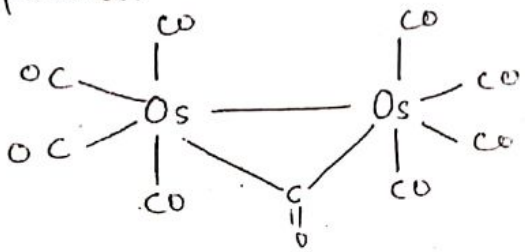
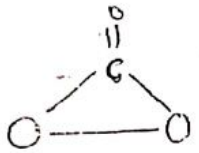
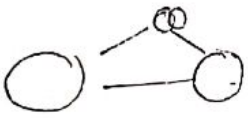
③ $Ru_2(CO)_9$ or $Os_2(CO)_9$:-

unstable compound.

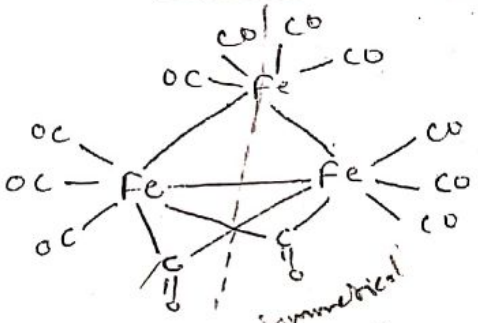


* Each Os → 4 terminal CO gp.
* Their is one doubly bridged CO
* One Os – Os bond.

Note:-  → 3d - element smaller, bridging can be do.

 → 4d & 5d elements ~~smaller~~ greater size, bridging strength lower, that's why 4d & 5d elements have less no of bridging CO gp.

→ $Fe_3(CO)_{12}$: Tri iron dodecacarbonyl:



* There is a triangle of 3- iron.
* One iron atom linked with 4 terminal CO & has no doubly bridged CO.
* The other two Fe atom are linked with 3 Terminal CO gp. and also linked with 2 doubly bridging CO gp.

e⁻ count : Symmetrical

Fe = 8e⁻

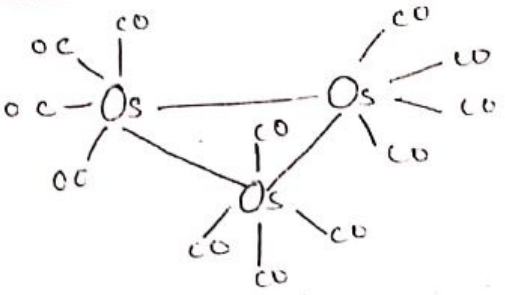
3 Ter. CO = 6e⁻

2 Brid. CO = 2e⁻

2 Fe-Fe = 2e⁻

18e⁻

÷ $[Os_3(CO)_{12}]$ or $[Ru_3(CO)_{12}]$ ÷

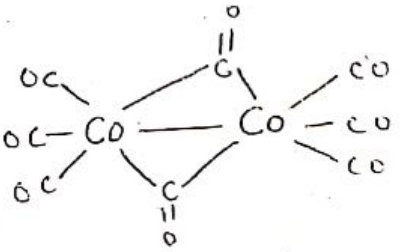


→ triangle of 3 Os elemen

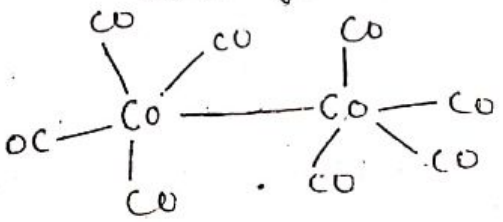
→ There is no briding co gp. & all the Os gps are attached with 4- co gps.

→ There is three Os-O single bonds which make a triangle.

→ $[Co_2(CO)_8]$:→



Bridge structure in solid form.



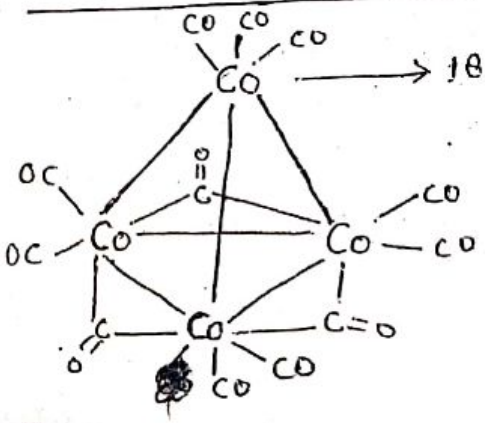
Non bridge structure

→* In solid state only brid structure is found whi in solution an equilibriu of bridge or non bridge structure are formed.

→ With increase in temp. the Bridge structure is converted into non-brid structure

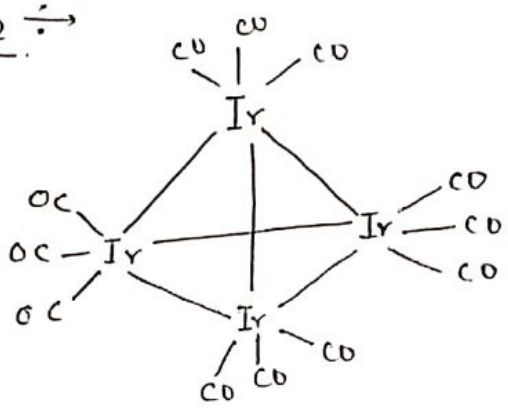
÷ It gives 18 e⁻ count per metal atom.

÷ $Co_4(CO)_{12}$ & $Rh_4(CO)_{12}$ ÷



→ 18 e⁻ count

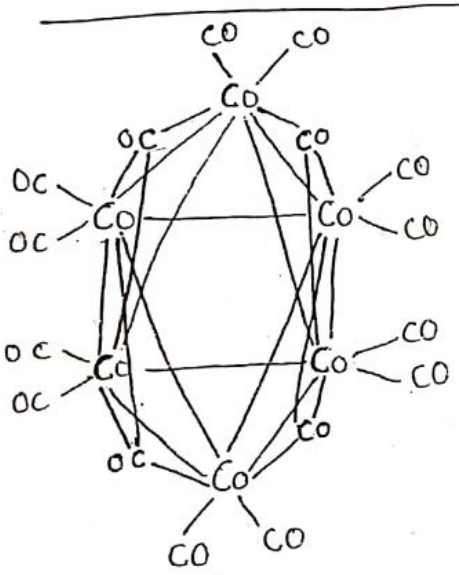
∴ $Ir_4(CO)_{12}$ ∴



→ Since Ir has bigger size so it has no bridging CO-gp.

→ It also give 18e⁻ count at each metal atom

∴ $[Co_6(CO)_{16}]$; $[Rh_6(CO)_{16}]$; $[Ir_6(CO)_{16}]$ ∴



→ These all of the compounds have similar structure

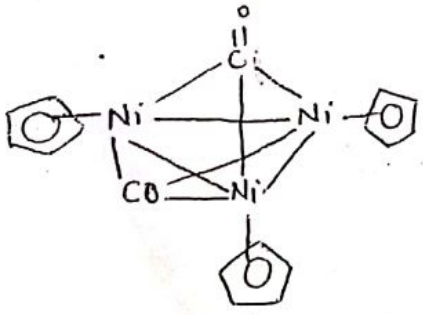
→ They do not follow the 18e⁻ Rule.

e⁻ count :

CO	= 9e⁻
2 Ter. CO	= 4e⁻
4 CO-Co	= 4e⁻
	17e⁻
2 Three bridging CO	= $\frac{4}{3}$e⁻
	18 $\frac{1}{3}$e⁻

∴ $Ni_3Cp_3(CO)_2$ ∴

Cp =  C_5H_5 cyclopenta diene gp.

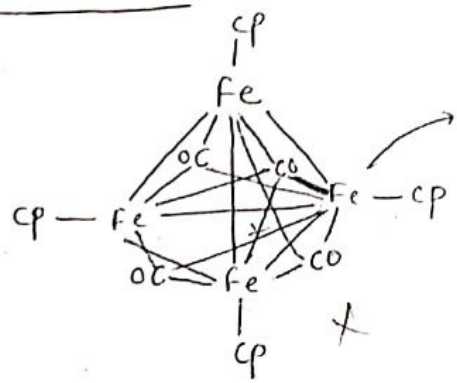


e⁻ count :

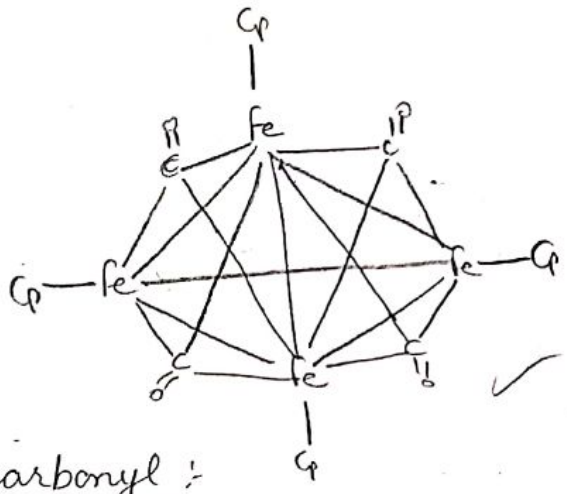
	10 e⁻
	5 e⁻
	2 e⁻
	4/3 e⁻
	18 1/3 e⁻

paramag-netic

∴ $Fe_4Cp_4(CO)_4$ ⟶



e⁻ count : $8 + 5 + 3 + 4 \times \frac{2}{3} = 18\frac{1}{3}$ e⁻



→ Preparation of metal carbonyl :-

① Direct reaction of metal (Finally divided with CO :-

$$Ni + 4CO \underset{100^\circ C}{\overset{60^\circ C}{\rightleftharpoons}} Ni(CO)_4 \quad \text{(Colourless liq.)}$$

$$Fe + 5CO \xrightarrow[100\ atm]{200^\circ C} Fe(CO)_5 \quad \text{(Yellow liq.)}$$

② By reductive carbonylation of metal salts :-

$$CrCl_3 + CO \xrightarrow[150^\circ C,\ 175\ atm]{LiAlH_4} Cr(CO)_6 + \ldots$$

$$OsO_4 + CO \xrightarrow[350\ atm]{250^\circ C} Os(CO)_5$$

↓ acts as reducing as well as CO

③ By UV radiation of metal carbonyls (only for Fe & Os) :-

$$2\,Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9$$

$$2\,Os(CO)_5 \xrightarrow{h\nu} Os_2(CO)_9$$

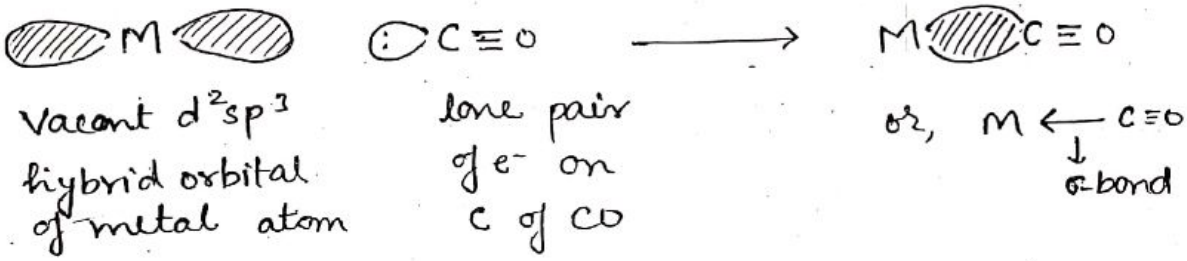
Nature of Bonding in metal carbonyls:

M ⇄ :CO (π-acceptor, σ-donor)

(CO is called π acid ligand due to having π* orbital vacant)

This type of bonding is called Synergic effect.

(i) M ← CO ⟶ σ bonding

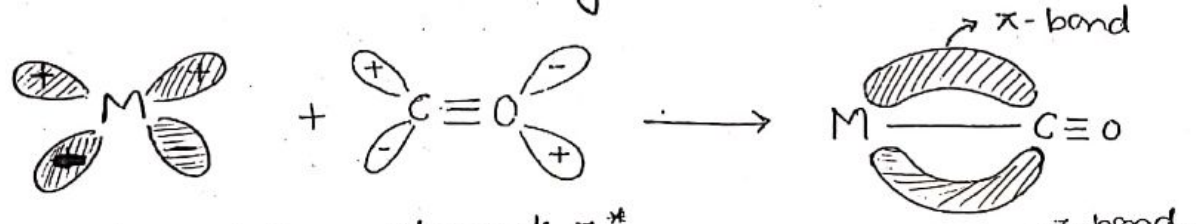


Vacant d^2sp^3 hybrid orbital of metal atom

lone pair of e⁻ on C of CO

or, M ← C≡O (↓ σ-bond)

(ii) M ⟶ CO π - bonding



Filled metal orbital

Vacant π* MO on CO

or, M ⟶ CO (π-bond.)

Synergic effect: Due to this, both σ- bond & π- bond strengthening each other.

÷ Vibrational frequency ÷→

$$M \longleftarrow C \equiv O$$

Bond order : 1 3

÷ In case of π- acceptor & σ-donor the bond order of M–C bond increases & C–O bond decreases.

$$M \cdots C \equiv O$$

b.o. → 1-2 2-3

÷ evidence of synergism :-

① shorter M–C bond, longer C–O bond.

$C \equiv O$ — X ray diff. = 1.128 A°

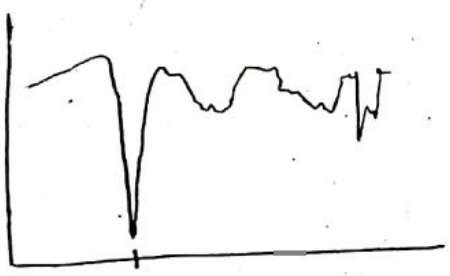
$C \equiv O$ — 1.15 A°

② ν_{M-C} – increases

ν_{C-O} – decreases

This is due to there that

B.O. ∝ Bond strength
bond energy
∝ stretching fre
$\propto \frac{1}{\text{Bond length}}$



ν_{CO} – frequency will differentiate, sharp & strong

$\simeq 2000\ cm^{-1}$

∴ Information convable by $\bar{\nu}_{CO}$:

(1) Nature of CO gp:-

Neutral CO ⟶ 2143 cm^{-1}

Terminal CO → 2125 — 1850 cm^{-1}

Doubly bridged. → 1850 - 1750 cm^{-1}

Triply bridged → 1750 - 1620 cm^{-1}

$\overset{\oplus}{C}O$ ⟶ 2184 cm^{-1}

$BH_3 \leftarrow CO$ ⟶ 2164 - 2184 cm^{-1}

Que: Explain the following band of frequencies of $Fe_3(CO)_{12}$

2000 cm^{-1}, 1900 cm^{-1}, 1860 cm^{-1}, 1820 cm^{-1}, 1775 cm^{-1}

Ans: solution 2000 cm^{-1}, 1900 cm^{-1}, 1860 cm^{-1} → Terminal CO

1820 cm^{-1}, 1775 cm^{-1} ⟶ Bridged CO

(11) Nature of metal carbonyls :-

wheather metal carbonyls are neutral, cationic or anionic

∴ Greater the +ve charge on metal less will be the back bonding ⟶ greater CO bond order ⟶ greater frequency.

∴ Greater the e^- density on metal larger will be the back bonding ⟶ Smaller will be the CO bond order ⟶ shorter frequency.

eg:- ① $[Mn(CO)_6]^+$ ⟶ 2090 cm^{-1}

$[Cr(CO)_6]$ ⟶ 2000 cm^{-1}

$[V(CO)_6]^-$ ⟶ 1860 cm^{-1}

② $[Ni(CO)_4]$ ⟶ 2060 cm^{-1}

$[Co(CO)_4]$ ⟶ 1890 cm^{-1}

$[Fe(CO)_4]^{-2}$ ⟶ 1790 cm^{-1}

(iii) Nature of ligand :-

Ligand

σ-donor

eg: NH_3, H_2O, $-X$

They have ability to donate lone pair of e⁻ to the metal that's why the e⁻ density increases on the mtal atom, hence the extent of back bonding increases which gives rise to decrease in C–O / bond order & ν_{CO} will decreases.

$M \rightleftharpoons C \equiv O$

ν_{CO} decreases.

σ-donor π-acceptor:

If the ligand has σ-donor & π-acceptor tendency same as that of CO then there will be No change in ν_{CO}.

$M \rightleftharpoons C \equiv O$

[ν_{CO} same]

∴ These ligands have vacant π* antibonding orbital

eg: CO, NO, CN^-

or vacand d-orbital

eg: S-ligand, PPh_3, $AsPh_3$, Aromatic/ hetehoaromatic

π-donor π-acceptor.

If the ligan is better π-don & better π-accel -tor, the e⁻ density on th metal atom decreases, This decreases the M – C≡O back bonding & ν_{CO} increases.

eg: $CH_2 = CH_2$

$CH \equiv CH$,

$=CR_2$ (carbene);

$\equiv CR$ (carbyne)

(iv) Nature of Product:-

$$L + M(CO)_6 \longrightarrow [M(CO)_5L]$$

→ Only one ν_{CO} band for $M(CO)_6$ T_{1u} mode $\approx 2000\ cm^{-1}$

→ $[M(CO)_5L]$ (C_{4v}) ⟶ 3-bands. (ν_{CO})

→ cis $[M(CO)_4L_2]$ (C_{2v}) ⟶ 4-Bands (ν_{CO})

trans $[M(CO)_4L_2]$ (D_{4h}) ⟶ 1-band (ν_{CO})

→ Expected explanation for Borane carbonyl:-

In case of $H_3B \leftarrow C \equiv O$; BH_3 is a excellent Lewis acid hence it will easily accept lone pair of e^- from CO (π-acid). But there is no back donation of e^- from BH_3 to CO & lone pair on the oxygen atom involves in increasing bond order. Hence, ν_{CO} is higher for $H_3B \leftarrow CO$ than free CO i.e. $2143\ cm^{-1}$.

$H_3B \longleftarrow C \equiv \ddot{O}:$ $\therefore \nu_{CO} > 2143\ cm^{-1}$