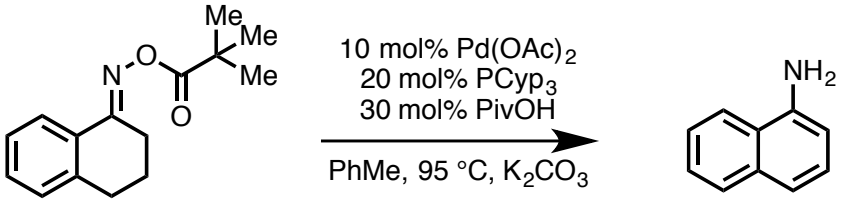
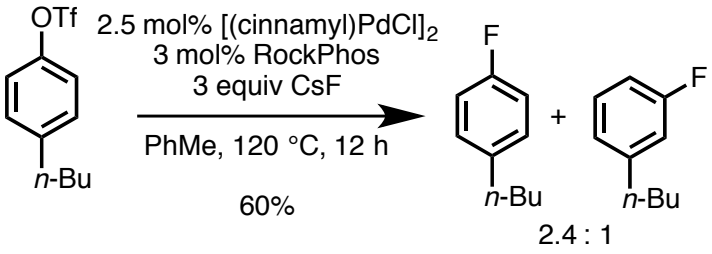
Organopalladium Mechanism Challenge. Palladium catalysis has continued to enriched organic synthesis since its advent in the 1960s. Based on our knowledge to date, oxidation states ranging from Pd(0) to Pd(IV) (including everything in between) have been implicated in catalysis. Working in teams, solve the following mechanistic puzzles and (when prompted) propose feasible experiments to elucidate their intricacies

A. In 2013, Stahl reported a palladium-catalyzed Semmler–Wolff reaction. Propose a catalytic cycle for this transformation.

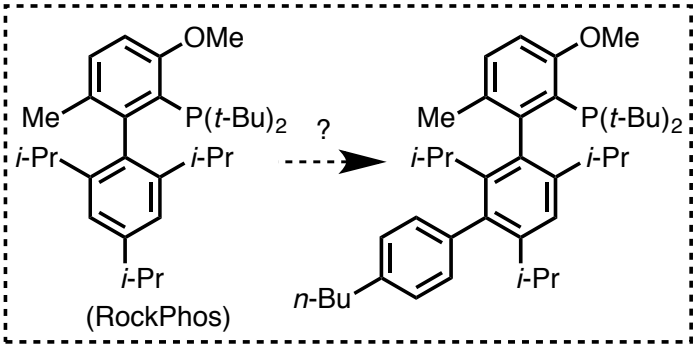


J. Am. Chem. Soc. **2013**, *135*, 13664–13667.

B. In a landmark publication in 2009, Buchwald report a catalytic system to perform fluorination of aryl triflates from inorganic fluoride (F^-) salts. Curiously, with certain substrates the reaction formed mixtures of regioisomers. (1) Propose one or more mechanisms that explain this phenomenon. (2) Design one mechanistic experiment that would potentially be consistent/inconsistent with your proposed mechanism. Under the reaction conditions, it was later found that the biarylphosphine ligand, RockPhos, was actually converted into a new, catalytically relevant species. (3) Propose a plausible reaction pathway to form this compound.

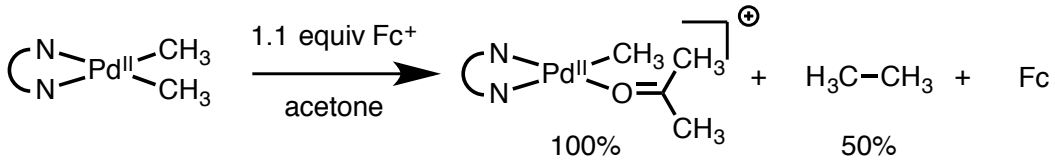


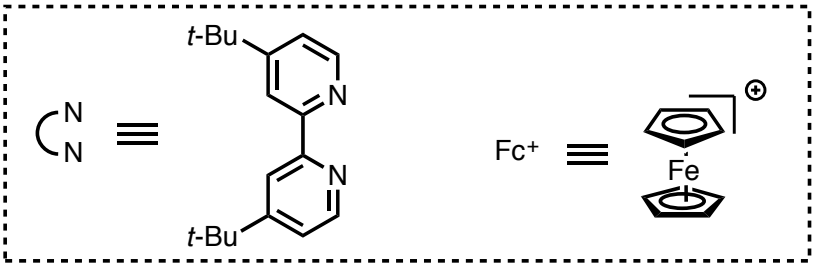
Science **2009**, *325*, 1661–1664.
J. Am. Chem. Soc. **2014,** *136*, 15757–15766.



J. Am. Chem. Soc. **2011**, *133*, 18106–18109.
J. Am. Chem. Soc. **2012**, *134*, 19922–19934.

C. In 2009, Sanford and Mayer reported the following reaction. (1) Draw out all possible mechanisms for this transformations (Hint: there are at least three). (2) Propose a series of experiments to disambiguate between these possibilities.





J. Am. Chem. Soc. **2009**, *131*,15618.