② On the basis of 18 $e^{\ominus}$ rule determine the unknown quantity.

→ ① $[Co(CO)_3]^{z}$ → Stable
↳ 18 $e^{\ominus}$ follow

TVE : $9 + 6 + z = 18$

$15 + z = 18$

$z = 18 - 15$

$z = 3$

$z = -3$

$[Co(CO)_3]^{-3}$ → charge.

(2) $[Ni(CO)_3(NO)]^{+1}$ → Whether NO is in linear / Bent mode?

NO

Binding Modes

$M-N\equiv O^{\oplus}$

Linear Mode

3 $e^{\ominus}$ donor

$M-\overset{\cdot\cdot}{N}=O$

Bent mode

1 $e^{\ominus}$ donor

$[Ni(CO)_3(NO)]^{(+1)}$ → Stable → follow 18 $e^{\ominus}$ rule

TVE = (18)

$10 + 6 + x - 1 = (18)$

$15 + x = 18$

$x = 3$

NO is 3 $e^{\ominus}$ donor

NO is in Linear Mode

Q $[(\eta^5\text{-}Cp)\ W(CO)_n]_2$ [W–W single bond]

$(5+6+2n)_d$

$n = ?$

(a) $n = 7$ (b) $n = 6$ (c) $n = 5$ ~~(d)~~ $n = 3$

$2 + 10 + 12 + 4n = 36$

$1\ CO \rightarrow 2e^{\ominus}$

$n\ CO \rightarrow 2ne^{\ominus}$

$2n\ CO \rightarrow 4ne^{\ominus}$

$24 + 4n = 36$

$4n = 36 - 24$

$4n = 12$

$\boxed{n = 3}$

Metal Carbonyl Complexes :-

1. Homonuclear Metal-carbonyl complex
2. Polynuclear metal-carbonyl complex-
   - → LNCC (Lower Nuclear Carbonyl Clusters)
   - → HNCC (Higher nuclear Carbonyl clusters).

IfAS

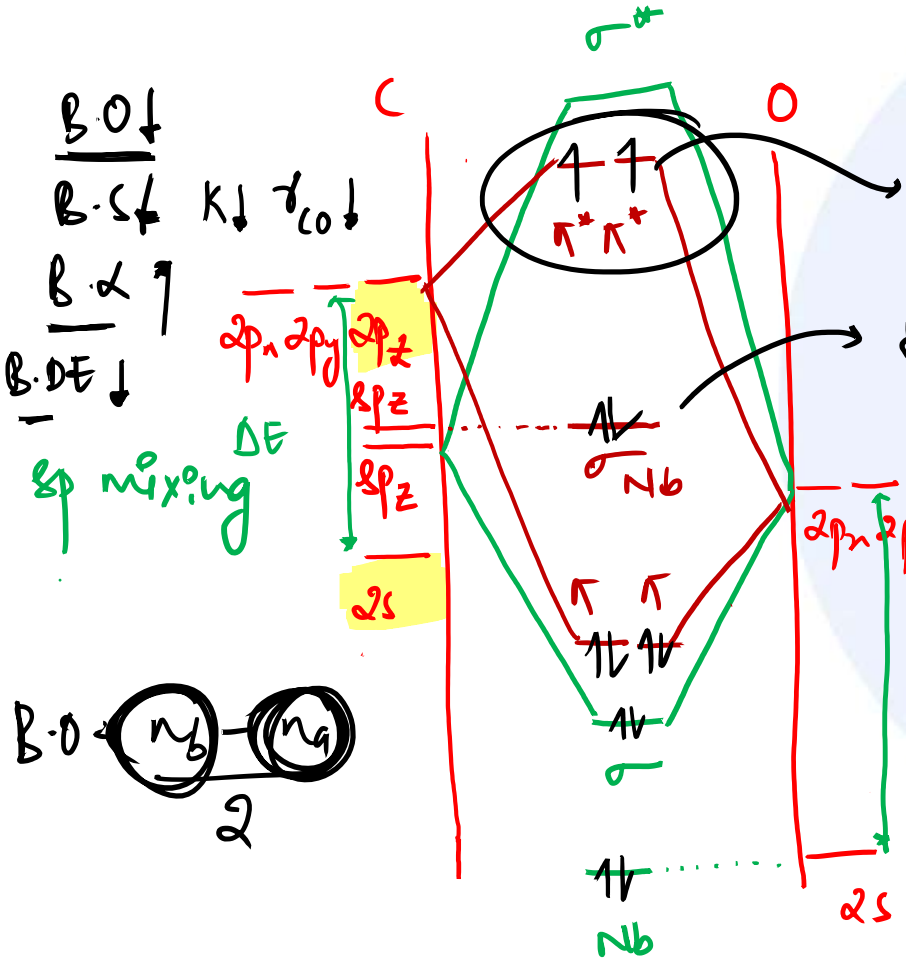
EN: C < O

CO: C : $2s^2 2p^2$

O : $2s^2 2p^4$

Mixing Condn. ① Symm. same

② Energy same



B.O ↓

B.St ↓ K ↓ γ_{CO} ↓

B.α ↑

B.DE ↓

B.O = $\frac{n_b - n_a}{2}$

(π acceptance).

① Bond Order = $\frac{N_{BMO} - N_{ABMO}}{2}$

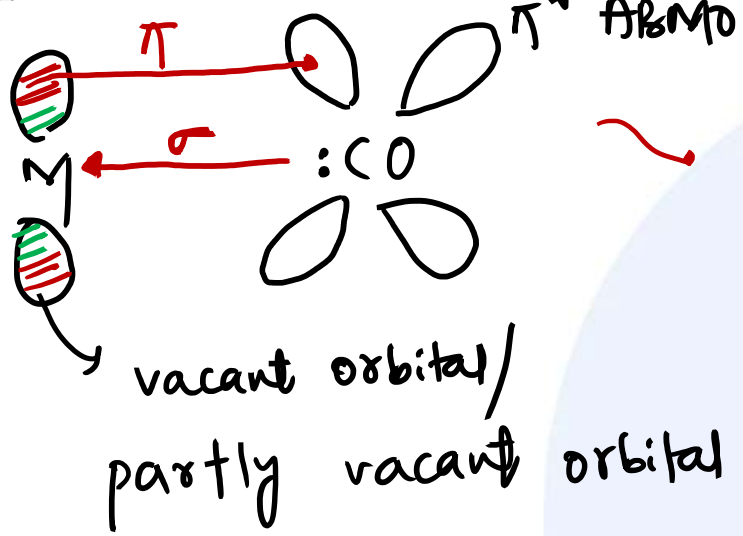
HOMO = $\frac{6 - 0}{2}$ = ③

② HOMO = σ_{sp_z} (N_{BMO}) (Small ABMO character)

③ LUMO = π^* (ABMO) (C-character)

④ $CO^{\oplus}$ (B.O = 3.5) > CO (B.O = 3)

Synergetic Effect:



σ bond is stabilised by Back donation from metal to C≡O (π*) ABMO.

→ If the above interactions shown are correct. then two techniques. i.e IR stretching freq. & X-ray crystallography will prove this.

① IR spectra :

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\nu \propto \sqrt{\frac{k}{\mu}}$$

IR stretching freq.

① $\nu \propto \sqrt{k}$

Bond strength ↑ k ↑ ν ↑

C≡O

② $\nu \propto \frac{1}{\sqrt{\mu}}$

Mass of atom ↑ μ ↑ ν ↓

free carbonyl : $C \equiv O^{\oplus}$

IR $\nu_{cm^{-1}}$ = 2143 cm^{-1}

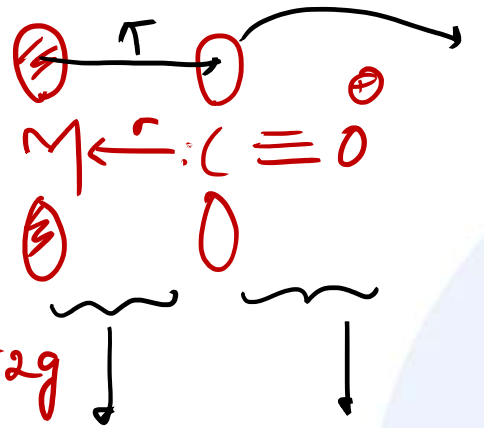
$M \rightleftarrows C \equiv O^{\oplus}$

k → force constant {tells about Bond strength.}

μ = Reduced mass.

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$m_1 m_2$ ↑ μ ↑



M=C=O

B.B / π interaction ↑

for C≡O

1. B.O ↓
2. B.S ↓
3. B α ↑
4. γ_{CO} ↓
5. γ_{M-C} ↑
6. B.D ↓ ↑ (M–C Bond)

TM

Factors affecting Back Bonding

(1) Charge on Central Metal ion :

Case (i)

$$M^{\oplus}-C\equiv O$$

Metal has less $e^{\ominus}$ density

$\therefore$ B.B ↓ γ_{CO} ↑

Complex stability ↓

Case (ii) :

$$M^{\ominus}-C\equiv O$$

Metal is $e^{\ominus}$ rich

B.B ↑ γ_{CO} ↓

Complex stability ↑

Q. (A) $[Ti(CO)_6]^{2-}$ (B) $[V(CO)_6]^{-1}$ (C) $[Cr(CO)_6]$ (D) $[Mn(CO)_6]^{\oplus}$

Arrange in ↑ng order of γ_{C-O} cm^{-1}. / γ_{m-c} cm^{-1}.

$Ti^{-2}—C\equiv O$ $V^{-1}—C\equiv O$ $Cr^{0}—C\equiv O$ $Mn^{+}—C\equiv O$

More $e^{\ominus}$ density → least $e^{\ominus}$ density

B.B ↑ γ_{CO} ↓ B.B ↓ γ_{CO} ↑ γ_{M-C} ↓

γ_{m-c} ↑

γ_{CO} cm^{-1} : (D) > (C) > (B) > (A)

γ_{MC} cm^{-1} : (A) > (B) > (C) > (D)

② If No. of carbonyl is different e⁻ (More ve charge)

(A) $[M(CO)_4]^{2+}$ $M^{+2} - CO \rightarrow +0.5$ → More e⁻ def. less B.B

(B) $[M(CO)_5]^{2+}$ $M^{+2} - \underline{CO} \rightarrow +0.4$

(C) $[M(CO)_6]^{2+}$ $M^{+2} - CO \rightarrow +0.37$ → less e⁻ def. ; More B.B.
(less ve charge)

$\gamma_{CO}\ cm^{-1}$: A > B > C

$\gamma_{M-C}\ cm^{-1}$: C > B > A

M^{+2} — 4CO $\quad \frac{+2}{4} = 0.5$

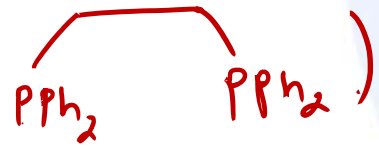
② Nature of Ligand :-

EDG.

σ-donor / π donor

Ex: PMe_3, $N(CH_3)_3$,

, $N(CH_3)_3$, en

dppe (

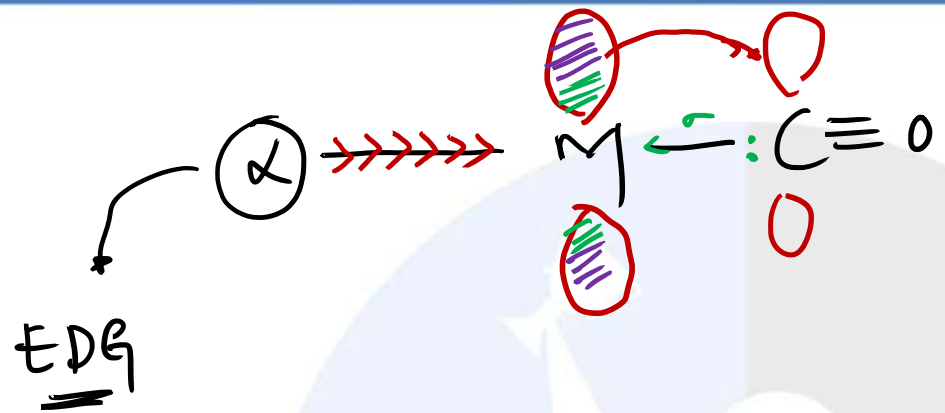
)

EWG

π-acceptor

CO, NO, PF_3, PCl_3, NO_2

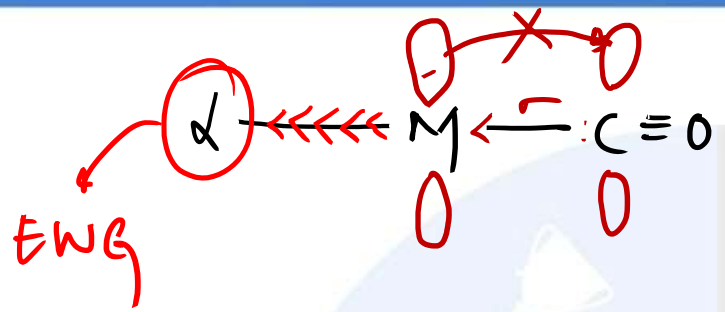
case (i) :



→ (1) If EDG. in complex ↑ B.B ↑ ν_{CO} ↓

→ (2) If EDG ↑ B.B ↑ Stability ↑

Case ② :



① If EWG in complex ↑ B.B ↓ γ_{CO} ↑

② If EWG ↑ B.B ↓ Stability ↓

↑ acceptor : $PF_3 > PCl_3 > P(OPh)_3 > P(OMe)_3 > PPh_3 > PMe_3 > P(Et)_3 > PCy_3$.

↓ donor : $PCy_3 > P(Et)_3 > P(Me)_3 > PPh_3 > P(OMe)_3 > P(OPh)_3 >$

$PCl_3 > PF_3$.

Q $[Mo(CO)_6] + 2PMe_3 \longrightarrow [Mo(CO)_4(PMe_3)_2]$

Ans

$[Mo(CO)_6] + 2PPh_3 \longrightarrow [Mo(CO)_4(PPh_3)_2]$

$[Mo(CO)_6] + 2PCl_3 \longrightarrow [Mo(CO)_4(PCl_3)_2]$

$[Mo(CO)_6] + 2PF_3 \longrightarrow [Mo(CO)_4(PF_3)_2]$

EWG : $PF_3 > PCl_3 > PPh_3 > PMe_3$

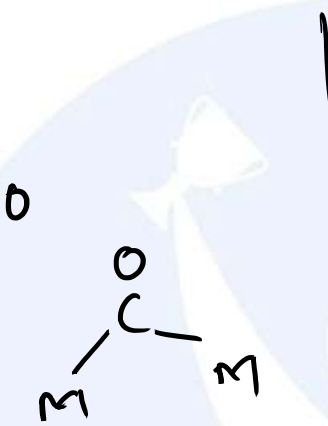
PF_3 → less B.B, γ_{CO} ↑

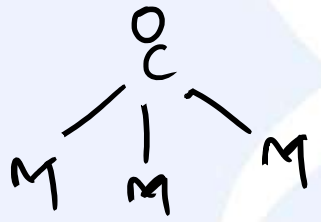
PMe_3 → More B.B, γ_{CO} ↓

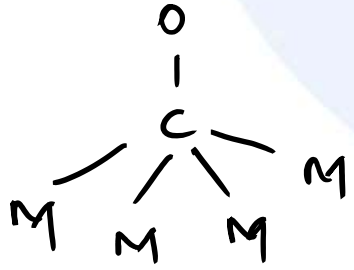
γ_{CO} : (D) > (C) > (B) > (A)

** Bridging Modes of CO :—

		$\nu\ cm^{-1}$ CO
①	free CO	2143
②	Terminal M—CO	1850 – 2120
③	Symm. μ_2–CO	1700 – 1860
④	Symm. μ_3–CO	1600 – 1700
⑤	μ_4 CO	< 1700 (few examples)



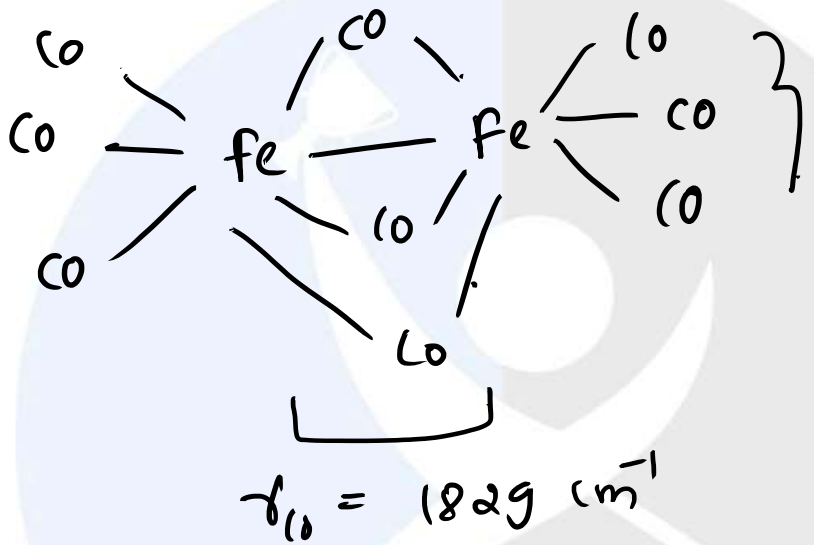




BB ↑

ν_{CO} ↓

Ex $Fe_2(CO)_9$



$\gamma_{CO} = 2082, 2019\ cm^{-1}$

$\gamma_{CO} = 1829\ cm^{-1}$

Complex	ν_{CO} cm^{-1}
$[Ti(CO)_6]^{2-}$	1748
$[V(CO)_6]^{-}$	1859
$[Cr(CO)_6]$	2000
$[Mn(CO)_6]^{+}$	2100
$[Fe(CO)_6]^{2+}$	2204

$[Ir(CO)_6]^{3+} \rightarrow T_1^{T_2} \rightarrow 2250\ cm^{-1}$.

free CO $\rightarrow$ 2143 cm^{-1} $<$ $[Fe(CO)_6]^{2+}$ ν_{CO}

Q HW $[Cr(CO)_6] + 3PPh_3 \longrightarrow$

Thank you