Asymmetric Miyaura–Michael Reaction with Polymeric Rh/Ag Catalysts

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

1) carbon black (CB) [Rh(OAc)\(_2\)]\(_2\), AgSbF\(_6\)
2) NaBH\(_4\), diglyme

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

R\(_1\)O

Ar

R\(_2\)O + ArB(OH)\(_2\)

0.3 mmol

0.45–0.6 mmol ligand 3

catalyst 2 (0.75–1.5 mol% Rh)

ligand 3 (1–2 mol%)

PhMe–H\(_2\)O (1:2)

100 °C, 7–24 h, argon

**Significance:** Polystyrene-based polymer-incarcerated bimetallic rhodium nanoparticle catalysts PI/CB Rh/Ag 2a–b were prepared from copolymer 1, carbon black (CB), [Rh(OAc)\(_2\)]\(_2\), and AgSbF\(_6\). 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).