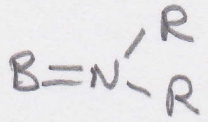
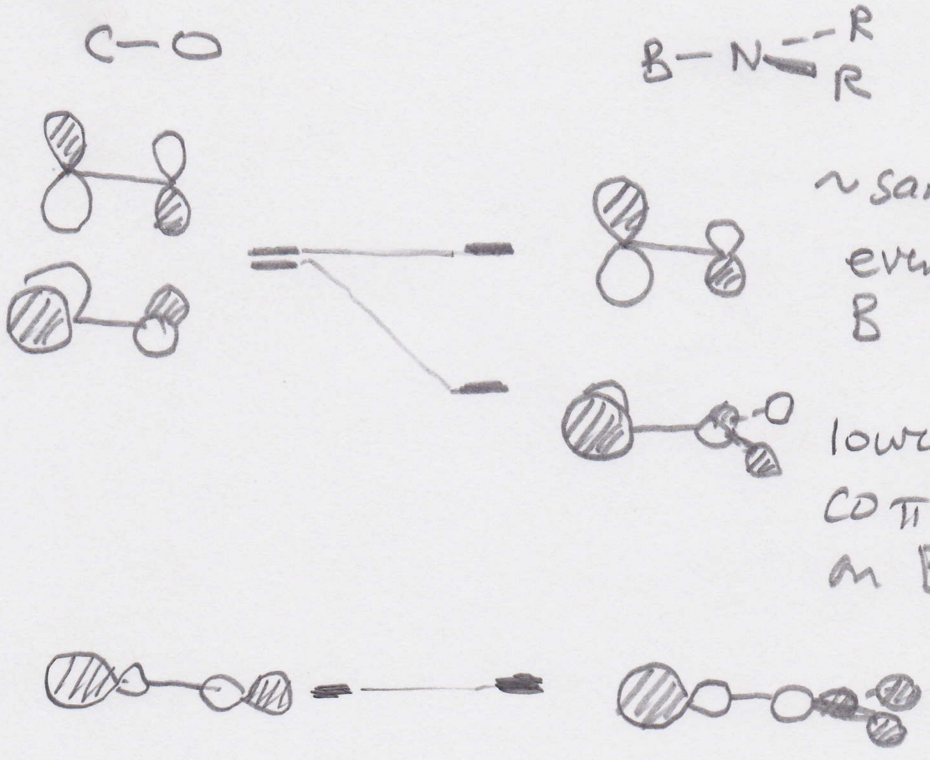
# Answers – Chapter 15

1. For CO vs



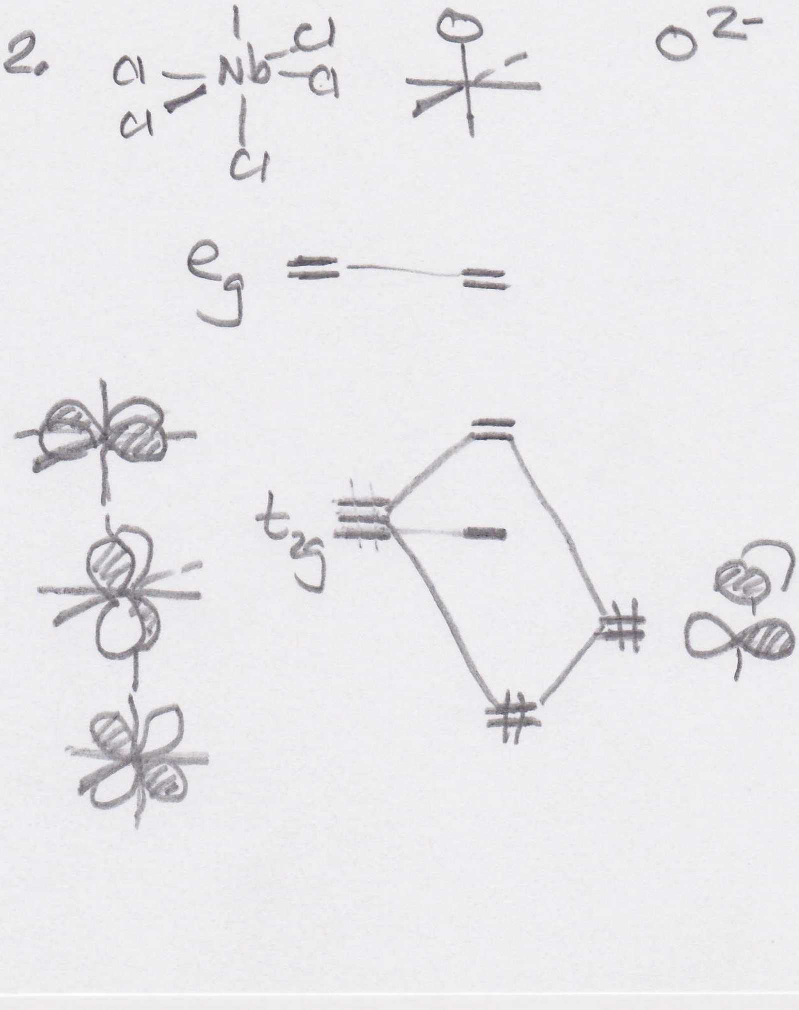


~same energy as CO π* even more localized on B

lower in energy than CO π* – almost exclusively on B

~same energy as CO σ – even more localized on B

2.

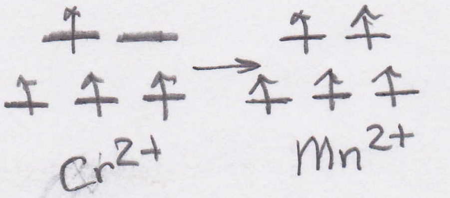


There are 5 $Cl^-$ & 1 $O^{2-}$

so Nb = 5+

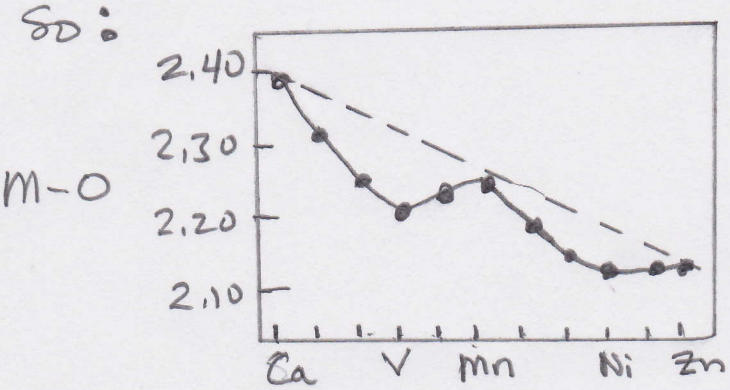
therefore no d electrons in $t_{2g}$ and $e_g$ ($d^0$)

3. There are two competiting factors in these molecules which are classic coordination compounds. Going from right to left causes the M-O distance to decrease since M is becoming more electronegative. However, put electrons into $e_g$ will cause the M-O distance to become longer since $e_g$ is M-O antibonding so from $M = Ca^{2+}$ $(d^0)$ to $V^{2+}$ $(d^3)$ $t_{2g}$ is filled and M-O decreases. When $M = Cr^{2+}$ to $Mn^{2+}$ ~~t~~ $e_g$ becomes progressively filled, i.e,



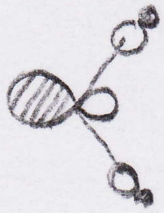
. For $Fe^{2+} \to Ni^{2+}$ $t_{2g}$ is again filled and so M-O decreases again. But then $t_{2g}$ is filled for $M = Cu^{2+}$ and $Zn^{2+}$ so M-O lengthens.

So:



For a full discussion see R. Åkesson, L.G.M. Pettersson, M. Sandström and U. Wahlgren, J. Am. Chem. Soc., **116**, 8691 (1994).

$NMe_2$ is a stronger $\sigma$ donor than CO is because in $NMe_2$ the lone pair orbital is essentially totally localized on N, i.e.

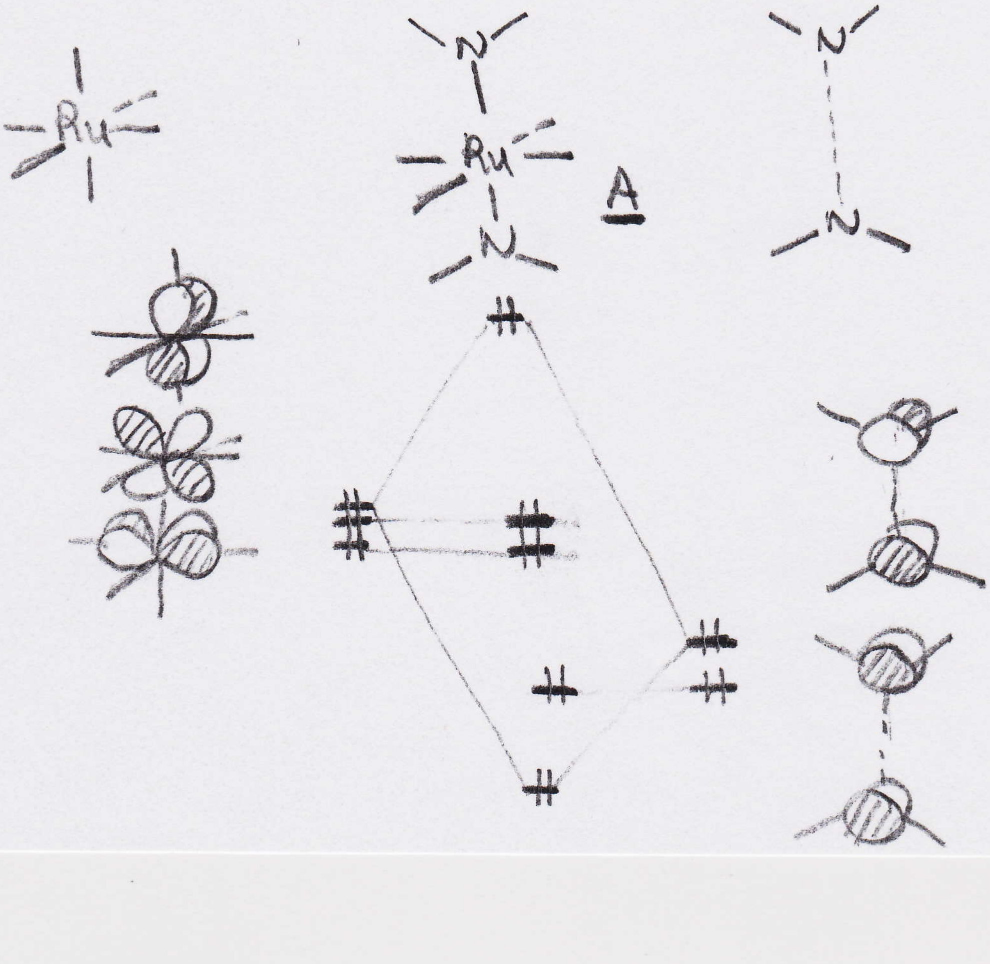


Whereas, in CO the maximal density in the lone pair orbital used for $\sigma$ bonding is on carbon, however, there is non-neglible density also on oxygen, i.e.

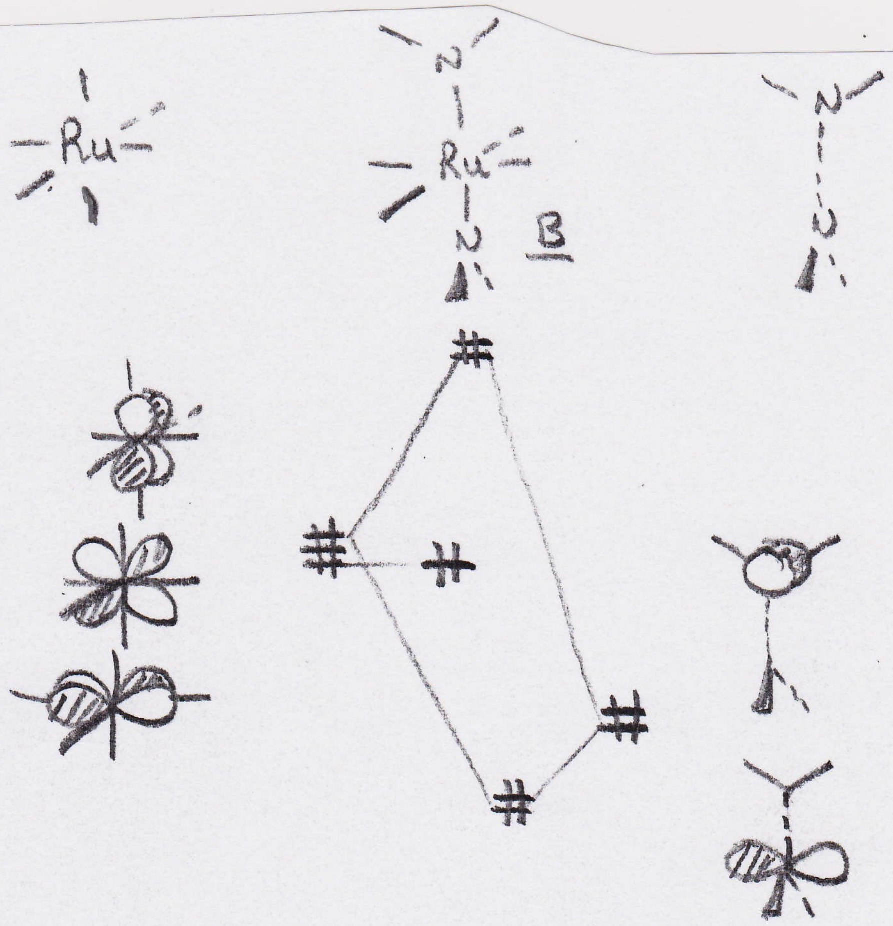
Thus, although the $\sigma$ orbital of CO is expected to lie at a higher energy than $^-NMe_2$ (because of electronegativity) its $\sigma$ overlap with the metal AOs is expected to be larger than the $\sigma$ overlap in CO. The overlap factor must dominate in this instance.

$Ru(NMe_2)_2(CO)_4$ is a $d^6$, 18 electron complex.

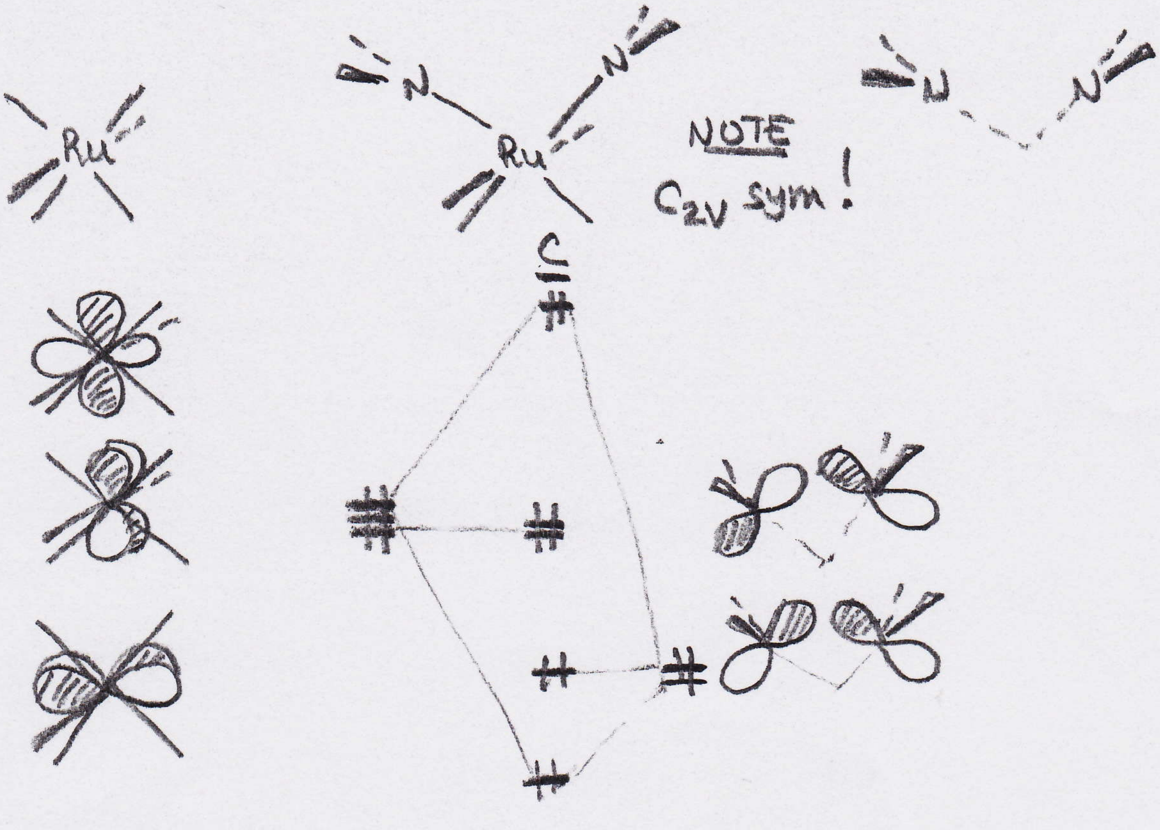
As outlined along the discussions associated with 15.28 - 15.36 in the book. It is more favorable to have the two strongest $\sigma$ donors in cis rather than trans positions (using then both $x^2-y^2$ and $z^2$ for $\sigma$ bonding). The relative stability ordering considering **only** $\sigma$ effects is thus C ~ D > A ~ B. The $\pi$ effects can manifest themselves in two possible ways. One can easily show that in A, B, C, and D, the CO $\pi^*$ combinations will overlap with and stabilize **all** three members of $t_{2g}$. Thus, $\pi$ acceptor effects do **not** differentiate between the four possible geometries. This is **not** true for the $\pi$-donor functions on the $-NMe_2$ groups. Looking at each geometry:



A



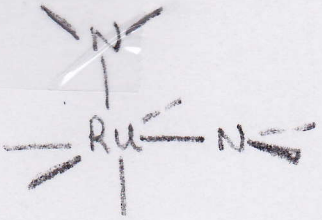
B

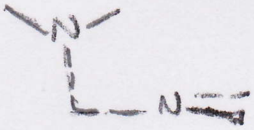


C

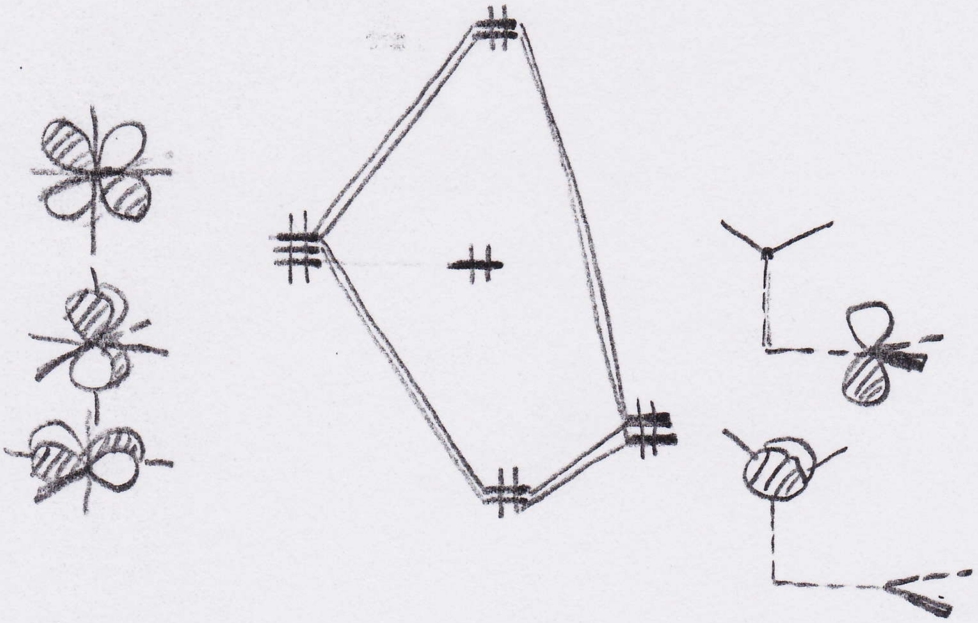
NOTE

$C_{2v}$ sym!





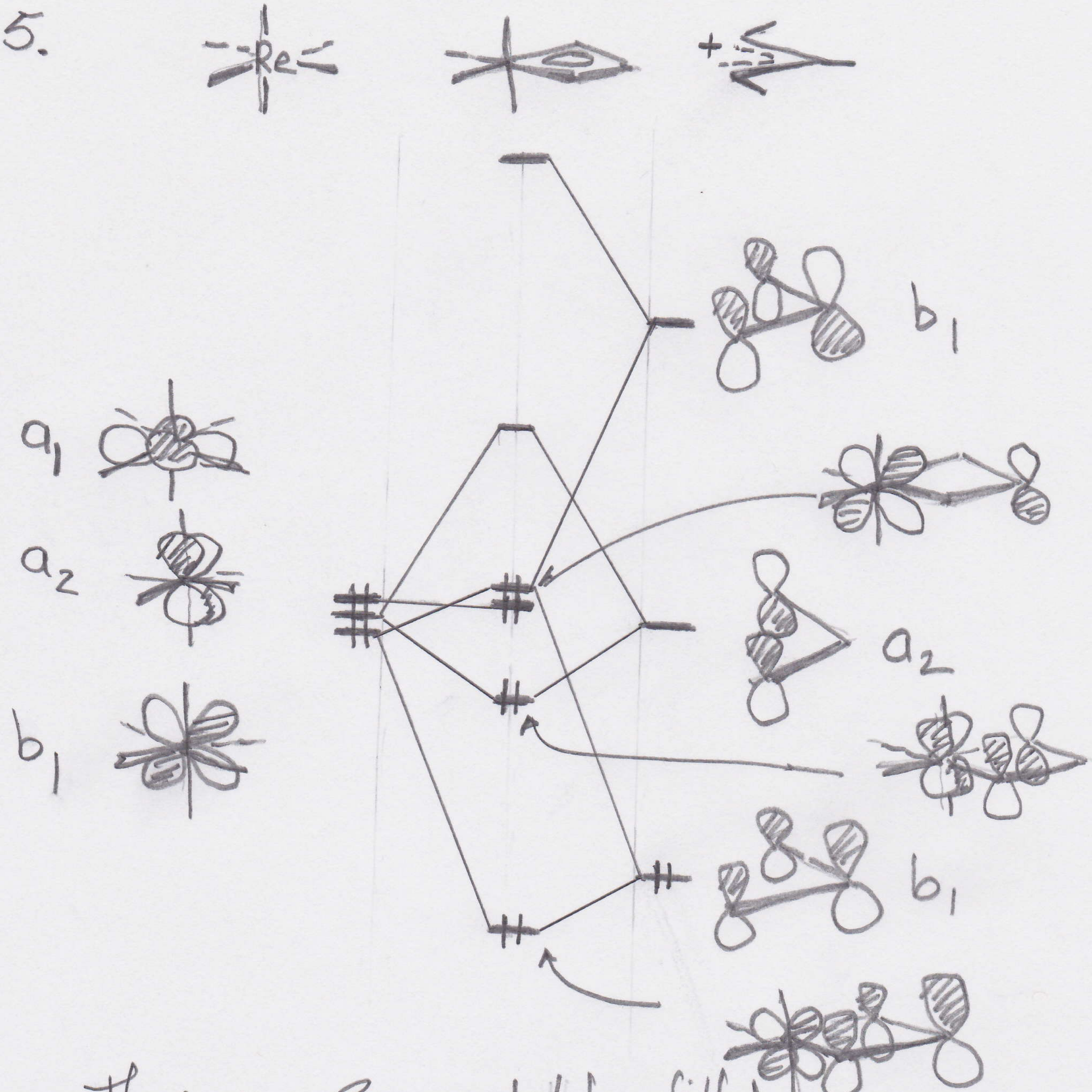
D



Thus the π-effects in A and C are identical and those in B and D are identical. The net destabilication in A and C (where one member of $t_{2g}$ is used) is **less** than that in B and C. Assuming that π and σ effects are approximately the same; the order of stability is then

$\underline{C} > \underline{D} \sim \underline{A} > \underline{B}$

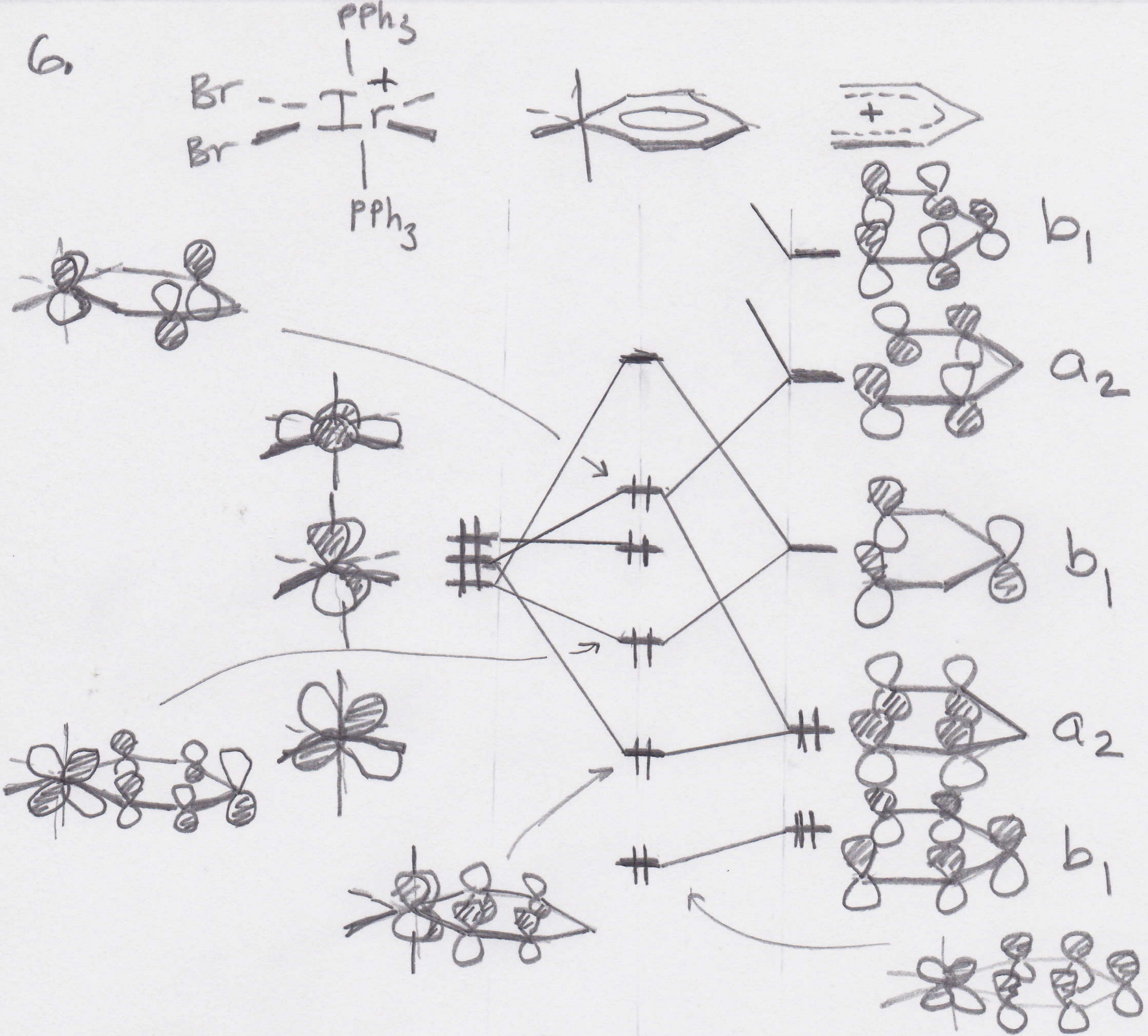
5.



There are 3 π orbitals filled.

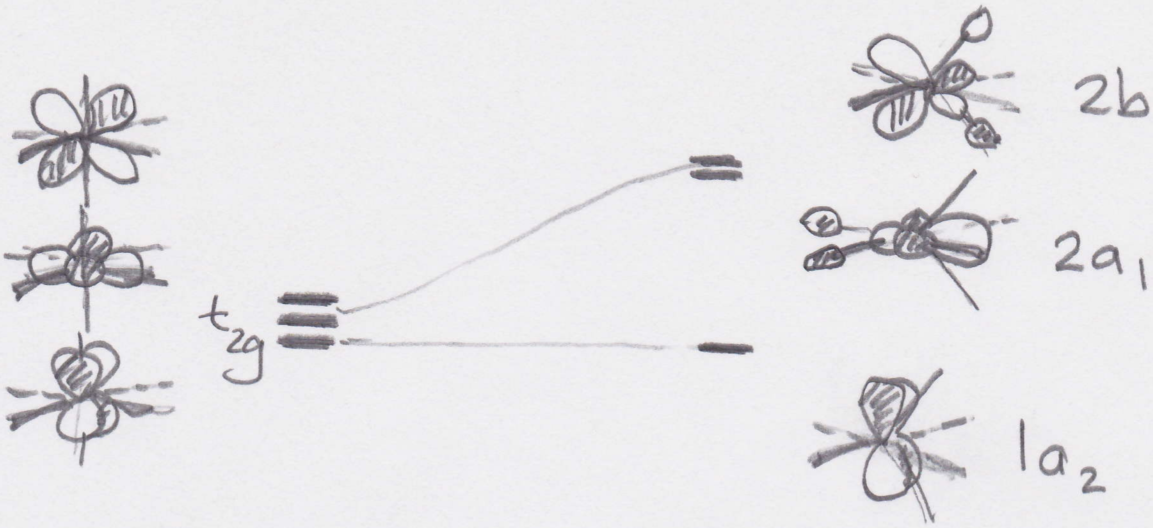
Is this then an "aromatic" molecule. There certainly is a large HOMO-LUMO gap unlike cyclobutadiene. Given that this metallacyclobutadiene is stable (or aromatic), then is the metallabenzene with 2 more π electrons unstable? We'll see in the next problem!

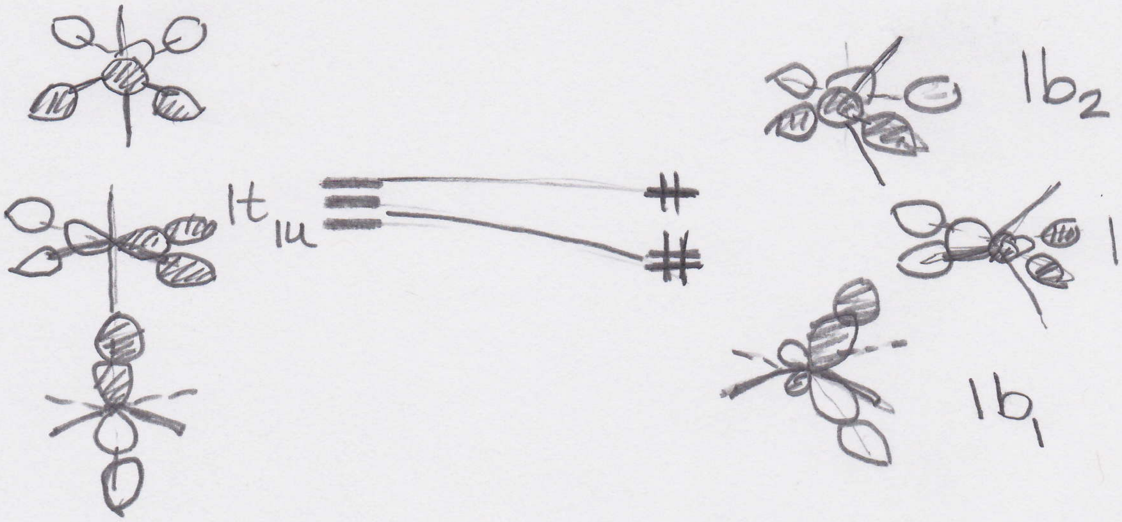
6.



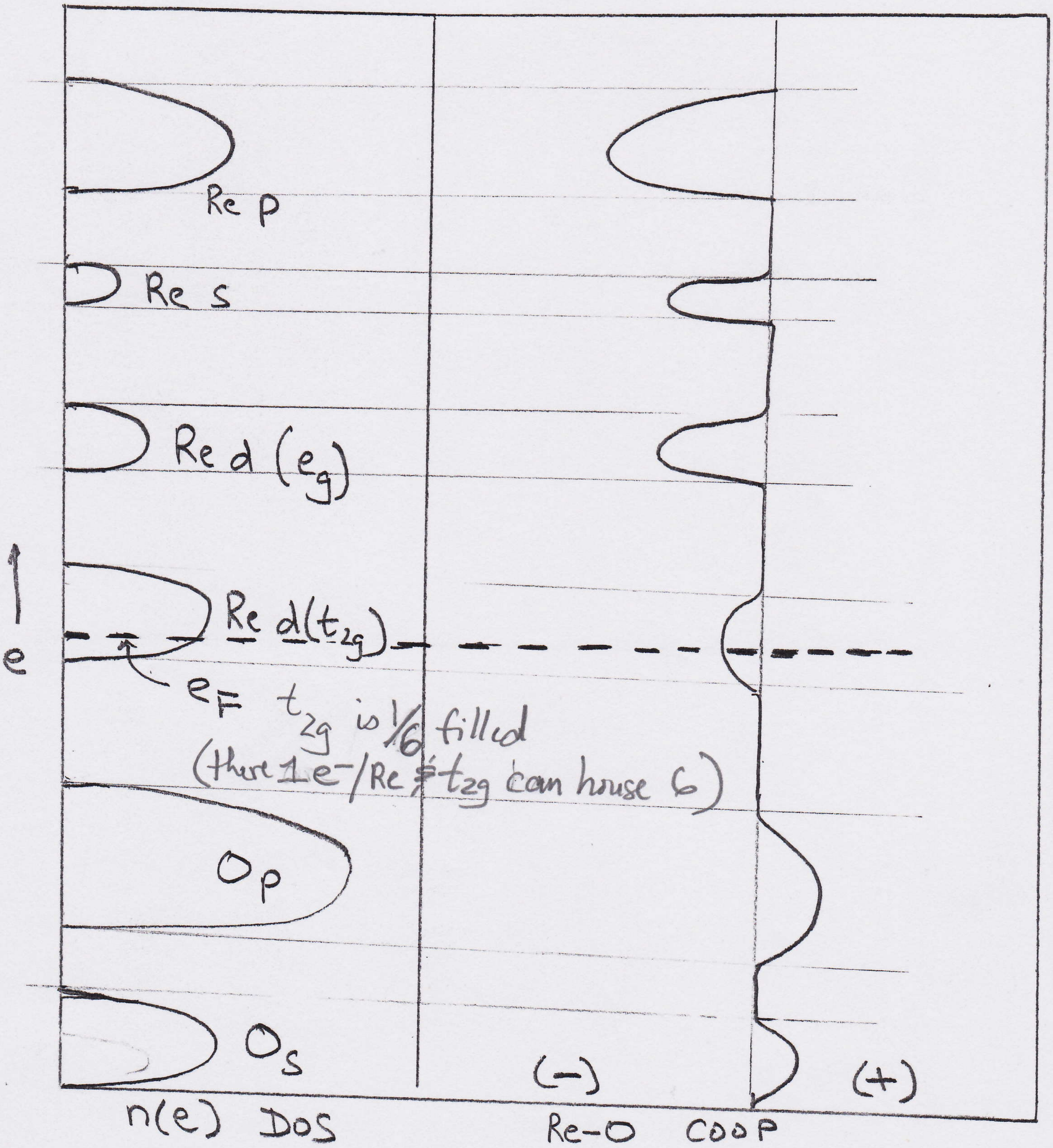
There still should be a good HOMO-LUMO gap! There are clearly 4 π-type MOs that are filled.

7. This is a combination of the two $ML_2$ bending motions discussed in Chapter 15.4. So


2b$_1$
2a$_1$
t$_{2g}$
1a$_2$

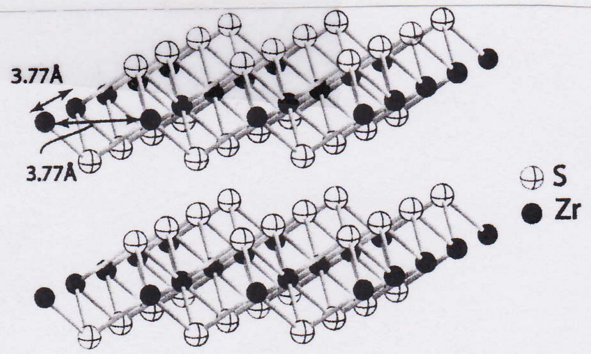

1b$_2$
1t$_{1u}$
1a$_1$
1b$_1$

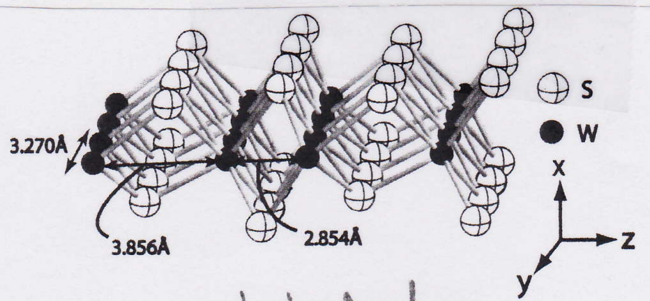
8.



$ReO_3 = [Re^{6+}][3O^{2-}]$ and $Re(6+) = d^1$ so $ReO_3$ is expected to be metallic.

9.





Octahedral based

$ZrS_2 = Zr^{(4+)} + 2S^{2-} = d^0$

$WS_2 = \boxed{d^2} \rightarrow t_{2g}$ set 1/3 filled