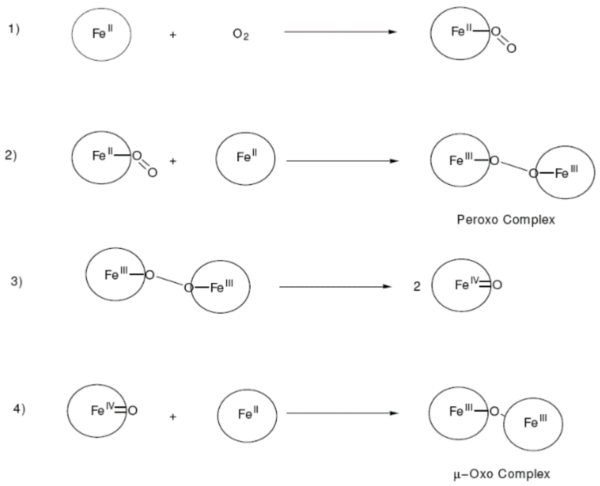
CHM102A
Problem Set 3

1. What is the role of protein chain (globin) in dioxygen transport proteins like hemoglobin or myoglobin?



Ans: Protein chain effectively provides protection and plays key role in preventing bimolecular contacts between heme groups. It prevents (i) irreversible oxidation of Fe(II) to Fe(III), (ii) formation of Fe-O_2-Fe dimer, (iii) makes Hb/Mb water-soluble and (iv) reduce heme affinity towards CO. Following unfavourable reactions do not take place when heme unit is packed within a protein chain.

2. Which of the following statement(s) are TRUE for Hemoglobin (Hb) and/or myoglobin (Mb).

(i) Hemoglobin is tetramer of myoglobin.

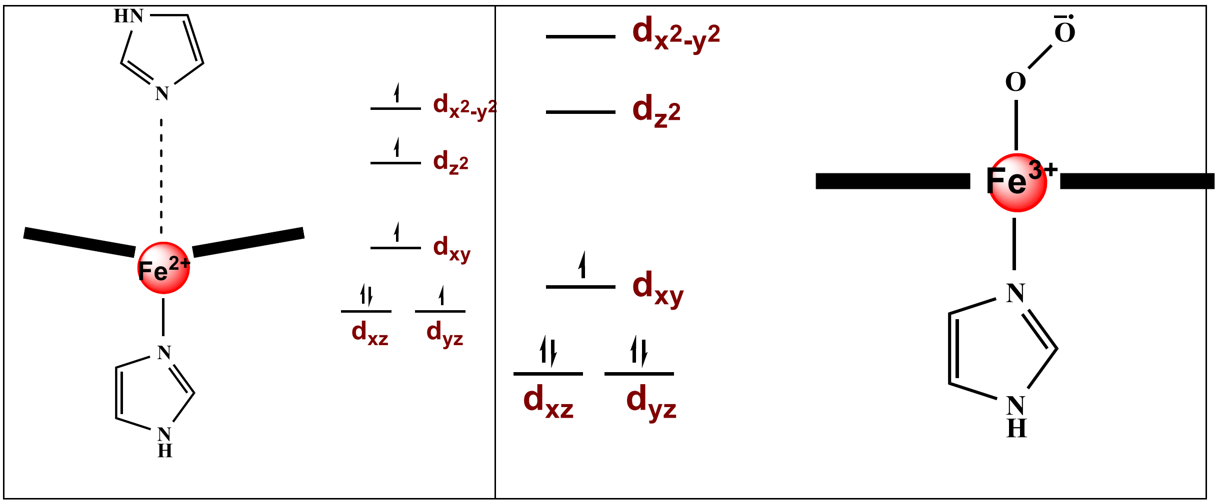
(ii) Proximal histidine makes a hydrogen bond with dioxygen at the active site of oxymyoglobin.

(iii) Iron atom move away from heme plane upon oxygenation in Mb.

(iv) Binding affinity of free heme group to CO is much higher compare to the binding affinity of CO to heme present in Mb.

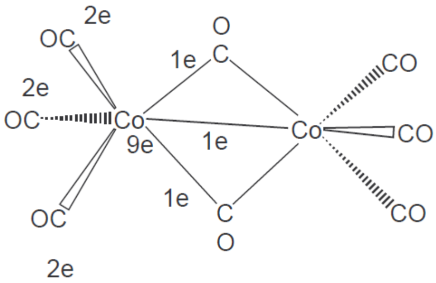
(v) Mb is having lower binding affinity than Hb at low partial pressure of O_2 (pO_2)

3. Draw the crystal field splitting diagram for deoxy-myoglobin and oxy-myoglobin with proper labelling and filling up of the electrons.



4. Do the electron count around central metal ion for the following compounds:

(a) $Co_2(CO)_8$

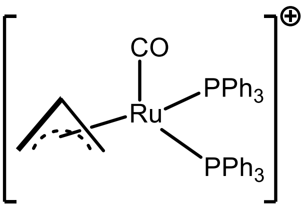
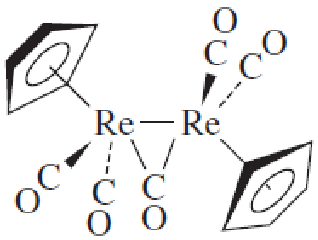


Co = 9
3 terminal CO = 3 x 2 = 6
2 bridging CO = 2 x 1 = 2
One Co-Co bond = 1

Total = 18 e^-

(b) $[HMn(CO)_3(PPh_3)_2]$
(Ionic method)
Mn^+ = 6
3 bridging CO = 3 x 2 = 6
2 PPh_3 = 2 x 2 = 4
H^- = 2

Total = 18 e^-

(c) 	Ru^{2+} = 6 η^3-allyl = 4 2 PPh_3 = 2 x 2 = 4 1 terminal CO = 2 ------------------------ Total = 16 e^-
(d) 	Re(I) = 6 η^5-C_5H_5 = 6 terminal CO = 2 x 2 = 4 bridging CO = 1 Re-Re bond = 1 --------------------------- Total = 18 e^-

5. Identify the first-row transition metal for the following 18-electron species:

(a) $[M(CO)_3(PPh_3)]^-$ (b) $HMn(CO)_5$ (c) $(\eta^4$-$C_8H_8)M(CO)_3$ (d) $[(\eta^5$-$C_5H_5)M(CO)_3]_2$ (assume single M-M bond) (e) $(\eta^5$-$C_5H_5)M(C_2H_4)_2$

Ans: **(a) $[M(CO)_3(PPh_3)]^-$:** 3 CO = 6 , PPh_3 = 2, (-)ve charge = 1: Total = 9, So need (18-9) = 9 e^- from metal, so, M= Cobalt (Co)

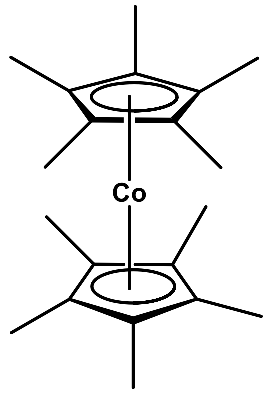
(b) $HMn(CO)_5$: 5 CO = 10, H = 1: Total = 11, need (18-11) = 7 e^- from M. Thus M = Mn.

(c) $(\eta^4$-$C_8H_8)M(CO)_3$: 3 CO = 6, η^4-C_8H_8 = 4; Total = 10, need (18-10) = 8 e^- from M, M = Fe

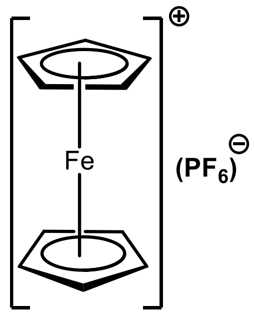
(d) [(η^5-C_5H_5)M(CO)$_3$]$_2$: 3 CO = 6, η^5-C_5H_5 = 5, M-M bond = 1; Total = 12, need (18-12) = 6 e^- from M, so, M = Cr.

(e) (η^5-C_5H_5)M(C_2H_4)$_2$: η^5-C_5H_5 = 5, 2 C_2H_4 = 2x 2 = 4, Total = 9 e^-, need (18-9) = 9 e^- from M, thus M = Co

6. Which of the following species will act as strong oxidizing or reducing agent?



Decamethylcobaltocene

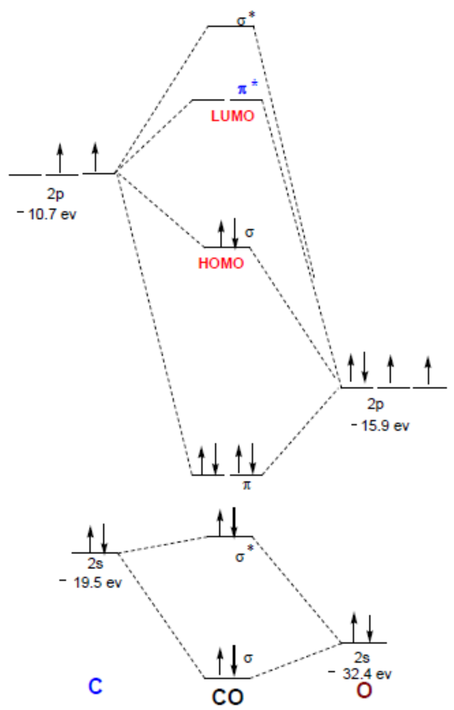


Ferrocenium hexafluorophosphate

[Co(η^5-C_5Me_5)$_2$] is a 19 electron system [Co = 9 e^- + 2(η^5-C_5Me_5) = 2x5 = 10 e^-, Total = 19 e^-) around cobalt, so to achieve stable 18 e^- count it will release one electron with ease to form [Co(η^5-C_5Me_5)$_2$]$^+$ and act as a strong reducing agent.

[Fe(η^5-C_5H_5)$_2$](PF_6): [Fe(η^5-C_5H_5)$_2$]$^+$ having 17 electron around iron [Fe = 8 e^- + 2(η^5-C_5H_5)= 2 x 5 = 10 e^-, (+) charge= -1 e^-, Total = 17 e^-], so to have 18 e^-, it need one more electron and get reduced itself, thus acting as efficient oxidizing agent.

7. Why does CO bind a metal through its less electronegative carbon atom than its more electronegative oxygen? What makes it a good π acceptor ligand? (THIS PROBLEM IS NOT FOR ANY FINAL TEST)



The highest occupied molecular orbital (HOMO) of CO is weakly antibonding (compared to O atomic orbitals) and mainly centered on the carbon. Moreover, π*-antibonding orbital which is the lowest unoccupied molecular orbital (LUMO) is also of comparatively lower energy making it possible to effectively interact with metal filled t_{2g} orbitals for π-back bonding. There exists a strong backbonding of metal electrons to the π* antibonding orbitals of CO.

8. The CO stretching frequency of the following species is listed below. Provide a convincing explanation.

Compound	**ν_{CO} (cm^{-1})**
free CO	**2143**
$[Mn(CO)_6]^+$	**2090**
$Cr(CO)_6$	**2000**
$[V(CO)_6]^-$	**1860**
$[Ti(CO)_6]^{2-}$	**1750**

Ans: CO stretching frequency depends on effective charge on the metal centre. As the electron density on a metal centre increases down the table, more π-back bonding to the CO ligands takes place. This weakens the C-O bond as more electron density from low-valent metal is pumped into π* antibonding orbitals of CO. Hence C-O bond order is lowered which is evident from the lowering of CO stretching frequency.

9. Identify A and B in the following reaction with proper justification.

$$2\,(\eta^5\text{-}C_5H_5)_2Co + I_2 \longrightarrow \boxed{A} + \boxed{B}$$

$$\underset{19\,e^-}{2(\eta^5\text{-}C_5H_5)_2Co} + I_2 \longrightarrow \underset{\substack{18\,e^- \\ \text{cobalticinium ion}}}{2[(\eta^5\text{-}C_5H_5)_2Co]^+} + 2\,I^-$$

(See reasoning in Q6, similar explanation is valid for $[Co(\eta^5\text{-}C_5Me_5)_2]$ and $[Co(\eta^5\text{-}C_5H_5)_2]$)