High Performance of a Chiral Diene-Rhodium Catalyst for the Rhodium-Catalyzed Asymmetric 1,4-Addition of Arylboroxines

Fu-Xue Chen, Asato Kina, and Tamio Hayashi*

*Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo,
Kyoto 606-8502, Japan*

Experimental

General

All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glovebox techniques under prepurified argon. NMR spectra were recorded at 500 MHz for ^1H and 125 MHz for ^{13}C NMR. Chemical shifts are reported in δ ppm referenced to an internal SiMe_4 standard or the residual peak of THF (δ 3.76) for ^1H NMR and chloroform-*d* (δ 77.05) or THF-*d*₈ (δ 67.0) for ^{13}C NMR. Optical rotations were measured on a JASCO DIP-370 polarimeter. CHCl_3 was distilled over P_2O_5 under N_2 . THF and 1,4-dioxane were distilled over benzophenone-ketyl under N_2 . H_2O was degassed by bubbling of N_2 .

2-Cyclohexenone and 2-cyclopentenone were distilled before use. Phenylboronic acid (Tokyo Kasei Kogyo Co., Ltd.) was used as received. Arylboroxines were prepared from purchased arylboronic acids (*vide infra*). $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ ¹ and (*S,S*)-Bn-bod*² were prepared following the reported procedures.

Preparation of $[\text{RhCl}((S,S)\text{-Bn-bod}^*)]_2$ (1)

A suspension of $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ (43 mg, 0.22 mmol) and (*S,S*)-Bn-bod* (60 mg, 0.21 mmol) in CHCl_3 (10 mL) was stirred for 2 h at room temperature. The mixture was filtered through celite pad. The solvent of the filtrate was removed under reduced pressure to give 89 mg of rhodium complex in a quantitative yield as a yellow solid.

^1H NMR (CDCl_3): δ 0.24 (m, 4H), 0.52 (m, 4H), 2.76 (d, J = 14.1 Hz, 4H), 3.52 (br, 4H), 3.54 (d, J = 14.0 Hz, 4H), 4.03 (d, J = 5.4 Hz, 4H), 7.21 (t, J = 7.3 Hz, 4H), 7.29 (t, J = 7.4 Hz, 8H), 7.35 (d, J = 7.4 Hz, 8H); ^{13}C NMR (CDCl_3): δ 25.9, 43.1, 45.6, 50.2 (d, $J_{\text{C-Rh}}$ = 10.9 Hz), 69.6

(d, $J_{\text{C-Rh}} = 11.4$ Hz), 126.4, 128.4, 128.9, 138.8; Anal. Calcd for $\text{C}_{44}\text{H}_{44}\text{Cl}_2\text{Rh}_2$: C, 62.21, H, 5.22; found C, 61.93; H, 5.32; $[\alpha]_{\text{D}_{25}}^{25} +571$ (c 0.769, CHCl_3).

Preparation of phenylboroxine (**5m**)

A solution of phenylboronic acid (5.0 g, 40 mmol) in benzene (100 mL) was refluxed for 2 h, during which H_2O was removed azeotropically. The mixture was concentrated under reduced pressure into ca. 30 mL, and it was cooled to room temperature. The precipitate obtained by filtration was washed 5 times with hexane to give 3.0 g of boroxine **5m** (71% yield) as a white crystal.

^1H NMR (CDCl_3): δ 7.50 (m, 6 H), 7.60 (m, 3 H), 8.25 (dd, $J = 8.0$ Hz, 1.3 Hz, 6 H).

Preparation of $[\text{Rh}(\text{OPh})((S,S)\text{-Bn-bod}^*)]_2$ (**6**)

The procedure reported for $[\text{Rh}(\text{OPh}(\text{cod}))]_2^3$ was modified as follows. A solution of $[\text{RhCl}((S,S)\text{-Bn-bod}^*)]_2$ (10.3 mg, 24.3 μmol) and potassium phenoxide (3.21 mg, 24.3 μmol), which was prepared from phenol and potassium hydride, in $\text{THF-}d_8$ (0.5 mL) was heated at 40 $^\circ\text{C}$ for 1 h. The formation of phenoxide-dimer **6** was determined by ^1H and ^{13}C NMR. The solvent was removed under reduced pressure. To the residue was added CH_2Cl_2 and it was filtered through celite for removal of the salt to give a quantitative yield of phenoxide-dimer **6**, which is contaminated with a small amount of impurity (less than ca. 5% by ^1H NMR). The crude sample was used for the next reaction as a catalyst without further purification.

^1H NMR ($\text{THF-}d_8$): δ 0.26 (m, 4H), 0.37 (m, 4H), 1.76 (d, $J = 13.8$ Hz, 4H), 2.78 (d, $J = 6.1$ Hz, 4H), 2.98 (d, $J = 14.0$ Hz, 4H), 3.90 (d, $J = 5.6$ Hz, 4H), 6.72 (t, $J = 7.2$ Hz, 2H), 7.09 (d, $J = 7.6$ Hz, 4H), 7.15 (t, $J = 7.6$ Hz, 4H), 7.31 (t, $J = 7.4$ Hz, 4H), 7.41 (t, $J = 7.6$ Hz, 8H), 7.46 (d, $J = 7.8$ Hz, 8H); ^{13}C NMR ($\text{THF-}d_8$): δ 25.2, 39.7, 44.2, 44.7 (d, $J_{\text{C-Rh}} = 11.4$ Hz), 61.9 (d, $J_{\text{C-Rh}} = 11.9$ Hz), 115.2, 119.0, 122.2, 125.8, 128.0, 128.9, 139.5, 166.0; $[\alpha]_{\text{D}_{25}}^{25} +945^\circ$ (c 0.665, THF).

Catalytic asymmetric 1,4-addition of arylboron reagents to α,β -unsaturated ketones

As a typical procedure, the addition of phenylboroxine (**5m**) to 2-cyclohexenone (**2a**) (entry 8 in Table 1) is shown below: To a suspension of [RhCl((*S,S*)-Bn-bod*)]₂ (0.13 mg, 0.30 μmol Rh) and phenylboroxine (**5m**, 371 mg, 3.60 mmol B) in 3.0 mL of 1,4-dioxane was added 2-cyclohexenone (**2a**, 288 mg, 3.00 mmol) and aqueous KOH (5.0 M, 0.30 mL, 1.5 mmol). The solution was stirred at 30 °C for 1 h. The resulting mixture was passed through a short silica gel pad and eluted with Et₂O. Evaporation of the solvent followed by preparative TLC (silica gel, hexane/ethyl acetate = 3/1) gave (*S*)-3-phenylcyclohexanone (**4am**) (501 mg, 96% yield, 96% ee) as a colorless oil. All of 1,4-addition products were reported in the literature.⁴

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1216-1

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[RhCl((S,S)-Bn-bod*)]₂ (1)

1216-1

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 QBFQ : 500.00 MHz
 IRSET : 128250.00 Hz
 IRPFW : 50.0 usec
 TRNS : 0

SCANS : 847 times

SLVNT : CDCl₃
 SPINNING : 9 Hz
 TEMP : 28.2 °C

[RhCl((S,S)-Bn-bod*)]₂ (1)