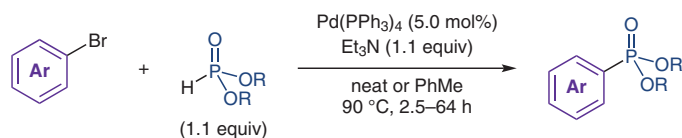
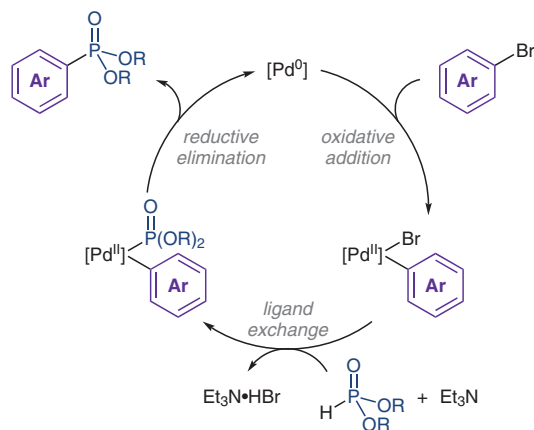


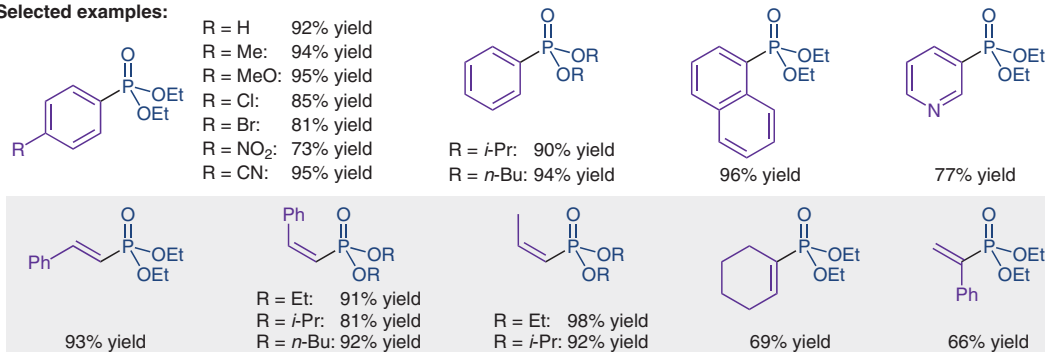
The Hirao Reaction: Palladium-Catalyzed Cross-Coupling of Dialkyl Phosphites with Aryl Halides



Proposed mechanism:



Selected examples:



Significance: In 1981, Hirao and co-workers disclosed the direct cross-coupling of aryl halides with dialkyl phosphites in the presence of a palladium(0) catalyst and an amine base to give the corresponding aryl phosphonates. In contrast to the Michaelis–Arbuzov reaction, this protocol enables the facile formation of C(sp²)–P bonds.

Comment: While most products were isolated in good to excellent yields, the cross-couplings of *para*-hydroxyphenyl and *para*-aminophenyl halides were ineffective. The substrate scope was successfully extended to vinyl halides (*Tetrahedron Lett.* 1980, 21, 3595), affording the corresponding vinyl phosphonates in high yields (see grey box).