Solutions to Section 3 Text Questions

13-1 (a)

Fe^0		= 8 e^-
5 CO	= 5*2	= 10 e^-
		18 e^-

(b) bipy is a bipyridyl, or 2 pyridine (C_5H_5N) rings donating through N lone pair (so one bipy is neutral and donates a total of 4 e^-)

Rh^{2+}		= 7 e^-
Cl^-		= 2 e^-
2 bipy	= 2*4	= 8 e^-
		17 e^-

(c) think of the =O like you would a carbene (=CR2, which is CR_2^{-2} and donates 4 e^-)

Re^{7+}		= 0 e^-
3 =O	= 3*4	= 12 e^-
Cp^{*-}		= 6 e^-
		18 e^-

(d) think of N as ≡N which is N^{3-} and a 6 e^- donor

Re^{5+}		= 2 e^-
≡N		= 6 e^-
2 PR_3	= 2*2	= 4 e^-
2 Cl^-	= 2*2	= 4 e^-
		16 e^-

(e) ≡CPh is like ≡N

Os^{4+}		= 4 e^-
CO		= 2 e^-
2 PR_3	= 2*2	= 4 e^-
Cl^-		= 2 e^-
≡CR		= 6 e^-
		18 e^-

13-2 (a)

Ir^+		= 8 e^-
CO		= 2 e^-
Cl^-		= 2 e^-
2 PR_3	= 2*2	= 4 e^-
		16 e^-

(b)

Rh^+		= 8 e^-
Cl^-		= 2 e^-
3 PR_3	= 3*2	= 6 e^-
		16 e^-

(c) Ni^{2+} = 8 e^-
4 CN^- = 4*2 = 8 e^-
16 e^-

(d) Pt^{2+} = 8 e^-
2 Cl^- = 2*2 = 4 e^-
2 NH_3 = 2*2 = 4 e^-
16 e^-

13-3 (a) V (b) Mn (c) Co (d) Mn (e) Cr (f) Ni
(g) Cr (h) Ti

13-4 (a) total number of e^- is 2 Fe^+ = 2*7 = 14 e^-
2 Cp^- = 2*6 = 12 e^-
4 CO = 4*2 = 8 e^-
34 e^-
M-M bonds = [18(# M) - N] / 2 = [18 (2) - 34] / 2 = 1

(b) Note: the question is supposed to be $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2^{2-}$
total number of e^- is 2 Mo = 2*6 = 12 e^-
2 Cp^- = 2*6 = 12 e^-
4 CO = 4*2 = 8 e^-
32 e^-
M-M bonds = [18(# M) - N] / 2 = [18 (2) - 32] / 2 = 2

13-5 (a) Ru (b) Rh (c) Tc (d) Cu (or Rh if this is a 16 e^- complex)

13-6 (a) 3- (b) 1+ (c) 1- (d) 0 (e) 1+
(f) cannot be done without assuming a set number of Ni-Ni bonds, and making an assumption about the nature of the CO bonding (how they are bridging and the type of bridge); basically this is a stupid question

13-7 (a) makes no sense (b) $x = 4$ (c) $z = 3-$ (d) $z = 2+$ (e) $x = 2$

13-11 When there is more electron density on the metal, there is more electron density available for back-donation to the ligands, so there is a greater V=C (double) bond character in the $V(CO)_6^-$. Corollory: the CO bonds will be weaker.

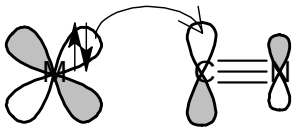
13-12

<u>σ-donation</u>

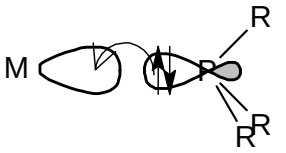


σ_{nb} on CN^-

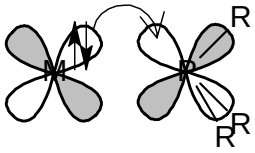
<u>π-acceptance</u>



π* on CN^-



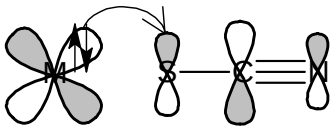
sp^3 hybrid (lone pair) on P



empty 3*d*-orbital on P

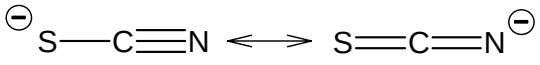


some σ-symmetry orbital on S

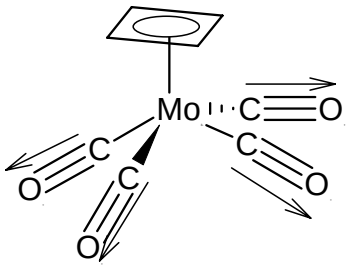


π* on SCN^-

(remember SCN's resonance structures)



13-15 (a) If you really want to find the number of CO bonds, perform the symmetry operations of C_{4v} on the following (as usual, signs that stay the same are +1, 180° change are -1, if the bond moves it is 0.



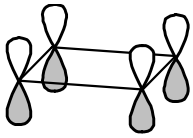
reducible representation:

E	2 C_4	C_2	2 σ_v	2 σ_d
4	0	0	2	0

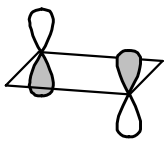
Factors into: $E + A_1 + B_1$

E and A_1 are IR active, therefore 2 CO stretches

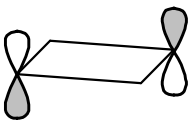
(b) Using the orbitals I gave you on the assignment:



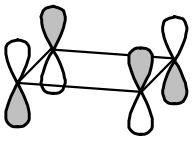
will interact with *s*, p_z, or d_{z^2}



p_x or d_{xz}



p_y or d_{yz}



$d_{x^2-y^2}$

13-16 2-node orbitals, *l* to *r*: first and third orbitals = E_2' second and 4th = E_2''
interact with: d_{xy} & $d_{x^2-y^2}$ NONE

I wouldn't expect you to come up with these exact orbital symmetry for , except to recognise that they don't interact with any metal orbitals

The rest of these are easier to assign if you look at the metal orbital that will interact with it, then the ligand set will have the same symmetry.

1-node orbitals, *l* to *r*: 1st and 3rd = E_1' 2nd and 4th = E_1''
interact with: p_x & p_y d_{xz} & d_{yz}

0-node orbitals, *l* to *r*: 1st = A_1' 2nd = A_2''
interact with: *s* & d_{z^2} p_z

13-26 The carbonyl stretches in the NS compound are higher energy (larger wavenumber) so the CO stretches are stronger. This implies there is less backbonding to the CO, and consequently more to the NS. Therefore, NS is a stronger π-acceptor.

13-29 Remember that the more electron withdrawing the substituent on the P, the more available (stronger) the back-bonding. Therefore, the strength of back-bonding from the PR_3 should follow the order: $P(^tBu)_3 < P(p\text{-tol})_3 < P(p\text{-}C_6H_4F)_3 < P(C_6F_5)_3$

The stronger the backbonding to P, the less to CO, therefore, the strongest CO stretch (weakest CO backbonding, largest ν_{CO}) should correspond to the strongest phosphine ($P(C_6F_5)_3$) and so on.
$P(^tBu)_3$ (1923); $P(p\text{-tol})_3$ (1965); $P(p\text{-}C_6H_4F)_3$ (1984); $P(C_6F_5)_3$ (2004 cm^{-1})

13-30 The highest CO stretch will occur with the weakest back-bonding to CO. Therefore, the best π-acceptor other than CO will lead to the highest CO stretch.

(a) $Fe(CO)_4PF_3$ (or $Fe(CO)_5$)
(b) $Re(CO)_6^+$ (highest positive charge = least amount of back-bonding)
(c) $Mo(CO)_3(PCl_3)_3$ (Cl is more withdrawing than Ph)

13-32 A stretch will only be IR active if there is a change in the dipole moment, but N_2 is nonpolar, so no stretch can meet this criterion. You can see it in the Raman (scattering) spectrum, though.

Coordinated N_2 should be lower in energy (weaker bond) because N_2's orbitals are similar to CO (if bonded end-on) or ethene (if side-bound). In either case, back-donation will go into a π* orbital, thus weakening the N≡N bond.

13-36 (a) $Fe(NO)(mnt)_2^-$ (weaker back-bond because of lower charge)
(b) $(CO)_5Cr\text{-}N{\equiv}N\text{-}Cr(CO)_5$ (back-bonding from both metals weakens N≡N)
(c) $Ta{=}CH_2$ (carbene is a M=C rather than a M-C)
(d) CrCCH3 in *trans*-.... (is a carbyne, Cr≡C)
(e) $Fe(CO)_4^{2-}$ (most backbonding (most -ve charge) makes weakest CO stretch)