Take-Home Section, Chem 450 Exam 2
Name Key

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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 11.

(7)(15 pts) For the reaction below, the following kinetic data was found.

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

L (for Y = PMe_3)	Relative Rate	$\Delta S^{\ddagger}$
NMe_3	105	75
NH_3	25	60
PPh_3	5	45
Cl^-	200	-30
NO_2^-	205	-15
OH^-	220	-5

Explain the following data with respect to possible mechanisms.

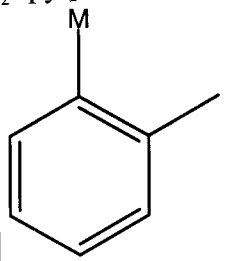
If you notice, the rate of substitution for neutral ligands is dependent on the leaving group and has a positive $\Delta S^{\ddagger}$, indicating a dissociative mechanism. For the anionic ligands, however, the rate is independent of the leaving ligands identity and $\Delta S^{\ddagger}$ is negative.

There is a change of mechanism when the ligands are changed. For the neutral ligands, the substitution is dissociative or I_d. For the anionic ligands the substitution is A or I_a.

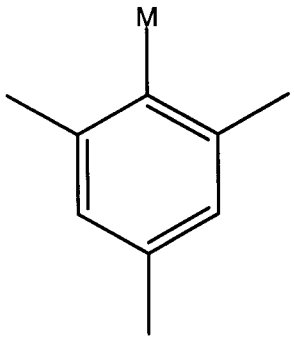
(8)(15 pts) For the following reaction, come up with an explanation for the following rate data. Do you think the reaction is associative or dissociative (why?)?

cis-$Pt(PEt_3)_2LCl$ + py ------> *cis*-$[Pt(PEt_3)_2Lpy]^+ + Cl^-$

L	relative rate
Cl^-	1
methyl	6
phenyl	8
o-tolyl	0.02
mesityl	0.0006



o-tolyl



mesityl

L is not the incoming or outgoing ligand.
As L becomes bulkier, the rate of substitution slows.
This suggests the incoming ligand is blocked by the bulkier groups and the mechanism is A or Ia. If the substitution was dissociative, the bulkier groups would cause more rapid dissociation, not a less rapid rate.

(9)(15 pts) Some substitutions can be accellerated by acid in solution. The acid protonates the outgoing ligand, decreasing the metal-ligand bond strength.

$$[M(H_2O)_5X]^{n+} + H_3O^+ \text{ ------> } [M(H_2O)_5HX]^{(n+1)+} + H_2O$$

$$[M(H_2O)_5HX]^{(n+1)+} + L \text{ -----> } [M(H_2O)_5L]^{(n)+1+} + HX$$

For which of the following ligands, decide which one should show the greatest accelleration of substitution rate by the addition of acid and explain why.

X	K_b
F^-	1.4×10^{-11}
S^{2-}	0.083
CN^-	1.7×10^{-5}

The strongest base is S^{2-}. Assuming it is still the strongest base when coordinated, it should be protonated to a much larger extent than CN^- or F^- and so the acceleration of its substitution rate should be greatest

(10)(15 pts) In metal carbonyl compounds, the rate of CO substitution is often found to increase with increasing CO streching frequency. Give an explanation for this.

The more backbonding to CO, the more electron density is in the CO π^* orbital, and the weaker the C≡O bond. the weaker the CO bond, the lower the ν_{CO} is. If the compound has high energy ν_{CO} streches, it has little backbondy to the CO ligand and weak M-CO bonds resulting in a rapid substitution rate for dissociative substitution

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

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

Cp 5
W 6
I 1
2CO 4
16 ← 2 short ∴ 2 M-M bonds

(b) $Ir_4(CO)_{10}(PPh_3)_3$

Cluster should have 18×4 = 72e⁻

4 Ir 36
10 CO 20
3 PPh_3 6
62

Short 10 e⁻ ∴ 5 M-M bonds

(c) $Mo_2(en)_4$

en = N N

each Mo has 4 N: bound to it

Mo 6e⁻
4N 8e⁻
14e⁻

∴ 4 M-M bonds