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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):

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\text{Allylic arylation–alkenylation of allylic acetates/carbonates:}
\]

\[
\begin{align*}
R^1 \text{X} &+ \text{R}^2 \text{B(OH)}_2 \\
\text{MEPI-Pd 3} & (0.8–40 \text{ mol ppm}) \\
\text{TBAF, K}_2\text{CO}_3, \text{H}_2\text{O} & 100 \degree \text{C}, 2–20 \text{ h}
\end{align*}
\]

\[
\begin{align*}
\text{X} = \text{Cl} &; (20 \text{h}) \\
1\text{st run: 98\% yield, 5th run: 97\% yield} \\
\text{X} = \text{Br} &; (3 \text{ mol ppm}) \\
\text{X} = \text{Br} &; (40 \text{ mol ppm})
\end{align*}
\]

The Suzuki–Miyaura coupling:

\[
\begin{align*}
\text{MEPI-Pd 3} & (66 \text{ mol ppm}) \\
\text{TBAF, K}_2\text{CO}_3, \text{H}_2\text{O} & 100 \degree \text{C}, 22 \text{ h}
\end{align*}
\]

\[
\begin{align*}
\text{7b} \text{ X} = \text{Cl}, & 96\% \text{ yield} \\
\text{7c} \text{ X} = \text{Cl}, & 98\% \text{ yield} \\
\text{7d} \text{ X} = \text{Cl}, & 95\% \text{ yield}
\end{align*}
\]

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)]2]. 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).