

Organometallic Chemistry

Problem Set #1

Due: Sept. 8, 2011

Name: Hurricane Irene

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).

Me- (H_3C^-) ligand exerts a greater trans effect than Cl^- thereby stabilizing the transition state for substitution. This trans effect lowers the kinetic barrier to ligand substitution of the COD by the CO making this process more facile than with the $\text{PtCl}_2(\text{COD})$ complex.

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.

C-'s are X-type and N-'s are all L-type. Cl-'s are X type to one Pd and L type to the other.

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

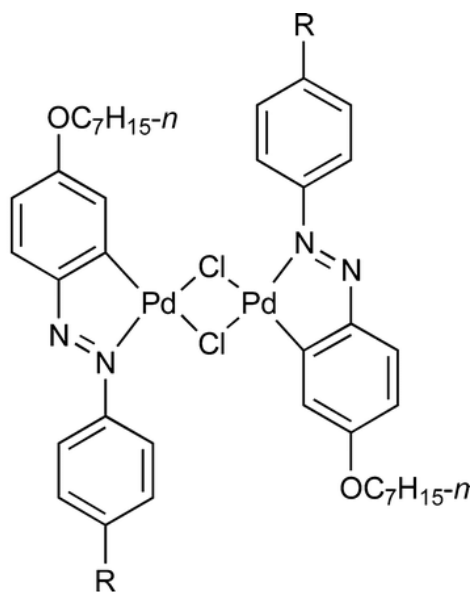
The Cl's are bridging ligands.

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

Pd(II)

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

The Pd is d^8 and has a total electron count of 16 (8 Pd e-'s and 4 ligands with 2 e-'s each).



R = NO_2 (1), CN (2), F (3), CO_2Et (4)

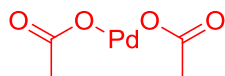
3. $\text{Pd}(\text{OAc})_2$ and PdCl_2 are two common forms of palladium that are commercially available and useful for performing catalytic reactions. Based on our discussions in class, why would these be good forms of palladium to use as starting materials in catalytic reactions?

Both Cl^- and $-\text{OAc}$ (acetate) are low field ligands which have weaker M-L bonds thereby permitting easy substitution of those ligands for others that might be necessary for catalytic processes to occur. Also, Pd is a 12 e- complex and therefore is probably eager to add more ligands.

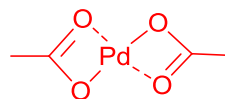
4. The acetate ligands of Pd can bind as monodentate or bidentate ligands.

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

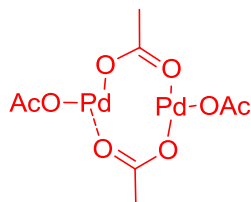
Monodentate acetate binding in $\text{Pd}(\text{OAc})_2$



Bidentate acetate binding in $\text{Pd}(\text{OAc})_2$



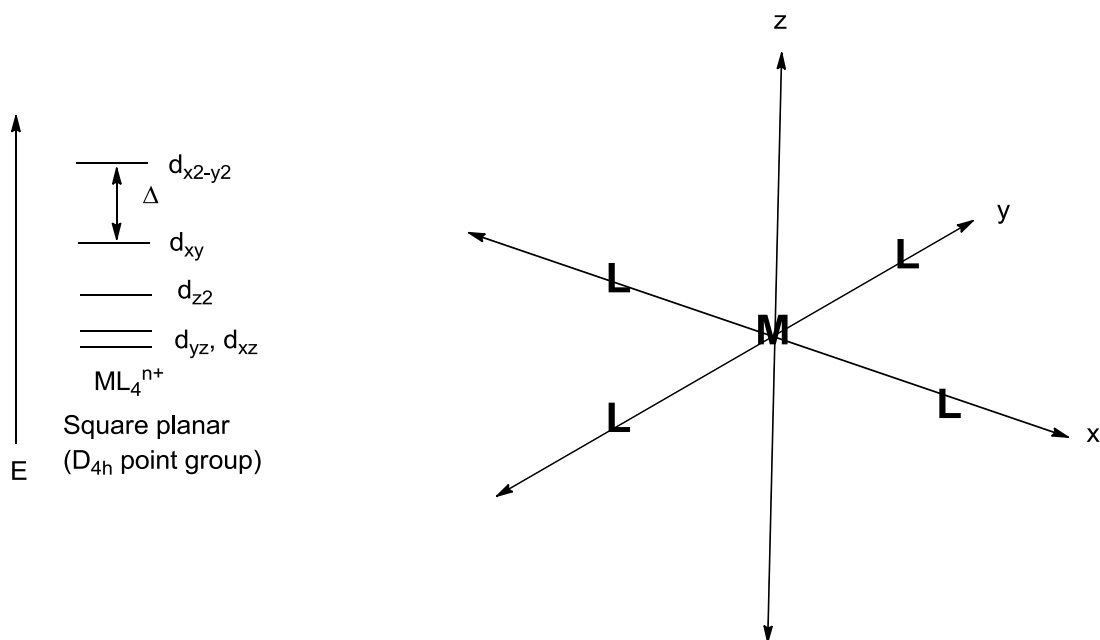
b) The acetate groups can also act as bridging ligands. Draw an example of $\text{Pd}(\text{OAc})_2$ that illustrates the acetate group as a bridging ligand.

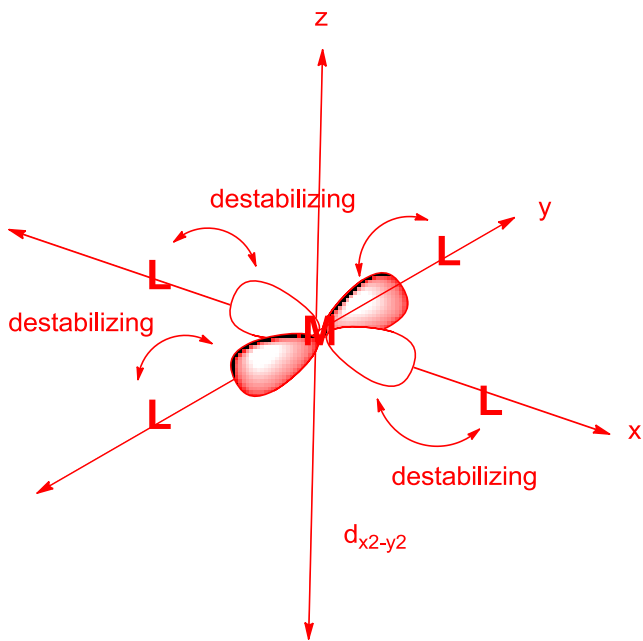


c) Which would seem to be the more favorable configuration for the $-\text{OAc}$ group, as a bidentate ligand or as a bridging ligand? Briefly explain your answer.

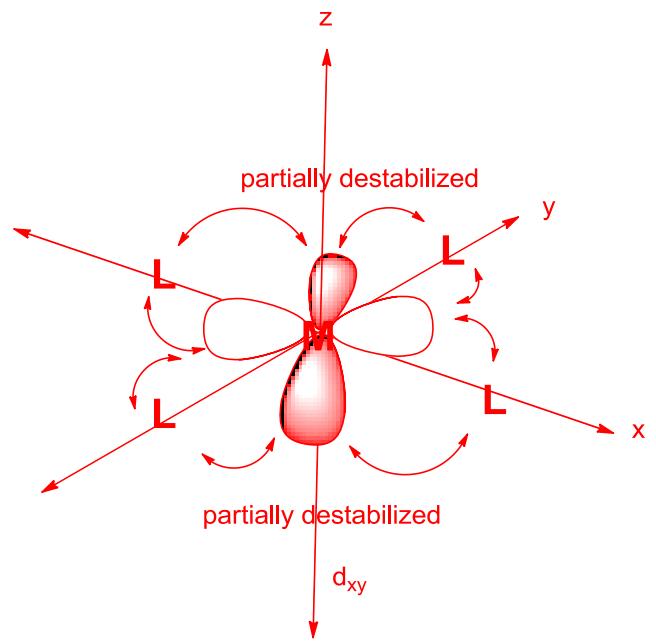
The bridging ligand would seem more reasonable since the bidentate acetate group forms a strained four member ring.

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.

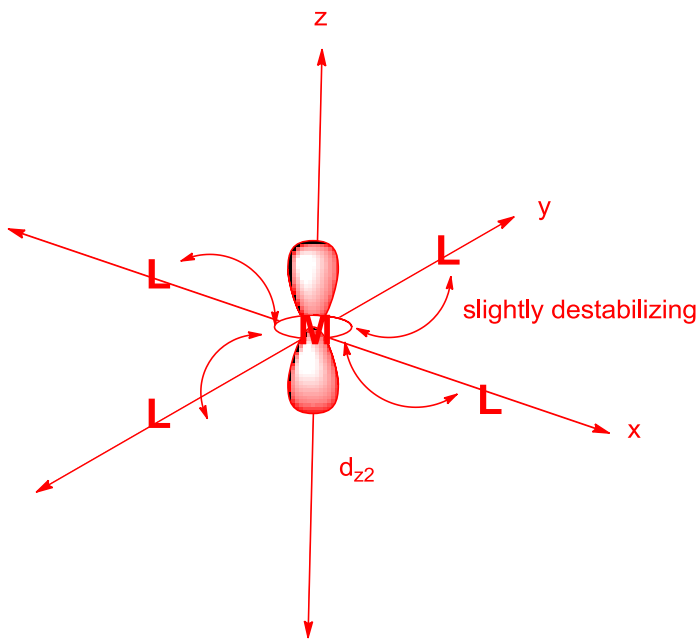




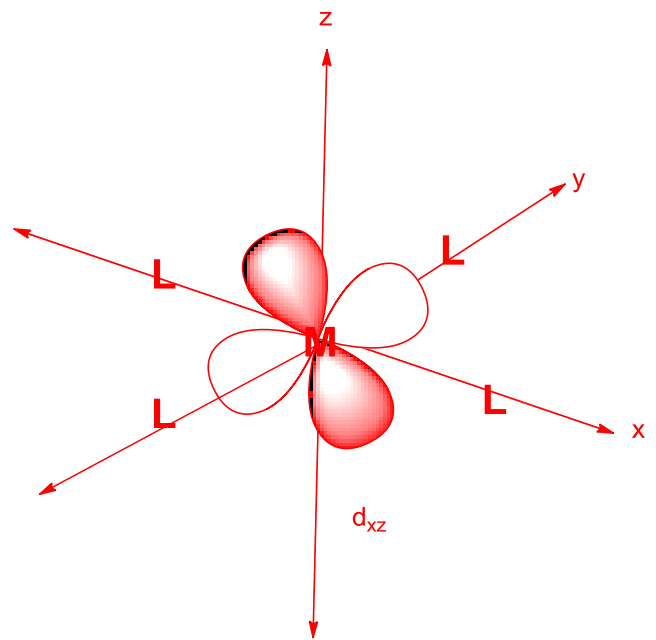
$d_{x^2-y^2}$ is the least stable because the orbitals project along the x and y axis directly at the incoming L's.



d_{xy} is found in the x-y plane of the L's, but not pointing directly at the L's. This creates some destabilization due to electrostatic repulsions, but not quite as great as for $d_{x^2-y^2}$.

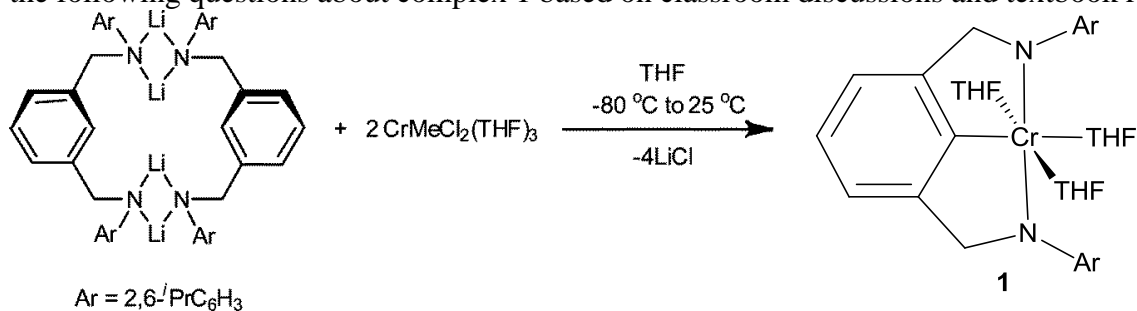


d_{z^2} has a central ring that projects, albeit only slightly, in the x-y plane. Most of the d_{z^2} orbital points away from the L's and therefore this orbital is more stable relative to $d_{x^2-y^2}$ and d_{xy} .



d_{xz} has no electron density in the x-y plane and therefore has the least amount of destabilization and is the most stable of the d orbitals. d_{yz} has a similar interaction with the ligands as d_{xz} .

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**.

oxidation state for Cr= 3 X-type ligands + 0 charge on complex = +3 or Cr(III)

d^n configuration= (6 valence e^- 's in neutral Cr atom) – (3 for oxidation state)= 3 or d^3

total electron count= $d^3 + [2 \times (6 \text{ total ligands})] = 15 e^-$'s around Cr.

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

octahedral

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

With a d^3 configuration, the Cr will be paramagnetic as it will most likely have three half-filled d orbitals.

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

The THF ligands since they are O ligands that have weaker bonds with the metal. In particular, the THF that is trans to the benzene C would be the most labile as the C:- (carbanion) group should have the strongest trans effect.