# Chemistry 423/523 Organometallic Chemistry

Introduction

- ◆ concerned with complexes containing M-C bonds but usually expanded to include hydrides (M-H) and carbonyls (M-CO) as well.

- ◆ relevance:
  - industrial catalysis
  - pharmaceutical industry
  - organic synthesis

- ◆ organometallic chemistry of the d-block has a long history dating back to Zeise's salt ($Na^+[PtCl_3(C_2H_4)]^-$) in the early part of the 19th century but most of the developments in this field date from 1950 on.

- ◆ major developments since 1950:
  - synthesis and structure of ferrocene (Pauson, Wilkinson and Fischer, Nobel 1973)
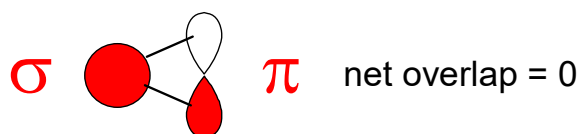 - Ziegler-Natta alkene polymerization (Nobel 1963)

A] Basic Bonding Concepts and M.O. Theory

A reminder of simple orbital interactions:

axial nodes

σ σ^* zero

π π^* one

δ δ^* two
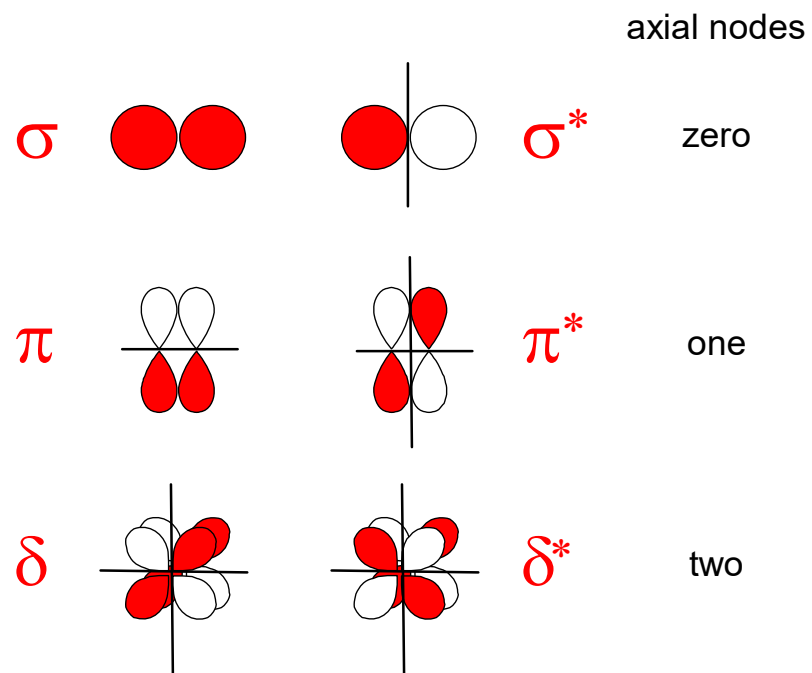
•symmetry is defined w.r.t. the internuclear axis

σ, π and δ bonding orbitals can always be treated separately because overlap between different classes of orbitals is identically zero.

σ π net overlap = 0

Criteria for strong orbital interactions:

• correct symmetry (σ, π or δ)

• spatial overlap - must occupy the same region in space

• similar energy - minimal interaction if very different in energy

eg. H_2 vs. HCl
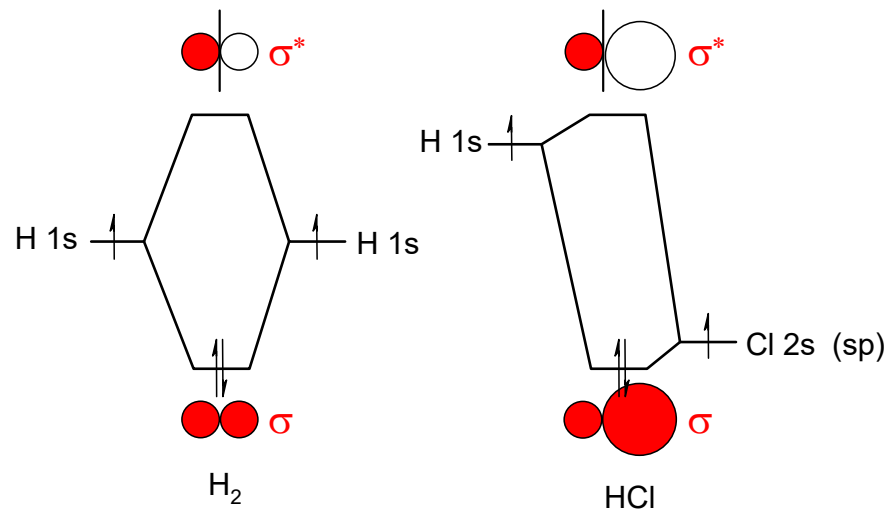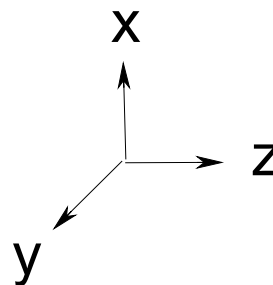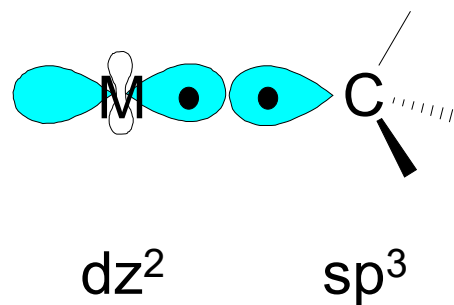

Note what the HCl diagram is telling you:
- the HOMO is mainly Cl in character and LUMO is mainly H in character
- the bond is very polar: H^+Cl^- is not a bad description

Metal-Ligand Bonding

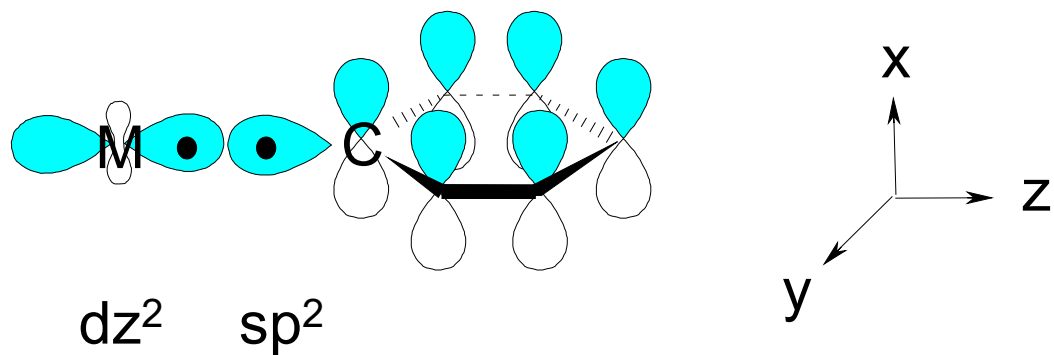**σ-Bonding:** no different from organic chemistry

M-C(alkyl) σ-bonding

dz^2 sp^3

M-C π-bonding can't occur: all available orbitals on C are involved in C-H (or C-R) bonding.

M-C(aryl) σ-bonding

dz²   sp²

x

z

y

M-C π-bonding does not occur because it would disrupt the aromaticity of the phenyl ring.

Trends in M-Me and M-H bond strengths

M-Me bonds are NOT weak

C-C single bond ~350 kJ/mol
H-H single bond ~436 kJ/mol
Cl-Cl single bond ~240 kJ/mol

- eg. Ta-Me 260 kJ/mol   Ge-Me 240 kJ/mol
- high reactivity is **kinetic** in origin

M-H bonds are stronger than M-Me for a given metal

- eg. Zr-Me 244 kJ/mol   Zr-H 249 kJ/mol
- *Rationale:* better overlap with spherical 1s orbital, no nonbonding electron repulsions and minimal steric repulsion for H

M-Me bond strength increases DOWN a group

- eg. Ti-Me 200 kJ/mol   Zr-Me 244 kJ/mol
- *Rationale:* overlap between the C 2s and 2p hybrids and TM d orbitals improves with increasing principal quantum number (3d are too contracted, projection of valence d orbitals beyond filled s and p shells is greater for 2nd and 3rd row TM).
- Note this trend is the ***opposite*** of that observed in the main group: Si-Me 290 kJ/mol vs Pb-Me 130 kJ/mol

M-Me bond strength increases to the left in the d-block

(early metals form stronger bonds to carbon)

- eg. Zr-Me 244 kJ/mol   Pd-Me 174 kJ/mol*   (* P.E.M. Siegbahn, J. Phys. Chem. 1995, 99, 12723)
- *Rationale:* better radial extension for the d orbitals and a better energy match with C 2s and 2p orbitals (the latter reaches a maximum latter for groups 6-8).

The difference in M-H and M-Me ($\Delta_{Me/H}$) bond strengths increases from left to right across the d-block
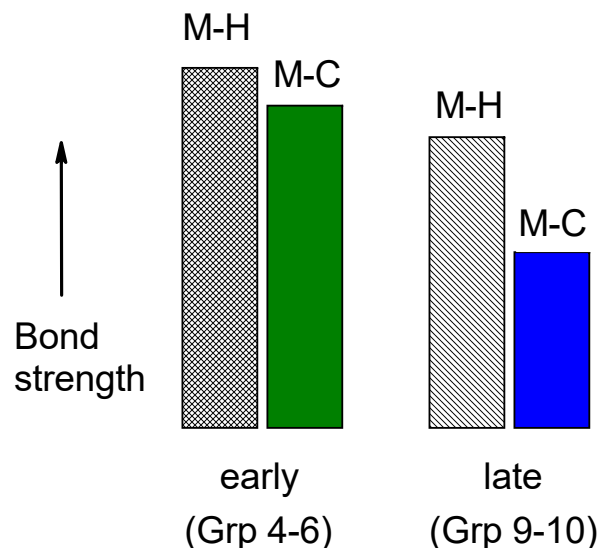
• *Rationale:* late d-block metals (groups 9-10) possess more nonbonding electrons than do early metals and this results in greatly increased repulsions with alkyl nonbonding electrons (in C-H or C-C bonds); H has no such electrons so this effect does not apply. It should be noted that electron density in C-H bonds is known to stabilize early transition metal alkyls (agostic bonding).

this point is one factor favouring **β-H elimination in late metals** (there are other factors involved too):

M — C(H$_2$) — CH$_2$ — H ⟶ M(H) — CH$_2$=CH$_2$
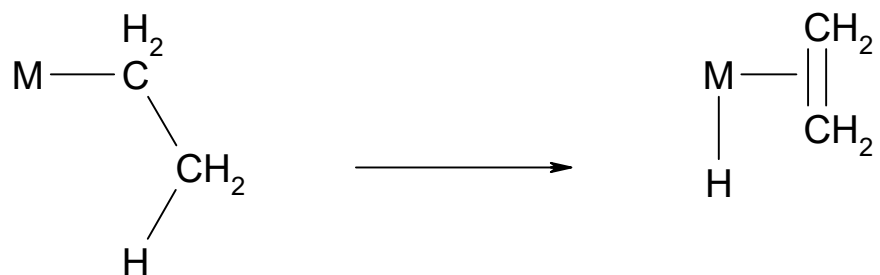
in contrast, early metals are known to **undergo β-alkyl elimination** even in cases where β-H elimination is possible:
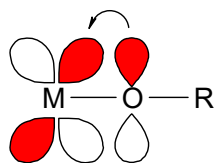
π-Bonding: **donor (ligand π → M) OR acceptor (M → ligand π*)**

π-donors: eg. amides and alkoxides
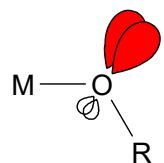
bent alkoxide (σ-only)

sp³ at O

linear alkoxide (σ and π donor)

sp at O (there is a second set of orbitals perpendicular to that shown)
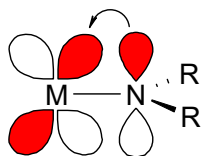
well supported by structural evidence:

Grp 4-6 M-O-R linear   *Grp 8-10*   M-O-R bent

M-NR₂ planar   M-NR₂ pyramidal

pyramidal amide (σ-only)

sp³ at N

planar amide (σ and π donor)

sp² at N

π-acceptors: **eg. carbon monoxide and alkenes**

Carbonyl Bonding

a) σ-donation: from the *HOMO of CO* (5σ orbital) to an *empty metal orbital* (s, p or d) of correct symmetry

b) π-back donation: from a *filled metal orbital* to the *empty LUMO* of CO (2π)

empty ⬅ filled

dz^2 5σ

(a)

filled ➡ empty

d_{xz} 2π

(b)
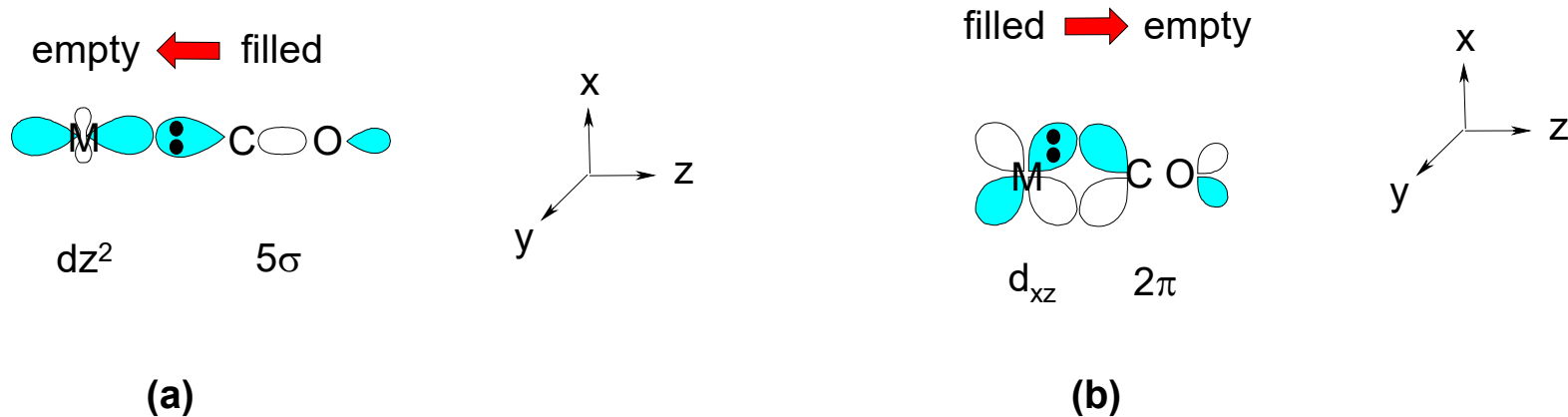
NB: Removes negative charge from the metal

Synergic effects:

π promotes σ

- ♦ back donation maintains electron density on C while preventing excessive negative charge buildup on M

σ promotes π

- ♦ donation makes the metal more electron rich and therefore more willing to engage in back donation

- ♦ The two types of bonding are ***COOPERATIVE***

- ♦ This type of bonding is **not unique** to CO; it also applies to N_2, CN^-, NO^+ (an isoelectronic series) and many others

Net effect: electron density is removed from the weakly C-O bonding 5σ level and put it into the strongly C-O antibonding 2π level.

Predictions:

♦ **M-C** bond should be ***stronger*** and ***shorter*** than a normal single bond

♦ **C-O** bond should be ***weaker*** and ***longer*** than a normal triple bond

♦ Both of these predictions are born out by experiment:

 ▪ **IR** for stretching frequencies (ie. bond strength)
 ▪ **X-ray** for bond length

IR evidence is most compelling for CO stretching vibrations but M-C can also provide some useful information:

***free* CO** $\qquad$ ν_{CO} **= 2143 cm^{-1}**
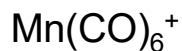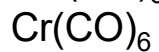
$Mn(CO)_6^+$	ν_{CO} = 2090 cm^{-1}	ν_{MC} = 416 cm^{-1}
$Cr(CO)_6$	ν_{CO} = 2000 cm^{-1}	ν_{MC} = 441 cm^{-1}
$V(CO)_6^-$	ν_{CO} = 1859 cm^{-1}	ν_{MC} = 460 cm^{-1}

Alkene Bonding

σ-donation

z
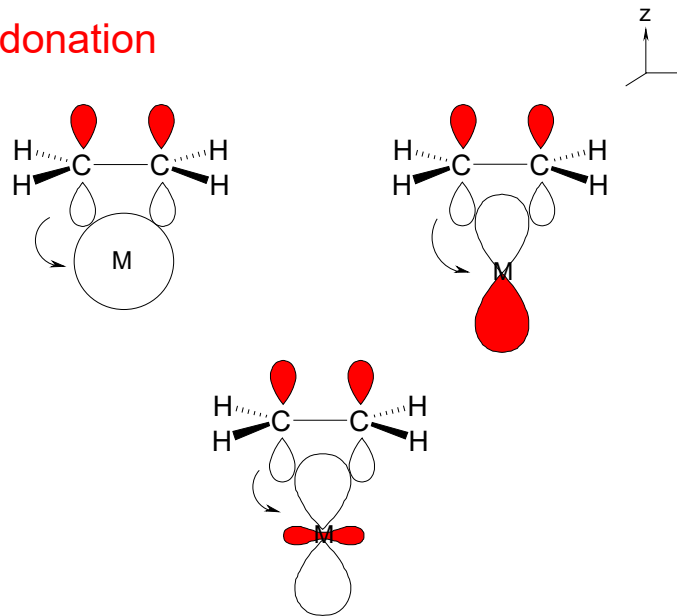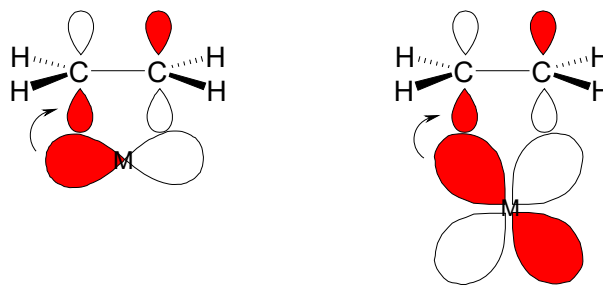
π-back donation

Effects on C=C bond

σ-donation:

removes e⁻ density from the C-C π bonding HOMO

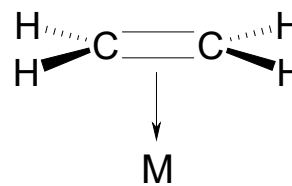**π-back donation:**

places e⁻ density in the C-C π* antibonding LUMO

Both LOWER the C-C bond order ∴ weaker (longer) C-C bond and $\upsilon_{C=C}$ decreases by 50-150 cm^{-1} in the IR on complexation (free C$_2$H$_4$ $\upsilon_{C=C}$ = 1623 cm^{-1})

Bending back of alkene substituents.   **A metallacyclopropane**

Alkene bonding falls between two extremes:
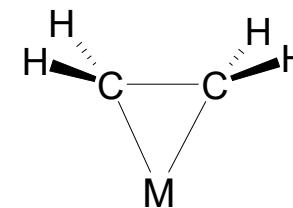
Planar alkene   **Alkene substituents bent back (sp³ C)**

σ donation dominant   π back donation dominant

Dual π-Donor/Acceptor Ligands:

Alkynes and Conjugated π-systems

$\pi^*_{\parallel}$

H—C≡C—H

d_{xz}

(p_x)

π back donation

$\pi^*_{\perp}$

H—C≡C—H

d_{xy}

δ back donation

$\pi_{\parallel}$

H—C≡C—H

d_{z^2}

(s, p_z)

σ donation

$\pi_{\perp}$

H—C≡C—H

d_{yz}

(p_y)

π donation

z
y   x

40°

Ph

Ph_3P

Pt

Ph_3P

Ph

1.32 A

$\nu_{cc} = 1750$ cm^{-1}

free HCCH 2100 cm^{-1}
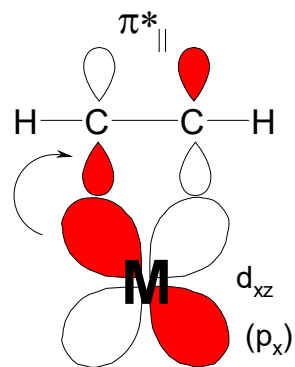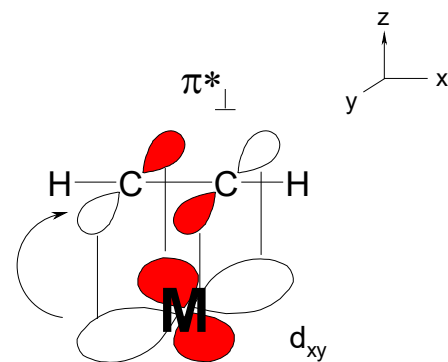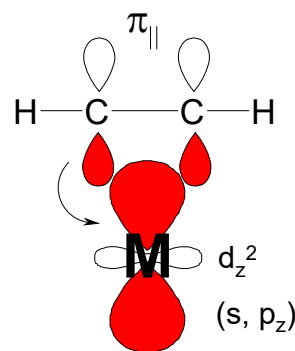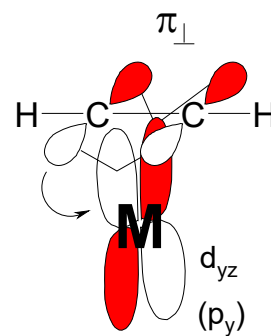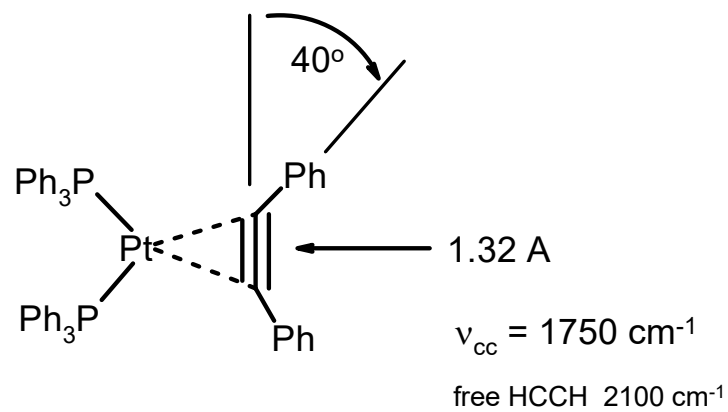
Alkynes as 2 e$^-$ donors:

real situation falls between two extremes

Ph_3P Ph

Pt

Ph_3P Ph

OR

Ph

Ph_3P

Pt

Ph_3P

Ph
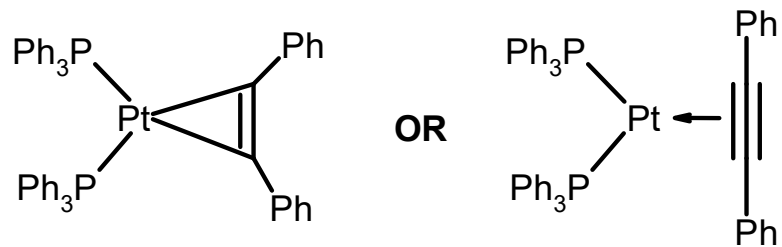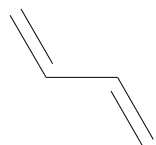
A metallacyclopropene

Conjugated diene complexes

dienes usually coordinate to metals
through the s-cis conformer

Increasing energy ⟶

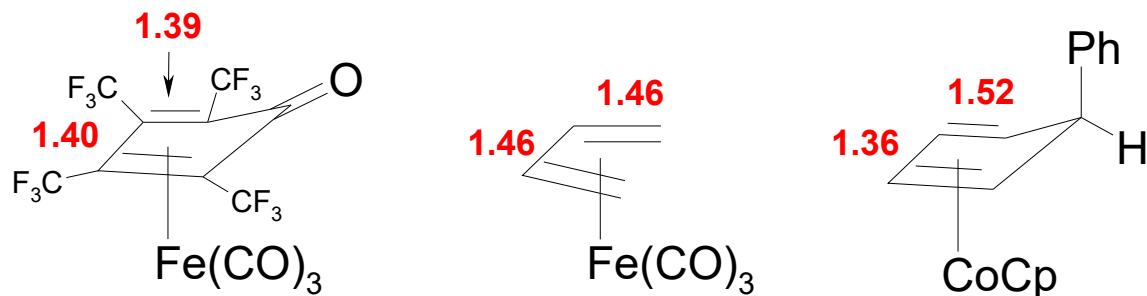π_1 π_2 π_3 π_4

s-cis   s-trans

Metal
orbitals $d_z{}^2$ d_{yz} d_{xz} d_{xy}

(s, p_z) (p_y) (p_x)

σ π π δ

donation   donation   back   back
                 donation   donation
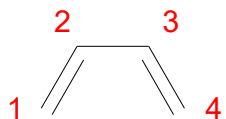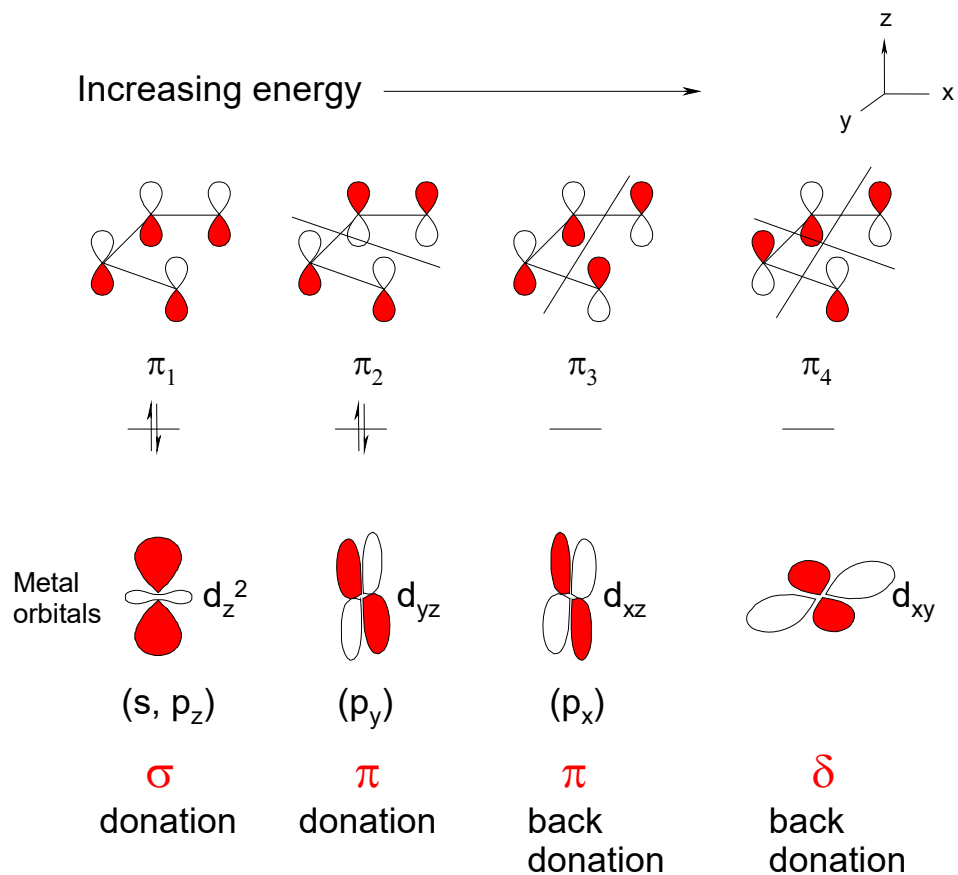
Net effect:

C1-C2 and **C3-C4** *bond lengthens* [π^3 antibonding]

C2-C3 *bond shortens* [π^3 bonding]

- degree of bond lengthening depends on the metal and the other ligands present

- real situation is again found between two extreme views:

A metallacyclopentene

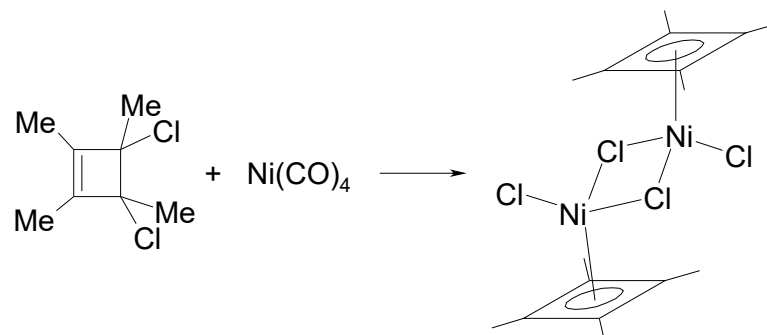# Cyclobutadiene complexes

Free cyclobutadiene is unstable

1956   Orgel predicted stable cyclobutadiene TM complexes on the basis of MO theory
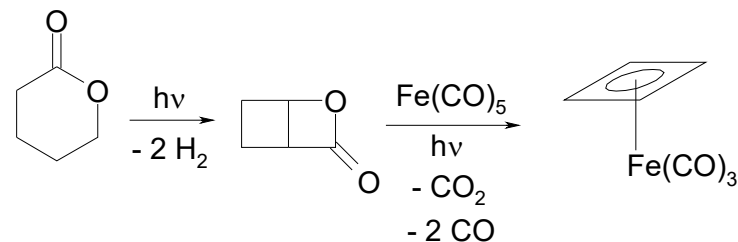1959   Criegee prepared 1st cyclobutadiene complex

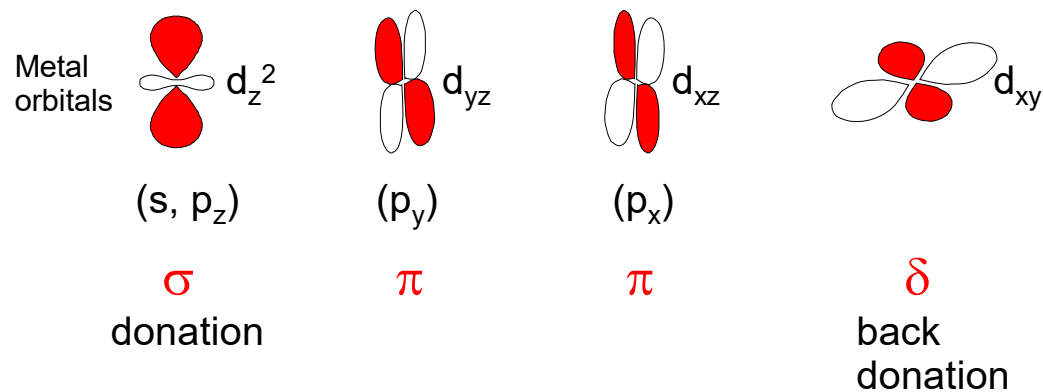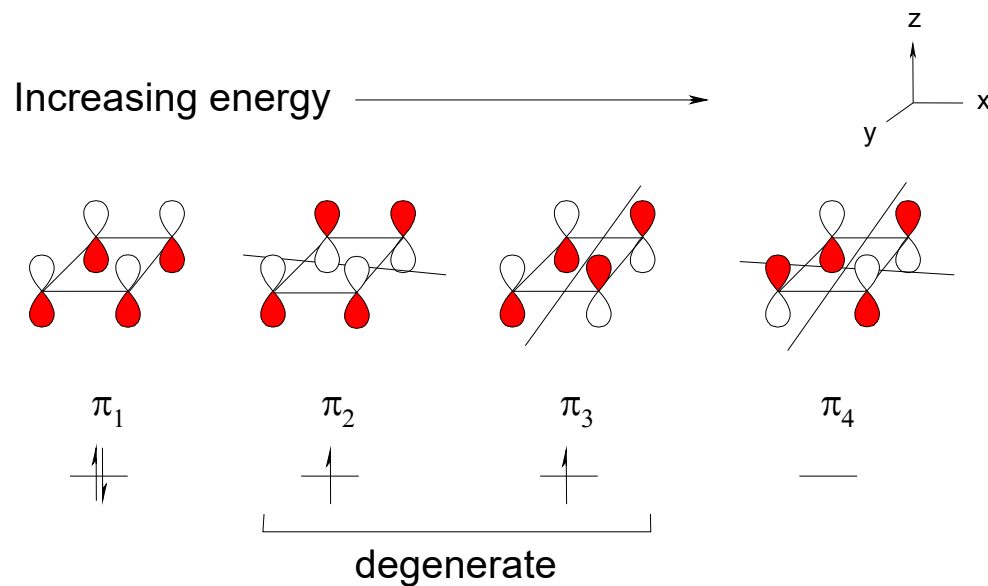4π electrons
anti-aromatic

rectangular
(diradical if square)

Later:

Planar C_4R_4 units, equal C-C bonds lengths, very e⁻ rich
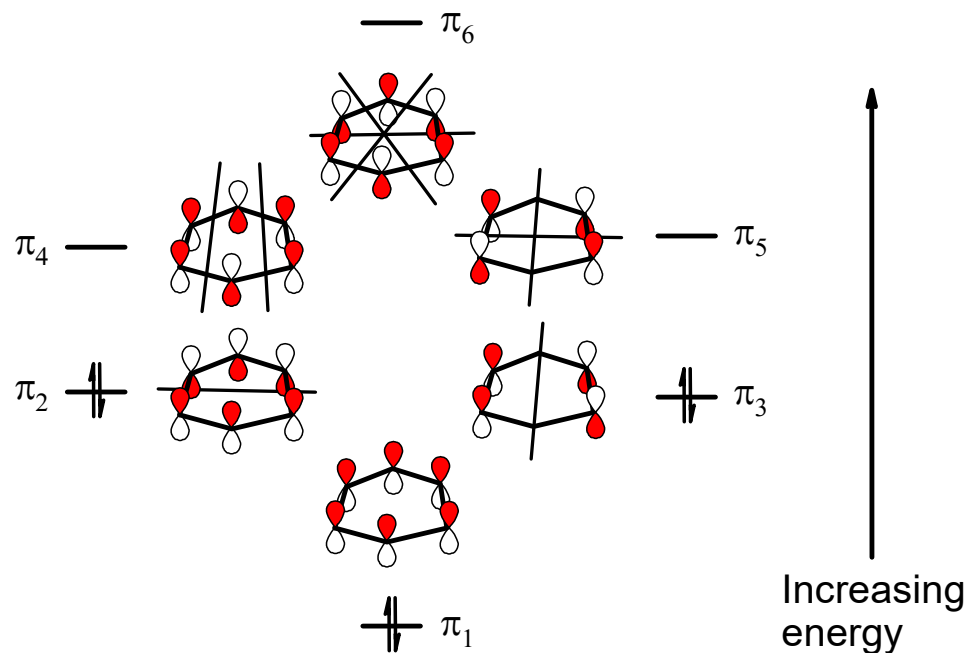
Bonding is very similar to butadiene

Increasing energy ⟶

z, x, y

π_1 π_2 π_3 π_4

degenerate

Metal orbitals

d_{z^2} d_{yz} d_{xz} d_{xy}

(s, p_z) (p_y) (p_x)

σ π π δ

donation   back donation

Cyclic conjugated π-systems

polygon trick: a useful device for remembering the π-**orbital pattern for cyclic conjugated systems**

- **with the polygon representing the cyclic π-system point placed point downwards, the orbital pattern energy pattern is given by drawing energy levels at each corner**

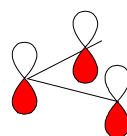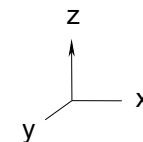- **number of nodes increases by one for each energy step**
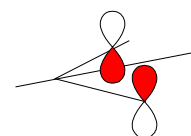
eg. benzene

3 nodes
2 nodes

1 node

0 nodes

π_6

π_4 π_5

π_2 π_3

π_1
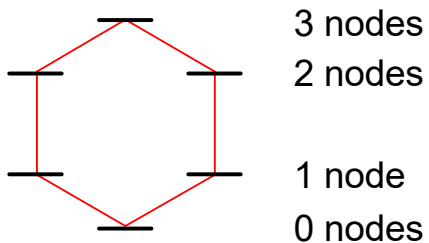
Increasing energy

Allylic systems

Increasing energy ⟶

z ↑ / x, y

π_1 π_2 π_3

⇅   ⇅   —

Metal orbitals d_{z^2} d_{yz} d_{xz}

(s, p_z) (p_y) (p_x)

σ π π

donation   donation   back donation