CHEM-651 (F14)
Problem Set 4

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1. For each of the following sets of complexes, predict which will more rapidly undergo substitution following the pathway below. Please rationalize your choice.

$$ML_5X \rightleftharpoons ML_5 + X \xrightarrow{Y} ML_5Y$$

   (a) $[Co(H_2O)_5Cl]^{2+}$ versus $[Cr(H_2O)_5Cl]^{+}$
   (b) $[Re(bpy)_2(H_2O)Br]$ versus $[Ir(bpy)_2(H_2O)Br]^{2+}$
   (c) $[Fe(CN)_5(H_2O)]$ versus $[Os(CN)_5(H_2O)]$ (4 pts)
   (d) $W(CO)_6$ versus $[V(CO)_6]^{3+}$

2. Consider the following outer sphere electron transfer reaction (note: ⁎ = radioactive label):

$$[{}^*Ru(L)_6]^{2+} + [Ru(L)_6]^{3+} \rightleftarrows [{}^*Ru(L)_6]^{3+} + [Ru(L)_6]^{2+}$$

   (a) Draw a Marcus plot for this ET reaction. Please be sure to label the reorganization energy (λ), activation energy ($\Delta G^{\ddagger}$) and driving force ($\Delta G°$).

   (b) Crystallographic studies show that the change in Ru–L bond length between reduced and oxidized species is 0.09(2) Å for L = H_2O, but only 0.04(1) Å for L = NH_3. Based on this information, for which L is the rate of ET faster? Please be sure to rationalize your answer.

3. Consider the following reaction and kinetic data (taken at 30 °C in $CHCl_3$):

$$Ni(CO)_4 + L \rightarrow Ni(CO)_3L + CO$$

L	**[L] (M)**	***k*** **(10^5 s^{-1})**
PPh_3	0.133	6.7
PPh_3	0.344	6.8
$AsPh_3$	0.134	6.6
$SbPh_3$	0.135	6.6

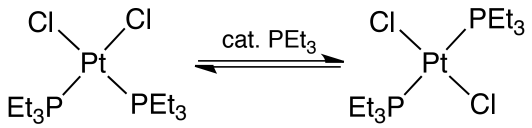
Activation Parameters for the Reaction of $Ni(CO)_4$ with Nucleophile			
L	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)	k (10^4 s^{-1})
PPh_3	24	13	50
$C^{18}O$	24	14	52

(a) What is the metal oxidation state, *d*-electron count and LFSE for the starting $Ni(CO)_4$?
(b) Propose a mechanism for this reaction and explain how it is consistent with the above data.
(c) Write an expression for the experimentally observed rate law.

5. Rank the following complexes in order of increasing rate of aquation.

$[Rh(NH_3)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Ir(NH_3)_6]^{3+}$, $[Mn(NH_3)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$

6. *cis*-$Pt(Cl)_2(PEt_3)_2$ is stable in benzene solution, however, addition of a catalytic amount of free PEt_3 facilitates an equilibrium with the *trans* isomer.



(a) Provide an explanation for why the trans-isomer is thermodynamically more stable than the starting *cis*-$Pt(Cl)_2(PEt_3)_2$.
(b) Propose a mechanism for this isomerization.