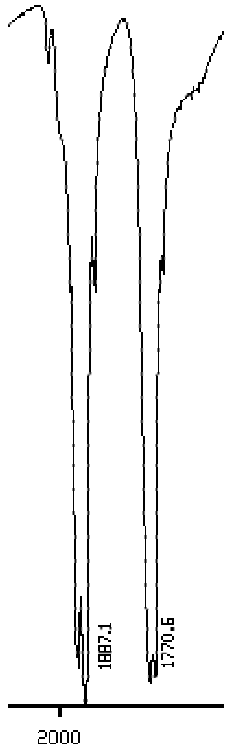
6. Exceptions to the rule occur at the two ends of the transition series where *nd, (n+1)s, and (n+1)p* valence orbitals are less well matched in energy.

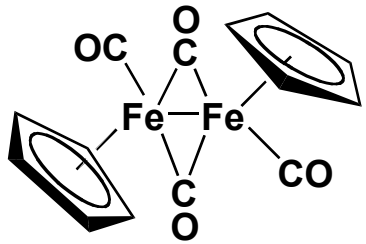
This Rule allows for prediction of structures, reactivity, and reaction mechanisms.

Bridging or Terminal CO



Terminal CO bonding at 2021.5 cm^{-1} and 1975.7 cm^{-1} also, because of very small symmetry differences between carbon monoxides.

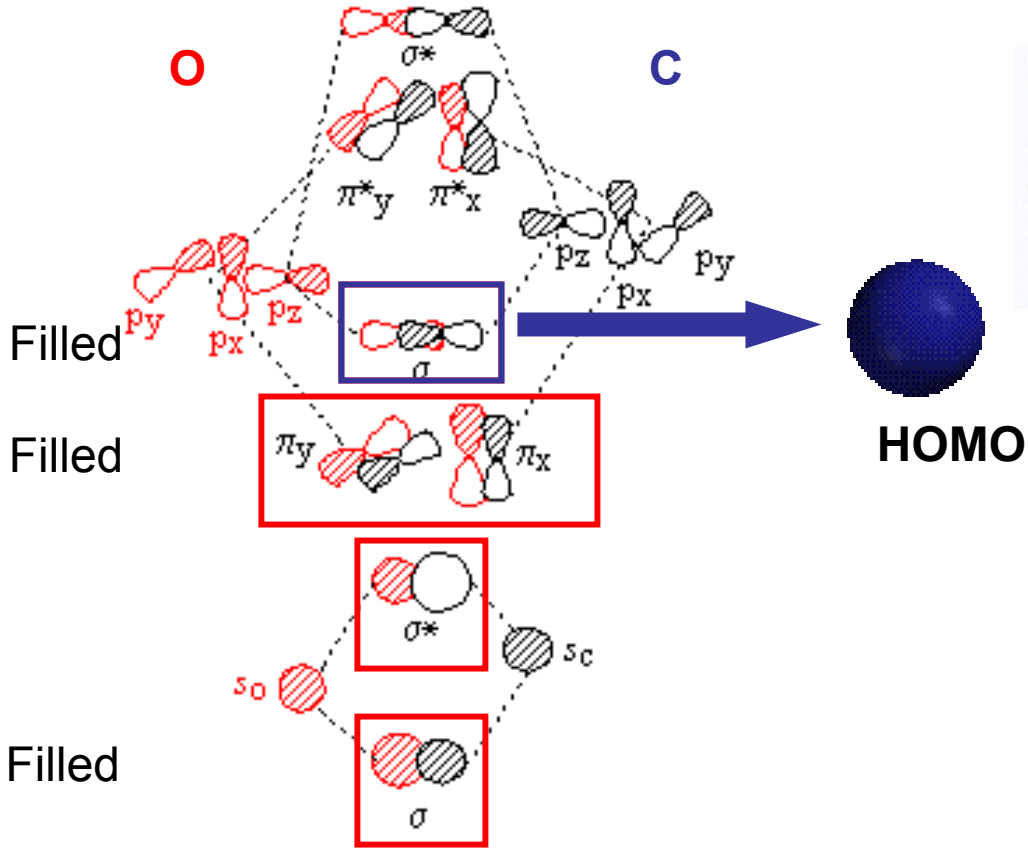




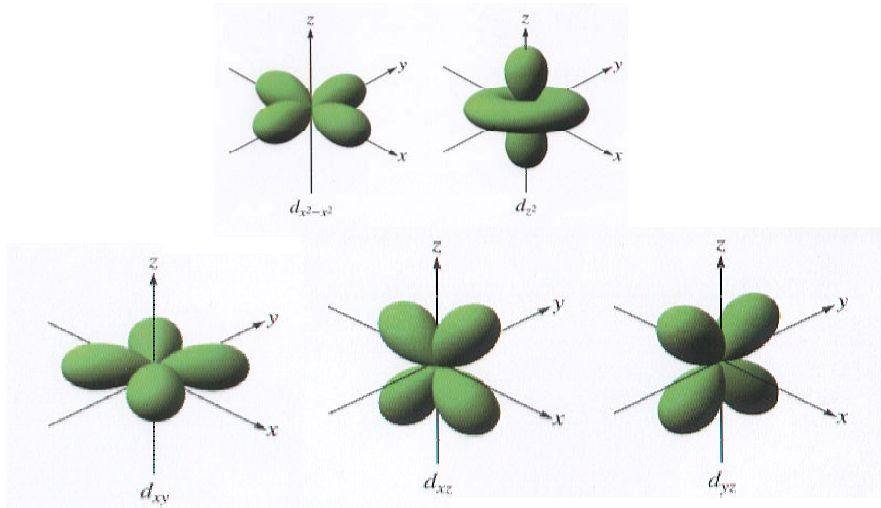
Terminal CO bond1887 cm^{-1}
Bridging CO bond at 1770 cm^{-1}

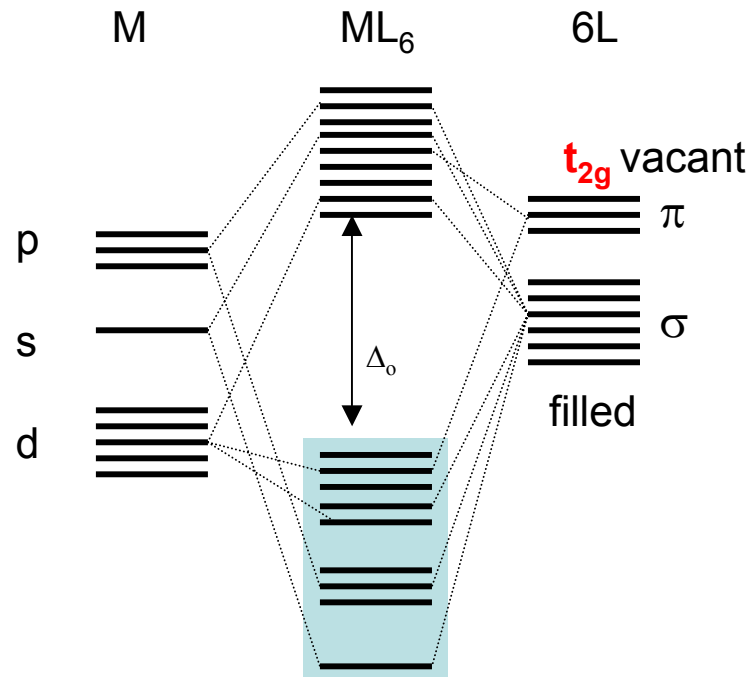
Bonding in TM Carbonyls

CO bonding-the orbital picture



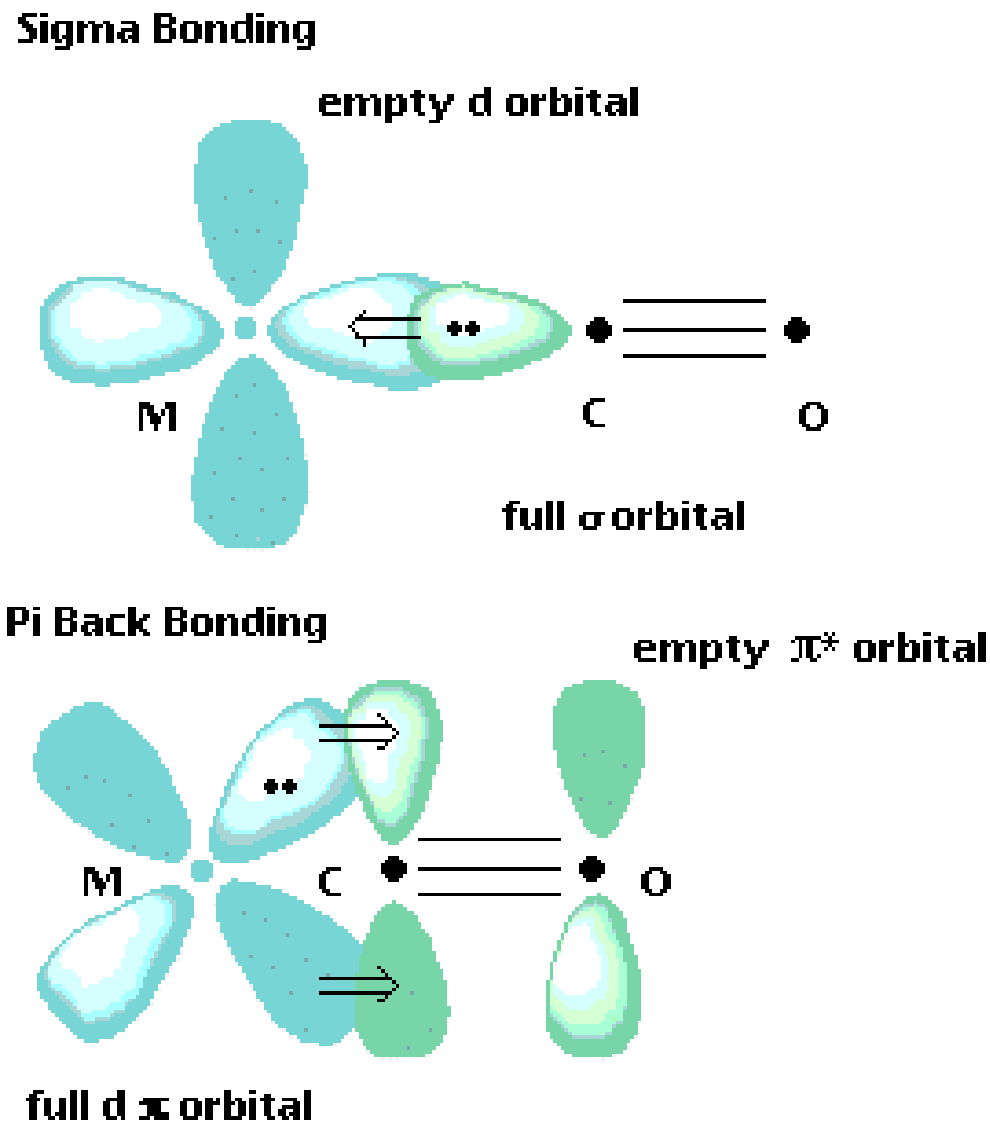
10 valence electrons
C (4), O(6)





Strong sigma interaction and **strong pi acceptor interaction** by 6L.

A cartoon of M-CO bonding.



The HOMO in carbon monoxide is the high energy σ^{NB} which is primarily derived from a carbon 2p orbital.

This means a lone pair of electrons is residing on the C atom.

The LUMO on CO is the π^*_{2p} which are antibonding orbitals with significant 2p character.

CO acts as a Lewis Base and a Lewis Acid.

The back bond appearing in this systems is known as a **synergistic effect**.

Reactions of Metal Carbonyls.

i) Substitution of CO by other L

(L is often a π-acid or Soft Lewis base; L= PR_3, polyolefins, SR_2, CH_3CN)

Recall that TM carbonyls obey the 18 electron rule.

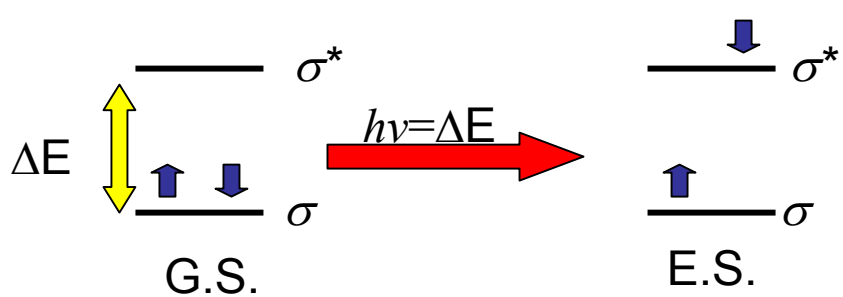
This means two things….

They are inert toward substitution.

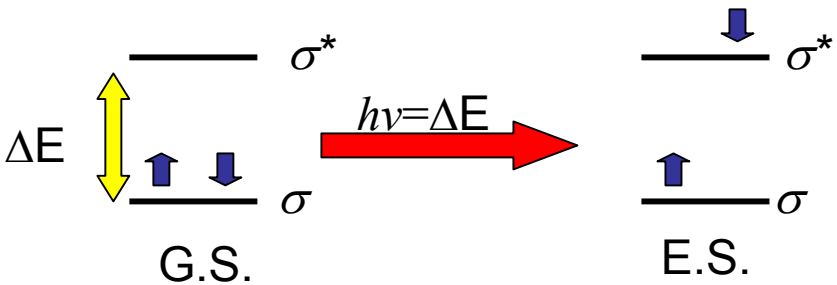
Reactions must proceed via a Dissociative mechanism (via M-CO bond cleavage)

This provides a basis for photochemistry:

If light of a suitable energy is supplied such that $\sigma \Rightarrow \sigma^*$ can occur some interesting things happen.



M-CO Photochemistry



B.O.= 0

This negates the M-CO σ bond.

Bond Order = 1/2 (electrons in bonding orbitals - electrons in anti-bonding orbitals)

CO is photoejected!

L_nM-CO $\xrightarrow{h\nu}$ $[L_nM]$ $\xrightarrow{L'}$ $L_nM\ L'$

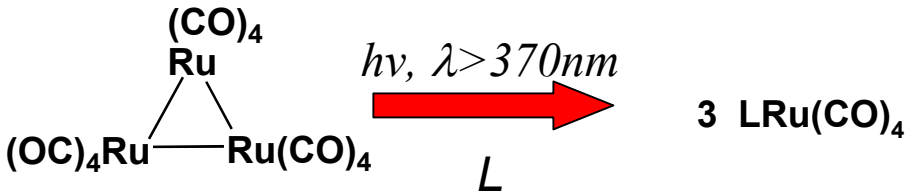
18 electrons — *slow* - CO — 16 electrons High energy reactive intermediate. — *fast* — 18 electrons

ΔE~390nm

In theory, by filtering the excitation light it should be possible to remove only 1 CO.

This is not simple given the broad nature of the UV-vis bands.

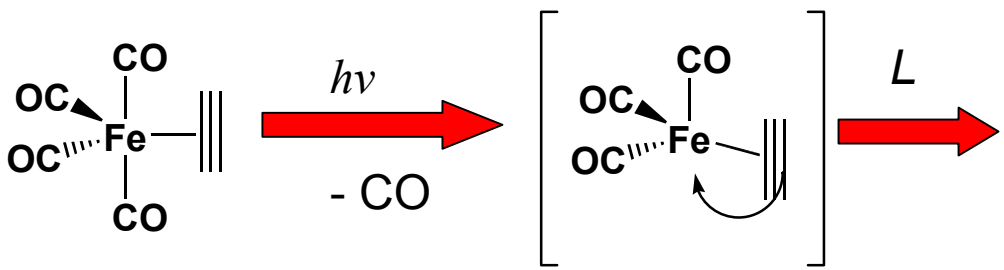
M-CO photochemistry Examples



(L= olefin)

Orange, colour arises from $\sigma \Rightarrow \sigma^*_{(Ru\text{-}Ru)}$ λ~390nm

Another example involving Fe and an 18 electron transition state



18 electrons
alkyne $2e^-$ donor

18 electrons
alkyne $4e^-$ donor

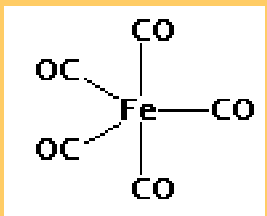
This intermediate is not 16e- and is stabilized by a 4e- donor alkyne.

It substitutes 10^{13}x faster than $Fe(CO)_5$.

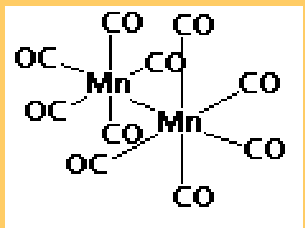
Reduction of TM Carbonyls

What will happen if electrons are added to $18e^-$ TM carbonyls?

High energy 19 or 20 electron systems will result and CO will be ejected.
(This can be viewed as the two electrons taking the place of the CO or breaking M-M bonds)



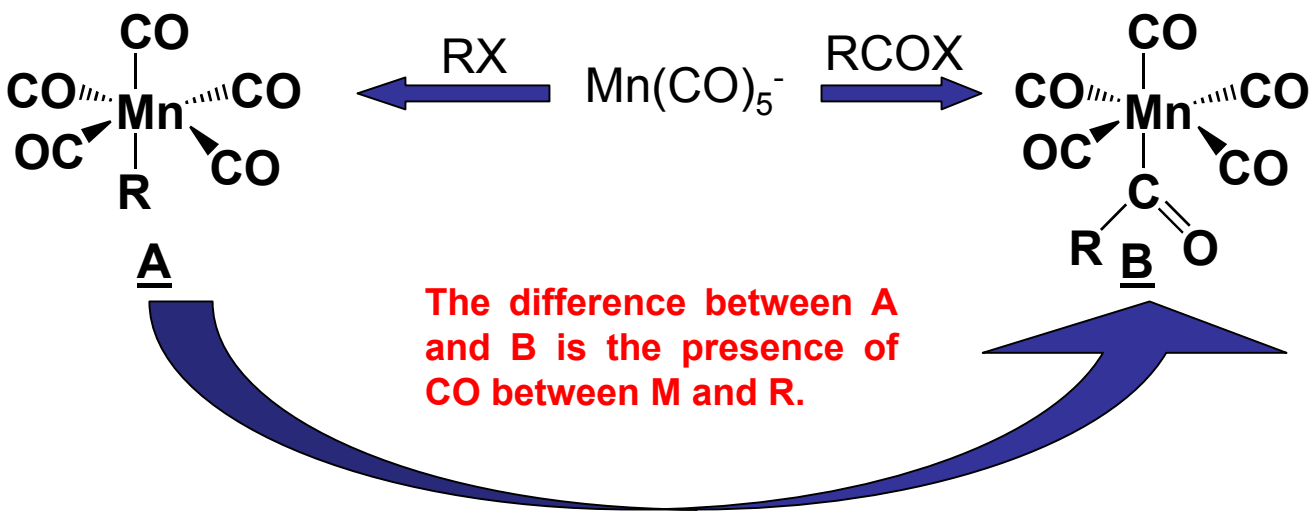
2Na/Hg → $Fe(CO)_4^{2-}$

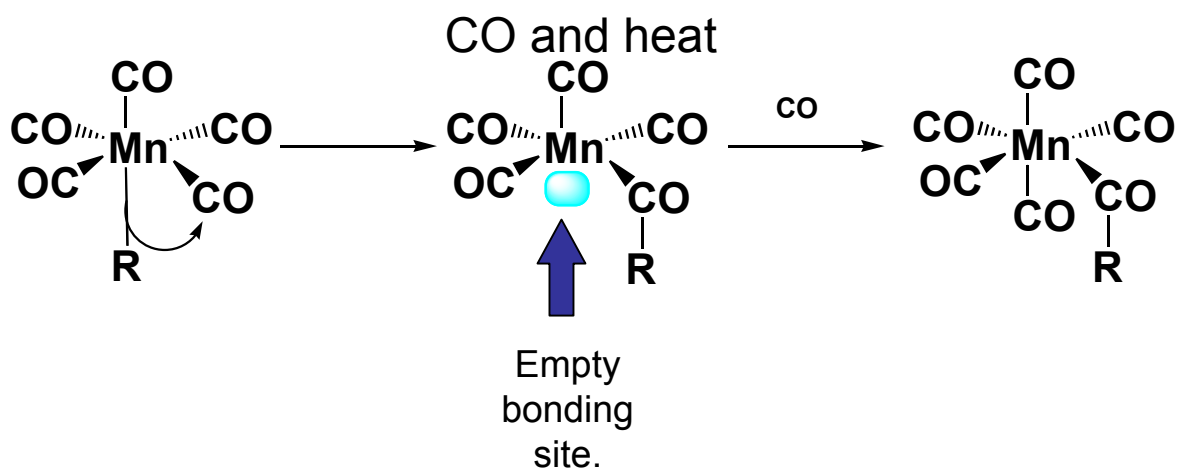


2Na/Hg → $2Mn(CO)_5^-$

These anions are of significant importance. They are nucleophiles and react further to form M-C and M-H bonds.

Formation of M-H and M-C bonds



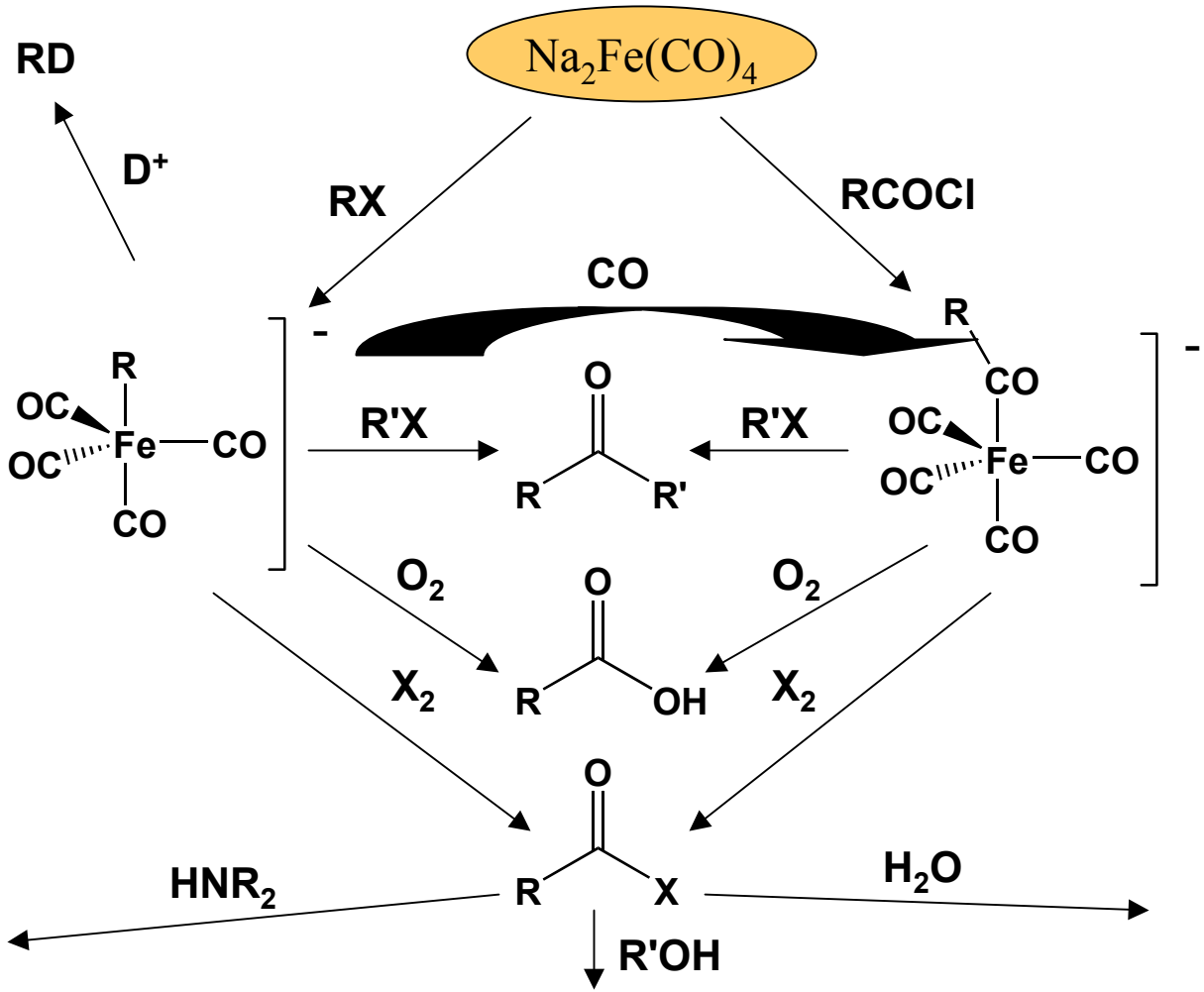


This is referred to as “CO insertion” although the mechanism involves migration of R.

$$Mn(CO)_5^- + H^+ \longrightarrow H\text{-}Mn(CO)_5^-$$

Collman's Reagent

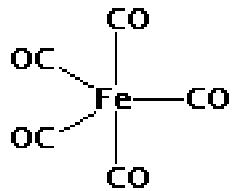
Application of "carbonylmetallates" in organic synthesis.



Disodium tetracarbonylferrate is useful in the functionalization of organic halides.

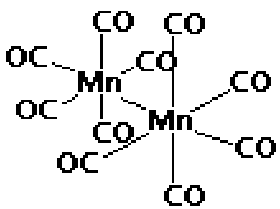
Oxidation of TM Carbonyls

Oxidation weakens the M-CO or M-M bonds and results in CO elimination or M-M cleavage with the formation of TM carbonyl halides.

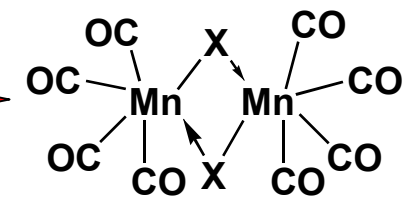


$+ X_2$ → $Fe(CO)_4X_2 + CO$

18 electrons



$+ X_2$ → $2Mn(CO)_5X$ → (heat) →

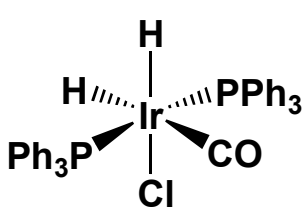


18 electrons

18 electrons

$Mn(CO)_5X$ → (RLi / RMgX) → $Mn(CO)_5R$

Special Case. Oxidative Addition (4-coordinate Vaska's Compound 1961, 16 electron species)

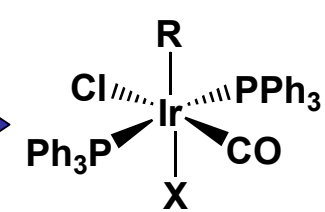


(activation of H_2)

← H_2

Ir(I), d^8, $16e^-$

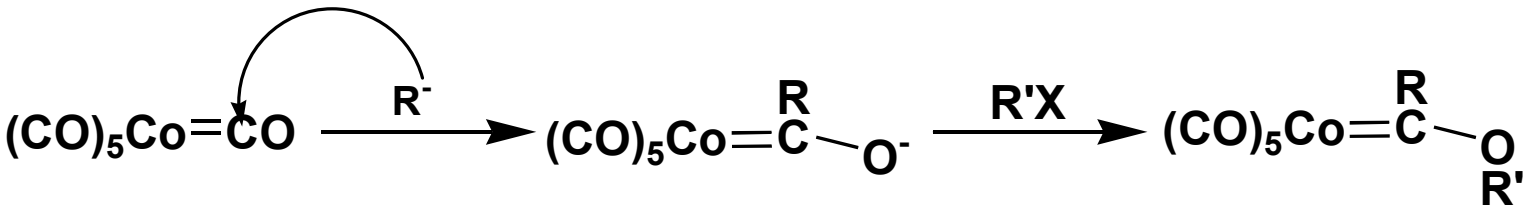
→ RX



Ir(III), d^6, $18e^-$

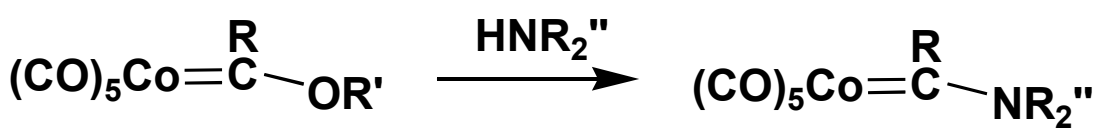
Reactions of Coordinated M-CO

The attachment of CO to a TM makes the C electrophillic and may be attacked by a nucleophile)



This is a carbene complex; E.O. Fischer discovered this type of molecule and shared the Nobel Prize with Wilkinson.

The "$(CO)_5Co$" structural unit acts as an electron withdrawing; It is a pseudo ester.



Trans-esterification

The Mond Process

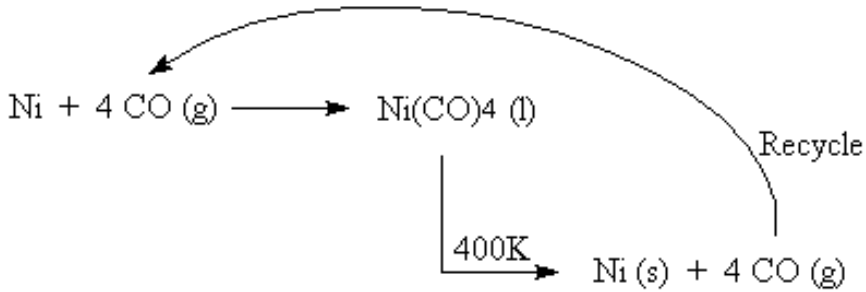
Nickel carbonyl, a gas formed from carbon monoxide and metallic nickel.

Scientific Serendipity

In 1890 Ludwig Mond, was investigating the rapid corrosion of nickel valves used in apparatus for the **Solvay process***, and discovered $Ni(CO)_4$.

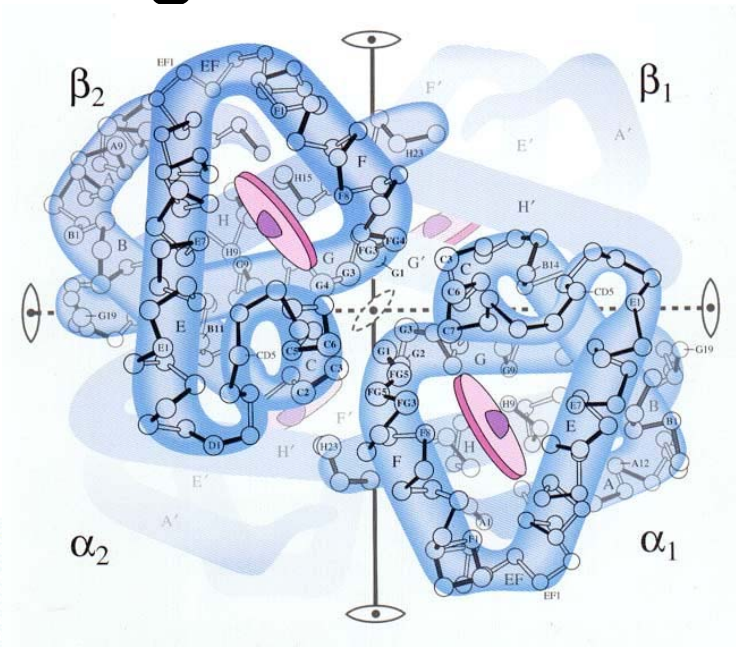
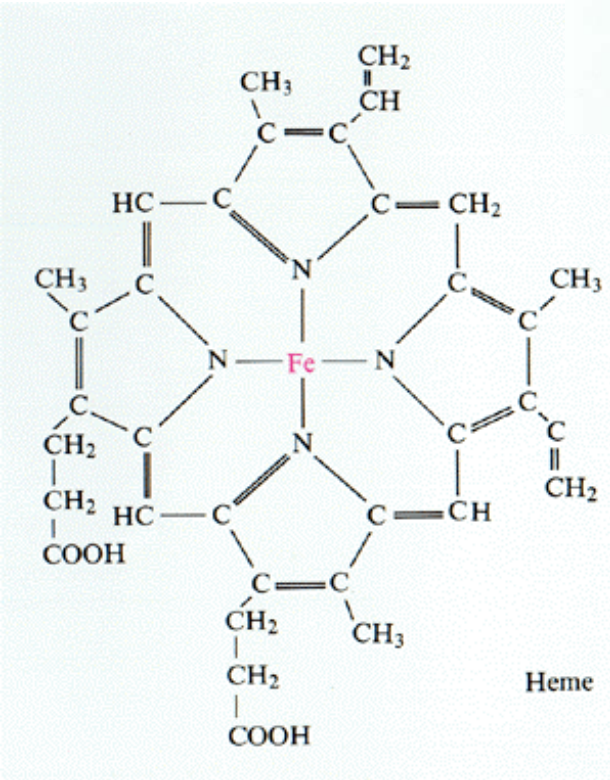
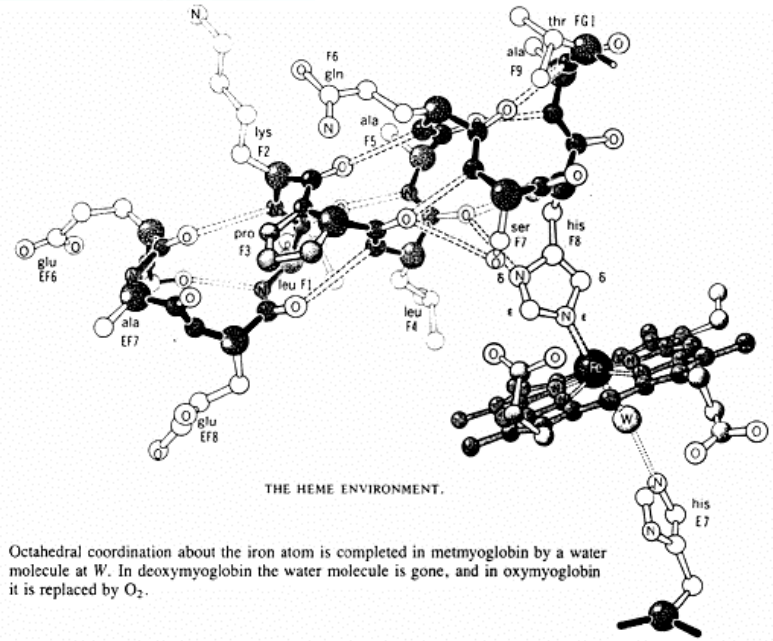
In contrast to many nickel compounds which are usually green solids, $Ni(CO)_4$ is a colourless, volatile, toxic liquid with a very "organic character".

He used it as the basis of a method to purify nickel, called the **"Mond process".**



Ni reacts with CO (leaving the impurities behind), to form $Ni(CO)_4$.

The $Ni(CO)_4$ is passed through a tower filled with nickel pellets at a high velocity and 400 K. Pure Ni plates out on the pellets.

* A commercial process for the manufacture of Na_2CO_3. NH_3 and CO_2 are passed into a sat'd $NaCl_{(aq)}$ solution to form soluble $(NH_4)(HCO_3)$, which reacts with the NaCl to form soluble NH_4Cl and solid $NaHCO_3$ if the reactor temperature is maintained below 15°C. The $NaHCO_3$ is filtered off and heated to produce Na_2CO_3.

Hemoglobin and Heme