

## Organometallic Chemistry

Name: \_\_\_\_\_

### Problem Set #1

Due: Sept. 8, 2011

1. Consider the following reactions:

reaction 1:  $\text{PtCl}_2(\text{COD}) + \text{excess CO} \rightarrow \text{no reaction}$

reaction 2:  $\text{PtMe}_2(\text{COD}) + \text{excess CO} \rightarrow \text{PtMe}_2(\text{CO})_2 + \text{COD}$

(COD = 1,5-cyclooctadiene)

Explain the discrepancy in rates between reaction 1 (very slow) and reaction 2 (fast).

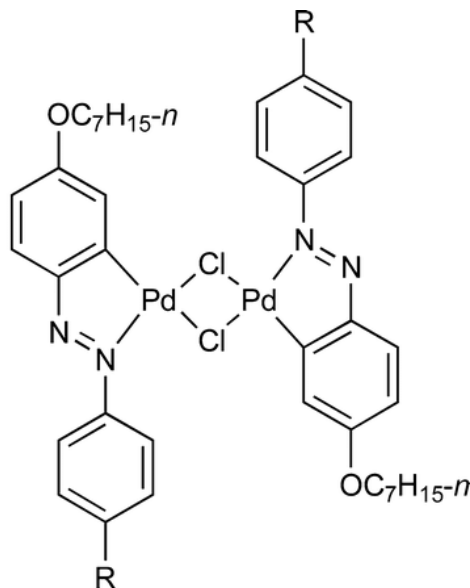
2. The following palladacyclic complex was reported in the journal *Organometallics* (2011 ASAP) by Benjamin Coe and co-workers. Use your knowledge of organometallic complexes to answer the following questions.

a) Identify all metal ligands as X-type or L-type.

b) The Cl's are a special type of ligand. What is this called?

c) What is the formal oxidation state of the Pd atoms?

d) What is the  $d^n$  electron count and the total electron count for the Pd in the complex?



R = NO<sub>2</sub> (1), CN (2), F (3), CO<sub>2</sub>Et (4)

3.  $\text{Pd}(\text{OAc})_2$  and  $\text{PdCl}_2$  are two common forms of palladium that are commercially available and useful for performing catalytic reactions. Based on our discussions in class, why would these be good forms of palladium to use as starting materials in catalytic reactions?

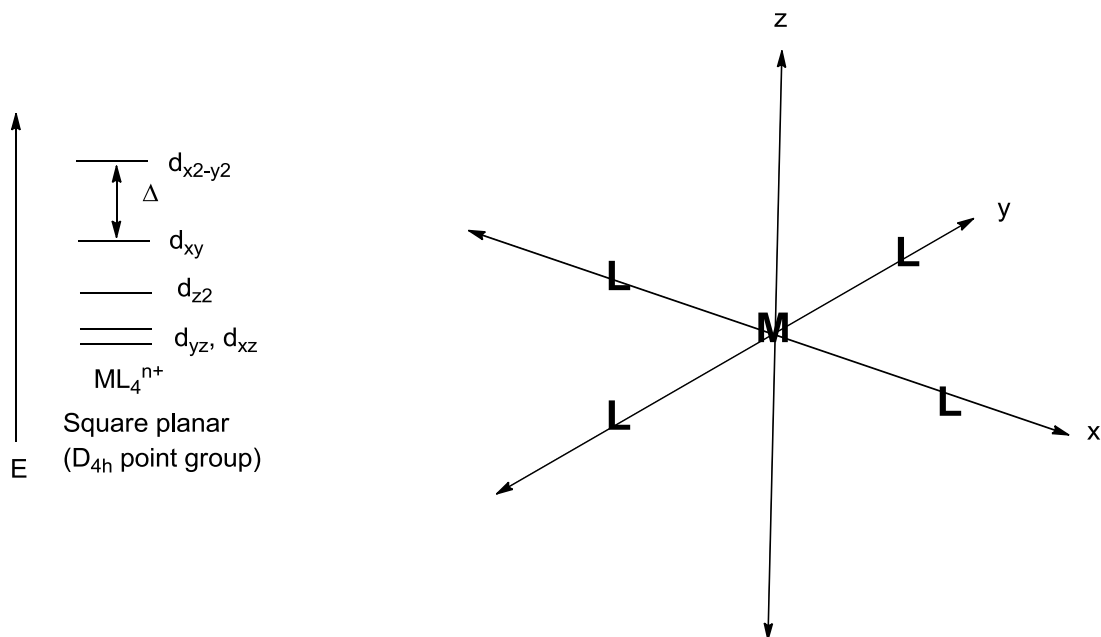
4. The acetate ligands of Pd can bind as monodentate or bidentate ligands.

a) Draw  $\text{Pd}(\text{OAc})_2$  with the acetates as monodentate ligands in one organometallic complex and bidentate ligands in another.

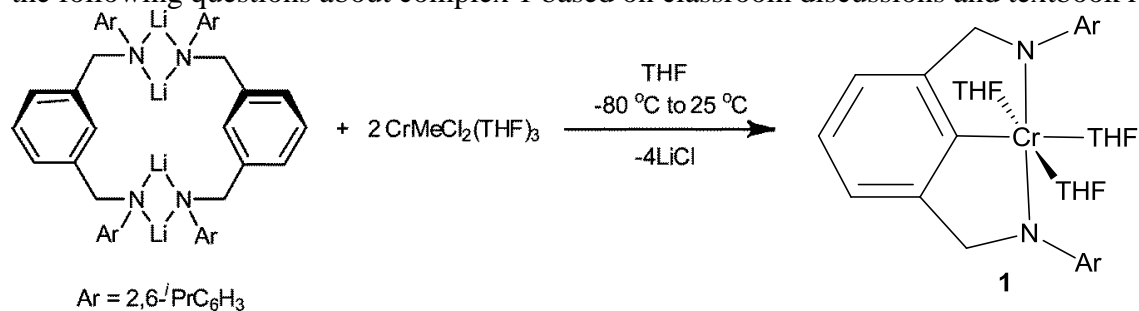
b) The acetate groups can also act as bridging ligands. Draw an example of  $\text{Pd}(\text{OAc})_2$  that illustrates the acetate group as a bridging ligand.

c) Which would seem to be the more favorable configuration for the  $-\text{OAc}$  group, as a bidentate ligand or as a bridging ligand? Briefly explain your answer.

5. The electronic orbital structure for square planar transition metal complexes is shown below. Create a diagram like the one shown below for each of the different d orbitals and rationalize why the orbital has the relative energy as shown, i.e. why is  $d_{x^2-y^2}$  the highest energy and so forth.



6. The following reaction was recently reported in the journal *Organometallics* (2011 ASAP). Answer the following questions about complex **1** based on classroom discussions and textbook reading.



Note: THF=tetrahydrofuran =

a) Determine the formal oxidation state for Cr, the  $d^n$  configuration and the total electron count for **1**.

b) What type of geometry is complex **1**?

c) Will complex **1** be diamagnetic or paramagnetic? Briefly explain.

c) Which ligand(s) would you expect to be the most labile in complex **1**?