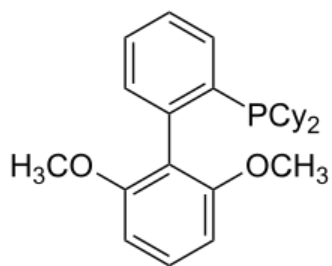
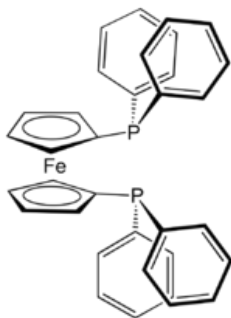


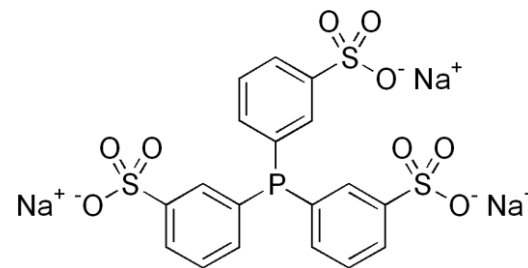
1. (a) Associate the most suitable phosphine ligands below for the following Pd-catalyzed cross-coupling reaction. (b) Give a brief explanation for each of your choice.



A, S-Phos



B, DPPF



C, TPPTS

Reactions:

- (i) Suzuki coupling of sterically hindered aryl chlorides; why?
- (ii) Suzuki coupling in water medium; why?
- (iii) Kumada and Suzuki coupling of alkyl nucleophiles; why?

(i) Suzuki coupling of sterically hindered aryl chlorides; why?

A: S-Phos. Because this ligand can stabilize one-coordinate Pd(0) species (along this line)

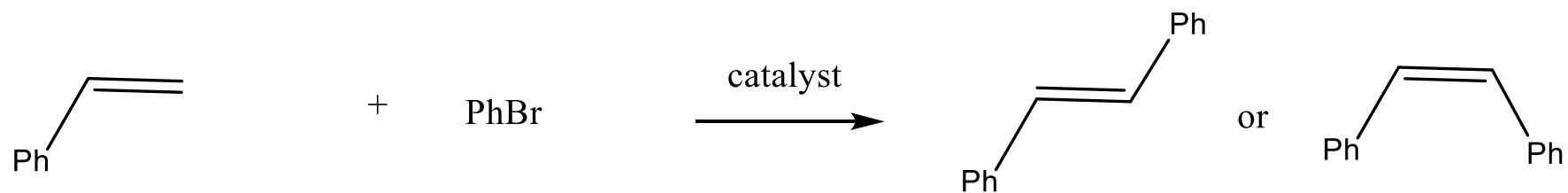
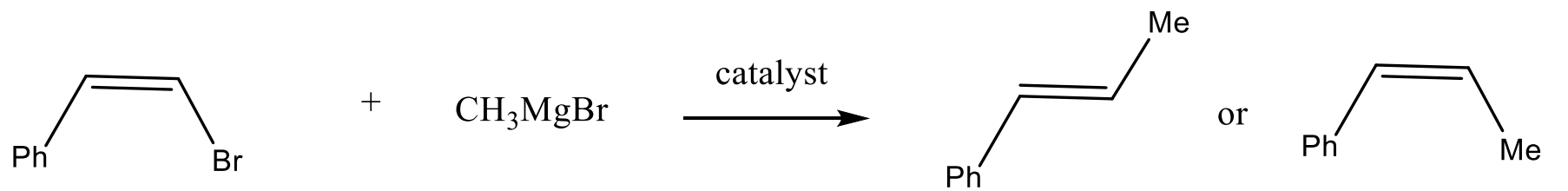
(ii) Suzuki coupling in water medium; why?

C: TPPTS. Because this ligand is water soluble (charged).

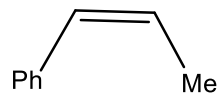
(iii) Kumada and Suzuki coupling of alkyl nucleophiles; why?

B: DPPF. Because this ligand is bidentate and suppress β -elimination. (second answer, promote reductive elimination)

Choose the correct major product in the following cross-coupling reactions. Explain why.

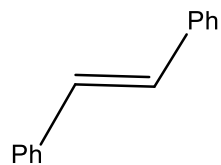


1:



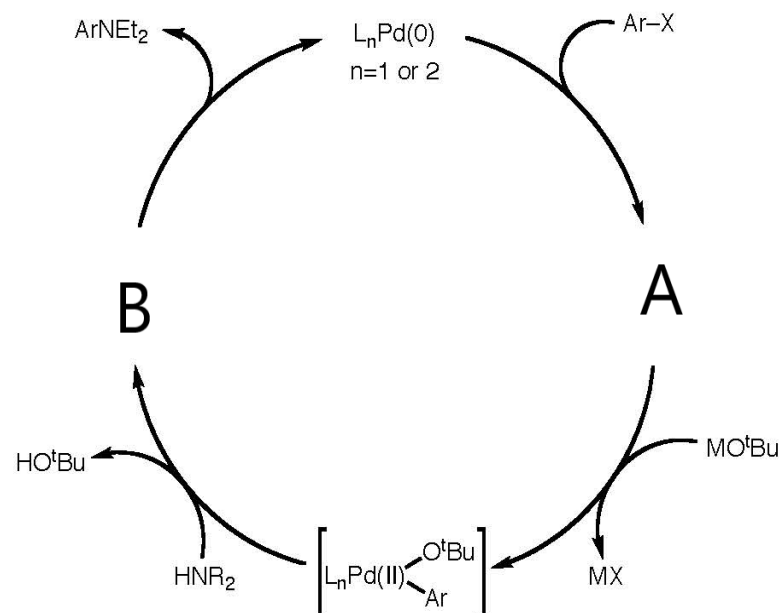
. Because cross coupling is stereospecific, or because the cis/trans configuration is conserved.

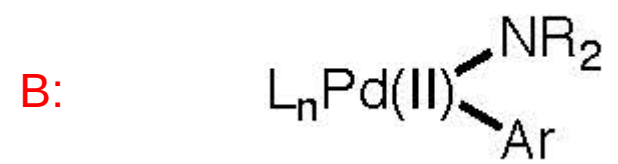
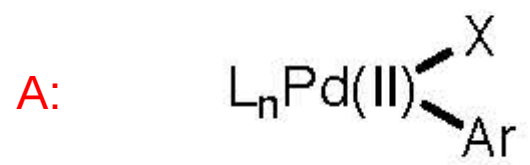
2:



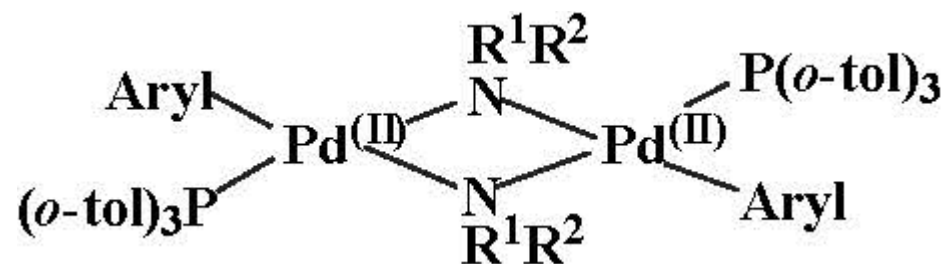
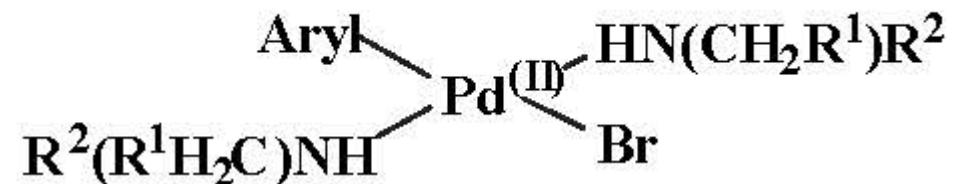
. Because heck reaction gives the trans isomer as the major product (due to the syn-elimination).

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?



Answer:

1. They are formed by replacement of $P(o\text{-tol})_3$ ligands of the Pd catalysts by the amine nucleophile, which is in excess.
2. Yes, a bidentate ligand will inhibit the replacement. As a result, the catalyst is more stable and expect to have higher turnovers.