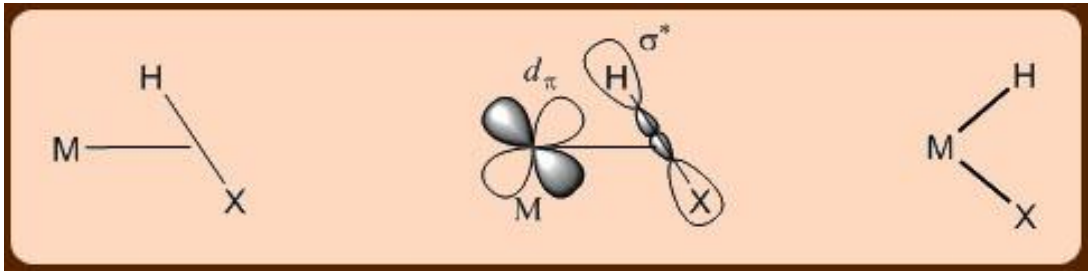
Classification of Ligands

Classification of Ligands

σ -bonded Alkyl, Aryl, and Related Ligands

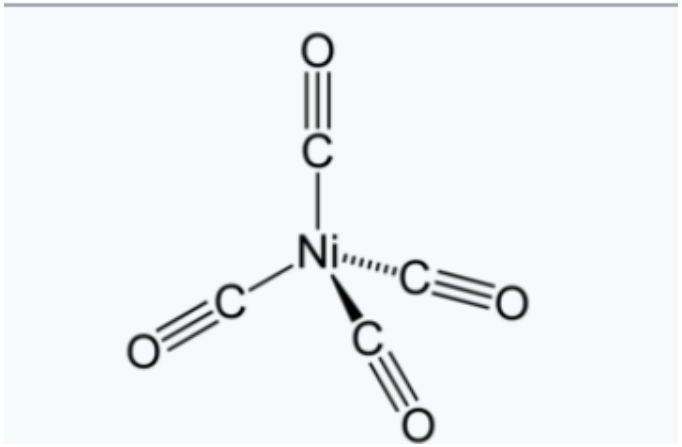
- σ−complexes are rare compounds, in which the σ bonding electrons of a X−H bond further participate in bonding with a metal center (X = H, Si, Sn, B, and P).
- The σ complexes thus exhibit an a skewed binding to a metal center with the hydrogen atom, containing no lone pair, being more close to the metal center and thereby resulting in a side−on structure.
- Many times if the metal center is electron rich, then further back donation to the σ* orbital of the metal bound X−H moiety may occur resulting in a complete cleavage of the X−H bond.



Carbonyl Ligands

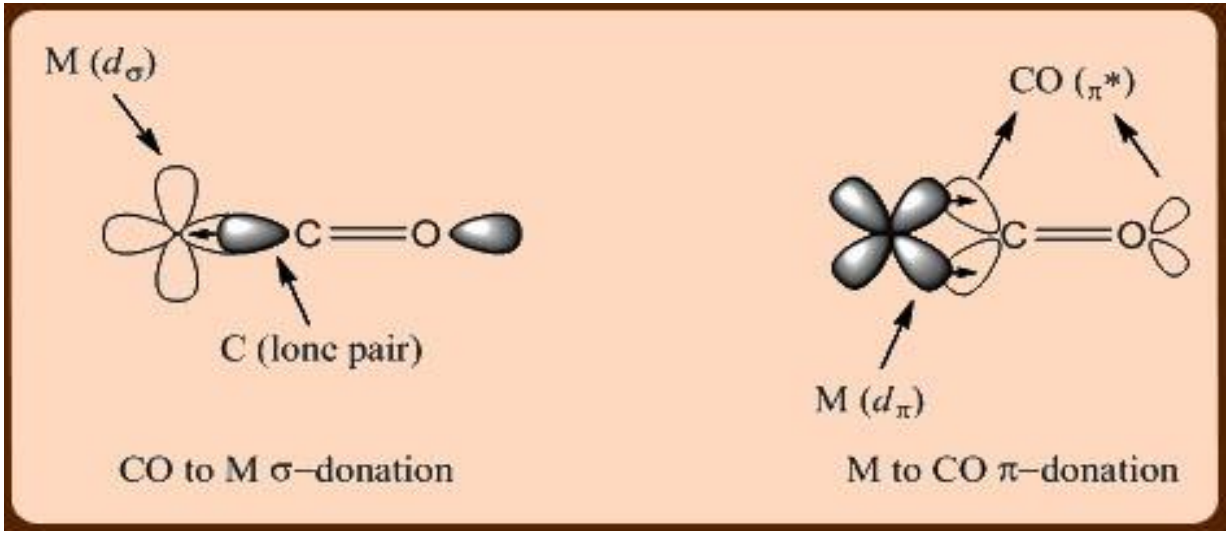
- Metal carbonyls are important class of organometallic compounds that have been studied for a long time.
- Way back in 1884, Ludwig Mond, upon observing that the nickel valves were being eating away by CO gas in a nickel refining industry, heated nickel powder in a stream of CO gas to synthesize the first known metal carbonyl compound in the form **$Ni(CO)_4$**.
- The famous Mond refining process was thus born, grounded on the premise that the volatile $Ni(CO)_4$ compound can be **decomposed** to pure metal at elevated temperature.

Nickel tetracarbonyl



Carbonyl Ligands

- The carbonyl ligand (CO) distinguishes itself from other ligands in many respects.
- For example, unlike the alkyl ligands, the carbonyl (CO) ligand is **unsaturated** thus allowing not only the ligand to σ**−donate but also to accept electrons in its π* orbital from d_π metal orbitals** and thereby making the CO ligand π−acidic.
- The other difference lies in the fact that CO is a soft ligand compared to the other common σ−and π−basic ligands like H_2O or the alkoxides (RO−), which are considered as hard ligands.



Preparation of metal carbonyl complexes

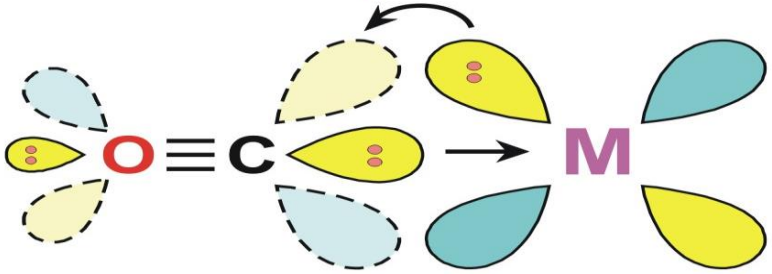
The common methods of the preparation of the metal carbonyl compounds are,

1.Directly using CO

The main requirement of this method is that the metal center must be in a **reduced low oxidation state** in order to facilitate CO binding to the metal center through metal to ligand π−back donation.

Carbonyl Ligands - C≡O

empty π-acceptor orbitals on carbonyl*



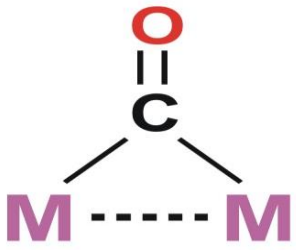
powerful π-acceptor ligand!

excellent ligand, therefore, for stabilizing electron-rich low-valent metal centers

Standard Bonding Modes:

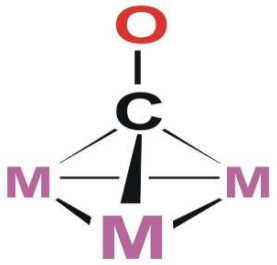
terminal mode

2e⁻ neutral donor



μ_2– bridging mode

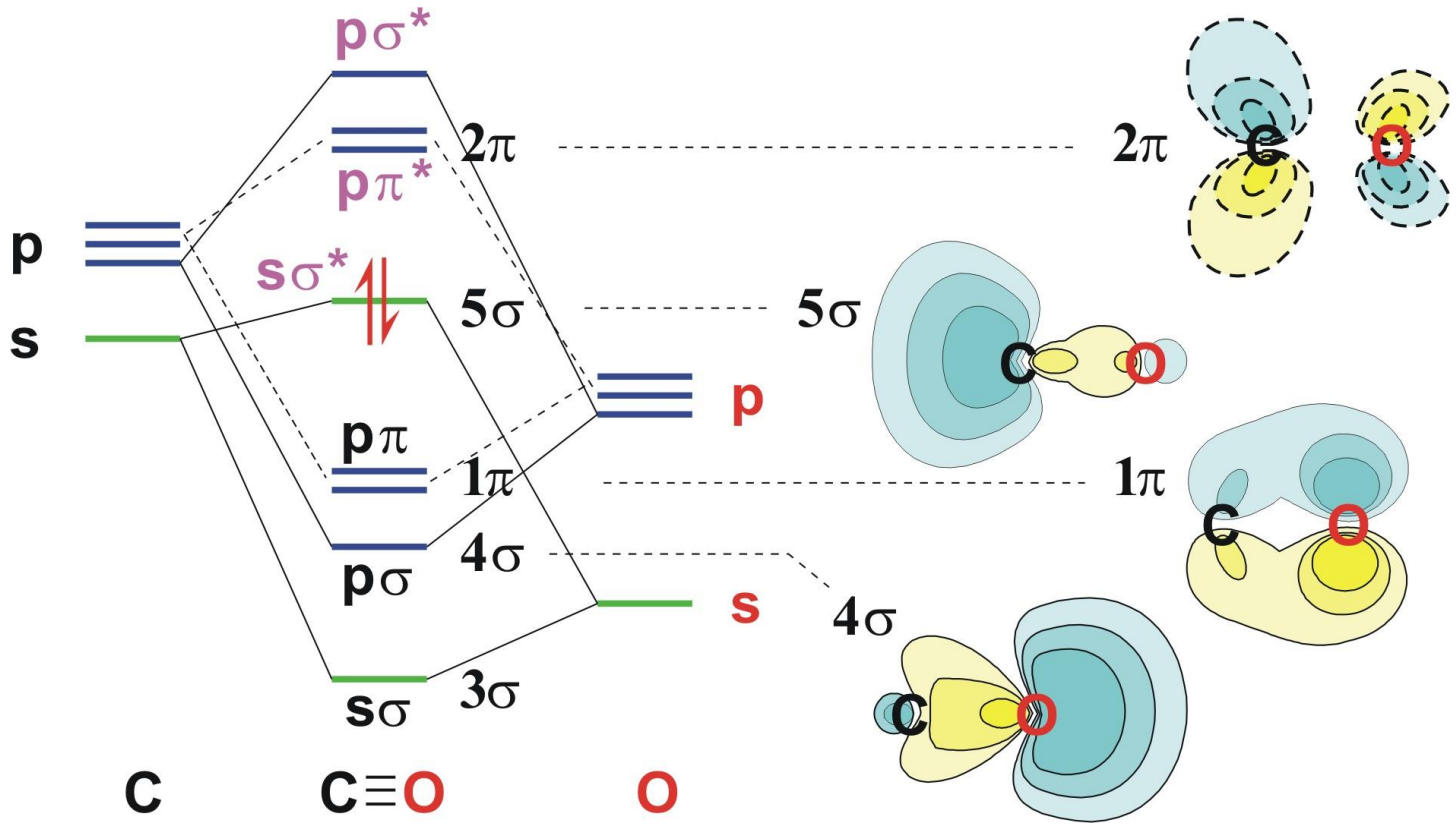
2e⁻ neutral donor



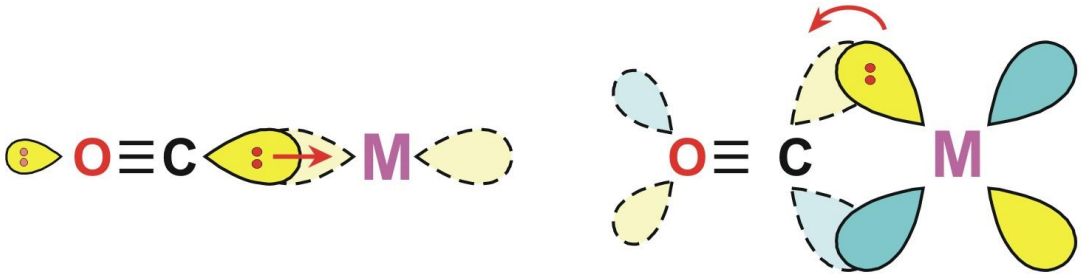
μ_3– bridging mode

3e⁻ neutral donor

Molecular Orbital (MO) Diagram



Types of CO- Metal bonding interactions:



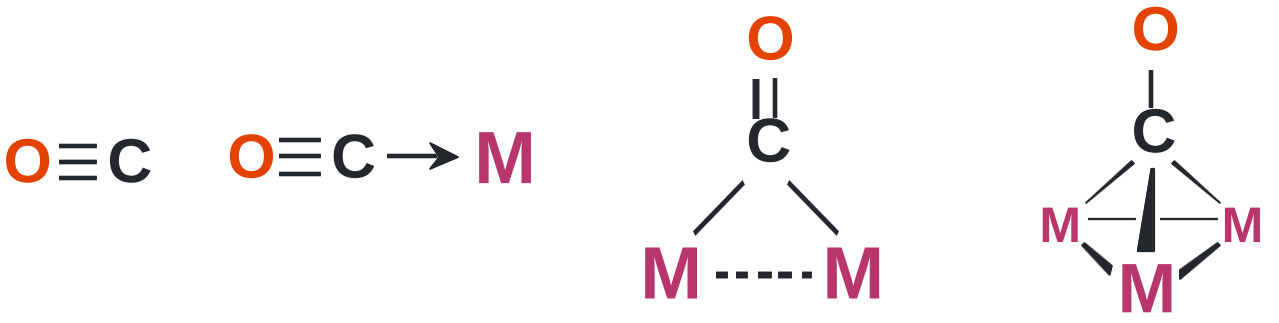
CO-M sigma bond

M to CO pi backbonding

M-C bond:	increases	increases
C-O bond:	increases	decreases
ν_{CO} freq:	increases	decreases

Carbonyl Infrared (IR) Stretching Frequencies

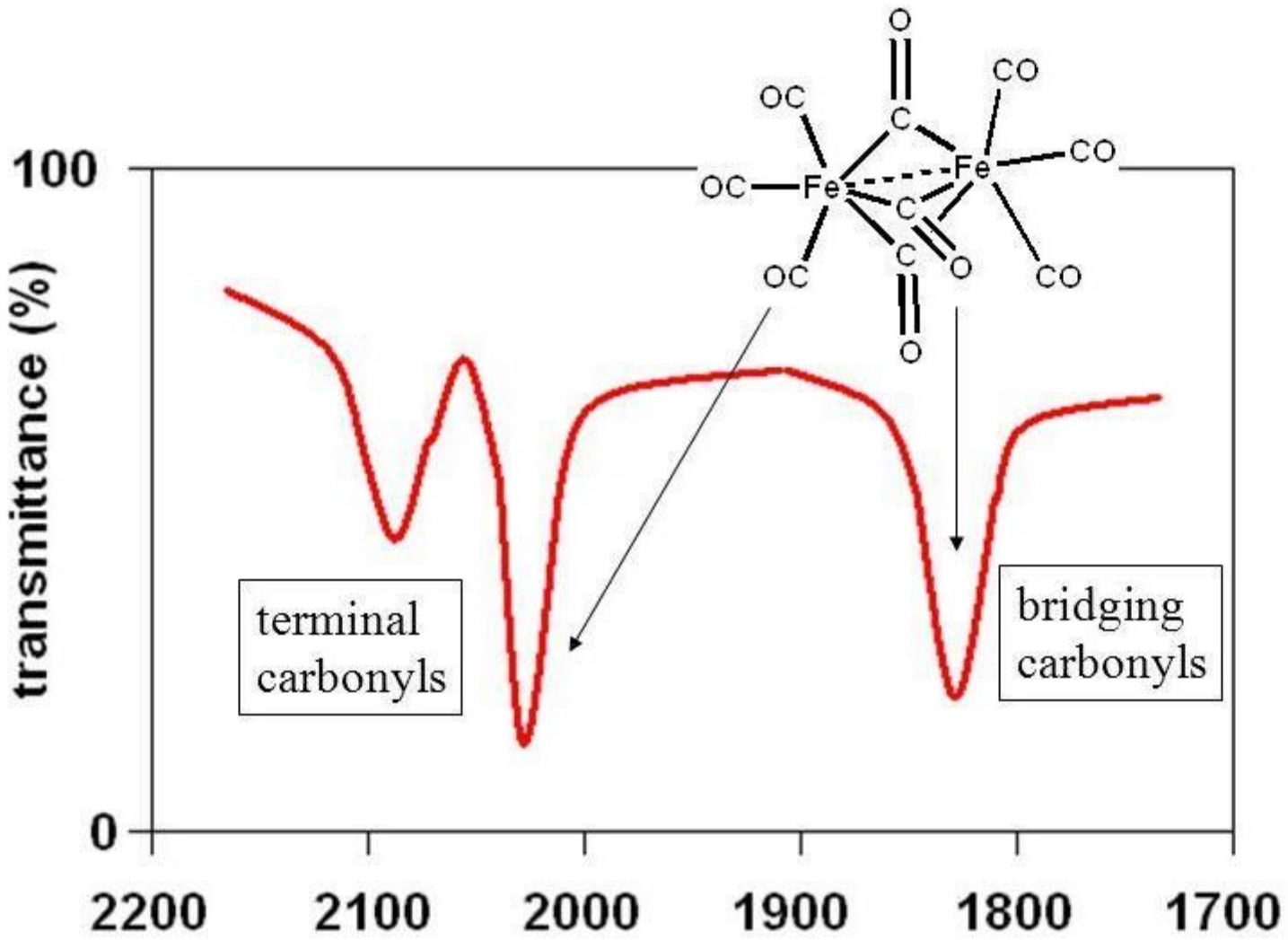
- The **position** of the carbonyl bands in the IR depends mainly on the bonding mode of the CO (terminal, bridging) and the amount of electron density on the metal being π-backbonded to the CO.
- The **number** (and intensity) of the carbonyl bands observed depends on the number of CO ligands present and the symmetry of the metal complex. There are also secondary effects such as Fermi resonance and overtone interactions that can complicate carbonyl IR spectra.



	free CO	*terminal mode*	μ_2 – *bridging*	μ_3 – *bridging*
ν_{CO} IR (cm^{-1})	2143	2120 - 1850	1850 - 1720	1730 - 1500

(for neutral metal complexes)

IR spectrum and bridging versus terminal carbonyls in $[Fe_2(CO)_9]$



Electronic Effects on ν_{CO}

As the electron density on a metal center increases, more π-back bonding to the CO ligand(s) takes place.

This further weakens the C-O bond by pumping more electron density into the formally empty carbonyl π^* orbital.

This increases the M-CO bond strength making it more double- bond-like, i.e., the resonance structure M=C=O assumes more importance.

Based on CO IR stretching frequencies, the following ligands can be ranked from **best** π-acceptor to **worst**:

NO^+ > CO > PF_3 > RN≡C > PCl_3 > $P(OR)_3$ > PR_3 > RC≡N > NH_3

Classifications of ligands

Metal-ligand bonding can be divided into three basic classes:

- σ- donor

e.g. H, CH_3 (or any alkyl or aryl group, R), H_2O, NH_3, NR_2 (bent)

- σ - donor, π acceptor (sometimes referred to as 'π-acceptors' or 'π-acids')

e.g. CO, CN, NO, H_2, C_2H_4, N_2, O_2, PR_3, BR_2

- σ - donor, π donor (sometimes referred to as 'π donors')

e.g. F, Cl, Br, I, O, OR, S, SR, N, NR_2(linear), NR (bent and linear), P,η^3-C_3H_5, η^5-C_5H_5, η^6-C_6H_6

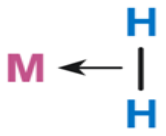
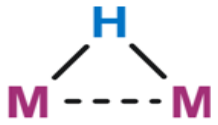
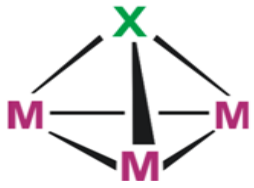
- In terms of bond strength the σ-bond is much more important than π-bonding (donor or acceptor)

Classifications of ligands

Cationic 2e- donor:	NO^+ (nitrosyl)
Neutral 2e- donors:	PR_3 (phosphines), CO (carbonyl), $R_2C{=}CR_2$ (alkenes), RCCR (alkynes, can also donate 4 e-), NCR (nitriles)
Anionic 2e- donors:	Cl^- (chloride), Br^- (bromide), I^- (iodide), CH_3^- (methyl), CR_3^- (alkyl), Ph^- (phenyl), H^- (hydride) *The following can also donate 4 e- if needed, but initially count them as 2e- donors (unless they are acting as bridging ligands):* OR^- (alkoxide), SR^- (thiolate), NR_2^- (inorganic amide), PR_2^- (phosphide)
Anionic 4e- donors:	$C_3H_5^-$ (allyl), O^{2-} (oxide), S^{2-} (sulfide), NR^{2-} (imido), CR_2^{2-} (alkylidene) *and from the previous list:* OR^- (alkoxide), SR^- (thiolate), NR_2^- (inorganic amide), PR_2^-
Anionic 6e- donors:	Cp^- (cyclopentadienyl), N^{3-} (nitride)

- Electron counts can depend on the complex's specific electronic and geometric structure and bonding type of sigma bonds, pi bonds, or a combination

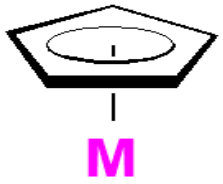
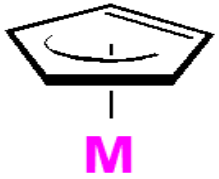
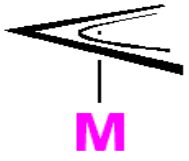
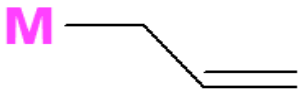
Classifications of ligands

Ligand Name	Bonding Type	Formal Charge	Electrons Donated
Molecular Hydrogen: H_2		0	2
Hydride: H^-	M-H	-1	2
Hydride: H^-		-1	2
Halide: X^-	M-X	-1	2
Halide: X^- μ bridging		-1	4 (2 to each M)
Halide: X^- μ_3 bridging		-1	6 (2 to each M)

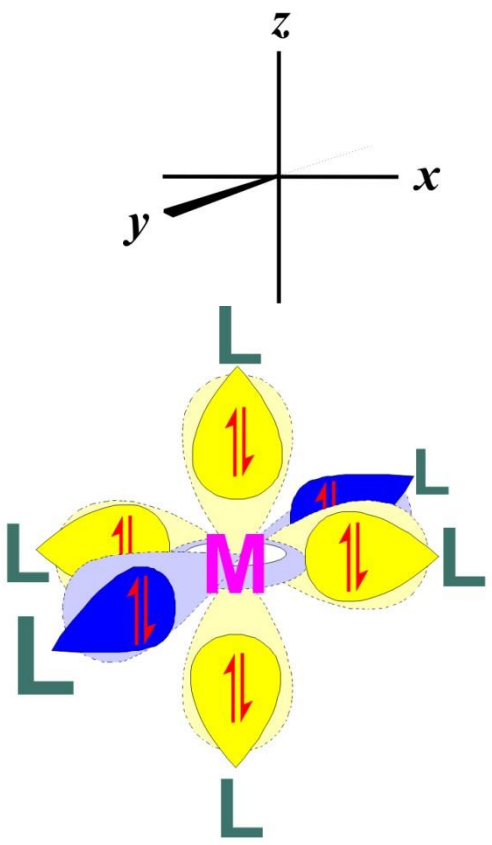
Classification of ligands

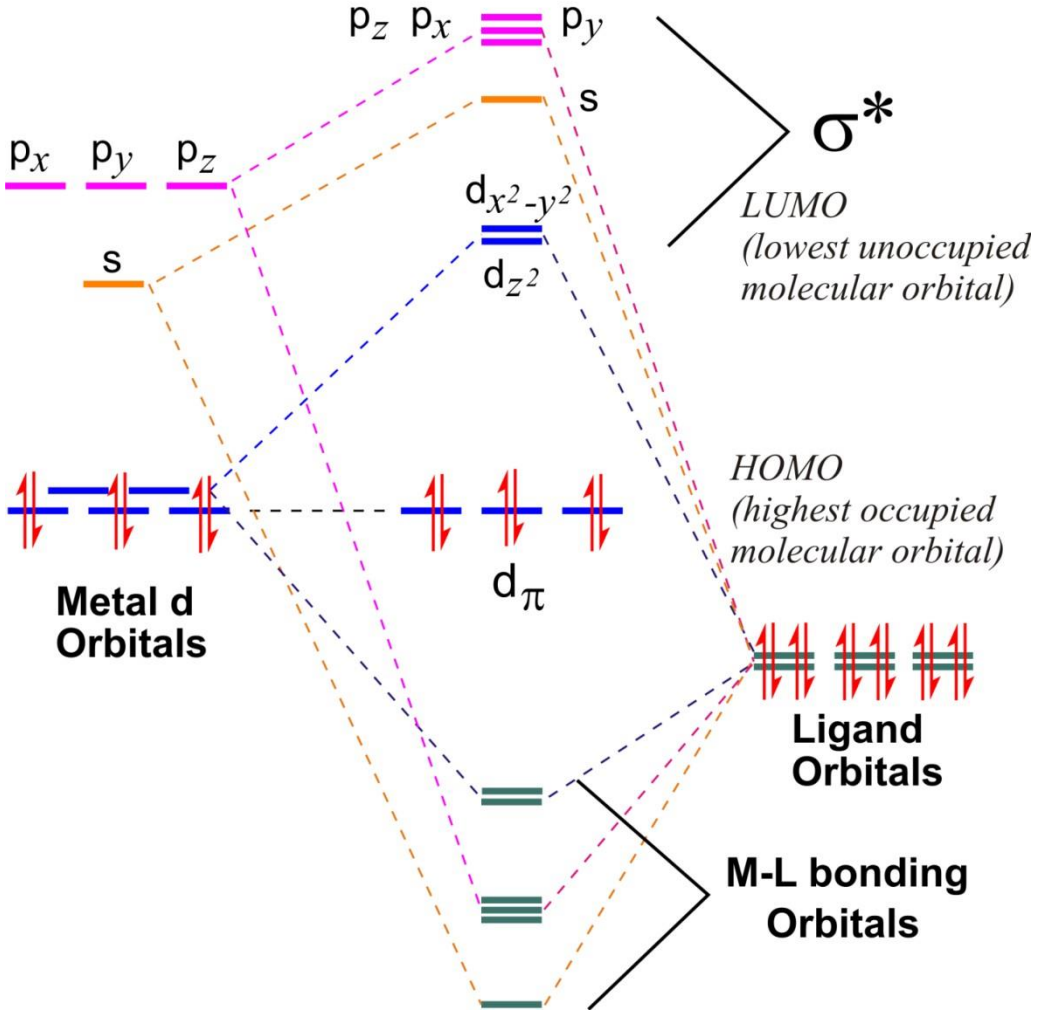
- η^x "eta-*x*" was originally developed to indicate how many *contiguous* donor atoms of a p-system were coordinated to a metal center. Hapticity is another word used to describe the bonding mode of a ligand to a metal center. An h^5-cyclopentadienyl ligand, for example, has all five carbons of the ring bonding to the transition metal center.

- η^x values for all-carbon based ligands where the x value is odd usually indicate *anionic* carbon ligands (e.g., η^5-Cp, η^1-CH3, η^1-allyl or η^3-allyl, η^1-CH=CH2). The # of electrons donated (ionic method of electron counting) by the ligand is usually equal to $x + 1$. Even η^x values usually indicate *neutral* carbon p-system ligands (e.g., η^6-C6H6, η^2-CH2=CH2, η4-butadiene, η^4-cyclooctadiene). The # of electrons donated by the ligand in the even (*neutral*) case is usually just equal to *x*.

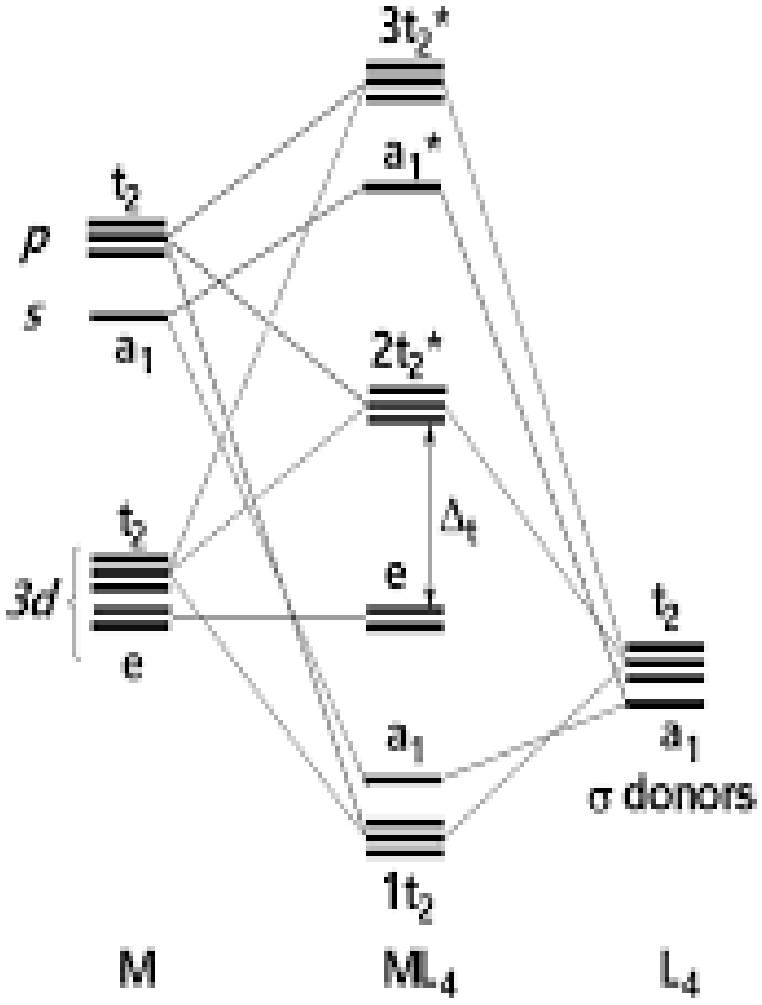
			
η^5-Cp	η^3-Cp	η^3-allyl	η^1-allyl

Stability of 18 e or 16e complexes according to MO theory





Stability of 18 e or 16e complexes according to MO theory



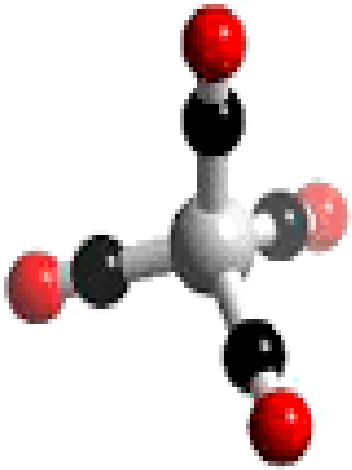
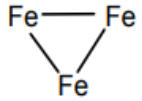
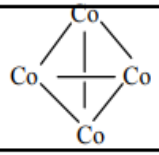


Table of various metal carbonyl complexes, including their total valence electron count (TVE), metal-metal bonds, and the basic geometry of the metal atoms in each complex.

Molecule	TVE (*A*)	(18 × *n*) – *A* (*B*)	Total M–M bonds (*B*/2)	Bonds per metal	Basic geometry of metal atoms
$Fe_3(CO)_{12}$	48	54 – 48 = 6	6/2 = 3	48/3 = 16; 2	
$Co_4(CO)_{12}$	60	72 – 60 = 12	12/2 = 6	60/4 = 15; 3	
$[\eta^5\text{-}CpMo(CO)_2]_2$	30	36 – 30 = 6	6/2 = 3	30/2 = 15; 3	Mo≡Mo
$(\eta^4\text{-}C_4H_4)_2Fe_2(CO)_3$	30	36 – 30 = 6	6/2 = 3	30/2 = 15; 3	Fe≡Fe
$Fe_2(CO)_9$	34	36 – 34 = 2	2/2 = 1	34/2 = 16; 1	Fe–Fe

-(18 x n) - A = B : how many electrons are needed to reach this ideal state from the actual TVE count (n = number of transition metals)

-Total M-M Bonds: count of metal-metal bonds within each complex

-Bonds per Metal: shows how many bonds can make for **each** metal

- **$Fe_3(CO)_{12}$**:
- **TVE = 48**: Total valence electrons present:

Electron configuration of Iron (Fe):$[Ar]3d^6 4s^2$

Valence electrons per Fe in the 0 oxidation state: $3d^6+4s^2=8$ electrons, so 3Fe*8=24 electrons

Electrons donated per CO ligand are 2 electrons, so for 12CO=2*12= 24 electrons

- **(B electrons needed): (18 x 3) - 48 = 6**: Six more electrons are needed for all iron atoms together to reach a stable 18-electron configuration.
- **Total M-M Bonds (B/2) = 3**: There are three Fe-Fe bonds.
- **Bonds per Metal (48/3) = 16;2**: Each iron atom is bonded to two other iron atoms.
- **Geometry**: Triangular arrangement of iron atoms.

Classification of Ligands by donor atoms

Classification of Ligands by donor atoms:

- Ligand is a molecule or an ion that has at least one electron pair that can be donated.
- Ligands may also be called Lewis bases; in terms of organic chemistry, they are ‘nucleophiles’.
- Metal ions or molecules such as BF_3 (with incomplete valence electron shells (electron deficient) are called Lewis acids or electrophiles).

Hydrocarbon complexes

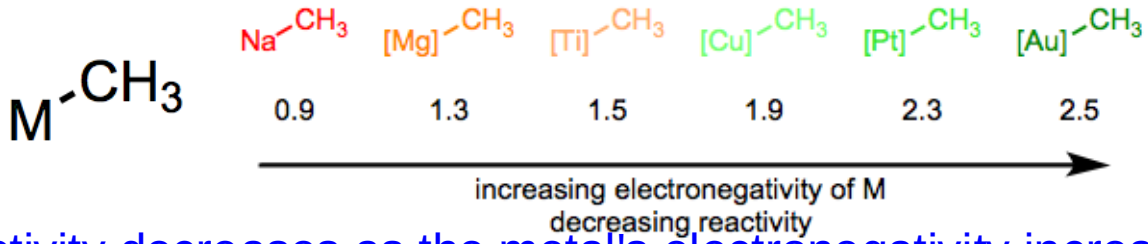
An organometallic compound is one which has metal-carbon bonds, and between one and eight carbon atoms in a hydrocarbon ligand bond to a metal. **Hapticity** describes the number of atoms in a ligand that have direct coordinative interaction with the metal and the number is added to **η**. An example is η^5 (pentahapto)-cyclopentadienyl (Table below).

Table Hapticity and number of donating electrons of hydrocarbon ligands

Name	Hapticity	Number of electrons	Example
Alkyl	η^1	1	$W(CH_3)_6$
Alkylidene	η^1	2	$Cr(CO)_5\{C(OCH_3)C_6H_5\}$
Alkene	η^2	2	$K[PtCl_3(C_2H_4)]$
π-allyl	η^3	3	$Ni(\eta^3\text{-}C_3H_5)_2$
Diene	η^4	4	$Fe(CO)_3(\eta^4\text{-}C_4H_6)$
Cyclopentadienyl	η^5	5	$Fe(\eta^5\text{-}C_5H_5)_2$
Arene	η^6	6	$Cr(\eta^6\text{-}C_6H_6)_2$
Tropylium	η^7	7	$V(CO)_3(\eta^8\text{-}C_7H_7)$,
Cyclooctatetraene	η^8	8	$U(\eta^8\text{-}C_8H_8)_2$

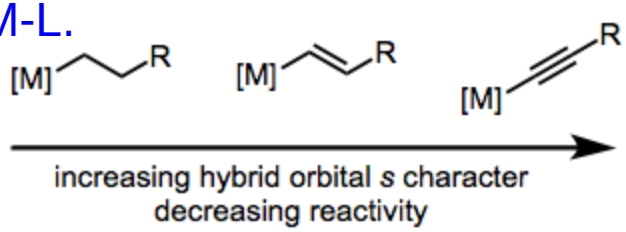
Metal Alkyls

With this post we finally reach the defining ligands of organometallic chemistry, alkyls. Metal alkyls feature a metal-carbon σ bond and are usually actor ligands, although some alkyl ligands behave as spectators.



Reactivity decreases as the metal's electronegativity increases because of the tight bonds between M-L. Values given are Pauling electronegativities.

The hybridization of the carbon atom is also important, and the trend here follows the trend in nucleophilicity as a function of hybridization in organic chemistry. sp-Hybridized ligands are the least nucleophilic, followed by sp^2 and sp^3 ligands respectively because of the close e- in s orbital to tight bonds between M-L.



Note that this trend is similar to the nucleophilicity of carbanions as a function of hybridization.

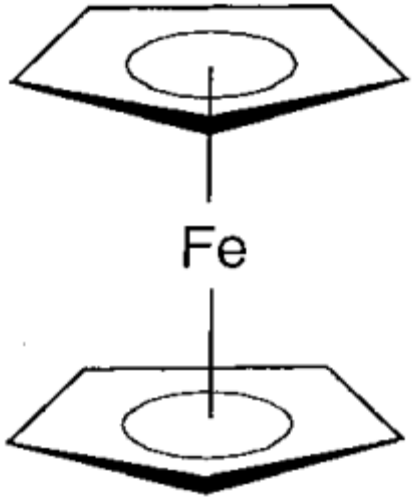
π allyl complexes

If an allyl group, CH_2=CH-CH_2^-, is bonded to a metal via a carbon atom, it is a 1-electron ligand like an alkyl group. If the double bond delocalizes, three carbon atoms bond to the metal simultaneously as a 3-electron ligand. This is also an odd electron and formally anionic ligand and is stabilized by being coordinated to the metal.

$Pd(C_3H_5)(Ac)(PPh_3)$, $Co(C_3H_5)_3$, etc are well-known examples. Since η^1, η^2, and η^3 coordination modes are possible in the catalytic reactions of unsaturated hydrocarbons, various reactions occur.

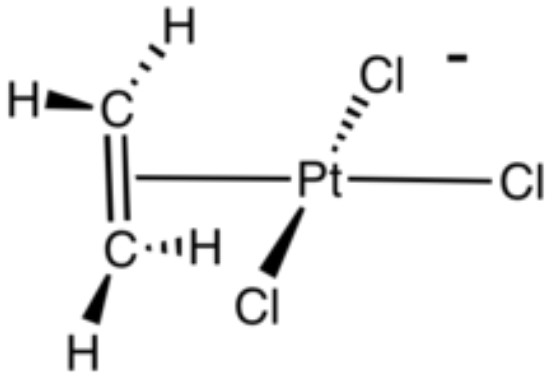
π cyclopentadienl complexes

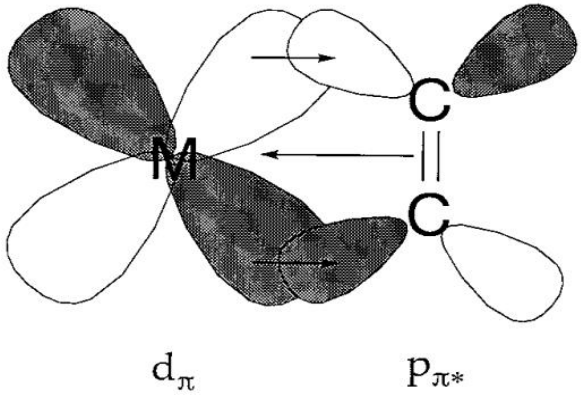
The cyclopentadienyl ligand, C_5H_5, is abbreviated as Cp. C_5Me_5, in which the hydrogen atoms of Cp are replaced with methyl groups, is a useful ligand called **Cp star** and is denoted by Cp*. Ferrocene, Cp_2Fe, is a very stable orange-colored iron compound in which two cyclopentadienyl groups are bonded to iron. It was discovered independently in two laboratories, but the discoverers proposed incorrect structures. The correct structure was clarified by the group of G. Wilkinson, who won a Nobel Prize (1973)

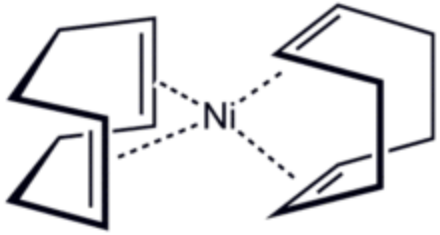


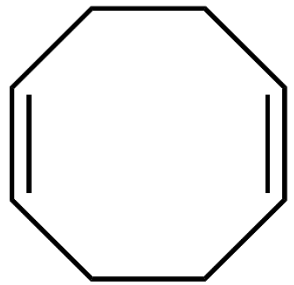
Olefin complexes

Zeise's salt, $K[PtCl_3(C_2H_4)]$, is the oldest known organometallic compound and was synthesized and analyzed in ca. 1825 by Zeise. An olefin is a 2-electron ligand and there are many olefin complexes in which the central metal is in a relatively low oxidation state. Dienes or trienes with two or more double bonds coordinate to a metal as 4-electron or 6-electron ligands. $Fe(CO)_3(C_4H_6)$ and $Ni(cod)_2$, in which a butadiene or cyclooctadienes (cod) are coordinated to the metal, are well-known examples. Since cyclooctadienes are easily eliminated from $Ni(cod)_2$, it is conveniently used for generating atomic, zero valent nickel. This complex is sometimes called **naked nickel** with no ligands.





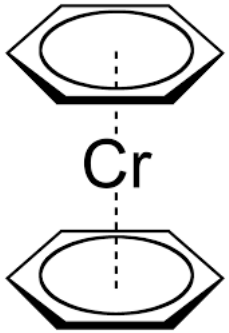




Cyclooctadienes (cod)

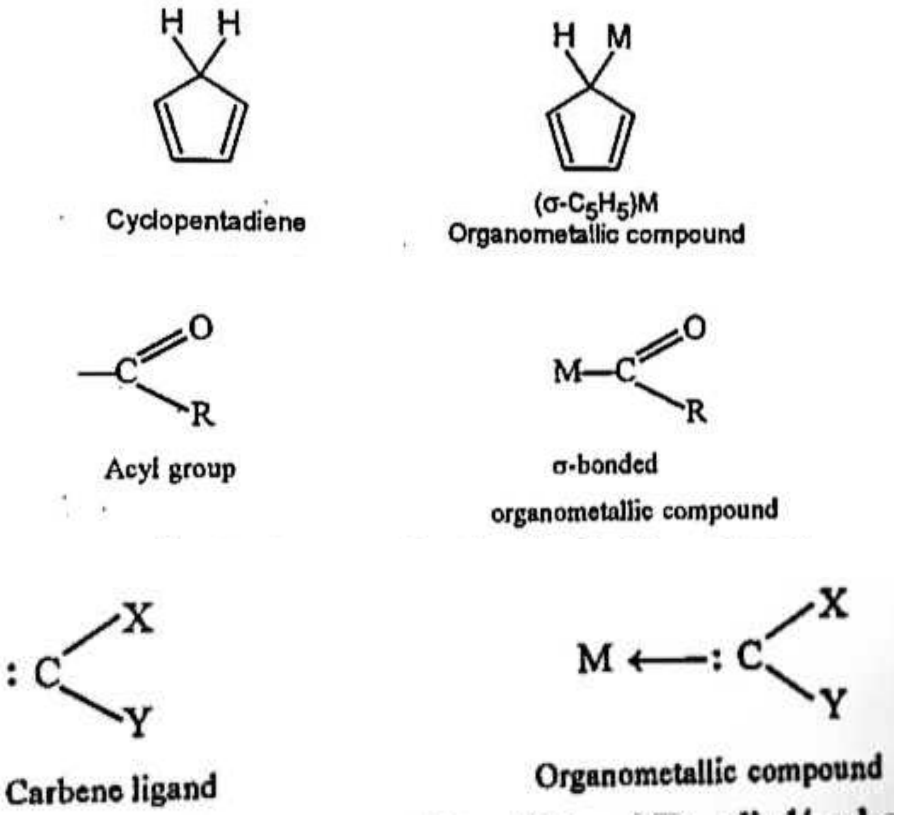
•Arene complexes

Aromatic compounds are 6-electron donors that coordinate to transition metals in the η^6 coordination mode with six carbon atoms. Bisbenzenechromium, $Cr(C_6H_6)_2$, is a typical example of such a compound. The compound is prepared by reducing chromium chloride in benzene and it has a sandwich structure in which a chromium atom is inserted between two benzene rings. When a benzene ligand is replaced by three carbonyls, $Cr(CO)_3(C_6H_6)$ is obtained.

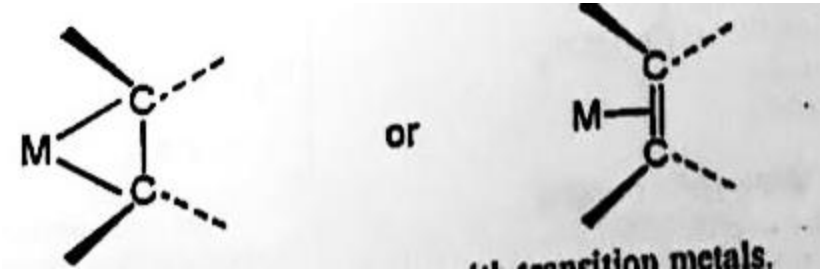


Some electron donors ligands are classified as below:

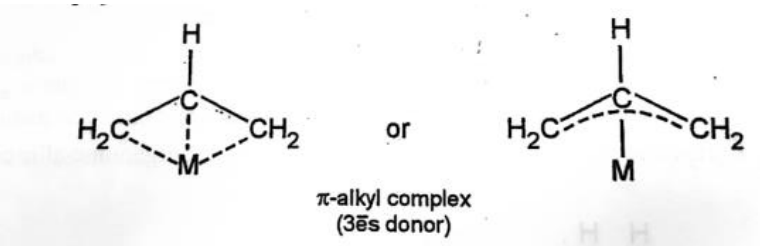
(1) One electron donor: when the metal ions attached with one carbon such as:



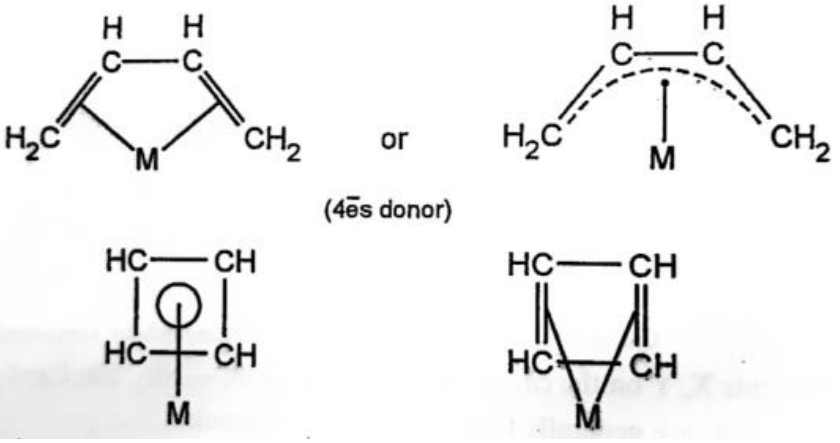
(2) two electrons donor: two carbon bonded ligands are those ligands in which two carbon atoms of the same ligand are bonded to the metal atom as



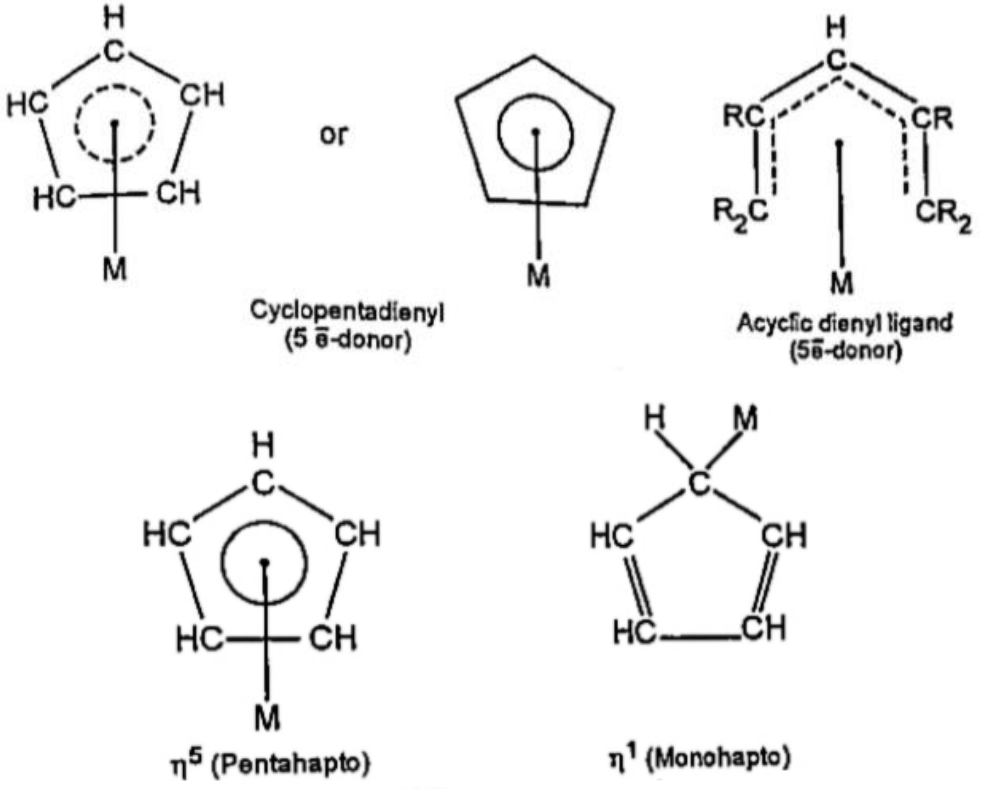
(3) Three electrons donors: *three carbon bonded ligands are those ligands in which three carbon atoms of the same ligand are bonded to the metal atom*



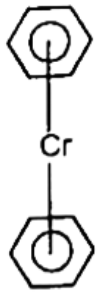
(4) Four electrons donors



Five electrons donor

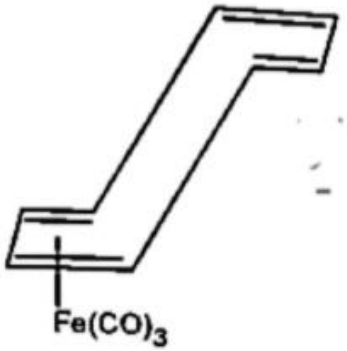


Six electrons donor

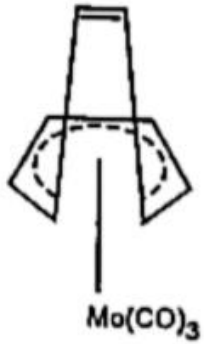


benzene chromium, $(C_6H_6)Cr$
($6e^-$-donor)

Cycloheptatriene acting as six electron donor

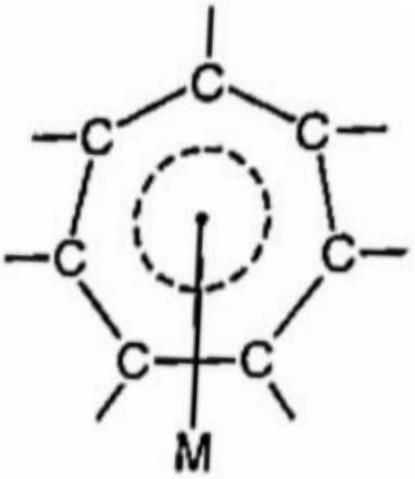


Cyclooctatetraene
(4 $\bar{e}$ donor)

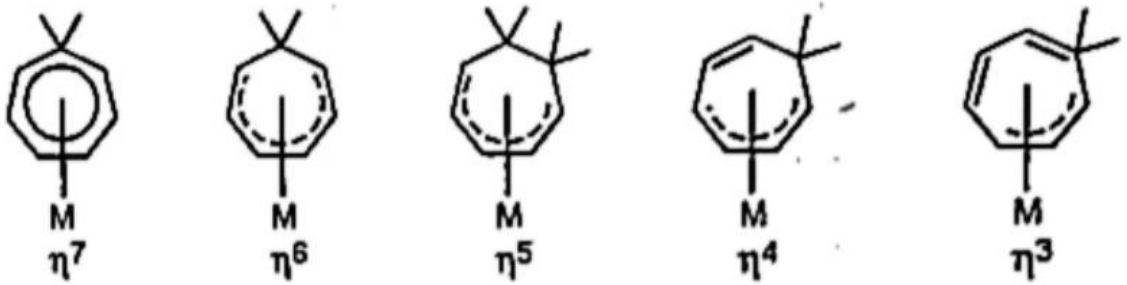


Cyclooctatetraene
(6 $\bar{e}$ donor)

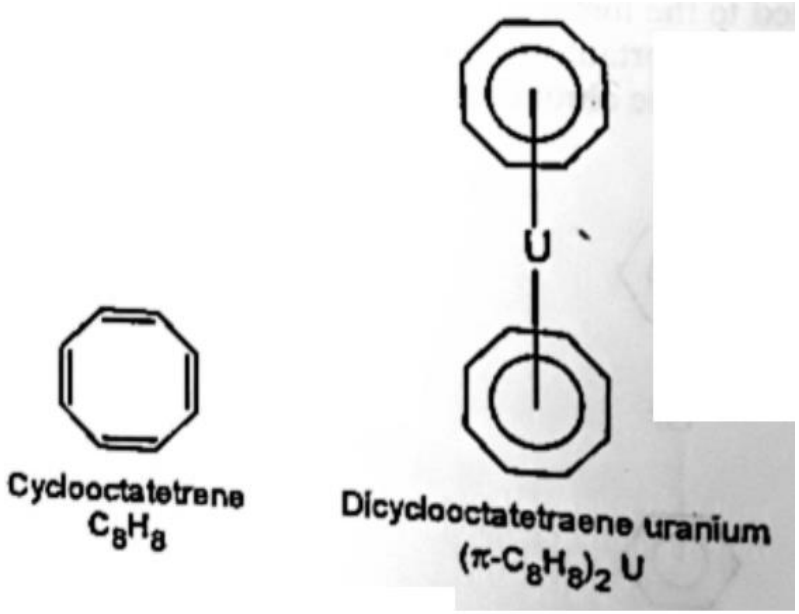
Seven electrons donors

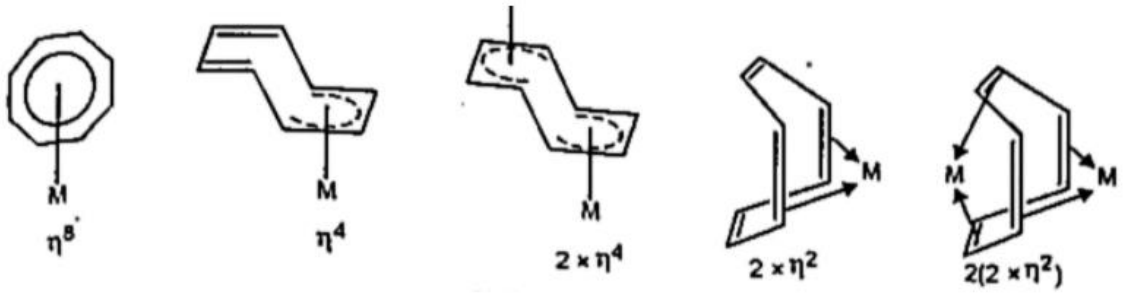


Cycloheptatrienyl η^7($7\bar{e}$ donor)



Eight electrons donors





Ligand	Neutral atom	Oxidation state		Ligand	Neutral atom	Oxidation state	
		Electron contribution	Formal charge			Electron contribution	Formal charge
Carbonyl (M–CO)	2	2	0	Halogen (M–X)	1	2	–1
Phosphine ($M–PR_3$)	2	2	0	Alkyl (M–R)	1	2	–1
Amine ($M–NR_3$)	2	2	0	Aryl (M–Ar)	1	2	–1
Amide ($M–NR_2$)	1	2	–1	acyl (M–C(O)–R	1	2	–1
Hydrogen (M–H)	1	2	–1	η^1-cyclopentadienyl	1	2	–1
Alkene (sidewise) η^2-	2	2	0	η^1-allyl	1	2	–1
Alkyne (sidewise) η^2-	2	2	0	η^3-allyl	3	4	–1
η^2-C_{60}	2	2	0	η^5-cyclopentadienyl	5	6	–1
Nitrosyl bent	1	2	–1	η^6-benzene	6	6	0
Nitrosyl linear	3	2	+1	η^7-cycloheptatrienyl	7	6	+1
Carbene ($M=CR_2$)	2	4	–2	Carbyne (M≡CR)	3	6	–3
Alkoxide (M–OR)	1	2	–1	Thiolate (M–SR)	1	2	–1
μ-CO (M–(CO)–M)	2	2	0	μ-H	1	2	–1
μ-alkyne	4	4	0	μ-X (M–X–M) X = halogen	3	4	–1
μ-alkyl	1	2	–1	μ-amido ($M–(NR_2)–M$	3	4	–1
μ-phosphido ($M–(PR_2)–M$	3	4	–1	μ-alkoxide (M–(OR)–M	3	4	–1