Chemistry 432 Exam 2

Name Key

Trans effect CN^-, CO, NO, C_2H_4>PR_3, H^->CH_3^-, $C_6H_5^-$, SR_2>SO_3H>NO_2^-, I^-,SCN^-> Br^-> Cl^-> py> NH_3> OH^-> H_2O

(1)(15 pts) For the reaction below, the following kinetic data was found.

$ML_6 + Y$ -------> $ML_5Y + L$

Y	Relative Rate
PMe_3	1.5
Br^-	1.2
NH_3	1.2
H_2O	1

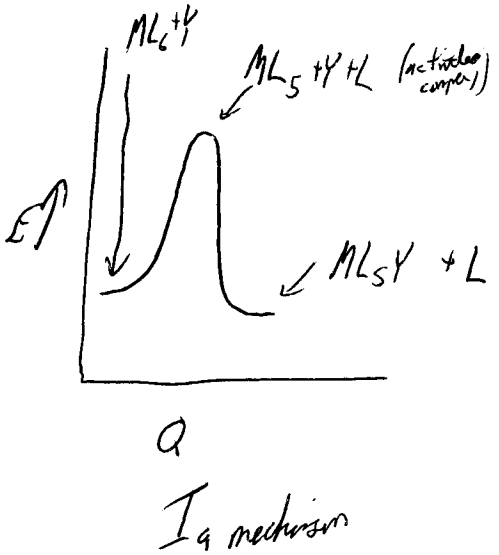
L (for Y = PMe_3)	Relative Rate
NMe_3	105
NH_3	25
SO_3R^-	1

(a) Propose a mechanism that is consistent with the rate data and explain your reasons.

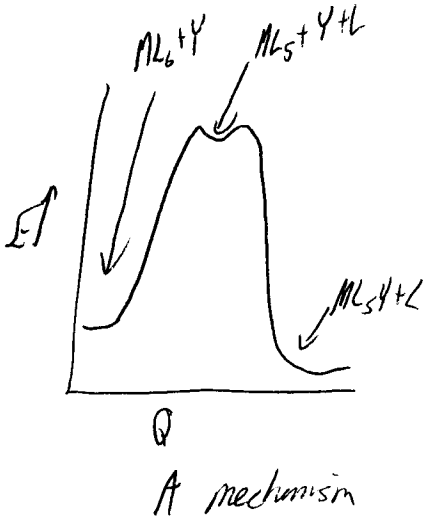
The rate has very little dependence on the incoming ligand and a lot of dependence on the outgoing ligand. This suggests that the rate determining step is the dissociation of one of the L ligands.

The mechanism seems to be D or Id.

(b)Draw a reaction coordinate diagram with starting materials, products, and activated complex/intermediate for the mechanism proposed above.



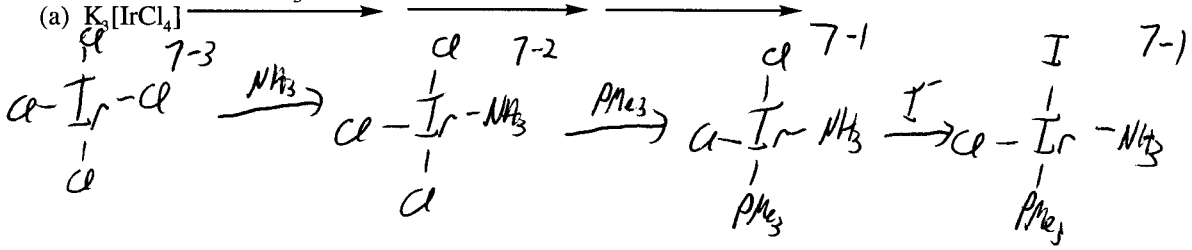
I a mechanism



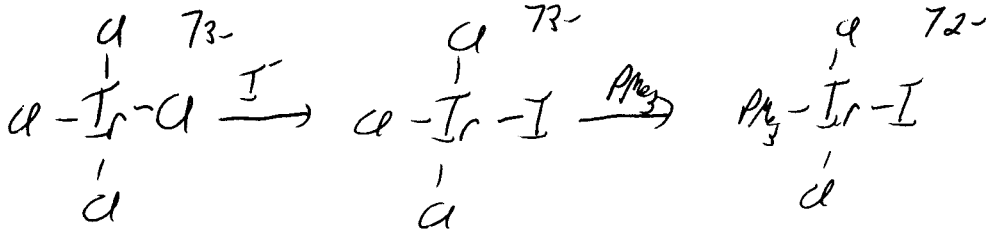
A mechanism

(2)(10 pts) Predict the product of the following reaction sequences

(a) $K_3[IrCl_4]$ $\xrightarrow{NH_3}$ $\xrightarrow{PMe_3}$ $\xrightarrow{I^-}$



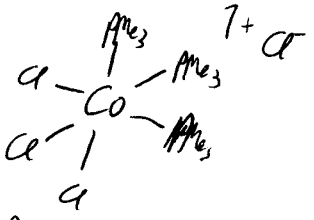
(b) $K_3[IrCl_4]$ $\xrightarrow{I^-}$ $\xrightarrow{PMe_3}$



(3)(10 pts) Name the following compounds and draw the structure

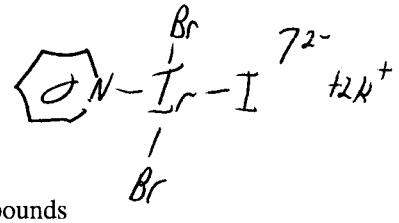
(a) *fac*-$[CoCl_3(PMe_3)_3]Cl$

fac-trichloro tris trimethylphosphine cobalt(III) chloride



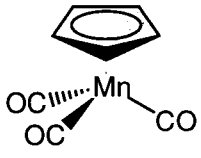
(b) *trans*-$K_2[IrBr_2I(C_5H_5N)]$

trans potassium dibromo iodo pyridyl iridium(I)



(4)(10 pts) Write the formulas for the following compounds

(a)



$Cp\,Mn(CO)_3$ $(\eta^5\text{-}C_5H_5)Mo(CO)_3$

(b) trichlorotris(diphenylphosphino) iron(III)

$FeCl_3(PPh_2H)_2$

(5)(20 pts) What is the trans effect? Explain what causes the trans effect.

The trans effect is a kinetic effect of substitution. Ligands that have a strong trans effect cause the ligands trans to them in a complex to substitute at a more rapid rate.

There are both σ-bonding and π bonding aspects to the trans effect. Ligands that form strong M-L σ bonds tie up electron density thus causes the σ bonds trans to them to be weak. Good π -acceptor ligands stabilize the intermediate (excited state) of associative reactions by withdrawing excess electron density.

(6)(15 pts) List the ground state term symbols for the following valence shell electron configurations or ions.

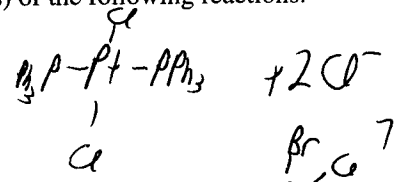
(a) $3d^5$ — $L = 0$; $S = \frac{5}{2}$; multiplicity = 6 → **6S**

(b) $4p^5$ — $L = 1$; $S = \frac{1}{2}$ → **2P**

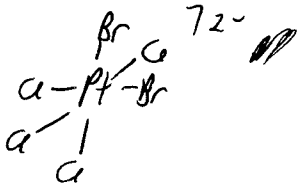
(c) Cr^{3+} — $L = 3$; $S = \frac{3}{2}$; multiplicity = 4 → **4F**

(7)(20 pts) Predict the product(s) of the following reactions.

(a) $[PtCl_4]^{2-} + 2PPh_3$ ---> (draw correct isomer)

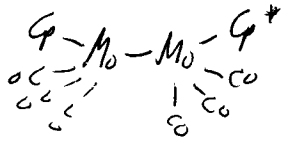


(b) $[PtCl_4]^{2-} + Br_2$ ---->

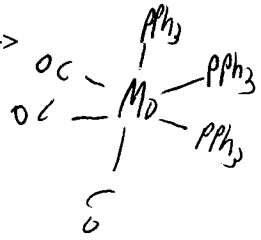


(c) $CpMo(CO)_3I + Na[Cp^*Mo(CO)_3]$ ----->

$Cp^* = C_5Me_5$



(d) $Mo(CO)_6 + 3PPh_3$ -------> (draw correct isomer) Δ



Take-Home Section, Chem 432 Exam 2
Name key

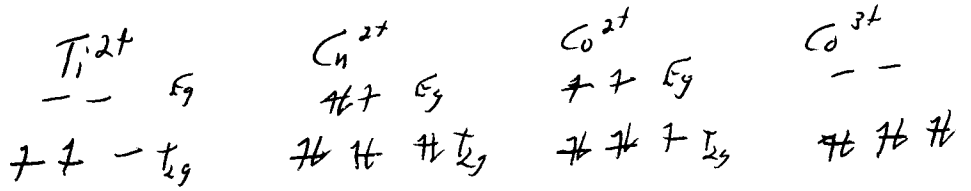
You may only use the course textbook and notes as a reference for this exam. This exam is due by 5:00 PM Monday, November 5.

(8)(15 pts) $Mo(CO)_6$ and $Nb(CO)_5(NO)$ are isoelectronic (linear NO), but the Nb compound has a larger substitution rate constant. Give a possible explanation for this observation.

$M(CO)_6$ is an 18e⁻ species and 6 coordinate. An associative substitution mechanism is unlikely because it would result in a 20e⁻ intermediate or activated complex. NO has 2 binding modes that donate 3 or 1 electrons. If an associative mechanism occurs, the NO can bend and accomodate the 2 extra electrons while maintaining an 18e⁻ count. This gives the $Nb(CO)_5(NO)$ species an added possible reaction mechanism that $Mo(CO)_6$ doesn't have available (or is at least unfavorable).

(9)(15 pts) Place the metal complexes below in order from slowest to most rapid ligand exchange rates and explain your reasoning.

$[Ti(NH_3)_6]^{2+}$, $[Cu(NH_3)_6]^{2+}$, $[Co(NH_3)_6]^{2+}$, $[Co(NH_3)_6]^{3+}$



Ti^{2+} & Co^{3+} have no electrons in the E_g set, so they will be slowest. Co^{3+} has a higher charge and most likely a larger CFSE so it is the slowest of the two

Co^{2+} & Cu^{2+} both have e⁻'s in the E_g set, but Cu^{2+} has a degenerate E_g set and will be Jahn-Teller distorted making it have the fastest substitution rate.

$[Co(NH_3)_5]^{3+} < [Ti(NH_3)_6]^{2+} < [Co(NH_3)_6]^{2+} < [Cu(NH_3)_2]^{2+}$

(10)(15 pts) $V(CO)_6$ has a rather rapid CO exchange rate. What do you think would happen to the exchange rate if $V(CO)_6$ were reduced by one electron and why? What do you think would happen to the CO exchange rate of $Mo(CO)_6$ if it were reduced by one electron? Why?

V 5e⁻ $V(CO)_6$ is a 17e⁻ species. If it were reduced to form

6 COs 12e⁻ $[V(CO)_6]^-$, an 18e⁻ species, its CO substitution rate would likely

17e⁻ decrease. The e⁻ deficient 17e⁻ species is more reactive because it wants to add ligands to reach 18e⁻'s.

$Mo(CO)_6$ is an 18e⁻ species. If it is reduced to $[Mo(CO)_6]^-$, a 19e⁻ species, it would be less stable. It would want to lose e⁻'s and may do it by losing a CO ligand resulting in a 17e⁻ species (that tries to gain e⁻ density by adding a ligand).

(11)(10 pts) Predict the number of metal metal bonds in the following compounds

(a) $[CpFeI(CO)]_2$

Cp 5e⁻
Fe 5e⁻
I 1e⁻
CO 2e⁻
16e⁻

each Fe is 2e⁻ deficient, so 2 M–M bonds

(b) $[ReI_2(CO)_2]_2^{2-}$

Re 7e⁻
2 I 2e⁻
2 CO 4e⁻
14e⁻

each Metal is 4e⁻ short, so 4 M–M bonds form

(12)(15 pts) Data for the d-d transitions of 2 Cr^{3+} octahedral molecules is shown in the table below. Calculate 10 Dq for each ion. Which ligand is the stronger field ligand?

$[CrF_6]^{3-}$	$[Cr(en)]^{3+}$
34,800 cm^{-1}	46,500 cm^{-1}
22,400 cm^{-1}	28,700 cm^{-1}
14,900 cm^{-1}	21, 850 cm^{-1}

For $[CrF_6]^{3-}$ the best fit is $\frac{Dq}{B} = 1.9$

The $\frac{E}{B}$ value here is 17 for the lowest energy transition ($E = 14,900 cm^{-1}$)

$\frac{14,900 cm^{-1}}{B} = 17 \quad \therefore B = 876 cm^{-1}$

$\frac{Dq}{B} = 1.9 \quad \frac{Dq}{876 cm^{-1}} = 1.9 \quad Dq = 789 cm^{-1}$

$10Dq = 7.9 \times 10^3 cm^{-1}$

For $[Cr(en)_3]^{3+}$, the best fit is $\frac{Dq}{B} = 3.0$ The $\frac{E}{B}$ value here for the lowest energy transition is 30 ($21,850 cm^{-1}$).

$\therefore \frac{21,850 cm^{-1}}{B} = 30$

$B = 728 cm^{-1}$

$\frac{Dq}{B} = 3.0 \therefore \frac{Dq}{728 cm^{-1}} = 3.0$

$Dq = 2185$

$10Dq = 2.2 \times 10^4 cm^{-1}$

$\therefore$ en is a stronger field ligand