Rank Enhancer

This column is specially designed to make your concepts crystal clear.

METAL CARBONYLS

Compounds of metals with CO (carbon monoxide) as a ligand are called metal carbonyls.

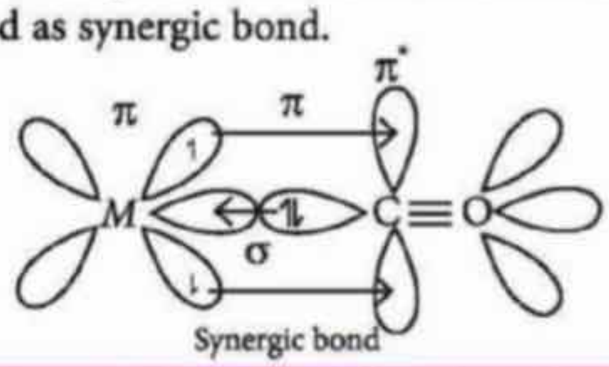
Classification Based on Number of Metals :

	Monomeric metal carbonyls		Polymeric metal carbonyls
1.	Those metal carbonyls which contain only one metal atom per molecule are called monomeric metal carbonyls.	1.	Metal carbonyls which contain two or more than two metal atoms per molecule are called polymeric metal carbonyls.
2.	More volatile	2.	Less volatile
3.	Either colourless or light coloured	3.	Deep coloured
4.	Examples: (1) $Ni(CO)_4$ (2) $Fe(CO)_5$ (3) $Cr(CO)_6$ (4) $V(CO)_6$	4.	Examples: (1) $Mn_2(CO)_{10}$ (2) $Co_2(CO)_8$

Bonding in Metal Carbonyls

Metal-carbon bond in metal carbonyls possesses both *s*- and *p*-character and they form two types of bonds :

- **σ-Bond :** It is formed by donation of lone pair of electrons from carbonyl carbon into a vacant hybrid *d*-orbital of metal.
- **π-Bond :** It is formed by sidewise overlapping of filled unhybrid *d*-orbital of metal with vacant π*-orbital of carbon of CO.
- During bonds formation, carbon acts as σ donor and π-acceptor. These two interactions combinely called as synergic bond.



Synergic bond

Consequences of Synergic Bond :

- **Bond energy of CO :** As metal-carbon π-bonding increases, bond between C and O weakens.

  (a) If same metal with different +ve oxidation number then

  +ve oxidation number of metal increases
  ⇓
  its donating tendency decreases
  ⇓
  $(M - C)$ π-bond weakens
  ⇓
  $(C - O)$ bond becomes stronger
  ⇓
  ∴ Bond energy of C — O Bond ∝ oxidation number of metal

  (b) If isoelectronic : In anionic complexes, metal has a greater electron density to be dispersed, $M - C$, π bond strength increases, σ bond strength between C — O decreases *i.e.*,

  −ve charge on complex increases
  ⇓
  more electron density on metal
  ⇓
  $M - C$ π-bond becomes stronger
  ⇓
  C — O bond becomes weaker

  ∴ Bond energy of C — O bond $\propto \dfrac{1}{\text{−ve charge on complex}}$

Example: Decreasing order of bond energy of C—O bond:
$[Ni(CO)_4] > [Co(CO)_4]^- > [Fe(CO)_4]^{2-}$

- **Bond order :** We know, bond energy is directly proportional to bond order, we can use above concept for bond order.

  Metal–carbon π bond strength increases
  ⇓
  Carbon-oxygen bond strength decreases
  ⇓
  Carbon-oxygen bond order decreases

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- **Bond length :** As we know bond length inversely proportional to bond energy and bond order.

Example :

In $[V(CO)_5]^{3-}$ $[Cr(CO)_5]^{2-}$ $[Mn(CO)_5]^{-}$ $\longrightarrow$

Metal-carbon bond strength decreases
Carbon-oxygen bond strength increases
Carbon-oxygen bond order increases
Carbon-oxygen bond length decreases

Use of EAN Rule to Identify Oxidising Nature :

(1) EAN of V in $[V(CO)_6]$

$\Rightarrow$ At. No. + C.No. (2) – Ox. No.

$= 23 + 6(2) - 0 = 35$

To get next inert gas EAN, it gains an electron and reduces, acts as an oxidising agent.

$[V(CO)_6] + e^- \longrightarrow [V(CO)_6]^-$

EAN = 35 EAN = 36

(2) EAN of Co in $[Co(CO)_4]$

$\Rightarrow$ At. No. + C.No. (2) – Ox. No.

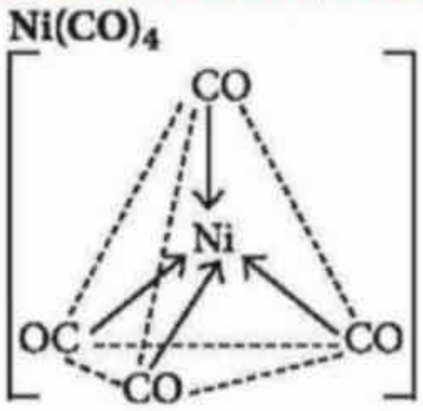
$\Rightarrow 27 + 4(2) - 0 \Rightarrow 35$

To get next inert gas EAN, it dimerises and acts as an oxidising agent.

$2Co(CO)_4 \longrightarrow Co_2(CO)_8$

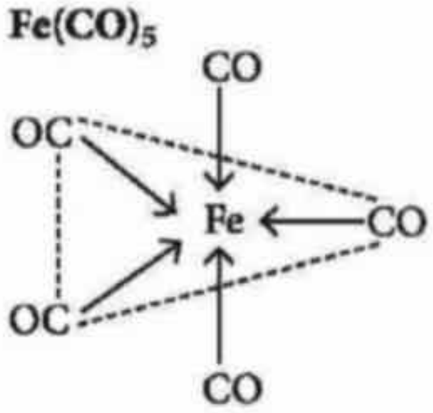
Structures of Some Important Carbonyl Compounds :

1. **$Ni(CO)_4$**



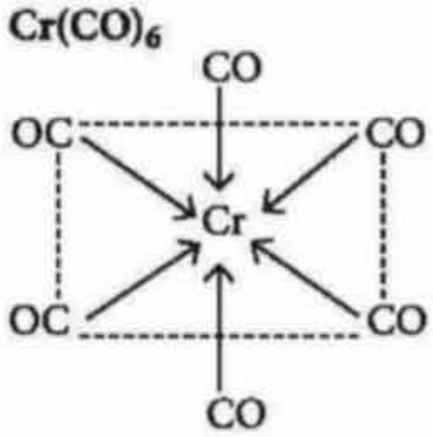
sp^3 hybridisation
Tetrahedral
EAN = 28 + 4(2) + 0
EAN = 36

2. **$Fe(CO)_5$**



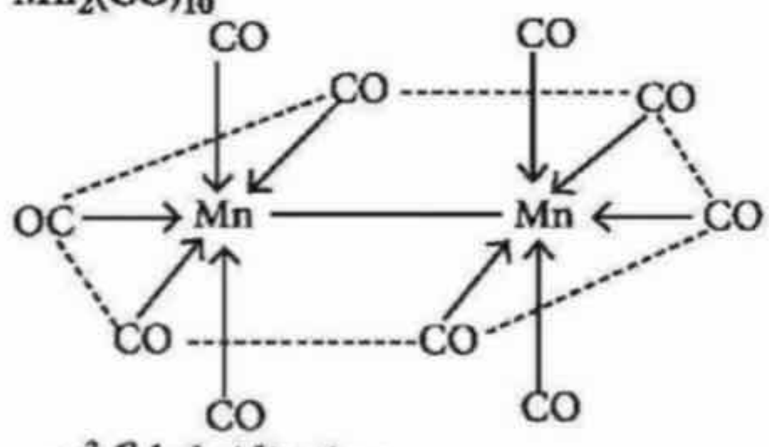
sp^3d hybridisation
Trigonal bipyramidal
EAN = 26 + 5(2) + 0
EAN = 36

3. **$Cr(CO)_6$**



sp^3d^2 hybridisation
octahedral or Square bipyramidal
EAN = 24 + 6(2) + 0
EAN = 36

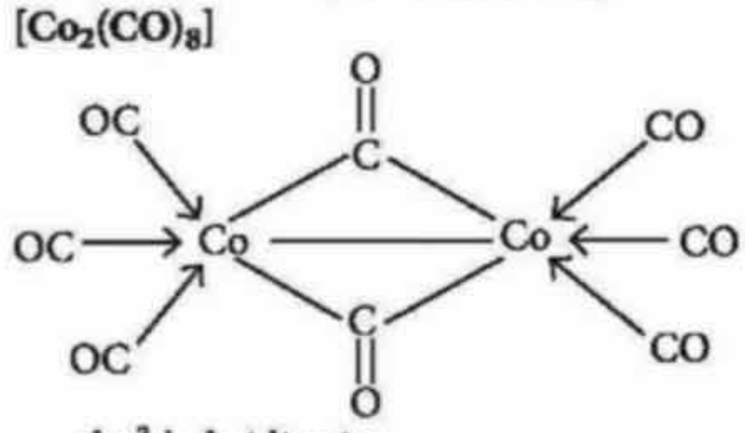
4. **$Mn_2(CO)_{10}$**



sp^3d^2 hybridisation

EAN = 25 + 5(2) + 1 = 36
(Metal-metal bond)

5. **$[Co_2(CO)_8]$**



dsp^3 hybridisation

EAN = 27 + 3(2) + 2 + 1 = 36
(Co–C bond) (Co–Co bond)

PROBLEMS

1. Which of the following is/are paramagnetic?

(a) $[V(CO)_6]$ (b) $[Cr(CO)_6]$
(c) $[Co_2(CO)_8]$ (d) $[Fe(CO)_5]$

2. In which of the following metal-carbonyl compounds, metal-carbon bond order is lowest?

(a) $[Fe(CO)_5]$ (b) $[Cr(CO)_6]$
(c) $[Mn(CO)_6]^+$ (d) $[V(CO)_6]^-$

3. Oxidation number of Co in $Na[Co(CO)_4]$ is

(a) 0 (b) +1 (c) –1 (d) +3

4. Bond between Cr and C in $Cr(CO)_6$ possesses

(a) σ character (b) π character
(c) ionic character (d) both (a) and (b).

5. Which of the following species is not expected to be a ligand?

(a) NO (b) NH_4^+
(c) $NH_2CH_2CH_2NH_2$ (d) CO

6. Correct order of C — O bond strength is

(a) $[Ti(CO)_6]^{2-} > [V(CO)_6]^- > [Cr(CO)_6] > [Mn(CO)_6]^+$
(b) $[Mn(CO)_6]^+ > [Cr(CO)_6] > [V(CO)_6]^- > [Ti(CO)_6]^{2-}$
(c) $[V(CO)_6]^- > [Ti(CO)_6]^{2-} > [Mn(CO)_6]^+ > [Cr(CO)_6]$
(d) $[Ti(CO)_6]^{2-} > [V(CO)_6]^- > [Mn(CO)_6]^+ > [Cr(CO)_6]$