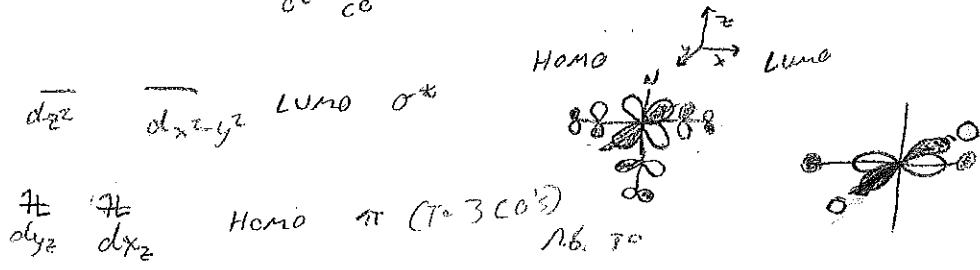
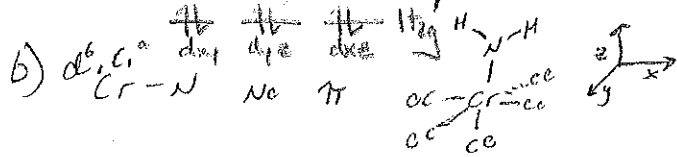
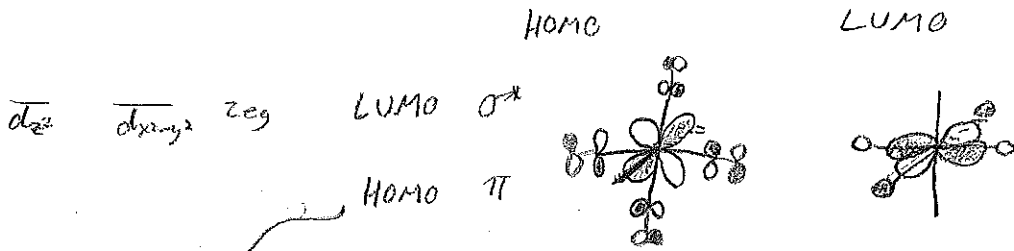


#1

A

a)  $d^6, Cr^0$

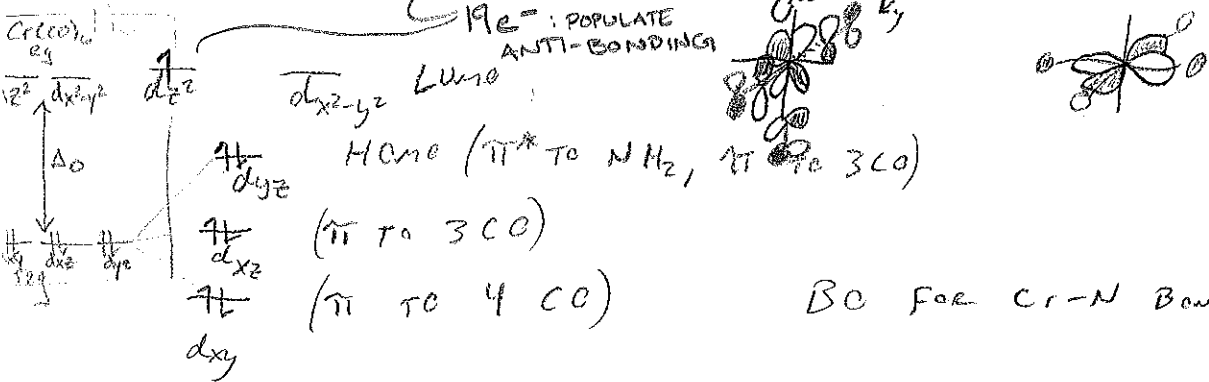


$\pi$  (to 4 CO's)

$Cr-N$  STRONG  $\pi$  DONATION  
 $d^6, Cr^0$

$\rightarrow$  AMIDE = LX DONOR HOMO

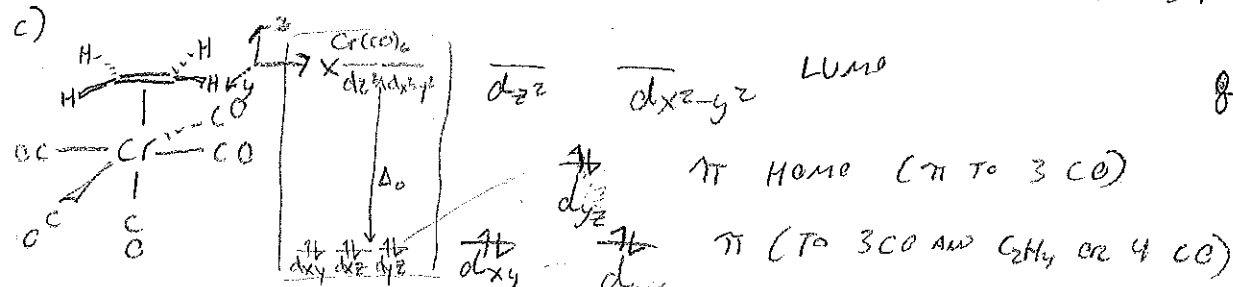
$\rightarrow$   $\pi$  = POPULATE ANTI-BONDING



BC FOR  $Cr-N$  BOND IS 1 (ONLY  $\sigma$ )

$\pi$ -DONATION FROM  $NH_2^-$  TO  $Cr^0$  IS DESTABILIZING, AS IT RAISES THE ENERGY OF THE  $d_{yz}$  ORBITAL

$Cr-C_2H_4$  ML ( $\pi$  BONDING)

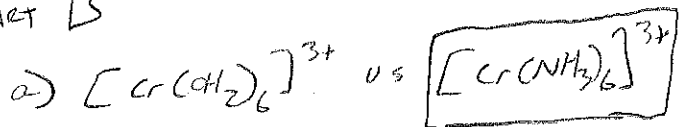


\* ASSUMING  $C_2H_4$   $\sigma$ -DONATION IS THE SAME AS CO, AND  $\pi$ -ACIDITY IS SIMILAR

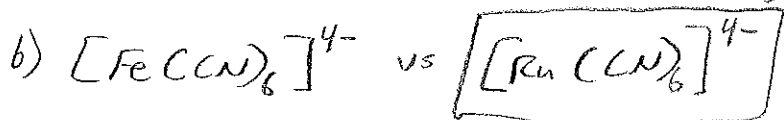
$d^6, Cr^0$

AVERAGE C-O STRETCH SHOULD BE HIGHER THAN QUESTION 6 DUE TO THE PRESENCE OF MORE BACKBONDING LIGANDS - Cr WILL HAVE LESS  $\sigma$  DENSITY TO DONATE

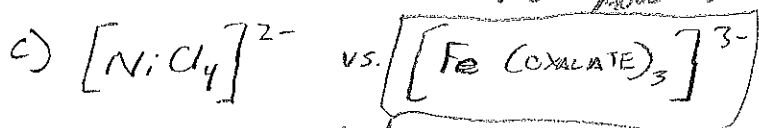
PART B



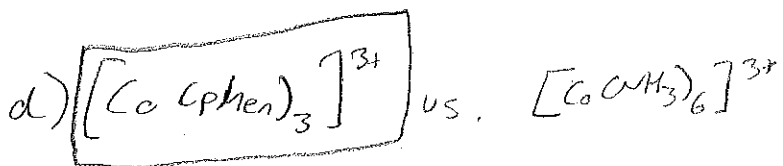
$\text{NH}_3$  IS ABOVE  $\text{H}_2\text{O}$  ON THE SPECTROPHOTOCHEMICAL SERIES;  $\text{NH}_3$  LP IS MORE BASIC THAN  $\text{OH}_2$  LP (HIGHER ZEG MO)



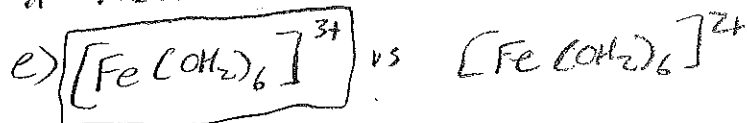
$\Delta_o$  INCREASES AS YOU MOVE DOWN A GROUP; LARGER d ORBITALS BIND BETTER WITH LIGAND ORBITALS



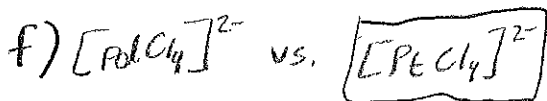
TETRAHEDRAL d-d SPLITTING IS MUCH SMALLER THAN OCTAHEDRAL GEOMETRY



PHEN. IS ABOVE AMMONIA ON THE SPECTROPHOTOCHEMICAL SERIES; LP ON N IN PHEN IS  $\text{sp}^2$  HYBRIDIZED (MORE S CHARACTER) AND ARENE RING IS A  $\pi$  ACID



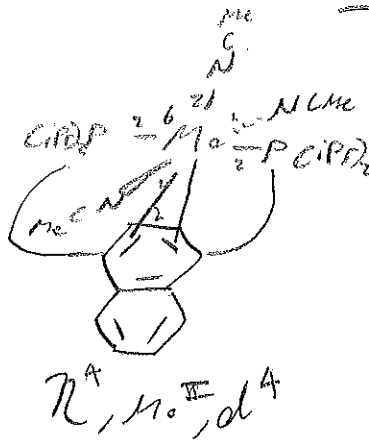
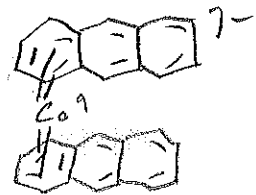
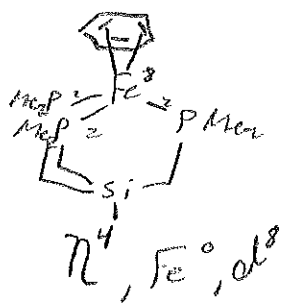
$\Delta_o$  INCREASES WITH INCREASING OXIDATION STATE;  $\text{Fe}^{3+}$  IS MORE LEWIS ACIDIC, LEADING TO SHORTER M-L BONDS (HIGHER  $\sigma^*/\text{Zeg}$ )



SAME REASON AS b)

#2

PART B



72+

PART C

$1860 \text{ cm}^{-1}$   
 $1840 \text{ cm}^{-1}$   $\nu_{C=O}$

$^{13}C=O$  COMPLEX:

$$\frac{\nu_{^{12}C=O}}{\nu_{^{13}C=O}} = \sqrt{\frac{M_{C=O}}{\mu_{^{12}C=O}}}$$

$$\mu_{C=O} = \frac{13 \cdot 16}{13+16} = 7.1724$$

$$\mu_{^{12}C=O} = \frac{12 \cdot 16}{12+16} = 6.8571$$

$$\mu = \frac{m_A \cdot m_B}{m_A + m_B}$$

$$\frac{\nu_{^{12}C=O}}{\nu_{^{13}C=O}} = \sqrt{\frac{7.1724}{6.8571}} = 1.0227$$

$$\nu_{^{13}C=O} = \frac{\nu_{^{12}C=O}}{1.0227}$$

$$\nu_{^{13}C=O} = \frac{1860 \text{ cm}^{-1}}{1.0227} = 1819 \text{ cm}^{-1}$$

$$\nu_{^{13}C=O} = \frac{1840 \text{ cm}^{-1}}{1.0227} = 1799 \text{ cm}^{-1}$$

$C=O$  STRETCHES REMAIN @  $1600 \text{ cm}^{-1}$

$C^{18}O$  COMPLEX:

$$\frac{\nu_{C=^{16}O}}{\nu_{C=^{18}O}} = \sqrt{\frac{\mu_{C=^{18}O}}{\mu_{C=^{16}O}}}$$

$$\mu_{C=^{18}O} = \frac{12 \cdot 18}{12+18} = 7.2$$

$$\mu_{C=^{16}O} = \frac{12 \cdot 16}{12+16} = 6.8571$$

$$\frac{\nu_{C=^{16}O}}{\nu_{C=^{18}O}} = \sqrt{\frac{7.2}{6.8571}} = 1.0247$$

CO LIGANDS

$$\nu_{C=^{18}O} = \frac{1860 \text{ cm}^{-1}}{1.0247} = 1815 \text{ cm}^{-1}$$

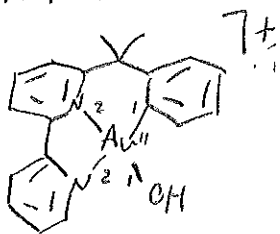
$$\nu_{C=^{18}O} = \frac{1840 \text{ cm}^{-1}}{1.0247} = 1795 \text{ cm}^{-1}$$

For QUINONE  $C=O$

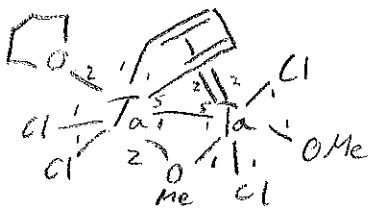
$$\nu_{C=^{18}O} = \frac{1600 \text{ cm}^{-1}}{1.0247} = 1561 \text{ cm}^{-1}$$

Z

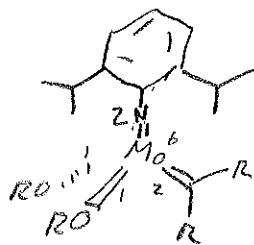
PART A



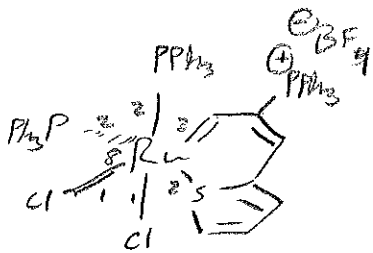
Au 11  
 2xN 4  
 C<sub>sp2</sub> 1  
 OH 1  
 +  $\frac{-1}{-1}$   
 16e<sup>-</sup>, Au<sup>III</sup>, d<sup>8</sup>



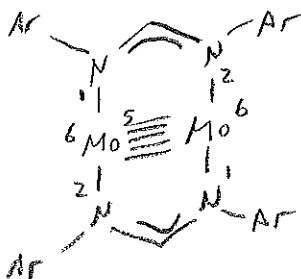
Ta 5	Ta 5
2xCl 2	2xCl 2
L:OMe 2	X:OMe 1
THF 2	OMe 1
2xC <sub>sp2</sub> 2	2xALKENE 4
M-M 1	M-M 1
<hr/> 14	<hr/> 14
Ta <sup>IV</sup> , d <sup>1</sup>	Ta <sup>IV</sup> , d <sup>1</sup>



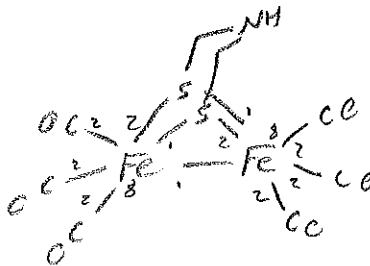
Mo 6	6
2x RO 2	2
CARBENE 1	2
IMIDO 1	2
<hr/> 12e <sup>-</sup>	<hr/> 14e <sup>-</sup>
Mo <sup>VI</sup> , d <sup>0</sup>	OR IMIDO: 4



Ru 8  
 2xPPh<sub>3</sub> 4  
 2xCl 2  
 CARBENE 2  
 5 2  
 18e<sup>-</sup>  
 Ru<sup>IV</sup>, d<sup>4</sup>



Mo 6	Mo 6
N(CX-TYPE) 1	N(CX-TYPE) 1
N(LL-TYPE) 2	N(LL-TYPE) 2
M-M 5	M-M 5
<hr/> 14	<hr/> 14
Mo <sup>I</sup> , d <sup>5</sup>	



Fe 8	Fe 8
5(CX-TYPE) 1	5(CX-TYPE) 1
5(LL-TYPE) 2	5(LL-TYPE) 2
3xCO 6	3xCO 6
M-M 1	M-M 1
<hr/> 18e <sup>-</sup>	<hr/> 18e <sup>-</sup>
Fe <sup>I</sup> , d <sup>7</sup>	

③

MeOH · DME  
ACID      BASE

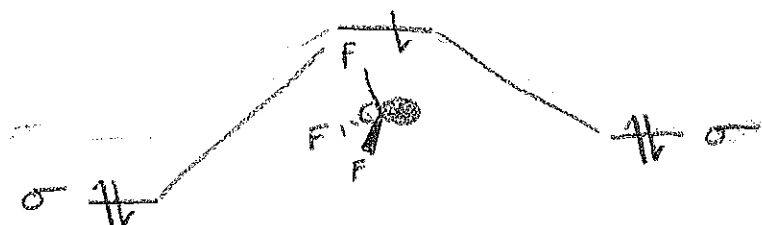
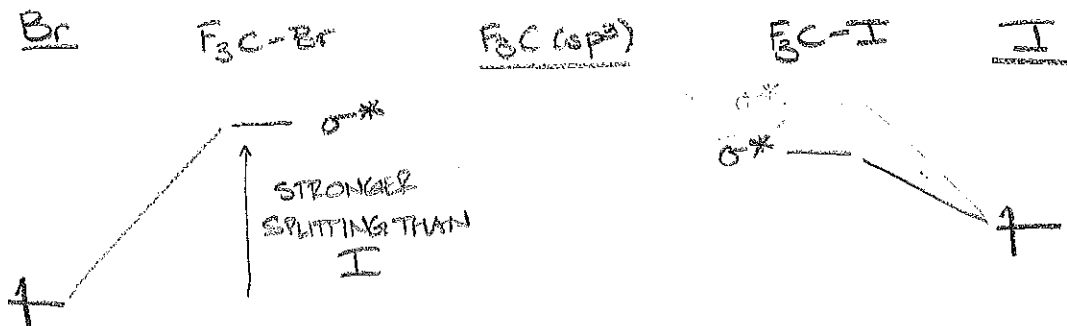
MeOH · DMS  
ACID      BASE

CF<sub>3</sub>I · DME  
ACID      BASE

CF<sub>3</sub>I · DMS  
ACID      BASE

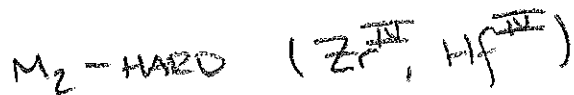
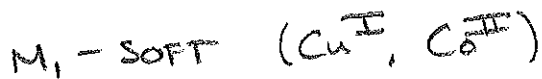
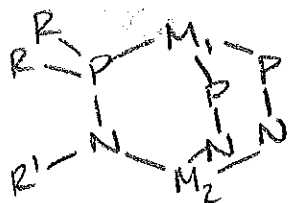
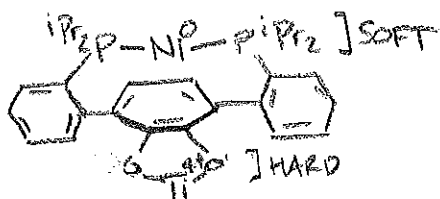
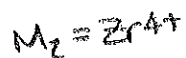
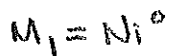
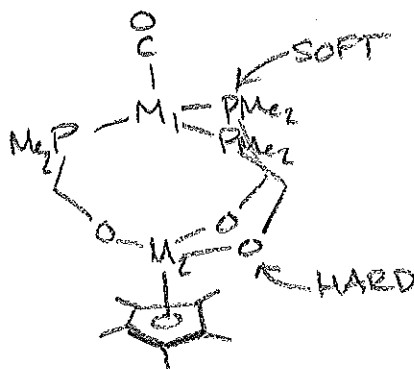
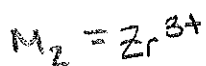
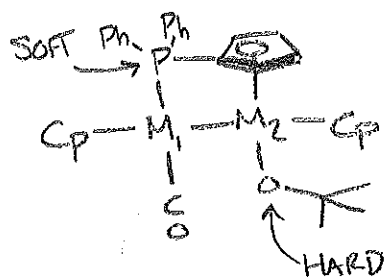
→ MeOH <sup>HARD ACID</sup> HAS STRONGER INTERACTIONS (LOWER ΔH) W/ DME THAN DMS B/C MeOH · DME IS MATCHED HARD · HARD, MeOH · DMS IS MISMATCHED HARD · SOFT

→ CF<sub>3</sub>I <sup>SOFT ACID</sup> IS MATCHED W/ DMS (SOFT · SOFT) + MISMATCHED WITH DME (SOFT · HARD).



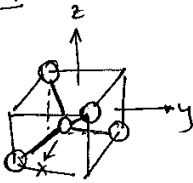
I HAS WEAKER OVERLAP W/ F<sub>3</sub>C(sp<sup>3</sup>) + THE σ\* RESIDES MOSTLY ON I, MORESO COMPARED W/ Br.

PART B



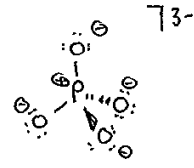
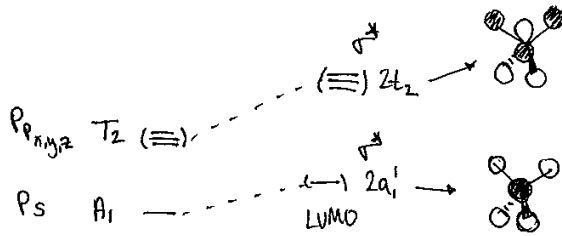
PROBLEM 4

a)

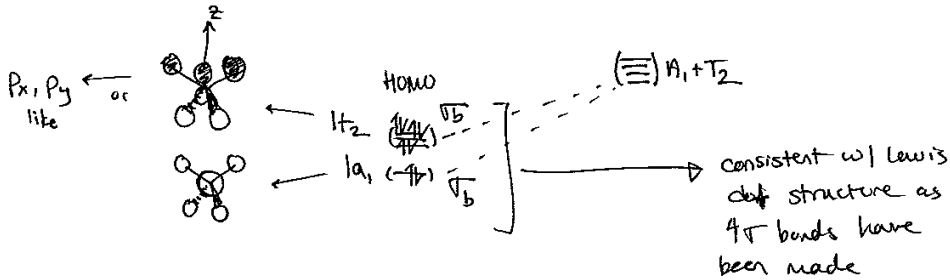


$T_d$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\Gamma_{4\sigma}$	4	1	0	0	2 $\Rightarrow A_1 + T_2$
$\Gamma_M$	$A_1 + T_2 + E + T_2$				
	s	3p orbitals	$(z^2, x^2-y^2)$	$(xz, yz, xy)$	
$\Gamma_P$	$A_1 + T_2$				
	s	3p orbitals			

b)  $PO_4^{3-}$  - P-only



73-  
think Lewis dot structure.  
Expect 4  $\sigma$  bonds

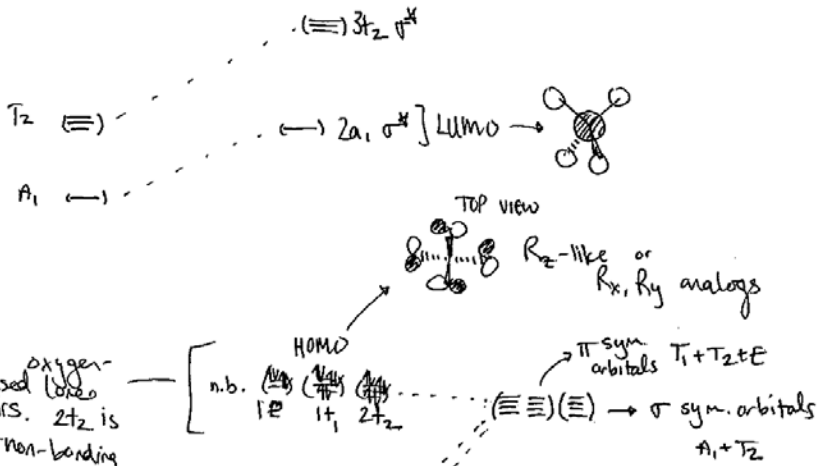


c)

$T_d$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\Gamma_{\text{oxygen } p_{x,y}}$	8	-1	0	0	0 = $T_1 + T_2 + E$

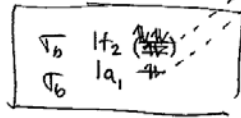
d)

(P)



12 pairs of  $e^-$

oxygen-based lone pairs.  $2t_2$  is net non-bonding since only 3  $t_2$  sym. bonds can be formed because P only has one  $T_2$  set. Consequently  $\pi$  bonding comes at the expense of  $\sigma$ -bonding

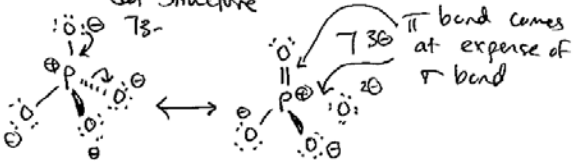


orbitals contributing to  $\sigma$ -bonding framework has contribution from  $2t_2$   $\pi$ -sym. orbitals, but still dominated by  $\sigma$ -bonding picture

(by this count 4  $\sigma$  sym. orbitals for  $4 \times 2 e^-$  total of  $8e^-$ )

can make  $\pi$ -bonds or  $\sigma$  bonds but can't have both since only one  $t_2$  set can be bonding energywise.

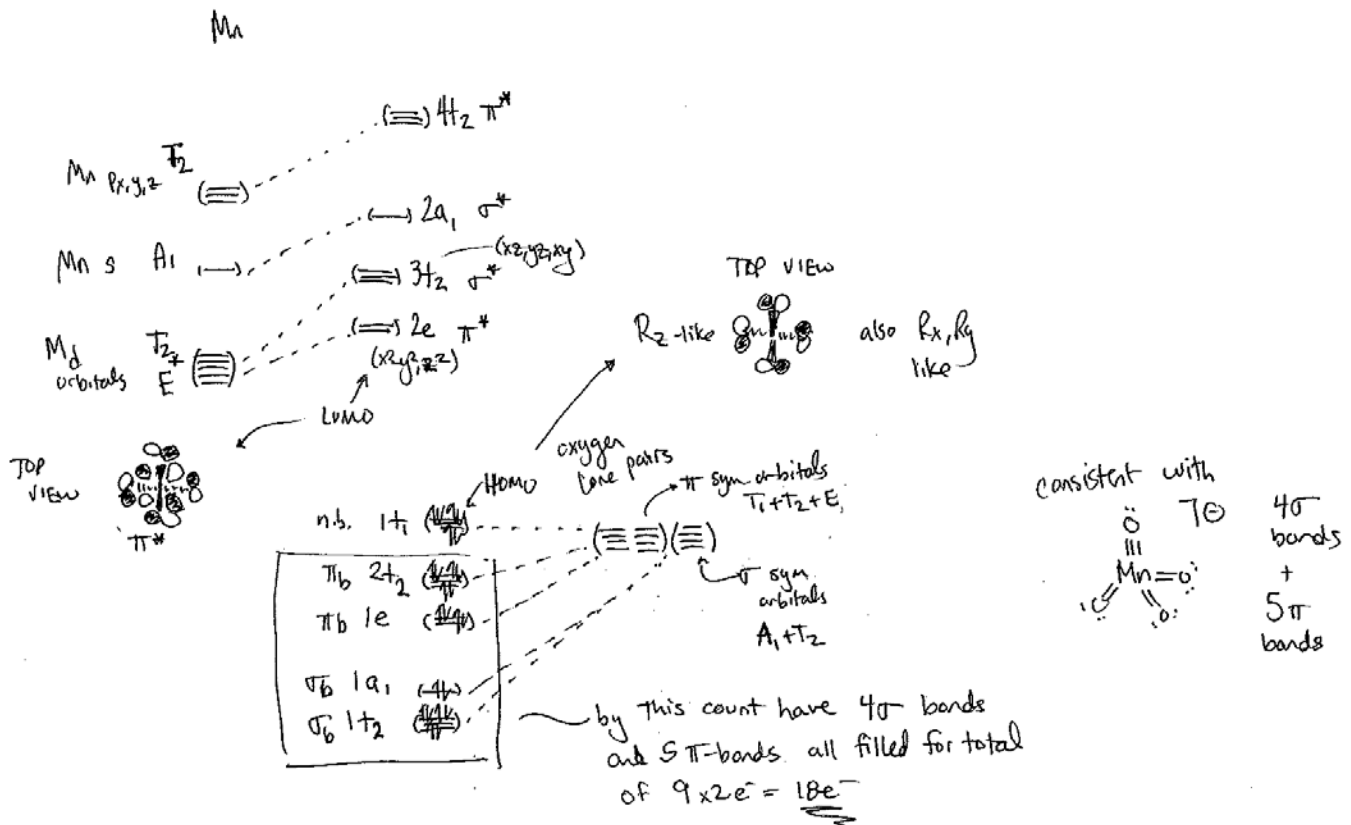
$\Rightarrow$  consistent w/ Lewis dot structure







f)  $\pi$ -sym allowed  $MnO_4^-$



g)  $PO_4^{3-}$  have 4  $\sigma$  bonding orbitals for total of  $8e^-$  shared at P valence shell  
 $\therefore 8e^-$  which is consistent with octet rule.  
 no also consistent with resonance structure that obeys octet rule

$MnO_4^-$  have 4  $\sigma$  bonding and 5  $\pi$  bonding orbitals for total of  $18e^-$  in valence shell  
 $\therefore 18e^-$  is consistent w/  $18e^-$  rule for metal complexes  
 no also consistent w/ Lewis dot structure.