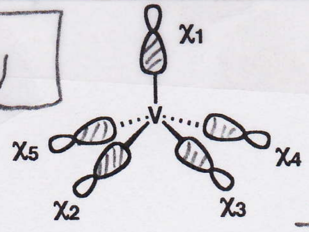
Answers—Chapter 17

1. a) $\boxed{C_{4v}}$



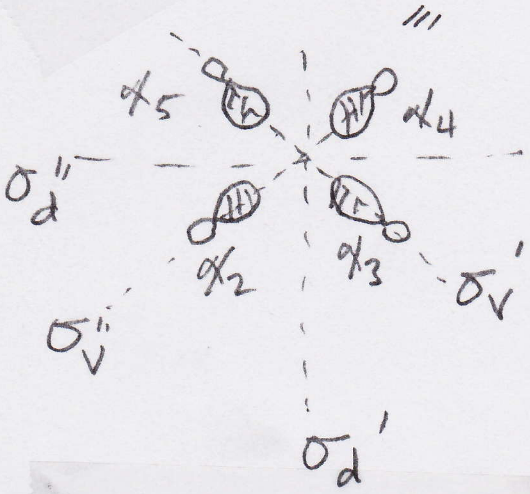
Basis 1 - $\Gamma_1 = \chi_1$

Basis 2 - $\Gamma_2 = \chi_2, \chi_3, \chi_4$ & χ_5

	E	C_4	C_2	σ_v	σ_d
Γ_1	1	1	1	1	1 $\Rightarrow a_1$
Γ_2	4	0	0	2	0

$\Rightarrow a_1 + b_1 + e$

(if you changed σ_v & σ_d around - $a_1 + b_2 + e$)



	E	C_4	C_4^3	C_2	σ_v'	σ_v''	σ_d'	σ_d''
χ_1	χ_1	χ_1	χ_1	χ_1	χ_1	χ_1	χ_1	χ_1
χ_2	χ_2	χ_5	χ_3	χ_4	χ_4	χ_2	χ_3	χ_5
χ_3	χ_3	χ_2	χ_4	χ_5	χ_3	χ_5	χ_2	χ_4

For Γ_1; $\psi_{a_1} \propto \chi_1$

For Γ_2;

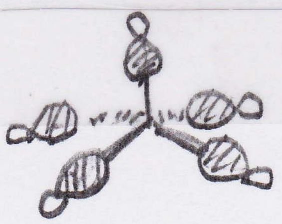
$$\psi_{a_1} \propto \chi_2+\chi_5+\chi_3+\chi_4+\chi_4+\chi_2+\chi_3+\chi_5$$
$$\propto \chi_2+\chi_3+\chi_4+\chi_5$$

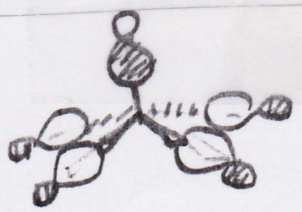
Combining the two SALCS

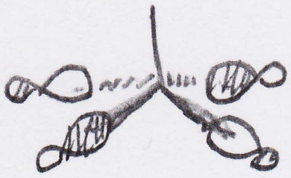
$$\psi'_{a_1} \propto \chi_1+\chi_2+\chi_3+\chi_4+\chi_5$$
$$\psi''_{a_1} \propto \chi_1-\chi_2-\chi_3-\chi_4-\chi_5$$
$$\psi_{b_1} \propto \chi_2-\chi_5-\chi_3+\chi_4+\chi_4+\chi_2-\chi_3-\chi_5$$

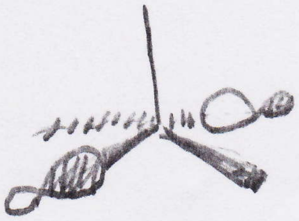
(or b_2) → $\propto \chi_2-\chi_3+\chi_4-\chi_5$

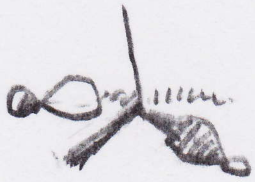
$$\psi'_e \propto 2\chi_2-2\chi_4 \propto \chi_2-\chi_4$$
$$\psi''_e \propto 2\chi_3-2\chi_5 \propto \chi_3-\chi_5$$

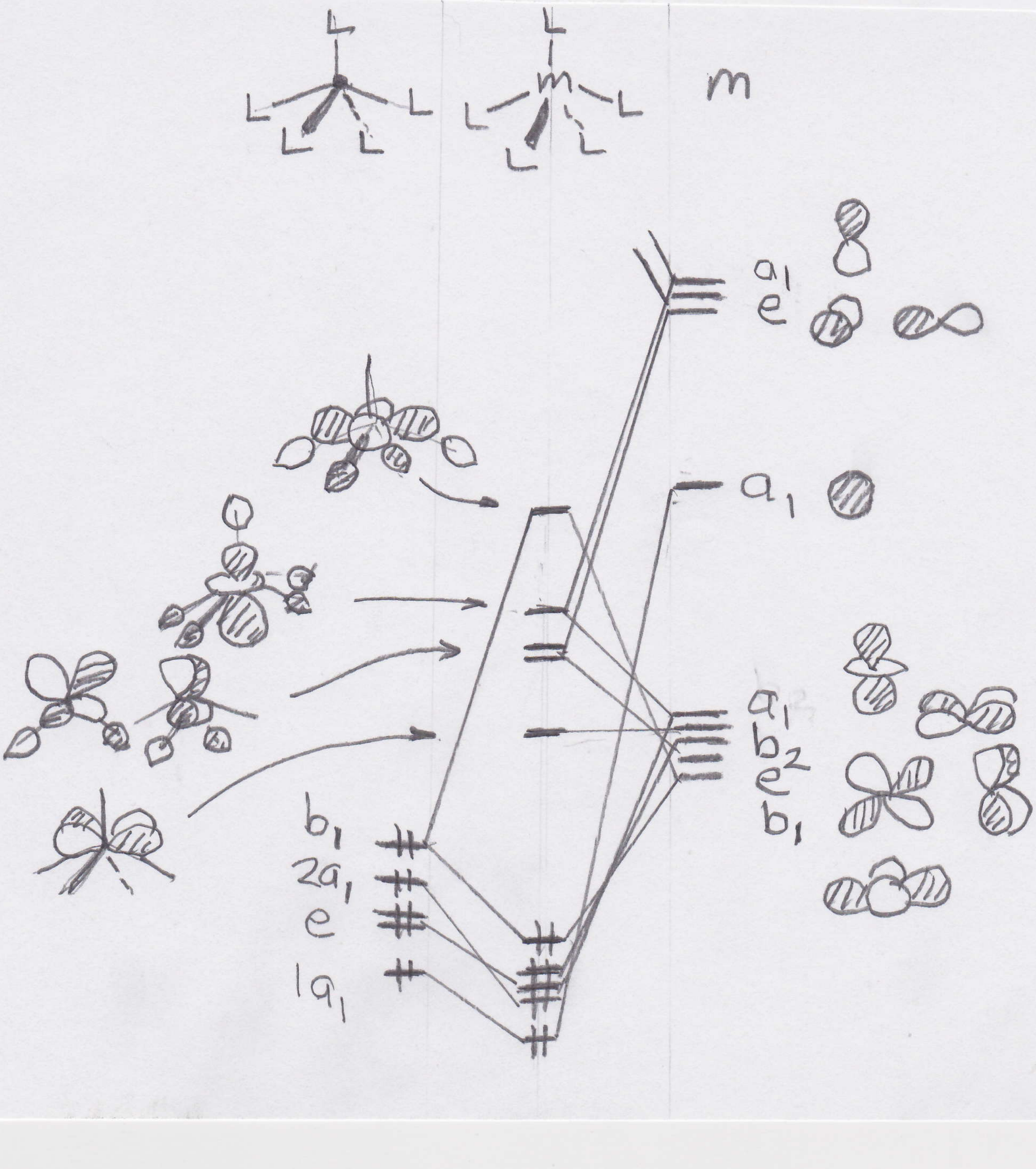
$\psi'_{a_1} =$ 

$\psi''_{a_1} =$ 

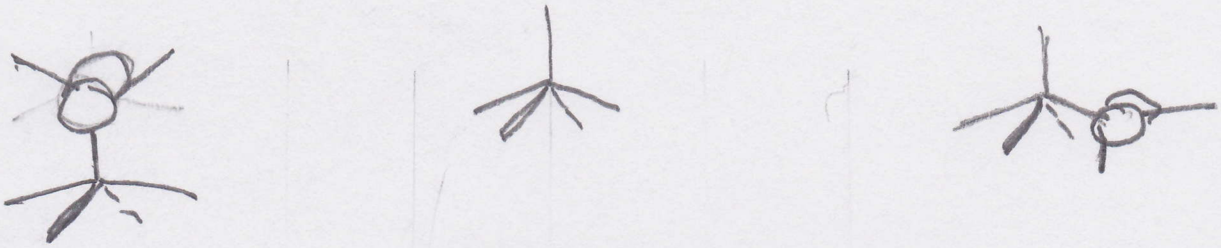
ψ_{b_1} (or b_2) $\rightarrow$ $=$ 

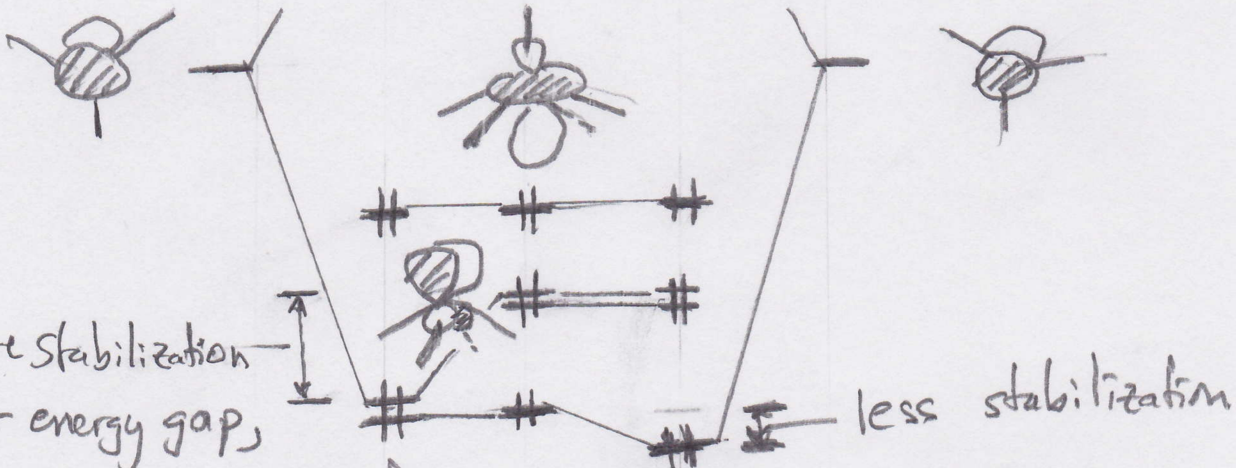
$\psi'_e =$ 

$\psi''_e =$ 



2.





more stabilization

smaller energy gap, larger overlap because of hybridization

less stabilization

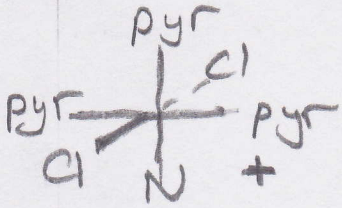
3. $N^{3-} = 2e^-$

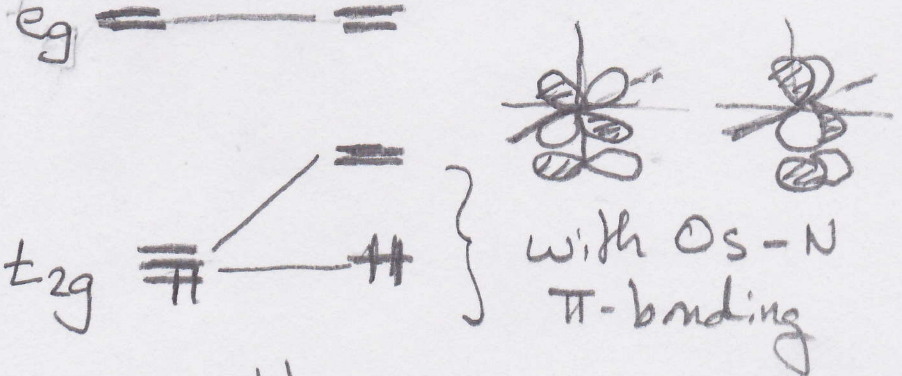
$2Cl^- = 4e^-$

3  N: $= 6e^-$

$Os(6+) = d^2 = \underline{2e^-}$

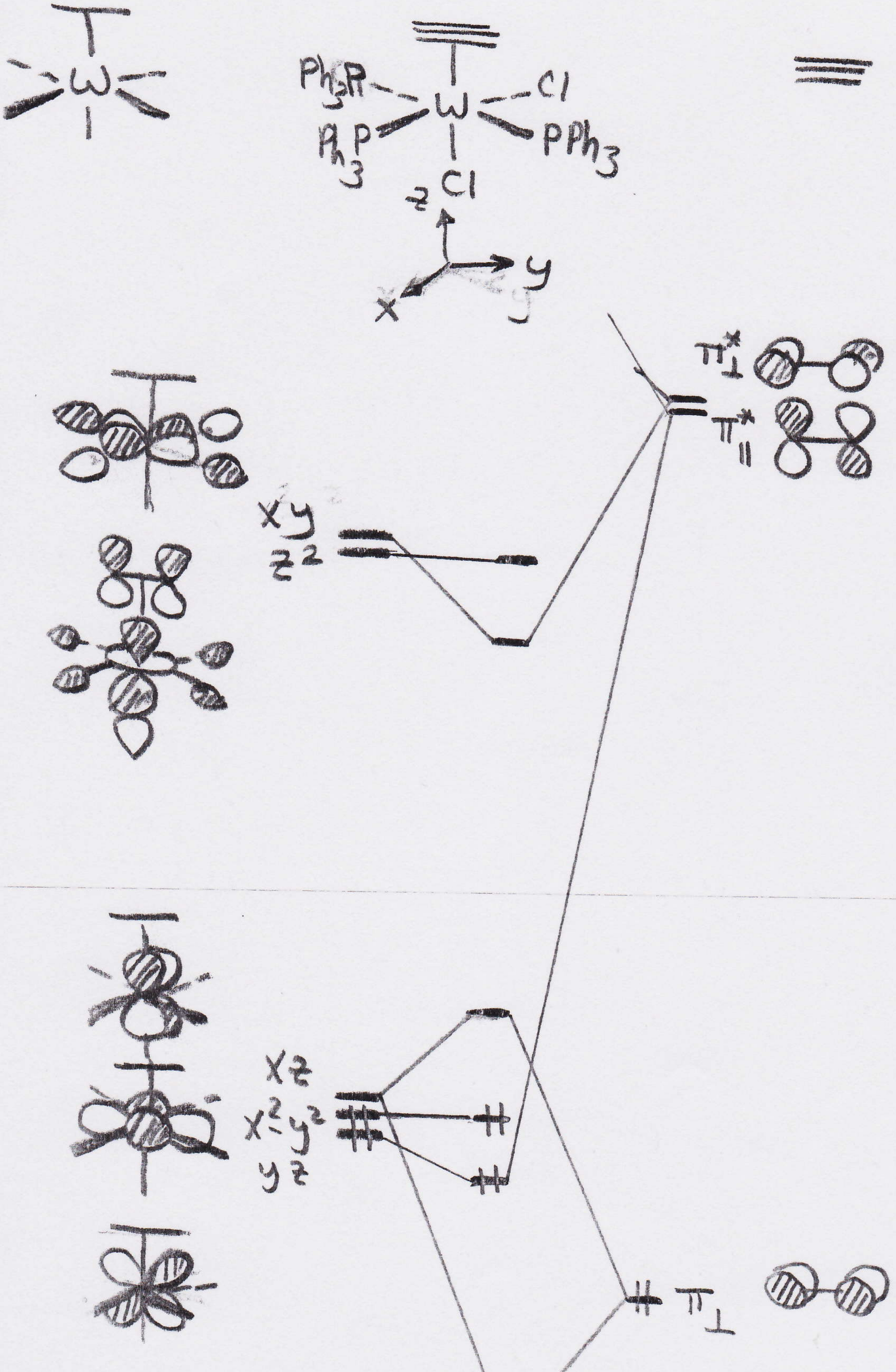
(remember +1 charge on molecule) $14e^-$!





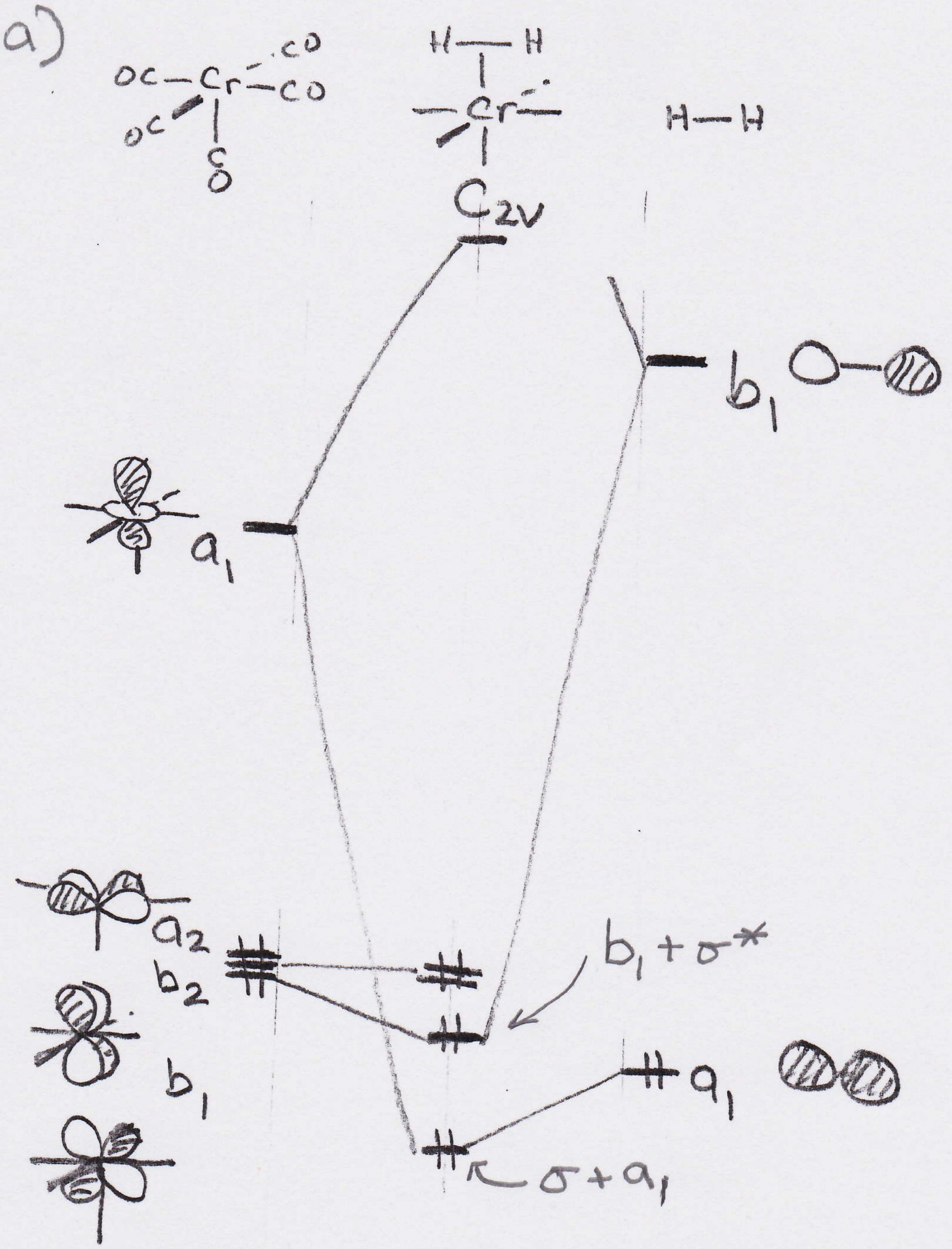
Therefore, one could assign an Os-N triple bond to this molecule

4.



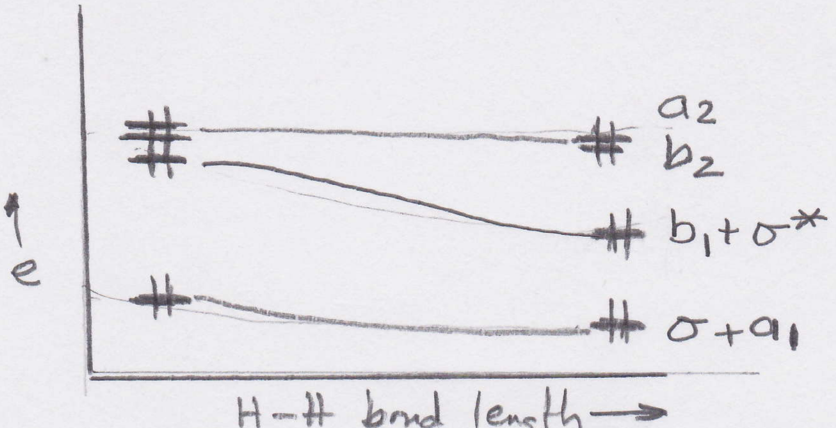
This problem can be worked several ways. One could take an ML_5 fragment splitting pattern and use both sets of π and π* orbitals. One could also split the t_{2g} set slightly to reflect the π donor characteristics of the Cl ligands (xz and yz would lie slightly higher in energy than x^2-y^2). What is done here is to use the octahedral splitting pattern where one π orbital ($\pi_{\parallel}$) is used as a σ donor. Then the remaining $\pi_{\perp}$ and $\pi_{\parallel}^*/\pi_{\perp}^*$ set are used to combine with the t_{2g}-like and e_g-like sets. Notice that in this conformation $\pi_{\perp}^*$ interacts with the xy member of "e_g". If the acetylene were rotated by 45°, $\pi_{\perp}^*$ would stabilize x^2-y^2 in "t_{2g}". This would be a more stable situation. One would take a linear combination of xz and yz so that the same interaction pattern with $\pi_{\perp}$ and $\pi_{\parallel}^*$ would exist.

5. a)



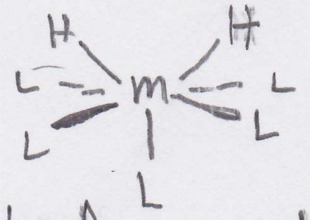
When the b_2 metal orbital interacts with H_2 σ^*, electron density flows from the metal to the H_2 ligand. Since H_2 σ^* is strongly H-H antibonding, this weakens the H-H bond and ultimately will break to form the metal dihydride. Electron donor groups on L or making the metal more electropositive (or putting a negative charge on the metal) will raise the energy of b_2 so the b_2-σ^* energy gap is smaller. This will create a larger interaction, therefore, σ^* has more electron density and the equilibrium is shifted towards the dihydride. With electron acceptors on L or a positive charge on the metal, the b_2 orbital lies lower and the σ^*–b_2 energy gap is larger. A smaller interaction keeps the complex at the η^2-H_2 side.

b) Plotting out a Walsh diagram for this transformation:

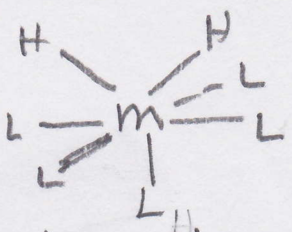


The two MOs smoothly transform from a loose H_2 complex to a dihydride

So there is no obvious barrier engendered along this rxn. path. What the problem is that a geometry like

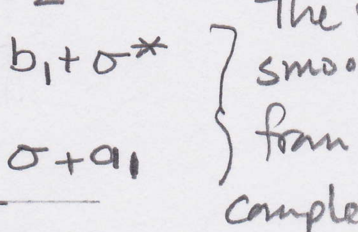


or



does not exist

Instead, geometries like



do.

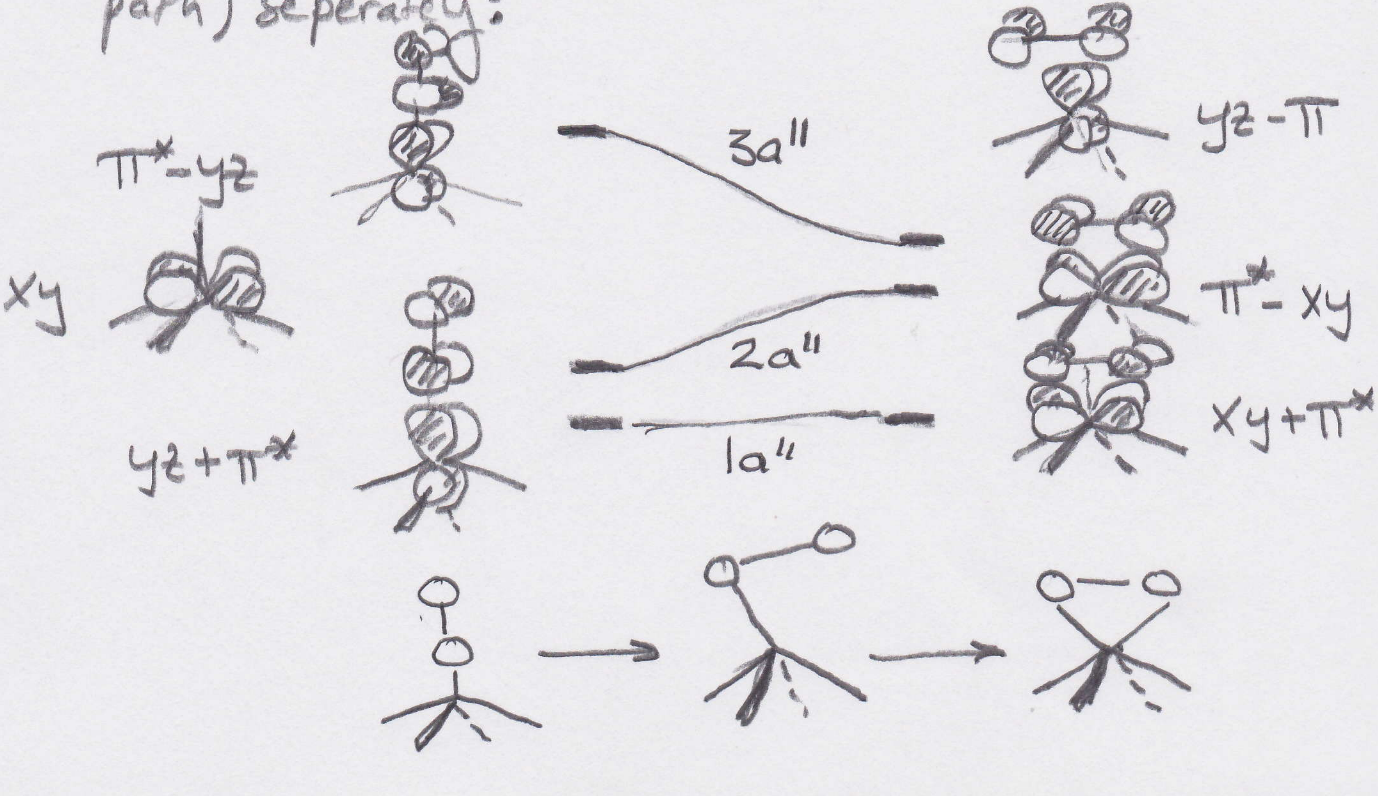
The barrier lies in a polytopal rearrangement occuring concerted with H--H bond breaking

6. a) Counting the porphyrin as 2− and O_2 as 2+ we have a Fe(0)-d^8 molecule. So using Figure 17.11, z^2-n is the HOMO and, therefore, the Fe-O-O angle should be less than 180°. For the initial complex this is a Fe(2+) high spin metal interacting with triplet O_2. So the electron configuration is:

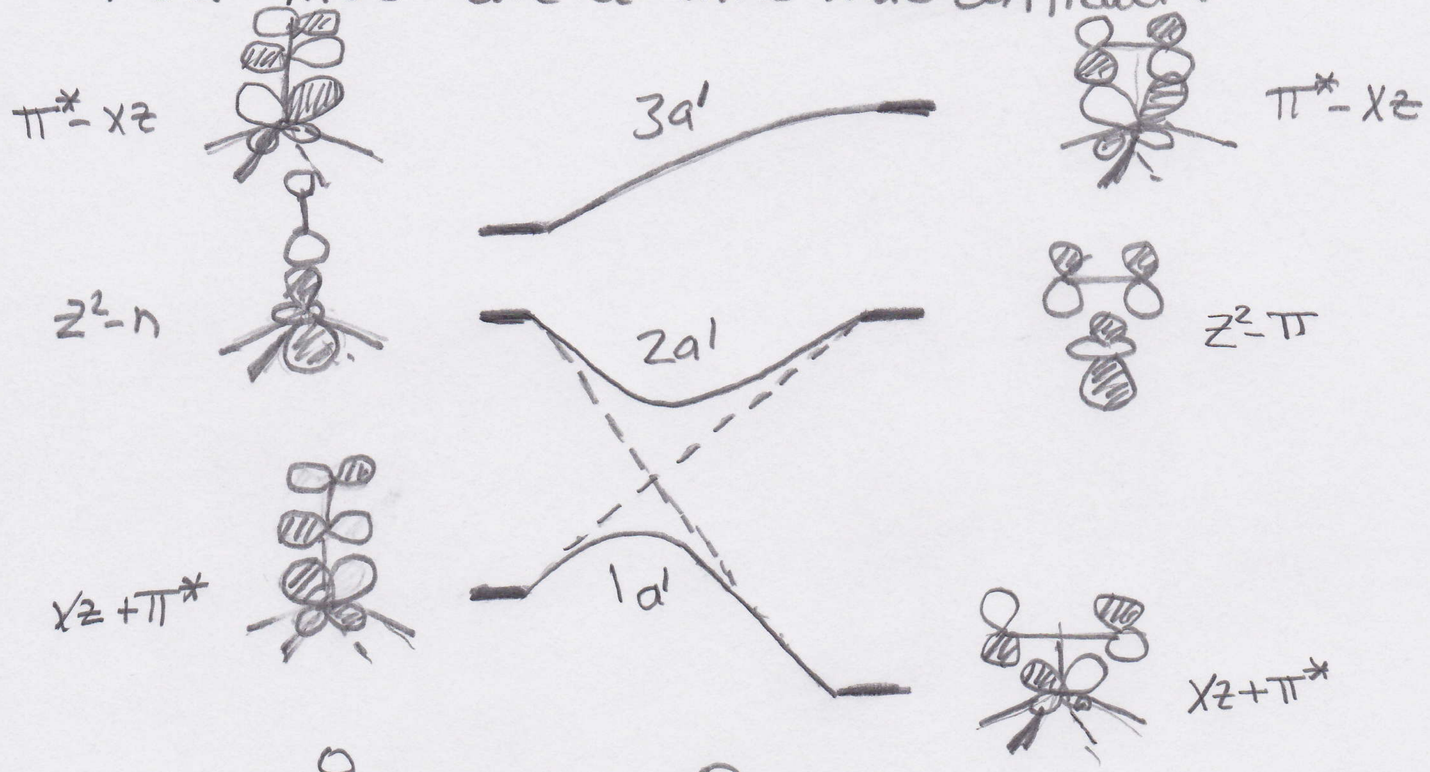
$(xz+\pi^*)^2(yz+\pi^*)^2(xy)^1(z^2-n)^1(\pi^*-yz)^1(\pi^*-xz)^1$

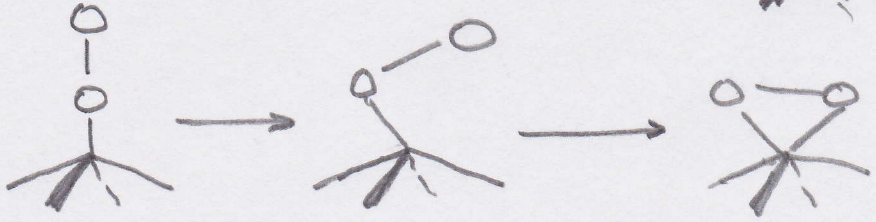
We'll see in b) that π^*-xz actually goes up in energy upon bending so the initial complex before spin pairing should be linear or close to it.

b) The easiest way to tackle this problem is to treat the orbitals symmetric and antisymmetric to the mirror plane (which is conserved along the reaction path) seperately:

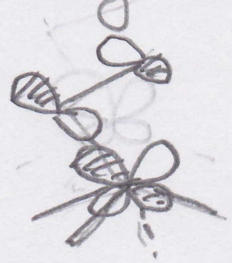


The a′ MOs are a little more difficult:



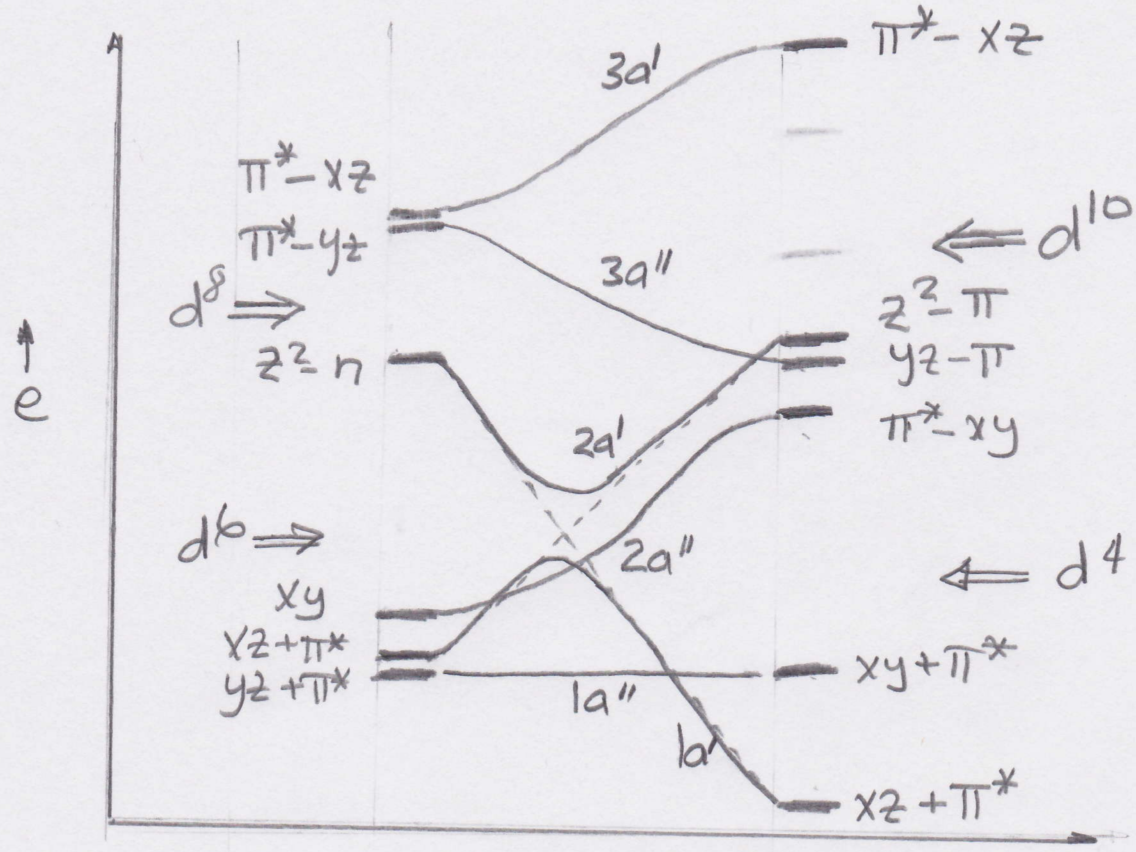


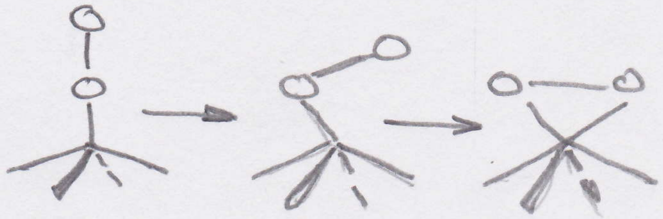
1a′ and 2a′ undergo an avoided crossing. Upon bending the $xz+\pi^*$ MO loses π bonding and so it is destabilized, i.e. at the midpoint:



Likewise, z^2-n loses the σ antibonding between O_2 and z^2 and so it is stabilized. But, $xz+\pi^*$ and z^2-n cannot cross. This is a weakly avoided crossing. There is little overlap between the two near the crossing point.

So putting these two together:

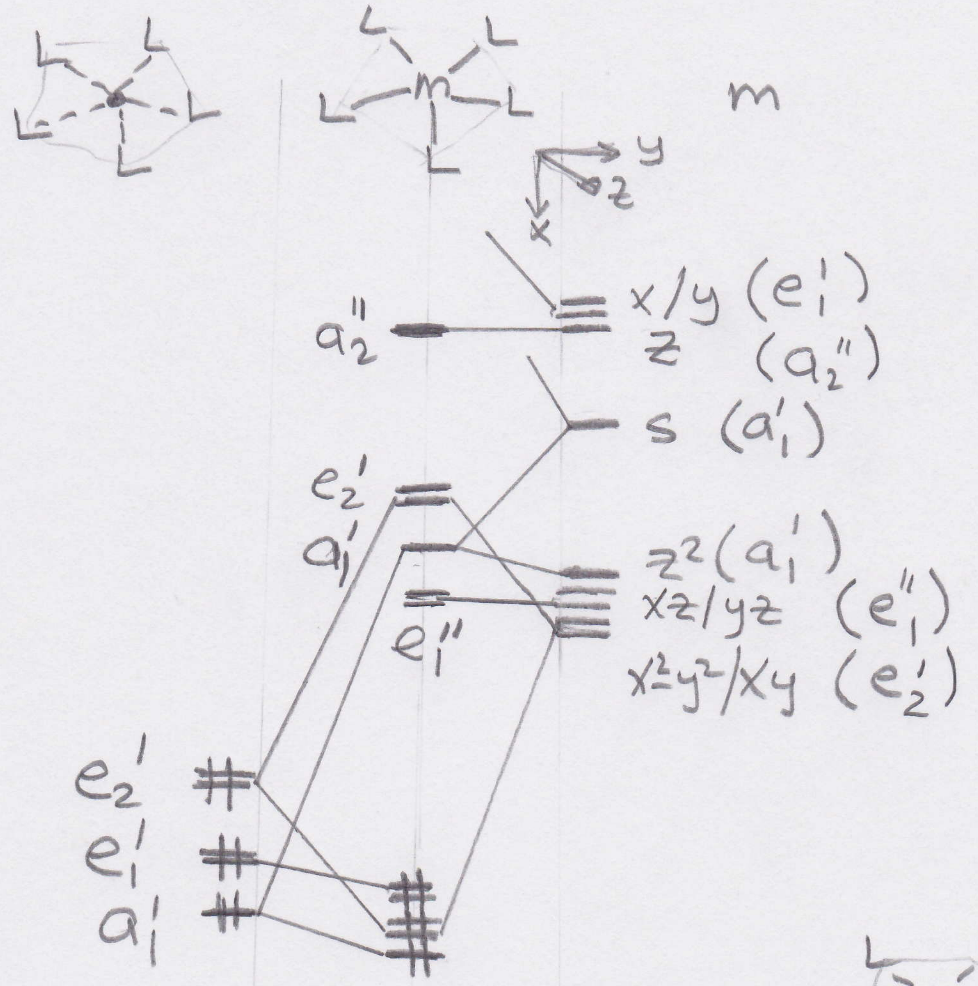




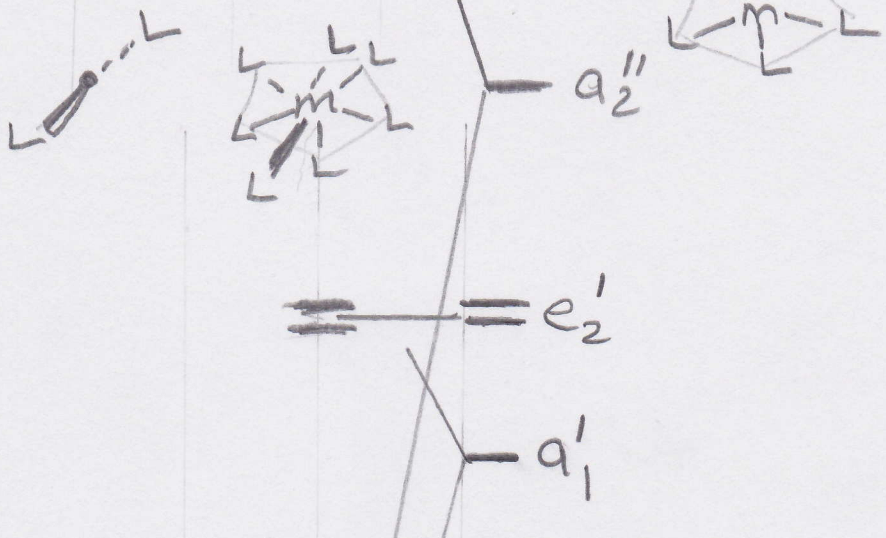
From the Walsh diagram, d^4 and d^{10} complexes will prefer to be side-bonded. The d^6 count should give rise to a linear structure. For d^8 compounds, either linear or bent but not side-bonded should be preferred.

7. The SALCs are:

a)



b)



In the absence of strong π bonding, a d^0 or d^4 complex should be stable.