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Rh-Catalyzed *Ortho*-Selective C–H Borylation of *N*-Functionalized Arenes with Silica-Supported Bridgehead Monophosphine Ligands

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Category

Polymer-Supported Synthesis

Key words

rhodium

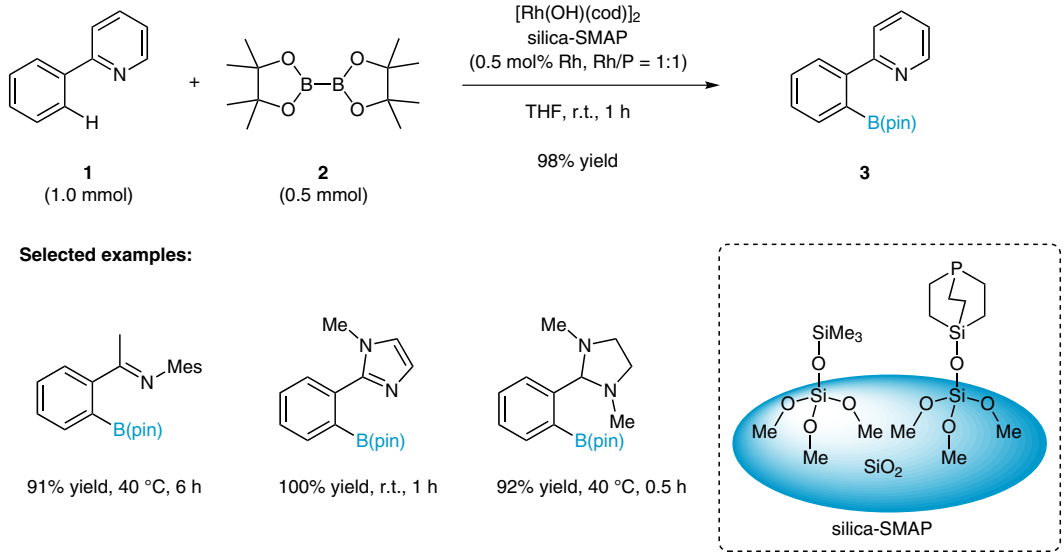
C–H activation

borylation

SMAP

silica-supported catalysis

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.

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