Supporting information for:

Applications of Ruthenium Hydride Borohydride Complexes Containing Phosphinite and Diamine Ligands to Asymmetric Catalytic Reactions

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Experimental section

All manipulations were carried out under an inert atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use. RuHCl(PPh3)3 was prepared by a slight modification of the published procedures.21 The phosphinite ligands were synthesized according to the literature.22 The other chemicals were purchased from Aldrich. The ketones were washed with saturated K2CO3 solution and dried with anhydrous Na2SO4, then distilled prior to use. The enantiomeric excess values of products were determined by use of a Perkin Elmer AutoSystem XL Gas Chromatograph system. Varian Gemini 300, Unity 400 and Unity 500 spectrometers were used to collect NMR data.

Synthesis of trans-RuH(η1-BH4)[(R)-binop][(R,R)-dpen] 1b. trans-RuHCl [(R)-binop][(R,R)-dpen] (150 mg, 0.15 mmol) and NaBH4 (86 mg, 2.25 mmol) were put in a 50 mL Schlenk flask under Ar. Benzene (3 mL) and ethanol (3mL) were added.
The mixture was stirred at 65 °C for 10 min and then ambient temperature for 1 hour. The solvent was removed in vacuo. The residues were extracted with benzene (3 x 6 mL) and the combined extracts were filtered through a Celite pad. Benzene was removed under vacuo and a brown powder was obtained in 94 % yield. Two isomers were obtained in a molar ratio of 1/3. The minor isomer changed to the major isomer upon recrystallization from benzene/hexanes. \(^1\)H NMR (400 MHz, C\(_6\)D\(_6\) ): Major isomer: \(\delta\) -13.97 (dd, \(J = 23.2\) Hz, \(J = 27.2\) Hz, 1H), -0.39 (br, 4H), 2.04 (d, \(J = 15.6\) Hz, 1H), 2.62-2.67 (m, 1H), 3.12 (m, 1H), 3.60-3.65 (m, 1H), 4.29-4.36 (m, 1H), 4.45-4.50 (m, 1H), 6.33-8.50 (m, 40H), 8.49-8.53 (m, 2H). Minor isomer: \(\delta\) -14.86 (m, 1H), 1.57-1.63 (m, 2H), 2.32 (m, 1H), 3.27-3.31 (m, 2H), 3.47-3.48 (m, 1H), 6.50-7.83 (m, 40H), 9.04-9.08 (m, 2H). \(^{31}\)P\(^{\{^1\}H}\)NMR (121.5 MHz, C\(_6\)D\(_6\) ): Major isomer: \(\delta\) 173.4 (AB, \(J_{pp} = 51.0\) Hz), 174.1 (AB, \(J_{pp} = 51.0\) Hz). Minor isomer: \(\delta\) 155.2 (d, \(J_{pp} = 52.1\) Hz). Anal. Calcd for C\(_{58}\)H\(_{53}\)BN\(_2\)O\(_2\)P\(_2\)Ru: C, 70.80; H, 5.43; N, 2.85. Found: C, 70.55; H, 5.27; N, 2.68.

**Synthesis of trans-RuH(\(\eta^1\)-BH\(_4\))[(R)-BINOP][(S,S)-DPEN] 2b.** The procedure for the synthesis of complex 2b is similar to that for complex 1b. The yield is about 90 %. Two isomers were obtained (molar ratio 1/2). \(^1\)H NMR (300 MHz, C\(_6\)D\(_6\) ): Major isomer: -14.85 (dd, \(J = 23.7\) Hz, \(J = 29.7\) Hz), 1.72-1.79 (m, 2H), 2.62 (d, \(J = 7.8\) Hz, 1H), 3.11 (br, 1H), 3.52-3.67 (m, 2H), 4.20-4.30 (m, 1H), 5.99 (d, \(J = 7.5\) Hz, 2H), 6.35-8.12 (m, 36H), 8.30 (t, \(J = 8.1\) Hz, 2H), 9.15-9.24 (m, 2H). Minor isomer: \(\delta\) -13.84 (dd, \(J = 27.0\) Hz, \(J = 36.9\) Hz), \(^{31}\)P\(^{\{^1\}H}\)NMR (121.5 MHz, C\(_6\)D\(_6\) ): Major isomer: \(\delta\) 164.0 (d, \(J = 53.69\) Hz), 167.6 (d, \(J = 53.69\) Hz). Minor isomer: \(\delta\) 162.4 (d, \(J = 54.66\) Hz).
(Hz), 174.5 (d, \(J = 54.66\) Hz). Anal. Calcd for \(C_{58}H_{53}BN_2O_2P_2Ru\): C, 70.80; H, 5.43; N, 2.85. Found: C, 71.02; H, 5.51; N, 2.77.

**Synthesis of \(\text{trans-RuH}^1\text{-BH}_4\)[Xyl-(\(R\))-BINOP][(\(R,R\))-DPEN] 3b.** The procedure for the synthesis of complex 3b is similar to that for complex 1b. Only one isomer was obtained. Yield: 94 %. The pale yellow crystals suitable for an X-ray diffraction study were obtained from benzene/hexanes. \(^1\)H NMR (300 MHz, \(C_6D_6\)): -14.35 (dd, \(J = 21.8\) Hz, \(J = 28.7\) Hz, 1H), -0.3 (br, 4H), 1.63 (s, 6H), 1.91 (s, 6H), 1.98 (s, 6H), 2.46 (s, 6H), 2.84-2.90 (m, 1H), 3.33-3.36 (m, 1H), 3.45-3.48 (m, 1H), 3.61-3.68 (m, 1H), 4.39-4.46 (m, 1H), 4.72-4.76 (m, 1H), 6.37-8.23 (m, 32H), 8.73 (d, \(J = 10.5\) Hz, 2H).

\(^{31}\)P\(^{1}\)H NMR (121.5 MHz, \(C_6D_6\)): 173.6 (AB, \(J = 53.44\) Hz), 174.7 (AB, \(J = 53.44\) Hz).

Anal. Calcd for \(C_{66}H_{69}BN_2O_2P_2Ru\): C, 72.32; H, 6.35; N, 2.56. Found: C, 72.05; H, 6.67; N, 2.42.

**Synthesis of \(\text{trans-RuH}^1\text{-BH}_4\)[Xyl-(\(R\))-BINOP][(\(S,S\))-DPEN] 4b.** The procedure for the synthesis of complex 4b is similar to that for complex 1b. The yield is about 80 %. The pale yellow crystals suitable for an X-ray diffraction study were obtained from benzene/hexanes. Only one isomer was obtained. \(^1\)H NMR (300 MHz, \(C_6D_6\)): -14.36 (dd, \(J = 24.3\) Hz, \(J = 26.1\) Hz, 1H), -0.2 (br, 4H), 1.63 (s, 6H), 1.89 (s, 6H), 2.06 (s, 6H), 2.13 (m, 1H), 2.40 (m, 1H), 2.45 (s, 6H), 3.65 (m, 1H), 3.85 (m, 1H), 4.23 (m, 1H), 4.35 (m, 1H), 6.14 (m, 2H), 6.28 (m, 2H), 6.73 (s, 1H), 6.49 (d, \(J = 12.9\) Hz, 2H), 6.62-6.83 (m, 10H), 6.99-7.09 (m, 4H), 7.27-7.32 (m, 2H), 7.55-7.56 (m, 4H), 7.87 (m, 3H), 7.96 (d, \(J = 8.7\) Hz, 1H), 8.12 (d, \(J = 8.7\) Hz, 1H), 8.75 (br, 2H). \(^{31}\)P\(^{1}\)H NMR: 173.1 (s). Anal. Calcd for \(C_{66}H_{69}BN_2O_2P_2Ru\): C, 72.32; H, 6.53; N, 2.56. Found: C,
Typical procedure for the ruthenium catalyzed asymmetric transfer hydrogenation of ketones. In a glovebox, the ruthenium complex \((4.0 \times 10^{-3} \text{ mmol})\) was placed in a 4 mL vial. Then 2-propanol (2 mL) was added. The mixture was stirred for 2 min. The substrate (0.4 mmol) was added and the solution was diluted with 2-propanol to the desired concentration. This mixture was stirred at room temperature. The conversion and enantiomeric excess of the products were determined by NMR and chiral GC analysis, respectively.

A typical procedure for the Michael addition reaction. In an argon glovebox, a ruthenium complex \((5.0 \times 10^{-3} \text{ mmol})\) was put into a 4 mL vial with a stirring bar and then dimethyl malonate (66 mg, 0.05 mmol) and 2-cyclohexene-1-one (49 mg, 0.05 mmol) were added. The mixture was diluted with the desired solvent to 2 mL and was stirred at 20 °C for 72 h. The conversion was determined by \(^1\text{H} \text{NMR}\) and GC. The product 3-[Bis(methoxycarbonyl)methyl]-cyclohexenone can be purified with silica gel chromatography (eluent: ethyl acetate/hexanes = 1/4). The ee value was determined with GC analysis using a chiral column (CP Chiral-DEX CB; 25 m × 0.25 mm, carrier gas, \(\text{H}_2\)). The oven temperature is 140 °C, the initial pressure is 5.0 psi: 41.2 min (R isomer), 42.8 min (S isomer). When the oven temperature is 135 °C, the initial pressure is 5.0 psi, \(R_t = 53.0\) min (R isomer), \(R_t = 55.1\) min (S isomer).

Procedure for the tandem Michael addition reaction/\(\text{H}_2\) hydrogenation to prepare \textit{trans}-3-hydroxycyclohexanepropandioic acid dimethyl ester.
In an argon glovebox, a ruthenium complex (5.0 × 10^{-3} mmol) was put into a 4 mL vial with a stirring bar then dimethyl malonate (66 mg, 0.05 mmol) and 2-cyclohexene-1-one (49 mg, 0.05 mmol) were added. The mixture was diluted with the benzene to 2 mL and was stirred at 20 °C for 24 h. Then more benzene (2 ml) was added to the mixture. The mixture was injected into an autoclave against a flow of H_2 and then the autoclave was pressurized with hydrogen to 400 psi. The reaction mixture was stirred at the ambient temperature for 48 h. The hydrogenation products are a mixture of *trans* and *cis* isomers (*trans/cis* = 10/1, monitored with NMR, quantitative yield). The product was purified with silica gel chromatography with the eluent of acetone/hexanes (1/3). The pure *trans* isomer was obtained (colorless oil). ¹H NMR (400MHz, CHCl₃): 1.04-1.14 (m, 1H), 1.32-1.53 (m, 3H), 1.64-1.76 (m, 4H), 1.97 (br, 1H), 2.48-2.58 (m, 1H), 3.20 (d, J = 8.8 Hz, 1H), 3.70 (s, 6H), 4.03-4.09 (m, 1H); ¹³C NMR (75 MHz, CHCl₃): 19.70, 29.88, 32.22, 32.34, 36.90, 52.37, 52.39, 57.15, 65.91, 169.10, 169.14; MS (EI⁺) 213 (MH⁺), 132 (100); HRMS (EI⁺) Calcd for [C₁₁H₁₉O₅]⁺: Anal. Calcd for 231.1232; Found: 231.1231; [α] = 5.66° (c = 1.1, CH₂Cl₂, 90 % ee, (R,R)-form).

**X-ray Structure Analysis.** Data were collected on a Nonius Kappa-CCD diffractometer using MoKα radiation. The CCD data were integrated and scaled using the DENZO-SMN software package and the structures were solved and refined using SHELXTL V6.0. The hydrides were located and refined with isotropic thermal
parameters.
