

Problem set 9

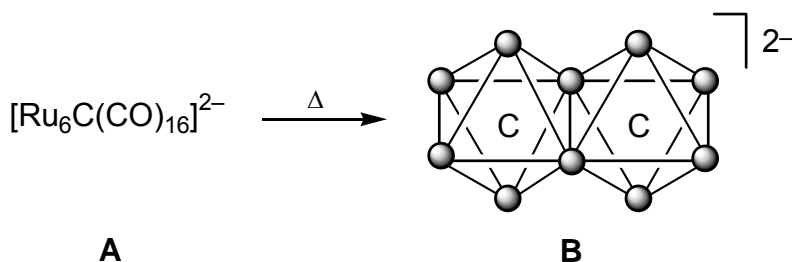
1. The solution ^{31}P NMR spectrum of the cluster $\text{PtRu}_5\text{C}(\text{CO})_{14}(\text{PMe}_2\text{Ph})_2$ shows five signals due to three isomers (note: J_{PtP} appear as satellites):

- A:** δ 9.62, $J_{\text{PtP}} = 63$ Hz
 δ -13.45, $J_{\text{PtP}} = 5999$ Hz
B: δ 4.35, $J_{\text{PtP}} = 63$ Hz
C: δ -1.11
 δ -11.80, $J_{\text{PtP}} = 6111$ Hz

Propose plausible structures for the three isomers.

2. How could NMR be used to determine the distribution of the metal atoms in the core of the trigonal prismatic cluster $[\text{Fe}_3\text{Rh}_3(\mu_6\text{-C})(\text{CO})_{17}]^-$? Consider both ^{103}Rh and $^{13}\text{C}_{\text{interstitial}}$ nuclei.

3. The ruthenium cluster $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$ (**A**) when heated in solution produces $[\text{Ru}_{10}\text{C}_2(\text{CO})_x]^{2-}$ (**B**):



Use suitable electron-counting rules to predict the structure of **A** and to calculate x , the number of CO ligands on cluster **B**.

[from 2004 midterm]

4. Use the following statements to help you illustrate the different types of electronic transition encountered in complexes of the heavy metals.

- (i) Rh^{III} complexes tend to have a characteristic rose color.
- (ii) $[\text{Ru}(\text{bipy})_3]^{2+}$ complexes are intensely colored (bipy = 2,2'-bipyridyl).
- (iii) $[\text{Re}_2\text{Cl}_8]^{2-}$ is royal blue and $[\text{Mo}_2\text{Cl}_8]^{4-}$ an intense red.

[part of a question from the 2004 final exam]