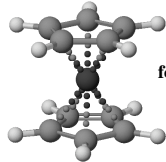
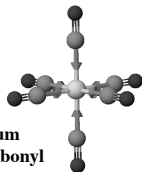


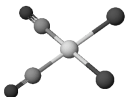
Organometallic Chemistry



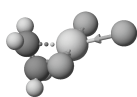
ferrocene



chromium hexacarbonyl



dicarbonyldiodorhodium(1+)



Zeise's salt

Ligands in Organometallic Chemistry

2 Electron Donors



HC≡CH

:C≡O:

halide ions

PR₃, phosphines

4 Electron Donor



6 Electron Donors



cyclopentadienide ion

16 & 18 Valence Electron Rule

C. A. Tolman, Chem. Soc. Rev., 1972, 1, 337

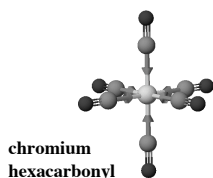
- Diamagnetic organometallic compounds of the transition metals may exist in significant concentration at moderate temperatures only if the metal's valence shell contains 16 or 18 valence electrons.

16 & 18 Valence Electron Rule

C. A. Tolman, Chem. Soc. Rev., 1972, 1, 337

- Organometallic reactions, including catalytic ones, proceed by elementary steps involving only intermediates with 16 or 18 metal valence electrons.

16 & 18 Valence Electron Rule



$$\begin{aligned} \text{Cr}^0 &= d^6 = 6 e^- \\ 6 \text{ CO} &= 6 \times 2 e^- \\ &= 12 e^- \end{aligned}$$

**Total = 18
valence
electrons**

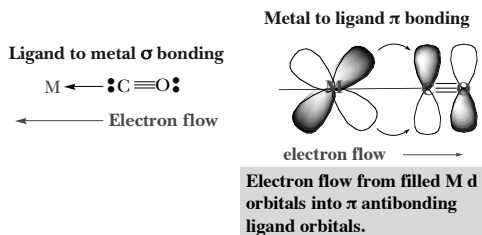
18 valence electrons lead to maximum bonding. All bonding molecular orbitals are filled.

Bonding in Coordination Compounds

- Consider Cr(NH₃)₆³⁺
- Cr³⁺ = 3 valence electrons
- 6 NH₃ ligands = 12 valence electrons
- TOTAL valence electrons = 15

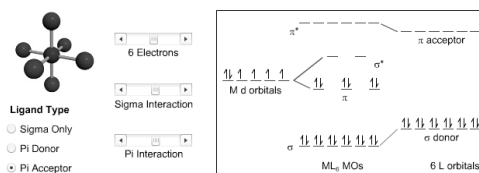
Ordinary coordination compounds do not generally have 18 (or 16) valence electrons.

Bonding in M—CO Complexes



This SYNERGY leads to stronger bonding than either sigma or pi bonding alone.

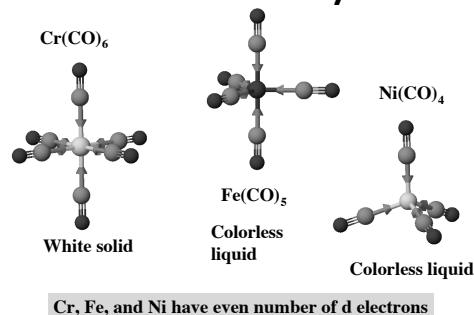
MO Stabilization by π Acceptor Ligands



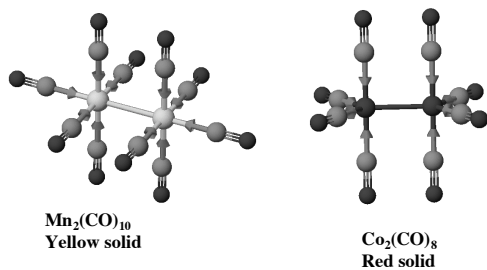
Bonding in Metal Carbonyls

- M-CO bonding illustrates why OM compounds of trans metals always use low-valent metals (< +2) (usually 0 or +1).
- M → L π^* bonding leads to stabilization.
- Low valence state of M means effective nuclear charge of M is low, so M → L charge flow is possible.

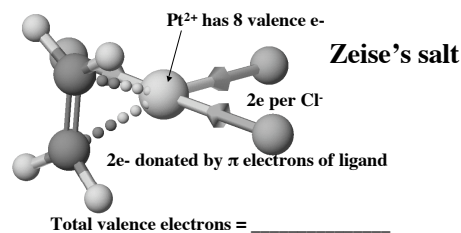
Metal Carbonyls



Metal Carbonyls

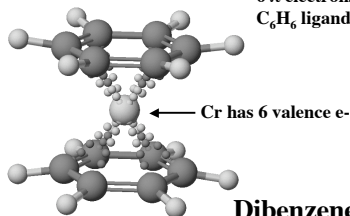


Metal-Olefin Complexes



Metal-Aromatic Complexes

6 π electrons of donated by C_6H_6 ligand

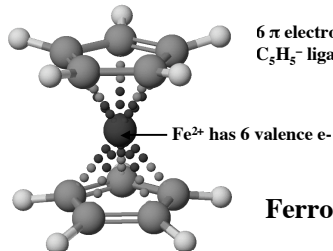


Dibenzenechromium

Total valence electrons = _____

Metal-Aromatic Complexes

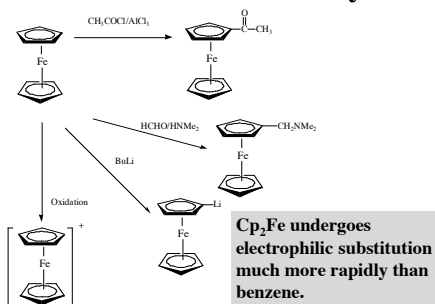
6 π electrons of donated by $C_5H_5^-$ ligand



Ferrocene

Total valence electrons = _____

Ferrocene Chemistry

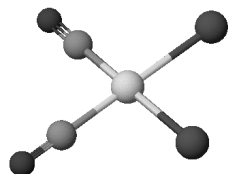


16 & 18 Valence Electron Rule

C. A. Tolman, Chem. Soc. Rev., 1972, 1, 337

- Organometallic reactions, including catalytic ones, proceed by elementary steps involving only intermediates with 16 or 18 metal valence electrons.

A Rhodium Catalyst

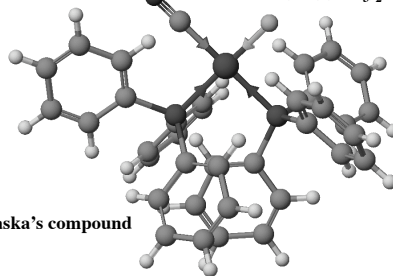


Total valence electrons?

dicarbonyldiiodorhodium(1+)

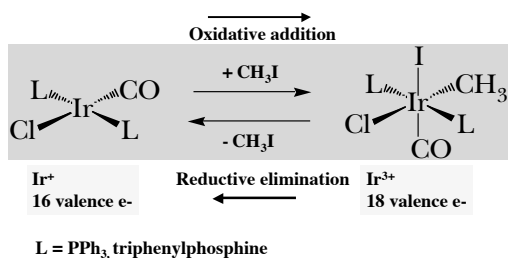
Reactions & Catalysis

$IrCl(CO)(PPh_3)_2$

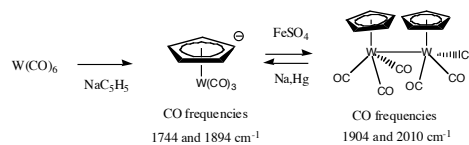


Vaska's compound

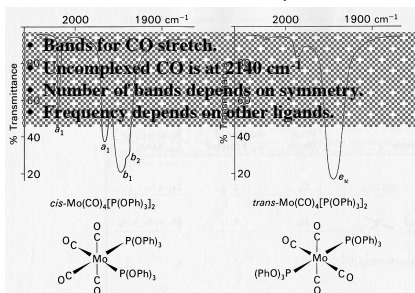
Oxidative Addition & Reductive Elimination



Organometallic Chemistry Problem 12



Infrared Spectroscopy of Metal Carbonyls



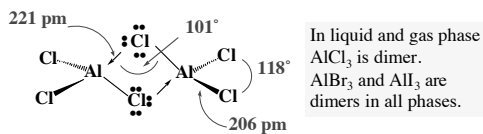
Metal Alkyls and Aryls

Grignard reagents
 RX + Mg in ether ----> RMgX
 Structure is more complex than RMgX.

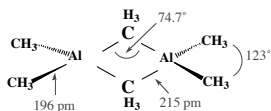
Organomercury compounds
 Hg + 2 Na + 2 RX ----> HgR₂ + 2 NaX
 Compounds like Hg(CH₃)₂ are EXTREMELY toxic

Organolithium compounds
 2 Li (dispersion) + RCl ----> RLi + LiCl
 Usually done in pet. Ether, benzene, or cyclohexane
 RLi can be used to transfer R groups to other compounds

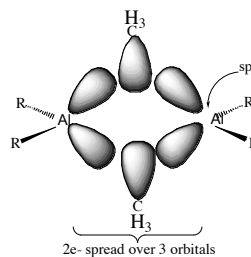
AlX₃: X = Cl, Br, I or R



Replace Cl with alkyl or aryl groups ---->
 organoaluminum compounds (AlR₃)₂

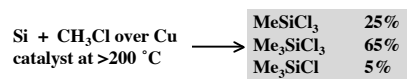


3-Center, 2-Electron Bond



Terminal and bridging R groups exchange positions rapidly at room temperature.

Organosilanes, R₄Si



This is the origin of silicone polymers

