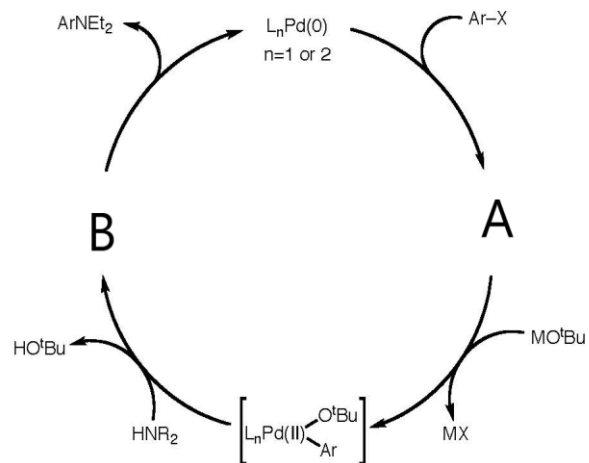
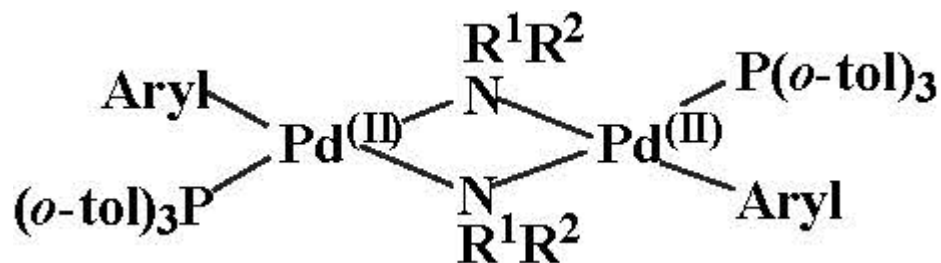
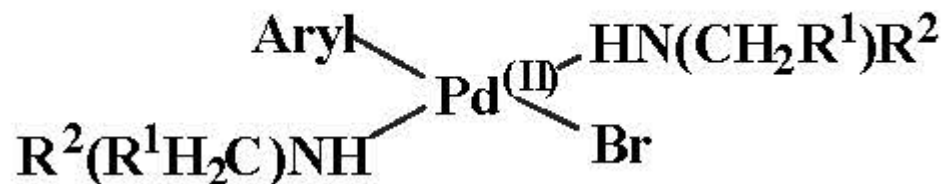


Pd-catalyzed C-N cross-coupling is similar to C-C cross coupling. Below is a catalytic cycle for Pd-catalyzed C-N coupling. Please draw the structures of intermediates A and B. And label their oxidation states.

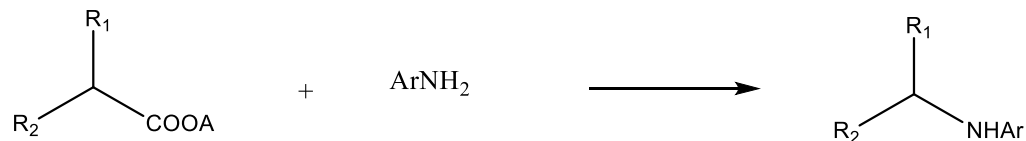


1. In Pd-P(*o*-tol)₃-catalyzed C-N coupling reactions, two compounds are formed in the reaction mixture. They are catalytically inactive. 1. Explain how they are formed. 2. Can a bidentate ligand influence the formation of these species? How? What is the net result?

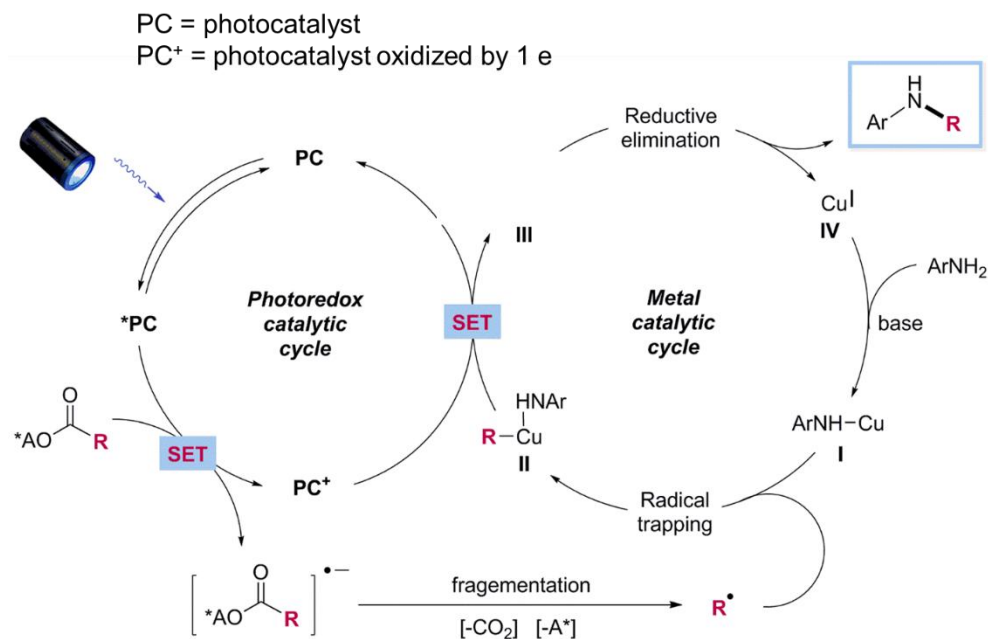


For Pd-catalyzed C-N coupling, the C-N reductive elimination is known to correlate with the electron density on the N nucleophiles. The more nucleophilic N is, the faster the reaction is. Based on this information, predict the order of the reaction rate for reductive elimination with (alkyl)NH⁻, (aryl)NH⁻, and (aryl)₂N⁻.

Cross coupling of alkyl electrophiles with nitrogen nucleophile is difficult. The group of Hu at EPFL developed a strategy to combine photocatalysis and Cu-catalyzed cross-coupling to achieve C(sp³)-N coupling.



They proposed the following catalytic cycle



- (i) Give the oxidation state of Cu in intermediates I, II, and III

- (ii) Draw a formula of intermediate III

- (iii) Explain why reductive elimination occurs on III, but not II.