Supporting Information
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Supporting Information

New Types of o-Carborane-Based Chiral Phosphinoxazoline (Cab-PHOX) Ligand Systems: Synthesis and Characterization of Chiral Cab-PHOX Ligands and Their Applications for Asymmetric Hydrogenation

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Experimental Section

General Procedures  All manipulations were performed under a dry, oxygen-free nitrogen or argon atmosphere using standard Schlenk techniques or in a vacuum atmosphere HE-493 glovebox. The THF was distilled under nitrogen from sodium/benzophenone. $\sigma$-Carborane was purchased from KatChem and used after sublimation. The starting materials phosphino-$\sigma$-carboranes (1–2), 2-bromo-4-isopropylloxazoline (3), [Ir(COD)$_2$]BARf$_2$, and [Rh(NBD)$_2$]BF$_4$ were prepared using a modification of the procedures reported in the literature. The $^1$H, $^{11}$B, $^{13}$C, and $^{31}$P NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1, 96.3, 75.4, and 121.5 MHz, respectively. All $^{11}$B chemical shifts were referenced to BF$_3$·O(C$_2$H$_5$)$_2$ (0.0 ppm) with a negative sign indicating an up-field shift. The $^{31}$P NMR spectra were recorded using 85% H$_3$PO$_4$ as an external reference. All proton and carbon chemical shifts were measured relative to internal residual peaks from the lock solvent (99.5% CDCl$_3$) and then referenced to Me$_4$Si (0.00 ppm). The IR spectra were recorded on a Biorad FTS–165 spectrophotometer. Elemental analyses were carried out on a Carlo Erba Instruments CHNS–O EA1108 analyzer. All melting points were uncorrected. High-resolution mass spectra were measured at the Korea Basic Science Institute. The gas chromatography (GC)-mass spectra were obtained using a Micromass
QUAT-TRO II GC8000 series model with an electron energy of 20 or 70 eV. The enantiomeric excesses were determined by GC (an ACME 6000E series model, Younglin Co., Korea) or high performance liquid chromatography (HPLC, a Spectra System P2000 series model, Thermo Separation Products).

**Synthesis of Cab-PHOX 4** To a stirred solution of Cab$_{2}^{PPh}$ 1 (0.99 g, 3.0 mmol) in 30 mL of THF, which was cooled to –10 °C, was added 2.5 M $n$-BuLi (1.2 mL, 3.0 mmol) via a syringe. The resulting solution was stirred at –10 °C for 1 h and then added 2-bromooxazoline 3 (0.63 g, 3.3 mmol) through a cannula. The reaction temperature was maintained at –10 °C for 1 h. Subsequently the reaction mixture was warmed slowly to room temperature. After stirring for an additional 12 h, the solvent was removed under vacuum, and the resulting residue was taken up by fresh column chromatography. Chiral Cab-PHOX 4 was isolated from the reaction solution in 93% yield (1.23 g, 2.8 mmol). HRMS: Calcd for [$^{11}$B$_{10}^{12}$C$_{20}^{14}$N$_{1}$H$_{30}^{16}$O$_{31}$P$]^{+}$ 439.5421, Found 439.5432. Anal. Calcd: C, 54.65; H, 6.88; N, 3.19. Found: C, 54.85; H, 7.02; N, 3.12.

IR spectrum (KBr pellet, cm$^{-1}$) $\nu$(B–H) 2604, $\nu$(C=N) 1700, $\nu$(C–H) 2982, 2990, 3014.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.92 (d, 3H, CH(CH$_3$)$_2$), $^3$$J$$_{CH-CH_3}$ = 6.6 Hz), 0.99 (d, 3H, CH(CH$_3$)$_2$), $^3$$J$$_{CH-CH_3}$ = 6.9 Hz), 1.92 (m, 1H, C(CH(CH$_3$)$_2$), 4.16 (m, 1H, C(N)), 4.19 (t, 1H,
CH$_2$O, $^2$J$_{C-H}$ = 8.4 Hz), 4.45 (t, 1H, CH$_2$O, $^2$J$_{C-H}$ = 8.1 Hz), 7.43–7.82 (m, 10H, PPh$_2$).

$^{11}$B NMR (96.3 MHz, CDCl$_3$) δ −3.12 (1H), −5.74 (1H), −8.93 (2H), −12.49 (2H), −14.02 (4H). $^{13}$C NMR (75.4 MHz, CDCl$_3$) δ 14.2, 18.6, 30.5, 67.3, 70.5, 73.8, 81.7, 126.3, 126.5, 127.1, 127.7, 128.3, 128.6, 129.2, 129.7, 130.7, 131.2, 131.6, 132.8, 168.5.

$^{31}$P NMR (121.5 MHz, CDCl$_3$) δ 12.7 (PPh$_2$).

5. A procedure analogous to the preparation of compound 4 was used but instead starting from Cab$_{PCy_2}$ 2 (1.02 g, 3.0 mmol). Compound 5 was obtained as pale yellow oil (1.19 g, 2.64 mmol, 88%). HRMS: Calcd for $[^{11}$B$_{10}$C$_{20}$N$_4$H$_{42}$O$_{31}$P]$^+$ 451.6373. Found: 451.6387. Anal. Calcd: C, 53.19; H, 9.37; N, 3.10. Found: C, 53.33; H, 9.34; N, 3.11. IR spectrum (KBr pellet, cm$^{-1}$) ν(B–H) 2600, ν(C=N) 1698, ν(C–H) 2985, 2996.

$^1$H NMR (300 MHz, CDCl$_3$) δ 0.87 (d, 3H, CH(CH$_3$)$_2$, $^3$J$_{CH-CH3}$ = 6.3 Hz), 0.97 (d, 3H, CH(CH$_3$)$_2$, $^3$J$_{CH-CH3}$ = 6.9 Hz), 1.25 (m, 1H, P–cyclo–CH), 1.35 (m, 2H, P–cyclo–CH$_2$), 1.79 (m, 2H, P–cyclo–CH$_2$), 1.86 (m, 1H, CHN), 1.99 (m, 2H, P–cyclo–CH$_2$), 3.97 (m, 1H, CHN), 4.08 (t, 1H, CH$_2$O, $^3$J$_{CH-CH2}$ = 8.7 Hz), 4.34 (t, 1H, CH$_2$O, $^3$J$_{CH-CH2}$ = 9.3 Hz). $^{11}$B NMR (96.3 MHz, CDCl$_3$) δ −4.24 (1B), −6.19 (1B), −9.48 (2B), −10.51 (2B), −14.90 (4B). $^{13}$C NMR (75.4 MHz, CDCl$_3$) δ 13.7, 16.9, 23.1, 23.4, 25.4, 25.8, 27.4, 27.7, 29.9, 30.3, 30.8, 64.2, 70.4, 73.5, 84.3, 168.2. $^{31}$P NMR (121.5 MHz, CDCl$_3$) δ 32.3 (PCy$_2$).
**General Procedure for the Rh-Catalyzed Hydrogenation of Functionalized Olefins**

To a solution of \([\text{Rh(NBD)}_2]\text{BF}_4\) (7.5 mg, 0.02 mmol) in fresh distilled and degassed THF (2 mL), which was placed in a nitrogen-filled glovebox, was added Cab–PHOX ligand 4 (9.2 mg, 0.021 mmol). The reaction mixture was stirred at room temperature for 30 min, which was followed by the addition of a solution of methyl 2-acetamidoacrylate 6 (0.14 g, 1.0 mmol) in 2 mL of THF. The mixture was transferred to a Parr stainless autoclave. The autoclave was purged three times with hydrogen, and maintained a hydrogen pressure of 10 bar. Hydrogenation was carried out at room temperature for 24 h. After carefully releasing the hydrogen, the solvent was removed. The residue was filtered through a short SiO₂ column to remove the catalyst. The filtrate was concentrated under reduced pressure, and the hydrogenated product was extracted with 3 mL of heptane (HPLC quality). The solution was applied directly to GC or HPLC for the chemical and optical yield measurements.

**General Procedure for the Ir-Catalyzed Hydrogenation of Unfunctionalized Olefins**

To a solution of \([\text{Ir(COD)}_2]\text{BARf}\) (21.8 mg, 0.02 mmol) in fresh distilled and degassed CH₂Cl₂ (2 mL), which was placed in a nitrogen-filled glovebox, was added 2.1 equiv. of Cab–PHOX 4 (9.2 mg, 0.021 mmol) at 48 °C for 2 h. The reaction mixture was then stirred at room temperature for an additional 30 min. A solution of \((E)\)-prop-1-
ene-1,2-diyl dibenzene 12 (0.19 g, 1.0 mmol) in 2 mL of CH$_2$Cl$_2$ was then added. The mixture was transferred to a Parr stainless autoclave. The autoclave was purged three times with hydrogen, and maintained a hydrogen pressure of 10 bar. Hydrogenation was carried out at room temperature for 24 h. After carefully releasing the hydrogen, the solvent was removed. The residue was filtered through a short SiO$_2$ column to remove the catalyst. The filtrate was concentrated under reduced pressure, followed by extraction of the hydrogenated product with 3 mL of heptane (HPLC quality). The solution was analyzed directly to GC or HPLC for chemical and optical yield measurements, respectively.