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Threefold Cross-Linked Polystyrene-Triphenylphospane Hybrids: Mono-P-Ligating Behavior and Catalytic Applications for Aryl Chloride Cross-Coupling and C(sp^3)–H Borylation
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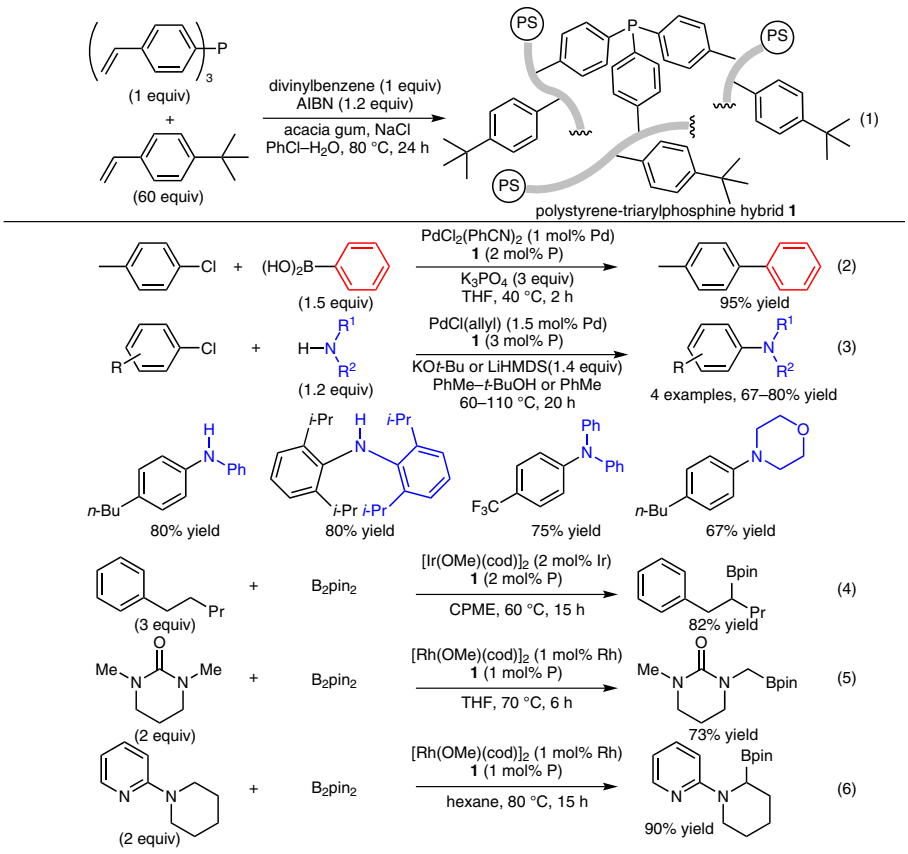
PS-PAr$_3$ Hybrid: Metal Complexation and Catalytic Applications



Significance: The polystyrene triarylphosphine hybrid **1** was prepared by radical emulsion polymerization of 4-*tert*-butylstyrene, divinylbenzene, and tris(4-vinylphenyl)phosphine (eq. 1). The cross-coupling of arylchlorides with phenylboronic acid and amines in the presence of Pd–**1** complexes, generated in situ, gave the corresponding coupling products (eqs. 2 and 3). Supported phosphine **1** was also effective for the iridium- or rhodium-catalyzed borylation of C(sp^3)–H bonds to afford the corresponding borylated products (eqs. 4–6).

Comment: PS-PAr$_3$ **1** was characterized with ^{13}C and ^{31}P CP-MAS NMR. In the Suzuki–Miyaura cross-coupling of 4-chlorotoluene with phenylboronic acid, the catalyst was recovered by simple filtration and reused with a decrease in catalytic activity (1st use: 91% yield, 3rd reuse: 94% yield, 4th reuse: 85% yield, 5th reuse: 70% yield, 6th reuse: 47% yield, 7th reuse: 24% yield). After the third reuse, TEM analysis of the recovered catalyst showed the aggregation of palladium metal.

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