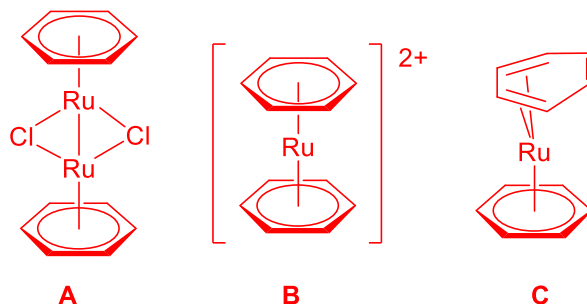


423/523 Organometallic Chemistry
Problem set 3

1. Rationalise the following observations:

- (a) On going from $\text{Fe}(\text{CO})_5$ to $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$, absorptions in the IR spectrum at 2025 and 2000 cm^{-1} are replaced by bands at 1944, 1886 and 1881 cm^{-1} .
 PPh_3 better σ -donor but poorer π -acceptor than CO, so the electron density pushed on to Fe by the phosphines is off-loaded on to the remaining COs, diminishing the C-O bond order.
- (b) On forming $\text{IrBr}(\text{CO})\{\eta^2\text{-C}_2(\text{CN})_4\}(\text{PPh}_3)_2$, the unique C-C bond in $\text{C}_2(\text{CN})_4$ lengthens from 135 to 151 pm.
Electron-withdrawing groups on alkene make it a relatively good π -acceptor, so metallacyclopropane approximation good for this complex; C-C bond order lowered.
- (c) The Tolman cone angles of PPh_3 and $\text{P}(p\text{-MeC}_6\text{H}_4)_3$ are 145° , but that of $\text{P}(o\text{-MeC}_6\text{H}_4)_3$ is 194° .
***Para*-Me doesn't affect geometry near the P, but *ortho*-Me has large effect (make a model).**
- (d) A single $\nu(\text{CO})$ band is observed for the ion $[\text{Co}(\text{CO})_3(\text{PPh}_3)_2]^+$.
 PPh_3 groups must be *trans* on a TBP complex.

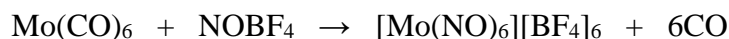
2. The reaction of $[(\text{C}_6\text{Me}_6)\text{RuCl}]_2$ (**A**) with C_6Me_6 in the presence of AgBF_4 gives $[(\text{C}_6\text{Me}_6)_2\text{Ru}][\text{BF}_4]_2$ containing cation **B**. Treatment of this compound with Na in liquid NH_3 yields a neutral Ru^0 complex, **C**. Suggest structures for **A**, **B** and **C**.



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

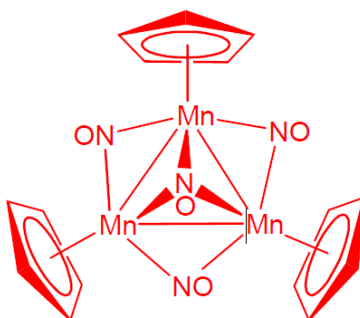
The more $\delta+$ the CO carbon, the easier the reaction, so the order is $[\text{Mn}(\text{CO})_6]^+ > \text{Mo}(\text{CO})_3(\text{NO})_2 > \text{Mo}(\text{CO})_6 > \text{Mo}(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2) > \text{Mo}(\text{CO})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2 > [\text{Mo}(\text{CO})_5]^{2-}$ (cations > neutrals > anions, and within each class, better π -acceptor ligands > less good π -acceptor ligands. IR.

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.



Net charge of $> \pm 2$ on complexes is rare, 6+ ridiculous. Mo would be incapable of π -donation in this complex.

5. A complex with the empirical formula $\text{Mn}_3(\text{C}_5\text{H}_5)_3(\text{NO})_4$ 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 $200\text{ }^\circ\text{C}$ has a molecular weight of 322. Find the formula and suggest possible isomers. Comment on the probable relative M-C and C-O bond lengths in these isomers. Can vibrational spectroscopy be used to distinguish between isomers?

$\text{PtCl}_2(\text{CO})_2$. $16e$, d^8 complex, most likely square-planar with *cis* and *trans* isomers. The *cis* isomer is likely to have the shortest M-C and longest C-O bonds, as the CO ligands in this complex are competing with the Cl ligands (π -donors) for π -electron density rather than with each other. Yes; the *cis* isomer will have 2 CO stretches, the *trans* just 1.