ORGANOMETALLIC CHEMISTRY

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Classification of organometallic compounds based of the metal-carbon bond

1) Ionic organometallic compounds
   - Ionic bonding
   - Alkali metals other than Li belongs to this class
   - Soluble in polar solvents
   - Eg:- $CH_3^- Na^+$

2) Organometallic compounds containing metal-carbon σ bonds

- Covalent bond
- Such compounds are formed by p-block elements with electronegativity values between 1 and 2.5
- d block elements can also form σ bonded organometallic compounds
- Eg: $Be(CH_3)_2$, $Si(CH_3)_4$, $W(CH_3)_6$

3) Organometallic compounds containing metal-carbon π bonds

- π donor ligands
- Hapticity- Number of carbon atoms that are bonded to the metal
- Alkenes, aromatics and alkynes form such complexes
- Metallocene
- π molecular orbital of organic compound overlaps with vacant orbital of metal
- Eg: Ferrocene, Ziese's salt

4) Organometallic compounds with multicenter bonds

- Bonding is different from conventional 2c, 2e bonds
- Few Organometallic compounds of Li, Be, Mg and Al forms multicentre bonds
- 3 center 2 electron bonds $[Be(CH_3)_2]_n$
- 4 centre 2-electron bonds $[Li_4(CH_3)_4]$

18-Electron Rule

- The number of ligands attached to a metal will be such that the sum of the electrons brought by the ligands plus the valence electrons of the metal equals 18.
- When the electron-count is less than 18, metal is said to be *coordinatively unsaturated* and can take on additional ligands.
- 18-Electron rule is to transition metals as the octet rule is to second-row elements.

- The 18-electron Rule
  - Counting Electrons
    - The octet rule governs organic and simple ionic compounds: s + 3p orbital
  - The 18-electron rule governs organometallics (with many exceptions)
    - s + 3p + 3d orbitals
    - Donor ligands provide the electrons other than the d-electrons

Examples of Electron Counting

- $Cr(CO)_6$
  - Total charge on ligands = 0, so charge on Cr = 0, so Cr = d^6
  - 6 CO ligands x 2 electrons each = 12 electrons
  - Total of 18 electrons

- $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$
  - Total charge on ligands = 2^-, so Fe^{2+} = d^6
  - $(\eta^5\text{-}C_5H_5^- = 6)$ + $(2CO \times 2 = 4)$ + $(Cl^- = 2)$ = 12 electro
  - Total of 18 electrons

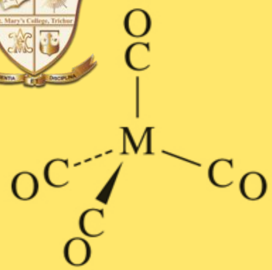
- Charged complex: $[Mn(CO)_6]^+$
  - Total ligand charge = 0, so Mn^+ = d^6
  - 12 electrons from 6 CO ligands gives a total of 18 electrons

- M—M Bond: $(CO)_5Mn—Mn(CO)_5$
  - Each bond between metals counts 1 electron per metal:
    Mn—Mn = 1 e^-
  - Total ligand charge = 0, so $Mn^0 = d^7$
  - 5 CO ligands per metal = 10 electrons for a total of 18 electrons per Mn

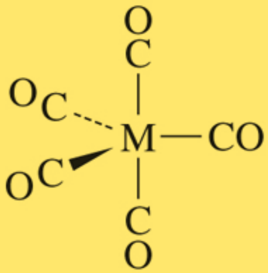
Metal Carbonyls

- CO is the ligand
- Homoleptic and heteroleptic carbonyl
- Classification
  - Mononuclear Carbonyl
  - Binuclear Carbonyl
  - Polynuclear Carbonyl
    - Bridged Carbonyl
    - Non bridged carbonyl

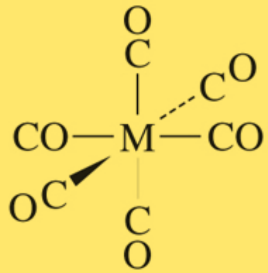
Mononuclear [$M(CO)_x$]



M = Ni, Pd

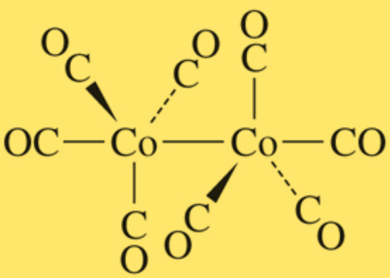


M = Fe, Ru, Os

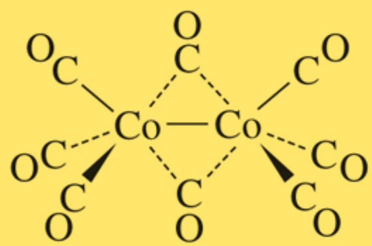


M = V, Cr, Mo, W

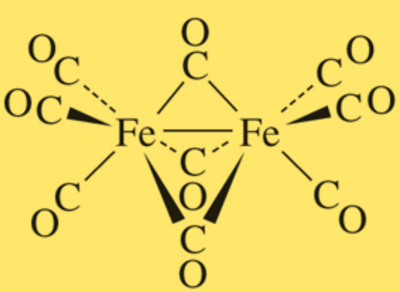
Binuclear [$M_2(CO)_x$]



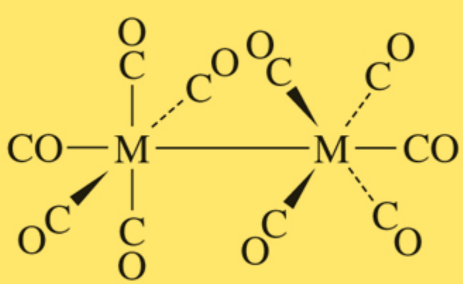
$Co_2(CO)_8$ (solution)



$Co_2(CO)_8$ (solid)

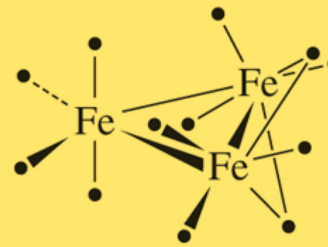


$Fe_2(CO)_9$

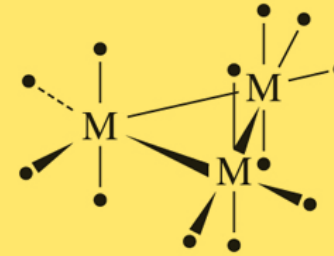


$M_2(CO)_{10}$
M = Mn, Tc, Re

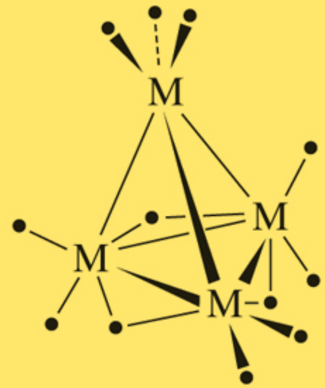
Polynuclear (CO represented by • for clarity)



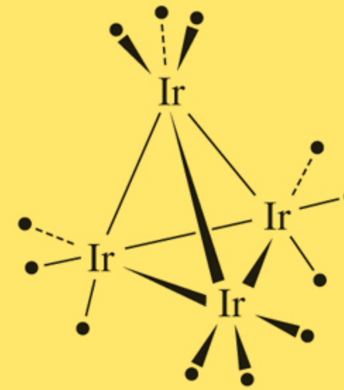
$Fe_3(CO)_{12}$



$M_3(CO)_{12}$
M = Ru, Os



$M_4(CO)_{12}$
M = Co, Rh



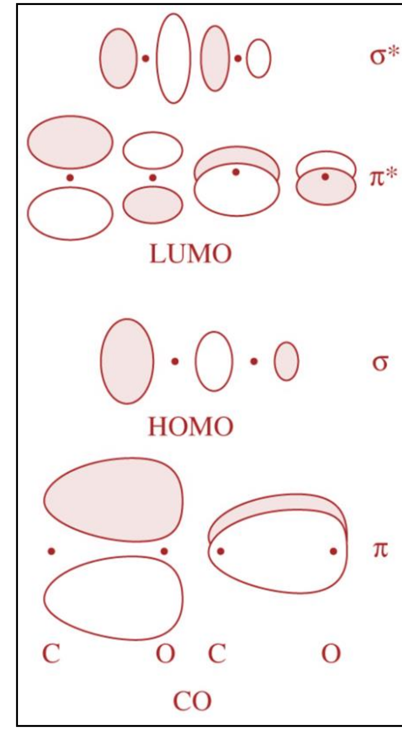
$Ir_4(CO)_{12}$

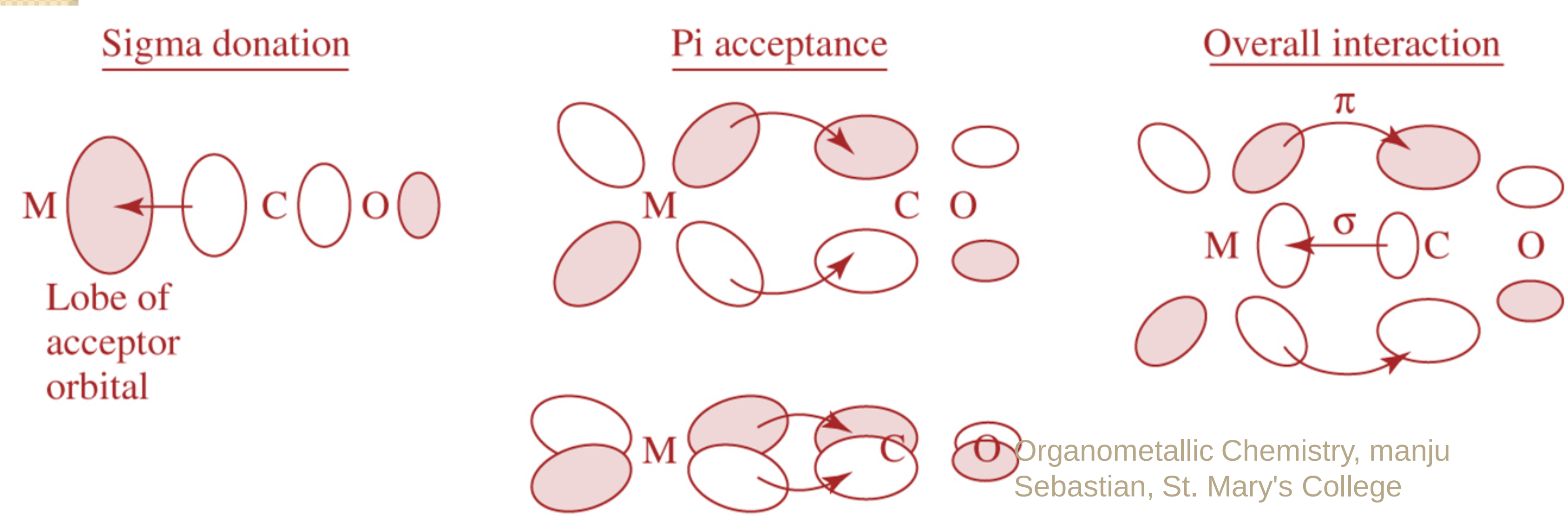
$M_6(CO)_{16}$
M = Co, Rh

Carbonyl Complexes (CO)

Bonding

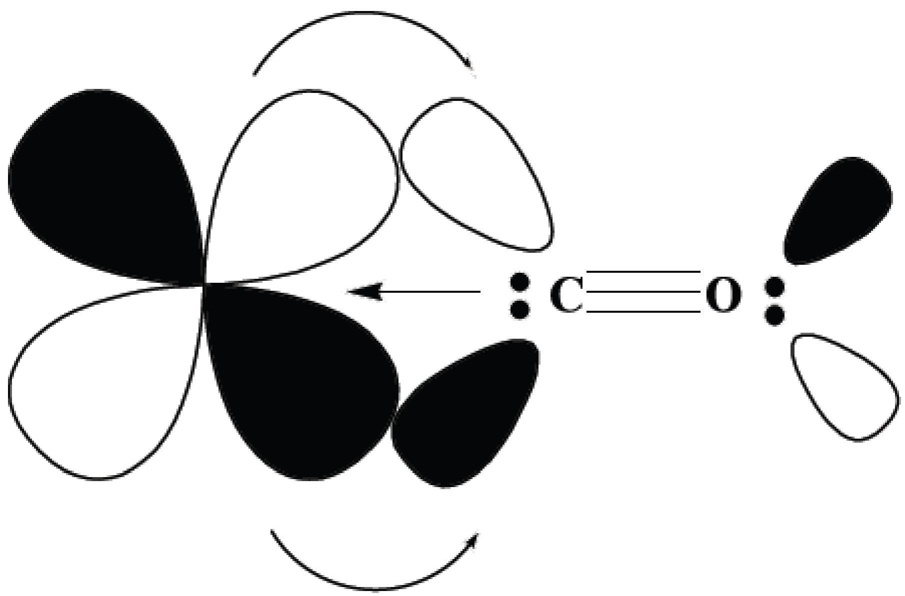
- Review of CO Molecular Orbitals
  - HOMO resides mostly on C = σ-donation
  - LUMO resides mostly on C = π-acceptance
  - Reinforce each other and provide strong bonding





The ***backbonding*** between the metal and the CO ligand, where the metal donates electron density to the CO ligand forms a ***dynamic synergism*** between the metal and ligand, which gives unusual stability to these compounds.

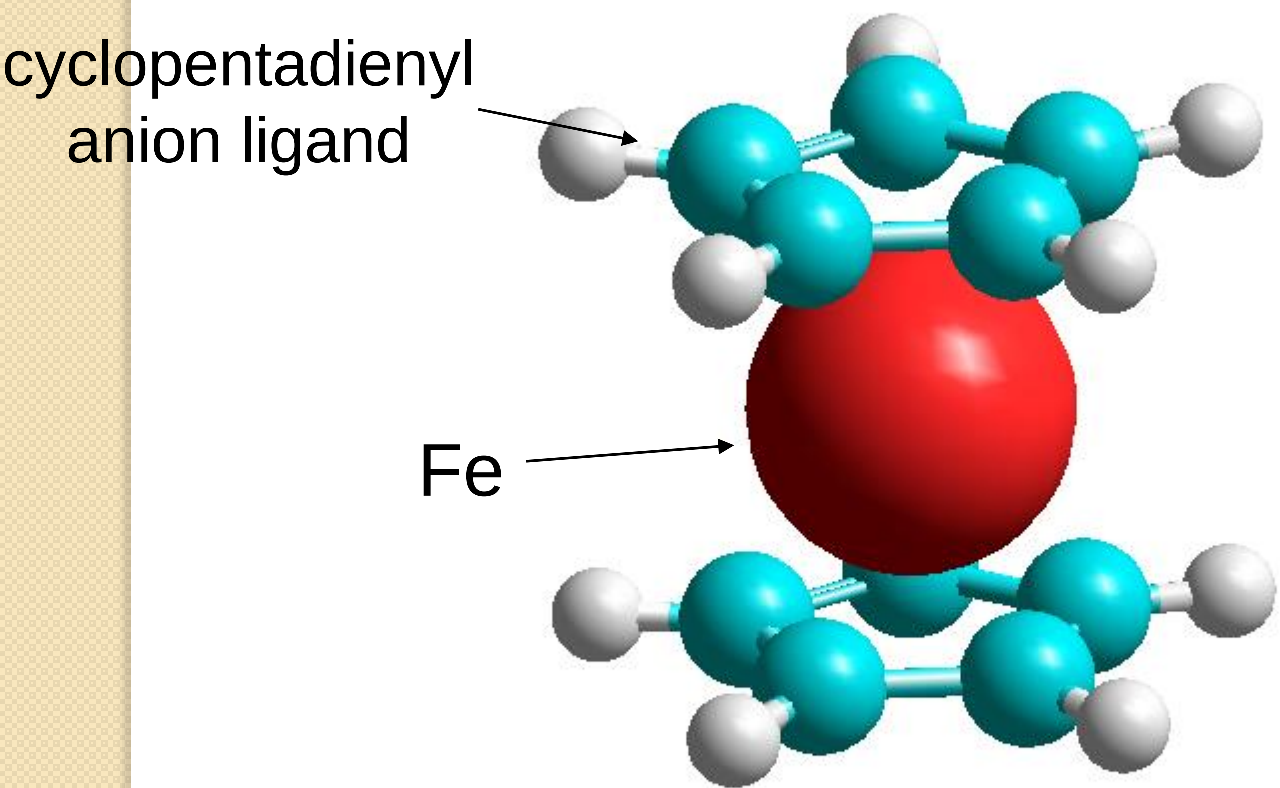
Dynamic synergism bonding



Valence Bond formalism: $\overset{-}{M}-C\equiv\overset{+}{O}: \longleftrightarrow M=C=\ddot{O}:$

FERROCENE

[(bis-cyclopentadienyl)iron] **$(\eta^5\text{-}C_5H_5)_2Fe$**



- Synthesis
  - Ferrous chloride with grignard reagent cyclopentadienyl magnesium halide
  - Metal cyclopentadienides ferrous halides in THF solvent
  - Cyclopentadiene on anh. Ferrous halide in presence of an amine
  - Iron or ferric oxide with cyclopentadiene at high temperature

Physical properties

- Orange coloured solid
- MP- 174˚C

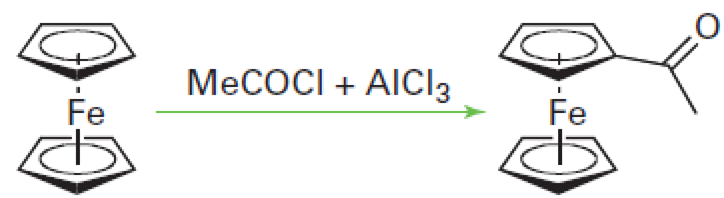
Chemical properties

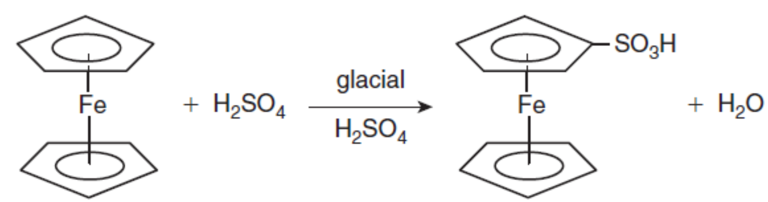
- Stable in air and thermally stable upto 500˚C
- It is stable towards hydrolysis, hydrogenation
- It does not undergo Diels Alder reaction showing unavailability of π electrons of the ring

Reactions of C_5H_5 rings

(Aromatic compound; undergo reactions like electrophilic substitution)

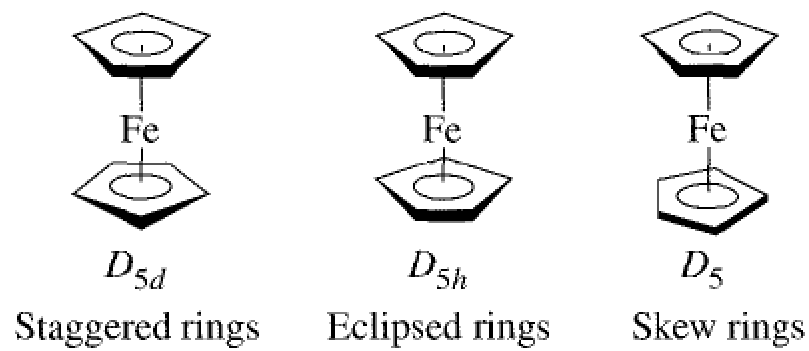
- Friedel Crafts Reaction (Alkylation and acylation)
- Sulphonation
- Nitration
- Bromination
- Mannich condensation
- Carboxylation

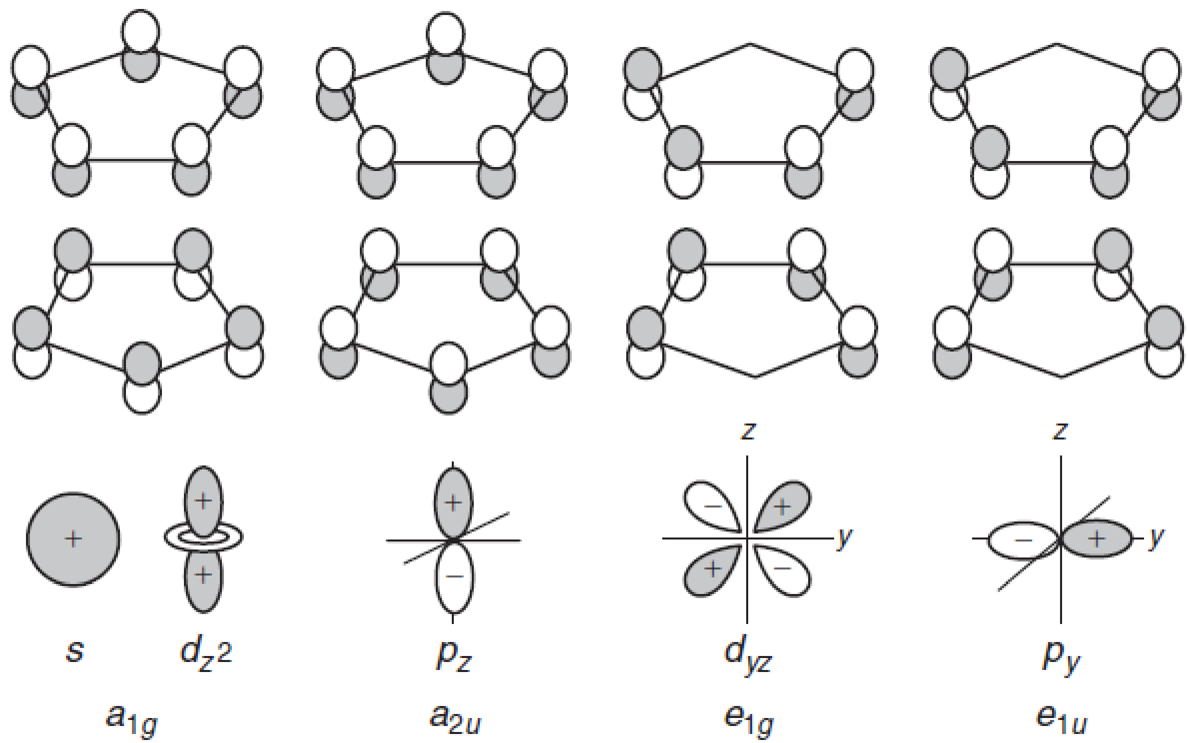




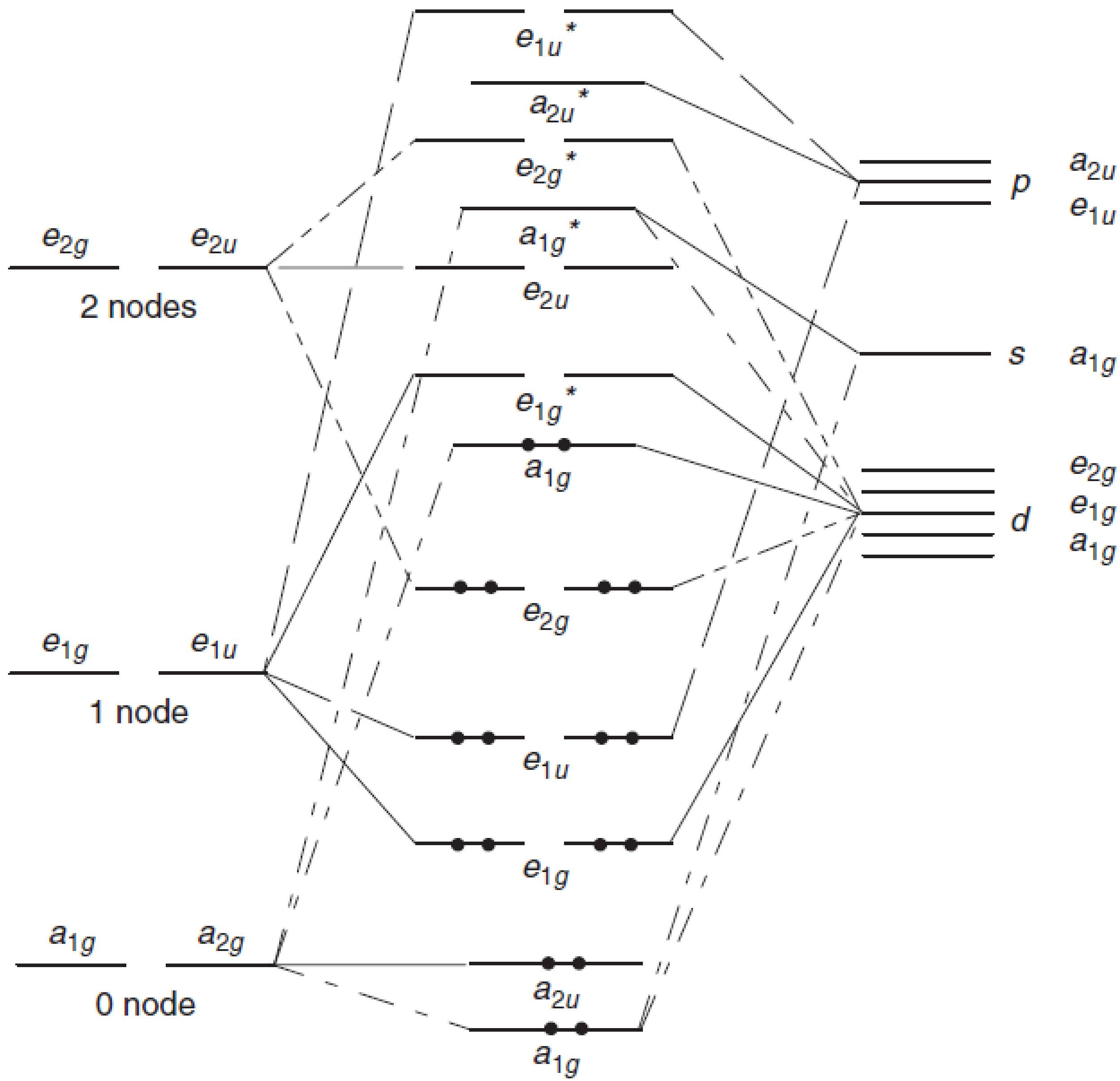
Structure and bonding in ferrocene

- Sandwich compound or metallocene
- Eclipsed and staggered ferrocene





The overlap of orbitals on Fe with the molecular orbitals on the cyclopentadienyl ion.



qualitative molecular orbital diagram for ferrocene.

Applications of organometallic compounds

- As synthetic reagents
  - Grignard reagents
  - Used widely in organic synthesis
- As catalysts
  - Many synthetic reactions like hydrogenation, polymerisation, hydroformylation etc.
  - Ziegler Natta Catalyst
  - Wilkinson catalyst

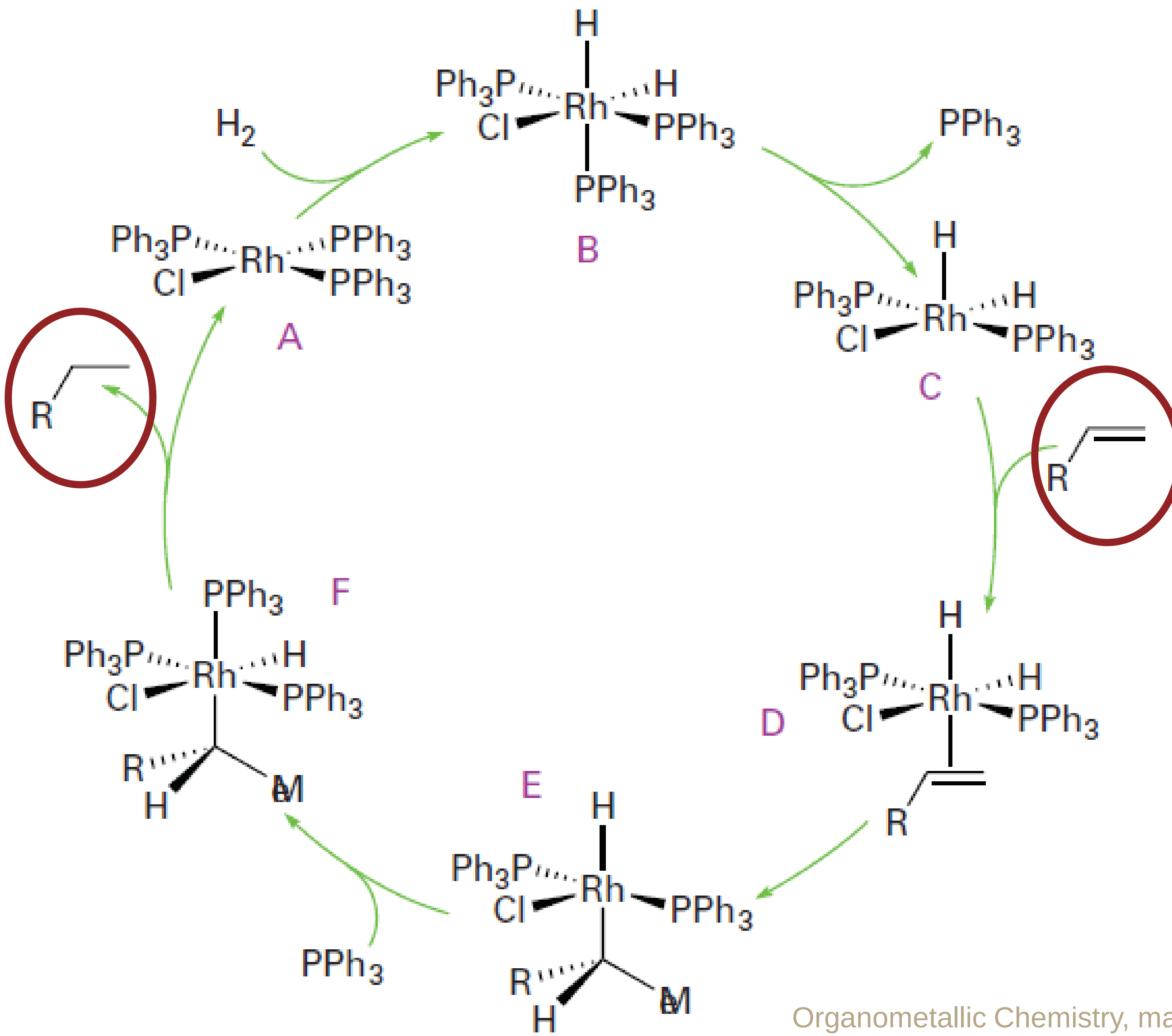
Ziegler-Natta Catalysts

Ziegler-Natta catalyst were a combination of $TiCl_4$ and $(CH_3CH_2)_3Al$

Used as a polymerisation catalyst

Wilkinson catalyst

- Selective Hydrogenation of terminal double bonds
- Tris(triphenylphosphine)rhodium(I)chloride $(PPh_3)_3RhCl$


A
B
C
D
E
F
H2
PPh3
PPh3
Ph3P
Cl
Rh
R


Thank You!