Counting the electrons and Interpreting CO stretching frequencies and phosphine complexes

Exercise 1: Count the valence electrons on the metal atom for a) $[Mo(CO)_6]$; b) $[Fe(CO)_4]^{2-}$; c) $[Fe(CO)_4(PEt_3)]$; d) $[Rh(Me)(CO)_2(PPh_3)]$.

Exercise 2: Count the valence electrons on the metal atom for a) $[Co_2(CO)_8]$; b) $[Fe_2(CO)_9]$.

Exercise 3: Which of the two isoelectronic compounds $[Cr(CO)_6]$ and $[V(CO)_6]^-$ will have the higher CO stretching frequency and why?

Exercise 4: Which of the two chromium compounds $[Cr(CO)_5(PEt_3)]$ and $[Cr(CO)_5(PPh_3)]$ will have the lower CO stretching frequency and why? And which will have a shorter M-C bond?

Interpreting CO stretching frequencies and phosphine complexes

Exercise 5: Which of the two iron compounds [$Fe(CO)_5$] and [$Fe(CO)_4(PEt_3)$] will have the higher CO stretching frequency and why? And which will have the longest M-C bond?

Exercise 6: Provide plausible reasons for the differencies in IR wavenumbers between each of the following pairs: a) [$Mo(CO)_3(PF_3)_3$] 2040, 1991 cm^{-1} versus [$Mo(CO)_3(PMe_3)_3$] 1945, 1851 cm^{-1}; b) [$MnCp(CO)_3$] 2023, 1939 cm^{-1} versus [$MnCp^*(CO)_3$] 2017, 1928 cm^{-1}.

Determining the structure of a carbonyl from IR data

Exercise 7: The complex $[Cr(CO)_4(PPh_3)_2]$ has one very strong IR absorption band at 1189 cm^{-1} and two other very weak bands in the CO stretching region. The ν_{CO} of $[Cr(CO)_6]$ is at 2000 cm^{-1}. a) Why in this compound is lower? b) What is the probable structure of this compound?

Exercise 8: The complex $[PtCl_2(CO)_2]$, a carbonyl of a third row M(II) metal, shows ν_{CO} = 2175 cm^{-1}. $[W(Cp)_2(CO)_2]$, another third row M(II) carbonyl, shows ν_{CO} = 1872 and 1955 cm^{-1}. What do these differences indicate in terms of M-CO bonding?

Exercise 9: Why is the rate of CO substitution of $[Co_2(CO)_8]$ much faster than that of $[Ni(CO)_4]$, even though the latter has fewer ligands?

Converting CO to carbene/acyl ligands

Exercise 10: Converting CO to carbene and acyl ligands

Starting from $[W(CO)_6]$ and using reagents of your choice propose a set of reactions for the synthesis of $[W(C(OMe)Ph)(CO)_5]$.

Exercise 11: Converting CO to an acyl ligands

Give a probable synthetic procedure to obtain *cis,trans*-$[IrCl_2(PPh_3)_2(COMe)(CO)]$ starting from *trans*-$[IrCl(PPh_3)_2(CO)]$.

Playing with carbonyl complexes

Exercise 12: When $[Fe(CO)_5]$ is reflux with cyclopentadiene, compound A is the product. A has formula $C_8H_6O_3Fe$ and a complicated ^1H NMR spectrum. A easily dissociates CO to yield compound B. ^1H NMR spectrum of B has two signals: one at negative chemical shift (relative intensity 1) and the other around 5 ppm (relative intensity 5). When B is warmed up, H_2 evolves with the formation of compound C. C has formula $C_7H_5O_2Fe$ and its ^1H NMR spectrum has only one signal. A, B, and C have 18 valence electrons. Identify A, B and C and explain their ^1H NMR spectra.