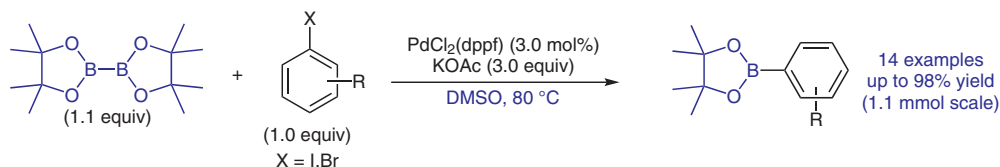
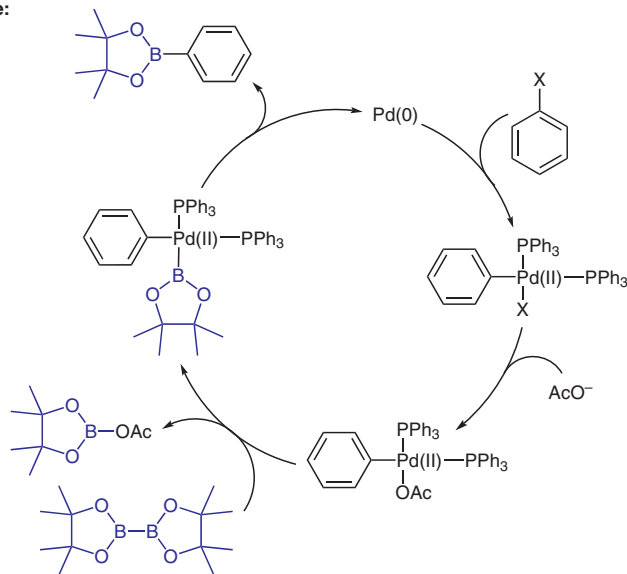


T. ISHIYAMA, M. MURATA, N. MIYAURA* (HOKKAIDO UNIVERSITY, SAPPORO, JAPAN)
Palladium(0)-Catalyzed Cross-Coupling Reaction of Alkoxydiboron with Haloarenes: A Direct Procedure for Arylboronic Esters
J. Org. Chem. **1995**, *60*, 7508–7510.

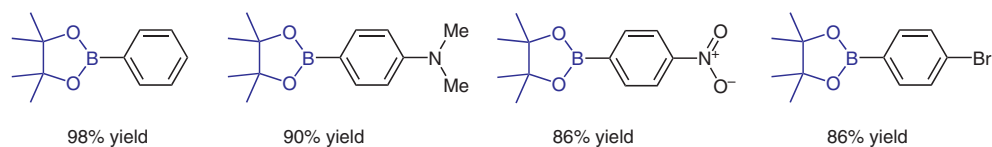
Miyaura Borylation Reaction



Proposed catalytic cycle:



Selected examples:



Significance: Miyaura and co-workers reported a direct catalytic approach for the preparation of arylboronic esters from aryl halides that proceeded in excellent yields and selectivity. This palladium-catalyzed reaction proved to have a broader functional group tolerance (e.g. to ketones, esters, nitriles) than prior syntheses of these useful synthetic linchpins via reactions with organometallic reagents.

Comment: The authors noted that the use of the KOAc as a base was critical to the formation of the desired aryl boronic esters in high yields and selectivities. They proposed that the base accelerates the transmetalation process, preventing the biaryl byproducts from being formed (see Review below).

Review: E. C. Neeve, S. J. Geier, I. A. I. Mkhallid, S. A. Westcott, T. B. Marder *Chem. Rev.* **2016**, *116*, 9091–9161.