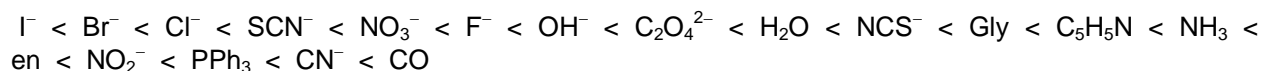


**SIGMA- AND PI- BONDING LIGANDS**

[Ref: Rodgers GE. Introduction to coordination, solid state and descriptive inorganic chemistry. McGraw Hill. 1994. p. 73-4.]

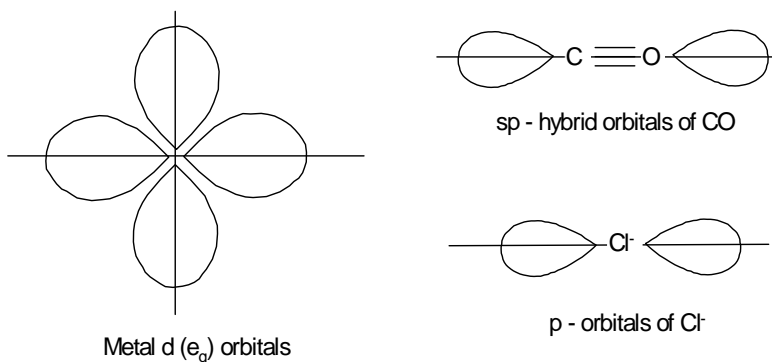
In the spectrochemical series, ligands are arranged according to their increasing ability to split metal *d*-orbitals.



According to arguments of CFT, it is expected that greater splitting of *d*-orbitals is favoured by:

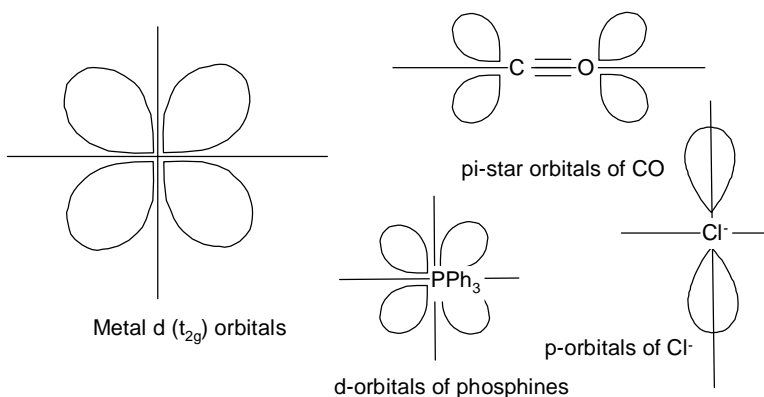
- (1) High negative charge on the ligand. Thus negative ligands should be better than neutral ones.
- (2) Smaller size of the negative ligand atom or molecule (= concentrated negative charge, less polarisability, high polarizing power). This effect is very clearly noticeable among the halides.
- (3) Higher dipole moment of the ligand, with more negative charge on the donor atom.

But it is not easy to explain the position of ligands in the spectrochemical series based only on the above assumptions. It can be noted that triphenyl phosphine, which is a very bulky ligand with a low dipole moment, is placed very high in the series. Carbon monoxide or 'carbonyl' ligand is a neutral molecule with a very small dipole moment, yet it is listed as the highest in the series. This means that explanations other than CFT such as covalent bond formation must also be taken into account. Ligand electrons, after all, must be associated with various orbitals that may be capable of overlapping various metal orbitals if they have "the correct symmetry".



Metal and ligand orbitals with the right symmetry along the axis

These can form sigma bonds



Metal and ligand orbitals with the right symmetry outside the internuclear axis

These can form pi bonds

**[Note on bonding in CO molecule:** Both C and O are supposed to be diagonally hybridized ( $sp$ ). One  $sp$ -hybrid orbital of each overlap to form the  $\sigma$ -bond between C and O. The other  $sp$ -hybrid orbital on C and O, directed along the internuclear axis, each contain a lone pair of electrons. The remaining  $p$ -orbitals overlap to form two  $\pi$ -bonds. This system requires the transfer of an electron from the O to the C, producing  $\delta^-C - O^{\delta+}$ . This is against the natural tendency of the more electronegative O atom. Measurement of dipole moment gives only a small value, indicating that these two effects almost cancel each other. It is the electron pair on the slightly negative C that is donated to the metal atom].

The metal  $e_g$  orbitals are usually empty, but lie along the internuclear axis ( $d_{x^2-y^2}$  and  $d_{z^2}$ ). These orbitals overlap with the  $sp$ -hybrid orbital of a ligand like CO, or the  $p_x$  orbital of ligands like  $Cl^-$ , to form a  $\sigma$ -bond. Electron density from the ligand is transferred to the metal atom through this  $\sigma$ -bond. Ligands capable of such bonding are called  **$\sigma$ -donor ligands**.

The  $t_{2g}$  orbitals on the metal atom ( $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ ) can then overlap with similar  $d$ -orbitals of P in phosphines, or with the  $\pi^*$  orbitals having the correct symmetry in ligands like CO, or the  $p_y$  (or  $p_z$ ) orbitals in halide ligands, forming  $\pi$ -bonds. Since the  $t_{2g}$  orbitals of the metal usually contain electrons and the  $\pi^*$  orbitals of the ligands are empty, electron density is transferred from **metal to ligand** through such  $\pi$ -bonds. This is therefore called "**back-bonding**". These give extra stability to the complex. Ligands capable of such bonding are called  **$\pi$ -acceptor ligands**.

In  $R_3P$ ,  $\sigma$ -bonding take place through the lone pair of the  $sp^3$ -hybrid orbital and  $\pi$ -bonding through the empty  $d$ -orbitals. The back-bonding is favoured by a positive or electron withdrawing group or atom on the ligand. Thus  $Ph_3P$  or  $Ar_3P$  is a stronger ligand than  $R_3P$ , because of the electron-withdrawing character of the benzene rings.

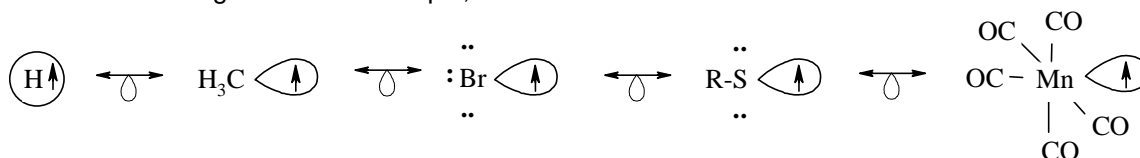
In  $\delta^-C-O^{\delta+}$ , the positive charge on the O atom favours back-bonding. In NO (nitrosyl ligand), there is one electron in the antibonding orbital. This is easily lost to form  $NO^+$ , which is then **isoelectronic** (= having same number of electrons) with CO. This too is a strong  $\pi$ -acceptor ligand. Since the electron in the antibonding orbital is also donated to the metal atom, NO is a **three-electron donor** ligand. Ligands such as  $N_2$  and  $CN^-$  are also isoelectronic with CO and hence  $\pi$ -acceptor ligands. CO,  $NO^+$  and  $CN^-$  are also **isolobal ligands** (see isolobal concept given on next page).

**Concepts of Frontier Orbitals, Isoelectronicity and Isolobality** [Shriver DF and Atkins PW, Inorganic Chemistry 3<sup>rd</sup> edition, Oxford University Press, (1999), p. 80].

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in an atom, molecule or a molecular fragment are called **frontier orbitals** (= orbitals at the boundary, containing valence electrons). These orbitals are important participants in further reactions of the species.

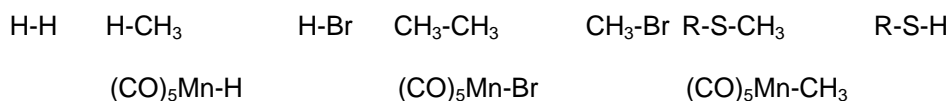
If different atoms, molecules or molecular fragments contain the same number of electrons in their frontier orbitals, they are said to be isoelectronic. For example,  $O^{2-}$ ,  $F^-$  and Ne are isoelectronic. CO and  $NO^+$  are isoelectronic.

Atoms, molecules or molecular fragments are said to be **isolobal** (= similar lobes) if their frontier orbitals have the same shape, symmetry and are isoelectronic. The concept of isolobality can be used to identify similarities in the structures and reactions of apparently unrelated molecules or fragments. Isolobality is indicated by a double-headed arrow with a tear-drop in the middle. A simple valence-bond viewpoint can be used for many of the applications of isolobality. This allows us to identify families of isolobal fragments. For example,

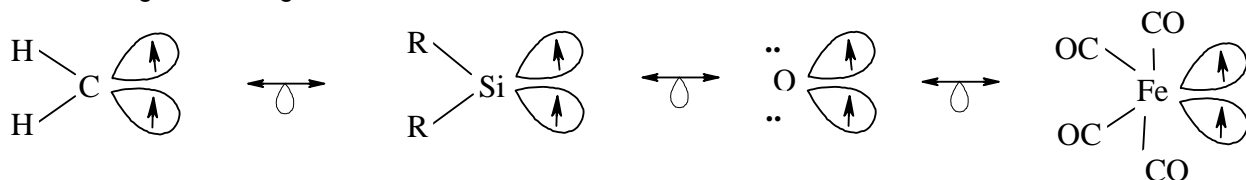


For hydrogen alone, the maximum number of electrons that can be accommodated in the  $1s$  orbital is 2. In the hydrogen atom, there is only one electron (ie. one less than the maximum). This is equivalent to having 7 electrons in the outer shell having  $p$ -orbitals and 17 electrons in the outer shell having  $d$ -orbitals

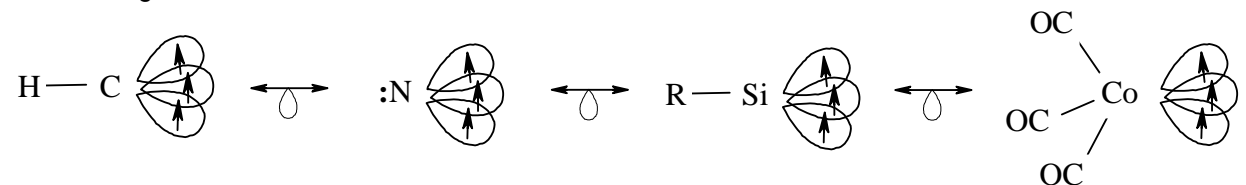
(all these have one less than the maximum and the last one electron is unpaired). In the methyl radical, there are three pairs of electrons around the C atom in the C-H bonds and an unpaired electron in an  $sp^3$ -hybrid orbital. Therefore the methyl radical is isolobal with a H atom, and can substitute a hydrogen atom in compounds. In the bromine atom, there are three lone pairs of electrons around the Br atom and an unpaired electron in a  $p$ -orbital. It is thus isolobal with hydrogen atom and the methyl radical; it can replace any of these in compounds. In the R-S- fragment, there are three pairs of electrons around the S atom (two lone pairs and one bond pair) and an unpaired electron in a  $p$ -orbital. Hence it is also isolobal with the others. Mn has the electronic configuration  $d^5s^2$  (7 electrons) and each CO ligand donates a pair of electrons, making a total of 17 electrons in 9 orbitals ( $d^5sp^3$ -hybrid, HOMO + LUMO). Therefore the fragment  $(CO)_5Mn-$  is isolobal with the other examples given. That all of these diverse species are similar and interchangeable in their compounds is shown by the following examples:



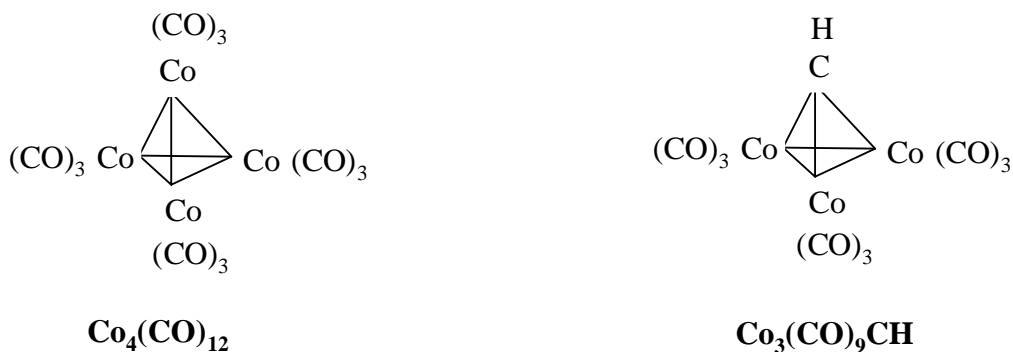
The existence of such isolobal families suggest that we can expect the formation of molecules like CH<sub>3</sub>-O-CH<sub>3</sub> (similar to H-O-H) and N(CH<sub>3</sub>)<sub>3</sub> (similar to NH<sub>3</sub>). All these are known. Some two-orbital isolobal fragments are given below:



In these, the  $Fe(CO)_4$  fragment contains 16 electrons and the others 6 electrons. Some three-orbital isolobal fragments are shown below:



The  $Co(CO)_3$  fragment contains 15 electrons and the others 5 electrons. This predicts the formation of complexes like  $Co_4(CO)_{12}$  and  $Co_3(CO)_9CH$ , and both are known showing that  $Co(CO)_3$  and CH fragments are interchangeable.



Although isolobal analogies are often helpful as show above, the predictions are not always valid. For example the above scheme also predicts molecules like  $(OC)_5Mn-O-(CO)_5$  and  $(OC)_4Fe=Fe(CO)_4$ , but both are unknown.

## ORGANOMETALLICS

[Ref: Emeleus HJ, Sharpe AG. Modern aspects of inorganic chemistry. ELBS. 1973. Chapters 15, 16, 17]

**Effective atomic number (E. A. N.) rule:** One of the earliest explanations for the formation of metal complexes was Sidgwick's E. A. N. rule. According to this rule, the central metal atom accepts electron

pairs from ligands in such a way as to attain the nearest inert gas configuration (Kr = 36, Xe = 54, Rn = 86). This is also known as the **18-electron rule**.

Example:  $[\text{Fe}(\text{CN})_6]^{4-}$  (first transition series)

Fe = 26 electrons;  $\text{Fe}^{2+} = 24$  electrons; 2 from each  $\text{CN}^- = 2 \times 6 = 12$  electrons;  
Total =  $24 + 12 = 36$  electrons  $\equiv$  Kr.

Example:  $[\text{Os}(\text{CO})_5]$  (third transition series)

Os = 76 electrons; 2 from each CO =  $2 \times 5 = 10$  electrons;  
Total =  $76 + 10 = 86$  electrons  $\equiv$  Rn.

Although this rule is very valuable in arriving at the structures of many metal carbonyls, the theory is not universally applicable. There are many examples where E. A. N. rule is not followed by metal complexes. Almost all metal carbonyls conform to the E. A. N. rule.  $[\text{V}(\text{CO})_6]$  is the most important exception.

Example:  $[\text{Fe}(\text{CN})_6]^{3-}$

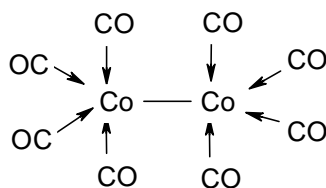
Fe = 26 electrons;  $\text{Fe}^{3+} = 23$  electrons; 2 from each  $\text{CN}^- = 2 \times 6 = 12$  electrons;  
Total =  $23 + 12 = 35$  electrons **(Not inert gas configuration!)**

The E. A. N. rule is very helpful in deriving structures of **polynuclear** metal carbonyls, which may have metal-metal bonds, or **bridging carbonyl groups**.

Example:  $\text{Co}_2(\text{CO})_8$

Since there are two Co atoms, and the formula is divisible by two, consider it as  $2 \times \text{Co}(\text{CO})_4$ . The halves may be joined together by a metal-metal (Co-Co) bond in which the metal atoms share one electron each. If so, for each half,

Co = 27 electrons; 2 from each CO =  $2 \times 4 = 8$  electrons; Total =  $27 + 8 = 35$  electrons; (not inert gas!)  
Add one electron from the other Co, then Total =  $35 + 1 = 36$  electrons; (inert gas!). So there may be a Co-Co bond and the structure may be:

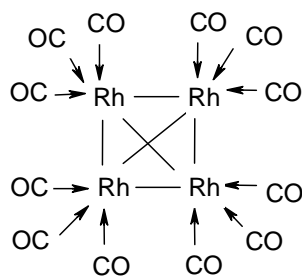


which is confirmed by X-ray studies. Thus this compound obeys the E. A. N. rule.

Example:  $\text{Rh}_4(\text{CO})_{12}$

Since there are four Rh atoms, and the formula is divisible by four, consider it as  $4 \times \text{Rh}(\text{CO})_3$ . Then, for each part,

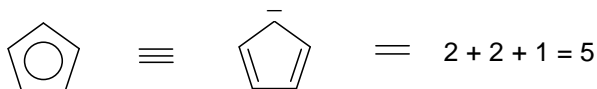
Rh = 45 electrons; 2 from each CO =  $2 \times 3 = 6$  electrons; Total =  $45 + 6 = 51$  electrons; (not inert gas!).  
Three more electrons, one from each remaining Rh atom, can make it 54 which is an inert gas configuration (Xe). Therefore the structure may be:



which is confirmed by X-ray studies. Thus this compound also obeys the E. A. N. rule.

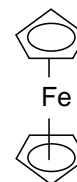
### Examples of E. A. N. rule using $\pi$ -bonding ligands

For this purpose, each  $\pi$ -bond is believed to contribute two electrons to the metal atom. Thus the cyclopentadienyl ligand contributes five electrons.

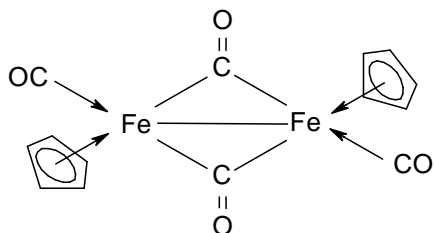


Example:  $\text{Fe}(\text{C}_5\text{H}_5)_2$

Fe = 26 electrons; Two cyclopentadienyl rings =  $2 \times 5 = 10$  electrons;  
Total =  $26 + 10 = 36$  electrons  $\equiv$  Kr



Example:  $[\pi\text{-(C}_5\text{H}_5)\text{Fe(CO)}_2]_2$



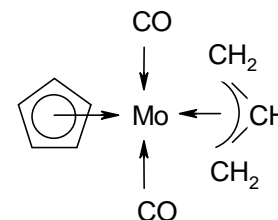
For each Fe atom:

Fe = 26 electrons; Cyclopentadienyl ring = 5 electrons; Terminal CO group = 2 electrons;  
One electron from each bridging CO = 2 electrons;  
One electron from the other Fe atom = 1 electron.  
Total =  $26 + 5 + 2 + 2 + 1 = 36$  electrons.  
(Inert gas configuration!)

Example:  $[\pi\text{-(C}_5\text{H}_5)\text{Mo(CO)}_2\pi\text{-(C}_3\text{H}_5)]$

$\text{C}_3\text{H}_5 \equiv \text{CH}_2=\text{CH}-\text{CH}_2^* \longleftrightarrow {}^*\text{CH}_2-\text{CH}=\text{CH}_2 = (\pi\text{-allyl})$  ligand

Mo = 42 electrons; Two CO groups =  $2 \times 2 = 4$  electrons;  
Cyclopentadienyl ring = 5 electrons;  $(\pi\text{-allyl}) = 3$  electrons;  
Total =  $42 + 4 + 5 + 3 = 54$  electrons.  $\equiv$  Xe.



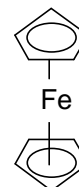
**THE HAPTO NOMENCLATURE**[Ref: Sharpe AG. Inorg. Chem. Int. Stu. Edn. 3<sup>rd</sup> edn, Addison-Wesley, 1992, p 544.]

Hapto (Gk = "fasten")

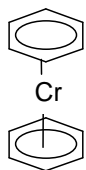
This is a method of naming  $\pi$ -complexes. In these, more than one atoms may be equidistant from the metal atom and contribute to forming a **single** metal-ligand bond. Depending on the contributing number of atoms, they are called monohapto-, dihapto-, trihapto- etc. These are represented as  $\eta^1$ -,  $\eta^2$ -,  $\eta^3$ - etc. (or  $h^1$ -,  $h^2$ -,  $h^3$ - etc.)

For example, the cyclopentadienyl ligand is an  $\eta^5$ -ligand (pentahapto ligand).

$(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$  or  
dicyclopentadienyl iron(II)

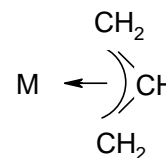


Benzene rings are  $\eta^6$ -ligands (hexahapto ligands).



$(\eta^6\text{-C}_6\text{H}_6)_2\text{Cr}$  or  
dibenzene chromium(0)

The allyl ligand is an  
 $\eta^3$ -ligand (trihapto).



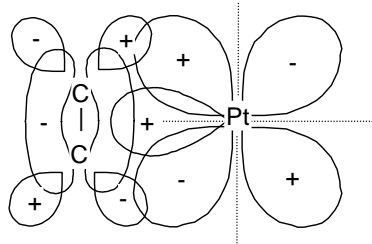
Note that all the atoms in the ligand taken together forms only **one** metal-ligand bond. Thus 'hapticity' of a ligand is different from 'denticity' of the ligand. For example, in a bidentate ligand, there are two metal-ligand bonds. The cyclopentadienyl ligand is a pentahapto ligand, but it is monodentate.

**ORGANOMETALLIC COMPLEXES WITH LINEAR  $\pi$ -DONOR LIGANDS**

Compounds containing double bonds and triple bonds ('enes' and 'ynes'), either linear or cyclic, can form complexes by donating electrons in their  $\pi$ -bonds to metal atoms. Each  $\pi$ -bond is assumed to donate two electrons in their  $\pi$ -bonds to metal atoms. Each  $\pi$ -bond is assumed to donate two electrons to the metal atom. The first such complex was discovered in 1830 by Zeise, and therefore potassium ethene trichloroplatinate(II),  $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$ , is usually known as **Zeise's salt**. Most of these compounds were discovered accidentally as unexpected products, and the structures were determined by a combination of physical methods.

**Structure of  $\pi$ -donor ligands – comparison with  $\sigma$ -donor  $\pi$ -acceptor ligands such as CO.**

The carbonyl C-atom uses its lone pair of electrons to form a  $\sigma$ -bond with the metal atom as the primary bond. The  $\pi^*$ -orbitals which are empty, accept electrons from the  $d$ -orbitals in the metal to form secondary bonds (back-bonding;  $\pi$ -acceptor ligands).

**Pt-ethene bonding in Zeise's salt.**

Note that the signs are not charges, but indicate the symmetry of the orbitals.

The  $\pi$ -bond of ethene donates electrons to Pt along the axis, while the empty  $\pi^*$ -orbitals of ethene receive electron density back from the metal through the  $d_{xy}$  orbitals.

In  $\pi$ -donor ligands, the electrons in the  $\pi$ -bonding MO are donated to the (empty)  $e_g$  metal orbitals to form the primary ligand-metal bond. The bond is reinforced through back-bonding involving the  $\pi^*$ -orbitals. As a result, the C-C multiple bond of the ligand is weakened due to the following reasons:

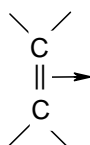
- (1) The electrons in the bonding MO are removed by the metal atom in primary bond formation.
- (2) Electrons are added to antibonding MO through back-bonding.

This weakening of the C-C bond is supported by the following observations:

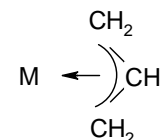
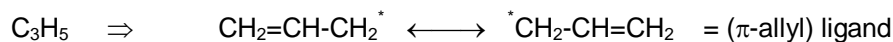
- (1) The C-C stretching frequency is lower in the complexed ligand compared to the free molecule. For example, the stretching frequency decreases from  $1623\text{ cm}^{-1}$  in free ethene to  $1460 - 1560\text{ cm}^{-1}$  range in complexes.
- (2) The C-C bond length in the complex is larger than that in the free molecule. For example, the bond length in ethene is  $132\text{ pm}$  while it is around  $137\text{ pm}$  in complexes.

Such  $\pi$ -donor ligands can be classified based on the number of electrons which are formally available for bonding (irrespective of whether these are really involved in bonding or not).

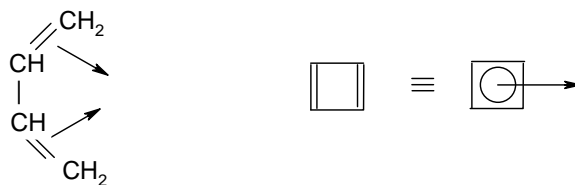
**2-electron donors:** Mono olefins (mono alkenes), e.g. ethene.



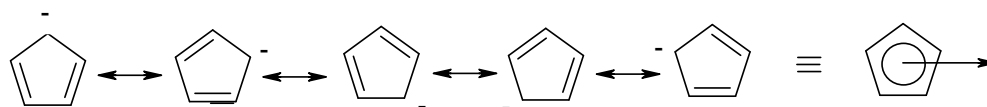
**3-electron donors:** e.g. enyl groups such as  $\pi$ -allyl.



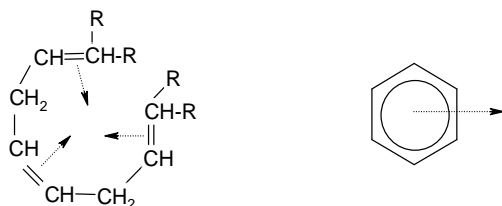
**4-electron donors:** e.g. dienes.



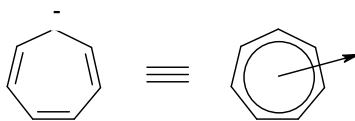
**5-electron donors:** e.g. dienyl groups like cyclopentadienyl.



**6-electron donors:** e.g. trienes and arenes.



**7-electron donors:** e.g. cycloheptatrienyl.



**8-electron donors:** e.g. tetrenes like cyclooctatetraene.



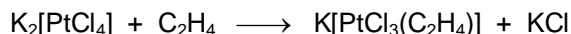
### General methods of preparation of $\pi$ -donor complexes.

Very few ligands react directly with transition metals to give organometallic derivatives because these organic substances are not very stable at the high temperatures required for the reaction. They are prepared usually by the displacement of existing CO ligands in carbonyl complexes. Reactions of metal chlorides with alkali metal derivatives of the ligand molecule are also used. In the case of 'enyl' ligands such as cyclopentadienyl or cycloheptatrienyl ions, a reducing agent must also be included in the reaction to produce the anionic ligand.

### Olefinic complexes (2-electron donors).

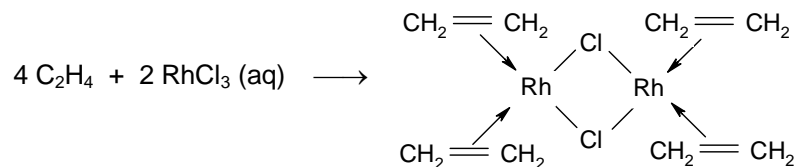
(1) Zeise's salt,  $K[PtCl_3(C_2H_4)] \cdot H_2O$  Potassium ethene trichloroplatinate(II) monohydrate.

It is prepared by passing ethene through a solution of potassium tetrachloroplatinate(II).

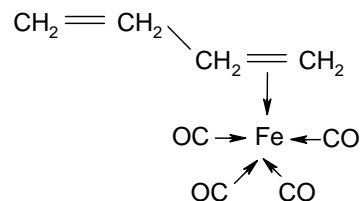


Less volatile olefins will displace ethene from this complex.

(2) Aqueous rhodium trichloride reacts with ethene directly.



(3) Butadiene +  $Fe(CO)_5 \xrightarrow{(40^\circ, n\text{-hexane})}$



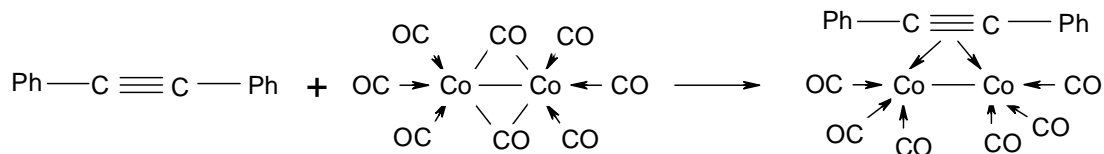
### Acetylenes or ethynes (4-electron donors).

Since there are two  $\pi$ -bonds in ethyne, it should be possible to complex a metal atom with each of them. The interaction of ethyne and organometallic compounds usually lead to the formation of extensively altered complex compounds. (**Note:** Reactions shown in these discussions are not balanced because other side products, not shown, are also obtained). Eg.,

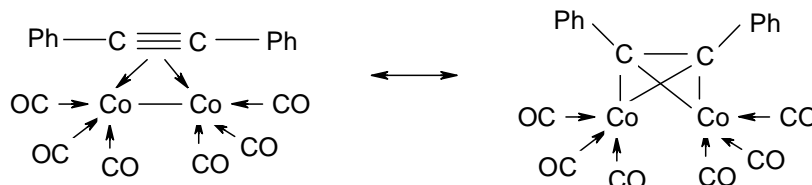




But still, a few relatively simple complexes containing an ethyne bonded to two metal atoms are known. Diphenyl ethyne displaces the bridging carbonyls from  $\text{Co}_2(\text{CO})_8$  when they are heated together in benzene.

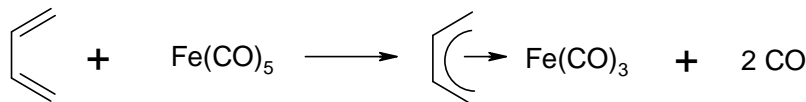


But the C-C bond length in the product (146 pm) indicates that its structure is intermediate between the following structures.



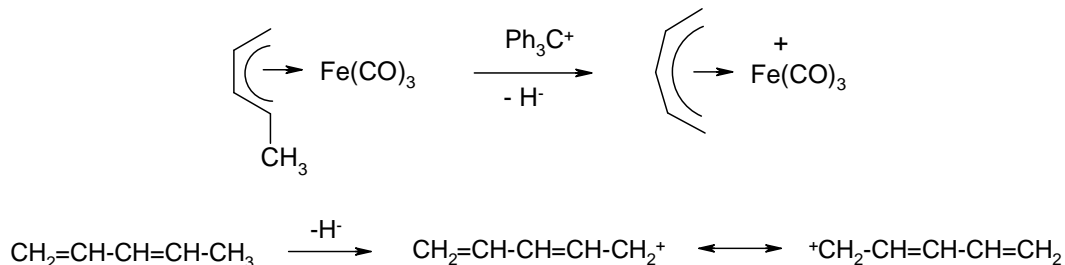
### Diene complexes

Butadiene iron tricarbonyl was first made in 1930 by heating butadiene with iron pentacarbonyl under pressure.

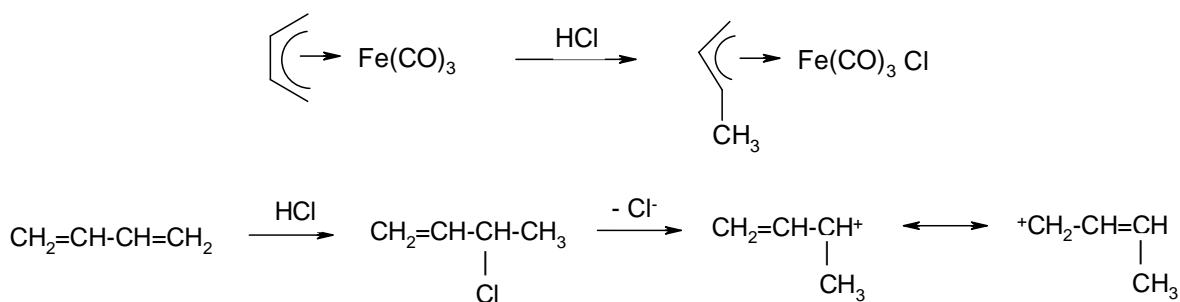


The product is a yellowish-brown oil which is soluble in most organic solvents and is slowly oxidized by air. The complexed ligand is difficult to hydrogenate and does not give the Diels-Alder reaction. The ligand is in the cis-configuration and the plane of the four C-atoms is nearly parallel to that of the three CO groups. The metal atom is equidistant from the four C-atoms and the C-C bond lengths are all 145 pm. All these observations suggest that it is a  $\pi$ -complex over all four C-atoms rather than two separate  $\pi$ -donor bonds. Iron carbonyls isomerise non-conjugated dienes to form  $\pi$ -complexes of conjugated compounds.

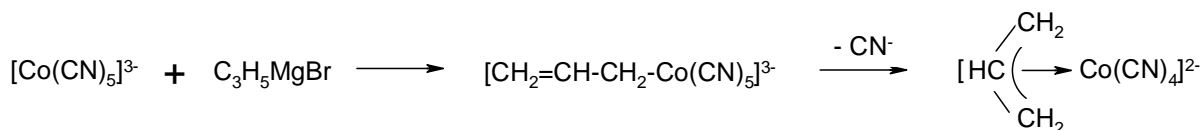
**$\pi$ -allyl complexes:** Hydride abstraction using  $\text{Ph}_3\text{C}^+\text{BF}_4^-$  converts complexes of conjugated dienes to 5-electron donor complexes. Eg.,



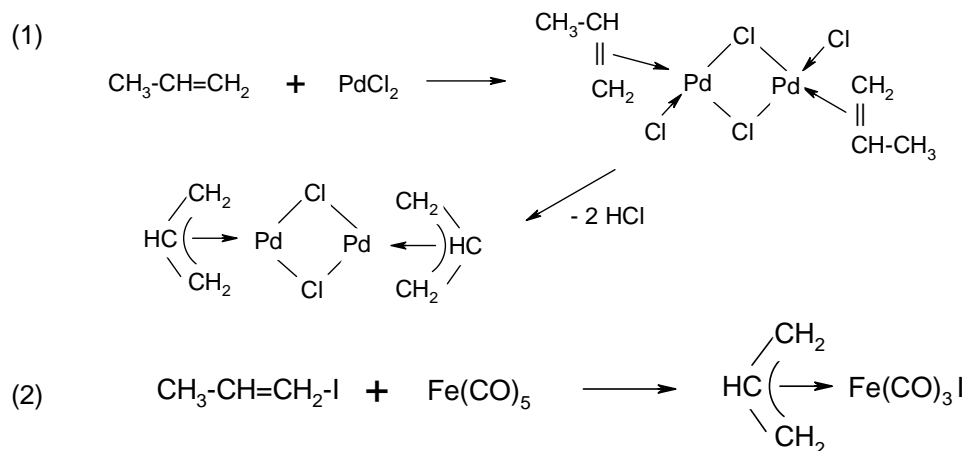
Proton addition (e.g. using HCl) converts complexes of conjugated olefins 3-electron  $\pi$ -enyl derivatives. E.g.,



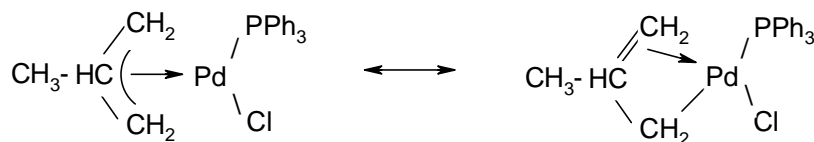
$\pi$ -allyl complexes can also be prepared from the reaction of metal halides, cyanides etc. with allyl Grignard reagents.



Some  $\pi$ -allyl complexes can also be prepared from olefins and metal halides or from allyl halides and metal carbonyls. E. g.,

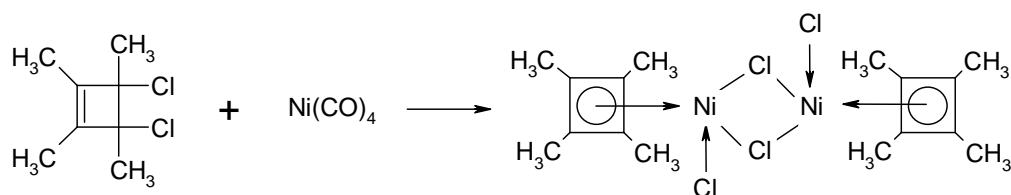


NMR studies show that, at low temperatures, these compounds exist as  $\pi$ -allyl complexes, but at higher temperatures they resonate between  $\sigma$ -bonded and  $\pi$ -allyl structures. E.g.,

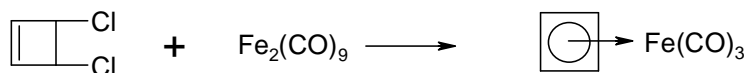


### Cyclic $\pi$ -donors

**Cyclobutadiene** is a 4-electron donor ligand. The existence of such ligands were theoretically predicted before the first one was isolated from the following reaction:

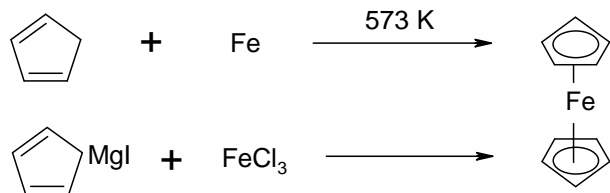


A complex of unsubstituted cyclobutadiene,  $\pi$ -cyclobutadiene iron tricarbonyl, is prepared as follows:



It is a remarkably stable compound and substitution reactions may be carried out on the ring. X-ray diffraction studies show that the  $\text{C}_4$ -ring is square-planar. Substituents are slightly displaced out of the plane of the ring on the side away from the metal atom.

**Cyclopentadienyl** system is a 5-electron donor ligand. The first compound with  $\pi$ -cyclopentadienyl system to be synthesized was ferrocene (dicyclopentadienyl iron). It can be prepared by the action of cyclopentadiene on reduced iron at 573 K, or by the action of cyclopentadienyl magnesium iodide on iron(II) chloride.



This is an orange crystalline solid, m. p. 447 K, sublimes at 373 K, insoluble in water and soluble in many organic solvents. It undergoes substitution reactions, but is more resistant to hydrogenation than benzene.

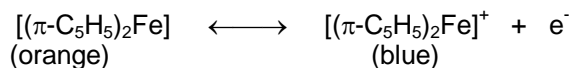
X-ray diffraction studies show



View from top

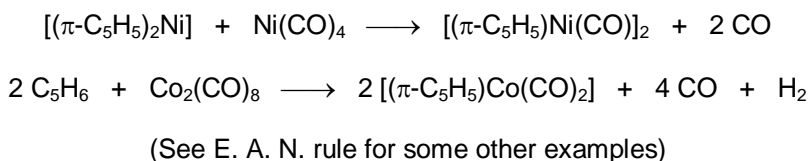
that it is a sandwich compound with the two cyclopentadiene groups staggered with respect to each other. Electron diffraction study of the vapour indicates that the rings are eclipsed in the vapour phase. All C-C distances in the ring are 140 pm, which is the same as that in benzene. The inter-ring distance is 332 pm and the Fe-C distance is 204 pm. The compound is diamagnetic, indicating the absence of unpaired electrons. Physical properties such as ionization potential and magnetic susceptibility indicated 18 electrons in nine available bonding orbitals.

Ferrocene is thermally stable up to 773 K and unattacked by boiling NaOH or HCl. It is easily oxidized by dilute nitric acid to the blue ferricinium ion.



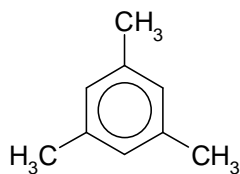
All metals of the transition series are now known to form such neutral sandwich complexes. They are called 'nickelocene', 'cobaltocene', 'manganocene' etc. Many  $\pi$ -cyclopentadienyl complexes of lanthanides and actinides are also known.

Among complexes containing  $\pi$ -cyclopentadienyl group and other ligands, carbonyl complexes are the most important. These are made by the action of cyclopentadiene on metal carbonyls, or by the action of carbon monoxide on  $\pi$ -cyclopentadienyl complexes.

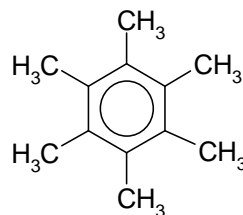


## Arene complexes

Benzene and substituted benzenes, particularly mesitylene and hexamethyl benzene act as 6-electron donor ligands. Complexes of naphthalene, anthracene and pyridine are also known.

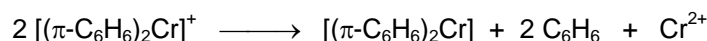
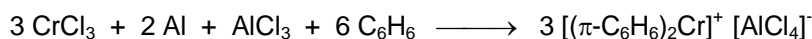


mesitylene



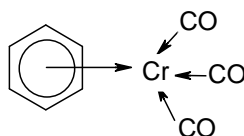
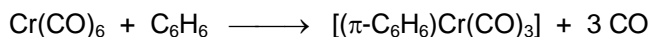
hexamethyl benzene

Neutral bis-arene complexes of vanadium, chromium, molybdenum, tungsten, iron and cobalt are known. Dibenzene chromium was the first arene complex to be correctly identified. It is prepared by the action of benzene on  $\text{CrCl}_3$  in presence of Al and  $\text{AlCl}_3$ . The resulting cation is hydrolysed in presence of alkali.



The neutral complexes are crystalline solids which sublime in vacuum at about 373 K. They are thermally stable up to about 573 K. They are soluble in organic solvents, but not in water. In both vapour and solid, dibenzene chromium is a sandwich molecule. The C-C distances in the ring are 142 pm, which is slightly more than in benzene (**why?**). The Cr-C distances are 215 pm. Dibenzene chromium is easily oxidized to form salts of  $[(\pi\text{-C}_6\text{H}_6)_2\text{Cr}]^+$  cation, but it is then resistant to further oxidation.

Arene metal carbonyls may be obtained by displacement of CO from metal carbonyls. E.g.,



**[Note:** How many CO molecules are replaced by cyclopentadiene from metal carbonyls? Why? How many are replaced by benzene? Why?]