1. Rationalise the following observations:

(a) On going from \( \text{Fe(CO)}_5 \) to \( \text{Fe(CO)}_3(\text{PPh}_3)_2 \), 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 \( \sigma \)-donor but poorer \( \pi \)-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 \( \text{IrBr(CO)} \{ \eta^2-\text{C}_2(\text{CN})_4 \}(\text{PPh}_3)_2 \), 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 \( \pi \)-acceptor, so metallacyclopropane approximation good for this complex; C-C bond order lowered.

(c) The Tolman cone angles of PPh\(_3\) and P(\( p \)-MeC\(_6\)H\(_4\))\(_3\) are 145°, but that of P(\( o \)-MeC\(_6\)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 \([\text{Co(CO)}_3(\text{PPh}_3)_2]^+\).

PPh\(_3\) groups must be \textit{trans} on a TBP complex.

2. The reaction of \( \left[ (\text{C}_6\text{Me}_6)\text{RuCl} \right]_2 \) (A) with C\(_6\)Me\(_6\) in the presence of AgBF\(_4\) gives \( \left[ (\text{C}_6\text{Me}_6)_2\text{Ru} \right][\text{BF}_4]_2 \) 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.

![Diagram of structures A, B, and C]

3. List the following in order of decreasing reactivity towards trimethylamine oxide: \( \text{Mo(CO)}_6 \), \([\text{Mn(CO)}_6]^+\), \( \text{Mo(CO)}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2 \), \([\text{Mo(CO)}_5]^2-\), \( \text{Mo(CO)}_4(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2 \), \( \text{Mo(CO)}_3(\text{NO})_2 \). 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 \([\text{Mn(CO)}_6]^+ > \text{Mo(CO)}_3(\text{NO})_2 > \text{Mo(CO)}_6 > \text{Mo(CO)}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2) > \text{Mo(CO)}_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2 > [\text{Mo(CO)}_5]^2-\) (cations > neutrals > anions, and within each class, better \( \pi \)-acceptor ligands > less good \( \pi \)-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.

\[
\text{Mo(CO)}_6 + \text{NOBF}_4 \rightarrow [\text{Mo(NO)}_6][\text{BF}_4]_6 + 6\text{CO}
\]

Net charge of > ±2 on complexes is rare, 6+ ridiculous. Mo would be incapable of \( \pi \)-donation in this complex.
5. A complex with the empirical formula Mn$_3$(C$_5$H$_5$)$_3$(NO)$_4$ has infrared absorptions at 1320 and 1495 cm$^{-1}$ and a single peak in the $^1$H NMR spectrum. Draw a plausible structure.

\[ \text{\includegraphics[width=0.5\textwidth]{complex.png}} \]

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?

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