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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

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

\[
\text{(2 mol equiv imidazole)} \quad + \quad \text{(NH}_4\text{)PdCl}_4 \quad \text{(1 mol equiv Pd)}
\]

\[
\text{MeOH-H}_2\text{O} \quad 80^\circ\text{C}, 30 \text{ min}
\]

**Significance:** A self-assembled polymeric palladium catalyst MEPI-Pd 3 was prepared via the molecular convolution of (NH\(_4\))\(_2\)PdCl\(_4\) 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/alkenylboron 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 of aryl 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).

**Key words**
- allylic arylation
- amphiphilic imidazole polymers
- heterogeneous palladium catalysis
- Suzuki–Miyaura coupling

**Category**
- Polymer-Supported Synthesis

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