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Self-Assembled Poly(imidazole-palladium): Highly Active, Reusable Catalyst at Parts per Million to Parts per Billion Levels


Polymeric Imidazole Pd Catalyst for Cross-Couplings

Significance: A self-assembled polymeric palladium catalyst MEPI-Pd 3 was prepared via the molecular convolution of (NH₄)₂PdCl₄ and poly[(N-vinylimidazole)-co-(N-isopropylacrylamide)] 5. MEPI-Pd 3 (0.8–40 mol ppm Pd) promoted the allylic arylation/alkenylation of allylic esters 4 with aryl/alkenyloboron reagents 5 in water and/or alcohol to give the corresponding products 6. MEPI-Pd 3 (0.28 mol ppm–0.1 mol% Pd) drove the Suzuki–Miyaura coupling of a variety ofaryl chlorides, bromides, and iodides in water to give the corresponding biaryls 7.

Comment: MEPI-Pd 3 was reused without loss of catalytic activity for the allylic arylation and the Suzuki–Miyaura coupling. MEPI-Pd with 0.28 mol ppm Pd efficiently promoted the Suzuki–Miyaura coupling of iodotoluene and phenylboronic acid to afford 7b quantitatively with a TON of 3,570,000 and a TOF of 119,000 h⁻¹. The authors reported a preliminary communication for the allylic arylation of allylic acetates (Angew. Chem. Int. Ed. 2011, 50, 9437; Synfacts 2011, 1380).

Preparation of an imidazole palladium catalyst (MEPI-Pd 3):

Allylic arylation–alkenylation of allylic acetates/carbonates:

The Suzuki–Miyaura coupling:

7b X = Cl, 92% yield (3: 0.1 mol%)
7c X = Cl, 91% yield (3: 0.1 mol%)
7d X = Cl, 91% yield (3: 40 mol ppm)
7b X = Cl, 98% yield (3: 40 mol ppm)