

a) For A

$$\text{rate}_{\text{MX}(\text{PPH}_3)(\text{CO})_2} = k_2 [\text{MX}(\text{CO})_2] [\text{PPH}_3]$$

$$\text{rate}_{\text{MX}(\text{CO})_2} = k_1 [\text{MX}(\text{CO})_3] - k_{-1} [\text{MX}(\text{CO})_2] [\text{CO}] - k_2 [\text{MX}(\text{CO})_2] [\text{PPH}_3] = 0 \quad \text{STEADY STATE APPROX.}$$

$$[\text{MX}(\text{CO})_2] = \frac{k_1 [\text{MX}(\text{CO})_3]}{k_{-1} [\text{CO}] + k_2 [\text{PPH}_3]}$$

$$\therefore \text{rate}_{\text{MX}(\text{PPH}_3)(\text{CO})_2} = \frac{k_2 k_1 [\text{MX}(\text{CO})_3]}{k_{-1} \frac{[\text{CO}]}{[\text{PPH}_3]} + k_2}$$

For B

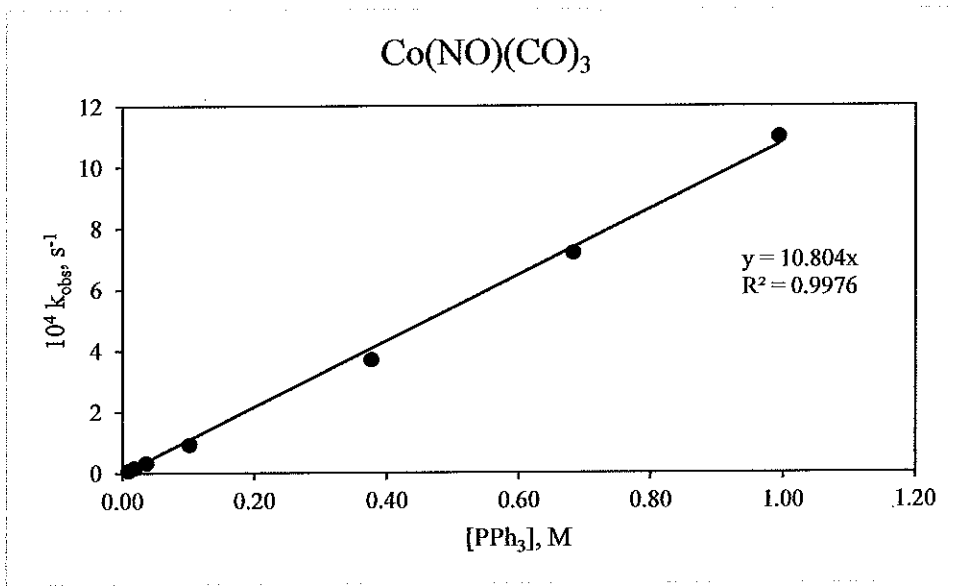
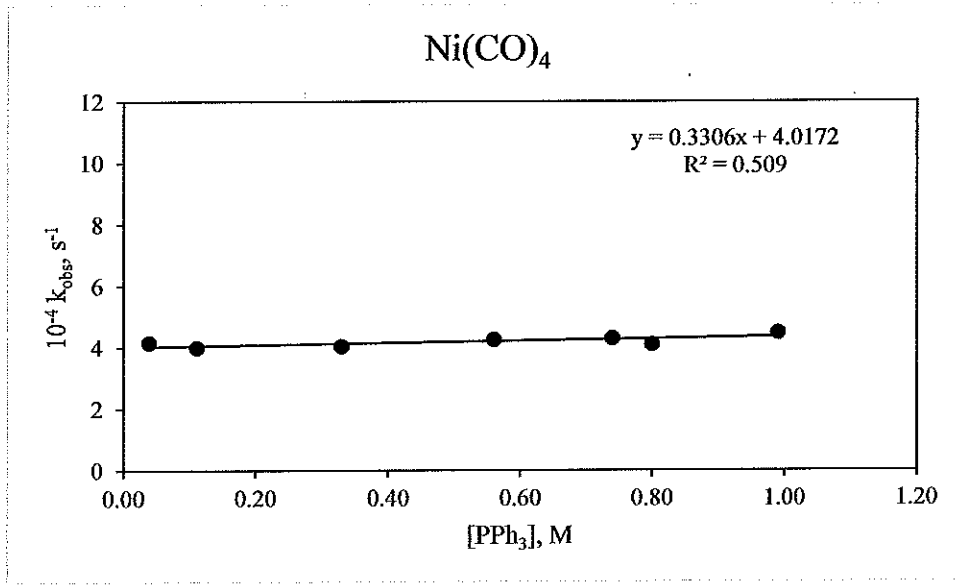
$$\text{rate}_{\text{MX}(\text{PPH}_3)(\text{CO})_2} = k_2 [\text{MX}(\text{CO})_3 (\text{PPH}_3)]$$

$$\text{rate}_{\text{MX}(\text{CO})_3 (\text{PPH}_3)} = k_1 [\text{MX}(\text{CO})_3] [\text{PPH}_3] - k_{-1} [\text{MX}(\text{CO})_3 (\text{PPH}_3)] - k_2 [\text{MX}(\text{CO})_3 (\text{PPH}_3)] = 0 \quad \text{SS}$$

$$[\text{MX}(\text{CO})_3 (\text{PPH}_3)] = \frac{k_1 [\text{MX}(\text{CO})_3] [\text{PPH}_3]}{k_{-1} + k_2}$$

$$\therefore \text{rate}_{\text{MX}(\text{PPH}_3)(\text{CO})_2} = \frac{k_2 k_1 [\text{MX}(\text{CO})_3] [\text{PPH}_3]}{k_{-1} + k_2}$$

b) NEXT PAGE



c) Ni(CO)₄ slope is nearly 0 ∴ zeroth order in [PPh₃]

Dissociative Mechanism

$$rate_{Ni(CO)_3 PPh_3} = k_{obs} [Ni(CO)_4]$$

FROM PART a)

$$k_{obs} = \frac{k_2 k_1}{k_{-1} [PPh_3] + k_2} \approx k_1$$

SINCE PSEUDO-FIRST ORDER CONDITIONS

MEANS LARGE EXCESS OF PPh₃

AND [PPh₃] >> [CO]

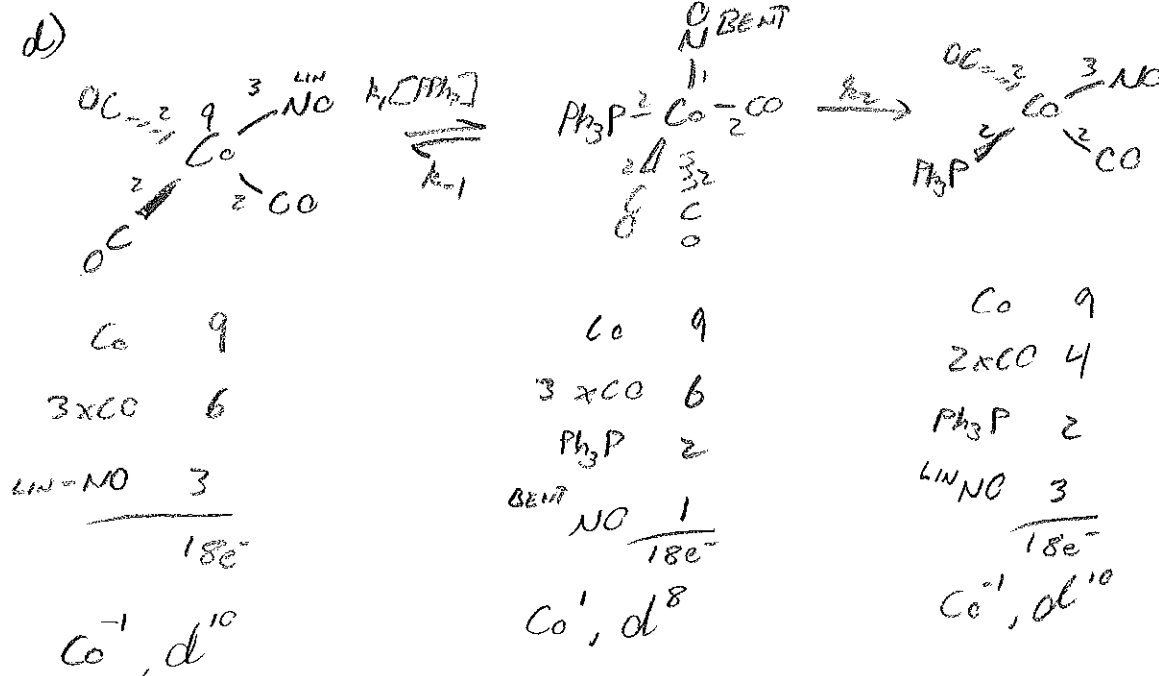
SO $k_{-1} \frac{[CO]}{[PPh_3]}$ GOES TO

ZERO

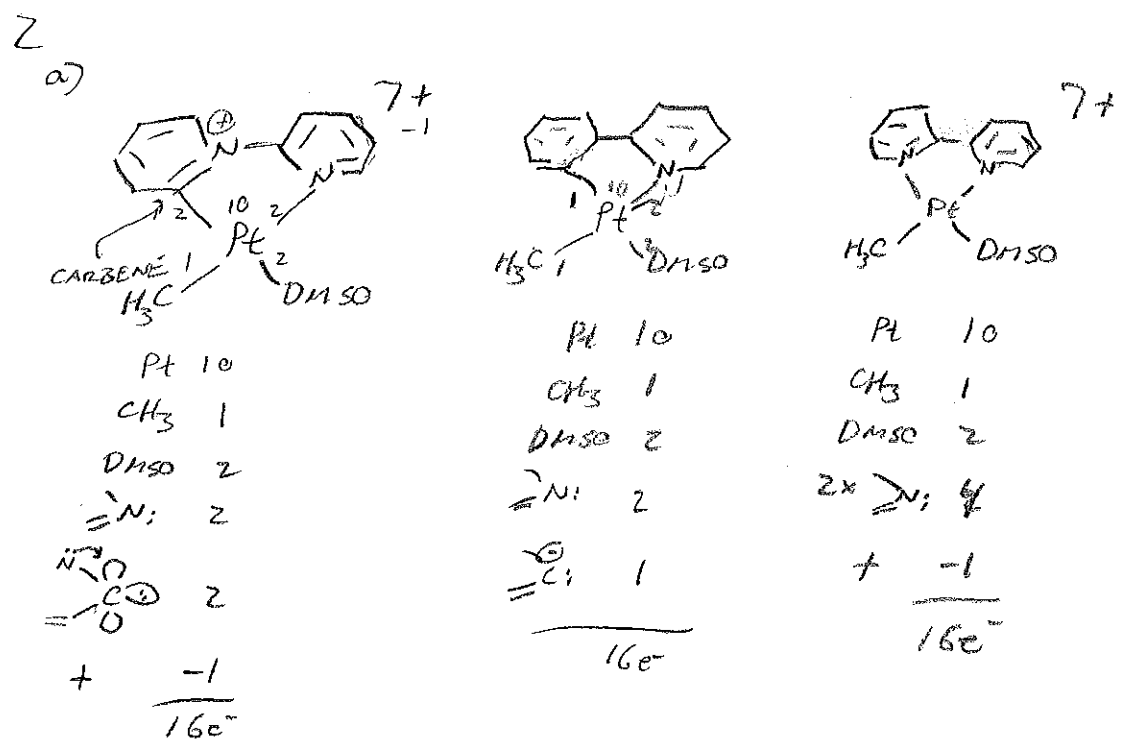
Co(NO)(CO)₃ RATE DEPENDS LINEARLY ON [PPh₃] ∴ FIRST ORDER IN [PPh₃]
ASSOCIATIVE MECHANISM

$$rate_{Co(NO)(CO)_2 PPh_3} = k [PPh_3] [Co(NO)(CO)_2 PPh_3]$$

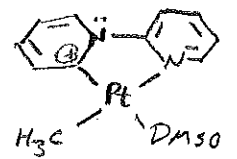
$$k = \frac{k_2 k_1}{k_{-1} + k_2}$$



e) ASSOCIATIVE PATHWAY OPERATIVE FOR $\text{Co}(\text{NO})(\text{CO})_3$ SINCE 5-COORDINATE INTERMEDIATE CAN BE $18e^-$ WITH BENT NO COORDINATION. 5-COORDINATE INTERMEDIATE FOR $\text{Ni}(\text{CO})_4$ ($\text{Ni}(\text{CO})_4\text{PPh}_3$) WOULD BE $20e^-$ AND VERY UNFAVORABLE. THEREFORE, DISSOCIATIVE PATHWAY IS MORE FAVORABLE FOR $\text{Ni}(\text{CO})_4$.

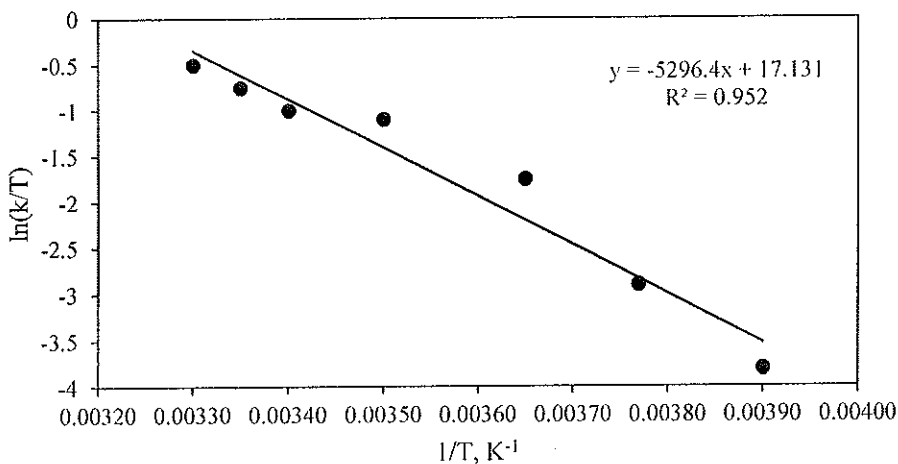


ALL ARE σ BASES, | WILL BE THE MOST π ACIDIC DUE TO RESONANCE!



b)

[Pt] Eyring Plot



$$\text{SLOPE} = \frac{-\Delta H^\ddagger}{R}$$

$$-5296.4 \text{ K} = \frac{\Delta H^\ddagger}{-1.98 \text{ cal K}^{-1} \text{ mol}^{-1}}$$

$$\Delta H^\ddagger = 10487 \text{ cal/mol} \text{ or } 10.5 \text{ kcal/mol} \text{ (43.96 kJ/mol)}$$

$$\text{INTERCEPT} = \ln \frac{k_b}{h} + \frac{\Delta S^\ddagger}{R}$$

$$17.131 = \ln \left(\frac{1.38 \times 10^{-23} \text{ J/K}}{6.626 \times 10^{-34} \text{ J/s}} \right) + \frac{\Delta S^\ddagger}{1.98 \text{ cal K}^{-1} \text{ mol}^{-1}}$$

$$17.131 = 23.76 + \frac{\Delta S^\ddagger}{1.98 \text{ cal K}^{-1} \text{ mol}^{-1}}$$

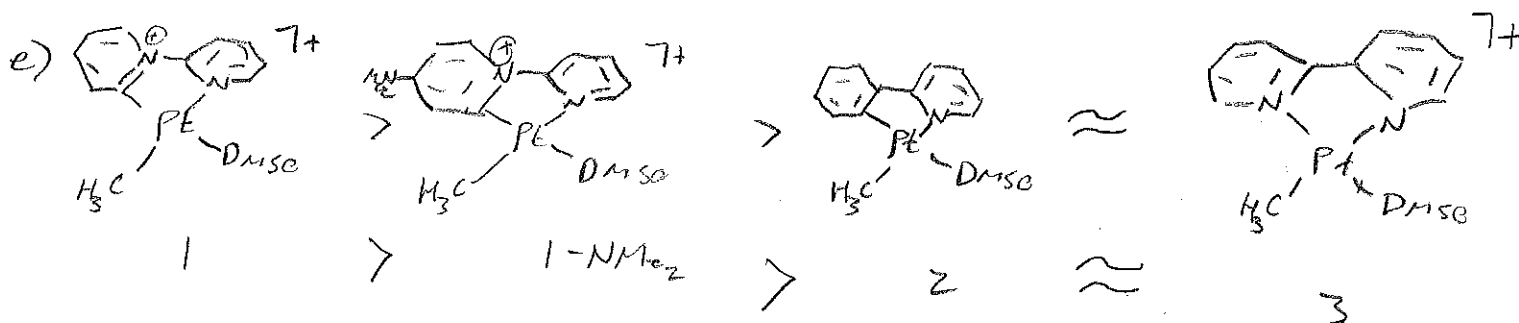
$$-6.629 = \frac{\Delta S^\ddagger}{1.98 \text{ cal K}^{-1} \text{ mol}^{-1}}$$

$$\Delta S^\ddagger = -13.1 \text{ cal/mol K} \text{ (-54.4 J/mol K)}$$

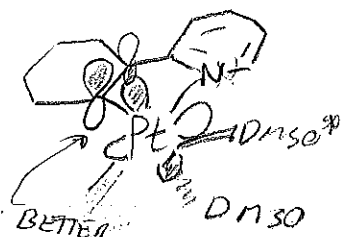
c) $16e^-$ SQUARE PLANAR PLATINUM AND $\Delta H^\ddagger = 10.5 \text{ kcal/mol}$ AND $\Delta S^\ddagger = -13 \text{ cal/molK}$
 ALL CONSISTENT WITH AN ASSOCIATIVE MECHANISM OF DMSO EXCHANGE

d) PLOTS ON PAGE 5

k_{OVERALL}	$[PE]$	k_{OVERALL} WITH INTERCEPT = 0
$3.82 \text{ M}^{-1} \text{ s}^{-1}$	1	$626.2 \text{ M}^{-1} \text{ s}^{-1}$
$0.247 \text{ M}^{-1} \text{ s}^{-1}$	2	$0.215 \text{ M}^{-1} \text{ s}^{-1}$
$6.39 \text{ M}^{-1} \text{ s}^{-1}$	1-NMe ₂	$6.49 \text{ M}^{-1} \text{ s}^{-1}$

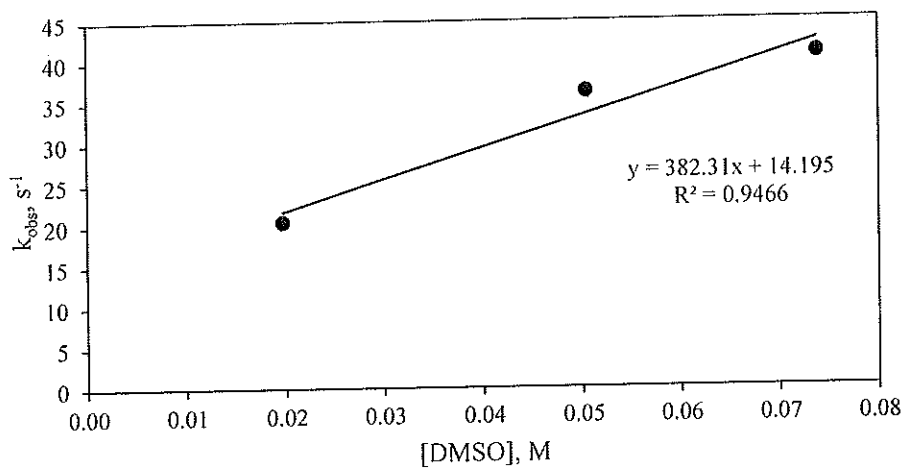


f) 1 IS THE BEST \uparrow ACID AS IT IS EXPECTED TO HAVE THE LOWEST ENERGY LUMO. THE PYRIDINIUM (N⁺) SUBSTITUTION ON THE RING MAKES THE AROMATIC PI SYSTEM MORE ELECTRON POOR (N⁺ BEING ELECTRON WITHDRAWING). THE POLAR $PE=N^+$ BOND ALSO MAKES THE LUMO MORE CENTERED ON THE CARBON BOUND TO PE. Z.E.3'S LUMOS WILL BE OF HIGHER ENERGY DUE TO THE INCREASED ELECTRON DENSITY OF THE RING, MAKING THE LUMO WORSE FOR BACKBONDING.
 1-NMe₂ IS SLOWER THAN 1 SINCE THE -NMe₂ GROUP DONATES ELECTRON DENSITY INTO THE AROMATIC RING, INCREASING THE ENERGY OF THE LUMO.

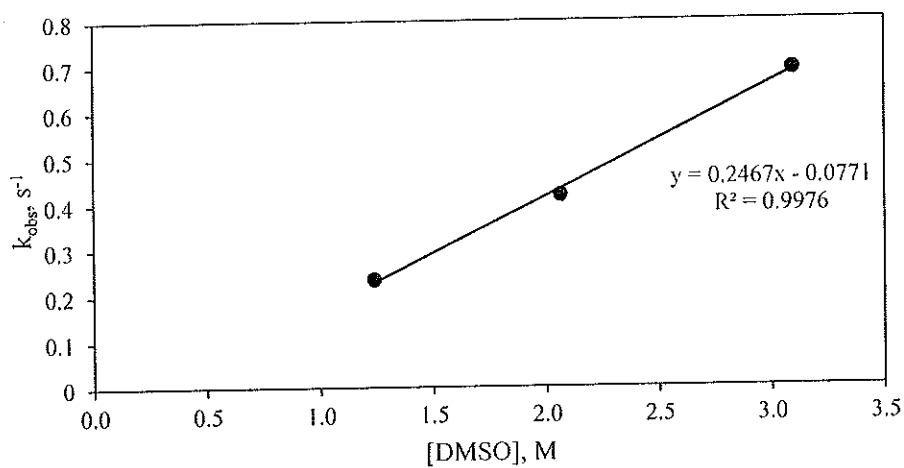


OVERLAP AND ENERGY MATCH INCREASES RATE OF SUBSTITUTION

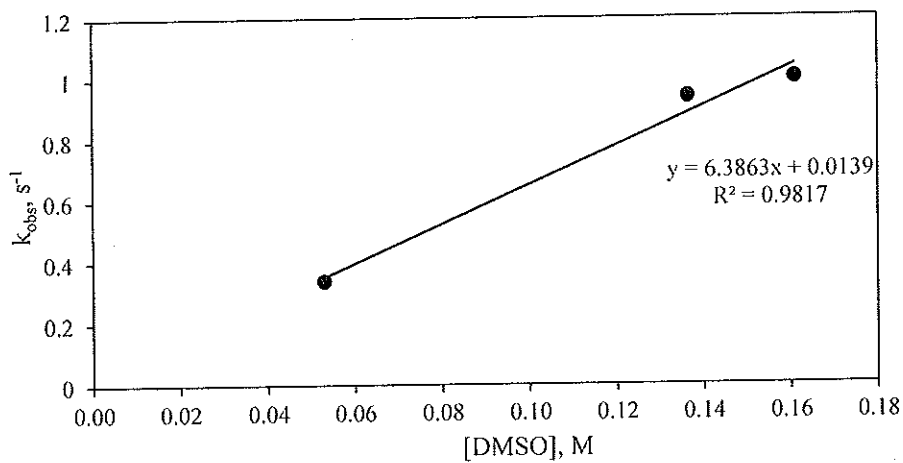
[Pt] 1 Pseudo First Order Plot



[Pt] 2 Pseudo First Order Plot

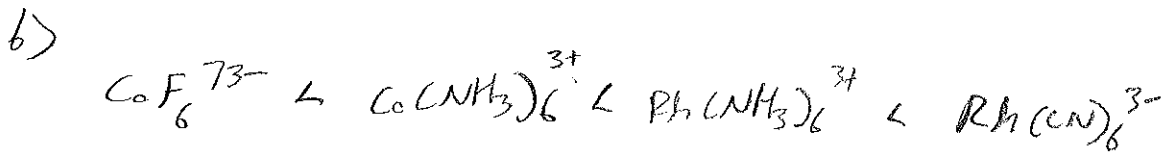


[Pt] 1-NMe₂ Pseudo First Order Plot



3 a) $\epsilon \sim 10 \text{ cm}^{-1} \text{ M}^{-1}$ WITHIN THE $1-1000 \text{ cm}^{-1} \text{ M}^{-1}$ RANGE

SPIN ALLOWED, LAPORTE FORBIDDEN



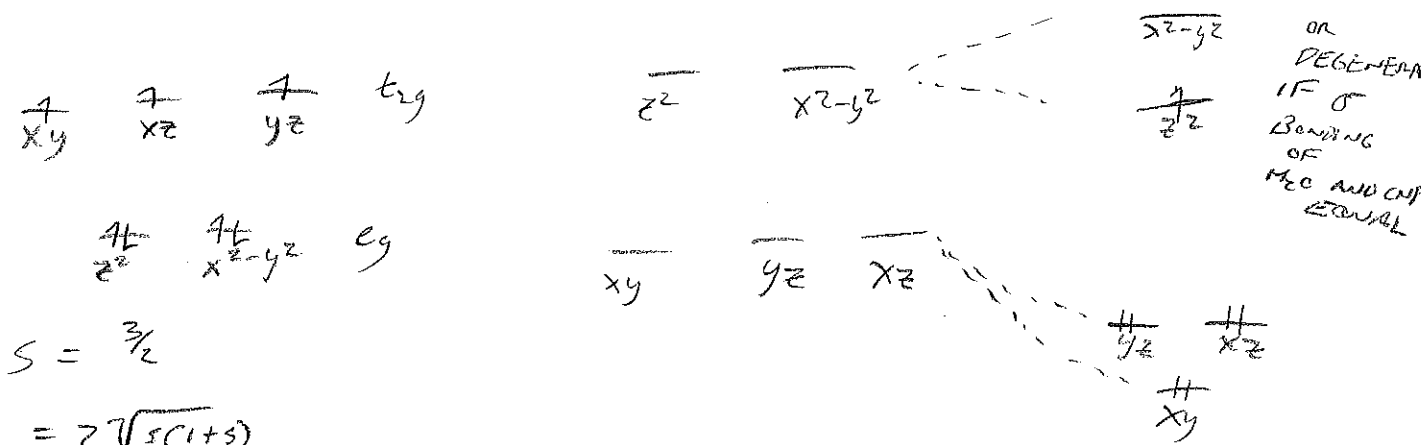
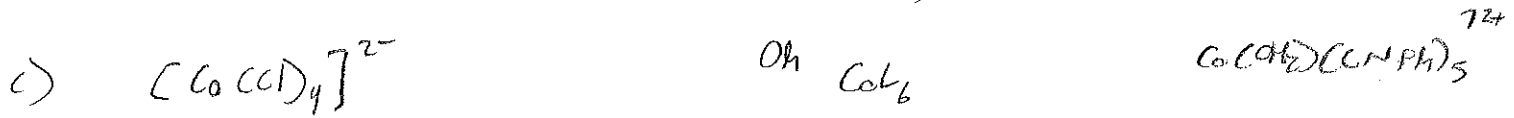
ALL O_h , ALL M^{III} , ALL d^6

CoF_6^{3-} - LOW Δ_o DUE TO FIRST ROW METAL AND π -BASIC LIGANDS RAISING e_g ORBITALS

$\text{Co}(\text{NH}_3)_6^{3+}$ - GREATER Δ_o THAN CoF_6^{3-} SINCE LIGANDS ARE NOT π -BASIC (σ -ONLY)

$\text{Rh}(\text{NH}_3)_6^{3+}$ - GREATER Δ_o THAN $\text{Co}(\text{NH}_3)_6^{3+}$ SINCE IT IS A 2ND ROW TRANSITION METAL (LARGER ORBITALS FOR BETTER M-L INTERACTIONS, HIGHER e_g ORBITALS)

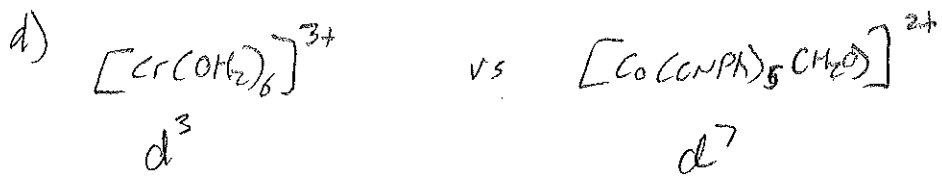
$\text{Rh}(\text{CN})_6^{3-}$ - GREATER Δ_o THAN $\text{Rh}(\text{NH}_3)_6^{3+}$ SINCE CN^- ARE π ACIDIC LIGANDS AND WILL LOWER THE ENERGY OF t_{2g} ORBITALS (ALSO STRONGER σ -DONORS, RAISING e_g)



$S = 3/2$

$\mu_{so} = 2\sqrt{S(S+1)}$
 $= 2\sqrt{\frac{3}{2}(1+\frac{3}{2})}$
 $= 2\sqrt{3.75}$
 $= 3.87$

$S = 1/2$
 $\mu_{so} = 2\sqrt{\frac{1}{2}(1+\frac{1}{2})}$
 $= 2\sqrt{0.75}$
 $= 1.73$

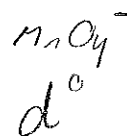
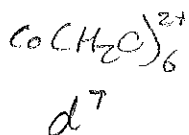
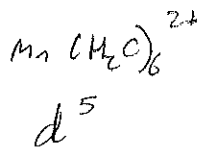
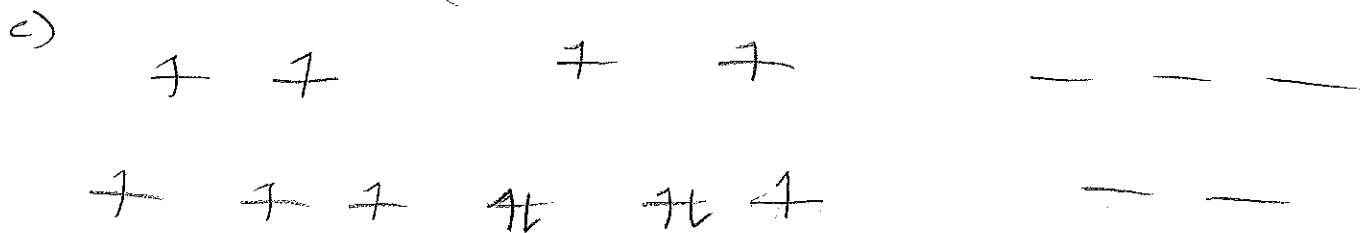


INERT

LABILE



EXPECTED TO HAVE FASTER WATER EXCHANGE KINETICS
DUE TO OCCUPIED σ^* ORBITAL

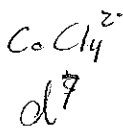
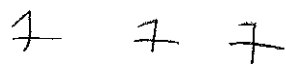


ONLY SPIN-FORBIDDEN
TRANSITIONS

SPIN-ALLOWED, BUT
LAPORTE FORBIDDEN
TRANSITIONS

LMCT FROM

FULLY ALLOWED



PEAK

a - $E \sim 10$ - LAPORTE FORBIDDEN, HIGHER E
THAN b - $Co(CH_2O)_6^{2+}$

b - $E \sim 800$ - LARGER E THAN: a - $CoCl_4^{2-}$

c - $E \sim 0.02$ - SPIN FORBIDDEN - $Mn(CH_2O)_6^{2+}$

d - $E \sim 2400$ - LMCT - MnO_4^-

NO INVERSION, NO LAPORTE RULE

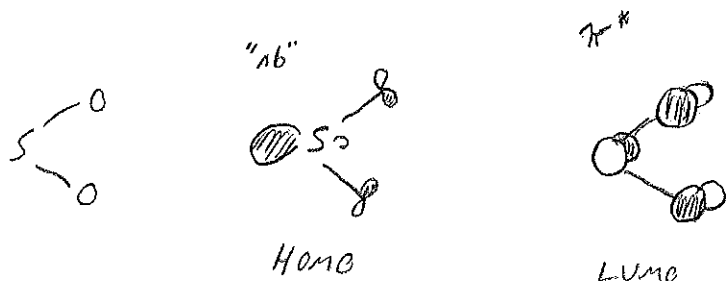
LOWER ENERGY THAN

$Co(CH_2O)_6^{2+}$ DUE TO
 π BASIC LIGANDS
AND TETRAHEDRAL
GEOMETRY

a) SO_2 $18e^-$



b) HOMO SULFUR sp , LUMO π^* - SIMILAR TO NHC'S

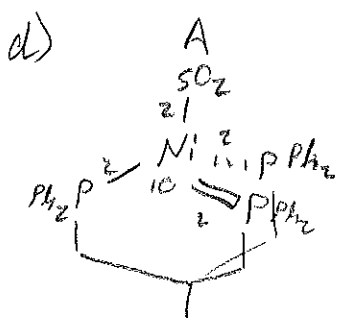


c) A - σ -BONDING WITH SO_2 HOMO - SO_2 σ -BASE

B - σ -BONDING WITH SO_2 LUMO - SO_2 σ -ACID

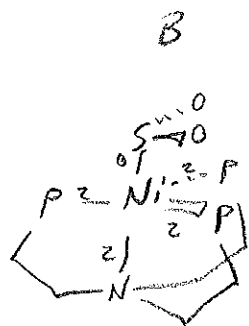
NiP_3 is $16e^-$ complex, so $2e^-$ donation BY SO_2 HOMO IS STABILIZING

$NiNP_3$ is $18e^-$ complex - BINDING OF SO_2 WITH HOMO WOULD BE GREATLY DESTABILIZING. Ni^0 IS d^{10} SO IS A VERY LEWIS BASIC METAL TO BIND SO_2 LUMO



Ni 10
 3xP 6
 SO₂ 2

 18e⁻
 Ni⁰, d¹⁰



Ni 10
 3xP 6
 N 2
 SO₂ 0 \rightarrow SO₂ IS LEWIS ACID,

 18e⁻ NOT DONATING ANY
 ELECTRONS
 Ni⁰, d¹⁰

e) B WOULD BE EXPECTED TO HAVE A LOWER S-O FREQUENCY SINCE THE S-O BONDS WILL BE WEAKENED BY DONATING ELECTRON DENSITY TO THE SO_2 LUMO, WHICH IS S-O π^*

