

## Reading Guide for

**“The mechanism of oxidative addition of Pd(0) to Si– H bonds: electronic effects, reaction mechanism, and hydrosilylation.”** Hurst, M. R.; Zakharov, L. N.; and Cook, A. K. *Chem. Sci.*, **2021**, *12*, 13045-13060. DOI: <http://dx.doi.org/10.1039/d1sc04419b>

## Preliminary questions

Why did the authors carry out this study? Why should the reader be interested in the hydrosilylation reaction? What is significant about the use of Pd?

Practice electron counting for complexes 1, 12, 13, and 14 (Figure 8). Classify them using CBC notation, give the  $d^n$  and valence electron counts, the LBN and the VN.

Use the information on page 13047, right, to explain what a  $\sigma$ -complex is. Start your analysis by considering that the authors use  $^{29}\text{Si}$  satellites as a marker for their structural hypothesis. What is an NMR satellite and how can it be used to guide their thinking? *Hint: through-bond coupling constants like a  $^1J_{\text{Si-H}}$  are larger for shorter bond lengths.*

Throughout the paper, the authors provide evidence that more electron poor silanes have higher conversion to the product. Briefly, does this claim make sense?

## Spectroscopy

When complex **1** was treated with silanes, new spectroscopic features were observed. What experimental evidence do they report to demonstrate the formation of a product that has a Pd-silane interaction?

Explain why cooling the  $L_2Pd(H)(SiR_3)$  complexes changed the  $^1H$  NMR signal from a triplet to a doublet, and the  $^{31}P\{^1H\}$  signal from a singlet to a doublet. The  $\{^1H\}$  notation means that the phosphorus signal was acquired with the proton decoupler on; no P-H coupling is observed. This is described on page 13047 and in the text near Figure 14.

In the text around figure 4, the authors discuss silanes as being strong trans influencing ligands. A ligand with a strong trans influence means that the ligand trans to it is more readily lost during a chemical reaction; this is a kinetic factor not a thermodynamic one. Use the information from Figure 4 to explain how silanes might be considered strong trans influencing ligands.

## Reaction equilibrium

On the first full paragraph on top right of page 13048 the authors claim that the evidence presented shows that the oxidative addition reaction of  $R_3Si-H$  to complex **1** is at equilibrium. How does this data show that? Given the information, is the reaction exo- or endothermic?

On page 13049, the authors show a van't Hoff plot (a plot of the  $\ln(K_{eq})$  vs  $1/T$  ( $K^{-1}$ ), Figure 6). The  $\Delta H$  and  $\Delta S$  of the reaction can be obtained from the slope and intercept of the plot. In the text, the authors justify the large and negative  $\Delta S$  due to the "reaction between three reactants to form two products." What are the three reactants and two products? Why would you expect a negative  $\Delta S$  for this reaction? Does the  $\Delta H$  of the reaction match your prediction from the previous equilibrium question?

What is a competition experiment? This is described in Figure 7. Why did they use this experiment instead of simply measuring the equilibrium like described on the previous page or in Scheme 1?

## Reaction kinetics

On the bottom left of page 13050, the authors present three possible pathways for the oxidative addition. Two of them are ruled out as being unlikely. What are they and why are they less likely than the mechanism shown in in Figure 8?

Are the mechanistic steps in Figure 8 reasonable? Use the electron counts for complexes **1**, **12**, **13**, and **14** to guide your thinking. Why doesn't complex **12** directly go to **14**; in other words, why are they invoking the  $\sigma$ -complex **13**?

A primary KIE (kinetic isotope effect) is a measure of the rate of the Si-H substrate divided by the rate of the Si-D substrate;  $k_H/k_D$ . The Si-H bond has a higher zero point energy, and if bond breaking were an important part of the mechanistic step, it would thus react faster than the corresponding Si-D bond. Why does the observation of a KIE point towards either step ii or iii being the rate determining step, and why does a larger KIE suggest step iii?

Figures 9 and 10 are a rare (in my experience) example of showing initial rate plots (usually introduced in a first year chemistry course) in a published primary literature article. How do these figures give the reaction order?

Figure 13 is an Eyring analysis which is plot of rate vs. reciprocal temperature and is used to determine the  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  of the reaction from the slope and intercept. The value of  $\Delta H^\ddagger$  ( $6 \pm 0.3$  kcal/mol) was not helpful but the large and negative value of  $\Delta S^\ddagger$  ( $-40 \pm 20$  cal/mol·K) was used to support the mechanism in Figure 8. How does the large and negative  $\Delta S^\ddagger$  support the mechanism?

Figure 15 summarizes the work presented in this paper. What Figure, equation, or table does each of the three listed numerical values ( $\Delta G$  values) come from? What do the numbers mean? Verify that the numbers are correct from the data they present (no need to propagate error 😊).