

Organometallic Compounds :-

Transition metals due to their special characteristic has tendency to combine with large number of neutral molecules like CO, NO, CN, N_2 , and with delocalised π -orbital like porphyrin to form metal complexes i.e., organometallic compounds.

Metallic Carbonyls :

Metallic complexes containing CO molecules as ligands are called metallic carbonyls.

Ex. $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{V}(\text{CO})_6$, $\text{Cr}(\text{CO})_6$, $\text{Rh}(\text{CO})_5$
 $\text{Fe}_3(\text{CO})_{12}$, $[\text{Pt}(\text{CO})_2(\text{CO})_2]$ etc.

There are two types of metallic carbonyls -

(I) Monomeric carbonyls, which contains only one metallic atom per molecule. They are hydrophobic but are soluble in non-polar solvents.

Ex. $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{V}(\text{CO})_6$, $\text{Cr}(\text{CO})_6$ etc.

II Polymetric carbonyls, which contain two or more metallic atoms per molecule. They may be

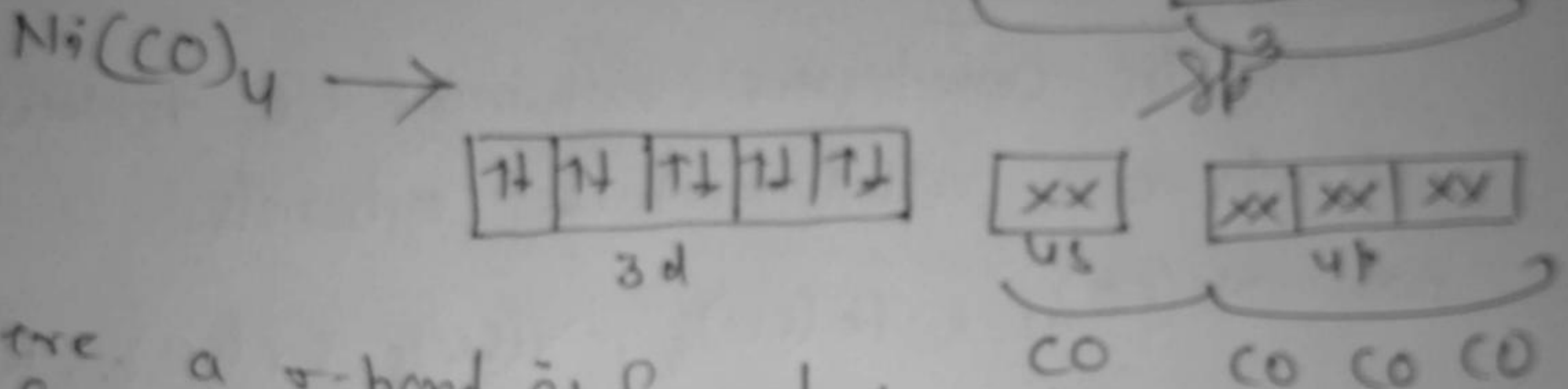
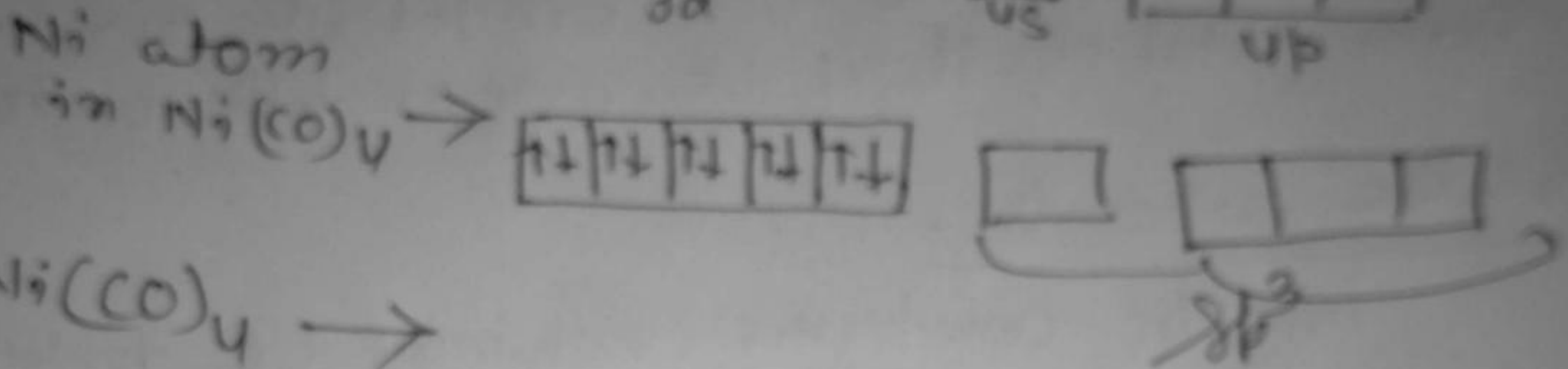
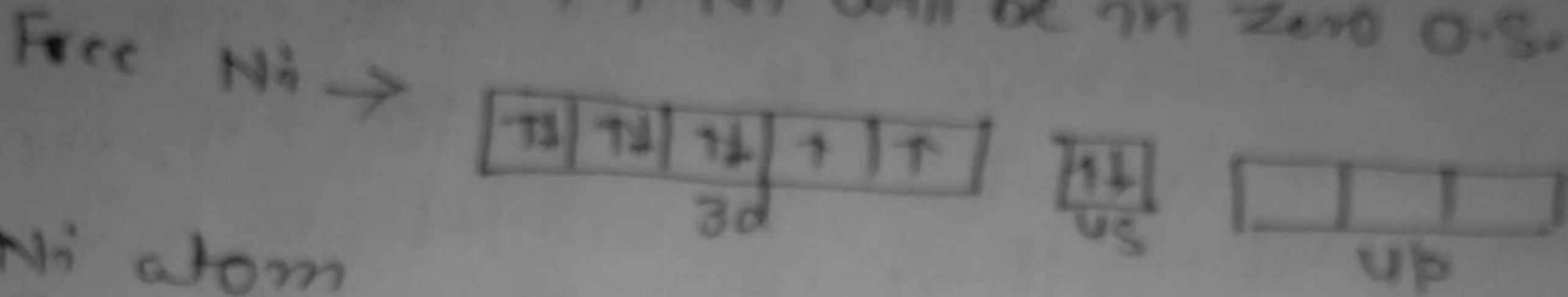
(a) Homonuclear i.e., $\text{Fe}_3(\text{CO})_{12}$

(b) Heteronuclear i.e., $[\text{Pt}(\text{CO})_2(\text{CO})_2]$

Bonding in metallic Carbonyl

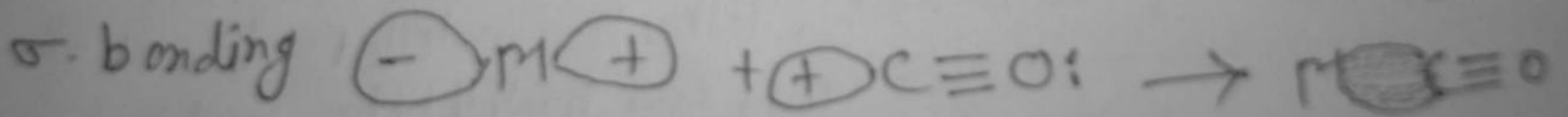
In metal carbonyls CO groups are attached to the metal atom through carbon atom, not with oxygen atoms due to having more electrophilicity than carbon. For explaining the bonding between metal carbonyl, let us take of $Ni(CO)_4$.

In $Ni(CO)_4$, Ni will be in zero O.S. $3d^8 4s^2$

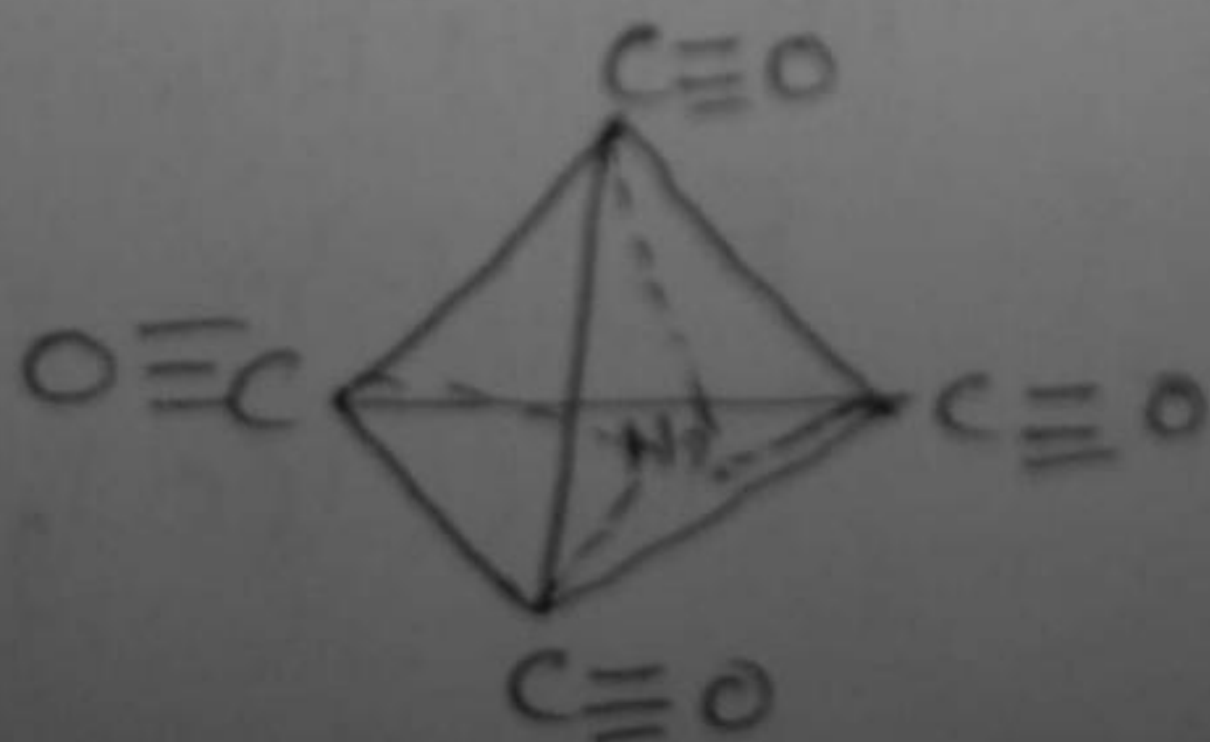


Here, a σ -bond is formed due to overlap of one pair of CO ^{electrons} with metal hybrid orbitals and form $M \leftarrow CO$ σ -bond.

The shape will be tetrahedral,



But the formation of $M \leftarrow CO$, σ -bond does not form a stable complex because in zero O.S. $M \leftarrow$ leads to accumulation of negative charge on metal which makes $M \leftarrow CO$ unstable.

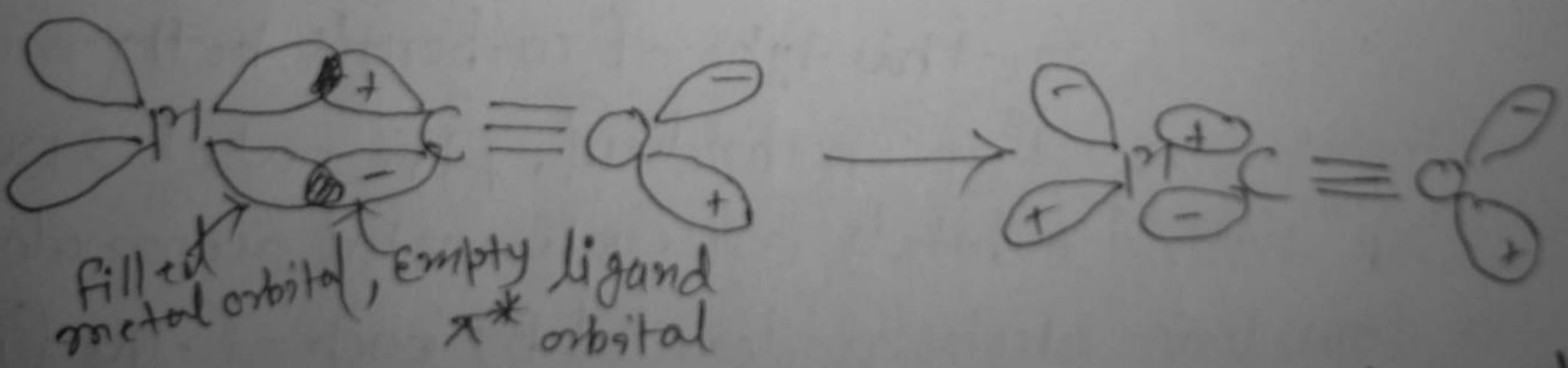
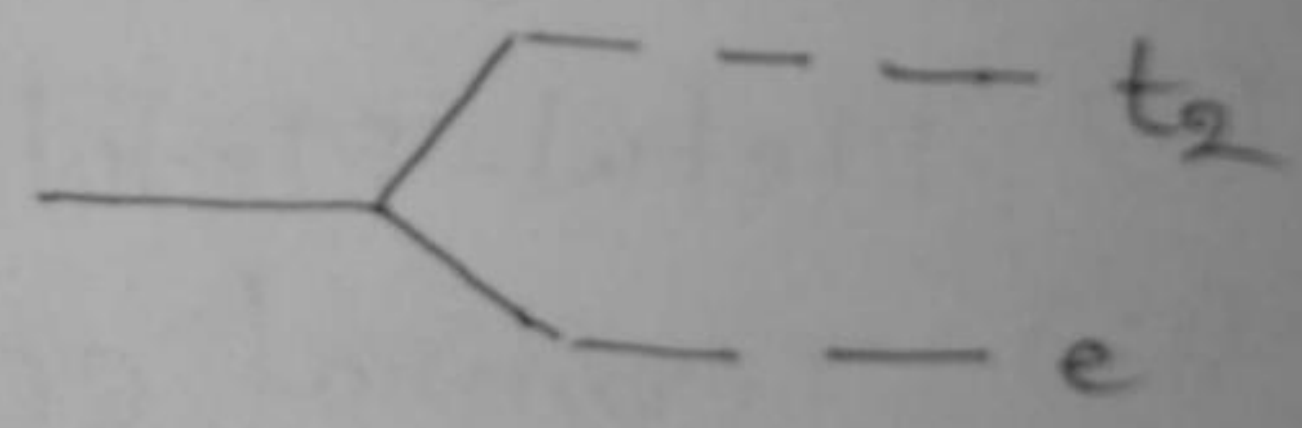
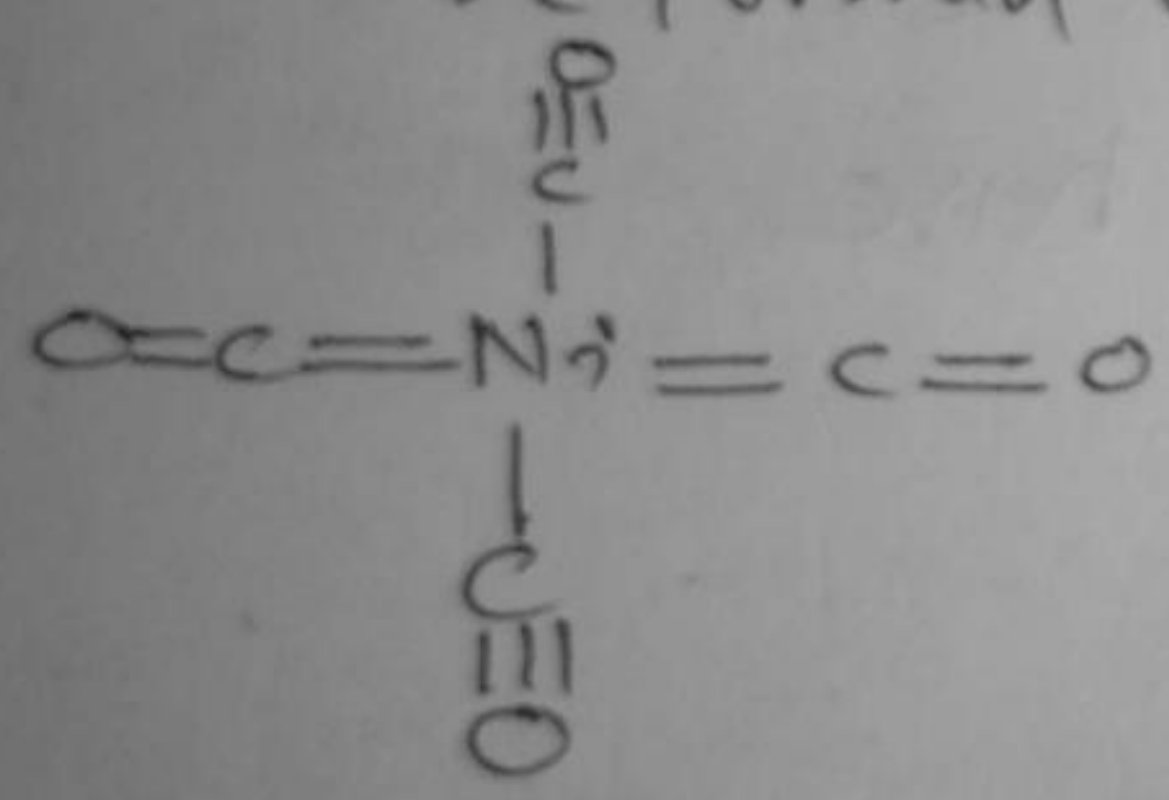


The accumulation of -ve charge on metal atom is countered by transferring some charge from metal to ligand i.e., $M \rightarrow CO$. This is done by overlapping of filled metal orbital with empty π^* orbital which CO has. Due to back bonding a $M \rightarrow CO \pi$ -type bond is formed.



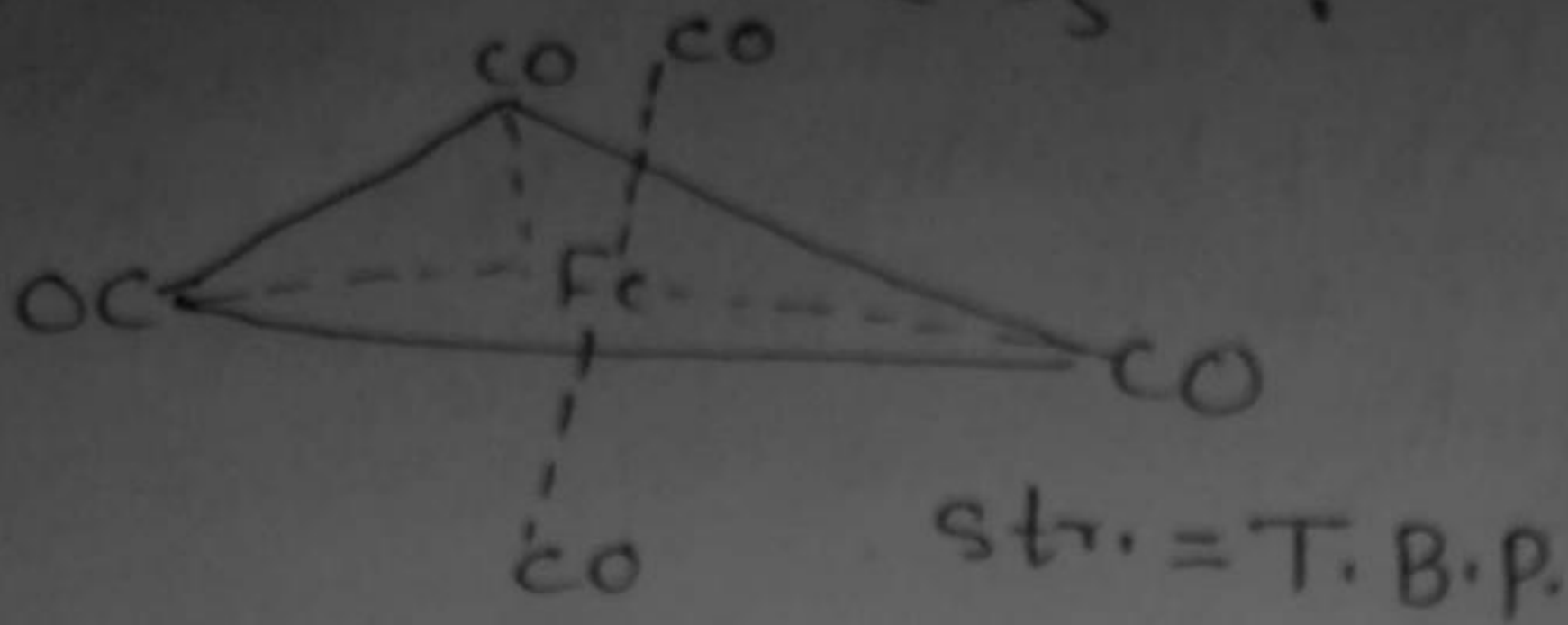
The formation of $M \rightarrow CO \pi$ bond, which is in opposite direction of $M \leftarrow CO \sigma$ bond, remove the excess of negative charge of the metal and consequently strengthens of the σ -bond.

In tetrahedral 'e' is non bonding and participate in π -bonding. So two $Ni=C$ bonds will be formed at a time and structure will be C_2v .



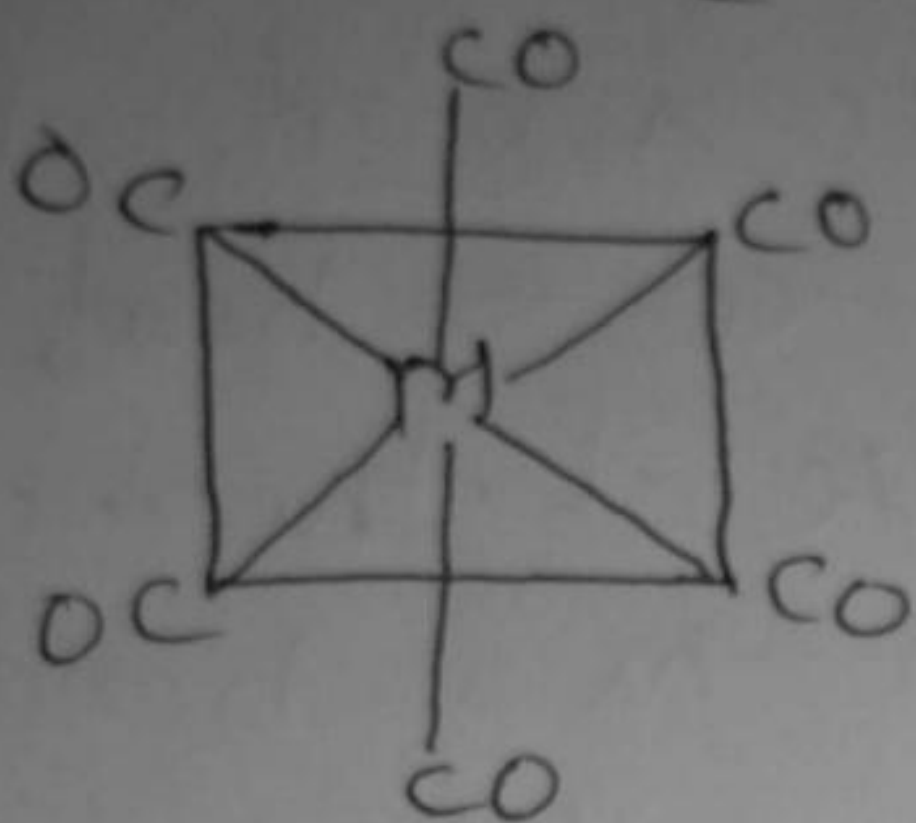
Thus we come to this conclusion that in metallic carbonyl both metal and ligand acts both as donor and acceptor.

(1) Structure of $Fe(CO)_5$:



str. will be same if Fe is replaced by Ru & Os.

(2) str. of $M(CO)_6$:-



It has regular octahedral shape.

where, $M = V, Cr, Mo, Ni$

(3) Structure of $M_2(CO)_{10}$ type carbonyls :-

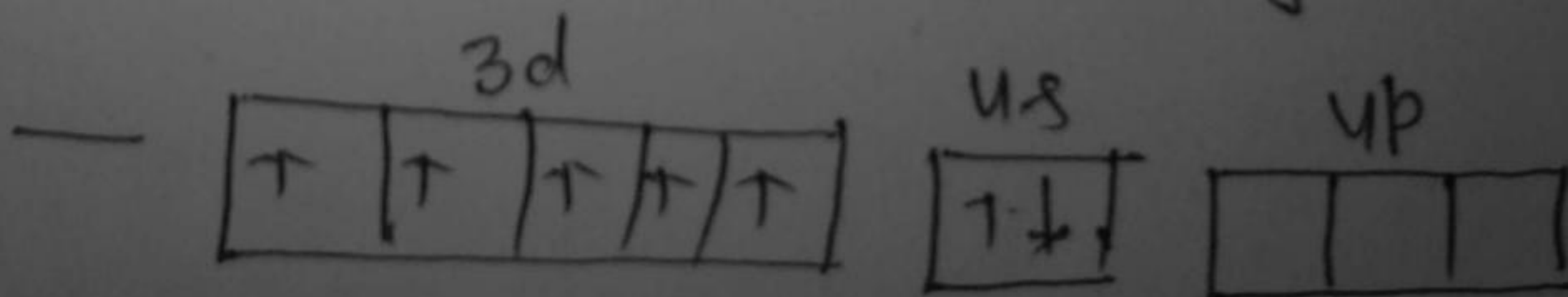
where, $M = Mn, Tc, Re$.

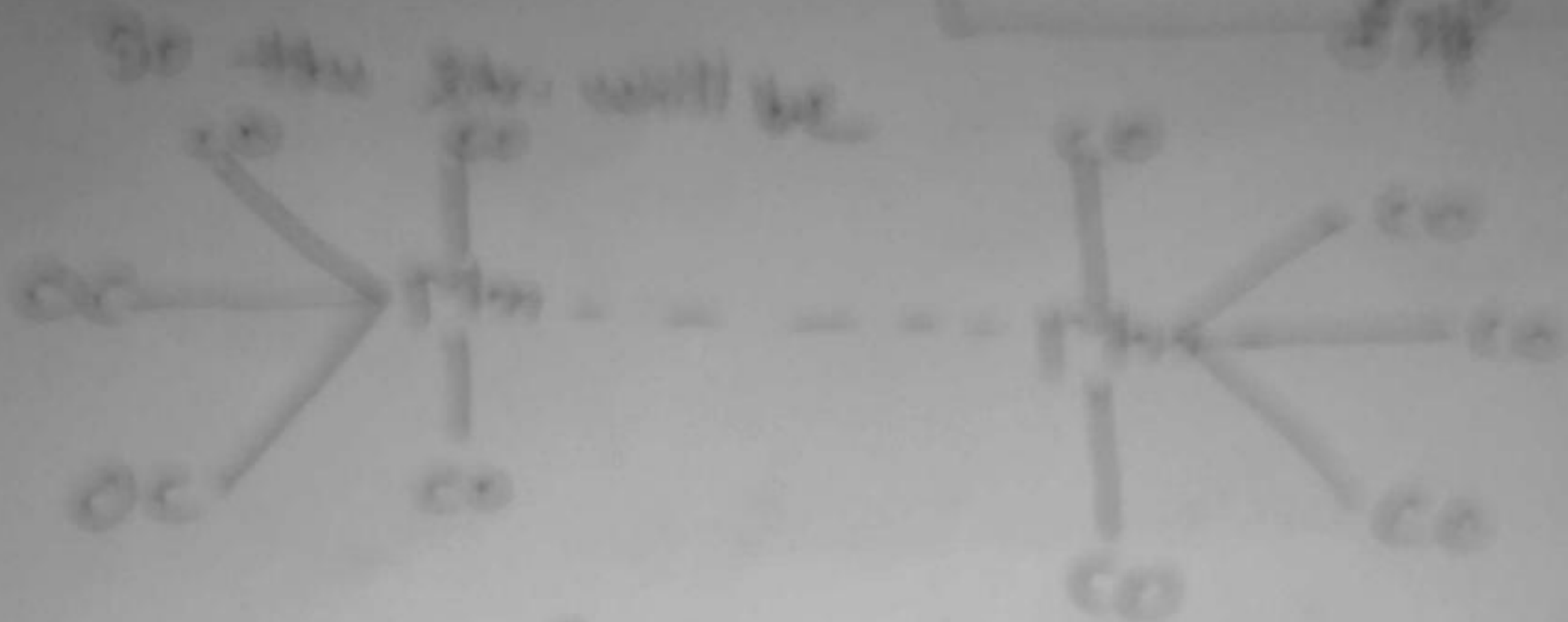
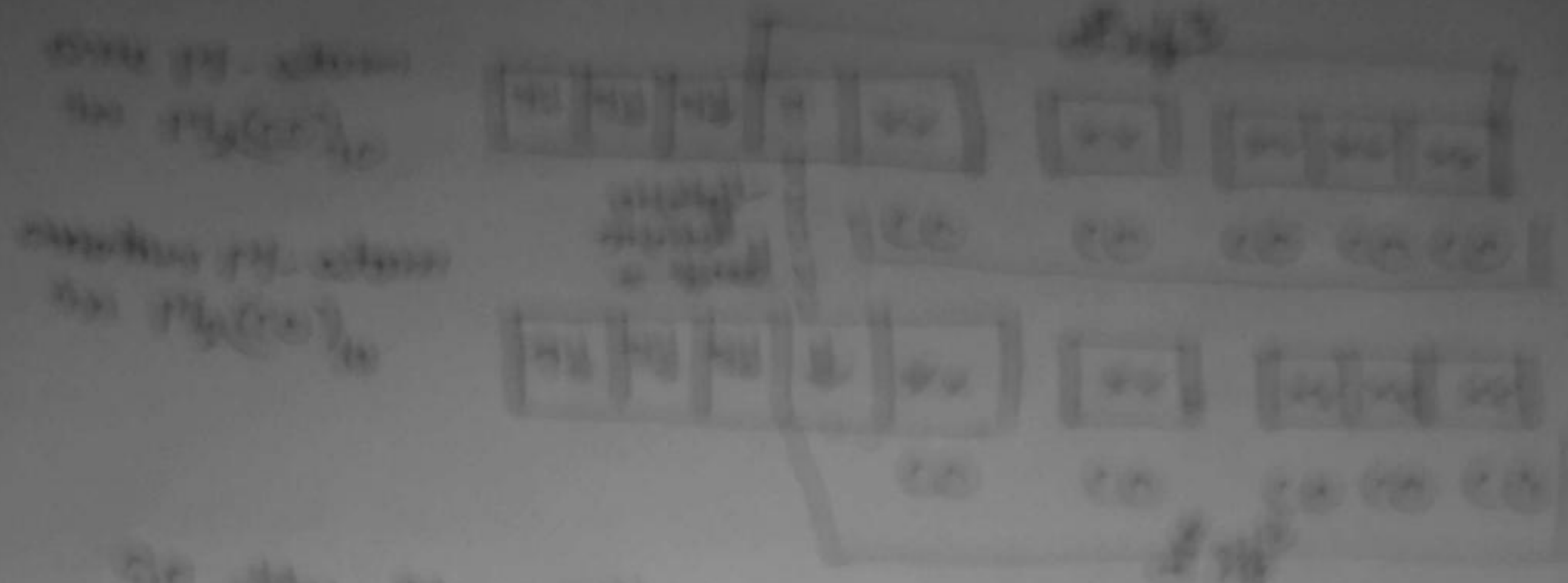
This type of carbonyls have

- (i) Metal-metal bond
- (ii) Terminal CO group.

In this type of carbonyls both metal atoms are d^2sp^3 hybridised. Five out of six d^2sp^3 hybrid orbitals on each metal accommodate a lone pair electrons donated by each of the five CO groups and sixth hybrid orbital on one metal overlap with a similar d^2sp^3 hybrid orbital to form metal-metal bond. This can be shown as

Free M-atom
($M = Mn, Tc, Re$)

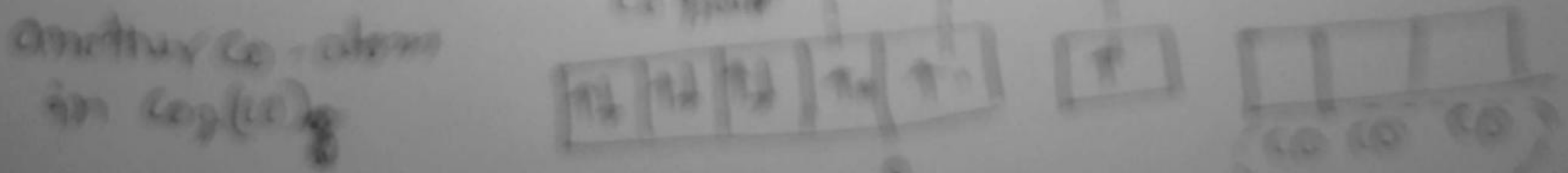
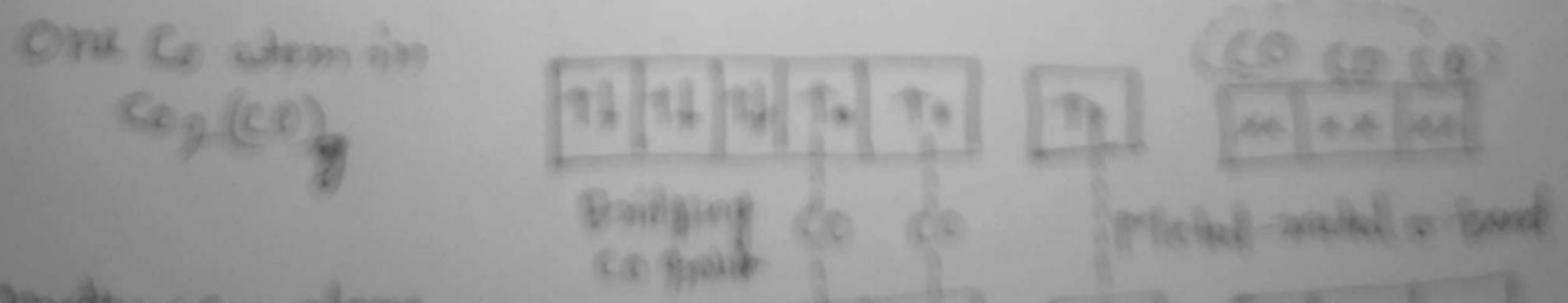




(4) Structure of $\text{Co}_2(\text{CO})_8$:-
 This will be in the type of carbonyl

- (i) Metal-metal bond
- (ii) Terminal CO-group
- (iii) Bridging CO-group

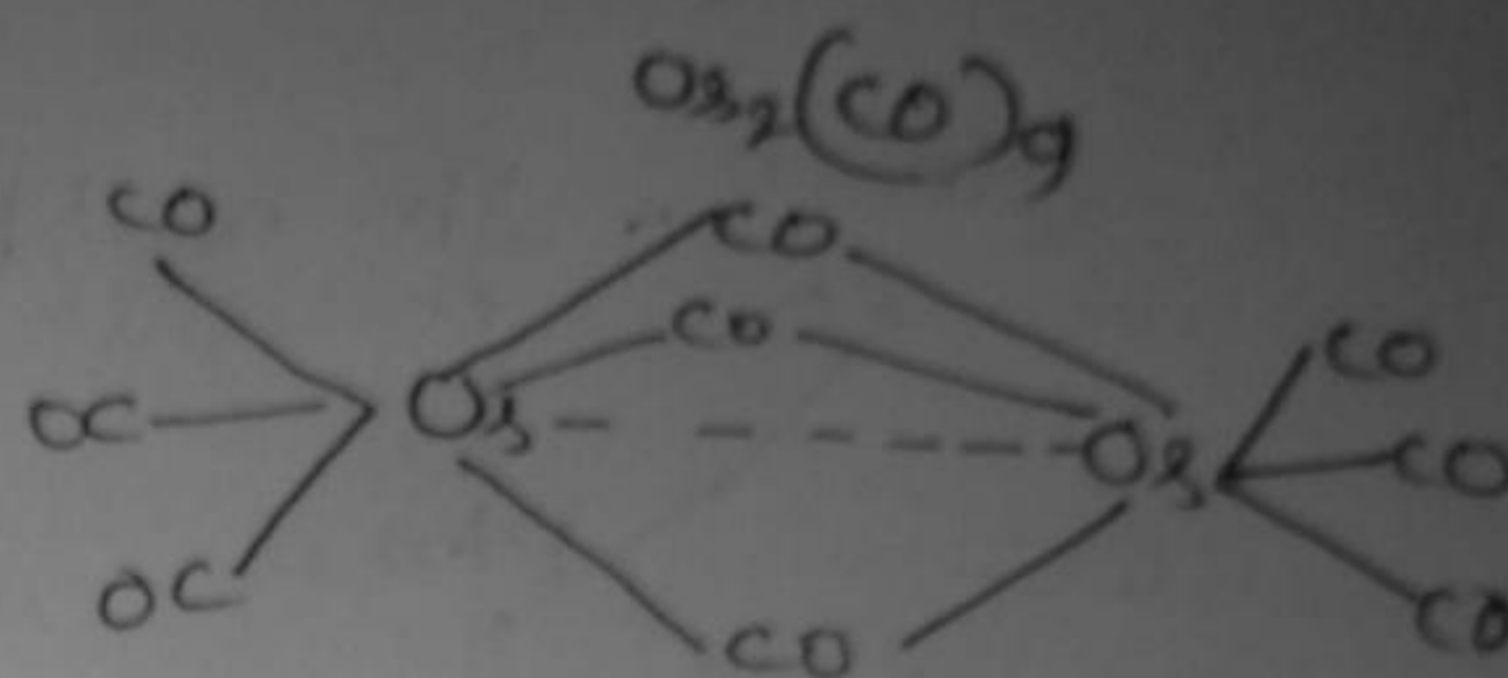
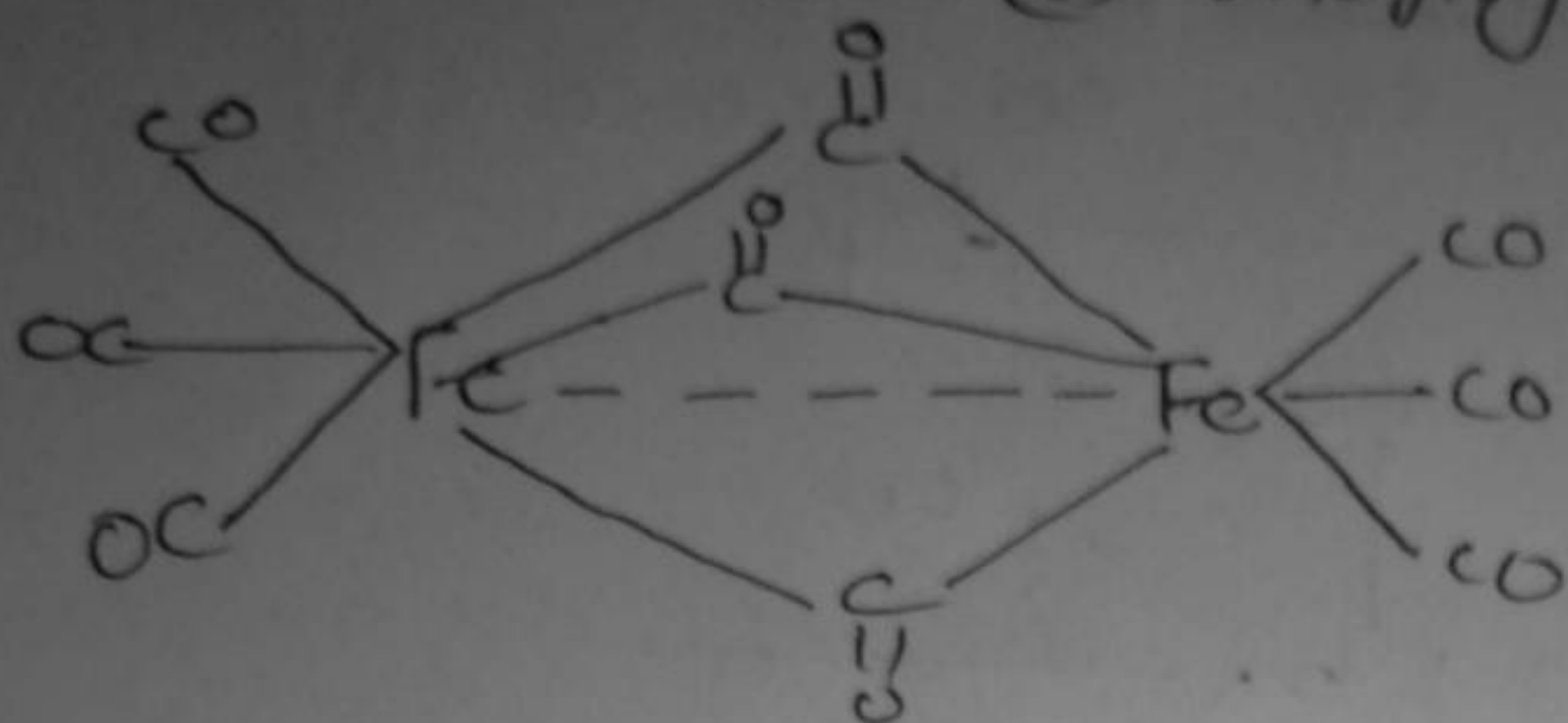
The str. will be as follows as —



(5) Structure of $\text{Fe}_2(\text{CO})_9$ or $\text{Os}_2(\text{CO})_9$:-

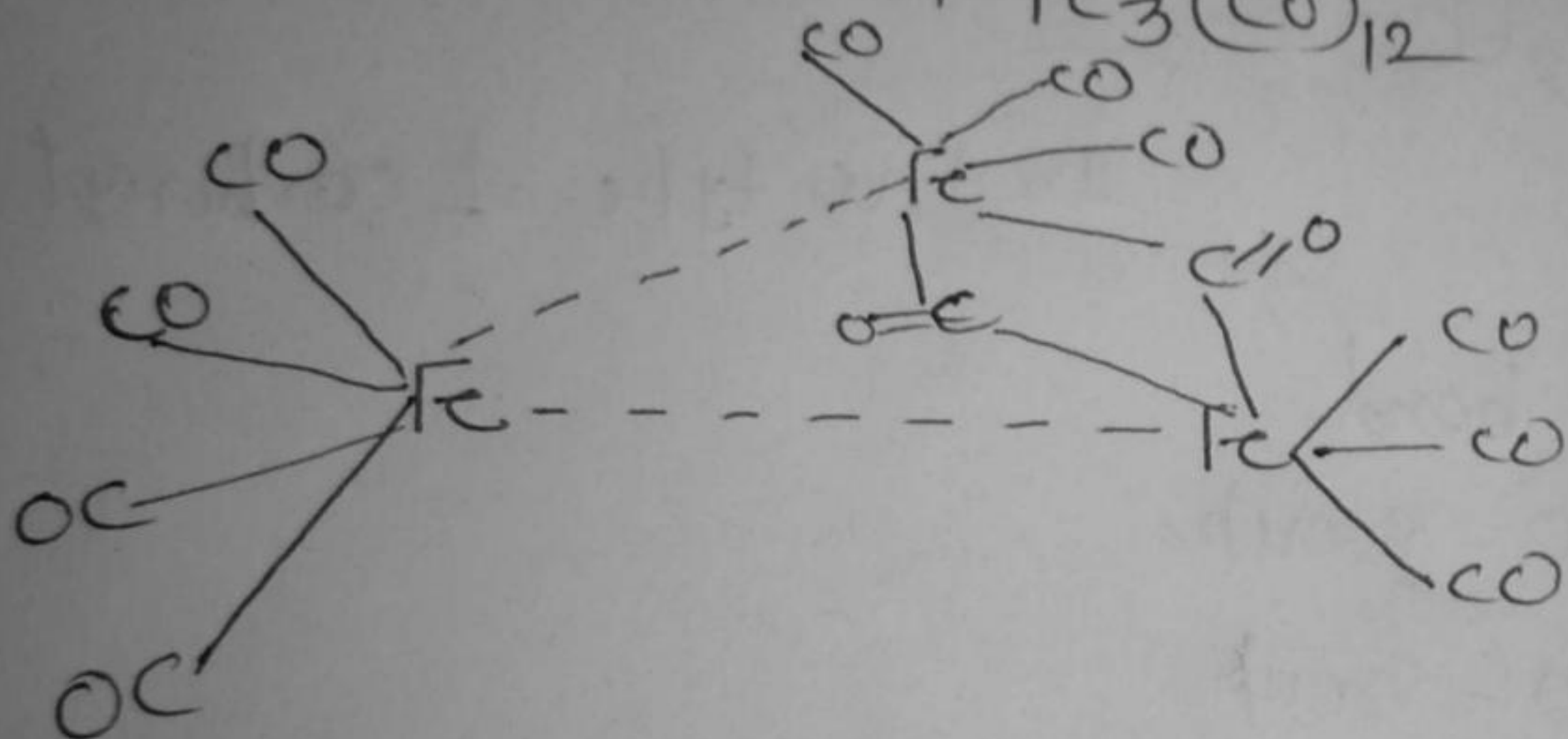
In this type of complex, there is

- (i) Metal-metal bond
- (ii) Six (6) terminal CO bond
- (iii) Three (3) bridging CO group.

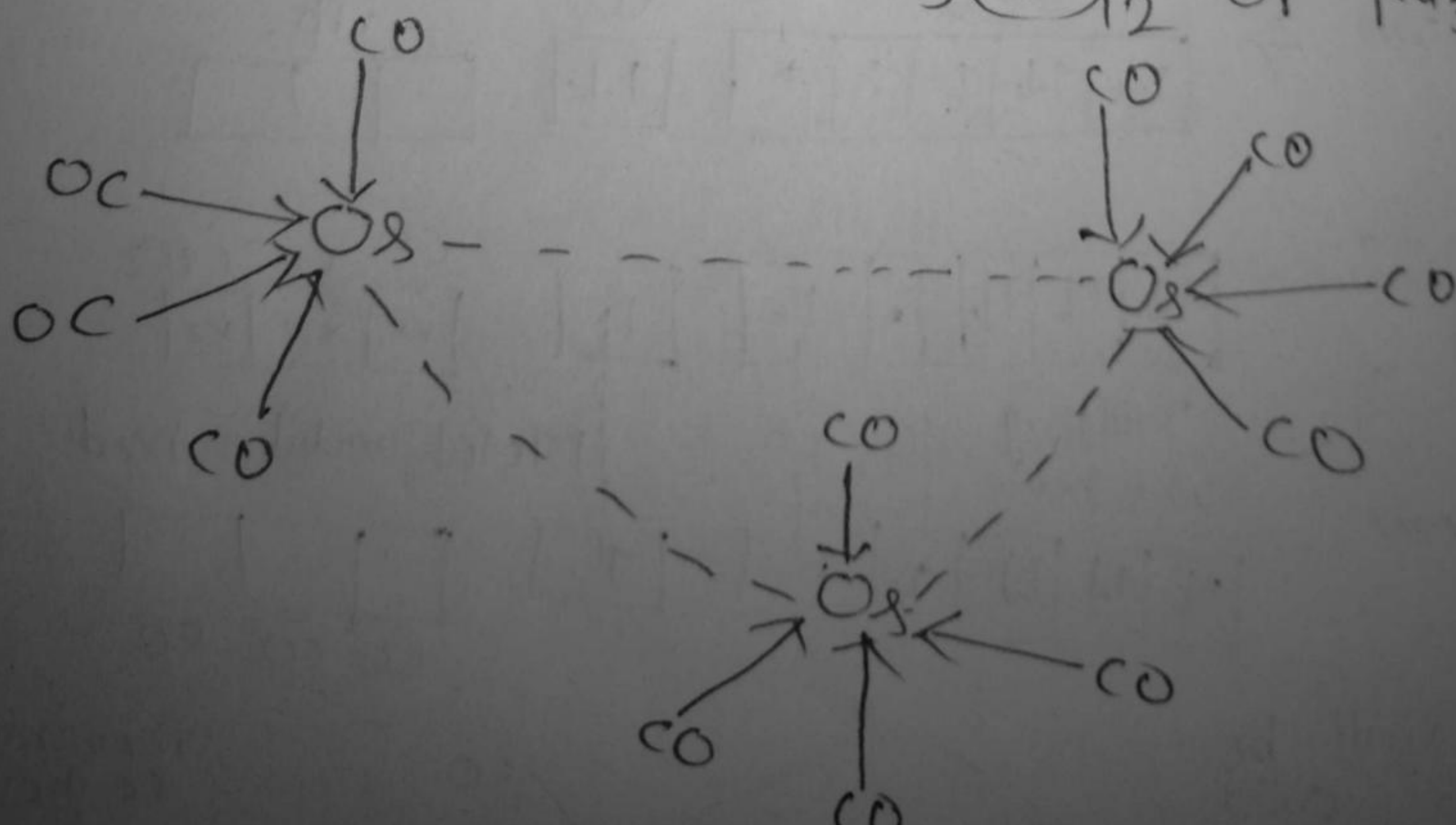


(6) ~~Tetra~~ Trinuclear carbonyls :- $\text{M}_3(\text{CO})_{12}$

Structure of $\text{Fe}_3(\text{CO})_{12}$



Structure of $\text{Os}_3(\text{CO})_{12}$ or $\text{Ru}_3(\text{CO})_{12}$



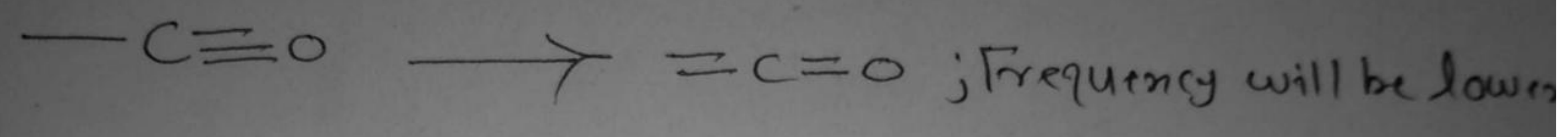
Determination of Terminal and Bridging CO group :-

Presence of terminal and bridging CO group is ascertained by I.R. Spectroscopy. From this -

For terminal CO ν will be 2143 cm^{-1} .

(ν is the range between $2125 - 1850 \text{ cm}^{-1}$)

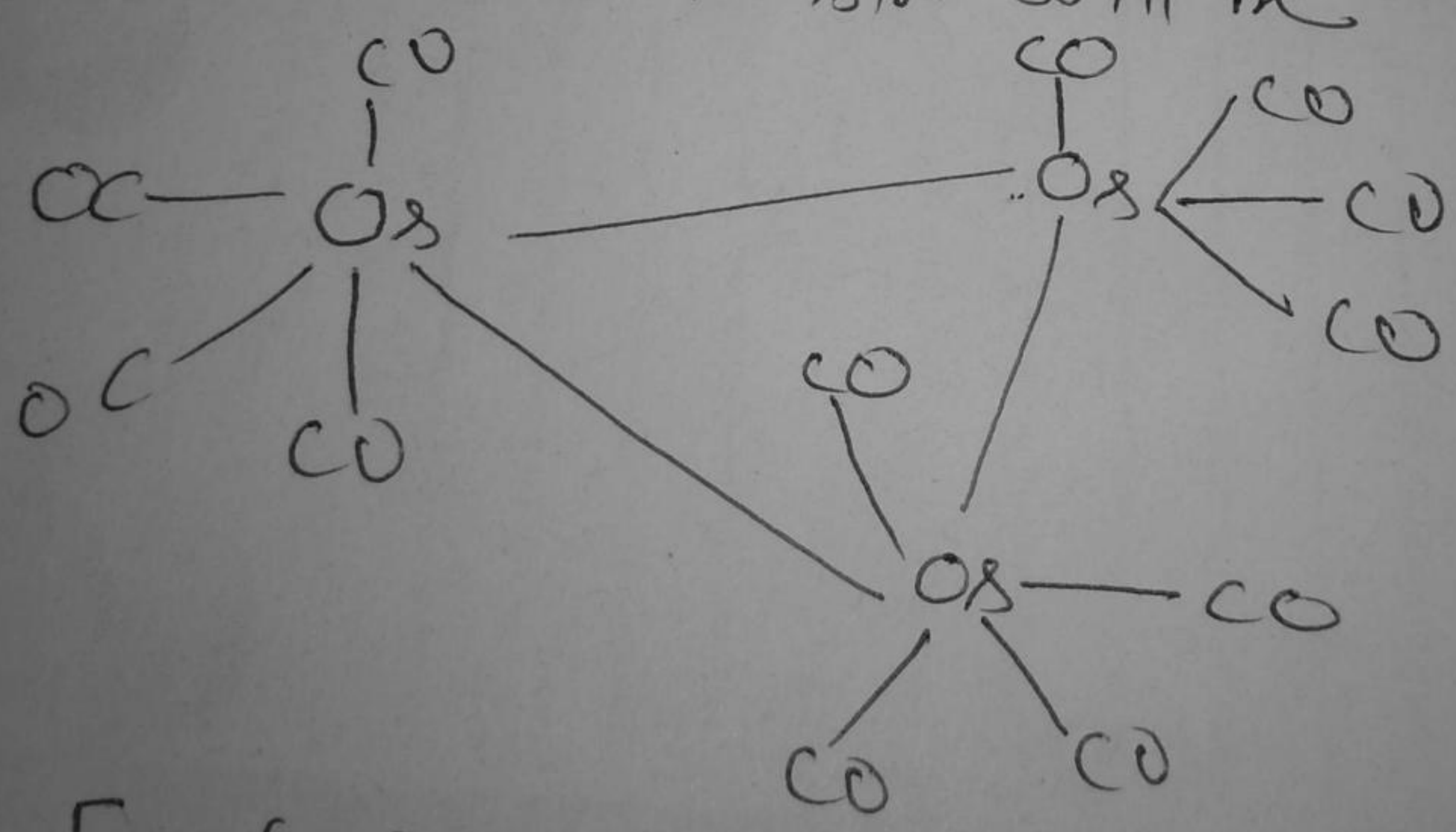
For bridging $>CO$ - ν is the range $1700 - 1850 \text{ cm}^{-1}$



EX.

$Os_3(CO)_{12}$ gives four I.R. Peaks. All the four peaks are in the range of terminal CO - Frequencies $2175, 2025, 2010$ and 2000 cm^{-1}

on this basis the str. will be



$Fe_2(CO)_9$ gives I.R. peaks in terminal CO and bridging range

$2100, 2010, 1860 \text{ cm}^{-1}$.