Polymer-Incarcerated Chiral Rh/Ag Nanoparticles for Asymmetric 1,4-Addition Reactions of Arylboronic Acids to Enones: Remarkable Effects of Bimetallic Structure on Activity and Metal Leaching


Asymmetric Miyaura–Michael Reaction with Polymeric Rh/Ag Catalysts

**Significance:** Polystyrene-based polymer-incarcerated bimetallic rhodium nanoparticle catalysts PI/CB Rh/Ag 2a–b were prepared from co-polymer 1, carbon black (CB), [Rh(OAc)₂]₂, and AgSbF₆. Asymmetric 1,4-addition of arylboronic acids to enones was carried out with 2 and chiral ligand 3 to give the corresponding ketones in 70–99% yield with 74–98% ee without leaching of rhodium.

**Comment:** Catalyst 2a was reused 13 times for the reaction of phenylboronic acid with 2-cyclohexenone. After the 10th use, the recovered catalyst was heated at 170 °C to regain its catalytic activity (1st–8th use: >94% yield, 9th use: 67% yield, 10th use: 60% yield, 11th–14th use: >90% yield, with 98% ee in all cycles).

**Preparation of PI/CB Rh/Ag catalyst 2:**

1) carbon black (CB) [Rh(OAc)₂]₂, AgSbF₆
2) NaBH₄, diglyme
3) NaBH₄, diglyme, 6 h
4) wash with H₂O–THF
5) wash with CH₂Cl₂ and THF

**Asymmetric 1,4-addition with PI/CB Rh/Ag catalyst 2:**

1) arylboronic acid (R₁ArB(OH)₂)
2) catalyst 2 (0.75–1.5 mol% Rh)
3) ligand 3 (1–2 mol%)
4) Me₆H₂O (1:2)
5) 100 °C, 7–24 h, argon

**SYNFACTS Contributors:** Yasuhiro Uozumi, Yoichi M. A. Yamada, Yoshinari Yuyama

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