Polymeric Imidazole Pd Catalyst for Cross-Couplings

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

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\begin{align*}
\text{(2 mol equiv imidazole)} & + (\text{NH}_4)_2\text{PdCl}_4 \\
(1 \text{ mol equiv Pd}) & \rightarrow \text{MeOH} - \text{H}_2\text{O} \\
80 ^\circ \text{C}, 30 \text{ min} & \rightarrow \text{MEPI-Pd 3} \\
M = \text{PdCl}_2 \text{ and Pd}^0
\end{align*}
\]

Allylic arylation–alkenylation of allylic acetates/carbonates:

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\begin{align*}
\text{R}_1^1 & + \text{R}_2^1 \text{B(OH)}_2 \\
\text{X} = \text{OAc or OCO}_2\text{Me} & \rightarrow \text{R}_1^2 \text{R}_3^2 \text{Na} \\
\text{MEPI-Pd 3} (0.8-40 \text{ mol ppm}) & \rightarrow \text{MeOH} - \text{H}_2\text{O} \\
\text{iPrOH} - \text{H}_2\text{O} (1:1) & \rightarrow \text{50 examples} \\
50 ^\circ \text{C}, 3-4 \text{ h} & \rightarrow \text{TON: 1,250,000; TOF: 104,000 h}^{-1}
\end{align*}
\]

The Suzuki–Miyaura coupling:

\[
\begin{align*}
\text{R}_1^1 \text{X} & + \text{R}_2^1 \text{B(OH)}_2 \\
\text{MEPI-Pd 3 (40 mol ppm–0.1 mol%)} & \rightarrow \text{TBAF, K}_2\text{CO}_3, \text{H}_2\text{O} \\
100 ^\circ \text{C}, 2-20 \text{ h} & \rightarrow \text{TON: 3,570,000; TOF: 119,000 h}^{-1}
\end{align*}
\]

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).