

## Problem Set #4

Due: Oct. 27, 2011

CHE-334: Complete 2 of 3 questions. CHE-534: Complete all 3 questions.

1. The following IR  $\nu_{\text{CO}}$  information was generated from reactions of Vaska's complex with the three reagents noted.

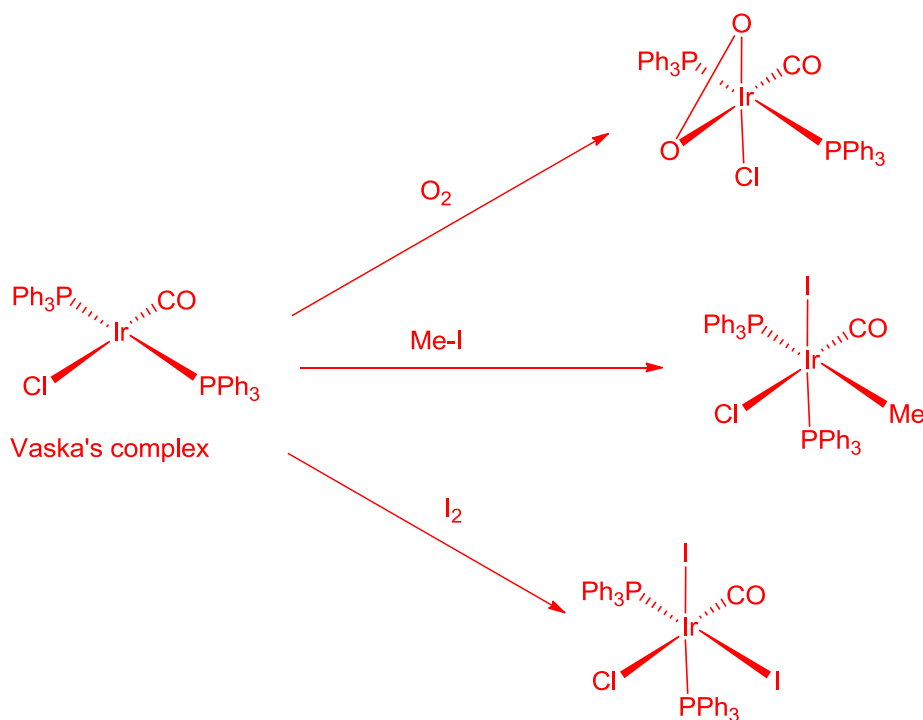
Vaska's Complex:  $1967 \text{ cm}^{-1}$

Vaska's +  $\text{O}_2$ :  $2015 \text{ cm}^{-1}$

Vaska's +  $\text{MeI}$ :  $2047 \text{ cm}^{-1}$

Vaska's +  $\text{I}_2$ :  $2067 \text{ cm}^{-1}$

a) Draw the reaction products that result from these three reactions.



b) Why do all three reactions result in a higher  $\nu_{\text{CO}}$ ?

All three are oxidative additions, so the Ir in Vaska's complex goes from  $\text{Ir}^+$  to  $\text{Ir}^{+3}$ . The higher oxidation state of Ir results in a weaker ability to backbond which results in a stronger CO bond and a higher  $\nu_{\text{CO}}$ .

c) What does the IR information say about the electron donating or withdrawing ability of the resulting ligands on the Ir?

The IR information shows that I- withdraws the most electron density from Ir, which makes the Ir the most electron deficient and the least capable of backbonding. In contrast, the  $\text{O}_2$  addition yields the least change in CO stretch and therefore does not withdraw as much electron density from the Ir metal.

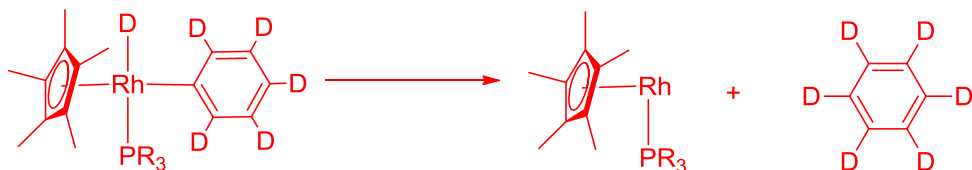
2. The results of a classic study of a reductive elimination process are shown below. Answer the questions below about this work based on the information in the table.

**Table V. Rates of Benzene Loss from  $(C_5Me_5)Rh(PR_3)(C_6D_5)D$  Complexes**

$PR_3$	cone angle, deg	$T$ , °C	$k$ , $s^{-1}$	$\Delta G^\ddagger$ , kcal/mol
$PMe_3$	118	23	$3.35 (17) \times 10^{-7}$	26.1
$PMe_2Ph$	122	23	$1.08 (5) \times 10^{-6}$	25.4
$PMePh_2$	136	24.5	$1.11 (6) \times 10^{-5}$	24.2
$PPh_3$	145	23	$3.85 (19) \times 10^{-4}$	21.9
$PMe_2(t-Bu)$	139	24.5	$6.6 (3) \times 10^{-6}$	24.5
$P(n-Bu)_3$	132	24.5	$2.4 (1) \times 10^{-6}$	25.1

W. D. Jones and V. L. Kuykendall, *Inorg. Chem.* **1991**, *30*, 2615.

a) Draw the reaction being studied.



b) Determine the oxidation state of the metal, total electron count and coordination number for both organometallic complexes.

starting material Rh complex:  $Rh^+$ , 18 e<sup>-</sup>, and CN=6

product Rh complex:  $Rh^{+3}$ , 16 e<sup>-</sup>, and CN=4

c) What do the experimental results say about the electronic effects of the phosphine ligands on the reductive elimination? Be as explicit as possible including citing at least three different phosphine groups that generate a trend that supports your answer.

The more electron withdrawing or  $\pi$  acidic (acceptor) the phosphine was, the faster the reductive elimination ( $k$  value) and the lower the energy of activation ( $\Delta G^\ddagger$ ). The following trend illustrates:

(most reactive)  $PPh_3$  >  $PMePh_2$  >  $PMe_2Ph$  >  $PMe_3$  (least reactive)  
 most  $\pi$  acidic and weakest  $\sigma$  donor least  $\pi$  acidic and strongest  $\sigma$  donor

d) What do the experimental results say about the steric effects of the phosphine ligands on the reductive elimination? Be as explicit as possible including citing at least three different phosphine groups that generate a trend that supports your answer.

The more sterically demanding the phosphine was, the faster the reductive elimination ( $k$  value) and the lower the energy of activation ( $\Delta G^\ddagger$ ). The following trend illustrates:

(most reactive)  $\text{PPh}_3$  >  $\text{PMe}_2(\text{t-Bu})$  >  $\text{P}(\text{n-Bu})_3$  >  $\text{PMe}_3$  (least reactive)  
 greatest cone angle least  $\pi$  acidic and strongest  $\sigma$  donor

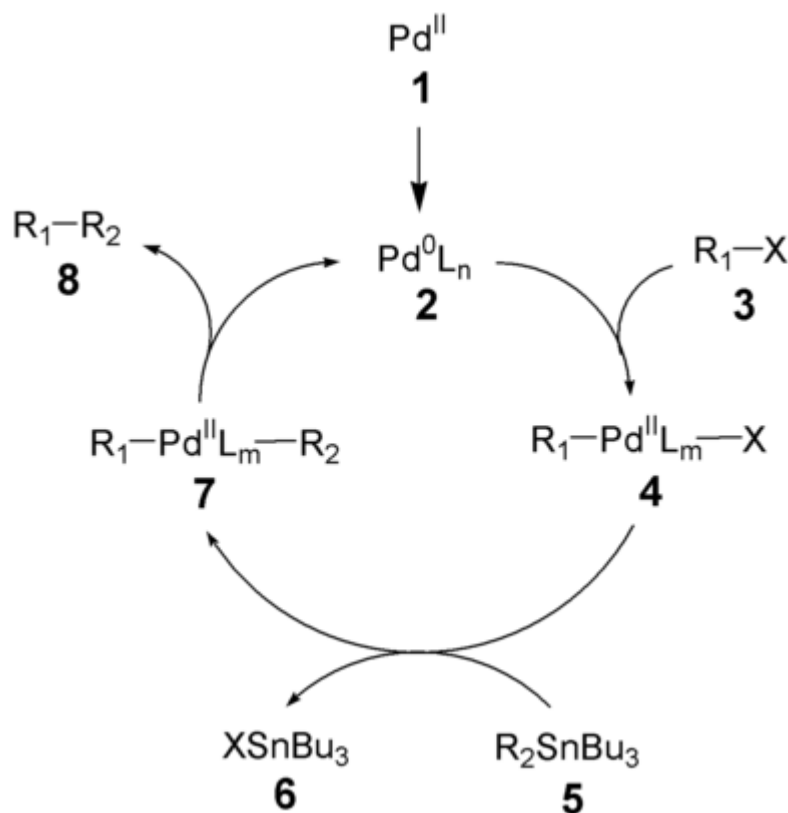
e) Explain why the trends described in part c and d are consistent with your understanding of the reductive elimination process.

Reductive elimination occurs more readily with a more electron poor, more sterically congested organometallic complex. The process of reductive elimination reduces the coordination number by two and reduces the formal metal oxidation state by two as well. Both processes are going to be thermodynamically favorable if the complex is more electron poor and more sterically congested.

3. The catalytic cycle of the Stille reaction, one of the first palladium-catalyzed cross coupling reactions discovered, is shown below.

a) Identify the three main steps in the catalytic cycle of the Stille reaction. Note:  $\text{R}_1$ =aryl or vinyl groups,  $\text{R}_2$ =alkyl, vinyl or aryl groups, X=a halide.

(figure taken from Wikipedia site for Stille reaction)



fundamental steps:

$2 \rightarrow 4$  is an oxidative addition

$4 \rightarrow 7$  is a ligand substitution or transmetalation

$7 \rightarrow 2$  is a reductive elimination

b) If you switched the ligand in the reaction from  $\text{PPh}_3$  to  $\text{PMe}_3$ , what effect you would expect on the transformation of 2 to 4?

Since 2 to 4 is an oxidative addition and the change in ligand from  $\text{PPh}_3$  to  $\text{PMe}_3$  adds a more electron rich and less sterically demanding ligand to the Pd, the oxidative addition should occur more rapidly.

The greater electron donation of the  $\text{PMe}_3$  would reduce the detrimental effects of the loss in electron density due to the Pd. Furthermore, the reduction in steric hindrance with  $\text{PMe}_3$  and its smaller cone angle would allow more space for the new ligands to fit around the Pd.

c) If you switched the ligand in the reaction from  $\text{PPh}_3$  to  $\text{PMe}_3$ , what effect you would expect on the transformation of **7** to **2**?

Since **7** to **2** is a reductive elimination and the change in ligand from  $\text{PPh}_3$  to  $\text{PMe}_3$  adds a more electron rich and less sterically demanding ligand to the Pd, the reductive elimination should occur less readily. The greater electron donation of the  $\text{PMe}_3$  would exacerbate the situation at the Pd where there is an increase in electron density during the reductive elimination. Furthermore, with less steric demands on the complex due to the smaller  $\text{PMe}_3$ , there is less need to reduce the congestion around the Pd.

d) If the slowest step in this particular catalytic cycle were the oxidative addition (as often happens), which would be the better choice in ligand?

$\text{PMe}_3$