**Mechanism of the Platinum(II)-Catalyzed Hydroamination of 4-Pentenylamines**

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*Organometallics* **2016** *35* (2), 113-125

DOI: 10.1021/acs.organomet.5b00821

**Discussion**

1. Why is this study important? What were the investigators hoping to improve and/or clarify?
2. Using the Covalent Bond Classification (CBC) method and [MLlXxZz]Q± notation, complete the following table (see Scheme 1 on page 114).

|  |  |  |  |
| --- | --- | --- | --- |
|  | Complex**3** | Complex **5a** | Complex **6a** |
| CBC [MLlXxZz]Q± |  |  |  |
| Valence number |  |  |  |
| Ligand bond number |  |  |  |
| Electron count |  |  |  |
| dn Configuration |  |  |  |

1. Rank Complexes **4**, **5**, and **6** in stability (pages 114 and 115). Justify your answer.
2. How did the investigators justify the structure of complex **6a** (pages 114 and 115)?
3. In Figure 1, the authors used 1H NMR with spin decoupling to help differentiate between diastereotopic protons in complex **6a**.
   1. Which nuclei were decoupled? For what purpose?
   2. Which spin-spin coupling is still present in Figure 1?
4. In Scheme 4 page 116, the authors investigate two possible pathways for the conversion of **4** to **5**.

A. Define the following terms:

1. Inner-sphere and outer-sphere

b. Syn or anti addition.

B. Label pathways a and b in Scheme 4 on page 116 with the terms defined in question 6A.

C. Why do equations 2 and 3 lead to different products (page 117)?

D. How did the investigators use the results depicted in equations 2 & 3 in their attempt to determine the pathway in Scheme 4 (pages 116 and 117)? How do the investigators defend their conclusion?

1. Draw which bonds are formed and which bonds are broken going from complex **5** to complex **6** in Scheme 10 (page 121).

1. Consider the mechanism of conversion of **4a** to **5a** illustrated in Scheme 5 and the corresponding Eyring plot in Figure 4 (page 117).

A Which step did the authors identify as the rate-determining step in Scheme 5?

B. What do the Eyring equation and the Arrhenius equation have in common?

C. What does the slope of an Eyring plot tell us about ΔH‡?  From the slope in Figure 4, do you expect ΔH‡to be positive or negative? What value did the investigators report?

D. What does the intercept of an Eyring plot tell us about ΔS‡?   What value did the investigators report?

E. From Scheme 4, would you expect the conversion of complex **4a** to **8a** to be a ligand substitution with an associative or dissociative mechanism? Is your answer consistent with question 7D?

1. In the complete conversion of **1** to **2**, the authors identified complex **6** as the catalyst resting state, and the protodemetalation of **6** as the turnover-limiting step (page 119).

A. Define protodemetalation.

B. Use equation 7 to write a rate law for the protodemetalation of **6** in the presence of ammonium (assume it is an elementary step). What do you expect the overall reaction order to be for this step?

C. What do the investigators conclude is the overall order of hydroamination catalysis (see Figure 9 page 120)?

D. What do the authors propose to explain this discrepancy (see Scheme 9 page 121)?

1. Consider the proposed catalytic cycle shown in Scheme 10 (page 121).

A. Indicate the turnover limiting step.

B.  Do investigators propose an intermediate or a transition state between **II** and **4**in Scheme 10? What is the evidence presented to support this proposition?

C. Propose future work that would add to what has been reported already about this mechanism.

