Supplementary Material (ESI) for Chemical Communications

Supporting information

Achiral Ligand for Perfect Enantiocontrol by Chiral Diamine: Asymmetric Transfer Hydrogenation by Rhodium Catalyst with Achiral Benzophenone Ligand

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<Experimental Part>

General. ^{1}H and ^{31}P NMR spectra were measured on a Varian GEMINI 2000 (300MHz) and Varian UNITY INOVA (400MHz) spectrometers. Chemical shifts of ^{1}H NMR were expressed in parts per million downfield from tetramethylsilane as an internal standard (δ= 0) in $CDCl_3$. Chemical shifts of ^{31}P NMR were expressed in parts per million downfield from 85% H_3PO_4 as an external standard (δ= 0) in $CDCl_3$. Capillary GC analyses were conducted on a Shimadzu GC-14B instrument equipped with flame ionization detector by using N_2 (75 kPa) as a carrier gas. Peak areas were calculated by a Shimadzu C-R6A as an automatic integrator; a chiral column was CP-Cyclodextrin- β-2,3,6-M-19 (i.d. 0.25 mm x 25 m; Chrompack, GL Sciences, Tokyo). Analytical TLC was performed on glass plates (Merck Kieselgal 60 F_{254}; layer thickness, 0.25 and 0.2 mm). Visualization was accomplished by UV light (254 nm) and anisaldehyde. Column chromatography was performed on Kanto Silica Gel 60N (spherical, neutral; Kanto Chemical Co., Tokyo).

Preparation of [Rh(dpbp)(cod)]SbF_6 [1]. To a mixture of [Rh(cod)$_2$]SbF_6 (55.5 mg, 0.1 mmol) and DPBP (55.0 mg, 0.1 mmol) was added CH_2Cl_2 (2 ml) at room temperature under argon atmosphere in Schlenk tube. After stirred for 5 h at room temperature, the reaction mixture concentrated under reduced pressure. The residue was washed with Et_2O (5 ml x 3) under argon atmosphere to give [Rh(dpbp)(cod)]SbF_6 **[1]**.

^{1}H NMR ($CDCl_3$, 300 MHz) δ2.14 (d, J = 6.3 Hz, 4H), 2.33 (d, J = 6.3 Hz, 4H), 4.45 (br, 4H), 7.24-7.54 (m, 28H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 24.94 (d, $J_{P\text{-}Rh}$ = 147 Hz, 2P).

Anal. Calcd for $C_{45}H_{40}F_6OP_2RhSb \cdot 1/2CH_2Cl_2 \cdot H_2O$: C, 51.66; H, 4.10%. Found: C, 51.53; H, 3.83%.

Preparation of [Rh(dpbp){(S,S)-dpen}]SbF_6 [3]. To a mixture of [Rh(dpbp)(cod)]SbF_6 (10.0 mg, 0.01 mmol) and (S,S)-dpen (2.1 mg, 0.01 mmol) was added $(CH_2Cl)_2$ (1 ml) at room temperature under argon atmosphere in Schlenk tube. A mixture was frozen and charged with hydrogen using balloon (1 atm), then stirred for 30 min at room temperature. Then the reaction mixture was concentrated under reduced pressure, to give [Rh(dpbp){(S,S)-dpen}]SbF_6 **(3)**.

^{1}H NMR ($CDCl_3$, 300 MHz) δ1.67 (br, 1H), 1.89 (br, 1H), 2.84 (br, 1H), 3.23 (br, 1H), 3.94 (br, 1H), 4.39 (br, 1H), 5.98-6.05 (m, 2H), 6.48-6.52 (m, 2H), 6.88-8.30 (m, 34H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 47.28 (dd, $J_{P\text{-}P}$ = 44.9 Hz, $J_{P\text{-}Rh}$ = 155 Hz, 1P), 57.40 (dd, $J_{P\text{-}P}$ = 44.9 Hz, $J_{P\text{-}Rh}$ = 158 Hz, 1P).

Anal. Calcd for $C_{51}H_{44}F_6N_2OP_2RhSb$: C, 55.61; H, 4.03; N, 2.54%. Found: C, 55.48; H, 4.31; N, 2.19%.

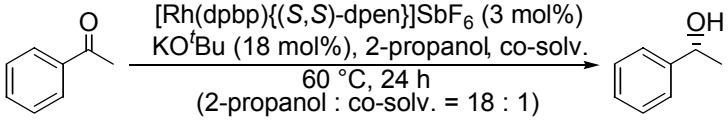
Typical procedure for Rh-catalyzed hydrogenation of ketones.

Table2, entry 1 and 3: To a solution of [Rh(dpbp){(S,S)-dpen}] SbF_6 (11.0 mg, 0.01 mmol) in 2-propanol (3.6 ml) and 0.1 M of ^{t}BuOK/2-propanol (0.6 ml, 0.06 mmol) at room temperature under argon atmosphere in Schlenk tube. After stirred for 20 min at room temperature, the reaction mixture was added ketone (0.33 mmol) and stirred for 24 h at room temperature under Ar atmosphere. After the reaction mixture was concentrated under reduced pressure, the residue was filtered through a short column of silica gel (hexane/ethyl acetate = 1/3) to give alcohol products.

Table2, entry 5 and 7: To a solution of [Rh(dpbp){(S,S)-dpen}] SbF_6 (11.0 mg, 0.01 mmol) in $(CH_2Cl)_2$ (0.23 ml) was added 2-propanol (3.6 ml) and 0.1 M of ^{t}BuOK/2-propanol (0.6 ml, 0.06 mmol) at room temperature under argon atmosphere in Schlenk tube. After stirred for 20 min at room temperature, the reaction mixture was added ketone (0.33 mmol) and stirred for 24 h at room temperature under Ar atmosphere. After the reaction mixture was concentrated under reduced pressure, the residue was filtered through a short column of silica gel (hexane/ethyl acetate = 1/3) to give alcohol products.

<Table Part>

Table S1. Transfer hydrogenation in a variety of solvents.



entry	Co-solvent	*ee* [%]	conversion [%]
1	-	63	98
2	toluene	37	99
3	THF	48	>99
4[a]	dichlorometane	68	99
5	*o*-dichlorobenzene	72	>99
6	1,2-dichloroethane	86	96
7[b]	**1,2-dichloroethane**	**89**	**97**

[a] The same conditions as in Table 1.
[b] At room temperature.