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Questions for Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543-6554 (doi: 10.1021/ja010624k).

1. Read the Introduction to the paper. The authors discuss a surprising finding in their earlier communication (Ref. 6). What was that surprising finding and how does that connect with the goals of this paper?
2. The authors studied phosphine exchange as a surrogate reaction for the olefin/phosphine exchange to understand whether associative or dissociative kinetics were favored for the first- and second-generation catalysts. Predict the sign of  $\Delta S^\ddagger$  for both reaction mechanisms.
3. Read the second paragraph of the section titled “Phosphine Exchange”. What technique do the authors use to track this reaction? Why were the reactions run at 80 °C?
4. Analyze the kinetics of phosphine exchange, as monitored by phosphorus NMR, in Table 1. Are these data consistent with an associative or dissociative mechanism for the first-generation catalysts? How about the second-generation catalysts?
5. Use the data in Table 1 to answer the following questions about phosphine exchange kinetics: (i) how does the halide influence  $k_B$ , (ii) how do the carbene substituents influence  $k_B$ , (iii) how does the phosphine substituent influence  $k_B$  (be careful of what is meant by “Cp”!), and (iv) how does NHC vs.  $PR_3$  influence  $k_B$ ?

*Break to discuss results as a class.*

6. Read the section “Initiation Kinetics” (two paragraphs only, not the following sections measuring the data). What is the authors’ hypothesis after observing the phosphine exchange kinetics? Which olefin is chosen to measure the initiation rate and why?
7. What technique was used to follow initiation kinetics? Why wasn’t the technique used to follow phosphine exchange used?
8. Analyze Table 2 and make two plots on the same graph in Excel with a linear fit (you need the slope): (i)  $k_{init}$  vs.  $k_B$  for the first-generation catalysts and (ii)  $k_{init}$  vs.  $k_B$  for the second-generation catalysts. If olefin saturation has been reached, the authors should observe a slope  $\sim 1$  because phosphine dissociation would be limiting. However, if olefin binding is competitive with the re-binding of phosphine a slope far from 1 should be observed. Have both catalyst generations reached saturation based on your analysis?

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**9.** Read the section “Initial Kinetics by NMR Spectroscopy”. Why is the lack of saturation in the first-generation catalysts such an issue?

**10.** The authors switch from NMR to UV-Vis spectroscopy to address the non-saturation of the first generation catalysts. What observable are they taking advantage of and what shortcoming of the NMR experiment does this new measurement address?

**11.** Analyze Table 3 and make a plot similar to those in problem **6** for the second-generation catalysts (but not on the same plot). Now that saturation has been achieved, is the hypothesis of phosphine dissociation being rate-limiting for initiation consistent with the conclusion for the first-generation catalysts?

**12.** Table 5 looks at the reactivity of back-reaction ( $k_{-1}$ ) with phosphine vs. forward reaction ( $k_2$ ) with olefin assuming a dissociative mechanism (Scheme 1b) is operative. Analyze Table 5 and interpret the difference between the first- and second-generation catalysts. What direct comparisons between the catalysts can be made?

*Read the first section of the Discussion, “Mechanism of Ruthenium-Catalyzed Olefin Metathesis Reactions”*

**13.** Which reaction pathway,  $I_a$  or  $I_d$ , has been conclusively demonstrated?

**Reflection.** Originally, the Grubbs group hypothesized that the superiority of the second-generation catalyst was due to the *trans* effect of the NHC ligand. Based on the  $k_{-1}/k_2$  analysis presented in this paper, what is the new hypothesis for its superiority?