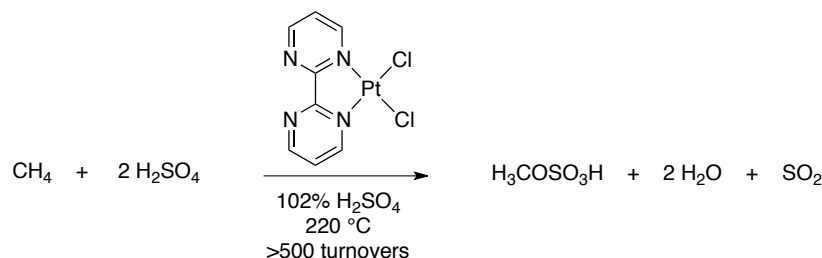


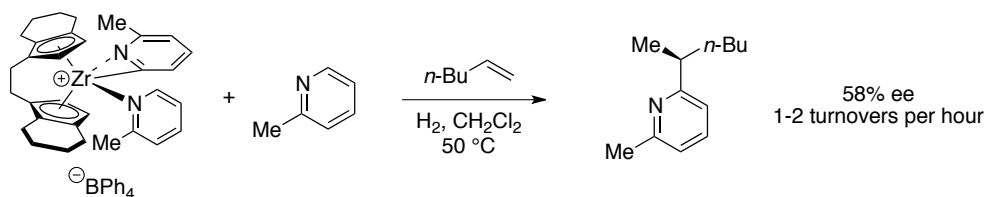
1. (20 points) Consider the following C–H functionalization reaction:



Ref. Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fuji, H. *Science* **1998**, *280*, 560-564.

- Draw a catalytic cycle for this reaction.
- Identify the special features of the bipyrimidine ligand that facilitates C–O bond formation.
Ref. Xu, X.; Kua, J.; Periana, R. A.; Goddard, W. A. III. *Organometallics*, **2003**, *22*, 2057-2068.
- The C–H bond activation selectivity is estimated to be >100:1. Based on the mechanism for C–H bond activation, propose an explanation for this selectivity.
- Based on the mechanism for this reaction, what would you expect the kinetic isotope effect to be? Use a reaction coordinate diagram and a potential energy diagram to illustrate your answer.

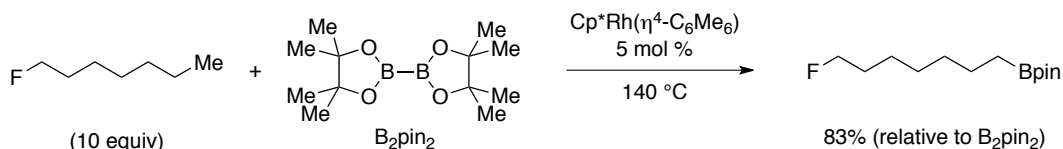
2. (15 points) Consider the following C–H functionalization reaction:



Ref. Rodewald, S.; Jordan, R. F. *J. Am. Chem. Soc.* **1989**, *111*, 778-779.

- Draw a catalytic cycle for this reaction. Your catalytic cycle should explain the mechanism for C–H bond cleavage with either a reactive intermediate or transition state.
- When the identity of the olefin is switched to styrene, the 1,2 insertion product is observed instead. Draw out the pertinent catalytic intermediates and critically analyze the differences that would lead to this selectivity.

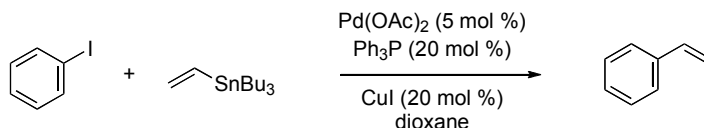
3. (15 points) Consider the following C–H bond borylation reaction:



Ref. Lawrence, J. D.; Takahashi, M.; Bae, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 15334-15335.

- Draw a catalytic cycle for this reaction. Your catalytic cycle should explain the mechanism for C–H bond cleavage with either a reactive intermediate or transition state.
- The by-product of the reaction H–Bpin was shown also to be a viable starting material for the borane. Draw a catalytic cycle that accommodates this observation.

4. (30 points) Consider the following Stille reaction:



- Provide a mechanism for the generation of the active Pd⁰ catalyst.

Ref. Amatore, C.; Jutland, A. *Acc. Chem. Res.* **2000**, *33*, 314.

- Using the Pd⁰ catalyst, draw a catalytic cycle for the reaction.

- What is the role of the Cu salt in this reaction?

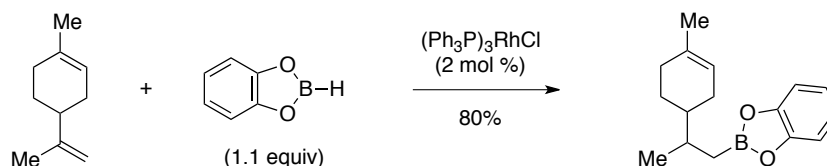
Ref. Farina, V.; Kapadia, S.; Krishnan, B.; Wang, C.; Liebeskind, L. *J. Org. Chem.* **1994**, *59*, 5905.

- Triphenylarsine can be used in place of the phosphine. When arsine ligands are used, no rate enhancement is observed when copper salts are added. Why?

Ref. Farina, V.; Kapadia, S.; Krishnan, B.; Wang, C.; Liebeskind, L. *J. Org. Chem.* **1994**, *59*, 5905.

Ref. Farina, V.; Krishnan, B. *J. Am. Chem. Soc.* **1991**, *113*, 9585.

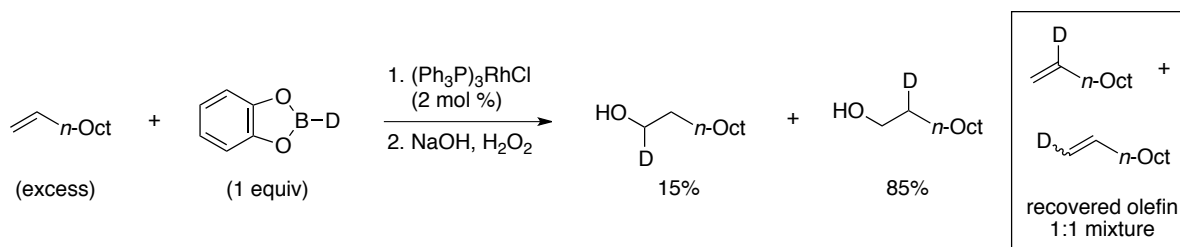
5. (20 points) Consider the following hydroboration reaction:



Ref. Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1992**, *114*, 6671-6679.

- Draw a catalytic cycle for this reaction.

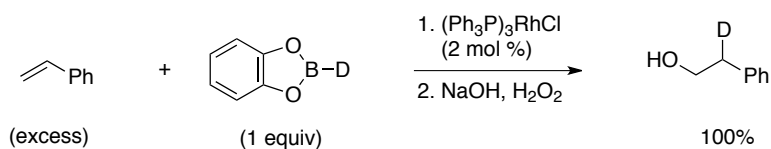
- b. In a subsequent study, the authors reported a deuterium labeling study using an excess of 1-decene:



Ref. Evans, D. A.; Fu, G. C.; Anderson, B. A. *J. Am. Chem. Soc.* **1992**, *114*, 6671-6685.

Draw a mechanism (and catalytic cycle) to accommodate these results.

- c. In contrast, when excess styrene was used as the olefin only a single isotopomer was observed:



Ref. Evans, D. A.; Fu, G. C.; Anderson, B. A. *J. Am. Chem. Soc.* **1992**, *114*, 6671-6685.

Why is only one isotopomer observed for styrene?