Metal Carbonyls

DEEPSHIKHA

Department of Chemistry

METAL CARBONYLS

- Metal carbonyls are the **transition metal complexes of carbon monoxid**e containing metal-carbon bond.
- Lone pair of electrons are available on both carbon and oxygen atoms of carbon monoxide ligand. However, as the **carbon atoms donate electrons to the metal**, these complexes are named as carbonyls.
- $Ni(CO)_4$ – Mond (purification of Ni).
- These compounds are widely studied due to industrial importance, catalytic properties and structural interest.

METAL CARBONYLS CONTD..

The carbonyls may be classified into two types:

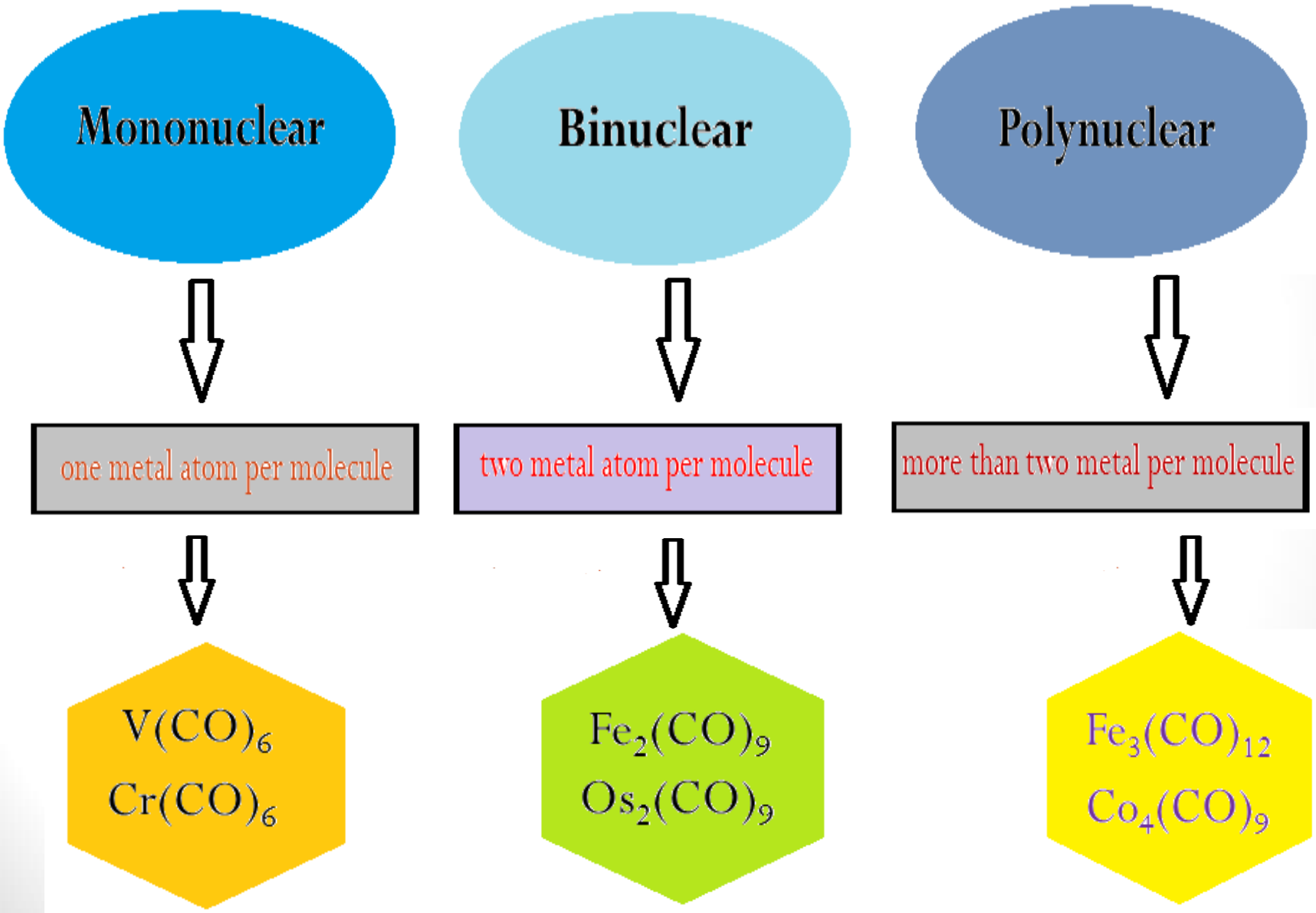
Mono nuclear carbonyls

a) They have the general formula M(CO)x
b) They contain only one atom of a metal per molecule of CO
c) Generally mono nuclear carbonyls are formed by metals which possess even atomic numbers.

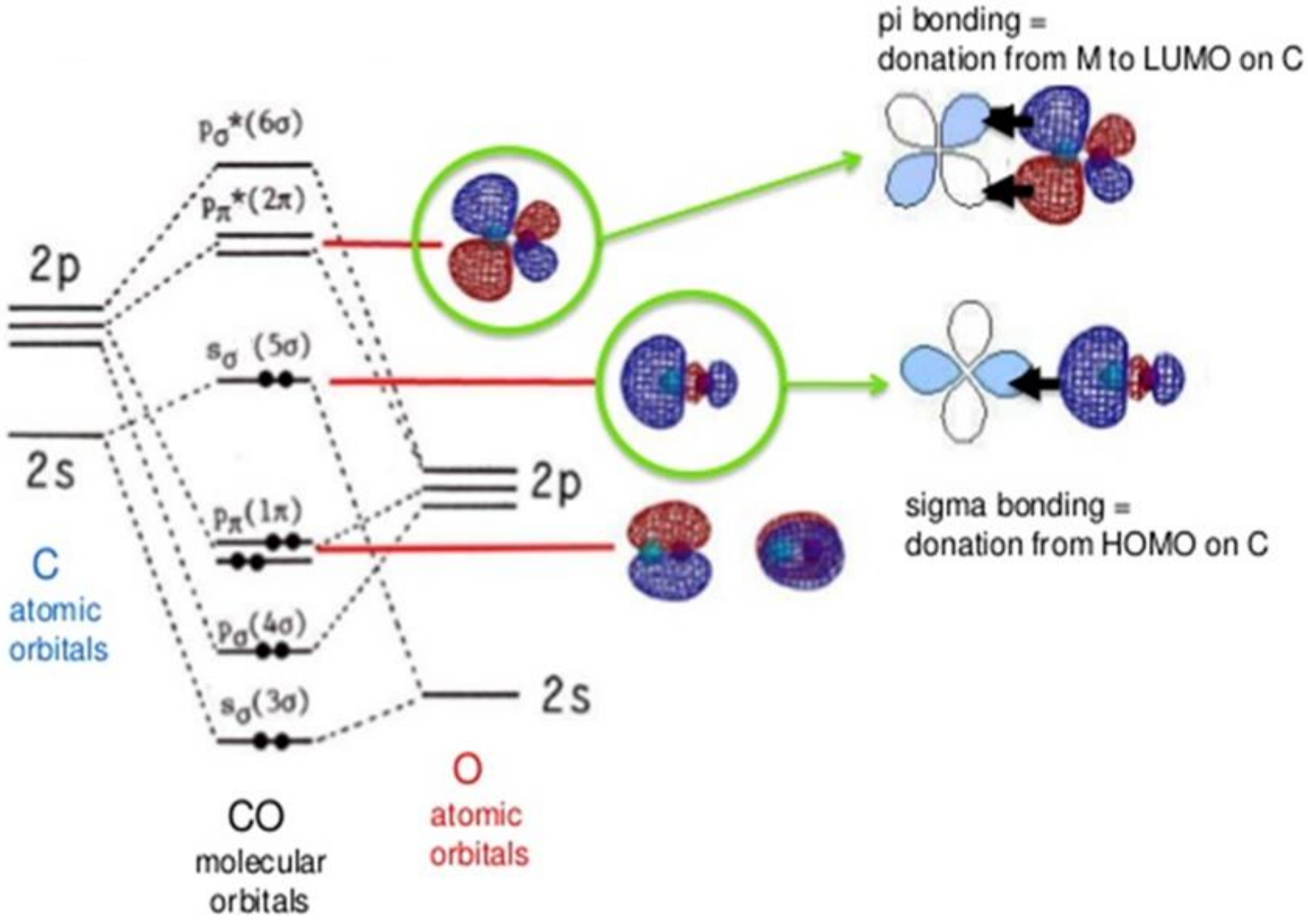
Poly nuclear metal carbonyls (Includes bi-nuclear carbonyls)

a) They have the general formula Mx(CO)y.
b) They contain more than one metal atom per molecule of CO.
c) If they contain two atoms of the metal per molecule, they are called binuclear carbonyls and they have the general formula M2(CO)

CLASSIFICATION OF METAL CARBONYLS



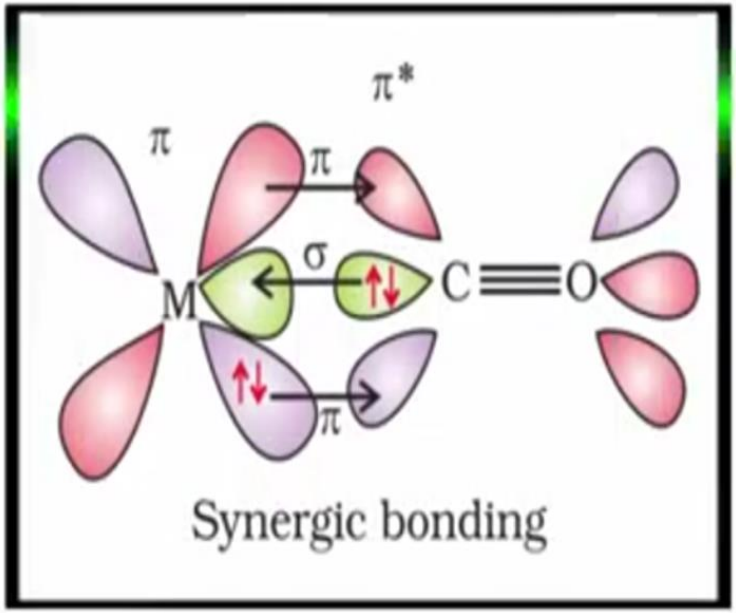
Bonding in Metal Carbonyls understood with MOT



BONDING IN METAL CARBONYLS

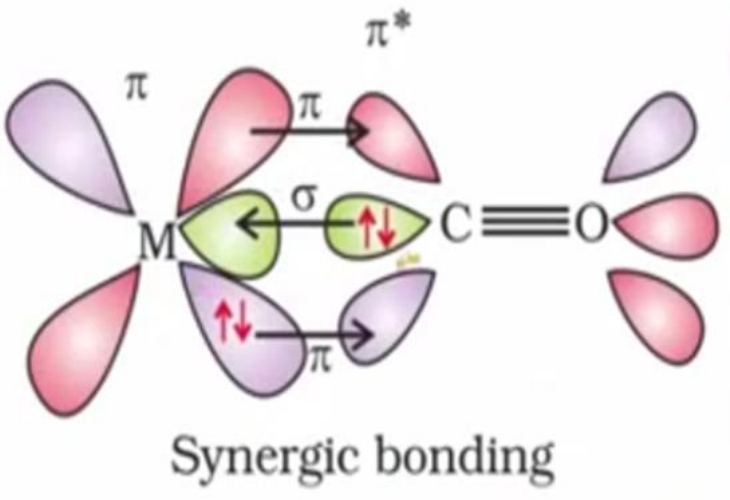
The Metal - carbon bond in metal carbonyls possess both s and p character

The M-C σ bond is formed by donation of loan pair of electrons on the carbonyl carbon into a vacant orbit of metal



Ni←CO σ-bonds in Ni(CO)4 takes place by the overlap between **empty sp3** hybrid orbital on **Ni** and **filled sp** orbital on carbon atom of **CO** molecule

BONDING IN METAL CARBONYLS(contd...)



The M-C π bond is formed by the donation of pair of a electron filled d orbital of metal into the π* carbon monoxide

The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and metal

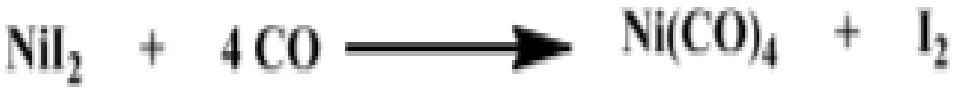
M→CO π-bond form by **overlap**ping with **filled dxy, dyz or dxz orbital of M** with **empty π* orbital on CO** molecule. Out of six CO, three are linked by M←CO σ-bond and remaining three is linked by M←CO and M→CO π-bond.

NICKEL CARBONYLS - PREPRATIONS

Nickel forms only mono nuclear carbonyl i.e., Ni(CO)

- Nickel carbonyl can be obtained by passing carbon monoxide over nickel at a temperature of about 60o C.

- When nickel iodide is heated with carbon monoxide in the presence of halogen, nickel carbonyl is formed

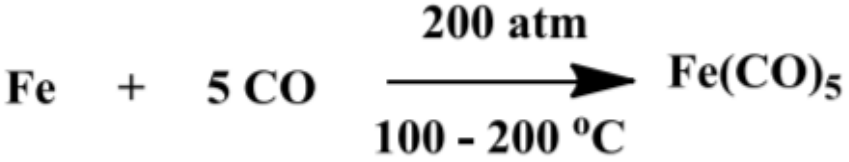


NICKEL CARBONYLS - PROPERTIES

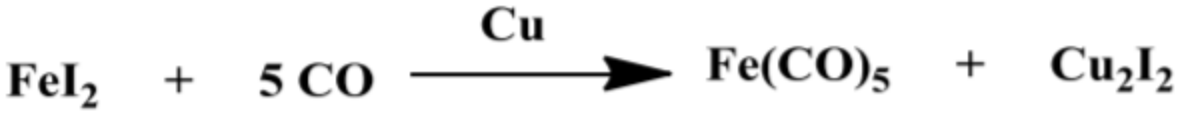
- Action of Heat: Nickel carbonyl is decomposed when heated to 180 – 200 o C.
- Action of Acids: Sulphuric acid reacts with nickel carbonyl and evolve carbon monoxide.
- Action of Bases: It reacts with barium hydroxide.
- Action of Halogens: It reacts with gaseous chlorine to form nickel chloride. Similarly it reacts with bromine.
- Displacement reaction: The CO group in carbonyls can be displaced by reagents such as PCl3, PF3 and NO2 etc.,
- With HI: It reacts rapidly with dry hydriodic acid.
- Action of nitric oxide: It reacts with nitric oxide to give a compound of intense blue colour Ni(NO)(OH).

IRON CARBONYLS - PREPRATIONS

- It is prepared by the action of carbon monoxide on iron powder at 200 atm and 100 – 200 o C.



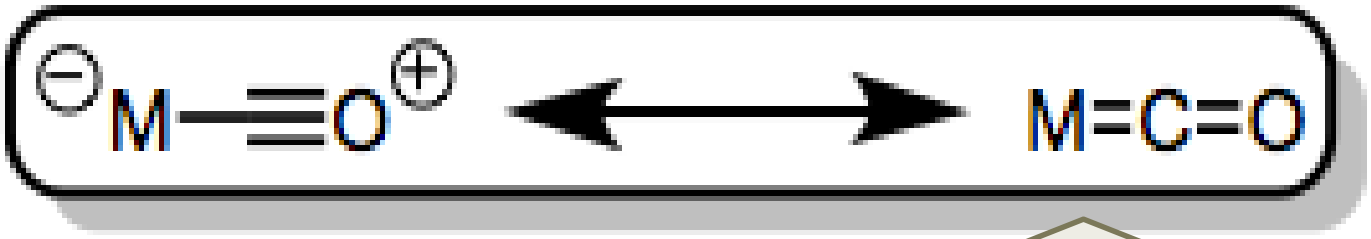
- Recently it has been prepared by the action of carbon monoxide on ferrous iodide



IRON CARBONYLS - PROPERTIES

- **Action of Heat:** When it is heated above 1300 o C it decomposes to give iron and carbon monoxide.
- **Action of Acids:** It is hydrolysed by sulphuric acid to give ferrous sulphate.
- **Action of Base:** It is hydrolysed by weak bases.
- **Reducing action:** It behaves as a reducing agent. The iron atom becomes divalent and either CO or CO2 is liberated.
- **With UV-light:** When Fe(CO)5 is irradiated by ultraviolet light, Fe2(CO)9 is formed.
- **With Cyclo pentadiene:** When Fe(CO)5 is heated with cyclo pentadiene at 300 o C, it gives the πcomplex ferrocene.
- **With Halogens:** It reacts with halogens to give stable tetracarbonyl halide, Fe(CO)4X2.

Consequences of bonding

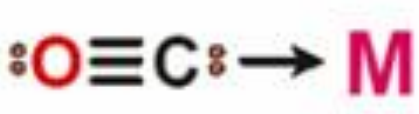


As **M-C** electron **donation increases**

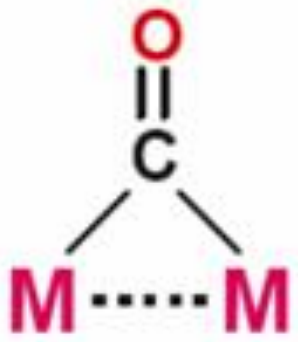
i.e π back bonding increases

M-C bond – strong	**C-O bond – weak**
M-C bond order increases	**C-O bond order decreases**
M-C bond length decreases	**C-O bond length increases**

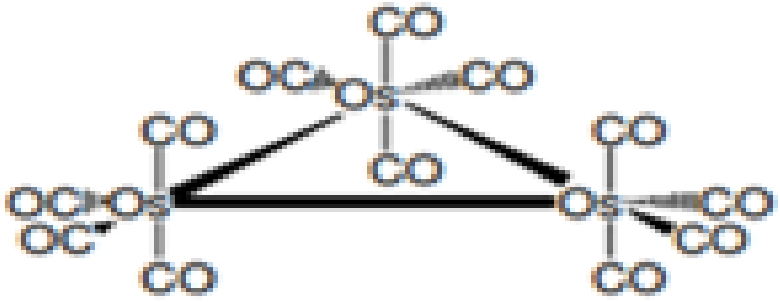
Standard Bonding Modes

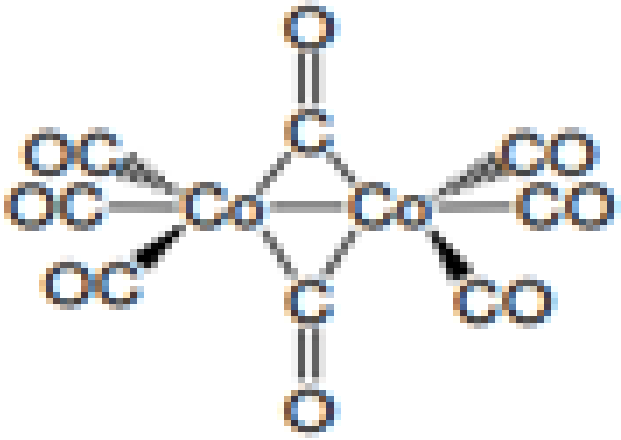


terminal mode



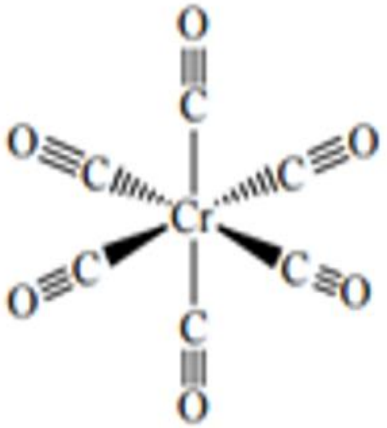
μ_2– bridging mode





Experimental evidence for bonding model

IR and Raman spectroscopy and single crystal X-Ray diffraction.
Characterisation of metal carbonyls



Cr-C = 195.5 pm

C-O = 114.0 pm

C-O = 112.8 pm

As ν(C-O) decreases C-O bonding decreases and M-C π-bonding increases

Bonding Modes

As one goes from a terminal CO-bonding mode to μ_2-bridging and finally μ_3 – bridging, there is a relatively dramatic drop in the CO stretching frequently seen in the IR

ν_{CO} IR (cm^{-1})	2143	2120 - 1850	1850 - 1720	1730 - 1500

References

1. **Adv. Inorganic chemistry Vol II,** SatyaPrakash, G.D. Tuli.
2. **Inorganic Chemistry**, Shriver and Atkins
3. **Inorganic Chemistry: Principles of Structure and Reactivity,** James E. Huheey, Ellen A. Keiter, Richard L. Keiter, Okhil K. Medhi

Thank You