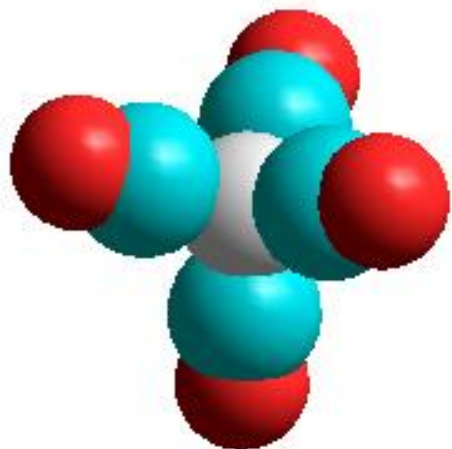
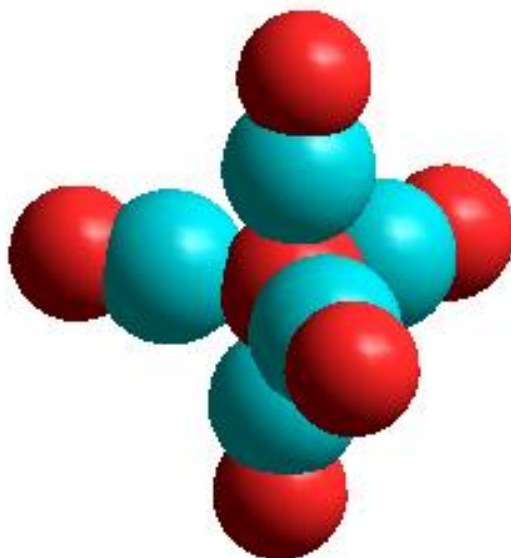


# METAL CARBONYLS

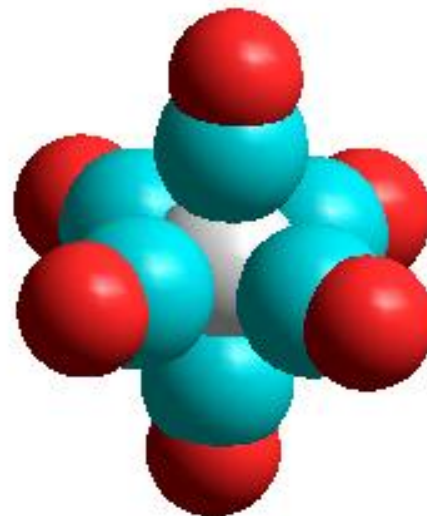
The carbonyl ligand forms a huge number of complexes with metal ions, most commonly in **ZERO oxidation states**, where it binds to the metal through its **C-donor**, as in the complexes below, where all the metal ions are zero-valent



$T_d$



TBP ( $D_{3h}$ )



$O_h$

**Effective Atomic Number** – Total no. of electrons present on a metal, its own and those gained during bond formation.

**EAN Rule** – Metals continue to accept pair of electrons from Ligands till their atomic number becomes equal to the atomic no. of the inert gas at the end of the period.

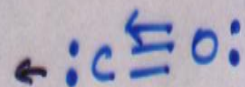
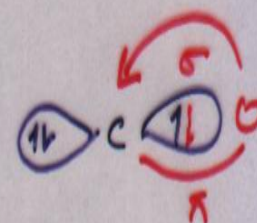
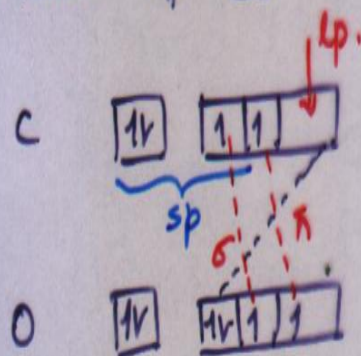
**EAN** = At.no. of metal + No. of e gained

**EAN of Carbonyls** = At. No. of metal + 2 x no. of CO molecules

| Metal Carbonyl    | At. No. of Metal | No. of e donated by CO mol. | EAN ( Inert gas)    |
|-------------------|------------------|-----------------------------|---------------------|
| $\text{Cr(CO)}_6$ | 24               | $6 \times 2 = 12$           | $24 + 12 = 36$ (Kr) |
| $\text{Ni(CO)}_4$ | 28               | $4 \times 2 = 8$            | $28 + 8 = 36$ (Kr)  |
| $\text{Fe(CO)}_5$ | 26               | $5 \times 2 = 10$           | $26 + 10 = 36$ (Kr) |
| $\text{Mo(CO)}_6$ | 42               | $6 \times 2 = 12$           | $42 + 12 = 54$ (Xe) |
| $\text{Os(CO)}_5$ | 76               | $5 \times 2 = 10$           | $76 + 10 = 86$ (Rn) |
| $\text{Mn(CO)}_5$ | 25               | $5 \times 2 = 10$           | $25 + 10 = 35$      |

CARBONYLS - CO as ligand.

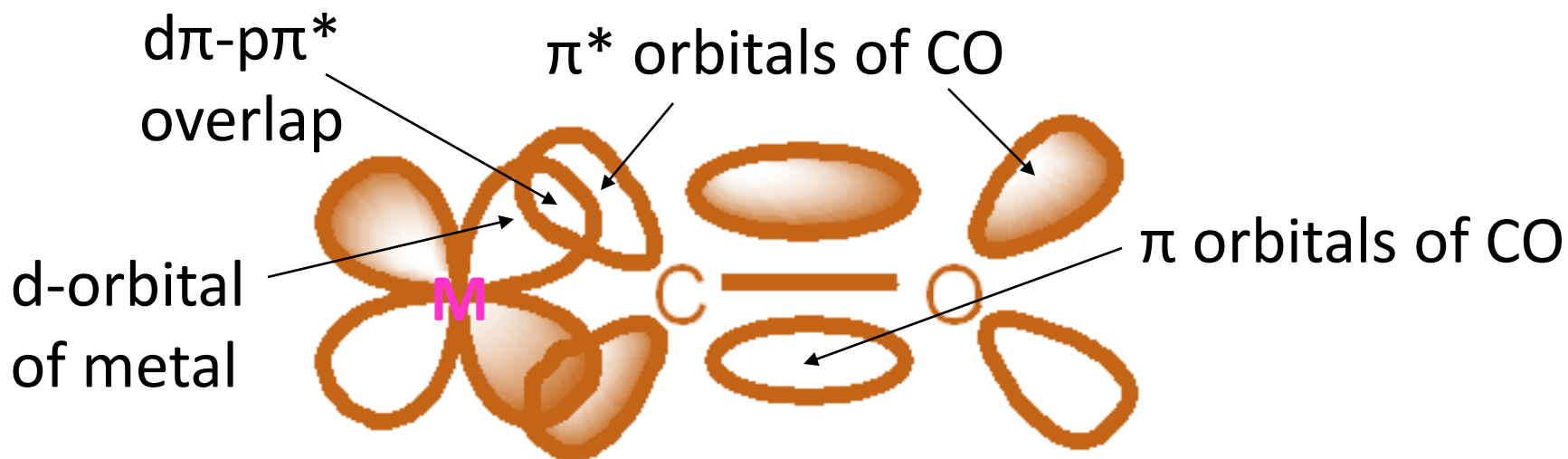
Structure of CO :



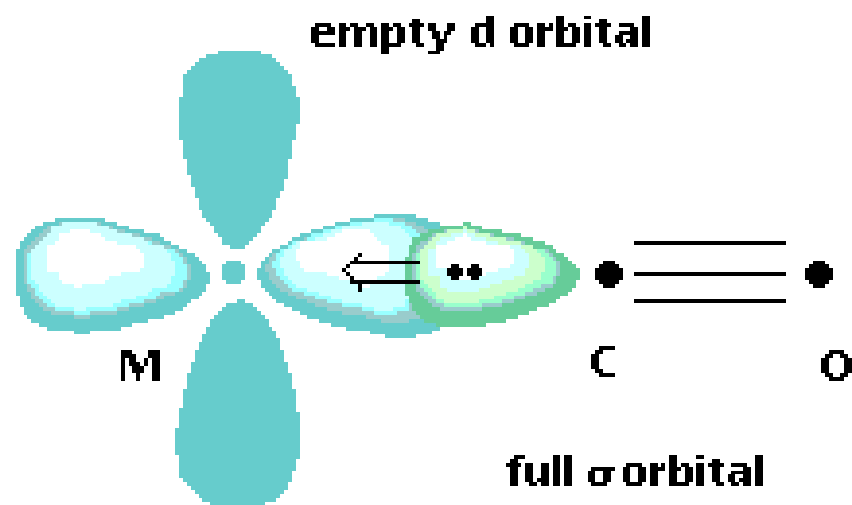
$\longleftrightarrow$   
112.8 pm

# Metal-Carbon bonding in carbonyl complexes

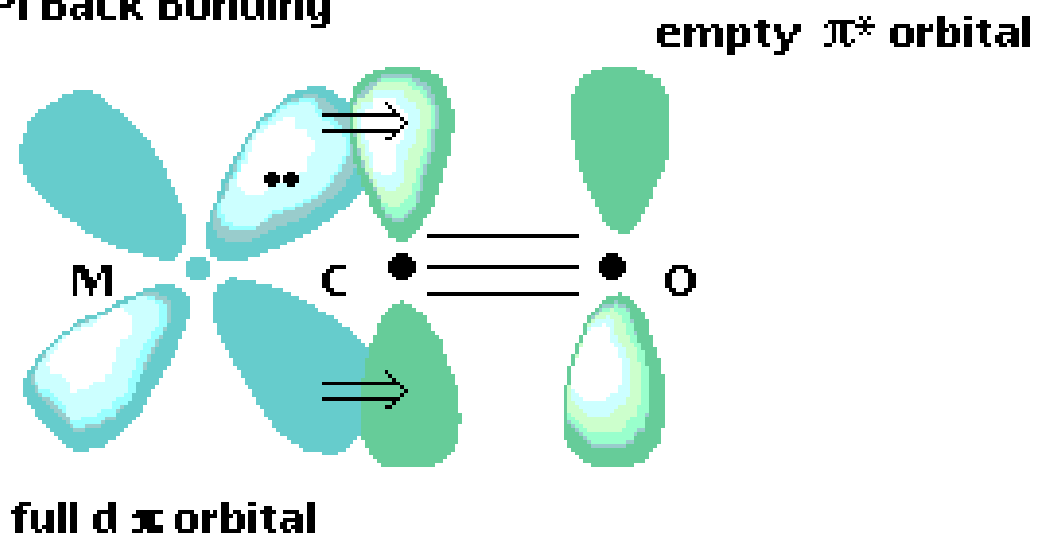
What stabilizes CO complexes is  $M \rightarrow C$   $\pi$ -bonding. The lower the formal charge on the metal ion, the more willing it is to donate electrons to the  $\pi$ -orbitals of the CO. Thus, metal ions with higher formal charges, e.g. Fe(II) form CO complexes with much greater difficulty than do zero-valent metal ions such as Cr(O) and Ni(O), or negatively charged metal ions such as V(-I). The  $\pi$ -overlap is envisaged as involving d-orbitals of the metal and the  $\pi^*$ -orbitals of the CO:



## Sigma Bonding

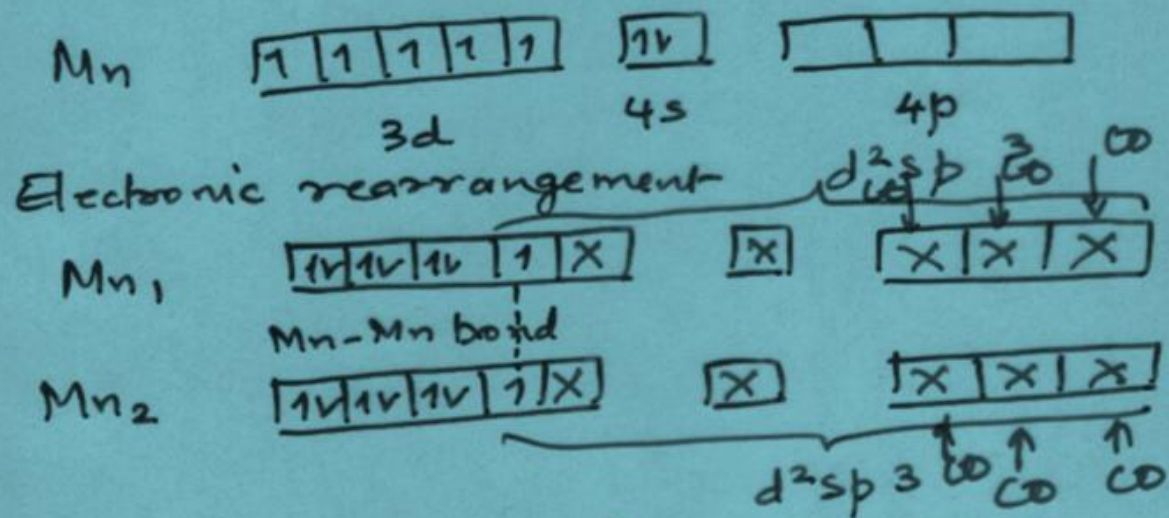


## Pi Back Bonding

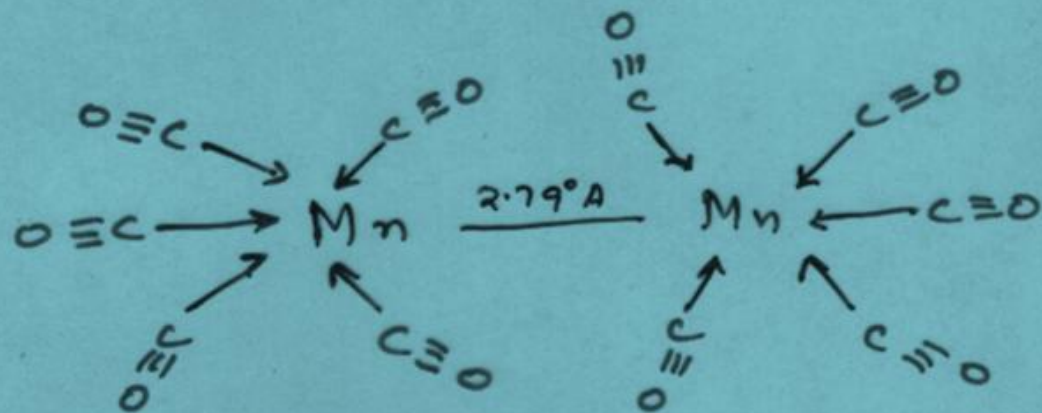


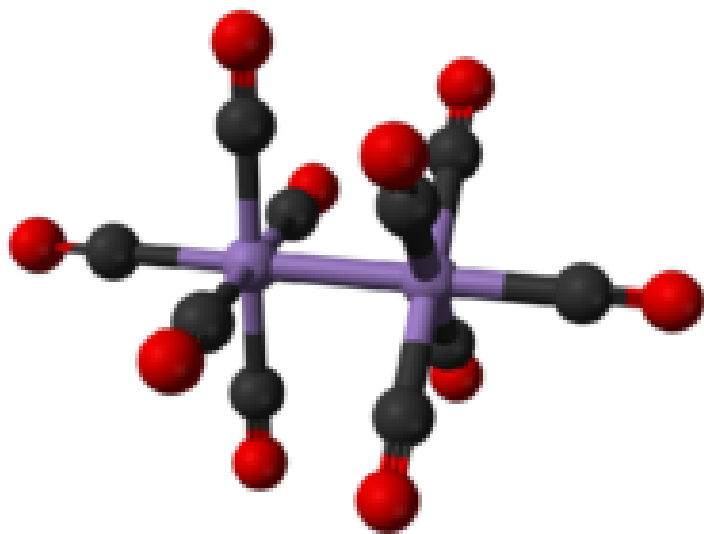
# POLYNUCLEAR CARBONYLS

## 1. $[Mn_2(CO)_{10}]$



Octahedral, diamagnetic

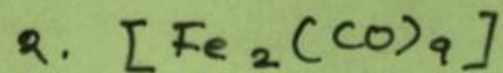




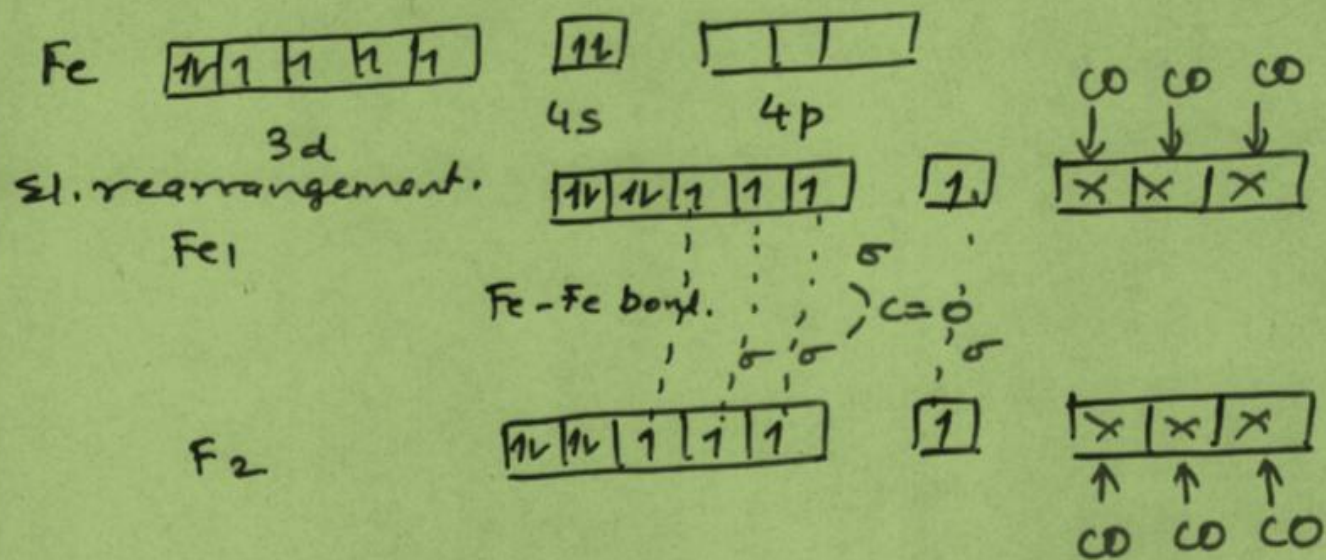
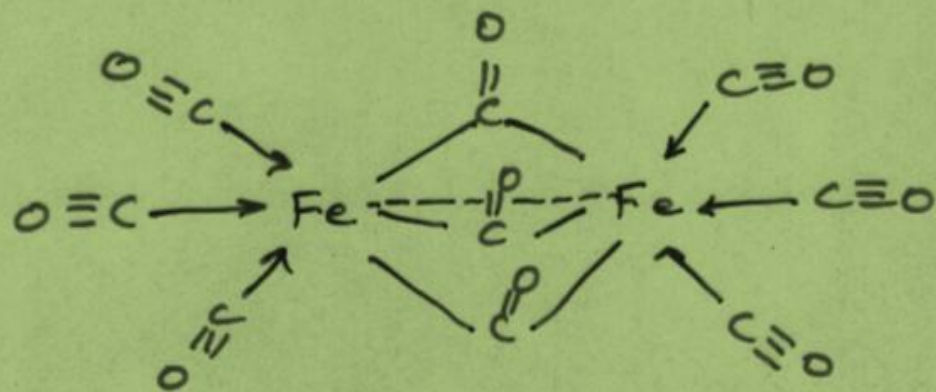
1. **five terminal CO's**,
2. and **one Mn – Mn** bond.





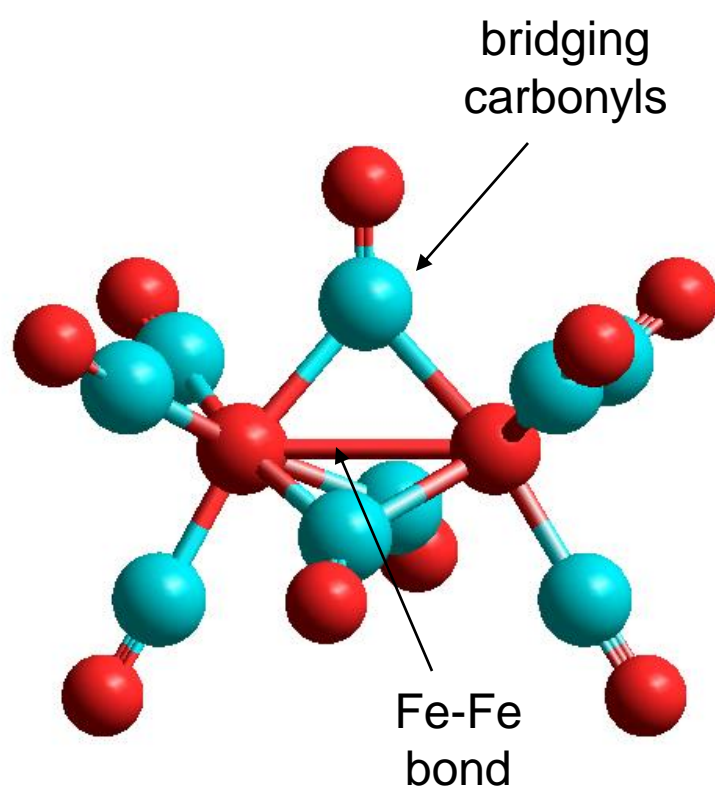


Octahedrally coordinated, 3 bridge carbonyls, 3 terminal carbonyls each. Diamagnetic





## Bridging Carbonyls in $\text{Fe}_2(\text{CO})_9$



$\text{Fe}_2(\text{CO})_9$  has each Fe with

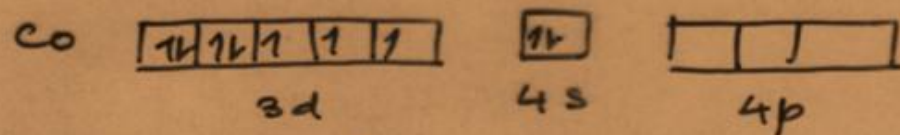
three terminal CO's,

three bridging CO's,

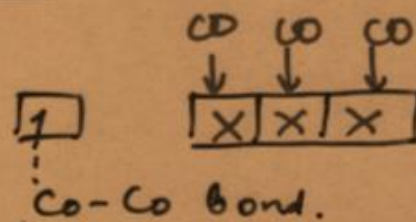
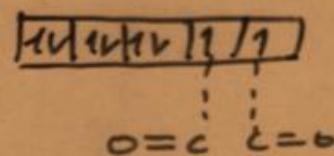
and an Fe-Fe bond.



# 4. $[Co_2(CO)_8]$

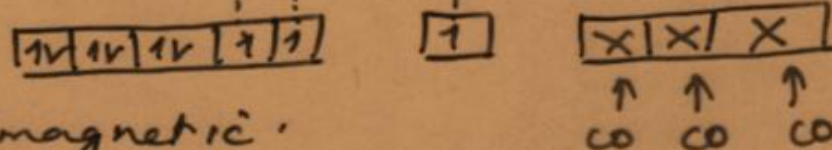


El. rearrangement  
Co<sub>1</sub>

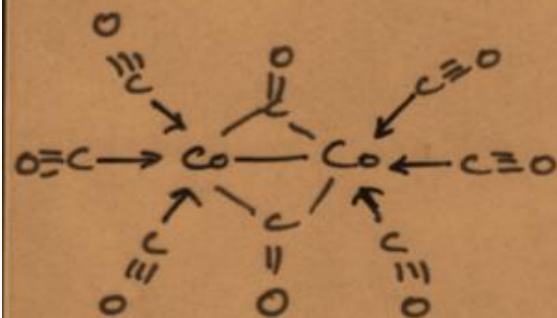


Bridge  
structure

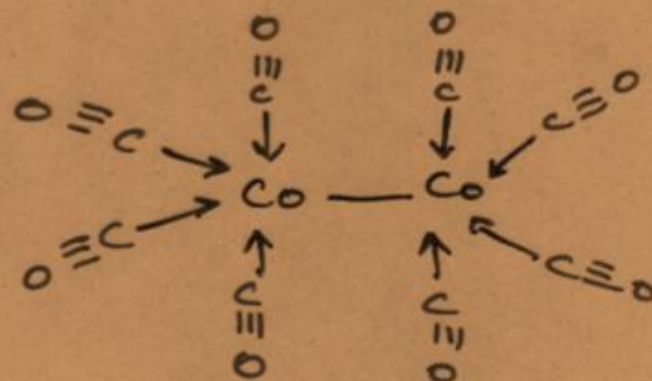
Co<sub>2</sub>



Octahedra, Diamagnetic.

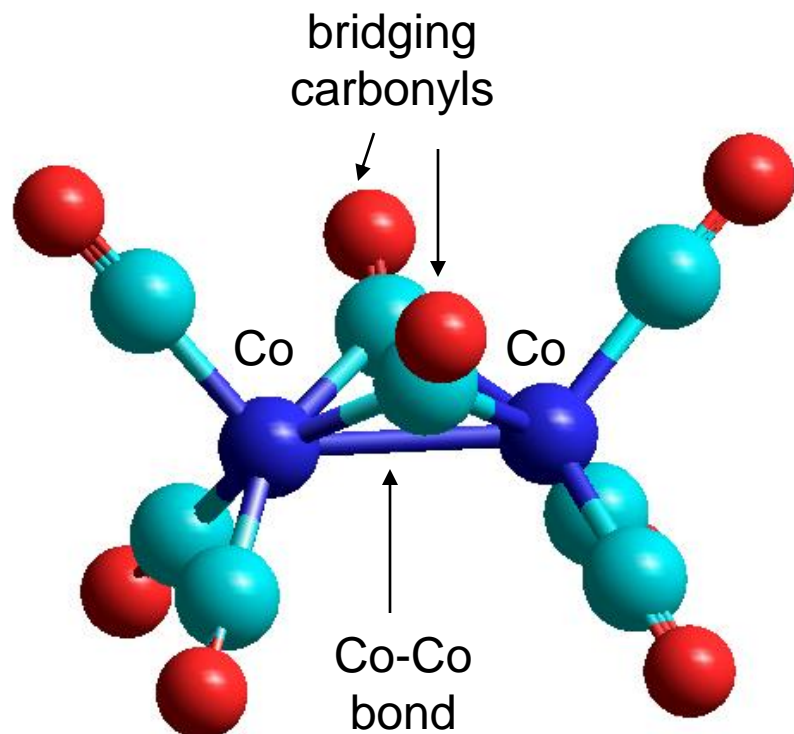


Bridge structure



Non-bridge structure

# Bridging Carbonyls in carbonyl complexes

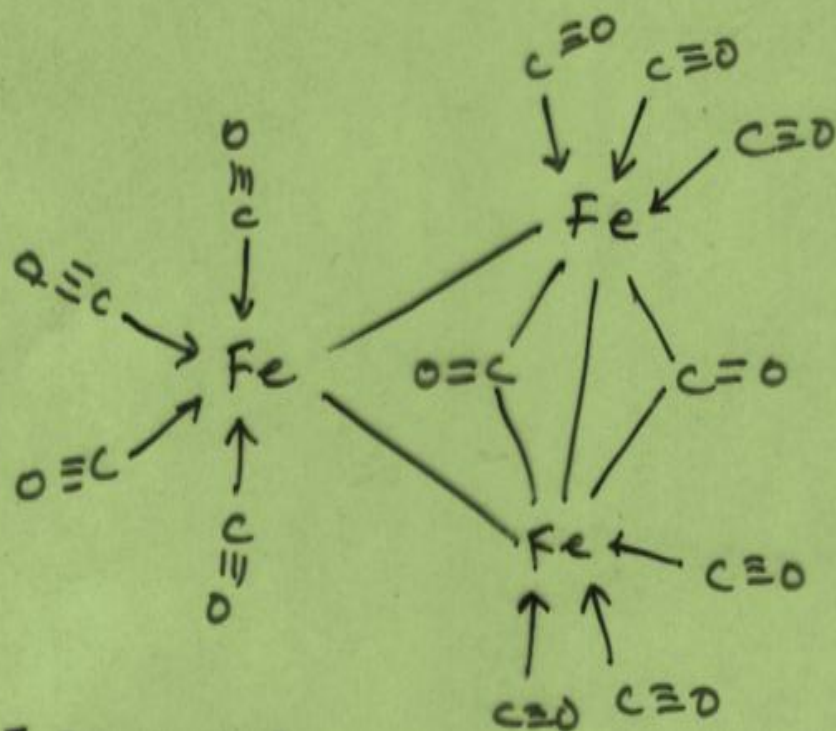


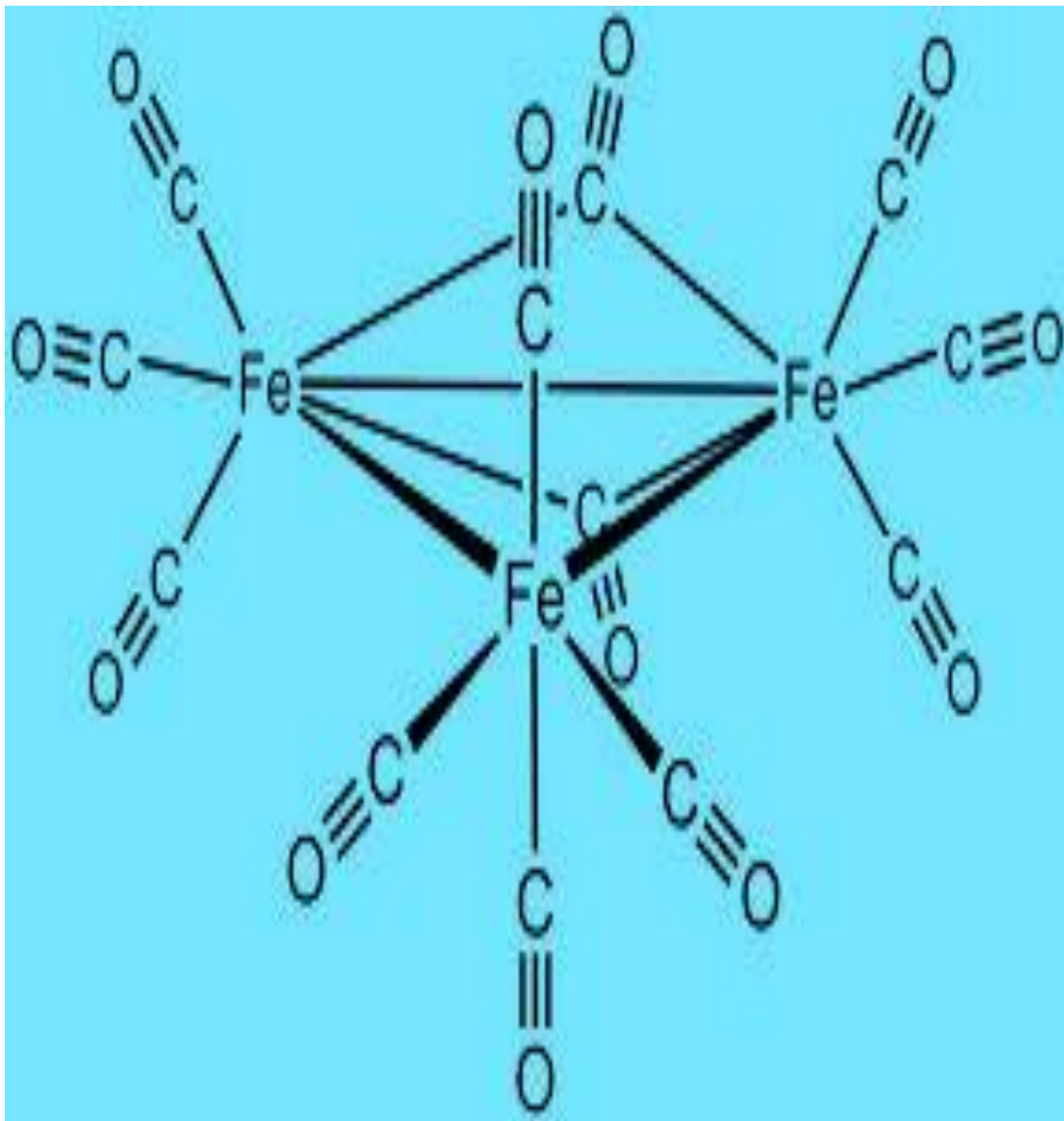
- **2 Carbonyls may form bridges** between two metals, where they donate one electron to each metal
- **1 Co – Co bond**



### 3. $[\text{Fe}_3(\text{CO})_{12}]$

- i) <sup>each</sup> 2 Fe atoms linked with 3 terminal carbonyl groups,  
2 bridge, and to 3<sup>rd</sup> Fe atom
- ii) 3<sup>rd</sup> Fe linked to 4 carbonyl terminal groups, & to 2 Fe atoms
- iii) Total of 3 Fe-Fe bonds.
- iv) Fe is  $\text{dsp}^3$  hybridised  
Trigonal bipyramidal



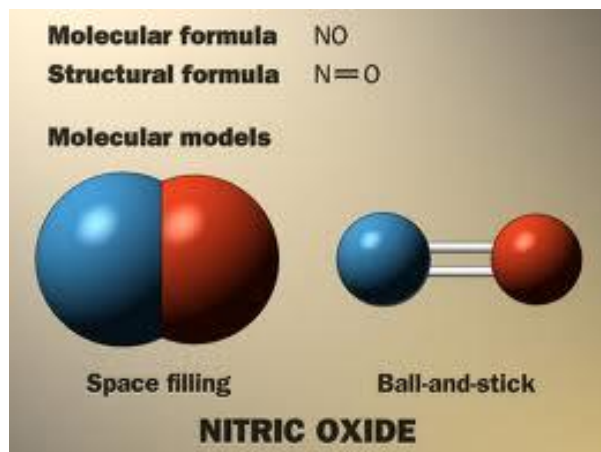


1. Each Fe bound to 2 other Fe
2. 1 Fe bound to 4 CO groups
3. 2 Fe bound to 3 CO group
4. And 2 bridging CO groups





# Metal Nitrosyls



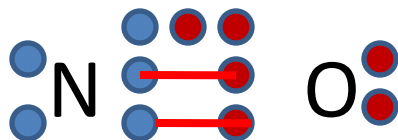
Nitrosyl complexes can be formed by the reaction of [nitric oxide](#) (NO) with many transition metal compounds or by reactions involving species containing nitrogen and oxygen. Some of these complexes have been known for many years: *e.g.*,  $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$  formed in the classical **brown ring test** for the qualitative detection of nitrate ion; Roussin's red ( $\text{K}_2[\text{Fe}_2\text{S}_2(\text{NO})_4]$ ) and black ( $\text{K}[\text{Fe}_4\text{S}_3(\text{NO})_7]$ ) salts; and **sodium nitroprusside**,  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ .

Such complexes, which can be **cationic, neutral, or anionic** and which are usually deeply coloured (red, brown, purple, or black

Because the nitrosonium ion ( $\text{NO}^+$ ) is isoelectronic with carbon monoxide and because its mode of coordination to transition metals is potentially similar to that of carbon monoxide, metal nitrosyls have been recognized as similar to carbonyls and are sometimes formulated as  $\text{NO}^+$  complexes.



# The structure and nature of Nitric Oxide



- Nitric oxide is a diatomic free radical consisting of one atom of nitrogen and one atom of oxygen
- Paramagnetic in gaseous state, diamagnetic in solid and liquid state as it dimerises  $-(\text{NO})_2$

**Structure of NO :** NO has eleven valence electrons. It is not possible to pair up all of them. So, it is an odd electron molecule and paramagnetic in gaseous state. In the liquid or solid state it is diamagnetic, because the molecule dimerises  $(\text{NO})_2$ .

The bond length N-O is  $1.15 \text{ \AA}$ , which is intermediate between a double and a triple bond.

Bonding is best described using molecular orbital theory. The bonding is similar to  $\text{N}_2$  and CO, with an extra unpaired electron which occupies an anti bonding  $2p$  orbital. If that electron is removed  $\text{NO}^+$  is formed. In  $\text{NO}^+$  the bond length is  $1.06 \text{ \AA}$ . Odd electron molecules are usually highly reactive. So, NO readily forms coordination complexes with transition metals.

# Types of compounds

Nitric oxide can combine with metals to form nitrosyl compounds by the following **three ways**.

**1. Simple compounds** containing the **A positive ion, NO<sup>+</sup>**, is produced by loss of electron

which then combine with atom or molecules.  **$[:N:::O:]^+$  or  $[:NO:]^+$**

Gen. formula **NO<sup>+</sup> X<sup>-</sup>** (X=F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NSO<sub>4</sub><sup>-</sup>)

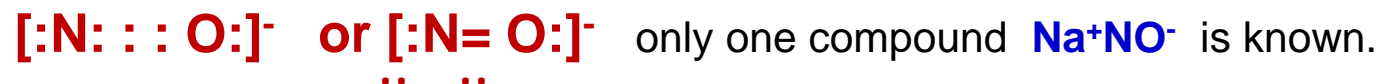
Presence of NO<sup>+</sup> confirmed by –

- NO has low I.P. so e<sup>-</sup> can be removed
- Electrolysis of NO<sup>+</sup>HSO<sub>4</sub><sup>-</sup> with Iron cathode, brown colour of [Fe(NO)]<sup>2+</sup> is formed around cathode showing migration of NO<sup>+</sup> to cathode.
- Conducting solution in nitro methane and behave like binary electrolyte.
- Salts of NO<sup>+</sup> HSO<sub>4</sub><sup>-</sup> can be prepared

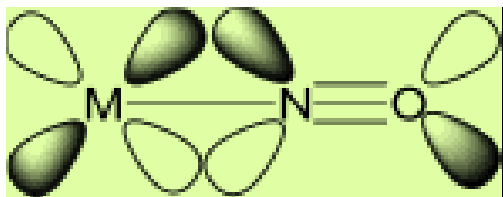


- Raman spectra confirms NO<sup>+</sup> ion

**2. Simple compound** containing **A negative ion,  $\text{NO}^-$** , is produced by gain of an electron from some electro positive material and it may have the structure.



**3. Metal complexes** - It may act as a **co-coordinating** group through donation of an electron pair involving the neutral molecule or the  $\text{NO}^+$  or  $\text{NO}^-$  group. It is mostly present as  $\text{NO}^+$ , where N is donor atom



- **Metal nitrosyl carbonyl** .  $[\text{Co}^- (\text{NO})^+ (\text{CO})_2]$  ,  $[\text{Fe}^{2-} (\text{NO})^+ {}_2(\text{CO})_2]$  , .

$[\text{Mn}(\text{NO})^+ (\text{CO})_4]$ , All these are iso electronic with  $[\text{Ni}(\text{CO})_4]$ ,

$[\text{Mn}^-(\text{NO})^+ (\text{CO})_4]$  with  $[\text{Fe}(\text{CO})_5]$

- **Metal nitrosyl halides** –  $[\text{Fe}^-(\text{NO})^+_2 \text{I}]_2$ ,  $[\text{Fe}^-(\text{NO})^+_2 \text{I}]$ ,  $\text{Ni}^-(\text{NO}^+) \text{X}$   
X= Cl, Br, I.

•**Metal Nitrosyl cyanides** -  $[\text{Mn}^+ (\text{NO}^+) (\text{CN})_5]^+{}^3-$

- **EAN Rule** – Nitrosyl cpx. follow EAN rule.  $[\text{Co}(\text{NO}^+)(\text{CO})_3]$

$$\text{Co}^- = 27 + 1e^- = 28, 3\text{CO} = 3 \times 2 = 6, \text{NO}^+ = 2 \quad \text{Total} = 28 + 6 + 4 = 36$$

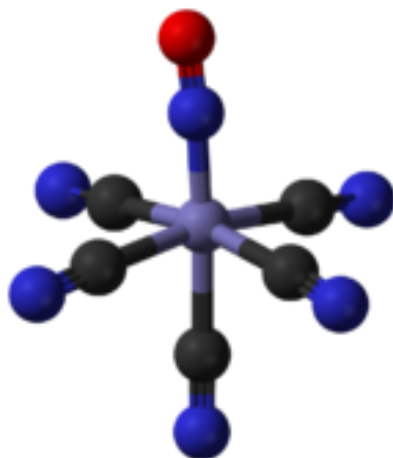
(At. No. of Kr)

# Bonding in Complexes

## Structure of Sodium nitroprusside $\text{Na}_2 [\text{Fe}^{+2} (\text{CN})_5 (\text{NO}^+)]$

$[\text{Fe}^{+2} (\text{CN})_5 (\text{NO})]^{-2}$  was formerly supposed to contain Fe (+3) ion. But Pauling and Sidgwick suggested that the odd electron of NO group enters the valence-shell of Fe (+3) ion making Fe as +2 oxidation state. Thus NO radical acquires one positive charge and gets coordinated to  $\text{Fe}^{+2+}$  ion as  $\text{NO}^+$  radical.

Thus there are total three +ve charges  $[\text{Fe}^2, \text{NO}^{+1}]$  and five negative charges ( $5\text{CN}^-$ ), hence total charges acquired by  $[\text{Fe}(\text{CN})_5 (\text{NO})]$  is -2, So, the formula of sodium nitroprusside is  $\text{Na}_2 [\text{Fe}^{+2} (\text{CN})_5 (\text{NO}^+)]$ . It has an octahedral structure with  $\text{Fe}^{+2}$  ion located at the centre of octahedron.



## Structure of Nitrosoferrous sulphate , $\text{FeSO}_4\text{NO}$ or $[\text{Fe}^+ (\text{NO}^+)]\text{SO}_4$ :

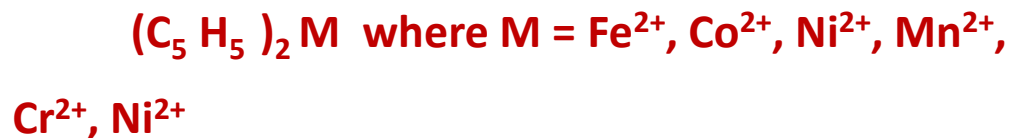
In aqueous solution  $[\text{Fe}^+ (\text{NO}^+)]^{+2}$  ion is better expressed as  $[\text{Fe}^+ (\text{NO}^+)(\text{H}_2\text{O}_5)]^{+2}$ , It is a paramagnetic substance having magnetic measurement 3.90 B.M. which corresponds to three unpaired electrons. This value supports the fact that Fe is in +1 oxidation state in this complex ion (i.e.  $3d^7$ ). i.e. it is a high spin complex of Fe (+1) with  $\text{NO}^+$ . The complex has N-O stretching frequency at  $1745 \text{ cm}^{-1}$  which indicates the presence of strong  $\pi$  bonding and the intense brown colour strongly suggests  $\text{Fe}^+ \leftrightarrow \text{NO}^+$  charge transfer.

# Metallocenes



**Ferrocene**

Transition metal atoms only generally form  $\pi$ -bonded compounds with multi  $\pi$  electron donors. **Ferrocene**, an iron compound, was the first compound of this type. Two  $C_5H_5$  rings are enclosing the iron atom. This is a sandwich compound.



In this compound all the Fe-C distances are identical. The ring structure is symmetric about the metal atom. The  $\pi$ -electrons of cyclopentadienyl anion overlap the vacant d-orbitals of the metal and form  $\pi$ -bonds. As a consequence these compounds are known as  $\pi$ -bonded compounds. Ethylene, acetylene, dienes like butadiene, aromatic molecules give these compounds