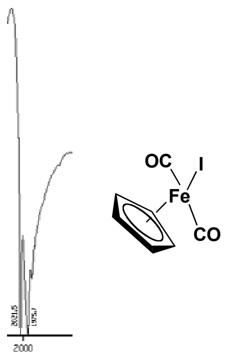
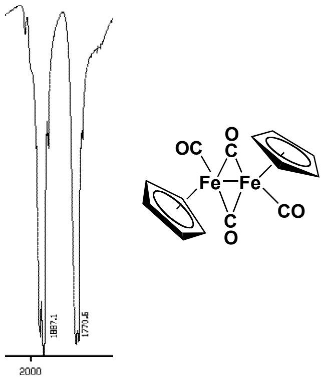
Bridging or Terminal CO



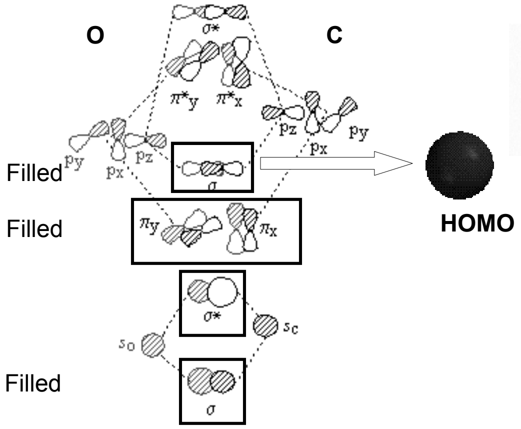
Terminal CO bonding at 2021.5 cm^{-1} and 1975.7 cm^{-1} also, because of very small symmetry differences between carbon monoxides.



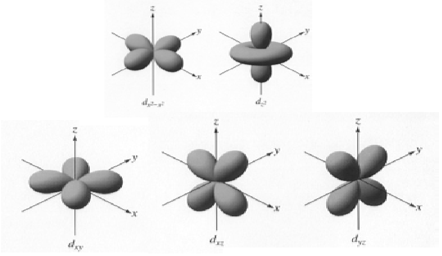
Terminal CO bond1887 cm^{-1}
Bridging CO bond at 1770 cm^{-1}

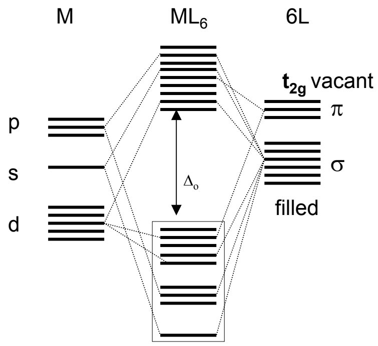
Bonding in TM Carbonyls

CO bonding-the orbital picture



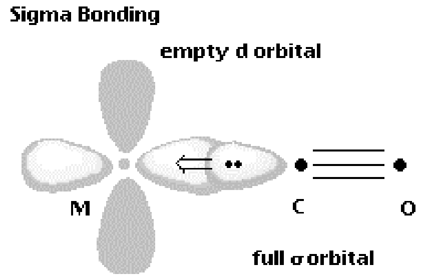
10 valence electrons
C (4), O(6)

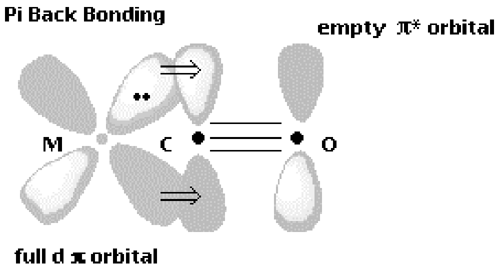




Strong sigma interaction and **strong pi acceptor interaction** by 6L.

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.

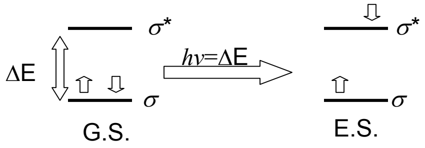
This means two things….

They are inert toward substitution.

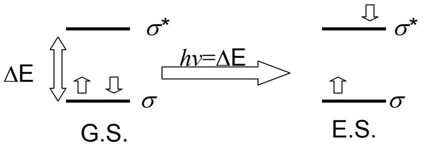
Reactions must proceed via a Dissociative mechanism (via M-CO bond cleavage)

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!

$$\underset{\text{18 electrons}}{L_nM\text{-}CO} \xrightarrow[\text{slow; - CO}]{h\nu} \underset{\text{16 electrons}}{[L_nM]} \xrightarrow[\text{fast}]{L'} \underset{\text{18 electrons}}{L_nM\,L'}$$

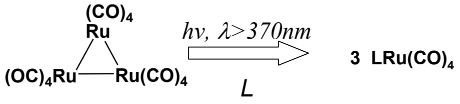
High energy reactive intermediate.

$\boxed{\Delta E\text{~}390\text{nm}}$

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.

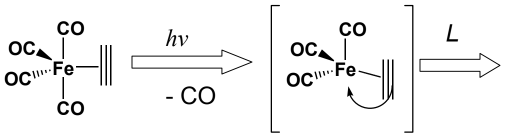
M-CO photochemistry Examples



(L= olefin)

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

Another example involving Fe and an 18 electron transition state



18 electrons alkyne 2e$^-$ donor

18 electrons alkyne 4e$^-$ donor

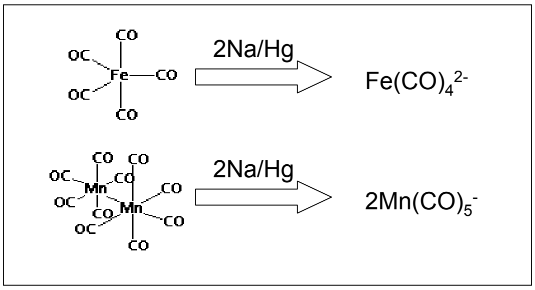
This intermediate is not 16e- and is stabilized by a 4e- donor alkyne.

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

Reduction of TM Carbonyls

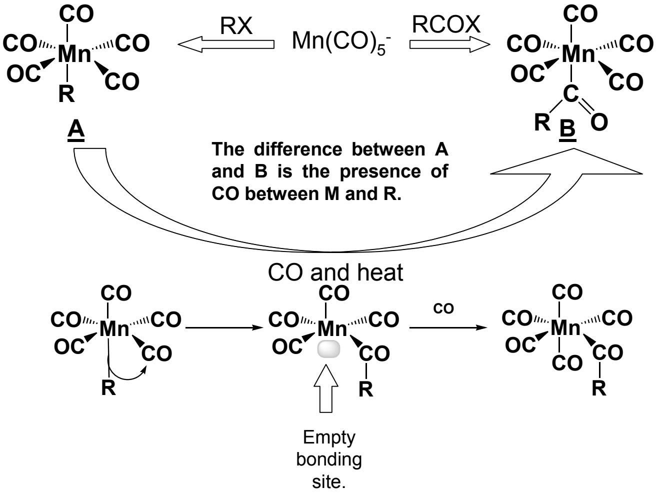
What will happen if electrons are added to 18e$^-$ TM carbonyls?

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)



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



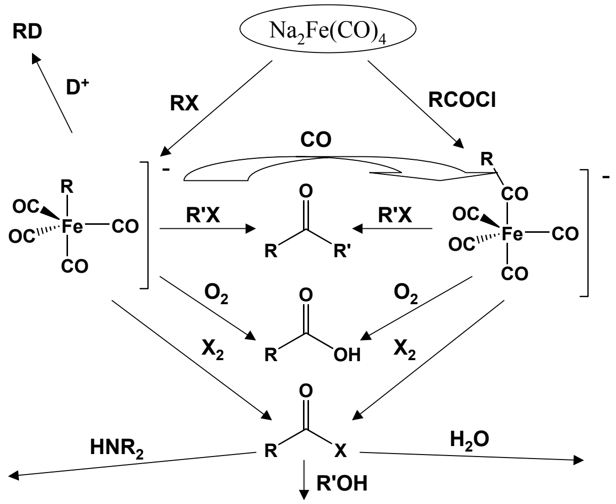
The difference between A and B is the presence of CO between M and R.

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

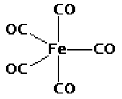
Application of "carbonylmetallates" in organic synthesis.



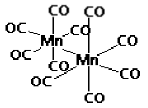
Disodium tetracarbonylferrate is useful in the functionalization of organic halides.

Oxidation of TM Carbonyls

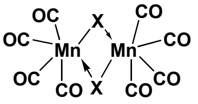
Oxidation weakens the M-CO or M-M bonds and results in CO elimination or M-M cleavage with the formation of TM carbonyl halides.



+ X_2 $\Longrightarrow$ $Fe(CO)_4X_2$ + CO
18 electrons



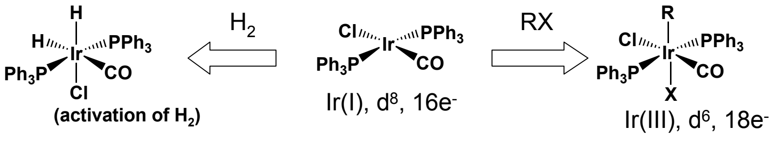
+ X_2 $\Longrightarrow$ $2Mn(CO)_5X$ $\xrightarrow{\text{heat}}$
18 electrons



18 electrons

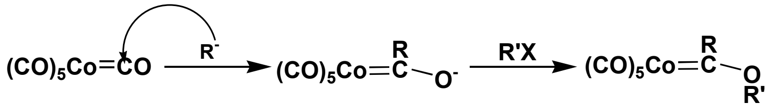
$$Mn(CO)_5X \xrightarrow[\text{RMgX}]{\text{RLi}} Mn(CO)_5R$$

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



Reactions of Coordinated M-CO

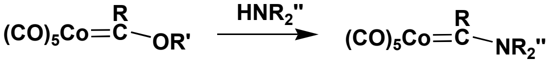
The attachment of CO to a TM makes the C electrophillic and may be attacked by a nucleophile)



$$(CO)_5Co{=}CO \xrightarrow{R^-} (CO)_5Co{=}\overset{R}{C}{-}O^- \xrightarrow{R'X} (CO)_5Co{=}\overset{R}{C}{-}\underset{R'}{O}$$

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.

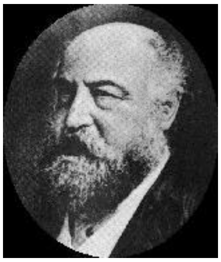


$$(CO)_5Co{=}\overset{R}{C}{-}OR' \xrightarrow{HNR_2''} (CO)_5Co{=}\overset{R}{C}{-}NR_2''$$

Trans-esterification

The Mond Process

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

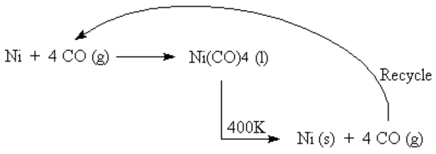


Scientific Serendipity

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".**



$$Ni + 4\,CO\,(g) \longrightarrow Ni(CO)_4\,(l)$$

$$Ni(CO)_4\,(l) \xrightarrow{400K} Ni\,(s) + 4\,CO\,(g)$$

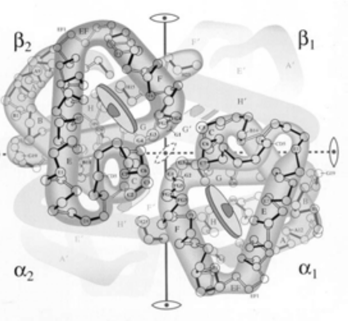
Ni reacts with CO (leaving the impurities behind), to form $Ni(CO)_4$.

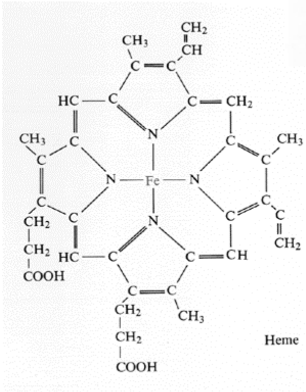
The $Ni(CO)_4$ is passed through a tower filled with nickel pellets at a high velocity and 400 K. Pure Ni plates out on the pellets.

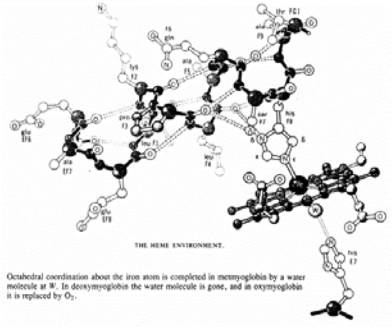
---

* 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







Octahedral coordination about the iron atom is completed in metmyoglobin by a water molecule at W. In deoxymyoglobin the water molecule is gone, and in oxymyoglobin it is replaced by O_2.

Formation and Reactions of TM Complexes

Very brief discussion in R-C pages 449-451.

What have we done so far?

1. What is the structure of these compounds?
   (Coordination Number, Geometry, Isomerization)

2. What holds these complexes together and how do we study them?
   (CFT d-orbital splitting, electronic spectroscopy, MO theory)

But….you can't study them if you can't get them…..

How are they made?

Where do we start?

How about with a Co and Pt complex? **$[Co(en)_2(NO_2)_2]^+$**, and **cis/trans platin.**

This is an interesting case:

We start with a Co^{2+} salt….**what is the oxidation state of Co in the product?**

Why do we use the Co^{2+}?

Ligand substitution occurs more readily than with Co^{3+}… but why?

$$CoCl_{2(aq)}\ \boxed{\{[Co(OH_2)_6]Cl_2\}} \xrightarrow[2NO_2^-]{2\ en} \xrightarrow{O_2} \mathbf{[Co(en)_2(NO_2)_2]^+}$$

If we change our starting material we can control stereochemistry…. but why?

$$[PtCl_4]^{2-} + 2NH_3 \longrightarrow \textit{cis}\text{-}PtCl_2(NH_3)_2$$

$$[Pt(NH_3)_4]^{2+} + 2Cl^- \longrightarrow \textit{trans}\text{-}PtCl_2(NH_3)_2$$

Why do these reactions occur the way they do?
We are going to look at influencing factors and mechanisms.

Stable vs. Unstable
Inert vs. Labile

When TM ions are dissolved in water the ions form aqua complexes.

UV-Vis, NMR indicate a six-coordinate octahedral species for 1st row TMs.

$[M(OH_2)_6]^{2+/3+}$

(neutron diffraction of these species was first reported in 1984)

Given that the ions are not "free" in solution, formation of TM complexes involves the replacement (substitution) of one ligand with another.

$$[M(OH_2)_6]^{2+/3+} + nL \Longleftrightarrow [ML_n]^{x+}$$

That these reactions occur in aqueous solution is VERY important to numerous disciplines including Inorganic Chemistry, Biochemistry, Analytical Chemistry, Environmental Chemistry and other applications.

TM Aqua Complexes

An IMPORTANT point about TM-aqua complexes.

The amount of time (residence time) the H_2O ligands spends attached to the TM can vary significantly from metal to metal.

$[Cr(OH_2)_6]^{3+}$ and $[Co(OH_2)_6]^{3+}$ fail to exchange with $^{18}OH_2/^{17}OH_2$ after several hours.

$$[Cr/Co^{16}(OH_2)_6]^{3+} + \text{large XS } ^{18}OH_2/^{17}OH_2 \xleftrightarrow{\text{hours}} [Cr/Co^{18/17}(OH_2)_6]^{3+}$$

Most other TMs exchange water rapidly.

What does this tell us about formation of TM complexes and what we need to consider?

1. **Thermodynamics**: When examining thermodynamics of a reaction we are entirely interested in the start and finish of a reaction. What is the extent of reaction? Where does the equilibrium lie? **How do we investigate this?** **ΔG^o**
2. **Kinetics:** How fast does a reaction reach equilibrium? This relates directly to the mechanism.