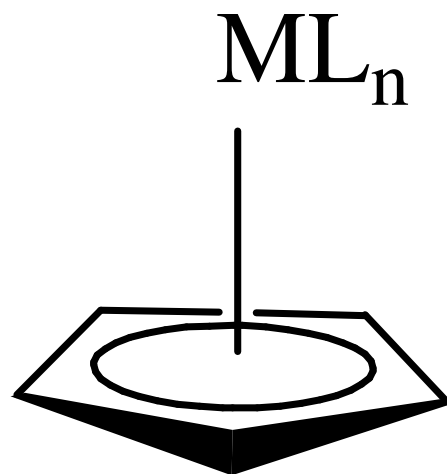
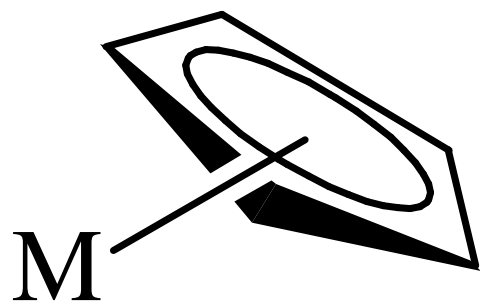


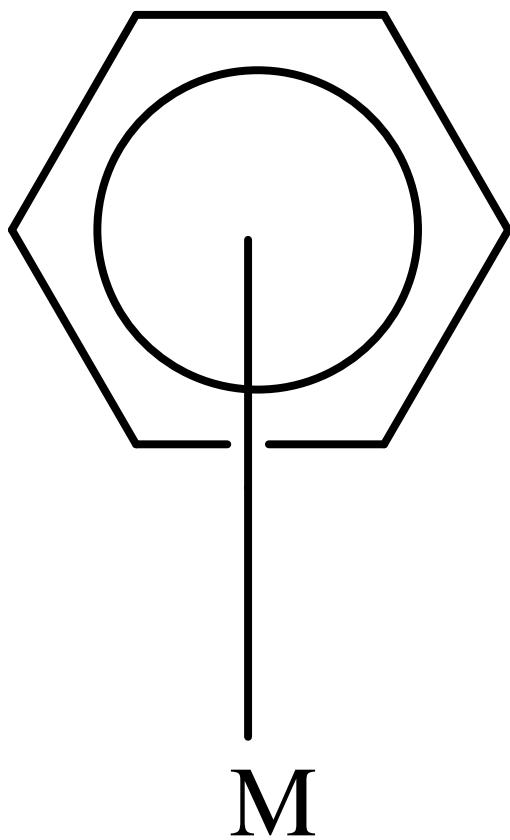
ORGANOMETALLICS

CHEM 245

- An organometallic compound contains one or more metal-carbon bonds.
- Haptacity of a ligand (η , eta): Number of atoms that are directly bonded to the metal centre.
- $[\eta^5\text{-C}_5\text{H}_5]^-$ cyclopentadienyl: Cp^-



$\eta^6\text{-C}_6\text{H}_6$



Some of the most common ligands found in organometallic chemistry:

σ -bonded alkyl, aryl and related ligands:

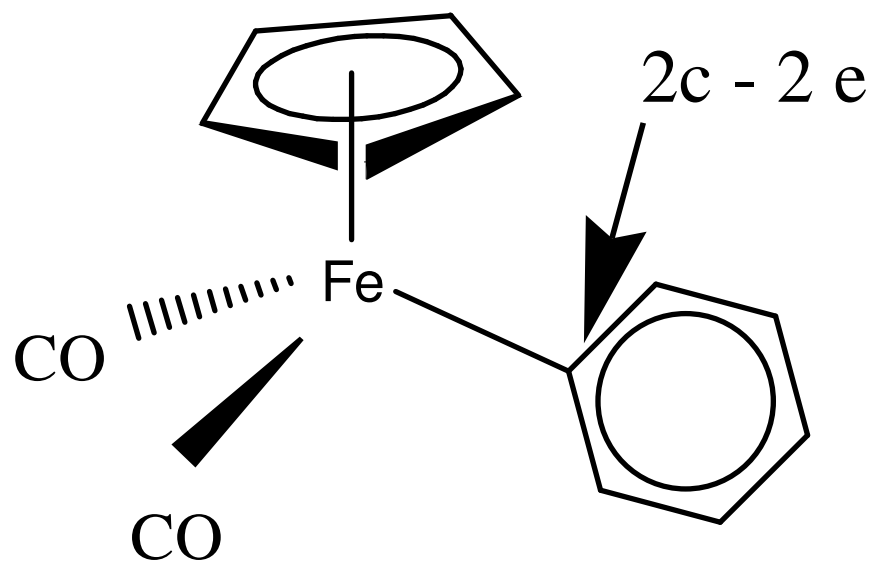
η^1 -mode:

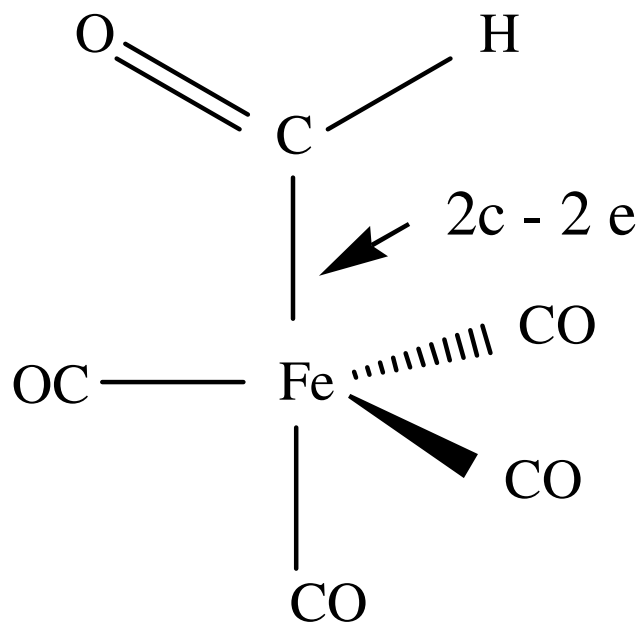
$WMe_6 \rightarrow M-C_{Me}$ bond
(single bond)

= localised bond

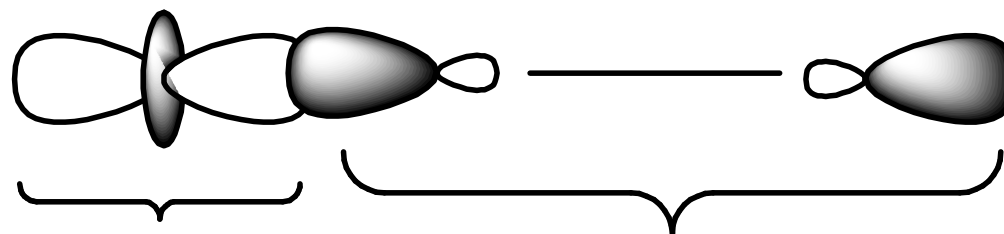
= 2 centre – 2 electron
interactions

= $2c - 2e$

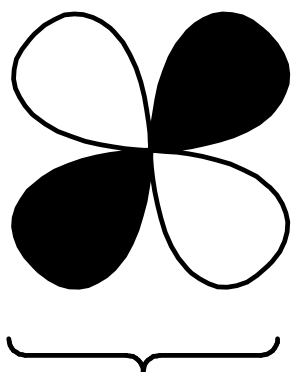




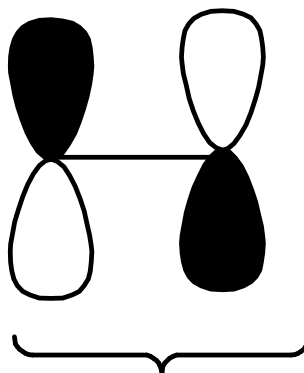
CARBONYL LIGAND:



Vacant metal orbital HOMO of CO
CO-to-M donation



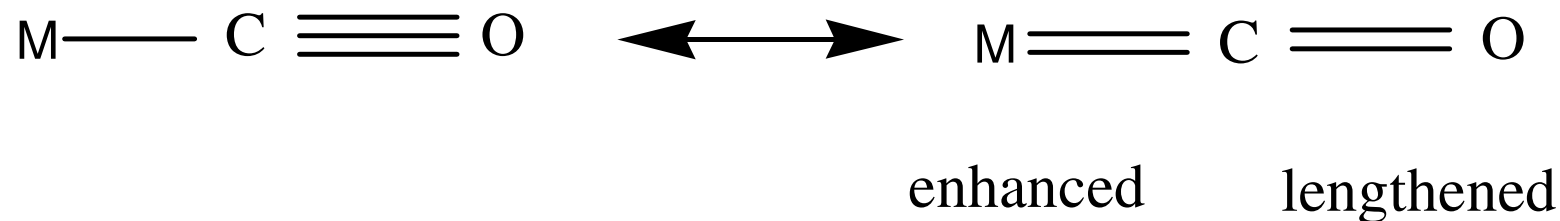
filled metal d_{xz}
or d_{yz} orbital



M-to-CO back donation

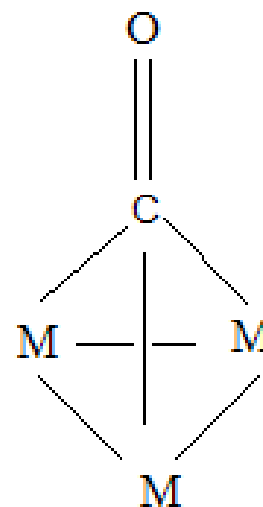
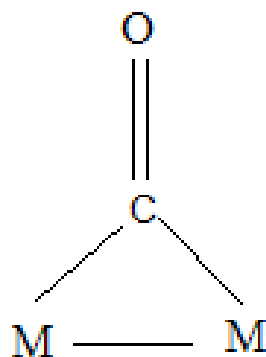
Vacant antibonding
pi orbital of CO

- HOMO of CO has predominantly C character.
- Vacant orbital of M ($sp_z d_{z^2}$ hybrid)
- Donation = back-donation model = Dewar-Chatt-Duncanson model
- CO \rightarrow weak σ -donor but strong π -acceptor (or π -acid)



Lowering of C-O bond order wrt free CO

In multinuclear metal species, CO ligands may adopt terminal, bridging modes.



μ^3 -CO

HYDRIDE LIGANDS: $\text{H}^{\delta-}$

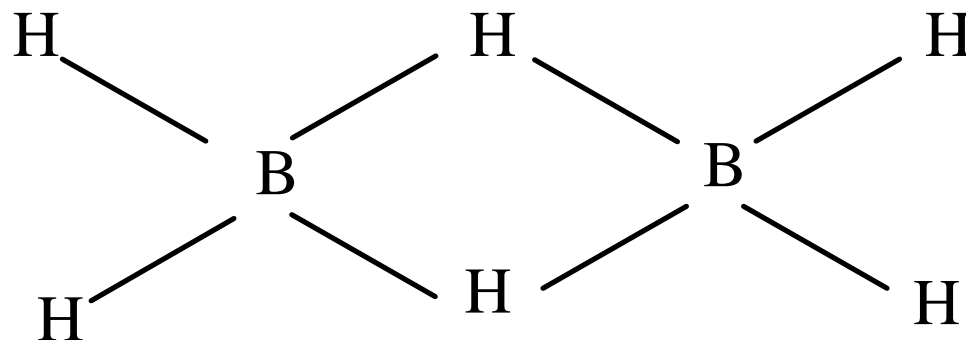
- (H atom attached to an electropositive metal centre)
- Bonding of H atom to M is simple because the only orbital of appropriate Energy for bonding on the hydrogen is 1s.
- M-H bond is based on σ -interactions.
- An M-H bond can sometimes be produced by protonation of an organometallic compound, such as neutral and anionic metal carbonyls.
- Ferrocene can be protonated in strong acid to produce Fe-H bond:
- $\text{Cp}'_2\text{Fe} + \text{HBrF}_4 \rightarrow [\text{Cp}_2\text{FeH}]^+[\text{BF}_4]^-$

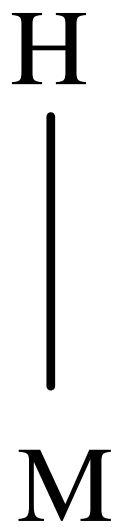
Bridging hydrides exist.

H-atom bridges 2 or 3 metal atoms

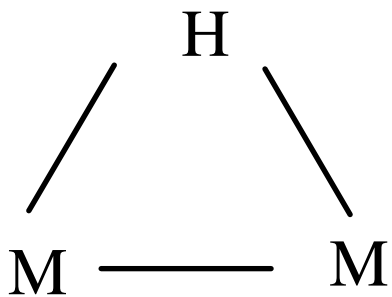
(like 3c-2e diborane B_2H_6 in which 2 electrons are shared between 3 atoms.)

Bridging bonds are longer and weaker than terminal ones:

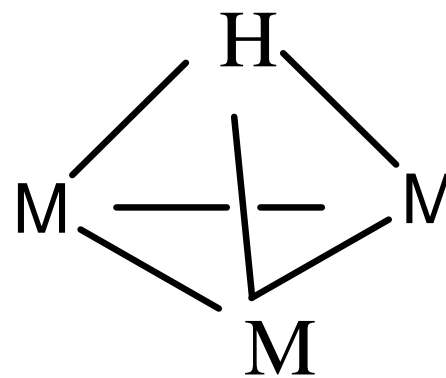




2c -2e (μ -H)



3c -2e (μ^2 -H)



4c -2e (μ^3 -H)

PHOSPHINES AND RELATED LIGANDS

- Monodentate organophosphines are:
 - TERTIARY: PR_3
 - SECONDARY: PR_2H or
 - PRIMARY: PRH_2
- They are terminally bound.
- Phosphines are σ -donor, π -acceptor ligands.
- Although they are not organometallic (i.e. no bonding to M through C), phosphines are discussed because of the similarities of their bonding to CO!

- PH_3 : Phosphine
 - Reactive, poisonous, flammable gas
 - Can behave as Lewis base
 - Rarely used as ligand
- Substituted phosphines(eg. PMe_3 , PEt_3 , triarylphosphines PPh_3 , etc)
 - Easy to handle, non toxic, air-stable solids
 - Widely used as ligands
- P atom is used as σ -donor.
- Empty orbitals on P atoms act as π -acceptors from M (analogous to CO-M)

Basicity of Phosphines (consider electronegativity of the substituent on P):



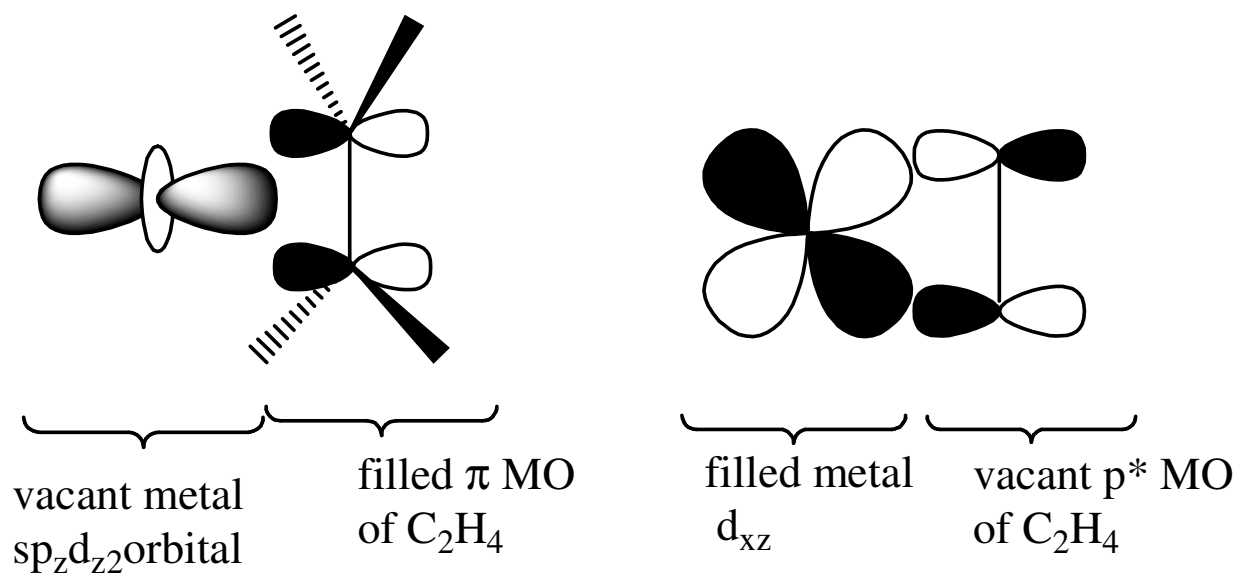
Good acceptor

π -BONDED ORGANIC LIGANDS:

ALKENES

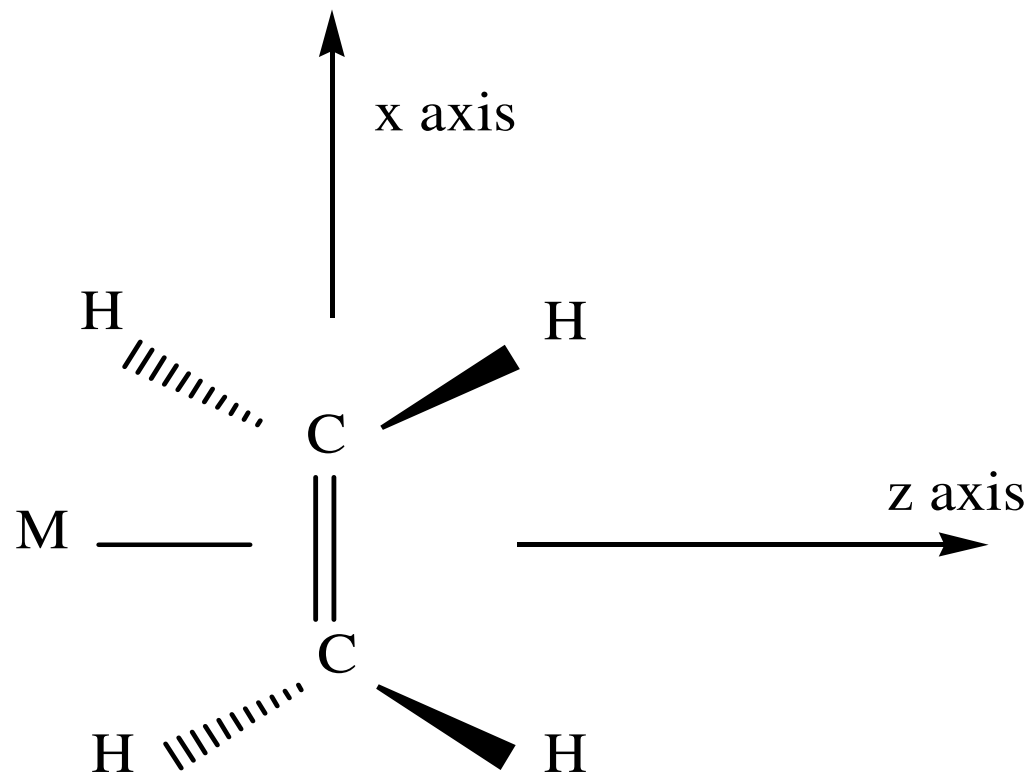
- These tend to bond to metal centres in a side-on (i.e. η^2) manner and behave as 2-electron donors.
- M-Ligand bond is described as Dewar-Chatt-Duncanson model.

The C=C π -bonding MO acts as an e-donor,
 π^* - MO is an e-acceptor (C-C bond lengthens)



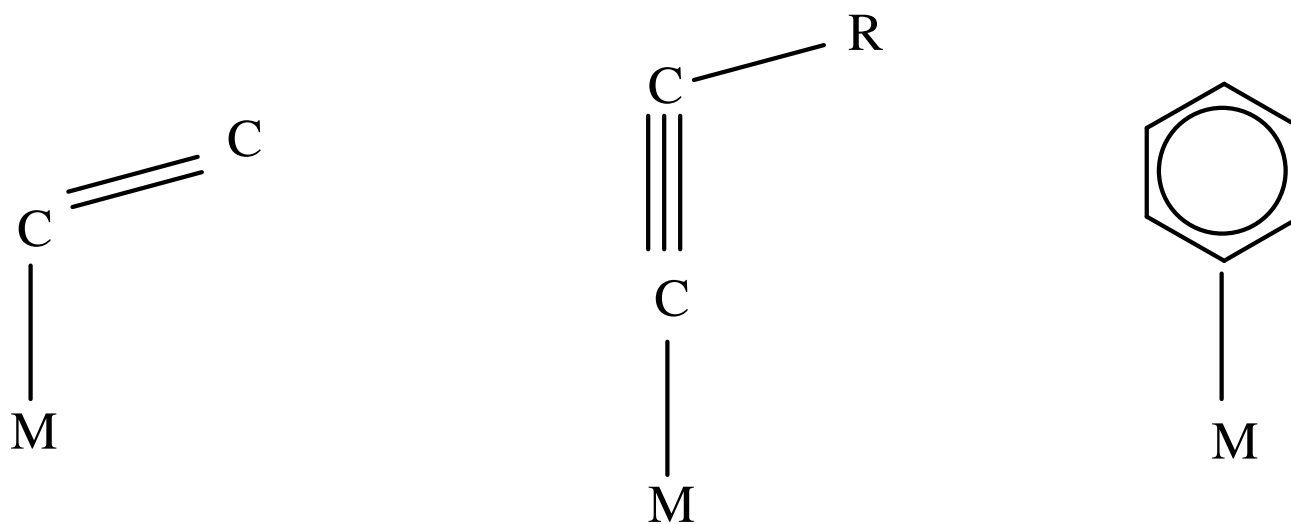
Alkene -to - M
donation

M - to - alkene
back donation



Extent of back-donation depends on R in $R_2C=CR_2$.
It is enhanced by e-withdrawing groups such as CN.

Metal-ligand bonding of η' -hydrocarbon ligand is σ -type:

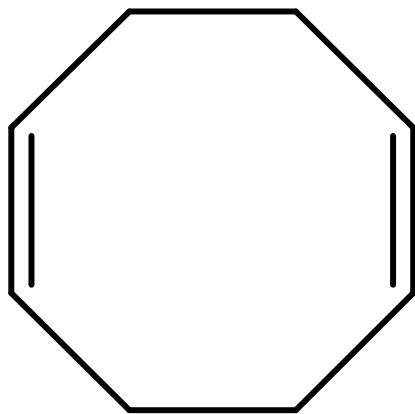


Monohapto = M-C bond

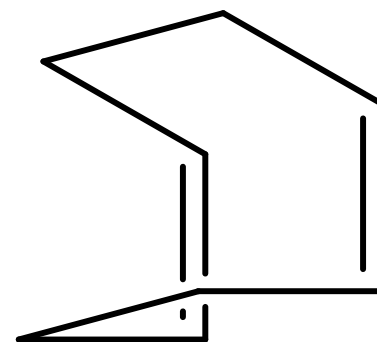
- Alkynes have 2 π -bonds and hence the potential to be 4-electron donors.
- When side-on to a single M atom, the η^2 -C-C triple bond (η^2 -C \equiv C) is considered a 2-electron donor. The π^* orbitals accept electrons from metal atom as in alkenes.
- When strongly electron-withdrawing substituents are attached, the ligand can become an excellent π -acceptor.
- Example: CH₃OCOC \equiv CCO₂CH₃
- The extent of back-donation to R₂C=CR₂ is influenced by the nature of R, and is enhanced by e-withdrawing groups such as CN.
- The bonding description of a coordinated alkene can be extended to other unsaturated organic ligands.

Polyalkenes may or may not be conjugated.

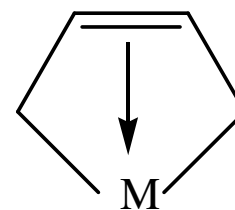
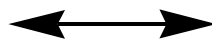
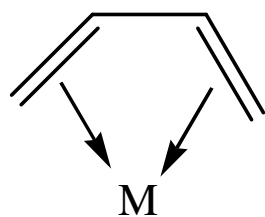
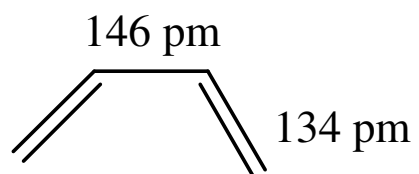
In **non-conjugated systems** (e.g. cycloocta-1,5-diene),
the M-L bonding is analogous to isolated alkene groups:



or



In conjugated polyenes such as buta-1, 3-diene, a delocalised bonding picture is appropriate:



Limiting resonance structures

The allyl ligand $[C_3H_5]$ - coordinates in an η^3 -mode.

