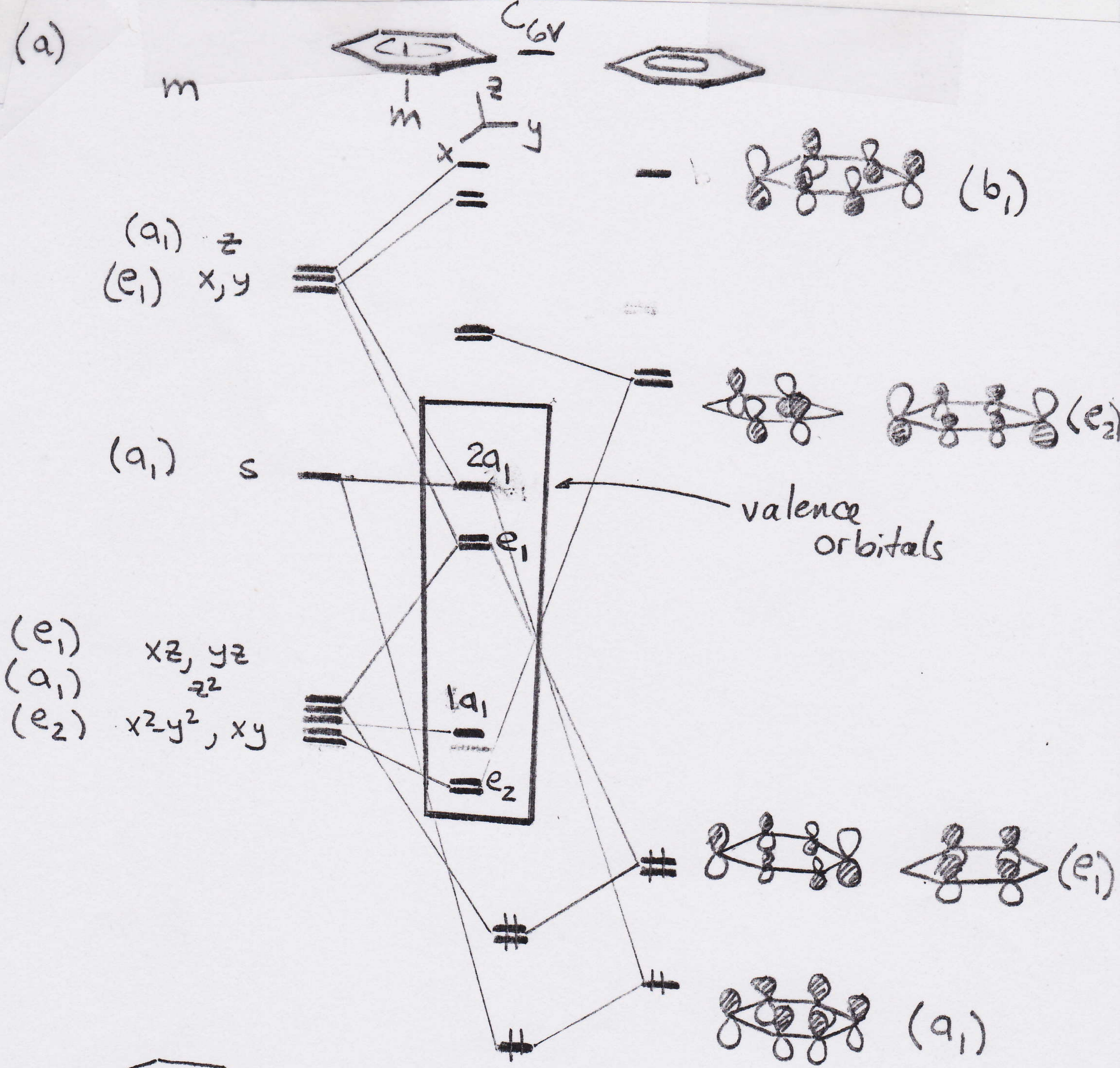
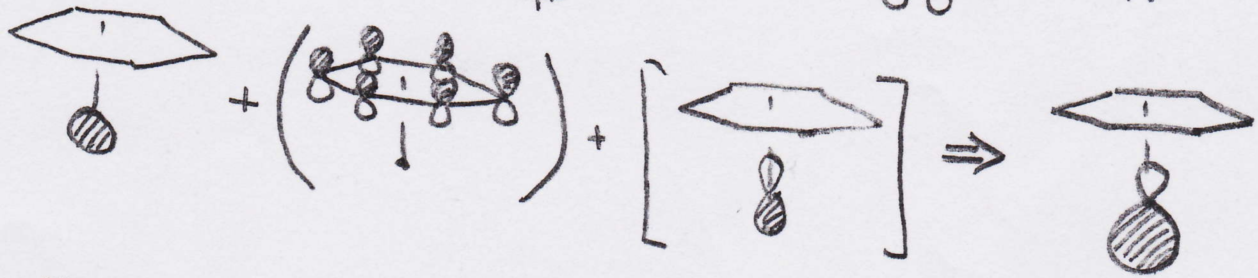
Answers - Chapter 20

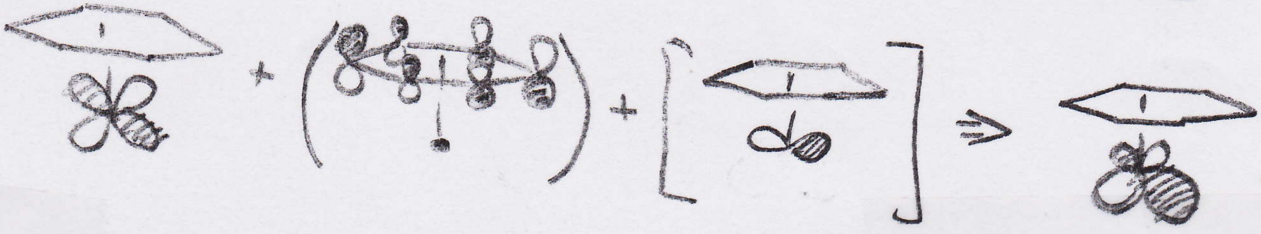
1. (a)

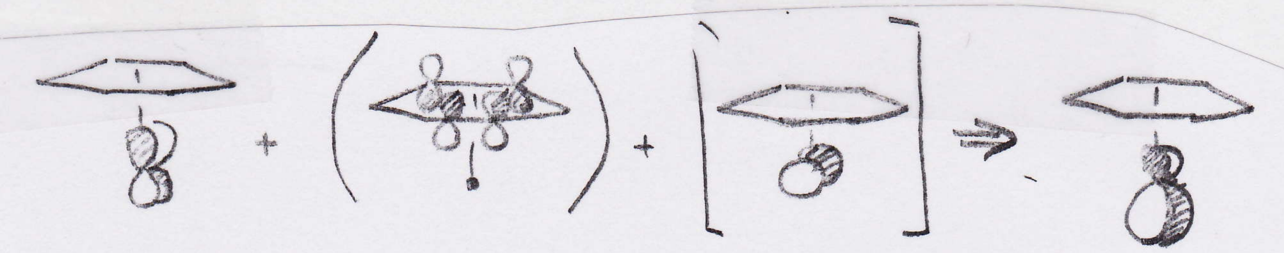


$2a_1 \equiv$

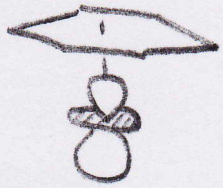


$e_1 \equiv$

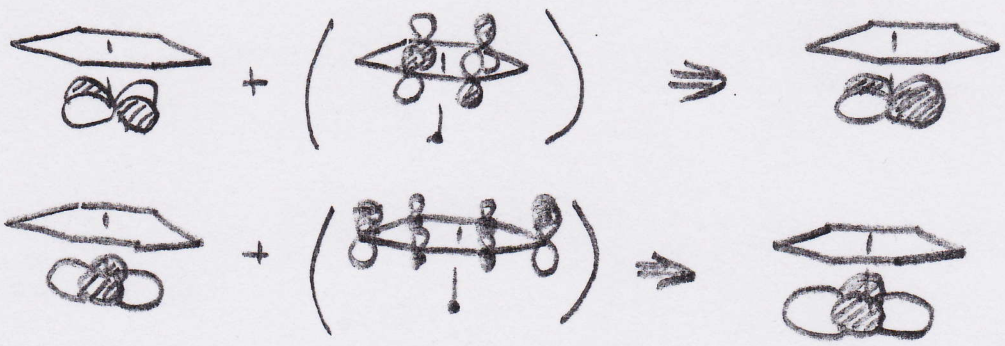




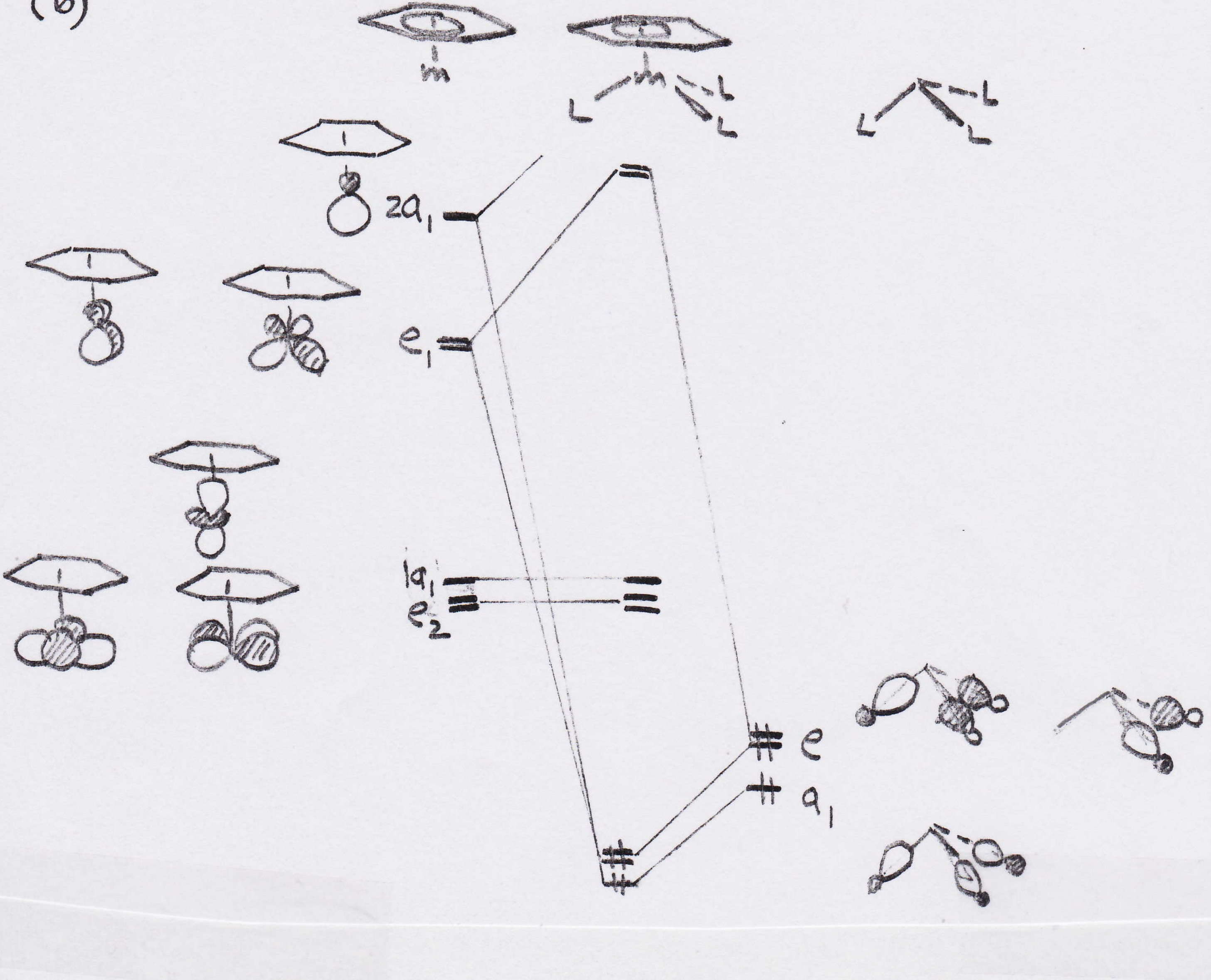
$1a_1 \equiv$



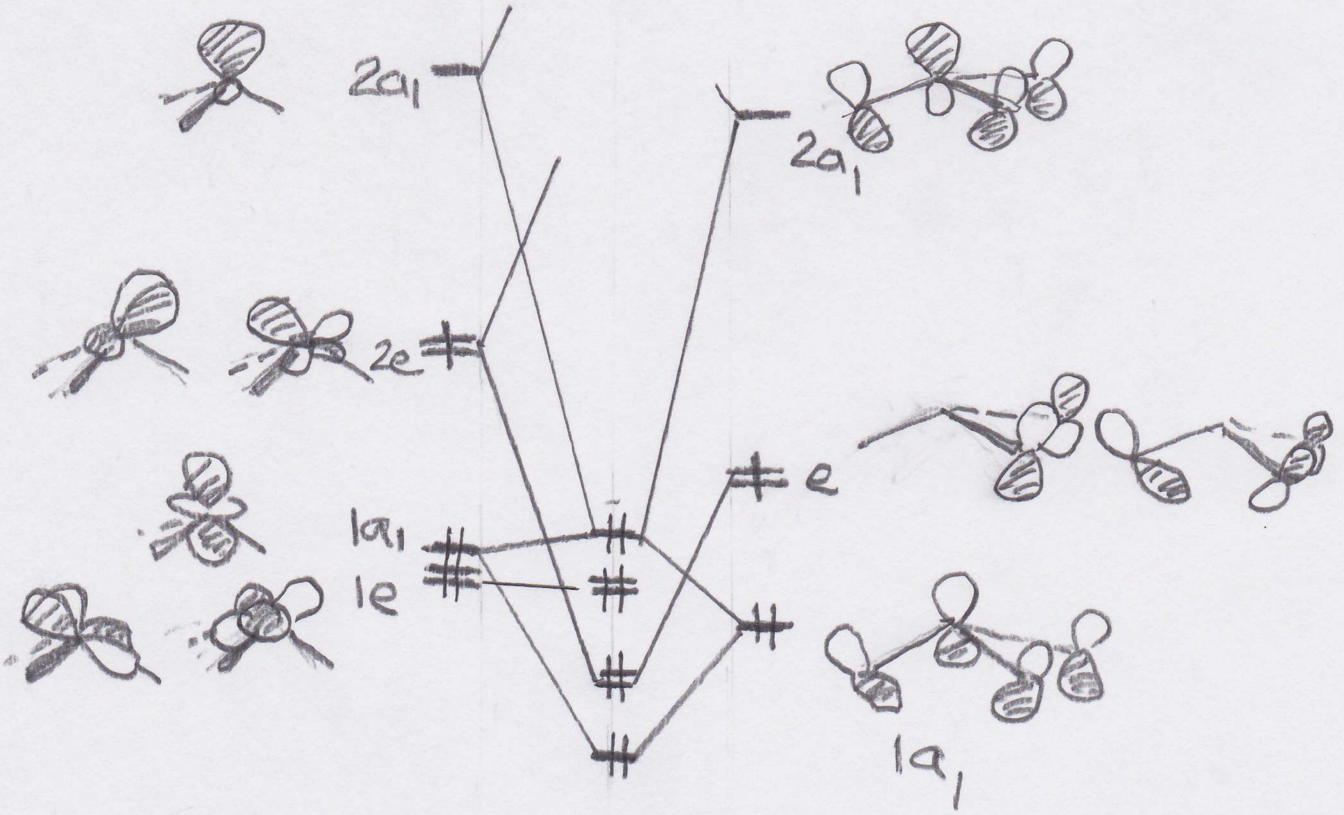
$e_2 \equiv$



(b)



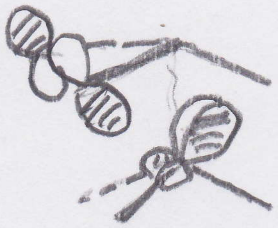
2. (a) An interaction diagram for TMM-Fe(CO)$_3$ at the staggered geometry is shown below:



The a$_1$ MO's do not change energy on rotation - they are cylindrically symmetric. This is not true for the e set - one combination is shown:

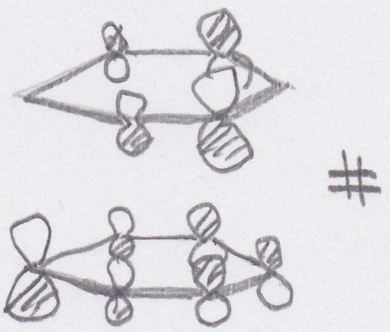
staggered: vs eclipsed:

more overlap - lower energy

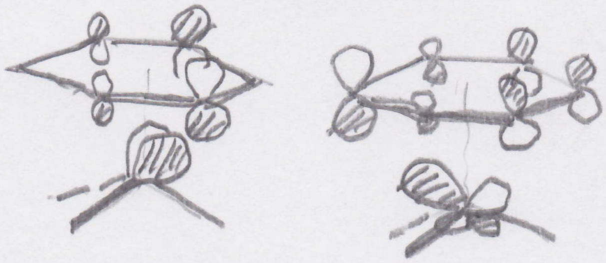


less overlap higher energy

(b) For 1,3,5-triazine the π orbitals are perturbed (you should be able to show this) as follows:

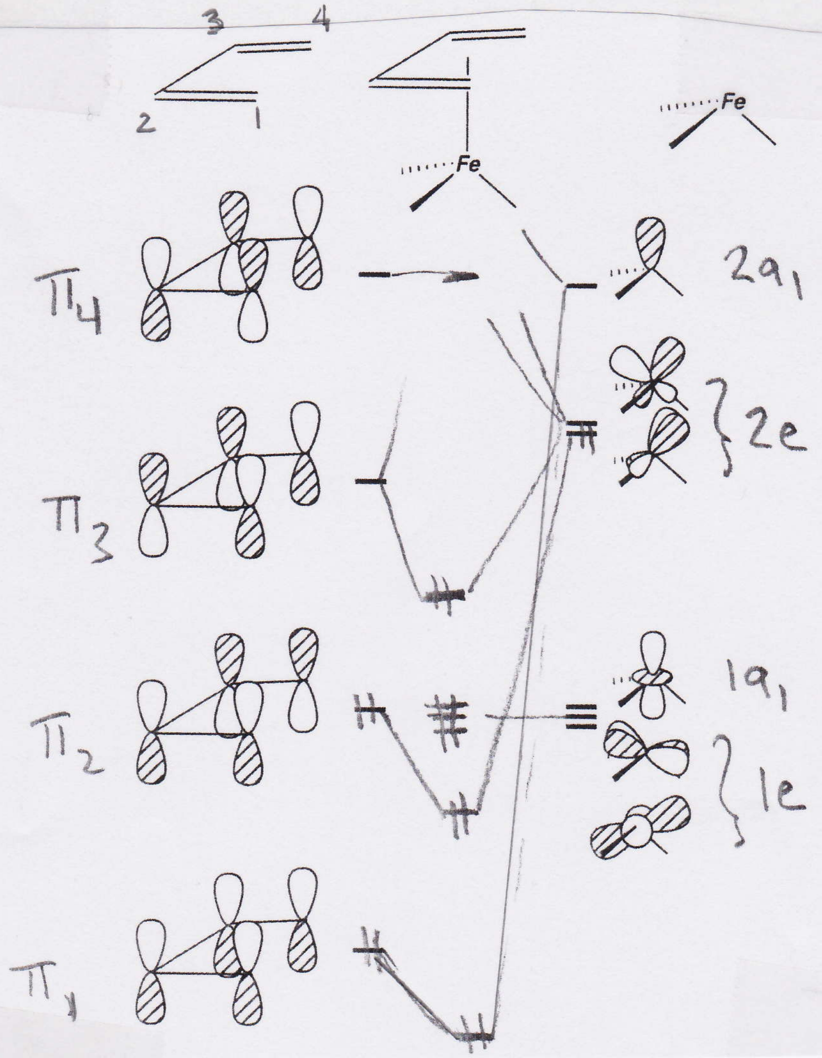


so the optimal orientation of the $Cr(CO)_3$ group is:



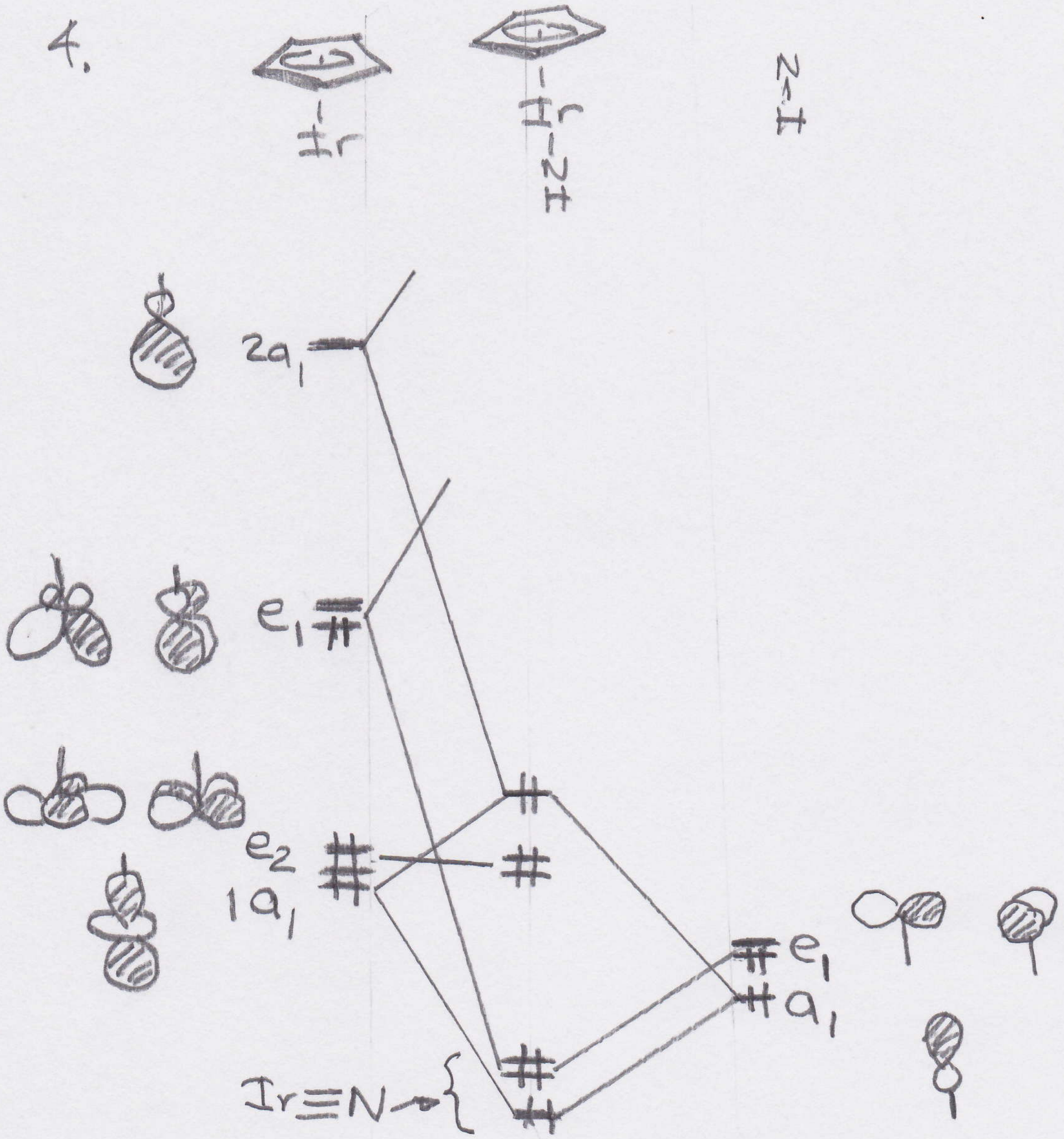
just like in TMM-$Fe(CO)_3$ - rotation by 60° causes the overlap between the 1,3,5-triazine π orbitals (in the 1e set) to lose overlap with $Cr(CO)_3$ 2e set. One can easily show that in benzene-$Cr(CO)_3$ rotation by 60° produces the same structure and rotation by 30° does not change the overlap.

3. (a)

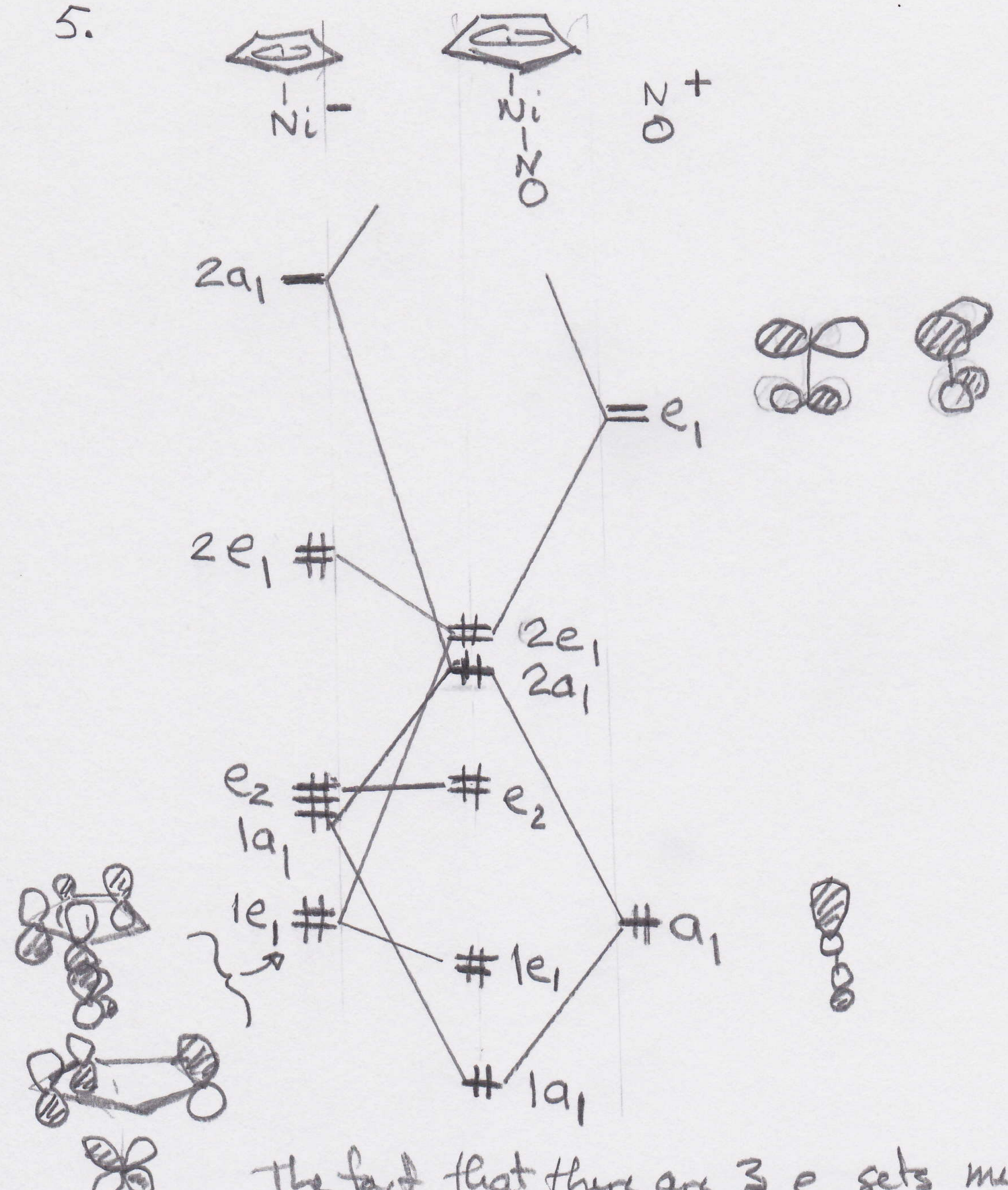


(b) For butadiene itself there is antibonding between C_2 and C_3 in π_2. This cancells the bonding between C_2 and C_3 in π_1. Both π_1 & π_2 have bonding between C_1-C_2 and C_3-C_4. So the alternation is C_1-C_2, short, C_2-C_3, long, and C_3-C_4, short. In butadiene-Fe(CO)$_3$ the $\pi_3 + 2e_s$ combination is filled. So electron density is transfered to π_3 which is C_2-C_3 bonding (and C_1-C_2/C_3-C_4 antibonding). Therefore, the bond alternation is considerably reduced.

4.



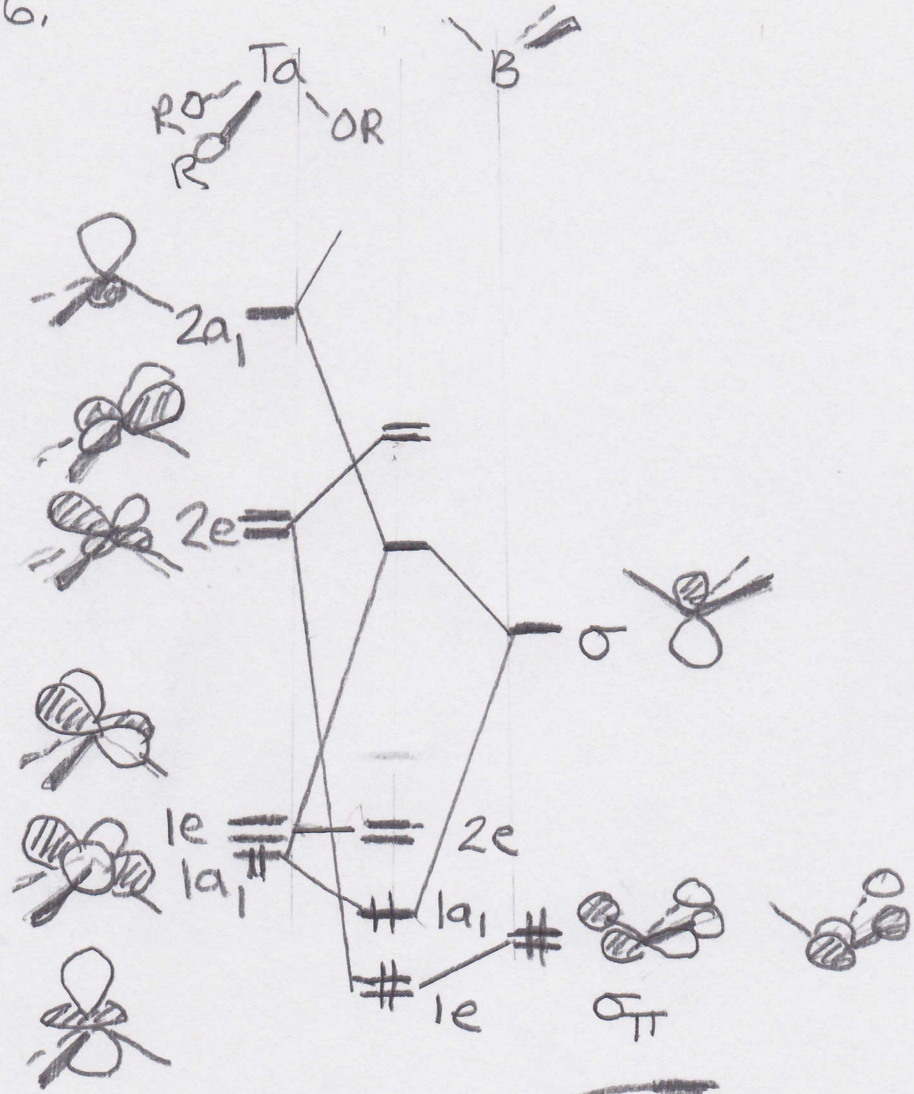
5.



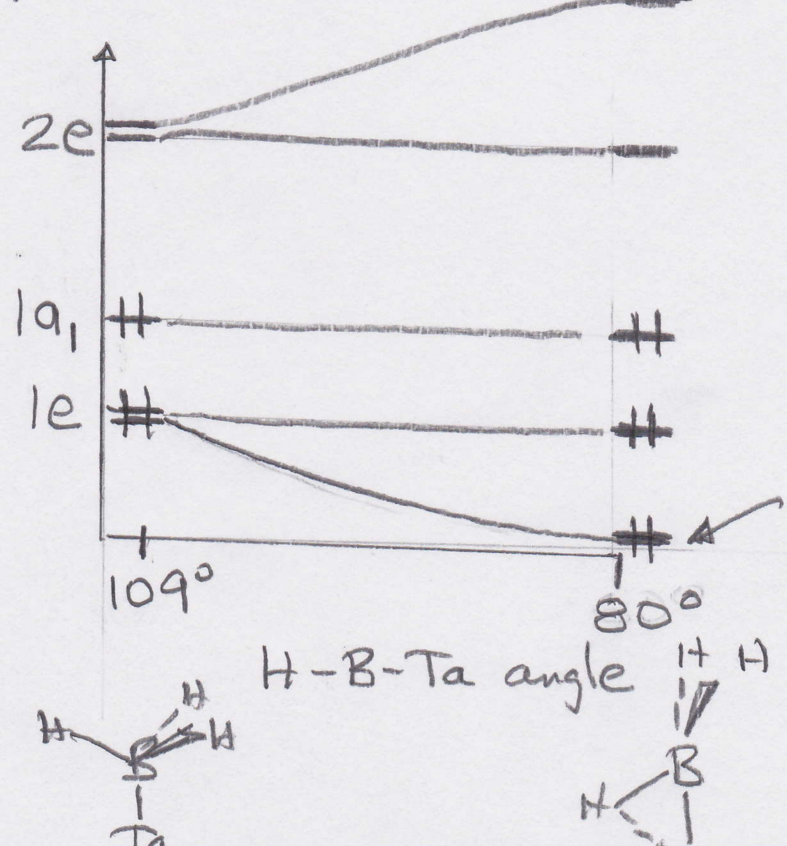
The fact that there are $\underline{\underline{3}}$ e sets means that peak ④ must correspond to the Cpπ $1e_1$ set.

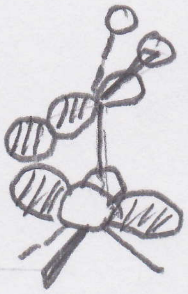
The level ordering above corresponds to the Bancroft proposal. Green's assignments put $2a_1$ at about the same energy as e_2. This can only occur if the mixing with CpNi $2a_1$ is very strong. It turns out that this latter assignment is more likely to be the case on the basis of high-level calculations and the PE of $Me_5C_5Ni(NO)$.

6.



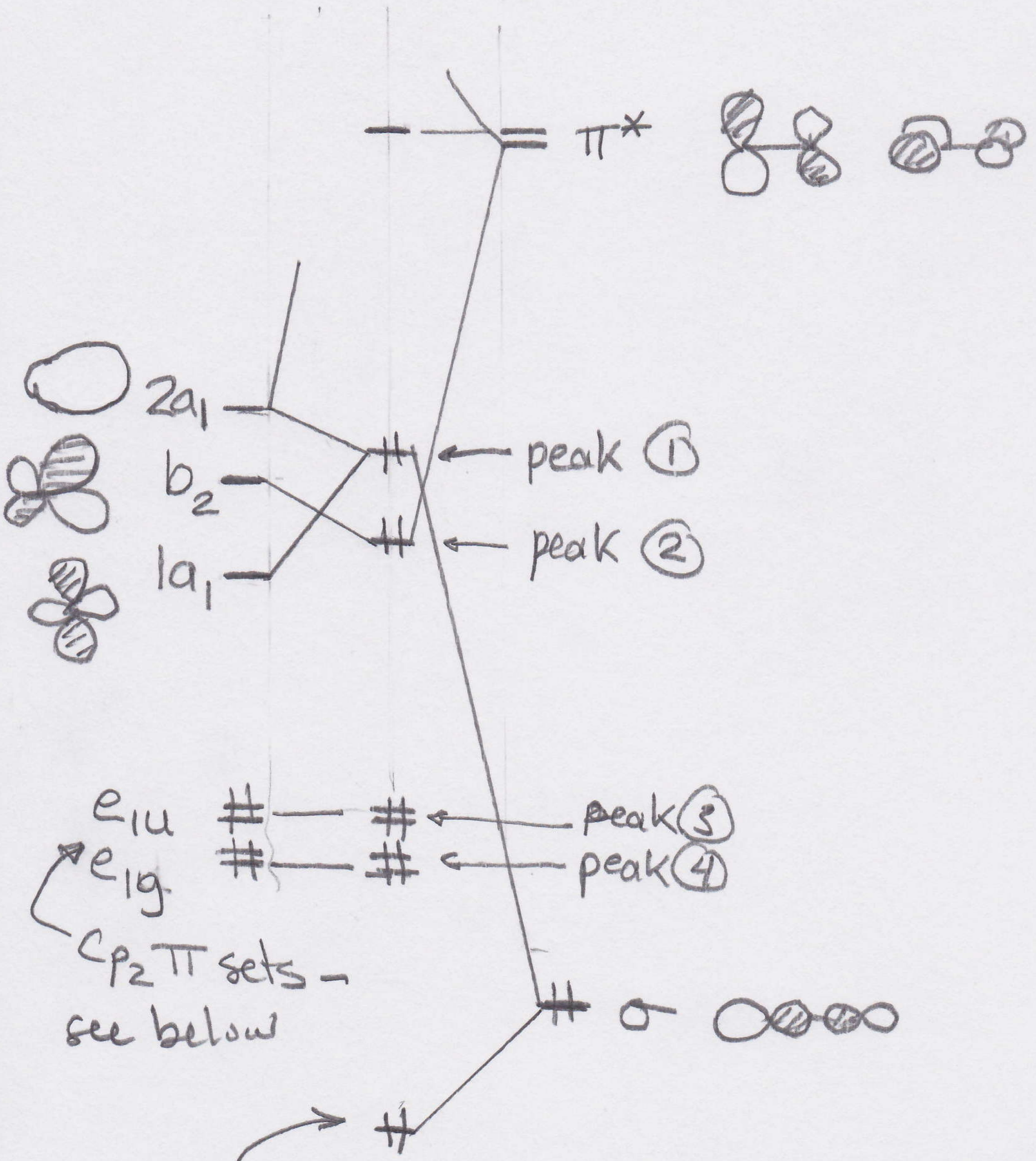
overlap primarily with 2e set





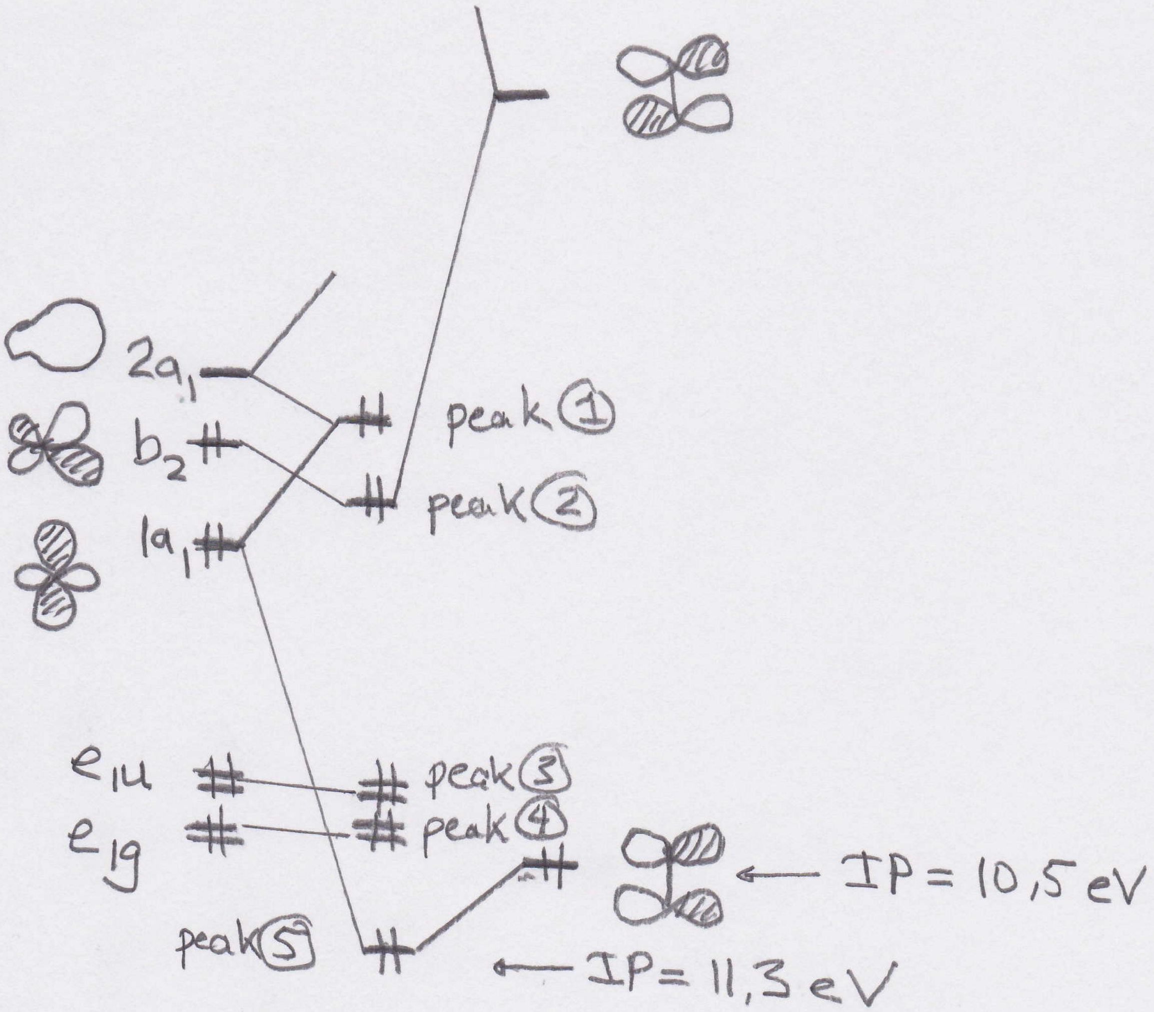
tilting the BH_3 group causes bonding between one component of σ_π and 1e to be enhanced

7. For $Cp_2Mo{-}CO$:



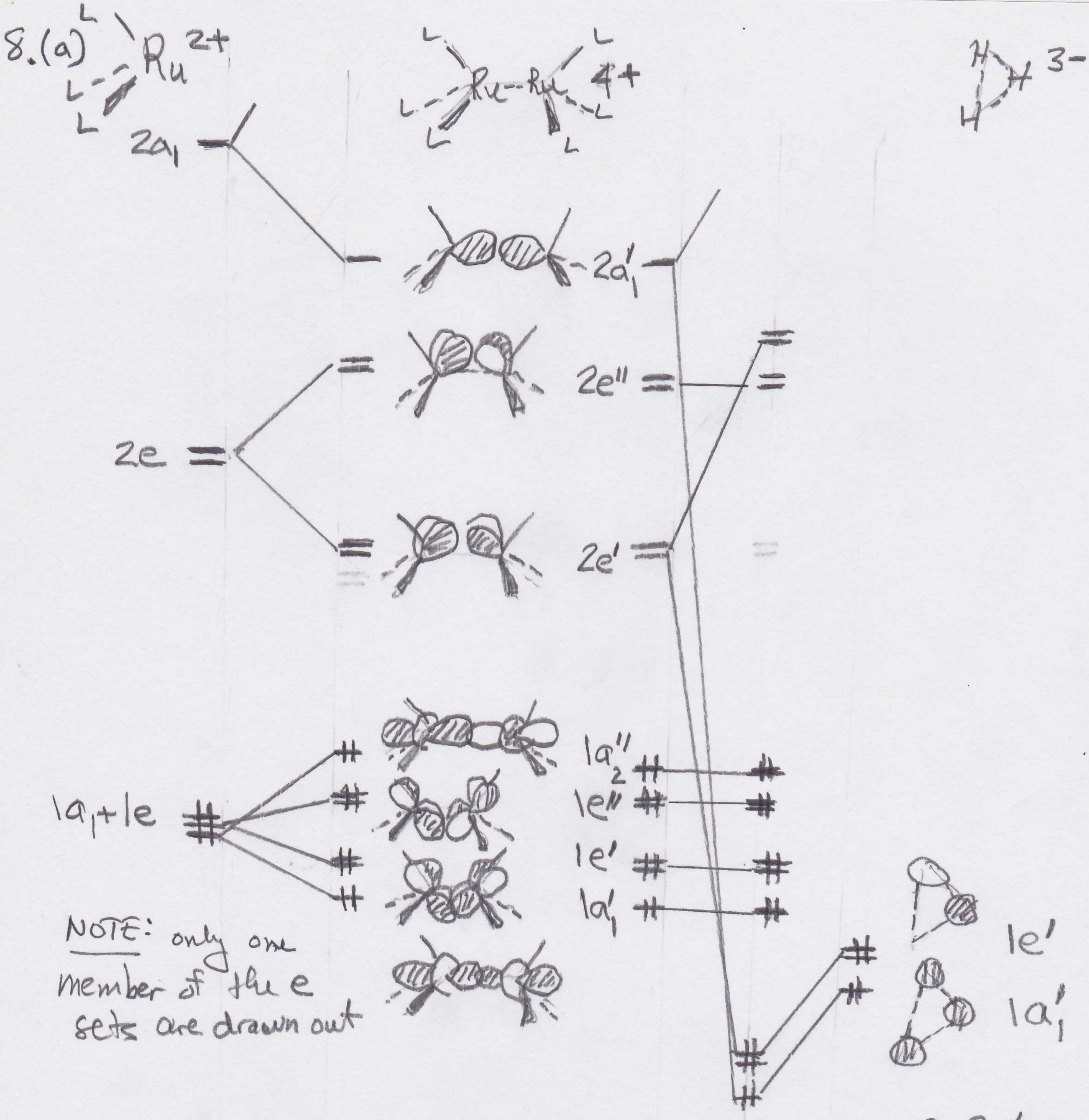
must be below −14 eV which would correspond to an IP of greater than 14 eV. This is buried in the large group if C–C and C–H, ionizations

$CpMo-\|$



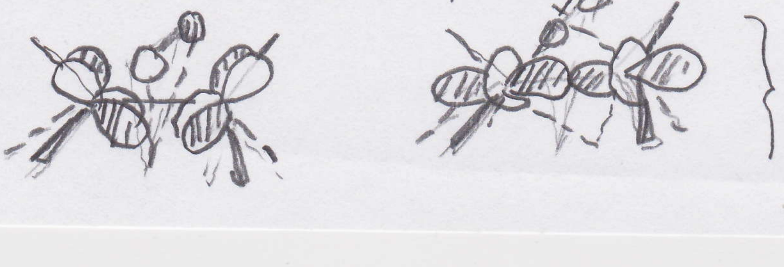
Notice that for both PE spectra the regions associated with peak ③ & ④ are very similiar which is consistent with ionization from the $Cp_2\pi$ sets (the combination of orbitals from Cp e_1'' - see Figure 20.13).

8.(a)



NOTE: only one member of the e sets are drawn out

Notice that the e′ set of H_3^{3-} overlaps strongly with the 2e′ fragment orbital. The overlap with 1e′ is *much* smaller. The a_1' combination of H_3^{3-} interacts mainly with $2a_1'$; again because of overlap reasons. a_1' lies in the nodal cone of $1a_1'$.



both have small overlaps with H_3^{3-}

(b) $(Me_3P)_6Ru_2H_3^+$

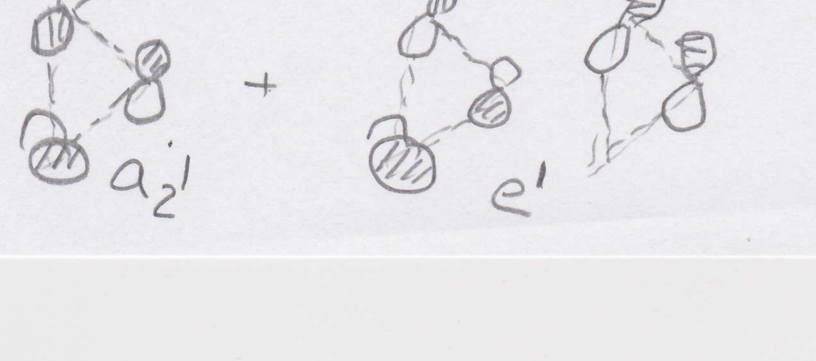
$6(Me_3P) = 12e^-$
$3H^- = 6e^-$
$1\oplus$ charge $= -1e^-$
$Ru_2^{3+} = d^7/d^6 = 13e^-$
$30e^-$

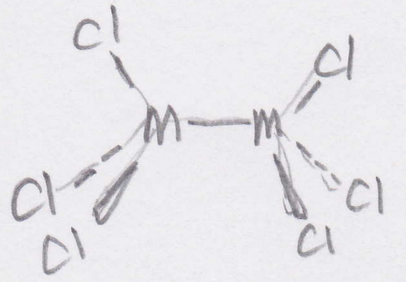
36 − 30 = 6 electrons short of 18e⁻ rule ∴ share 3e⁻ from each Ru → Ru≡Ru

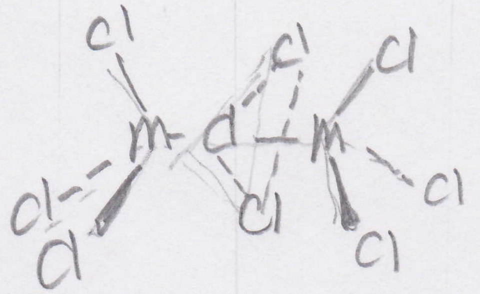
where is the triple bond? According to electron counting it should be derived from the $1a_1 + 1e$ combinations. Clearly this is not so. The "triple" bond comes from the bonding combination of $2a_1'$ and $2e'$ with the H_3^{3-} set. It is strongly Ru–H bonding but some Ru–Ru bonding remains. One wouldn't count this as a bond order of three...

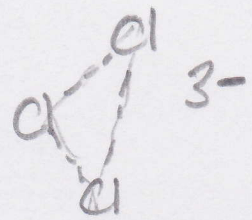
(c) $(R_3P)_6Rh_2H_3^{2+}$ has one more e⁻, therefore, it should go into the $2e''$ set. This is strongly M–M antibonding so the fact that the Rh–Rh distance elongates by 0.1 Å is consistent with occupation of the $2e''$ set. This molecule should undergo a first order Jahn-Teller distortion, the ML_3 groups are rotated about half way from the eclipsed (as shown) and staggered geometry so it has D_3 geometry which still should be J.-T. active. The $2e''$ is Rh–P antibonding so changing some of the Rh–P bond lengths would be an effective way to break the symmetry. The Rh–P bond lengths on one side are 2.33, 2.33 and 2.32 Å while on the other side they are 2.30, 2.30 and 2.32 Å. Three-fold symmetry is still present. The position of the hydrogens was not accurately located - see C. Bianchini, F. Laschi, D. Masi, C. Mealli, A. Meli, F.M. Ottaviani, D. M. Proserpio, M. Sabat and P. Zanello, *Inorg. Chem.*, **28**, 2552 (1989). Furthermore, since the hydrogens have no coefficients in $2e''$, it would be difficult to see how a distortion in the bridging hydrogen region will split $2e''$.

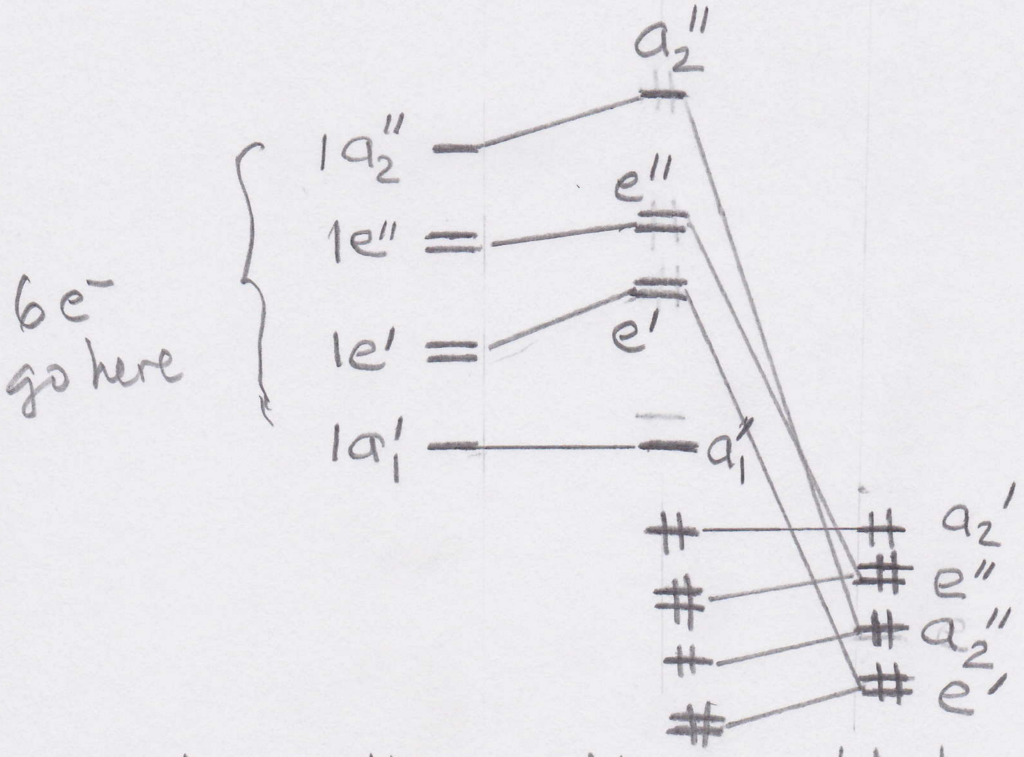
9.(a) The two sets of Cl p AOs are easy:











(b) There are three possible spin states:

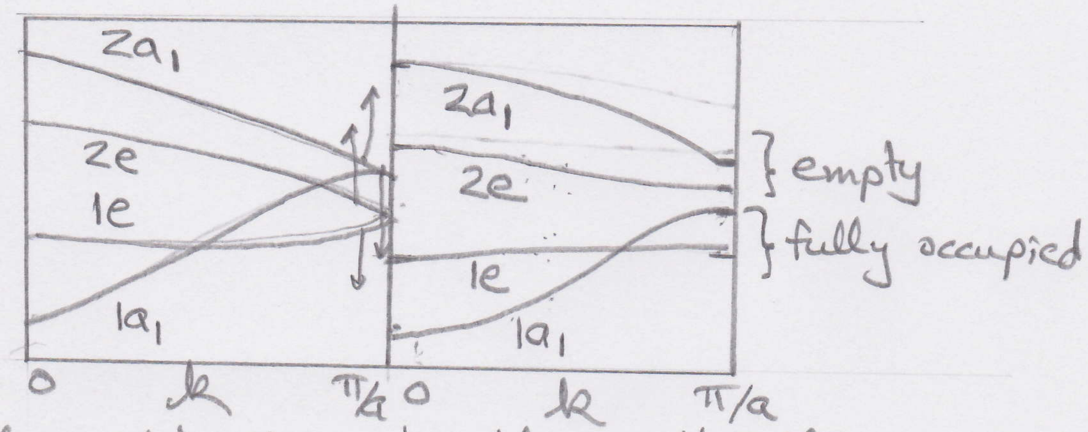
hs-$(a_1')^1(e')^2(e'')^2(a_2'')^1$ – there would be no M–M bond since all bonding & antibonding orbitals are filled. This is most consistent with $Cr_2Cl_9^{3-}$ – the long Cr–Cr distance and an enlarged Cr–Cl–Cr angle from the octahedral value are ~~the~~ clearest evidence

ls-$(a_1')^2(e')^4$ – this is consistent with $W_2Cl_9^{3-}$. The short W–W bond and narrow W–Cl–W angle give a W≡W. So what about $Mo_2Cl_9^{3-}$? It is certainly not h.s. A complete treatment of the $M_2X_9^{3-}$

series can be found in R. Stranger, A. Turner and C.D. Delfs, Inorg. Chem., **40**, 4093(2001). The calculated Mo-Mo bond length for the l.s. case was 2.38Å (the hs bond length was 3.40Å). The intermediate spin state is: $(a_1')^2(e')^2(e'')^2$. the calculated Mo-Mo was 2.83Å. So the experimental value of 2.65Å is right between the singlet and pentet states. There are three possibilities: the dimer is a singlet and the Mo-Mo stretching frequency is very low. The bond distance is set by crystal packing. In fact there are a varicty of Mo-Mo distances for $A_3Mo_3Cl_9$ compounds. Thermally one could populate the singlet and pentet states and the observed Mo-Mo distance is the averaged one. Finally, it could be, and likely is, a combination of both situations.

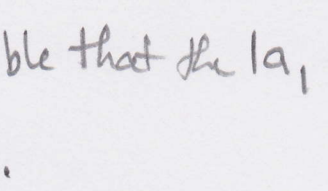
(c) For $CsVCl_3$ (and the hypothetical $CrCl_3$ along with $CsCrCl_3$) the long M-M distances are equivalent to the h.s. dimer states. Thus, the electrons in the 6 bands are all singly occupied. For $MoCl_3$

and $RuCl_3$ there is a Peierls distortion:



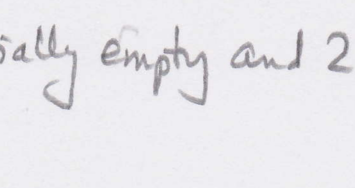
pushing the metals closer together within the unit cell makes the M-M distances between unit cells increase. So $RuCl_3$ has a band occupation $(1a_1)^2(1e)^4(2e)^4$. The situation for $MoCl_3$ is again not clear. It is quite possible that the $1a_1$ band is partially empty and $2e$ partially full.

(d) It is clear that this must be a result of M-Cl bonding in the bridging region. Notice in the interaction diagram that molecular e' is pushed up more and lies close to e''. The M-Cl overlap is larger in e' than in e'' - one compent in each of the e set is:



e'

vs

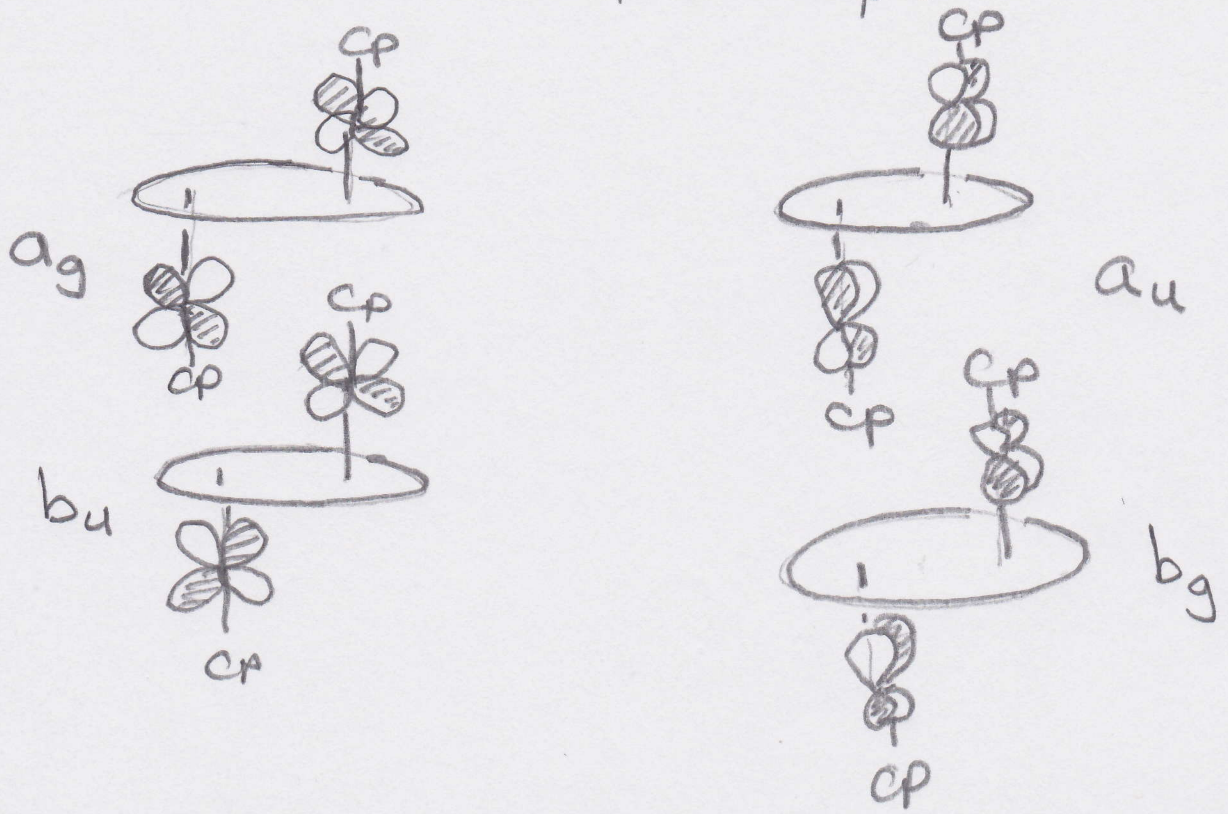


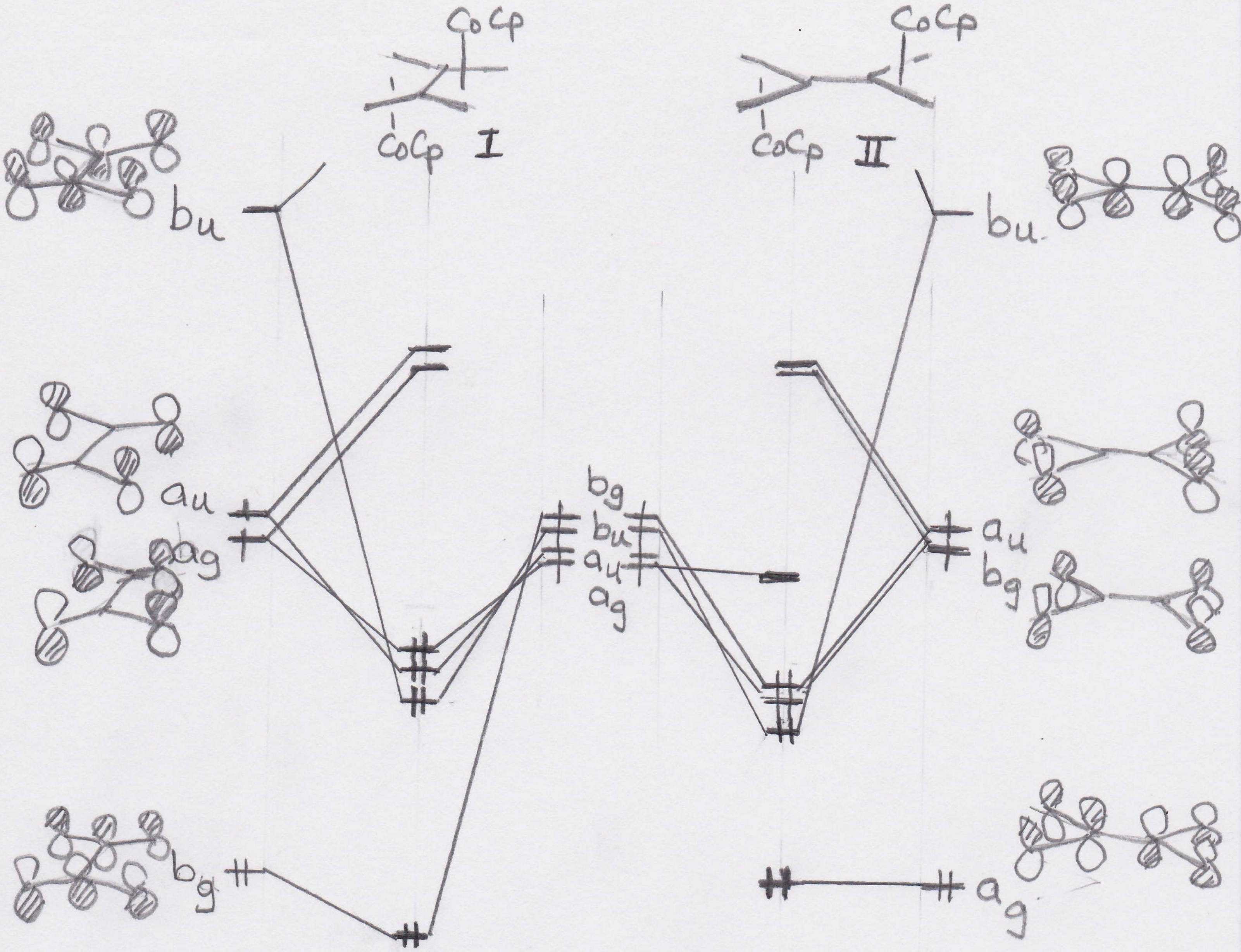
as M-Cl-M increases e' goes up in energy (gains overlap)

as M-Cl-M increases e'' goes down in energy (loses overlap)

So when the M-Cl-M angle increases, the M---M distance increases and direct M-M overlap decreases. The variation of bridging Cl lone pair overlap is exactly opposite so in terms of the Walsh diagram e″ can lie lower in energy than e′. This is what happens in the band structure where the M-Cl-M angles are close to 70°.

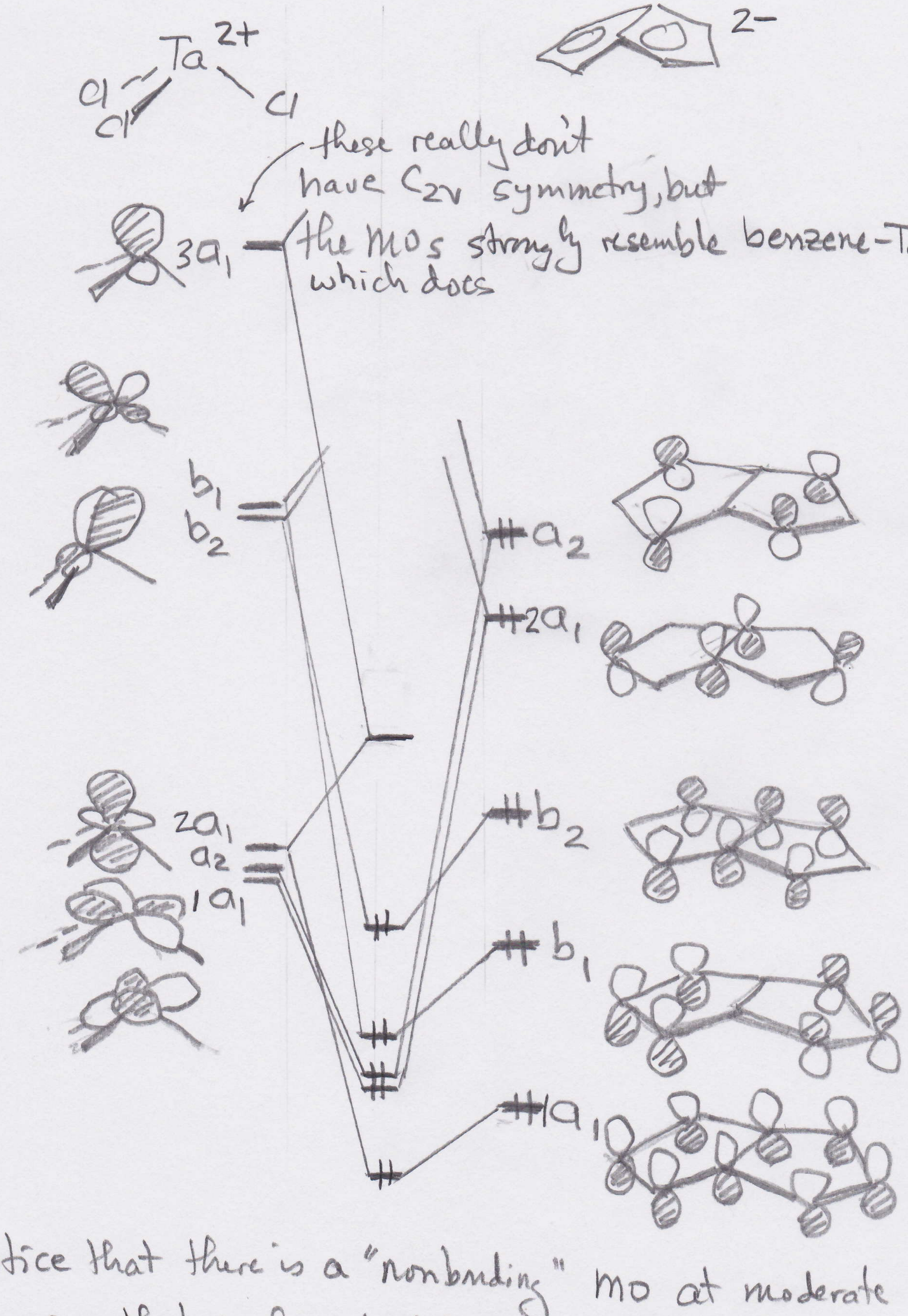
10. The critical feature is that both complexes have C_{2h} symmetry (but the symmetry elements are oriented differently), Taking the Cp as cylindrically symmetric we have SALC's of the e_1 sets on CpCo:





The essential difference here is that the Cp_2Co_2 a_g combination does not find a good overlap with the a_g tetramethylene combination in geometry II in geometry I this tetramethylene orbital has b_g symmetry and it does interact strongly with b_g Cp_2Co_2.

11.



these really don't have C_{2v} symmetry, but the MOs strongly resemble benzene-Ta^{5+} which does

Notice that there is a "nonbonding" MO at moderate energies that is formed. filling it creates an 18 electron complex and in fact pentalene-VCp is Known. A good review of pentalene complexes can be found in S. Bendjaballah, S. Kahlal, K. Costuas, E. Bévillon and J.-Y. Saillard, Chem. Eur. Journal, 12, 2048 (2006).