

*The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved.*

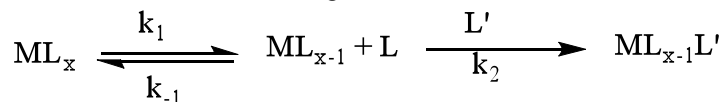
—Paul Dirac

*Chemistry is a class you take in high school or college, where you figure out two plus two is 10, or something.*

—Dennis Rodman

### Problem 1

Consider the following mechanism for a dissociative ligand substitution reaction:



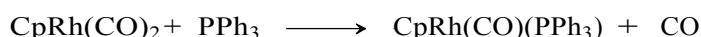
A) Applying the steady-state approximation to the intermediate  $\text{ML}_{x-1}$ , derive an empirical rate law for this reaction in terms of  $k_1$ ,  $k_{-1}$ ,  $k_2$ ,  $\text{ML}_x$ ,  $\text{L}$ , and  $\text{L}'$ .

B) Assume that the substitution reaction exhibits a rapid pre-equilibrium step, i.e.  $k_{-1} \gg k_2$ . What does the rate law simplify to in this case? Provide a physical interpretation of what this condition means.

C) The rate laws you derived in (A) and (B) are commonly encountered in reactions exhibiting either modest or rapid pre-equilibrium steps. Find two (organometallic) reactions in the literature that exhibit such a pre-equilibrium in their mechanisms. Write down the reaction mechanism and provide a reference.

### Problem 2

Consider the following reaction:



A) Propose two limiting mechanisms for the above ligand substitution. Include the structures and valence electron counts for all intermediates.

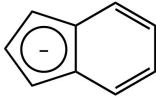
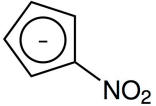
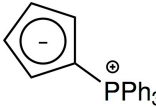
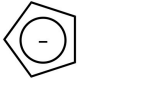
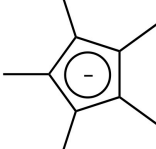
B) Under pseudo-first order conditions in  $\text{PPh}_3$ , the empirical rate law becomes  $v = k_{\text{obs}} [\text{Rh}]$ . For each of the limiting mechanisms derive expressions for  $k_{\text{obs}}$ . Show your work.

C) The following observations were made:

- In the presence of excess  $\text{PPh}_3$ , the rate is first order in rhodium complex.
- Plots of  $k_{\text{obs}}$  vs.  $[\text{PPh}_3]$  are linear with a zero intercept and indicate first order dependence on phosphine concentration
- The entropy of activation  $\Delta S^\ddagger = -20 \text{ e.u.}$

Based on these observations, which of the two mechanisms outlined in (A) is more consistent? Explain each observation above supports your conclusion.

D) The rate of substitution shows a dramatic ligand effect. As shown below, changes in the Cp ligand lead to changes in  $k_{\text{obs}}$  of over 10 orders of magnitude. Explain the differences in each case relative to the parent Cp ring. A discussion of reaction intermediates is required for a complete response.

	Cp ligand	$k_{\text{rel}}$
a		$4 \times 10^8$
b		$1.2 \times 10^3$
c		$1.1 \times 10^2$
d		1
e		$2.2 \times 10^{-2}$

E) The rate of substitution in complex (b) at room temperature shows some solvent effect. The rate constant increases by almost an order of magnitude moving from toluene to methanol. Explain how this observation is consistent with your answer to part (D).

### Problem 3

A reaction,



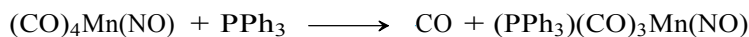
Has the following rate law:

$$v = k[\text{L}_n\text{ML}_1][\text{L}_2] + k'[\text{L}_n\text{ML}_1]$$

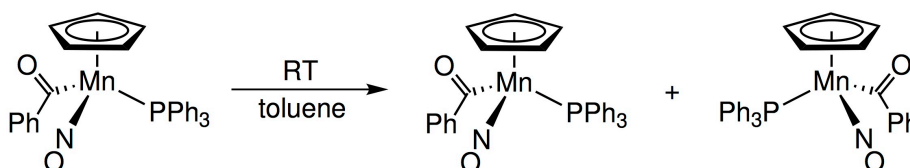
What does this rate law imply about the mechanism?

### Problem 4

When  $\text{PEt}_3$  reacts with  $\text{Mo}(\text{CO})_6$ , the reaction proceeds to *fac*- $\text{Mo}(\text{CO})_3(\text{PEt}_3)_3$ , but no further. Why do you think this is the case? Account for the stereochemistry of the product.

**Problem 5**

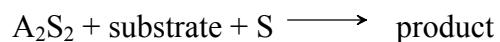
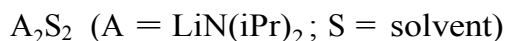
The reaction above shows a rate law that is second order overall, and first order in  $\text{PPh}_3$  and in metal complex. The entropy of activation is negative, and the following intermediate can be identified:  $(\text{PPh}_3)(\text{CO})_4\text{Mn}(\text{NO})$ . Give the mechanism, and describe the nature of the bonding of the NO ligand to Mn at each stage of the reaction.

**Problem 6**

Propose a mechanism for the above racemization reaction, whose rate is inversely proportional to  $[\text{PPh}_3]$ .

**Problem 7**

Read Collum's article on the kinetics of lithium diisopropylamide (LDA) reactions (*Angew. Chem. Int. Ed.* **2007**, 46, 3002.). In class we used the equations below to illustrate the principle that "the rate law provides the stoichiometry of the rate-limiting transition structure relative to the reactants".



$$d[\text{product}]/dt = k_{\text{obs}}[\text{substrate}]$$

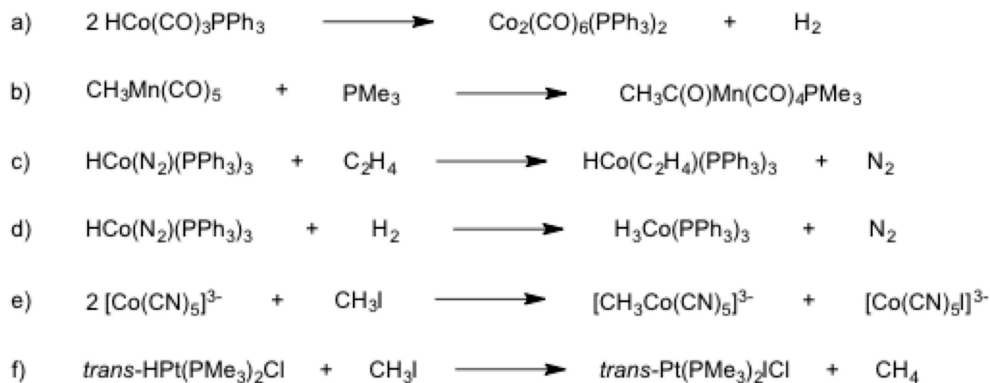
$$k_{\text{obs}} = k[\text{A}_2\text{S}_2]^a[\text{S}]^b$$

For the following values of  $a$  and  $b$ , sketch out a plausible, generalized mechanism that would be consistent with the observed rate law.

- A)  $a = 1/2, b = 0$
- B)  $a = 1/2, b = 1$
- C)  $a = 1, b = -1$

**Problem 8**

Assign the oxidation state of all of the transition metal complexes in the following reactions. Identify the reactions that involve oxidative-addition and/or reductive-elimination.

**Suggested Topics for Problem Writing Assignment (1-2 to be completed with PS #2)**

Valence Bond Theory

Electron Counting (Oxidation states, valence number, etc)

Kinetics

Trans effect/trans influence

Ligand substitution reactions

Oxidative additions/reductive eliminations

Migratory insertions

Dihydrogen/alkane complexes

Certainly, combinations of these topics can be used in a complete problem.