423/523 Organometallic Chemistry
Problem set 3

1. Rationalise the following observations:

   (a) On going from $Fe(CO)_5$ to $Fe(CO)_3(PPh_3)_2$, absorptions in the IR spectrum at 2025 and 2000 cm^{-1} are replaced by bands at 1944, 1886 and 1881 cm^{-1}.

   (b) On forming $IrBr(CO)\{\eta^2\text{-}C_2(CN)_4\}(PPh_3)_2$, the unique C-C bond in $C_2(CN)_4$ lengthens from 135 to 151 pm.

   (c) The Tolman cone angles of PPh_3 and $P(p\text{-}MeC_6H_4)_3$ are 145°, but that of $P(o\text{-}MeC_6H_4)_3$ is 194°.

   (d) A single ν(CO) band is observed for the ion $[Co(CO)_3(PPh_3)_2]^+$.

2. The reaction of $[(C_6Me_6)RuCl_2]_2$ (**A**) with C_6Me_6 in the presence of $AgBF_4$ gives $[(C_6Me_6)_2Ru][BF_4]_2$ containing cation **B**. Treatment of this compound with Na in liquid NH_3 yields a neutral Ru0 complex, **C**. Suggest structures for **A**, **B** and **C**.

3. List the following in order of decreasing reactivity towards trimethylamine oxide: $Mo(CO)_6$, $[Mn(CO)_6]^+$, $Mo(CO)_2(Ph_2PCH_2CH_2PPh_2)_2$, $[Mo(CO)_5]^{2-}$, $Mo(CO)_4(Ph_2PCH_2CH_2PPh_2)$, $Mo(CO)_3(NO)_2$. What physical data would you choose to measure as an aid to ordering these complexes?

4. NO^+ is isoelectronic with CO and often replaces CO in substitution reactions, so it might seem the reaction below is favourable. Comment on whether the process is likely.

$$Mo(CO)_6 + NOBF_4 \rightarrow [Mo(NO)_6][BF_4]_6 + 6CO$$

5. A complex with the empirical formula $Mn_3(C_5H_5)_3(NO)_4$ has infrared absorptions at 1320 and 1495 cm^{-1} and a single peak in the ^1H NMR spectrum. Draw a plausible structure.

6. The product of reaction between $PtCl_2$ and CO at high pressure and 200 °C has a molecular weight of 322. Find the formula and suggest possible isomers. Comment on the probable relative MC and CO bond lengths in these isomers. Can vibrational spectroscopy be used to distinguish between isomers?