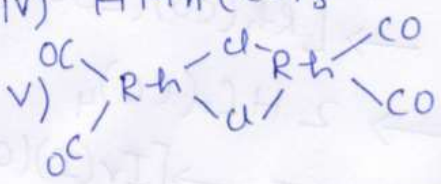
(1) Calculate the outershell electrons:

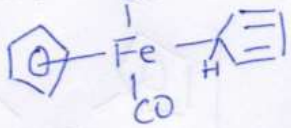
i) $Fe(CO)_4PPh_3$

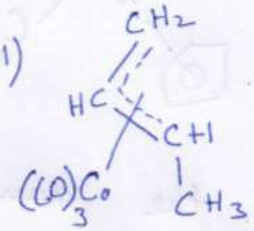
ii) $[Mn(CO)_5]^-$

iii) $Mn_2(CO)_{10}$

iv) $HMn(CO)_5$

v) 

vi) 

vii) 

(2) Draw the structures of these compounds:

i) $Os_4(CO)_{14}$

ii) $Co_4(CO)_{12}$

iii) $Ir_4(CO)_{12}$

(3) $Fe(\eta^5-C_5H_5)_2$ is more stable than $Ni(\eta^5-C_5H_5)_2$ or $Co(\eta^5-C_5H_5)_2$?

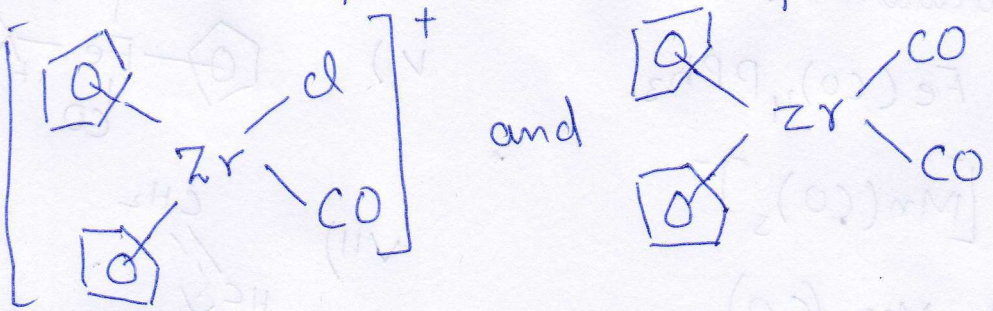
(4) V-C bond distances in $V(CO)_6^-$ and $V(CO)_6$ are 1.93 and 2.0 Å. Justify this bond length difference.

(5) $V(CO)_6$ readily reacts with Na to give $Na[V(CO)_6]$ why?

(6) Arrange the following in the decreasing order of back bonding:

$Cr(CO)_6$, $[Ti(CO)_6]^{2-}$, $[Mn(CO)_6]^+$, $[Ir(CO)_6]^{3+}$ and $[V(CO)_6]^-$

(7) Among these two complexes, which will show a lower carbonyl (CO) stretching frequency?



(8) Classify the ~~anon~~ name of reactions:

a) $[RhI_3(CO)_2CH_3]^- \longrightarrow [Rh(CO)(COCH_3)]^-$

b) $Co_2(CO)_8 + H_2 \longrightarrow 2\,HCo(CO)_4$

c) $[Ir(PPh_3)_2(CO)Cl] + CF_3I \longrightarrow [Ir(I)(CF_3)(PPh_3)_2(CO)Cl]$

d) $TiCl_4 + 2\,Et_3N \longrightarrow TiCl_4(NEt_3)_2$

(9) You have these three complexes: $[Ir(PPh_3)_2(CO)Cl]$, $[RhI_2(CO)_2]^-$, $[(\eta^5\text{-}Cp)_2Ti(Me)Cl]$ which will <u>not undergo</u> oxidative Addition Reaction.

(10) In hydroformylation reaction, $Co_2(CO)_8$ is the catalyst. An increase in partial pressure of CO decrease the rate of reaction. Why?

(1) i) $Fe(CO)_4PPh_3$

1 Fe = $8e^-$
4 CO = $8e^-$
1 PPh_3 = $2e^-$
$18e^-$

ii) $[Mn(CO)_5]^-$

1 Mn = $7e^-$
5 CO = $10e^-$
−charge = $1e^-$
$18e^-$

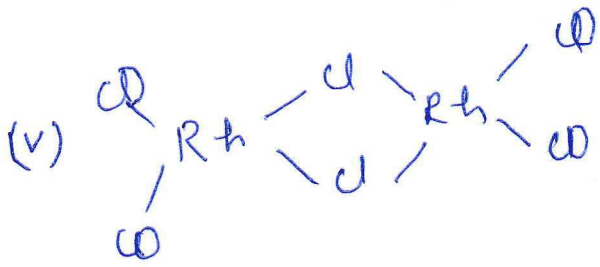
iii) $Mn_2(CO)_{10}$

1 Mn = $7e^-$
5 CO = $10e^-$
1 Mn–Mn bond = $1e^-$
$18e^-$

iv) $HMn(CO)_5$

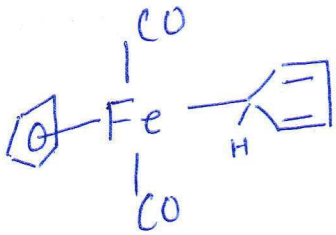
1 Mn = $7e^-$
5 CO = $10e^-$
1 H anion = $1e^-$
$18e^-$

(v)



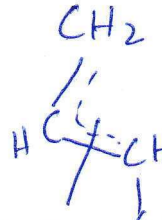
1 Rh = $9e^-$
2 CO = $4e^-$
2 Cl = $2e^-$
$15e^-$

vi)

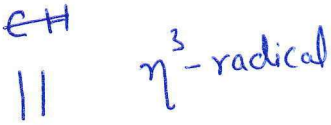


1 Fe = $8e^-$
2 CO = $4e^-$
η^5-Cp = $5e^-$
η^1-Cp = $1e^-$
$18e^-$

vii)

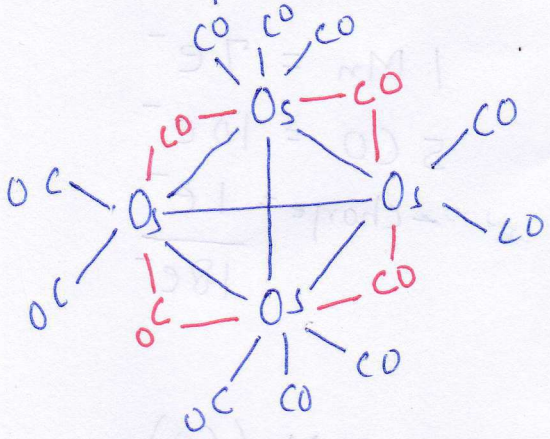


Co = $9e^-$
3 CO = $6e^-$
η^3 = $3e^-$

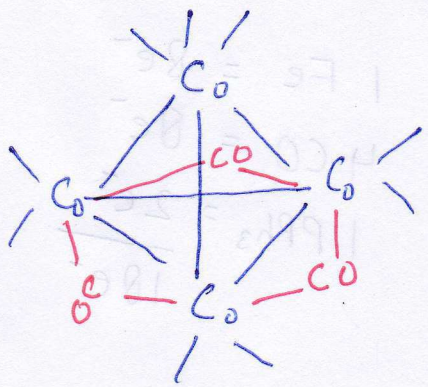


η^3-radical

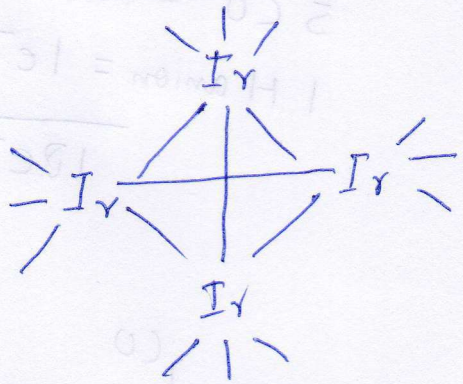
(2) i) $Os_4(CO)_{14}$



ii) $Co_4(CO)_{12}$



iii) $Ir_4(CO)_{12}$



(3) $Fe(\eta^5-C_5H_5)_2$ # outershell $e^- = 18$

$Ni(\eta^5-C_5H_5)_2$ # outershell $e^- = 19$

$Co(\eta^5-C_5H_5)_2$ # outershell $e^- = 20$

Therefore

$Fe(\eta^5-C_5H_5)_2$ is most stable. while

$Ni(\eta^5-C_5H_5)_2$ and $Co(\eta^5-C_5H_5)_2$ undergo oxidation to achieve 18 e^- configuration.

(4) $V(CO)_6^-$ has more back bonding because of additional negative charge on V. Hence decrease in bond order of CO and increase in bond order of V–C occurs in former case.

(5) $V(CO)_6$

$V = 5e^-$

$6\,CO = 12e^-$

$17e^-$

Since it has only $17e^-$ in outershell, it readily takes one e^- from Na to achieve inert $18e^-$ configuration.

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

(6) $[Ti(CO)_6]^{2-} > [V(CO)_6]^- > [Cr(CO)_6] > [Mn(CO)_6]^+ > [Ir(CO)_6]^{3+}$

(consider back bonding).

↳ (e^- donation from Metal to CO)

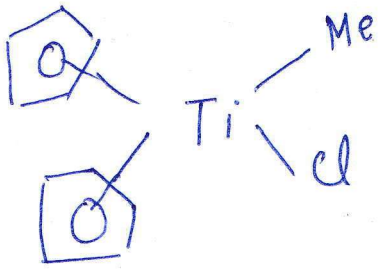
(7) The formal oxidation state of Zr is +4 in A and +2 in B. More back bonding to CO will occur in B and hence it will have lower CO

(8) a) Migratory insertion

b) oxidative addition

c) oxidative addition

d) Simple Addition)



Titanium is present in +4 oxidation state which is of its highest oxidation number. It can not further oxidize. Therefore this complex will not undergo oxidative addition Reaction!

(10) $Co_2(CO)_8 \xrightarrow{H_2} HCo(CO)_4$

Actual catalyst ($18e^-$)

↳ if you see the mechanism it must lose one CO before it enters into the catalytic cycle.

$$HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO$$

An increase in CO pressure will push the equilibrium to the reactant side and thus will decrease the concentration of $HCo(CO)_3$.