Chapter 16 - Answers

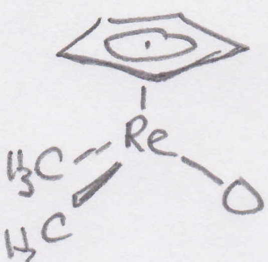
1. a) η^5-$Cp^- = 6e^-$

$2\ CH_3^- = 4e^-$

$O^{2-} = 2e^-$

$Re(5+) = d^2 = 2e^-$

$\overline{\quad 14e^- \quad}$



(For a $Re\equiv O$ one could count 4 more e^- = $18e^-$)

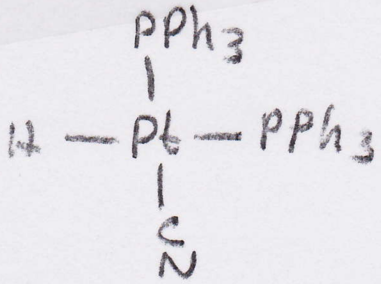
b) $2\ PPh_3 = 4e^-$

$H^- = 2e^-$

$CN^- = 2e^-$

$Pt(2+) = d^8 = 8e^-$

$\overline{\quad 16e^- \quad}$ ∴ square planar



c) (assume) η^5-$Cp^- = 6e^-$

$NO^+ = 2e^-$

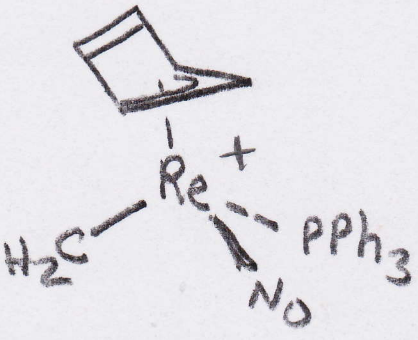
$PPh_3 = 2e^-$

$CH_2 = 2e^-$

$Re(1-) = d^8 = 8e^-$

(+1 charge on molecule)

$\overline{\quad 20e^- \quad}$ ∴ prob. η^3-Cp, T_d shape



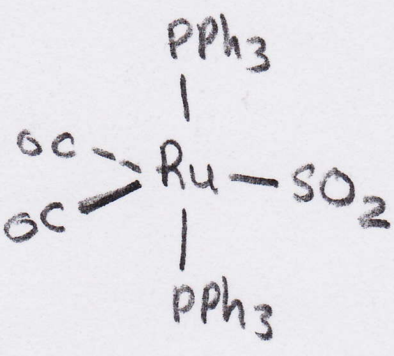
d) $2\ CO = 4e^-$

$SO_2 = 2e^-$

$2\ PPh_3 = 4e^-$

$Ru(0) = d^8 = 8e^-$

$\overline{\quad 18e^- \quad}$ with 5 ligands ∴ D_{3h} shape



We'll see in the next chapter how to put the SO_2 group

e) (assume) η^5-Cp^- = $6e^-$

(assume) η^6- benzene = $6e^-$ either

$Rh(1+) = d^8 = 8e^-$

$20e^-$

∴

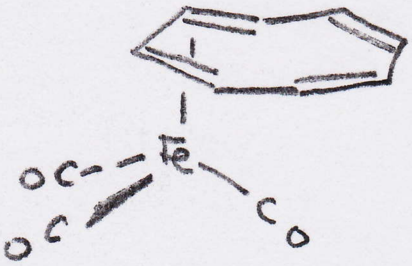
or

f) (assume) η^8-cyclooctatetraene = $8e^-$

$3CO = 6e^-$

$Fe(0) = d^8 = 8e^-$

$22e^-$ ∴ η^4- cyclooctatetraene



g) assume η^5 $Cp^- = 6e^-$

$Cl^- = 2e^-$

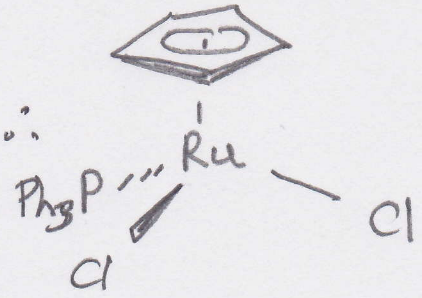
$CO = 2e^-$

$Ph_3P = 2e^-$

$Ru(2+) = d^6 = 6e^-$

$18e^-$

∴



h) assume η^5-$Cp^- = 6e^-$

$I^- = 2e^-$

$3CO = 6e^-$

$W(2+) = d^4 = 4e^-$

$18e^-$

∴

i) $Me_3Si^{\ominus} = 2e^-$

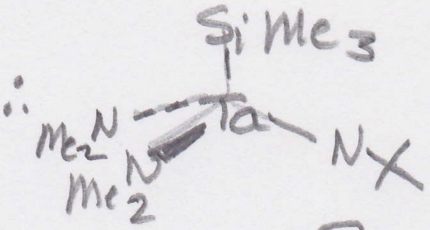
$2(Me_2N)^- = 4e^-$

$t\text{-}BuN^{2-} = 2e^-$

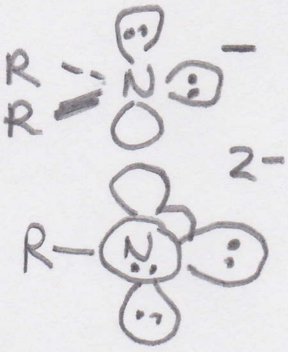
$Ta(5+) = d^0 = 0e^-$

$\overline{\quad 8e^- \quad}$

∴

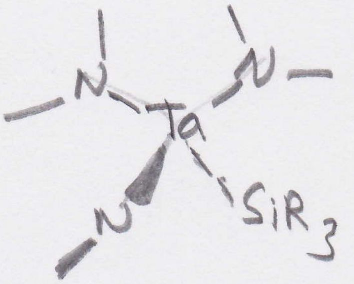


note



one could have 4 Ta−N π bonds formed, but this will only bring one up to a 16e⁻ count

As an exercise, use the metal orbitals of a tetrahedron and set up the Ta−N π interactions with the following geometry:



(you should find one component of the t set is left nonbonding)

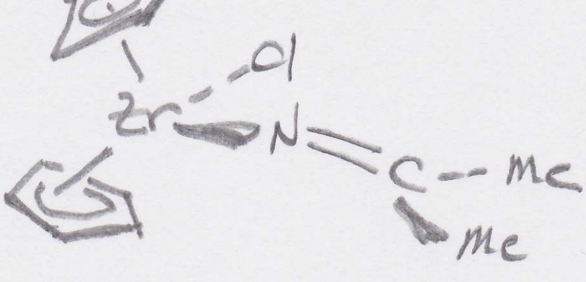
j) assume $2Cp^- = 12e^-$

$Cl^- = 2e^-$

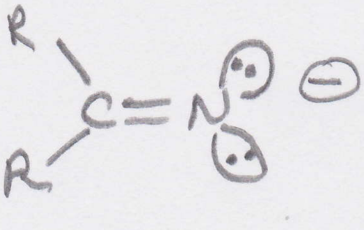
$Me_2C{=}N^- = 2e^-$

$Zr(4+) = d^0 = 0e^-$

$\overline{\quad 16e^- \quad}$



note:



k) assume η^5-$Cp^- = 6e^-$

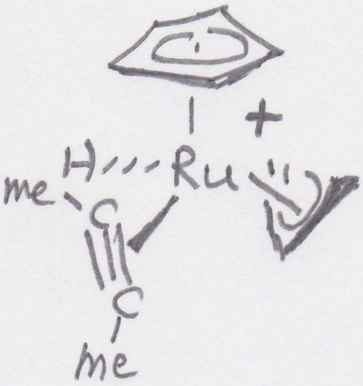
π-allyl$^- = 4e^-$

$H^- = 2e^-$

$meC\equiv Cme = 2$ or $4e^-$

$Ru(4+) = d^4 = 4e^-$

$18e^-$ (not $20e^-$)



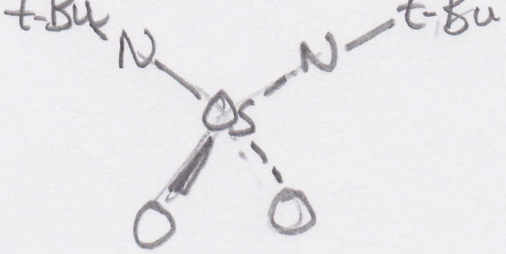
so acetylene here is a $2e^-$ donor

l) $2O^{2-} = 4e^-$

$2(t\text{Bu-N})^{2-} = 4e^-$

$Os(8+) = d^0 = 0e^-$

$8e^-$



Again one might count 4 Os-N π bonds + 4 Os-O π bonds which then would give $8+8+8 = 24$ e! Obviously not all of the combinations from N & O lone pairs form π bonds to Os. One can work this out in an easier fashion by forming SALC's of the 10 p AOs to be potentially used for π bonding in OsO_4.

2. a) around each Ta:

$2\ PPh_3 = 4e^-$

$2\ Cl^- = 4e^-$

bridging $Cl^- = 4e^-$ (count each Cl^- as donating a total of $4e^-$ to each Ta)

$Ta(3+) = d^2 = \underline{2e^-}$

counting the bridging Cl^- as [illegible] $14e^-$

a Ta=Ta is the maximum one can have for d^2

thus each Ta is $16e^-$

b) around each Co

$3CO = 6e^-$

(bridging) $1\ CO = 2e^-$ (counting each CO as donating two e^- to each Co)

$Co(0) = d^9 = \underline{9e^-}$

$17e^-$

∴ Co–Co single bond makes $18e^-$ around each Co

c) around each Re

$2\ PR_3 = 4e^-$

$2\ H^- = 4e^-$

(bridging) $2H^- = 4e^-$ (each H^- can donate only $2e^-$)

$Re(4+) = d^3 = \underline{3e^-}$

$15e^-$

∴ Re≡Re gives $18e^-$ around each Re

d) $\eta^5 Cp^- =$ $6e^-$

$NO^+ =$ $2e^-$

$Co(0) = d^9 =$ $9e^-$

$17e^-$

∴ Co—Co single bond gives an $18e^-$ count around each Co

e) $2(CO) = 4e^-$

$CN^- = 2e^-$

$CH_3S^{\ominus} = 4e^-$ (bridging unit)

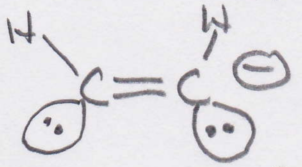
$Fe(+1) = d^7$ $7e^-$

$17e^-$ → ∴ Fe—Fe single bond

remember 2- charge on molecule

f) $Cl^- = 2e^-$

$2(PR_3) = 4e^-$



$= 2e^-$

$Pd(2+) = d^8 = 8e^-$

$16e^-$

So this could have a Pd=Pd – **BUT** – why not each Pd being a $16e^-$ square planar complex?

This is probably a better choice. We will look again at these compounds - called "A-frames" in Chapter 18.

3. Notice that in a) - d) a square planar or trigonal planar geometry is impossible, likewise in e) for $X=1$ an unreasonable $13\,e^-$ count will be obtained. Thus, <u>all</u> must be $18\,e^-$ complexes.

a) $4CO = 8\,e^-$
$xNO^+ = 2x$
$Mn(-X) = d^{7+X} = \underline{7+X}$
$18 = 15+3X$
$\underline{\underline{X=1}}$

b) $Cp^- = 6\,e^-$
$2NO^+ = 4$
$XCl^- = 2X$
$Cr(X-1) = d^{7-X} = \underline{7-X}$
$18 = 17-X$
$\underline{\underline{X=1}}$

c) $C_4H_4^{2-} = 6\,e^-$
$XCO = 2X$
$Fe(2+) = d^6 = \underline{6}$
$18 = 12+2X$
$\underline{\underline{X=3}}$

d) $2Cp^- = 12e^-$
$xH^- = 2X$
$W(X+2) = d^{4-X} = \underline{4-X}$
$18 = 16+X$
$\underline{\underline{X=2}}$

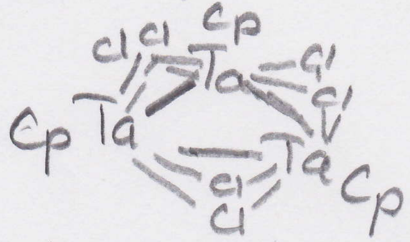
e) $3\,PPh_3 = 6e^-$
$xH^- = 2X$
$W(X) = d^{6-X} = \underline{6-X}$
$18 = 12+X$
$\underline{\underline{X=6}}$

4. For $Cp_2Ta_2Cl_4$:

$\eta^5\text{-}Cp^- = 6e^-$
$2Cl^- = 8e^-$ (4 bridging)
$Ta(3+) = d^2 = \underline{2e^-}$
$16e^-$

$\therefore Ta{=}Ta$

$Cp_3Ta_3Cl_6^+$ – same e^- count per $CpTaCl_2$ unit! So for a nuetral complex then a Ta–Ta single bond:



But this molecule is $1e^-$ short so the total Ta–Ta bonds is $\frac{6-1}{2} = 5/2$ Ta–Ta bonds spread out over 3 centers, or $\frac{5}{2\times 3} = \frac{5}{6}$ Ta–Ta for each

5. A R_2P Lewis base would be regarded as

Thus, the electron count around each Rh in the absence of any Rh-Rh bonds is:

$2CO = 4e^-$

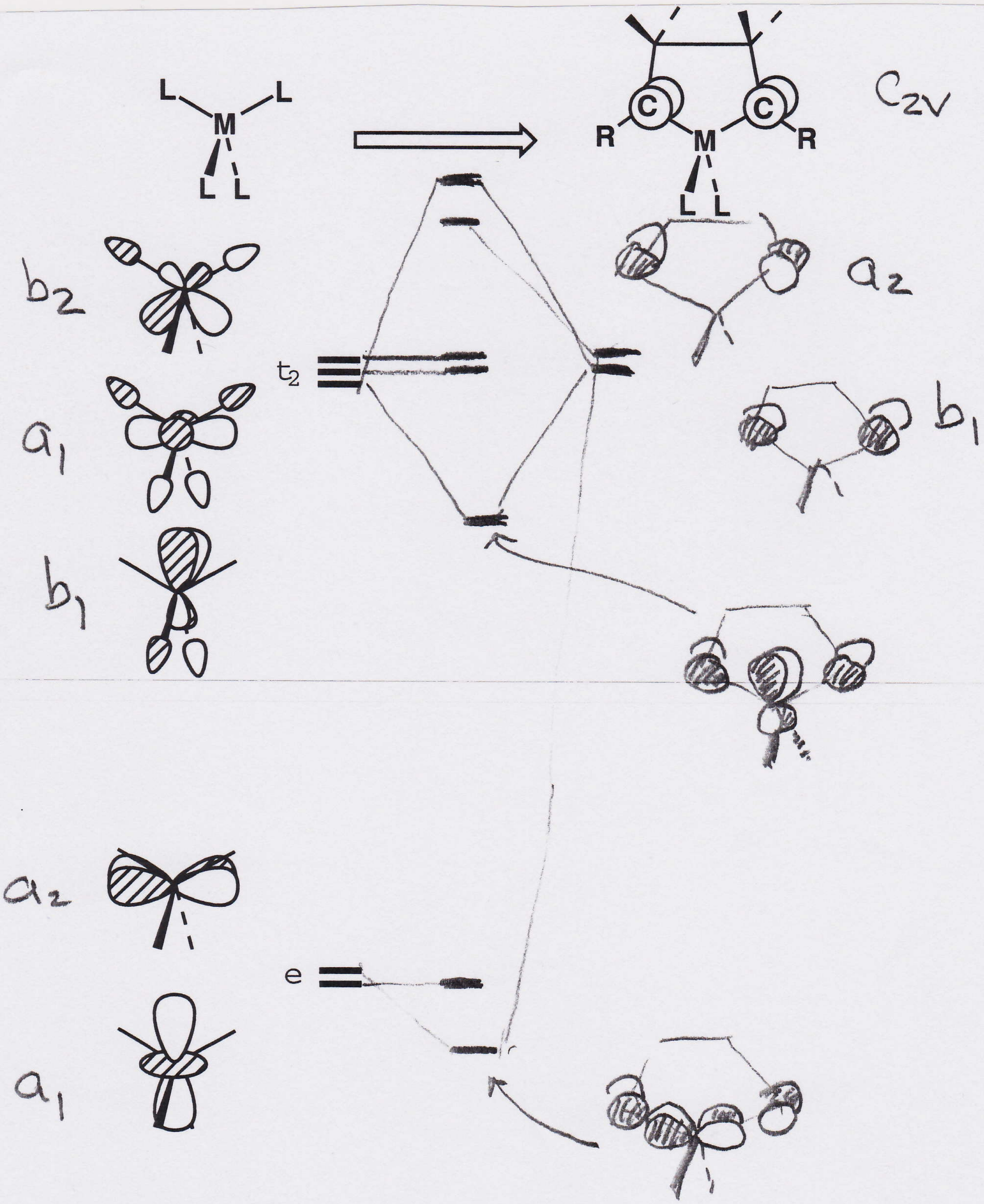
$PR_2^- = 4e^-$

$Rh(1+) = d^8 = 8e^-$

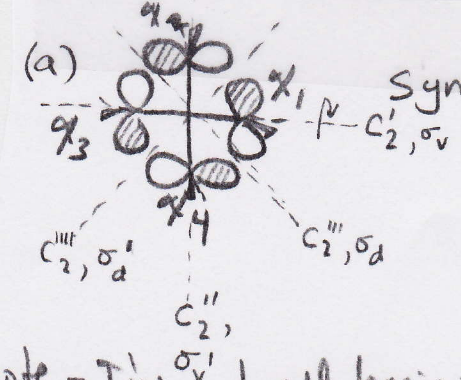
$16e^-$

In 1 the local coordination geometry around each Rh is square planar, thus, with a 16e^- count there should be no Rh-Rh bond. In 2 one Rh is square planar, the other is tetrahedral. Thus, to make an 18e^- count at the tetrahedral Rh one must use 2 nonbonding electrons on the square planar one to form a Rh-Rh single bond. The decrease of 1 Å on going from 1 to 2 is consistent with this. Finally in 3 both Rh atoms are tetrahedral. Thus, we now need to share 2 e^- from each Rh to make an 18e^- count and therefore a Rh=Rh double bond is expected. In agreement with this the Rh-Rh distance on going from 2 to 3 decreases by 0.21 Å.

6.



7. (a)



Symmetry = $\underline{\underline{D_{4h}}}$

	E	C_4	C_2	C_2'	C_2'''	i	S_4	σ_h	σ_v	σ
Γ	4	0	0	-2	0	0	0	4	-2	0
b_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
a_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
e_u	2	0	-2	0	0	-2	0	2	0	0

<u>note</u> - I've set all basis functions to have a negative overlap!

$$\Gamma = b_{2g} + a_{2g} + e_u$$

	E	C_4	C_4^3	C_2	C_2'	C_2''	C_2'''	C_2''''	i	S_4	S_4^3	σ_h	σ_v	σ_v'	σ_d	σ_d
χ_1	χ_1	χ_2	χ_4	χ_3	$-\chi_1$	$-\chi_3$	$-\chi_4$	$-\chi_2$	χ_3	χ_2	χ_4	χ_1	$-\chi_1$	$-\chi_3$	$-\chi_4$	$-\chi_2$
χ_2	χ_2	χ_3	χ_1	χ_4	$-\chi_4$	$-\chi_2$	$-\chi_3$	$-\chi_1$	χ_4	χ_3	χ_1	χ_2	$-\chi_4$	$-\chi_2$	$-\chi_3$	$-\chi_1$

Using χ_1:

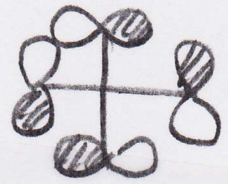
$$\psi_{b_{2g}} \propto (1)\chi_1 + (-1)\chi_2 + (-1)\chi_4 \overset{+(1)\chi_3}{\underset{\wedge}{+}} (-1)-\chi_1 + (-1)-\chi_3 + (1)-\chi_4 + (1)-\chi_2 + (1)\chi_3 + (-1)\chi_2$$
$$+ (-1)\chi_4 + (1)\chi_1 + (-1)-\chi_1 + (-1)-\chi_3 + (1)-\chi_4 + (1)-\chi_2$$
$$\propto 4\chi_1 - 4\chi_2 + 4\chi_3 - 4\chi_4 \propto \chi_1 - \chi_2 + \chi_3 - \chi_4$$

normalizing $\langle \psi_{b_{2g}} | \psi_{b_{2g}} \rangle = \langle \chi_1 - \chi_2 + \chi_3 - \chi_4 | \chi_1 - \chi_2 + \chi_3 - \chi_4 \rangle$

<u>note</u> $S_{12} = S_{23} = S_{34} = S_{14} = S$
$S_{13} = S_{24} = S'$

$$\langle \psi_{b_{2g}} | \psi_{b_{2g}} \rangle = 4 - 8S + 4S'$$

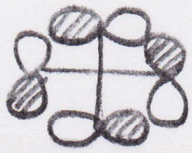
$$\therefore \psi_{b_{2g}} = \frac{1}{\sqrt{4 - 8S + 4S'}} (\chi_1 - \chi_2 + \chi_3 - \chi_4) =$$



$$\psi_{a_{2g}} \propto (1)\chi_1 + (1)\chi_2 + (1)\chi_4 + (1)\chi_3 + (-1)-\chi_1 + (-1)-\chi_3 + (-1)-\chi_4 + (-1)-\chi_2$$
$$+ (1)\chi_3 + (1)\chi_2 + (1)\chi_4 + (1)\chi_1 + (-1)-\chi_1 + (-1)-\chi_3 + (-1)-\chi_4 + (-1)-\chi_2$$
$$\propto 4\chi_1 + 4\chi_2 + 4\chi_3 + 4\chi_4 \propto \chi_1 + \chi_2 + \chi_3 + \chi_4$$

normalizing $\langle \psi_{a_{2g}} | \psi_{a_{2g}} \rangle = 4 + 8S + 4S'$

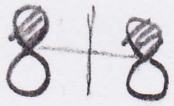
$$\therefore \psi_{a_{2g}} = \frac{1}{\sqrt{4+8S+4S'}}(\chi_1 + \chi_2 + \chi_3 + \chi_4) \equiv$$



$$\psi_{e_u} \propto (2)\chi_1 + (-2)\chi_3 + (-2)\chi_3 + (2)\chi_1$$
$$\propto \chi_1 - \chi_3$$

normalizing $\langle \psi_{e_u} | \psi_{e_u} \rangle = 2 - 2S'$

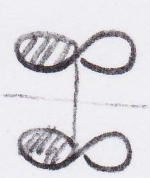
$$\therefore \psi_{e_u} = \frac{1}{\sqrt{2-2S'}}(\chi_1 - \chi_3) \equiv$$



using χ_2:

$$\psi'_{e_u} \propto (2)\chi_2 + (-2)\chi_4 + (-2)\chi_4 + (2)\chi_2$$
$$\propto \chi_2 - \chi_4$$

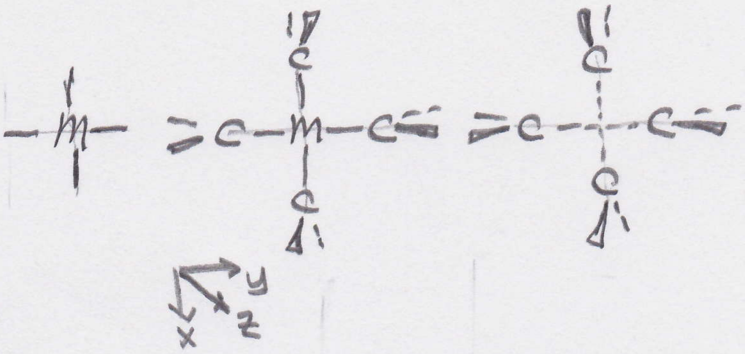
$$\therefore \psi'_{e_u} = \frac{1}{\sqrt{2-2S'}}(\chi_2 - \chi_4) \equiv$$

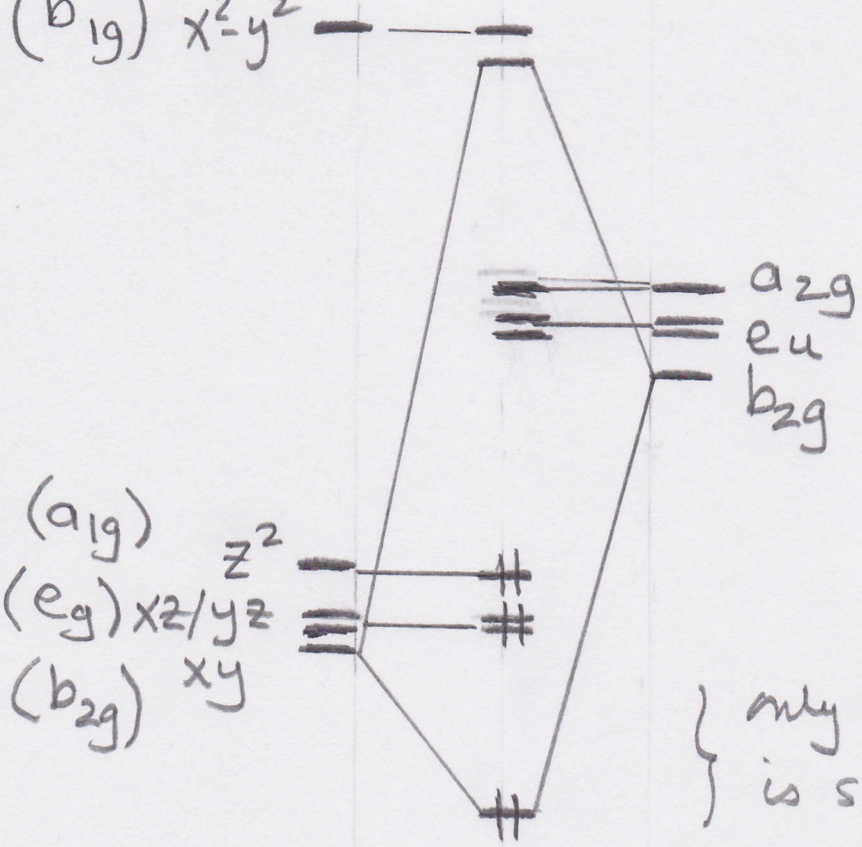


note $\langle \psi_{e_u} | \psi_{e_u'} \rangle = \frac{1}{2-2S'} \langle \chi_1 - \chi_3 | \chi_2 - \chi_4 \rangle = 0$

$\therefore$ the e_u set is just fine.

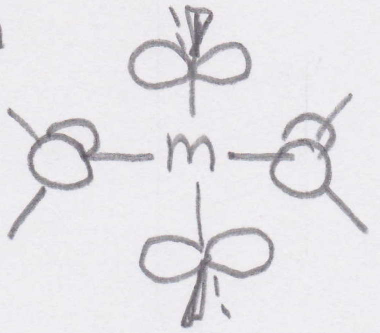
(b)

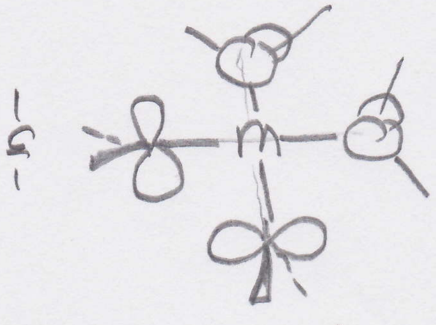




} only one π combination is stabilizing!

Please work out for yourself what will happen with

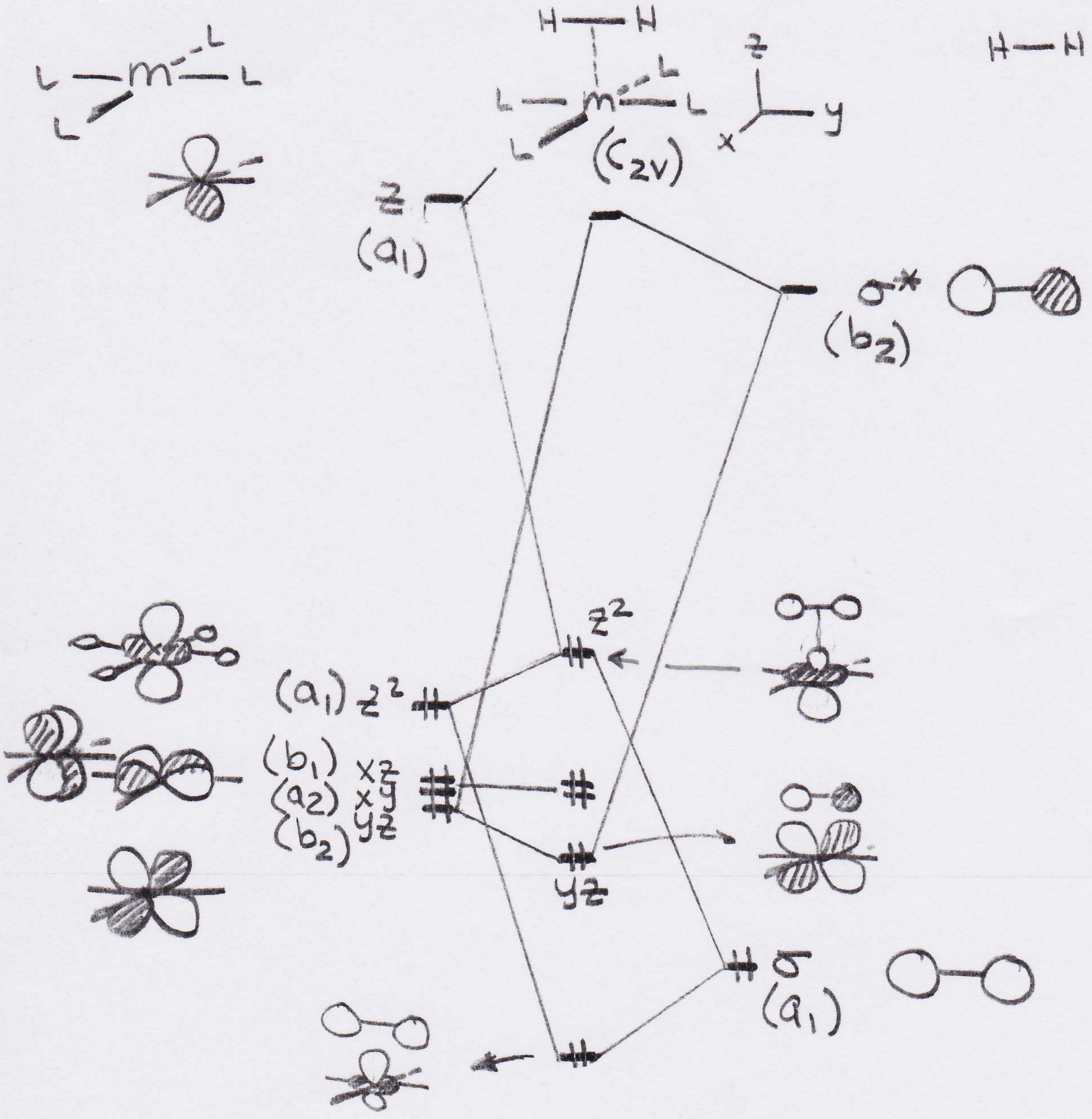




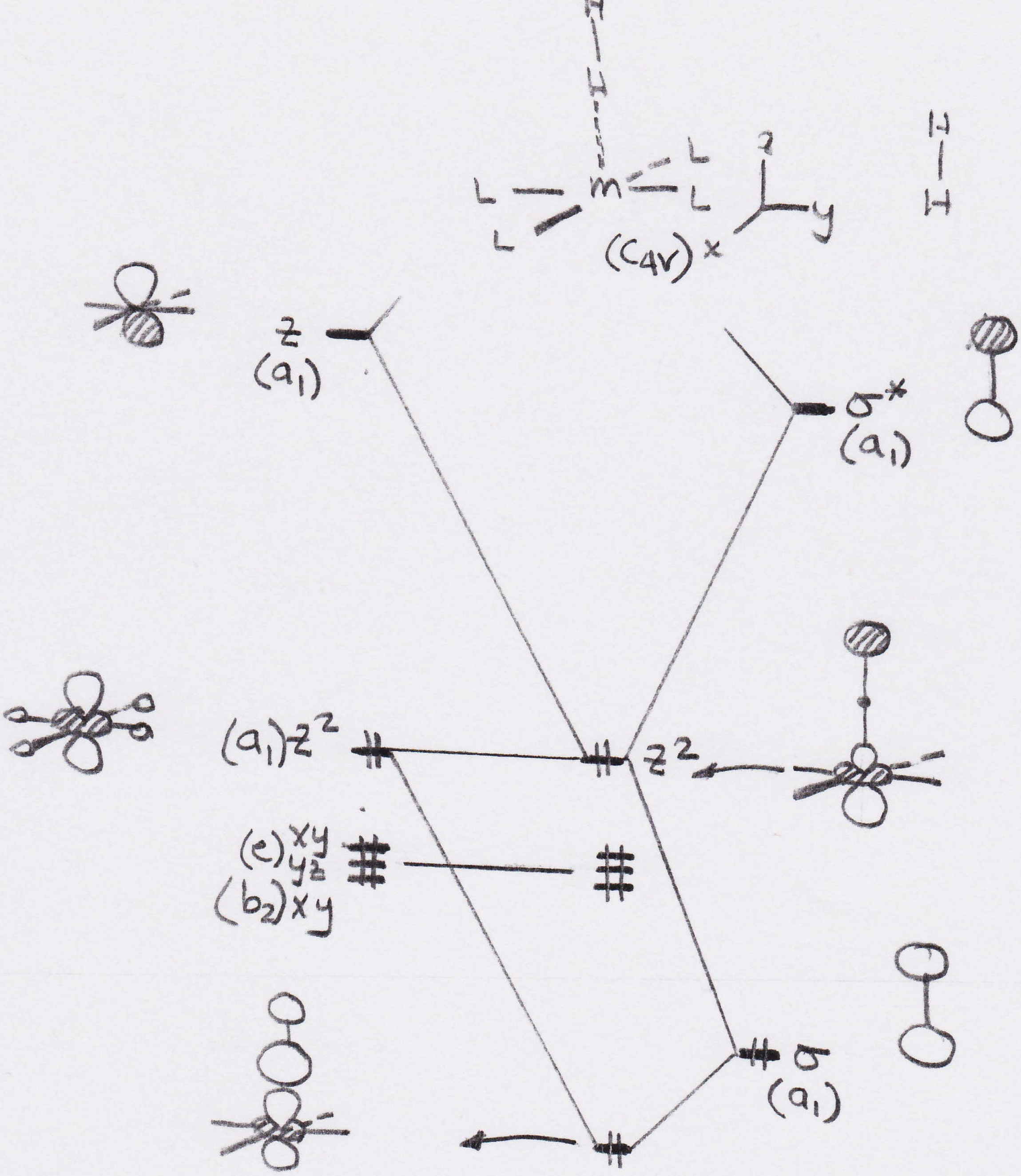
Both should be found to be more stabilizing for a d^8 metal than the above example.

8.

(a) For reaction (1):

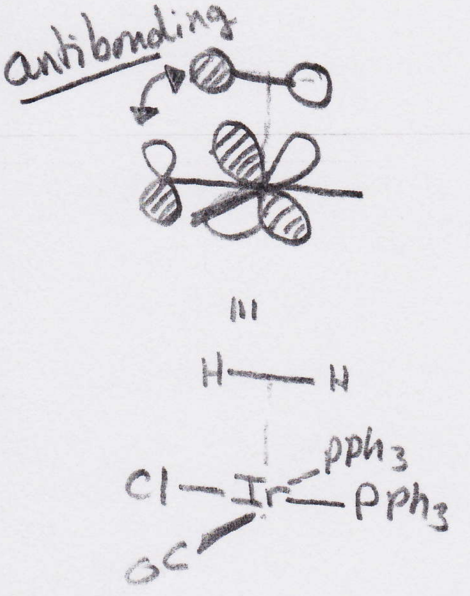


For reaction (2):

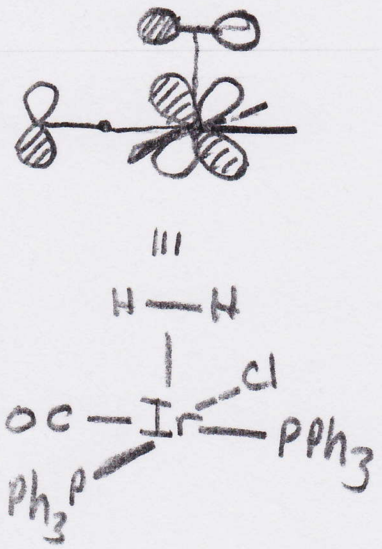


(b) There are two major differences. In reaction (1) there is bonding between yz and σ^* turned on and this stabilizes yz. In reaction (2) this is not possible. In reaction (1) there is some repulsion between H_2 σ and z^2. To a large extent this is removed by metal z. In reaction (2) one has an identical situation, however, H_2 σ^* can also mix into z^2 to releave the repulsion more. For reaction (1) to be more favorable the stabilization of yz by $H_2\sigma^*$ must be greater than the stabilization of z^2 by $H_2\sigma^*$ in reaction (2).

(c) If one does not consider π effects from Cl and CO then reactions (3) and (4) should occur at the same activation energy. However, considering the stabilization of yz or xz we have:

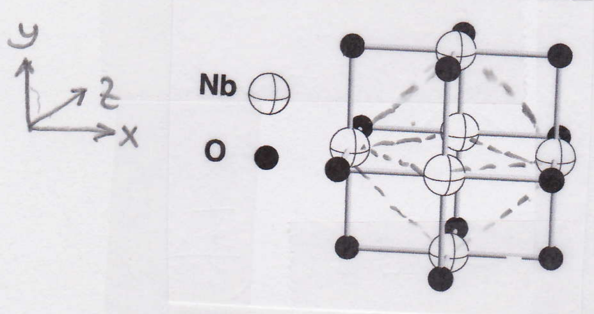


vs



The antibonding between $H_2\sigma^*$ and the Cl A.O. in yz leads to a smaller overlap than that between xz and $H_2\sigma^*$.

9. For each local unit:



— x^2-y^2 ← δ overlap

— z^2 ← σ overlap

= xz/yz ← π overlap

xy ← δ overlap

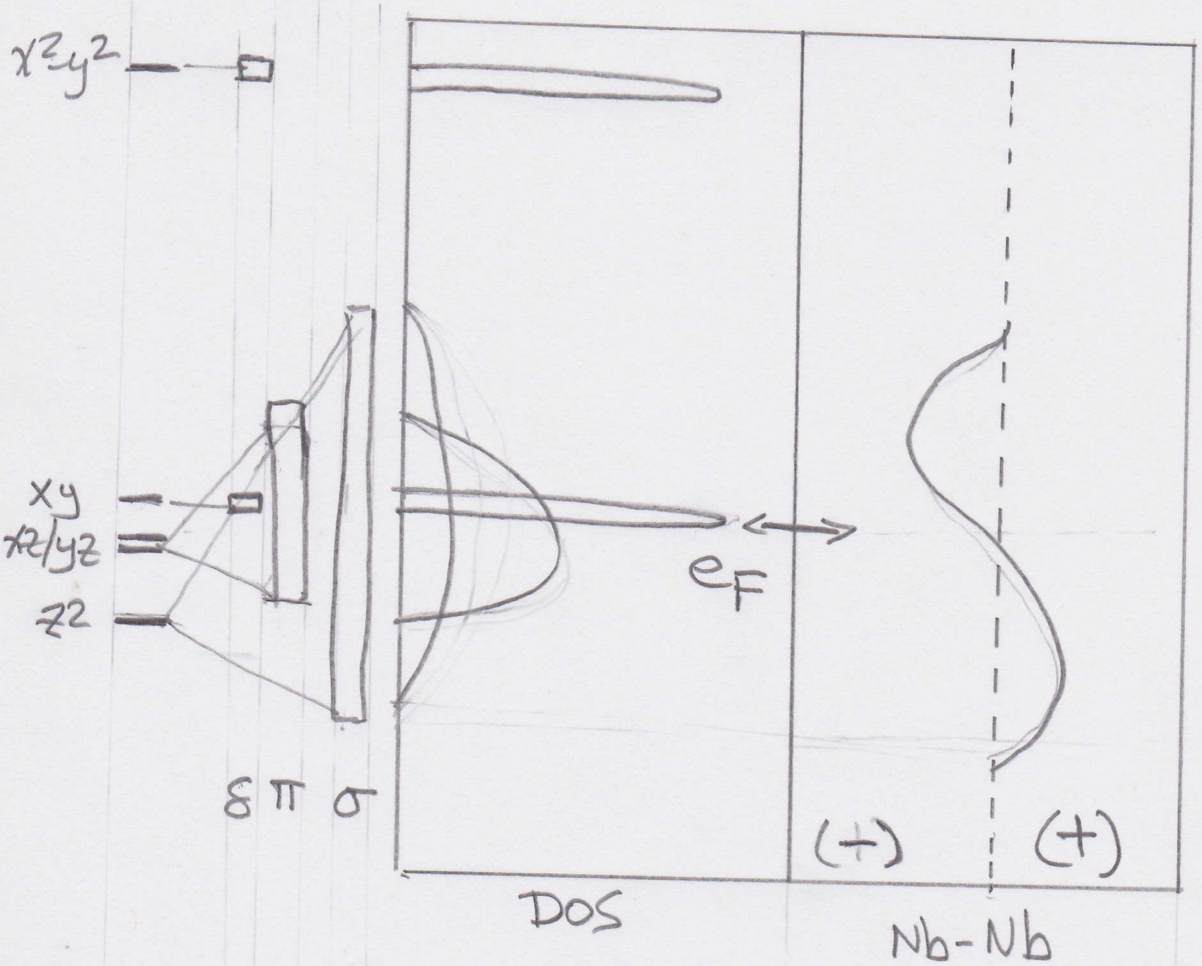
with π bonding to O, the sequence will be more like:

— xy

— — xz/yz

— z^2

Nb^{2+}/O^{2-} ∴ d^3



1e⁻ goes into $z^2//z^2$ bonding σ

2e⁻ goes into xz/yz // xz/yz bonding π

so e_F is right around xy orbitals

This is very simplified because there are strong Nb⋯Nb interactions along the dotted lines.