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 aryl chlorides 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<sup>3</sup>)–H bonds to afford the corresponding borylated products (eqs. 4–6).

Comment: PS-PA<sub>3</sub> 1 was characterized with <sup>13</sup>C and <sup>31</sup>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 (1<sup>st</sup> use: 91% yield, 3<sup>rd</sup> reuse: 94% yield, 4<sup>th</sup> reuse: 85% yield, 5<sup>th</sup> reuse: 70% yield, 6<sup>th</sup> reuse: 47% yield, 7<sup>th</sup> reuse: 24% yield). After the third reuse, TEM analysis of the recovered catalyst showed the aggregation of palladium metal.