423/523 Organometallic Chemistry
Problem set 2

1. Assign the oxidation state of each M. Assuming the 18-electron rule applies, identify the 1st row transition metal and sketch the complex:

(a) $\mathbf{Co^{I}}(CO)(CS)(PPh_3)_2Br$
(b) $[\mathbf{V^{I}}(CO)_7]^+$
(c) $[(\eta^3\text{-}C_3Ph_3)(\eta^4\text{-}C_4H_4)\mathbf{Fe^{II}}(NH_3)_2]^+$
(d) $[(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_6)\mathbf{Ni^{II}}]^+$
(e) $[(\eta^3\text{-}C_3H_5)\mathbf{Co^{III}}(CN)_4]^{2-}$

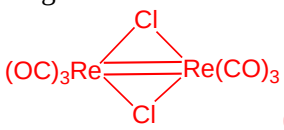
2. Assign the oxidation state of each M. Identify the 2nd row transition metal and sketch the complex:

(a) $(\eta^5\text{-}C_5H_5)(CO)_3\mathbf{Mo^{I}}\text{–}\mathbf{Mo^{I}}(CO)_3(\eta^5\text{-}C_5H_5)$
(b) $(\eta^5\text{-}C_5H_5)(CO)_2\mathbf{Tc^{I}}=\mathbf{Tc^{I}}(CO)_2(\eta^5\text{-}C_5H_5)$
(c) $[\mathbf{Ru^{-II}}(CO)_3(NO)]^-$ (linear NO)
(d) $(\eta^4\text{-}C_8H_8)\mathbf{Ru^{0}}(CO)_3$
(e) $[\mathbf{Rh^{-I}}(CO)_3(PMe_3)]^-$
(f) $(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_3H_5)(\eta^3\text{-}C_3H_5)_2\mathbf{Zr^{IV}}$ (16-electron molecule)

3. What charge, *z*, would be necessary for the following to obey the 18-electron rule?

(a) $[Ru(CO)_4(SiMe_3)]^{\mathbf{-1}}$
(b) $[(\eta^3\text{-}C_3H_5)V(CNMe)_5]^{\mathbf{0}}$
(c) $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^{\mathbf{+1}}$
(d) $[(\eta^6\text{-}C_6H_6)_2Ru]^{\mathbf{+2}}$
(e) $[W(CO)_5(SnPh_3)]^{\mathbf{-1}}$

4. A complex has the empirical formula $Re(CO)_3Cl$. How could it attain the 18-electron configuration without requiring any additional ligands?

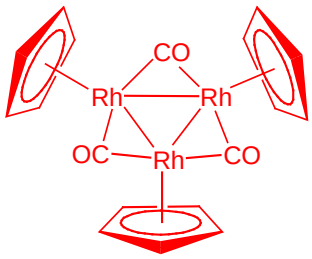


(or triangular cluster, etc with single bonds)

5. Predict the hapticity (i.e. what is *n* in η^n) of each Cp ring in **$(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)$**$W(CO)_2$, and the *n* in κ^n of each "triphos" ligand in $[Pd\{\mathbf{\kappa^2}\text{-}PPh_2CH_2CH_2)_3CPh\}_2]^{2+}$ **(if 16e; 18e requires 1 κ^3-, 1 κ^2-).**

6. Comment on the observation that the ν(CO) band in $[Fe(CO)_6]^{2+}$ appears at 2203 cm^{-1} (compare with free CO). **Higher than free CO, so no back-bonding; electrons donated from slightly anti-bonding electron pair on CO strengthens the CO bond; +ve charge on iron lowers energy of *d*-orbitals & ability to back-bond.**

7. When heated at low pressure, $(\eta^5\text{-}C_5Me_5)Rh(CO)_2$ reacts to give a gas and another product having a single peak in the ^1H NMR and a single band near 1850 cm^{-1} in the infrared. Suggest a structure for this product. **See right:**



8. Predict the distribution of products when carbon monoxide is lost from *cis*-$Mn(COMe)(CO)_4(^{13}CO)$ assuming the reaction proceeds by deinsertion of CO (as opposed to Me migration, i.e. it is CO that moves to the vacant coordination site, not Me).

25% $Mn(CO)_5Me$, 75% *cis*-$Mn(CO)_4(^{13}CO)Me$