Y. M. A. YAMADA,* S. M. SARKAR, Y. UOZUMI* (RIKEN ADVANCED SCIENCE INSTITUTE, WAKO, INSTITUTE FOR MOLECULAR SCIENCE AND THE GRADUATE SCHOOL FOR ADVANCED STUDIES, OKAZAKI, JAPAN)

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 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).

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

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

- \[R^1\text{Cl} + R^2\text{B(OH)}_2\rightarrow MEPI-Pd 3 (66 \text{ mol ppm}) \]
- \[\text{MeOH–H}_2\text{O, 100 °C, 22 h} \]
- \[7b \text{ X = Cl; 96% yield} \]
- \[\text{TON: 3,570,000; TOF: 119,000 h}^{-1} \]

**The Suzuki–Miyaura coupling:**

- \[X = \text{Cl; (20h)} \]
- \[7a X = \text{Cl; 98% yield, 5th run: 97% yield} \]
- \[7b X = \text{Cl, 92% yield} \]
- \[7c X = \text{Cl, 91% yield} \]
- \[7d X = \text{Cl, 91% yield} \]
- \[7e X = \text{Cl, 92% yield} \]
- \[7f X = \text{Cl, 98% yield} \]
- \[7g X = \text{Cl, 95% yield} \]

**SYNFACTS Contributors:** Yasuhiro Uozumi, Yoichi M. A. Yamada, Shaheen M. Sarkar

SYNFACTS 2012, 8(5), 0569 Published online: 18.04.2012

DOI: 10.1055/s-0031-1290933; Reg-No.: Y03912SF