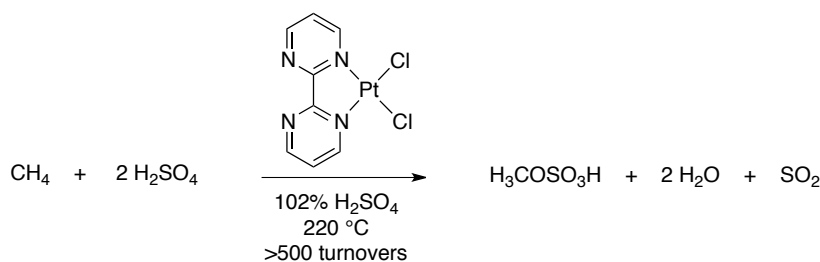


- (10 points) For the following combinations of transition metals and ligands, draw out their lowest energy structure. Use as many of each metal or ligand as necessary to achieve the formation of the lowest energy structure. Clearly define the geometry of the complex and if the complex is less than 18 e⁻ provide an explanation.
 - (Os)(O)
 - Re(Me)(O)
 - Ir(Cp^{*})(PMe₃)(H)
 - (bipy)PtCl₂
- (15 points) Draw the α- and π-bonding MO diagram for (Ph₃P)₂(CO)IrCl. Illustrate the orbital cartoons for the FMOs.
- (10 points) Which compound has the higher CO stretching frequency? Why?
 - Cr(CO)₆ or Ni(CO)₄
 - Mo(CO)₃(PF₃)₃ or Mo(CO)₃(PPh₃)₃
 - [Ag(CO)]⁺ or CO
- (20 points) Consider the following C–H functionalization reaction:

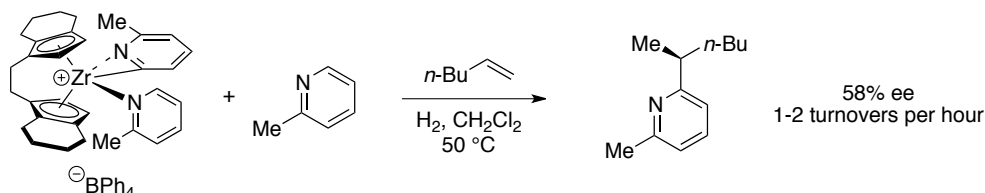


Ref. Periana, R. A.; Taube, D. J.; Gamble, S.; Taube, H.; Satoh, T.; Fuji, H. *Science* **1998**, *280*, 560-564.

- 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.

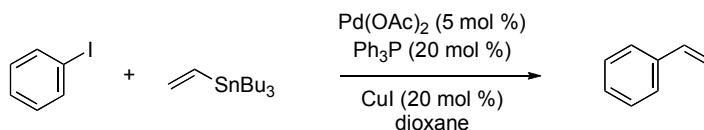
5. (15 points) Consider the following C–H functionalization reaction:



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.

6. (20 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.

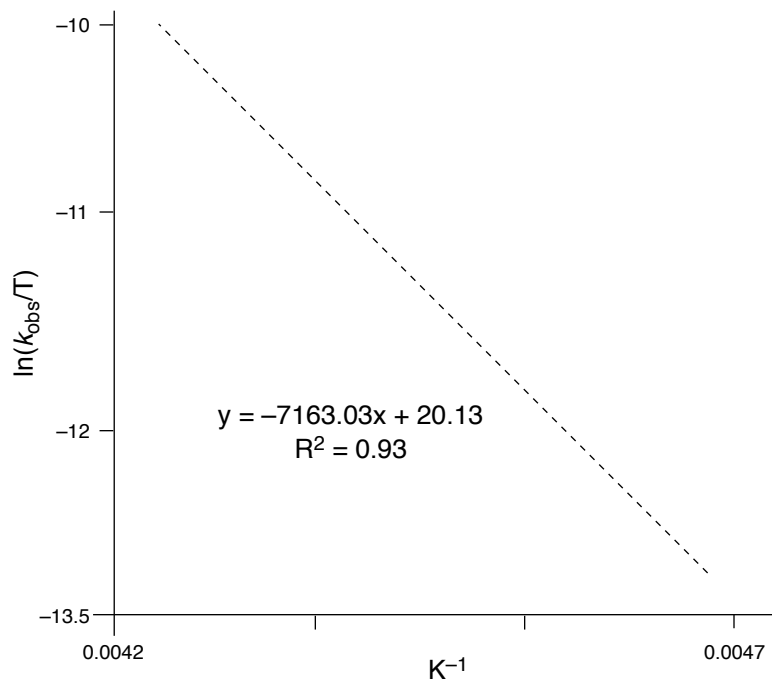
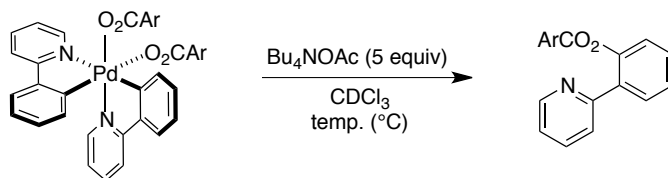
- What is the role of the Cu salt in this reaction?

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.

7. (10 points) Using the Eyring Equation, derive activation parameters from the following data. Place your answer in the box provided below.



ΔH^\ddagger (kcal·mol ⁻¹)	_____
ΔS^\ddagger (e.u.)	_____
$\kappa = 1.38 \times 10^{-23} \text{ m}^2\text{kg}\cdot\text{s}^{-2}\text{K}^{-1}$ $h = 6.626 \times 10^{-34} \text{ m}^2\text{kg}\cdot\text{s}^{-1}$	

Racowski, J. M.; Dick, A. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 10974.

What do the magnitude of the activation parameters tell you about the mechanism of this reaction?