ortho-C–H Borylation of Arenes Using Silica-Supported Rhodium Complexes

Significance: ortho-C–H Borylation of N-functionalized arenes with solid-supported Rh catalysts was described. A Rh complex prepared in situ from [Rh(OH)(cod)]_2 and silica-SMAP (a silica-supported 1-phospha-4-silabicyclo[2.2.2]octane derivative) was found to promote the ortho-borylation efficiently. In the presence of 0.5 mol% Rh (Rh/P = 1:1), the reaction of 2-phenylpyridine (1) with bis(pinacolato)diborone (2) gave 2-(2-pyridyl)phenylboronic acid pinacol ester (3) in 98% yield based on 2.

Comment: In the presence of Ph-SMAP (4-phenyl-1-phospha-4-silabicyclo[2.2.2]octane) instead of silica-SMAP, product 3 was obtained in only 17% GC yield. The catalyst was readily separated from the reaction mixture by filtration using Celite, although attempts to reuse the catalyst were unsuccessful.