

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) $M(\text{CO})(\text{CS})(\text{PPh}_3)_2\text{Br}$
- (b) $[\text{M}(\text{CO})_7]^+$
- (c) $[(\eta^3\text{-C}_3\text{Ph}_3)(\eta^4\text{-C}_4\text{H}_4)\text{M}(\text{NH}_3)_2]^+$
- (d) $[(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_6)\text{M}]^+$
- (e) $[(\eta^3\text{-C}_3\text{H}_5)\text{M}(\text{CN})_4]^{2-}$

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

- (a) $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{M}-\text{M}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)$
- (b) $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}=\text{M}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$
- (c) $[\text{M}(\text{CO})_3(\text{NO})]^-$ (linear NO)
- (d) $(\eta^4\text{-C}_8\text{H}_8)\text{M}(\text{CO})_3$
- (e) $[\text{M}(\text{CO})_3(\text{PMe}_3)]^-$
- (f) $(\eta^5\text{-C}_5\text{H}_5)(\eta^1\text{-C}_3\text{H}_5)(\eta^3\text{-C}_3\text{H}_5)_2\text{M}$ (16-electron complex)

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

- (a) $[\text{Ru}(\text{CO})_4(\text{SiMe}_3)]^z$
- (b) $[(\eta^3\text{-C}_3\text{H}_5)\text{V}(\text{CNMe})_5]^z$
- (c) $[(\eta^5\text{-C}_6\text{H}_7)\text{Fe}(\text{CO})_3]^z$
- (d) $[(\eta^6\text{-C}_6\text{H}_6)_2\text{Ru}]^z$
- (e) $[\text{W}(\text{CO})_5(\text{SnPh}_3)]^z$

4. A complex has the empirical formula $\text{Re}(\text{CO})_3\text{Cl}$. How could it attain the 18-electron configuration without requiring any additional ligands?

5. Predict the hapticity (i.e. what is n in η^n) of each Cp ring in $\text{Cp}_2\text{W}(\text{CO})_2$, and of each “triphos” ligand in $[\text{Pd}\{\text{PPh}_2\text{CH}_2\text{CH}_2\}_3\text{CPh}\}_2]^{2+}$.

6. Comment on the observation that the $\nu(\text{CO})$ band in $[\text{Fe}(\text{CO})_6]^{2+}$ appears at 2203 cm^{-1} (compare with free CO).

7. When heated at low pressure, $(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})_2$ 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.

8. Predict the distribution of products when carbon monoxide is lost from *cis*- $\text{Mn}(\text{COMe})(\text{CO})_4(^{13}\text{CO})$ 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).