Asymmetric Catalytic Synthesis of *P*-Stereogenic Phosphines via a Nucleophilic Ruthenium Phosphido Complex

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General Information. Unless otherwise noted, reactions and manipulations were performed at ambient temperature in an inert atmosphere (N₂) glovebox, or using standard Schlenk and high vacuum line techniques. Glassware was oven-dried overnight at 150 °C or flame-dried under vacuum immediately prior to use. All NMR spectra were obtained at ambient temperature using Bruker DRX-500, AV-500, AVB-400, AVQ-400, or AV-300 spectrometers. ¹H NMR chemical shifts (δ) are reported in parts per million (ppm) relative to residual protiated solvent. Data are reported as follows: (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in Hz; integration). ¹³C NMR chemical shifts (δ) are reported in ppm relative to the carbon resonance of the deuterated solvent. Infrared (IR) spectra were recorded on a ThermoNicolet Avatar 370 as a thin film on a ZnSe crystal or as a Nujol mull between NaCl plates. Elemental analyses were performed at the University of California, Berkeley Microanalytical facility on a Perkin Elmer 2400 Series II CHNO/S Analyzer. X-ray structural analyses were performed by Dr. Fred Hollander and Dr. Allen Oliver in the University of California, Berkeley CHEXRAY facility. Enantiomeric excess was determined using a Shimadzu 10A VP Series Chiral HPLC.

Materials. Reagents were purchased from commercial suppliers, checked for purity and used without further purification unless otherwise noted. Liquids were degassed using three freeze-pump-thaw cycles and dried over 4A activated molecular sieves. Solids were stored in an inert (N₂) atmosphere glove box. Tetrahydrofuran, pentane, hexanes, toluene, diethyl ether and benzene (Fisher) were passed through a column of activated alumina (type A2, size 12 x 32, Purify Co.) under nitrogen pressure and sparged with N₂ prior to use. Benzene-*d*₆ was dried over 4A sieves. THF-*d*₈ was vacuum transferred from purple sodium benzophenone/ketyl and stored under an inert atmosphere. (dmpe)₂Ru(H)₂¹, [Ru(H)(NH₂NMe₂)(cod)][BPh₄]², and (PPh₃)₃Ru(H)(Cl)³ were prepared according to literature procedures.

General Procedure for Asymmetric Alkylation. In a nitrogen atmosphere glovebox, a one-dram vial was charged with ruthenium catalyst **10** (24 mg, 0.020 mmol, 0.01 equiv) and sodium *tert*-amyloxide (27 mg, 0.24 mmol, 1.2 equiv), to which THF (0.8 mL) was added. Benzyl chloride (28 μ L, 0.24 mmol, 1.2 equiv) was syringed into the solution, which was then transferred into an NMR tube. The tube was fitted with a Cajon adapter and brought out of the glovebox. Using standard Schlenk techniques, the NMR tube was put under a positive pressure of nitrogen on a high vacuum manifold. The solution was cooled to $-78\text{ }^{\circ}\text{C}$, and methylphenylphosphine (26 μ L, 0.20 mmol, 1.0 equiv) was added directly to the reaction mixture using a Hamilton Gastight syringe. The NMR tube was then flame-sealed under an atmosphere of nitrogen. The contents were mixed by inverting the NMR tube, then warmed to $-30\text{ }^{\circ}\text{C}$. After 60 h, the solution was warmed to room temperature and brought into the glovebox. The NMR tube was opened and the solution was transferred to a five-dram scintillation vial equipped with a stirbar. A 1.0 M solution of $\text{BH}_3\cdot\text{THF}$ (2 mL, 2.0 mmol, 10 equiv) was added and the resulting solution was stirred for 30 min at room temperature. The following work-up was performed outside of the glovebox: Excess BH_3 was quenched by slow addition of water; the aqueous solution was then extracted with ethyl acetate (3 x 10 mL). The combined organic phase was washed with brine (10 mL), dried over Na_2SO_4 , filtered and concentrated in vacuo. The crude product was purified by silica gel chromatography (conditions indicated below).

***trans*-(dmpe)₂Ru(H)PMePh (1).** In a nitrogen glove box a 50 mL glass-walled

vessel equipped with a vacuum stopcock was charged with (dmpe)₂RuH₂ (0.50 g, 1.24 mmol, 1.0 equiv) and a stirbar. On a vacuum line using standard Schlenk techniques dry and degassed EtOH (25 mL) was added via cannula transfer. Methylphenylphosphine (0.15 mL, 1.24 mmol, 1.0 equiv) was then added via syringe. After 3 h, the volatile materials were removed in vacuo overnight, yielding the product as a bright orange solid (0.66 g, 100%). ¹H NMR (C₆D₆, 400 MHz) δ -14.02 (sextet, *J* = 24 Hz, 1H), 1.11 (s, 12H), 1.2 (br, 4H), 1.29 (s, 12H), 1.5 (br, 4H), 1.70 (d, *J* = 5 Hz, 3H) 7.00 (t, *J* = 7 Hz, 1H), 7.1 (br, 2H), 7.59 (t, *J* = 6 Hz, 2H) ppm; ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 16.2 (m), 27.5 (br), 31.4 (q, *J* = 13 Hz), 96.6 (m), 121.3 (s), 126.8 (d, *J* = 6 Hz), 131.9, 132. ppm; ³¹P{¹H} NMR (C₆D₆, 162 MHz) δ -58.3, 43.5 ppm; IR (ATR) 1277, 1421, 1475, 1571, 1796 cm⁻¹. Anal. Calcd. C, 43.43; H, 7.86. Found C, 43.81; H, 7.90.

[*trans*-(dmpe)₂Ru(H)P(H)MePh][BPh₄] (2-BPh₄). In a nitrogen glove box a 20

mL scintillation vial was charged with (dmpe)₂Ru(H)Cl (0.100 g, 0.23 mmol, 1.0 equiv), THF (5 mL) and a stirbar. To this solution sodium tetraphenylborate (0.080 g, 0.23 mmol, 1.0 equiv) and methylphenylphosphine (0.030 mL, 0.23 mmol, 1.0 equiv) were added via pipette. The solution was stirred overnight, and then filtered through a glass plug and concentrated to afford the desired product as a white solid (0.120 g, 60%). ¹H NMR (THF-*d*₈, 400 MHz) δ -11.85 (dq, *J* = 70, 24 Hz, 1H), 1.36 (s, 12H), 1.56 (s, 12H), 1.58 (t, *J* = 6 Hz, 3H), 1.7 (br, 8H), 5.41 (dm, *J* = 312 Hz, 1H), 6.70 (t, 7Hz, 4H), 6.85 (t, *J* = 8 Hz, 8H), 7.28 (br, 8H), 7.33 (br, 5H) ppm; ¹³C{¹H, ³¹P} NMR (THF-*d*₈, 125 MHz) δ 15.8, 17.5, 18.0, 31.7, 121.8, 125.7, 129.9, 130.0, 131.2, 137.3, 140.5, 165.3 (q, ¹³C-B coupling, *J* = 50 Hz) ppm; ³¹P{¹H} NMR (THF-*d*₈, 162

MHz) δ -16.5 (q, J = 25 Hz), 39.1 (br) ppm; IR (Nujol) 925, 1425, 1860 cm^{-1} . Anal. Calcd. C, 61.86; H, 7.61. Found C, 62.21; H, 7.43.

[*trans*-(dmpe)₂Ru(H)P(methylcyclopropylbenzene)MePh][Br] (5-Br). In a

nitrogen glove box a 20 mL scintillation vial was charged with **1** (0.105 g, 0.2 mmol, 1.0 equiv), THF (2 mL) and a stirbar. A solution of **4** (42 mg, 0.2 mmol, 1.0 equiv) in THF (2 mL) was added via pipette. The mixture was stirred for 4 h. The resulting suspension was filtered through a medium frit; the white solid collected was a mixture of the desired product contaminated with trace amounts of (dmpe)₂Ru(H)Br. Recrystallization from a concentrated solution in THF cooled to -30 °C afforded a 1:1 mixture of product diastereomers as a white crystalline solid (0.098 g, 66%). ¹H NMR (THF-*d*₈, 500 MHz) δ -12.7 (ddq, J = 71, 25, 11 Hz, 2H), 0.80 (br, 4H), 0.90 (br, 4H), 1.34 (s, 24H), 1.52 (s, 24H), 1.54 (br, 16H), 1.69 (d, J = 5 Hz, 3H), 1.79 (d, 3H, J = 5 Hz, 3H), 2.71 (br d, J = 16 Hz, 2H), 2.79 (br d, J = 16 Hz, 2H), 6.69 (d, 7 Hz, 2H), 6.84 (d, 8 Hz, 2H), 7.00-7.15 (m, 6H), 7.35-7.55 (m, 10H) ppm; ¹³C{¹H, ³¹P} NMR (THF-*d*₈, 125 MHz) δ 15.3, 17.1, 17.3, 17.5, 17.6, 18.4, 19.2, 22.3, 24.9, 26.6, 30.7, 31.0, 39.1, 39.2, 124.9, 125.0, 125.1, 127.8, 128.0, 128.3, 128.8, 129.5, 129.6 ppm; ³¹P{¹H} NMR (THF-*d*₈, 162 MHz) δ 4.3 (q, J = 24 Hz), 5.9 (q, J = 24 Hz), 39.7 (m) ppm; IR (ATR) 698, 890, 1065, 1427, 1871 cm^{-1} . Anal. Calcd. C, 47.29; H, 7.12. Found C, 47.50; H, 7.39.

Methyl-(2,2-dimethylpropyl)phenylphosphine borane (6). Note that this phosphine

borane was not prepared by the general procedure described above. In a nitrogen glovebox a 50 mL glass-walled vessel equipped with a vacuum stopcock was charged with **1** (0.105 g, 0.2 mmol, 1.0 equiv), 2,2-dimethyl-1-bromopropane (0.025 mL, 0.2 mmol, 1.0 equiv), THF (10 mL) and a stir bar. The flask was sealed and removed from the glovebox. After heating at 45 °C for

24 h, the solution was cooled to room temperature and a borane solution (2 mL, 1.0 M in THF) was added via syringe. The mixture was stirred for 1 h, and then washed with NH₄Cl (sat. aq.), dried with MgSO₄, filtered, and concentrated under reduced pressure to afford the desired product as a white solid (0.034 g, 82%). ¹H NMR (CDCl₃, 400 MHz) δ 0.5-1.2 (br, BH₃, 3H), 0.97 (s, 9H), 1.51 (d, *J* = 10 Hz, 3H), 1.87 (dd, *J* = 15, 10 Hz, 1H), 2.02 (t, *J* = 14 Hz, 1H), 7.46 (m, 3H), 7.76 (m, 2H) ppm; ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 14.3 (d, *J* = 41 Hz), 31.3 (d, *J* = 6 Hz), 32.2 (s), 42.7 (d, *J* = 31 Hz), 128.7 (d, *J* = 10 Hz), 131.0 (s), 131.4 (d, *J* = 9 Hz), 132.0 (s) ppm; ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ 4.1 (m) ppm; IR (ATR) 693, 744, 897, 1064, 1437, 2369, 2957 cm⁻¹. HR FAB-MS (M-BH₃⁺) Calcd: 194.1224. Found: 194.1224

***trans*-((*R,R*)-Me-BPE)₂Ru(H)PMePh (7).** In a nitrogen glove box a 20 mL scintillation vial was charged with **8-BPh₄** (0.100 g, 0.11 mmol, 1.0 equiv), THF (4 mL) and a stirbar. Methylphenylphosphine (0.014 mL, 0.11 mmol, 1.0 equiv) was added via syringe. The slurry was stirred for 5 min or until all of the ruthenium complex had dissolved. KHMDS (0.022 g, 0.11 mmol, 1.0 equiv) in THF (1 mL) was then added. The slurry was stirred for 10 min and then filtered through a glass plug, and the resulting clear, orange solution was concentrated to afford a yellow solid (0.081 g, 100 %). ¹H NMR (THF-*d*₈, 400 MHz) δ -14.29 (sextet, 1H, 27 Hz), 1.05 (quintet, *J* = 7 Hz, 16H), 1.15 (q, *J* = 7 Hz, 8H), 1.32 (d, *J* = 5 Hz, 3H), 1.38 (q, *J* = 7 Hz, 8H), 1.45-1.53 (m, 8H), 1.56-1.70 (m, 8H), 1.9-2.0 (m, 8H), 6.45 (t, *J* = 7 Hz, 1H), 6.74 (t, *J* = 7 Hz, 2H), 7.14 (t, *J* = 7 Hz, 1H), 7.32 (br, 1H) ppm; ¹³C{¹H} NMR (THF-*d*₈, 125 MHz) δ 14.4, 14.8, 15.8, 15.9, 16.0, 16.5, 16.9, 17.0, 18.2, 18.3, 18.4, 18.5, 19.3, 20.6-20.7 (m), 20.8, 23.0, 23.3, 24.9, 33.5, 33.8, 34.0, 34.5, 34.7, 35.1, 36.4, 36.5, 36.7, 36.8, 37.6, 37.9, 38.2, 40.0-40.1 (m), 41.1 (m), 42.4 (m), 126.6 (m), 128.9 (m), 129.7 (m), 131.9 (m) ppm; ³¹P{¹H} NMR

(THF-*d*₈, 162 MHz) δ -106.2, 76.2, 86.4 ppm; IR (Nujol) 1861 cm⁻¹. HR FAB-MS ($M+H^+$)
Calcd: 743.2896. Found: 743.2871.

In a nitrogen glovebox a 20 mL scintillation vial was charged with [Ru(H)(NH₂NMe₂)₂(cod)][BPh₄] (0.467 g, 0.63 mmol, 1.0 equiv), THF (5 mL) and a stirbar. To this solution 1,2-bis((2*R*,5*R*)-2,5-dimethylphospholano)ethane (0.326 mg, 1.26 mmol, 2.0 equiv) was added via pipette. The solution was stirred overnight and then concentrated to afford a red solid. Recrystallization from a concentrated THF solution afforded the desired product as red needles (0.525 g, 89%). ¹H NMR (THF-*d*₈, 400 MHz) δ -15.0 (br, 1H), 1.0-2.2 (br m, 56H), 6.71 (t, *J* = 7 Hz, 4H), 6.85 (t, *J* = 7 Hz, 8H), 7.27 (br, 8H) ppm; ¹³C{¹H, ³¹P} NMR (THF-*d*₈, 125 MHz) δ 11.4, 11.9, 33.9, 34.7, 35.0, 38.5, 118.7, 119.9, 122.5, 134.2, 162.0 (q, ¹³C-B coupling, *J* = 49 Hz) ppm; ³¹P{¹H} NMR (THF-*d*₈, 162 MHz) δ 69.6 (br), 72.2 (br) ppm; IR (Nujol) 2174 cm⁻¹. Anal. Calcd. C, 64.66; H, 8.03. Found C, 64.82; H, 8.03.⁴

Benzylmethylphenylphosphine borane (9). Flash chromatography

(80:20 hexanes:CH₂Cl₂) furnished product as a yellow solid (42 mg, 91%). ¹H NMR (CDCl₃, 400 MHz) δ 7.63–7.41 (m, 5H), 7.21 (m, 3H), 6.92 (m, 2H) 3.21 (d, *J* = 8.4 Hz, 2H), 1.51 (d, *J* = 10 Hz, 3H), 0.69 (br q, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 132.3 (d, *J* = 7 Hz), 131.7 (d, 9 Hz), 131.4, 129.7 (d, *J* = 4 Hz), 129.0, 128.5 (d, *J* = 10 Hz), 128.2 (d, *J* = 2 Hz), 126.9 (d, *J* = 3 Hz), 35.8 (d, *J* = 31 Hz), 8.8 (d, *J* = 39 Hz). ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ 10.3 (q, *J*_{B-P} = 63 Hz). IR: 3058, 3029, 2917, 2368, 2342, 2258, 1601, 1495, 1436, 1416, 1138, 1063, 915, 897, 845, 791, 744, 691 cm⁻¹. HRMS (FAB⁺) calcd for [C₁₄H₁₅BP]⁺ 225.1004, Found 225.1005. Analysis of enantiomers by chiral HPLC (Chiralcel OJ Column, flow rate 0.9 mL/min, 94:6

hexanes:*i*-PrOH, T_r minor 33.44, major 37.58 min) determined the ee to be 75%. Recrystallization of **7** from ethanol at $-30\text{ }^\circ\text{C}$ afforded the product as a white crystalline powder (12 mg, 29%) in 92% ee.

[(*R*)-(*i*-Pr-PHOX)₂Ru(H)][BPh₄] (10**).** To a 50-mL glass-walled vessel

equipped with a vacuum stopcock was added (PPh₃)₃Ru(H)(Cl) (600 mg, 0.65 mmol, 1.0 equiv), and (*R*)-*i*-Pr-PHOX (485 mg, 1.3 mmol, 2.0 equiv), and THF (10 mL). The sealed vessel was brought out of the glovebox and then degassed by three freeze-pump-thaw cycles. The solution was then heated to $105\text{ }^\circ\text{C}$; after 18 h, the solution was cooled to room temperature and concentrated to 5 mL. Under a nitrogen atmosphere, NaBPh₄ (222 mg, 0.65 mmol, 1.0 equiv) was added as a 1.0 M THF solution. After 10 h at room temperature, the reaction mixture was filtered through a pad of Celite. THF was removed in vacuo to afford a dark orange-red solid. The solid was then washed with Et₂O (3 x 1 mL) and benzene (3 x 1 mL). Further purification was accomplished by precipitation of **10** from a saturated THF solution by slow vapor diffusion of Et₂O at room temperature. **10** was obtained as a red crystalline solid (564 mg, 74%): mp $209.5\text{--}211\text{ }^\circ\text{C}$ (dec). Note that we cannot yet unambiguously assign the stereochemistry of this complex in solution. ¹H NMR (THF-*d*₈, 400 MHz) δ 8.08 (m, 1H), 8.01 (m 1H), 7.90–7.81 (m 3H), 7.64–7.14 (m, 22H), 6.86 (m, 12H), 6.68 (m, 8H), 5.98 (m, 1H), 4.49 (m, 3H), 4.27 (br t, 1H), 4.22 (m, 1H), 3.98 (br d, 1H), 2.80 (m, 1H), 0.82 (d, $J = 7.2\text{ Hz}$, 3H), 0.55 (br s, 4H), 0.33 (d, $J = 6.8\text{ Hz}$, 3H), -0.21 (br s, 3H), -20.9 (Ru–H, dd, $J = 27.6, 27.2, 35.8\text{ Hz}$, 1H). ¹¹B{¹H} NMR (THF-*d*₈), 128 MHz) δ -8.5. ³¹P{¹H} NMR (THF-*d*₈, 162 MHz) δ 67.4 (d, $J = 26\text{ Hz}$), 59.9 (d, $J = 24\text{ Hz}$). IR: 3054, 3000, 2960, 2931, 2361, 2342, 2048, 1644, 1627, 1580, 1479, 1434, 1372, 1238, 1142, 1094, 1058, 998, 955, 743, 694 cm⁻¹. Anal. Calcd for C₇₂H₆₉BN₂O₂P₂Ru: C 74.03, H 5.95, N 2.40; Found: C 73.65, H 5.98, N 2.39.

α -4-(chlorotolyl)methylphenylphosphine borane.

Flash

chromatography (80:20 hexanes:CH₂Cl₂) furnished product as a yellow oil, which solidified upon standing (51 mg, 96%). ¹H NMR (CDCl₃, 400 MHz) δ 7.58–7.42 (m, 5H), 7.18 (d, J = 8 Hz, 2H), 6.84 (d, J = 6.8 Hz, 2H), 3.17 (d, J = 10.8 Hz, 2H), 1.53 (d, J = 9.6 Hz, 3H), 0.77 (br q, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 132.9 (d, J = 3 Hz), 131.6 (d, J = 9 Hz), 131.5 (d, J = 2 Hz), 130.9 (d, J = 4 Hz), 130.7 (d, 7 Hz), 128.7 (d, J = 10 Hz), 128.3 (d, J = 3 Hz), 128.0, 35.3 (d, J = 31 Hz), 9.0 (d, J = 38 Hz). ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ 10.7 (q, J_{B-P} = 71 Hz). IR: 3057, 2913, 2395, 2375, 2342, 2261, 1490, 1435, 1407, 1091, 1067, 1014, 920, 900, 837, 734, 691 cm⁻¹. HRMS (FAB⁺) calcd for [C₁₄H₁₄BCIP]⁺ 259.0615, Found 259.0619. Analysis of enantiomers by chiral HPLC (Chiralpak AS Column, flow rate 1.1 mL/min, 96:4 hexanes:*i*-PrOH, T_r major 11.86, minor 13.29 min) determined the ee to be 41%.

α -(*p*-xylyl)methylphenylphosphine borane.

Flash chromatography

(70:30 hexanes:CH₂Cl₂) furnished product as a yellow oil (39 mg, 80%). ¹H NMR (CDCl₃, 400 MHz) δ 7.60–7.42 (m, 5H), 3.19 (m, 2H), 2.30 (s, 3H), 1.50 (d, J = 10 Hz, 3H), 0.79 (br q, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 136.6, 131.7 (d, J = 9 Hz), 131.3, 129.5 (d, J = 4 Hz), 129.0, 128.9, 128.6, 128.5, 35.4 (d, J = 31 Hz), 21.0, 8.8 (d, J = 39 Hz). ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ 10.0 (q, J_{B-P} = 75 Hz). IR: 3057, 2921, 2854, 2386, 2369, 2343, 1513, 1436, 1148, 1117, 1068, 914, 898, 837, 818, 785, 746, 723, 690 cm⁻¹. HRMS (FAB⁺) calcd for [C₁₅H₁₇BP]⁺ 239.1161, Found 239.1167. Analysis of enantiomers by chiral HPLC (Chiralpak AS Column, flow rate 1.1 mL/min, 99.5:0.5 hexanes:*i*-PrOH, T_r major 24.29, minor 29.28 min) determined the ee to be 83%.

α-(*p*-methoxy)methylphenylphosphine borane. Flash chromatography

(60:40 hexanes:CH₂Cl₂) furnished product as a yellow oil (44 mg, 85%). ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra agree with literature values.⁵ Analysis of enantiomers by chiral HPLC (Chiralpak AS Column, flow rate 0.8 mL/min, 98:2 hexanes:*i*-PrOH, T_r major 26.75, minor 30.29) determined the ee to be 85%.

α-(*o*-xylyl)methylphenylphosphine borane. Flash chromatography

(80:20 hexanes:CH₂Cl₂) furnished product as a yellow solid (45 mg, 92%). ¹H NMR (CDCl₃, 400 MHz) δ 7.52 (m, 3H), 7.41 (m, 2H), 7.17–7.07 (m, 3H), 6.89 (m, 1H), 3.24 (m, 2H), 1.96 (s, 3 H), 1.56 (d, *J* = 10 Hz, 3H), 0.83 (br q, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 136.9 (d, *J* = 4 Hz), 131.8 (d, *J* = 9 Hz), 131.4 (d, *J* = 2 Hz), 130.9 (d, *J* = 8 Hz), 130.6 (d, *J* = 3 Hz), 130.3 (d, *J* = 4 Hz), 129.2, 128.5 (d, *J* = 10 Hz), 127.1 (d, *J* = 3 Hz), 125.7 (d, *J* = 2 Hz), 32.5 (d, *J* = 30 Hz), 19.7, 9.1 (d, *J* = 39 Hz). ³¹P{¹H} NMR (CDCl₃, 162 MHz) δ 10.4 (q, *J*_{B-P} = 71 Hz). IR: 3057, 3025, 2904, 2373, 2342, 2250, 1494, 1438, 1417, 1116, 1063, 901, 823, 786, 738, 692 cm⁻¹. HRMS (FAB⁺) calcd for [C₁₅H₁₇BP]⁺ 239.1161, Found 239.1165. Analysis of enantiomers by chiral HPLC (Chiralcel OJ Column, flow rate 0.9 mL/min, 94:6 hexanes:*i*-PrOH, T_r major 30.54, minor 58.41 min) determined the ee to be 59%.

α-(1-naphthalenylmethyl)methylphenylphosphine borane. Flash

chromatography (80:20 hexanes:CH₂Cl₂) furnished product as a yellow oil (54 mg, 96%). ¹H NMR (CDCl₃, 400 MHz) δ 7.82 (d, *J* = 8 Hz, 1H), 7.75 (d, *J* = 8 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.58–7.31 (m, 8H), 7.06 (d, *J* = 6.4 Hz, 1H), 3.70 (d, *J* = 10.4 Hz, 2H), 1.46 (d, *J* = 9.6 Hz, 3H), 0.89 (br q, 3H). ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 133.7, 132.7 (d, *J* = 9 Hz), 131.9,

131.7 (d, $J = 9$ Hz), 131.3, 129.2, 128.9 (d, $J = 9$ Hz), 128.6, 128.5 (d, $J = 10$ Hz), 128.2 (d, $J = 5$ Hz), 127.8 (d, $J = 3$ Hz), 125.9, 125.7, 125.0 (d, $J = 3$ Hz), 123.8, 32.2 (d, $J = 31$ Hz), 9.0 (d, $J = 38$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ 11.4 (q, $J_{\text{B-P}} = 58$ Hz). IR: 3056, 2918, 2372, 2336, 2252, 1595, 1510, 1435, 1417, 1114, 1061, 1014, 899, 802, 781, 739, 692 cm^{-1} . HRMS (EI^+) calcd for $[\text{C}_{18}\text{H}_{19}\text{BP}]^+$ 277.1317, Found 277.1356. Analysis of enantiomers by chiral HPLC (Chiralcel OJ Column, flow rate 1.1 mL/min, 85:15 hexanes:*i*-PrOH, T_r major 31.04, minor 68.20 min) determined the ee to be 59%.

1,2-Bis((methylphenylphosphinoborane)methyl)benzene.

Flash

chromatography (70:30 hexanes:EtOAc) furnished product as a white solid (33 mg, 87%); isolated as a mixture of C_2 and meso diastereomers. ^1H NMR (CDCl_3 , 400 MHz) δ 7.55–7.43 (m, 6H), 7.42–7.38 (m, 4H), 7.08 (m, 2H), 6.80 (m, 2H), 3.01 (m, 4H), 1.50 (m, 6H), 1.02–0.31 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 131.8–131.6 (m), 131.2 (m), 128.8 (m), 128.7 (m), 127.1 (m), 32.9 (d, $J = 8$ Hz), 32.6 (d, $J = 9$ Hz), 10.0 (d, $J = 11$ Hz), 9.6 (d, $J = 10$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ 10.4 (m). IR: 3057, 2962, 2917, 2852, 2376, 2356, 2264, 1488, 1437, 1416, 1117, 1061, 922, 901, 785, 761, 743, 691 cm^{-1} . HRMS (FAB^+) calcd for $[\text{C}_{22}\text{H}_{25}\text{B}_2\text{P}_2]^+$ 373.1618, Found 373.1619. Analysis of enantiomers by chiral HPLC (Chiralpak AD Column, flow rate 1.0 mL/min, 80:20 hexanes:*i*-PrOH, C_2 : T_r minor 8.06, major 12.02 min, meso: T_r 9.05 min) determined the ee to be 74%. Ratio of C_2 :meso diastereomers found to be 33:67.

1,3-Bis((methylphenylphosphinoborane)methyl)benzene.

Flash

chromatography (75:25 hexanes:EtOAc) furnished product as a yellow oil (33 mg, 86%); isolated as a mixture of C_2 and meso diastereomers. ^1H NMR (CDCl_3 , 400 MHz) δ 7.58–7.42 (m, 10H), 7.02 (t J = 7.6 Hz, 1H), 6.76–6.63 (m, 3H), 3.12 (m, 4H), 1.52–1.44 (m, 6H), 1.08–0.42 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 132.7 (m), 131.7 (m), 131.4 (m), 128.6 (m), 128.38 (m), 35.7 (d, J = 32 Hz), 9.3 (d, J = 38 Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ 10.8 (m). IR: 3056, 2961, 2918, 2853, 2371, 2337, 2253, 1487, 1436, 1415, 1134, 1115, 1061, 942, 900, 806, 739, 691 cm^{-1} . HRMS (FAB^+) calcd for $[\text{C}_{22}\text{H}_{25}\text{B}_2\text{P}_2]^+$ 373.1618, Found 373.1622. Analysis of enantiomers by chiral HPLC (Chiralpak AS Column, flow rate 1.1 mL/min, 95:5 hexanes:EtOH, C_2 : T_r major 21.59, minor 30.35 min, meso: T_r 26.76 min) determined the ee to be 95%. Ratio of C_2 :meso diastereomers found to be 74:26.

1,3-Bis((methylphenylphosphinoborane)methyl)pyridine.

Flash

chromatography (60:40 hexanes:EtOAc) furnished product as a yellow oil (34 mg, 89%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.68–7.59 (m, 4H), 7.54–7.40 (m, 7H), 6.87–6.81 (m, 2H), 3.38–3.34 (m, 4H), 1.62–1.49 (m, 6H), 0.78 (br q, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 153.5 (m), 136.6, 131.7 (dd, J = 2, 9 Hz), 131.5, 129.3 (d, J = 10 Hz), 128.7 (m), 122.7 (m), 37.9 (d, J = 11 Hz), 37.6 (d, J = 10 Hz), 10.1 (d, J = 7 Hz), 9.7 (d, J = 6 Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ 11.5 (m). IR: 3057, 2960, 2918, 2370, 2336, 2252, 1589, 1573, 1451, 1435, 1413, 1135, 1115, 1061, 898, 830, 740, 691 cm^{-1} . HRMS (EI^+) calcd for $[\text{C}_{21}\text{H}_{26}\text{BNP}_2]^+$ 365.1634, Found

365.1590. Analysis of enantiomers by chiral HPLC (Chiralpak AS Column, flow rate 1.1 mL/min, 95:5 hexanes:EtOH, C_2 : T_r major 20.17, minor 31.62 min, meso: T_r 27.07 min) determined the ee to be 84%. Ratio of C_2 :meso diastereomers found to be 58:42.

(2-methylpyridyl)methylphenylphosphine borane.

Flash

chromatography (70:30 hexanes:EtOAc) furnished product as a yellow oil (43 mg, 94%). ^1H NMR (CDCl_3 , 400 MHz) δ 8.48 (d, $J = 4.8$ Hz, 1H), 7.64–7.60 (m, 2H), 7.56–7.46 (m, 2H), 7.43–7.39 (m, 2H), 7.14 (t, $J = 6.4$ Hz, 1H), 7.00 (d, $J = 8$ Hz, 1H), 3.41 (m, 2H), 1.61 (d, $J = 10.4$ Hz, 3H), 0.60 (br q, 3H). $^{11}\text{B}\{^1\text{H}\}$ NMR (CDCl_3 , 128 MHz) δ -39.1 (d, $J_{\text{B-P}} = 58$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 153.75 (d, $J = 7$ Hz), 149.3, 136.4, 131.7 (d, $J = 9$ Hz), 131.4, 129.3, 128.7 (d, $J = 10$ Hz), 124.7 (d, $J = 4$ Hz), 122.0, 38.0 (d, $J = 30$ Hz), 9.5 (d, $J = 38$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ 11.5 (q, $J_{\text{B-P}} = 65$ Hz). IR: 3054, 3033, 2960, 2924, 2867, 2373, 2338, 1953, 1581, 1455, 1435, 1259, 1062, 999, 925, 826, 799, 731, 699 cm^{-1} . HRMS (FAB^+) calcd for $[\text{C}_{13}\text{H}_{16}\text{BNP}]^+$ 228.1113, Found 228.1118. Analysis of enantiomers by chiral HPLC (Chiralcel OJ Column, flow rate 1.1 mL/min, 85:15 hexanes:*i*-PrOH, T_r major 46.05, minor 71.29 min) determined the ee to 48%.

(2-methylfuryl)methylphenylphosphine borane.

Flash chromatography (90:10 hexanes:EtOAc) furnished product as a yellow oil (35 mg, 80%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.61–7.42 (m, 5H), 7.31 (m, 1H), 6.29 (d, $J = 2.8$ Hz, 1H), 5.97 (dd, $J = 2.8, 3.2$ Hz, 1H), 3.27 (d, $J = 8.0$ Hz, 2H), 1.61 (d, $J = 10.0$ Hz, 3H), 0.78 (q, $J = 89.6$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 146.9 (d, $J = 9$ Hz), 142.0, 131.6 (d, $J = 9$ Hz), 131.5, 128.6 (m), 110.7, 108.6 (d, $J = 5$ Hz), 28.5 (d, $J = 33$ Hz), 9.5 (d, $J = 39$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ 11.1 (q, $J_{\text{B-P}} = 65$ Hz). IR: 3117, 3057, 2957, 2919, 2852, 2373, 2338, 2252, 1590,

1502, 1437, 1416, 1257, 1147, 1118, 1062, 1010, 934, 900, 735, 692 cm^{-1} . HRMS (EI^+) calcd for $[\text{C}_{12}\text{H}_{15}\text{BOP}]^+$ 217.0953, Found 217.0957. Analysis of enantiomers by chiral HPLC (Chiralcel OJ Column, flow rate 1.0 mL/min, 98:2 hexanes:EtOH, T_r minor 54.86, major 61.58 min) determined the ee to be 68%.

Ethylmethylphenylphosphine borane. Flash chromatography (70:30

hexanes: CH_2Cl_2) furnished product as a yellow oil (23 mg, 70%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.74–7.65 (m, 2H), 7.47 (m, 3H), 1.83 (m, 2H), 1.54 (d, $J = 10.4$ Hz, 3H), 1.09–0.39 (m, 6H, $\text{CH}_3 + \text{BH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100 MHz) δ 132.1 (d, $J = 8$ Hz), 131.4 (d, $J = 9$ Hz), 131.2, 128.8 (d, $J = 9$ Hz), 20.5 (d, $J = 37$ Hz), 10.2 (d, $J = 38$ Hz), 7.1. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 162 MHz) δ 11.1 (q, $J_{\text{B-P}} = 63$ Hz). IR: 3057, 2973, 2936, 2370, 2254, 1655, 1436, 1115, 1436, 1134, 1066, 902, 889, 743, 723, 692 cm^{-1} . HRMS (EI^+) calcd for $[\text{C}_9\text{H}_{15}\text{BP}]^+$ 165.1003, Found 165.1004. Analysis of enantiomers by chiral HPLC (Chiralcel OJ Column, flow rate 0.9 mL/min, 91:9 hexanes:*i*-PrOH, T_r minor 14.99, major 17.20 min) determined the ee to be 57%.

Figure S-1. ORTEP of *trans*-(dmpe)₂Ru(H)PMePh (**1**).

Figure S-2. ORTEP of cationic portion of $[trans-(dmpe)_2Ru(H)P(H)MePh][BPh_4]$ (**2-BPh₄**).

General Experimental Details for X-Ray Structure Determinations. A fragment of a crystal of was mounted on a glass fiber using Paratone N hydrocarbon oil. All measurements were made on either a SMART⁶ CCD (**1**) or a Bruker APEX⁷ CCD (**2-BPh₄**) area detector with graphite monochromated Mo-K α radiation. The data were collected at a temperature of **1**: -153 $\pm$ 1 $^{\circ}$ C; **2-BPh₄**: 0 $\pm$ 1 $^{\circ}$ C. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.3 $^{\circ}$ counted for a total of 10.0 seconds per frame. Data were integrated by the program SAINT⁸ to a maximum 2 θ value of **1**: 49.4 $^{\circ}$; **2-BPh₄**: 56.5 $^{\circ}$. The data were corrected for Lorentz and polarization effects. Data were analyzed for agreement and possible absorption using XPREP.⁹ An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS¹⁰ (**1**: Tmax = 1.00, Tmin = 0.54; **2-BPh₄**: Tmax=1.00, Tmin=0.89). The structure was solved by direct methods¹¹ and expanded using Fourier techniques.¹² The non-hydrogen atoms were refined anisotropically in **1**, while some were refined isotropically in **2-BPh₄**. The final cycle of full-matrix least-squares refinement¹³ was based on **1**: 2658 observed reflections ($I > 3.00\sigma(I)$) and 229 variable parameters; **2-BPh₄**: 8084 observed reflections ($I > 3.00\sigma(I)$) and 518 variable parameters. The standard deviation of an observation of unit weight¹⁴ was **1**: 1.29; **2-BPh₄**: 1.68. The weighting scheme was based on counting statistics and included a factor ($p = 0.030$) to downweight the intense reflections. Plots of $\sum w (|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin \theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to **1**: 0.89 and -0.85 e-/Å³; **2-BPh₄**: 0.65 and -0.26 e-/Å³, respectively. Neutral atom scattering factors were taken from Cromer and Waber.¹⁵ Anomalous dispersion effects were included in Fcalc;¹⁶ the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.¹⁷ The values for the mass attenuation coefficients are those of Creagh and Hubbel.¹⁸ All calculations were performed using the teXsan¹⁹ crystallographic software package of Molecular Structure Corporation.

Table S-1. Crystal and Data Collection Parameters for *trans*-(dmpe)₂Ru(H)P(Me)Ph (1).**A. Crystal Data**

Empirical Formula	P ₅ C ₁₉ H ₄₁ Ru
Formula Weight	525.47
Crystal Color, Habit	yellow, needles
Crystal Dimensions	0.16 X 0.07 X 0.07 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.4480(7) Å b = 15.478(1) Å c = 17.141(1) Å β = 94.165(1)° V = 2500.0(3) Å ³

Space Group	P2 ₁ /c (#14)
Z value	4
D _{calc}	1.396 g/cm ³
F ₀₀₀	1096.00
μ(MoKα)	9.50 cm ⁻¹

B. Intensity Measurements

Diffractometer	Bruker SMART CCD
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Detector Position	60.00 mm
Exposure Time	10.0 seconds per frame.
Scan Type	ω (0.3 degrees per frame)
2θ _{max}	49.4°
No. of Reflections Measured	Total: 11180 Unique: 2500 (R _{int} = 0.043)
Corrections	Lorentz-polarization Absorption (T _{max} = 1.00 T _{min} = 0.54)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares
Function Minimized	Σ w (Fo - Fc) ²
Least Squares Weights	1/σ ² (Fo) = 4Fo ² /σ ² (Fo ²)
p-factor	0.0300
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I > 3.00σ(I))	2658
No. Variables	229
Reflection/Parameter Ratio	11.61
Residuals: R; Rw; Rall	0.033 ; 0.036; 0.058
Goodness of Fit Indicator	1.29
Max Shift/Error in Final Cycle	0.04
Maximum peak in Final Diff. Map	0.89 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.85 e ⁻ /Å ³

Table S-2. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$ for *trans*-(dmpe)₂Ru(H)P(Me)Ph (**1**).

atom	x	y	z	B_{eq}
Ru(1)	-0.00300(5)	0.00305(2)	-0.00137(3)	0.864(8)
P(1)	0.1318(1)	-0.12496(8)	-0.04727(8)	1.17(3)
P(2)	0.0440(1)	0.09047(8)	-0.10435(8)	1.27(3)
P(3)	0.1980(1)	0.06532(9)	0.05740(8)	1.41(3)
P(4)	-0.2300(1)	-0.03087(8)	-0.04986(8)	1.08(3)
P(5)	-0.0636(1)	-0.07046(9)	0.10777(8)	1.33(3)
C(1)	0.2800(5)	-0.0978(3)	-0.1090(3)	1.8(1)
C(2)	0.0270(5)	-0.1939(3)	-0.1173(3)	1.0(1)
C(3)	0.0459(5)	-0.2002(3)	-0.1971(3)	1.5(1)
C(4)	-0.0341(6)	-0.2574(3)	-0.2456(3)	1.9(1)
C(5)	-0.1389(6)	-0.3080(3)	-0.2152(3)	1.9(1)
C(6)	-0.1609(5)	-0.3024(3)	-0.1359(3)	1.5(1)
C(7)	-0.0767(5)	-0.2480(3)	-0.0885(3)	1.3(1)
C(8)	0.2331(5)	0.1226(3)	-0.0962(3)	1.6(1)
C(9)	0.2790(5)	0.1409(3)	-0.0104(3)	1.6(1)
C(10)	0.0170(6)	0.0571(3)	-0.2065(3)	1.9(1)
C(11)	-0.0402(6)	0.1974(3)	-0.1100(3)	2.0(1)
C(12)	0.3469(5)	-0.0002(4)	0.0976(3)	2.2(1)
C(13)	0.1803(6)	0.1379(4)	0.1403(3)	2.4(1)
C(14)	-0.3073(5)	-0.1109(3)	0.0141(3)	1.3(1)
C(15)	-0.2570(5)	-0.0932(3)	0.0994(3)	1.6(1)
C(16)	-0.2825(5)	-0.0718(3)	-0.1471(3)	1.4(1)
C(17)	-0.3585(5)	0.0571(3)	-0.0451(3)	1.5(1)
C(18)	0.0132(6)	-0.1760(3)	0.1349(3)	2.0(1)
C(19)	-0.0502(6)	-0.0197(4)	0.2045(3)	2.2(1)
H(1)	0.3266	-0.1493	-0.1230	2.1238
H(2)	0.2432	-0.0690	-0.1551	2.1238
H(3)	0.3458	-0.0611	-0.0806	2.1238
H(4)	0.1149	-0.1647	-0.2190	1.7446
H(5)	-0.0170	-0.2618	-0.2994	2.2750
H(6)	-0.1948	-0.3460	-0.2482	2.2409
H(7)	-0.2332	-0.3358	-0.1146	1.8432
H(8)	-0.0895	-0.2472	-0.0340	1.6145
H(9)	0.2892	0.0772	-0.1148	1.9303
H(10)	0.2453	0.1731	-0.1264	1.9303
H(11)	0.2517	0.1981	0.0017	1.9643
H(12)	0.3793	0.1358	-0.0032	1.9643
H(13)	-0.0818	0.0556	-0.2215	2.3227
H(14)	0.0623	0.0970	-0.2386	2.3227

Table S-2. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$ for *trans*-(dmpe)₂Ru(H)P(Me)Ph (**1**) (continued).

atom	x	y	z	B_{eq}
H(15)	0.0563	0.0012	-0.2125	2.3227
H(16)	-0.0348	0.2230	-0.0595	2.3873
H(17)	0.0076	0.2331	-0.1447	2.3873
H(18)	-0.1369	0.1915	-0.1286	2.3873
H(19)	0.3211	-0.0288	0.1435	2.5933
H(20)	0.3705	-0.0419	0.0599	2.5933
H(21)	0.4266	0.0360	0.1101	2.5933
H(22)	0.2665	0.1688	0.1509	2.9208
H(23)	0.1052	0.1775	0.1280	2.9208
H(24)	0.1602	0.1051	0.1850	2.9208
H(25)	-0.4079	-0.1072	0.0080	1.6079
H(26)	-0.2782	-0.1672	-0.0000	1.6079
H(27)	-0.2758	-0.1423	0.1302	1.9730
H(28)	-0.3066	-0.0447	0.1177	1.9730
H(29)	-0.3787	-0.0901	-0.1490	1.6666
H(30)	-0.2726	-0.0273	-0.1845	1.6666
H(31)	-0.2238	-0.1192	-0.1585	1.6666
H(32)	-0.3444	0.0856	0.0040	1.7891
H(33)	-0.3459	0.0972	-0.0860	1.7891
H(34)	-0.4520	0.0343	-0.0507	1.7891
H(35)	-0.0430	-0.2033	0.1716	2.4437
H(36)	0.0153	-0.2111	0.0896	2.4437
H(37)	0.1070	-0.1683	0.1577	2.4437
H(38)	0.0455	-0.0038	0.2179	2.6350
H(39)	-0.1086	0.0303	0.2036	2.6350
H(40)	-0.0807	-0.0594	0.2421	2.6350
H(41)	-0.082(5)	0.086(3)	0.042(3)	2.2982
$B_{\text{eq}} = 8/3 \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \gamma + 2U_{13}(aa^*cc^*)\cos \beta + 2U_{23}(bb^*cc^*)\cos \alpha)$				

Table S-3. Anisotropic Displacement Parameters for *trans*-(dmpe)₂Ru(H)P(Me)Ph (1).

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ru(1)	0.0094(2)	0.0097(2)	0.0137(2)	-0.0004(2)	0.0003(1)	-0.0009(2)
P(1)	0.0136(7)	0.0115(7)	0.0191(8)	-0.0002(6)	0.0003(6)	-0.0014(6)
P(2)	0.0163(7)	0.0124(7)	0.0196(8)	-0.0007(6)	0.0017(6)	-0.0001(6)
P(3)	0.0132(7)	0.0179(8)	0.0223(8)	-0.0029(6)	-0.0005(6)	-0.0045(7)
P(4)	0.0112(7)	0.0139(7)	0.0158(8)	0.0002(6)	0.0008(6)	-0.0019(6)
P(5)	0.0182(8)	0.0172(7)	0.0152(8)	-0.0011(6)	0.0004(6)	0.0002(6)
C(1)	0.013(3)	0.021(3)	0.033(4)	0.001(2)	0.005(3)	-0.008(3)
C(2)	0.012(3)	0.009(3)	0.018(3)	0.004(2)	-0.002(2)	0.001(2)
C(3)	0.020(3)	0.014(3)	0.022(3)	0.004(2)	-0.000(2)	0.001(2)
C(4)	0.025(3)	0.024(3)	0.022(3)	0.012(3)	-0.004(3)	-0.005(3)
C(5)	0.023(3)	0.019(3)	0.026(4)	0.003(2)	-0.012(3)	-0.004(3)
C(6)	0.016(3)	0.016(3)	0.026(3)	-0.002(2)	-0.002(3)	-0.000(2)
C(7)	0.021(3)	0.014(3)	0.017(3)	0.003(2)	0.003(2)	0.001(2)
C(8)	0.016(3)	0.016(3)	0.030(4)	-0.005(2)	0.007(3)	0.002(2)
C(9)	0.017(3)	0.013(3)	0.032(4)	-0.003(2)	0.002(3)	-0.002(2)
C(10)	0.029(3)	0.027(3)	0.018(3)	-0.005(3)	0.005(3)	0.003(3)
C(11)	0.025(3)	0.016(3)	0.034(4)	0.001(2)	0.001(3)	0.005(3)
C(12)	0.015(3)	0.038(3)	0.029(4)	-0.004(3)	-0.008(3)	0.001(3)
C(13)	0.030(3)	0.033(4)	0.030(4)	-0.013(3)	0.006(3)	-0.020(3)
C(14)	0.010(3)	0.019(3)	0.023(3)	-0.002(2)	0.002(2)	0.003(2)
C(15)	0.018(3)	0.023(3)	0.023(3)	-0.005(2)	0.008(3)	0.002(3)
C(16)	0.016(3)	0.018(3)	0.018(3)	0.002(2)	-0.001(2)	-0.003(2)
C(17)	0.010(3)	0.022(3)	0.024(3)	0.001(2)	-0.001(2)	-0.004(3)
C(18)	0.030(3)	0.022(3)	0.026(4)	0.002(3)	0.003(3)	0.010(3)
C(19)	0.031(3)	0.036(4)	0.017(3)	-0.005(3)	0.008(3)	-0.001(3)

The general temperature factor expression:

$$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$

Table S-4. Bond Lengths(Å) for *trans*-(dmpe)₂Ru(H)P(Me)Ph (1).

atom	atom	distance	atom	atom	distance
Ru1	P1	2.513(1)	Ru1	P2	2.293(1)
Ru1	P3	2.296(1)	Ru1	P4	2.304(1)
Ru1	P5	2.297(1)	P1	C1	1.864(5)
P1	C2	1.840(5)	P2	C8	1.850(5)
P2	C10	1.826(5)	P2	C11	1.836(5)
P3	C9	1.853(5)	P3	C12	1.829(5)
P3	C13	1.828(5)	P4	C14	1.839(5)
P4	C16	1.818(5)	P4	C17	1.830(5)
P5	C15	1.856(5)	P5	C18	1.834(5)
P5	C19	1.830(5)	C2	C3	1.396(7)
C2	C7	1.406(6)	C3	C4	1.399(7)
C4	C5	1.393(7)	C5	C6	1.392(7)
C6	C7	1.381(7)	C8	C9	1.528(7)
C14	C15	1.529(7)	Ru1	H41	1.68(4)

Table S-5. Bond Angles(°) for *trans*-(dmpe)₂Ru(H)P(Me)Ph (1).

atom	atom	atom	angle	atom	atom	atom	angle
P1	Ru1	P2	95.35(5)	P1	Ru1	P3	92.67(5)
P1	Ru1	P4	100.79(4)	P1	Ru1	P5	91.52(5)
P2	Ru1	P3	83.67(5)	P2	Ru1	P4	94.83(5)
P2	Ru1	P5	173.12(5)	P3	Ru1	P4	166.54(5)
P3	Ru1	P5	95.61(5)	P4	Ru1	P5	84.27(5)
Ru1	P1	C1	114.8(2)	Ru1	P1	C2	113.6(2)
C1	P1	C2	98.7(2)	Ru1	P2	C8	109.9(2)
Ru1	P2	C10	123.4(2)	Ru1	P2	C11	117.7(2)
C8	P2	C10	102.5(2)	C8	P2	C11	100.0(2)
C10	P2	C11	100.1(2)	Ru1	P3	C9	110.8(2)
Ru1	P3	C12	121.4(2)	Ru1	P3	C13	118.7(2)
C9	P3	C12	104.1(2)	C9	P3	C13	99.5(2)
C12	P3	C13	99.2(3)	Ru1	P4	C14	109.7(2)
Ru1	P4	C16	126.5(2)	Ru1	P4	C17	114.7(2)
C14	P4	C16	102.6(2)	C14	P4	C17	100.4(2)
C16	P4	C17	99.3(2)	Ru1	P5	C15	109.5(2)
Ru1	P5	C18	122.0(2)	Ru1	P5	C19	121.3(2)
C15	P5	C18	102.7(2)	C15	P5	C19	98.9(2)
C18	P5	C19	98.8(3)	P1	C2	C3	125.3(4)
P1	C2	C7	118.2(4)	C3	C2	C7	116.4(4)
C2	C3	C4	121.7(5)	C3	C4	C5	120.1(5)
C4	C5	C6	119.4(5)	C5	C6	C7	119.5(5)
C2	C7	C6	122.9(5)	P2	C8	C9	109.1(3)
P3	C9	C8	112.6(3)	P4	C14	C15	109.9(3)
P5	C15	C14	110.1(3)	P2	Ru1	H41	90(1)
P1	Ru1	H41	172(1)	P4	Ru1	H41	84(1)
P3	Ru1	H41	82(1)	P5	Ru1	H41	82(1)

Table S-6. Torsion Angles(°) for *trans*-(dmpe)₂Ru(H)P(Me)Ph (**1**).

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
Ru1	P1	C2	C3	108.3(4)	Ru1	P1	C2	C7	-74.9(4)
Ru1	P2	C8	C9	-39.5(4)	Ru1	P3	C9	C8	-21.1(4)
Ru1	P4	C14	C15	35.9(4)	Ru1	P5	C15	C14	34.9(4)
P1	Ru1	P2	C8	-71.0(2)	P1	Ru1	P2	C10	49.9(2)
P1	Ru1	P2	C11	175.5(2)	P1	Ru1	P3	C9	92.6(2)
P1	Ru1	P3	C12	-30.0(2)	P1	Ru1	P3	C13	-153.2(2)
P1	Ru1	P4	C14	79.1(2)	P1	Ru1	P4	C16	-44.6(2)
P1	Ru1	P4	C17	-168.8(2)	P1	Ru1	P5	C15	-110.9(2)
P1	Ru1	P5	C18	8.9(2)	P1	Ru1	P5	C19	135.1(2)
P1	C2	C3	C4	176.9(4)	P1	C2	C7	C6	-179.8(4)
P2	Ru1	P1	C1	27.1(2)	P2	Ru1	P1	C2	-85.5(2)
P2	Ru1	P3	C9	-2.5(2)	P2	Ru1	P3	C12	-125.1(2)
P2	Ru1	P3	C13	111.7(2)	P2	Ru1	P4	C14	175.4(2)
P2	Ru1	P4	C16	51.8(2)	P2	Ru1	P4	C17	-72.4(2)
P2	Ru1	P5	C15	72.6(5)	P2	Ru1	P5	C18	-167.6(4)
P2	Ru1	P5	C19	-41.4(5)	P2	C8	C9	P3	37.8(4)
P3	Ru1	P1	C1	-56.8(2)	P3	Ru1	P1	C2	-169.4(2)
P3	Ru1	P2	C8	21.1(2)	P3	Ru1	P2	C10	142.0(2)
P3	Ru1	P2	C11	-92.4(2)	P3	Ru1	P4	C14	-101.6(3)
P3	Ru1	P4	C16	134.8(3)	P3	Ru1	P4	C17	10.5(3)
P3	Ru1	P5	C15	156.3(2)	P3	Ru1	P5	C18	-84.0(2)
P3	Ru1	P5	C19	42.3(2)	P4	Ru1	P1	C1	123.0(2)
P4	Ru1	P1	C2	10.5(2)	P4	Ru1	P2	C8	-172.3(2)
P4	Ru1	P2	C10	-51.5(2)	P4	Ru1	P2	C11	74.1(2)
P4	Ru1	P3	C9	-86.8(3)	P4	Ru1	P3	C12	150.6(3)
P4	Ru1	P3	C13	27.4(3)	P4	Ru1	P5	C15	-10.2(2)
P4	Ru1	P5	C18	109.6(2)	P4	Ru1	P5	C19	-124.2(2)
P4	C14	C15	P5	-44.6(4)	P5	Ru1	P1	C1	-152.5(2)
P5	Ru1	P1	C2	94.9(2)	P5	Ru1	P2	C8	105.5(5)
P5	Ru1	P2	C10	-133.6(4)	P5	Ru1	P2	C11	-8.1(5)
P5	Ru1	P3	C9	-175.6(2)	P5	Ru1	P3	C12	61.8(2)
P5	Ru1	P3	C13	-61.4(2)	P5	Ru1	P4	C14	-11.4(2)
P5	Ru1	P4	C16	-135.0(2)	P5	Ru1	P4	C17	100.7(2)
C1	P1	C2	C3	-13.6(5)	C1	P1	C2	C7	163.2(4)
C2	C3	C4	C5	2.0(8)	C2	C7	C6	C5	3.4(8)
C3	C2	C7	C6	-2.7(7)	C3	C4	C5	C6	-1.4(8)
C4	C3	C2	C7	0.0(7)	C4	C5	C6	C7	-1.2(8)
C8	C9	P3	C12	111.1(4)	C8	C9	P3	C13	-146.8(4)
C9	C8	P2	C10	-172.3(3)	C9	C8	P2	C11	85.0(4)
C14	C15	P5	C18	-96.1(4)	C14	C15	P5	C19	162.8(4)
C15	C14	P4	C16	172.6(3)	C15	C14	P4	C17	-85.2(4)

Table S-7. Crystal and Data Collection Parameters for [*trans*-(dmpe)₂Ru(H)PH(Me)Ph][BPh₄] (**2-BPh₄**).**A. Crystal Data**

Empirical Formula	RuP ₅ C ₄₉ H ₇₄ BO _{1.50}
Formula Weight	953.87
Crystal Color, Habit	colorless, rod-like
Crystal Dimensions	0.17 X 0.15 X 0.15 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 16.354(1) Å b = 13.2884(9) Å c = 22.9689 Å β = 95.501(2)° V = 4968.5(5) Å ³

Space Group	P2 ₁ /n (#14)
Z value	4
D _{calc}	1.275 g/cm ³
F ₀₀₀	2016.00
μ(MoKα)	5.12 cm ⁻¹

B. Intensity Measurements

Diffractometer	Bruker APEX CCD
Radiation	MoKα (λ = 0.71069 Å) graphite monochromated
Detector Position	60.00 mm
Exposure Time	10.0 seconds per frame.
Scan Type	ω (0.3 degrees per frame)
2θ _{max}	56.5°
No. of Reflections Measured	Total: 32598 Unique: 7725 (R _{int} = 0.026)
Corrections	Lorentz-polarization Absorption (T _{max} = 1.00 T _{min} = 0.89)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares
Function Minimized	Σ w (Fo - Fc) ²
Least Squares Weights	1/σ ² (Fo) = 4Fo ² /σ ² (Fo ²)
p-factor	0.0300
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I > 3.00σ(I))	8084
No. Variables	518
Reflection/Parameter Ratio	15.61
Residuals: R; Rw; Rall	0.040 ; 0.052; 0.068
Goodness of Fit Indicator	1.68
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.65 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.26 e ⁻ /Å ³

Table S-8. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$ and occupancy for [*trans*-(dmpe)₂Ru(H)PH(Me)Ph][BPh₄] (2-BPh₄).

atom	x	y	z	B_{eq}	occupancy
Ru1	0.52803(1)	0.25013(2)	0.232834(9)	2.037(5)	
P1	0.64286(5)	0.35114(6)	0.22167(4)	2.49(2)	
P2	0.46755(6)	0.25320(6)	0.13739(4)	3.03(2)	
P3	0.44596(5)	0.38946(6)	0.24411(4)	2.94(2)	
P4	0.55739(6)	0.22107(7)	0.33187(4)	3.56(2)	
P5	0.58585(6)	0.09201(6)	0.22364(4)	3.40(2)	
O1	0.9035(4)	0.6865(5)	-0.0223(2)	13.0(2)	
O2	1.0123(5)	0.0647(7)	-0.0563(3)	9.1(3)	1/2
C1	0.6360(2)	0.4636(3)	0.1742(2)	4.45(9)	
C2	0.7415(2)	0.3023(2)	0.2033(1)	2.35(6)	
C3	0.7592(2)	0.2926(3)	0.1458(1)	3.29(7)	
C4	0.8334(2)	0.2535(3)	0.1322(2)	3.87(8)	
C5	0.8923(2)	0.2239(3)	0.1763(2)	3.78(8)	
C6	0.8765(2)	0.2333(2)	0.2338(2)	3.43(8)	
C7	0.8021(2)	0.2721(2)	0.2469(1)	2.86(7)	
C8	0.3839(3)	0.3447(3)	0.1331(2)	5.2(1)	
C9	0.4062(3)	0.4336(3)	0.1711(2)	5.3(1)	
C10	0.5237(3)	0.2868(4)	0.0758(2)	5.4(1)	
C11	0.4129(3)	0.1428(3)	0.1083(2)	6.0(1)	
C12	0.4871(3)	0.5025(3)	0.2803(2)	5.6(1)	
C13	0.3518(3)	0.3753(3)	0.2793(2)	5.6(1)	
C14	0.5949(3)	0.0917(3)	0.3424(2)	6.2(1)	
C15	0.6440(3)	0.0616(3)	0.2942(2)	5.4(1)	
C16	0.6350(2)	0.2929(3)	0.3768(2)	4.89(10)	
C17	0.4738(3)	0.2211(4)	0.3791(2)	6.0(1)	
C18	0.5158(3)	-0.0148(3)	0.2150(2)	5.4(1)	
C19	0.6580(3)	0.0606(3)	0.1712(2)	6.1(1)	
C20	0.5511(2)	0.2258(2)	-0.0818(1)	2.38(6)	
C21	0.4887(2)	0.2907(2)	-0.1067(1)	2.86(7)	
C22	0.4066(2)	0.2731(2)	-0.1045(1)	3.18(7)	
C23	0.3805(2)	0.1878(3)	-0.0772(1)	3.61(8)	
C24	0.4383(2)	0.1205(2)	-0.0534(1)	3.34(8)	
C25	0.5216(2)	0.1400(2)	-0.0560(1)	2.66(7)	
C26	0.6695(2)	0.2827(2)	-0.1487(1)	2.60(6)	
C27	0.6246(2)	0.2417(2)	-0.1985(1)	3.53(8)	
C28	0.6428(3)	0.2639(3)	-0.2553(2)	4.43(10)	
C29	0.7067(3)	0.3273(3)	-0.2646(2)	4.6(1)	
C30	0.7523(2)	0.3684(3)	-0.2173(2)	3.97(9)	
C31	0.7336(2)	0.3463(2)	-0.1611(1)	3.14(7)	

Table S-8. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$ and occupancy for [*trans*-(dmpe)2Ru(H)PH(Me)Ph][BPh₄] (2-BPh₄) (continued).

atom	x	y	z	B_{eq}	occupancy
C32	0.7031(2)	0.1526(2)	-0.0597(1)	2.55(7)	
C33	0.7158(2)	0.1279(2)	-0.0003(1)	3.12(7)	
C34	0.7540(2)	0.0397(3)	0.0199(1)	3.75(8)	
C35	0.7818(2)	-0.0282(3)	-0.0190(2)	3.89(9)	
C36	0.7714(2)	-0.0052(3)	-0.0775(2)	3.86(8)	
C37	0.7324(2)	0.0822(2)	-0.0974(1)	2.91(7)	
C38	0.6753(2)	0.3487(2)	-0.0384(1)	2.50(6)	
C39	0.7570(2)	0.3633(2)	-0.0155(1)	3.23(8)	
C40	0.7815(2)	0.4461(3)	0.0191(2)	3.90(9)	
C41	0.7256(2)	0.5178(3)	0.0322(1)	3.77(9)	
C42	0.6452(2)	0.5062(2)	0.0107(1)	3.34(8)	
C43	0.6206(2)	0.4230(2)	-0.0234(1)	2.75(7)	
C44	0.8392(4)	0.6959(4)	-0.0639(3)	8.6(2)	
C45	0.8355(4)	0.6099(4)	-0.1021(2)	7.0(1)	
C46	0.9217(6)	0.5731(6)	-0.0991(4)	12.4(3)	
C47	0.9645(5)	0.635(1)	-0.0546(5)	17.3(5)	
C48	1.0196(5)	-0.0864(6)	0.0107(3)	12.1(3)	
C49	1.0094(4)	-0.0357(6)	-0.0463(3)	9.3(2)	
B1	0.6497(2)	0.2528(2)	-0.0820(1)	2.45(5)	
$B_{\text{eq}} = 8/3 \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \gamma + 2U_{13}(aa^*cc^*)\cos \beta + 2U_{23}(bb^*cc^*)\cos \alpha)$					

Table S-9. Anisotropic Displacement Parameters for [*trans*-(dmpe)₂Ru(H)PH(Me)Ph][BPh₄] (**2-BPh₄**).

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Ru1	0.0263(1)	0.0233(1)	0.0277(1)	-0.0012(1)	0.00192(9)	0.00027(10)
P1	0.0289(4)	0.0277(4)	0.0382(4)	-0.0028(3)	0.0034(3)	0.0008(3)
P2	0.0377(5)	0.0471(5)	0.0296(4)	-0.0066(4)	-0.0000(3)	0.0013(4)
P3	0.0348(5)	0.0279(4)	0.0508(5)	0.0021(3)	0.0122(4)	-0.0009(4)
P4	0.0449(5)	0.0566(6)	0.0323(5)	-0.0079(4)	-0.0042(4)	0.0066(4)
P5	0.0398(5)	0.0256(4)	0.0645(6)	0.0009(4)	0.0094(4)	0.0006(4)
O1	0.112(4)	0.239(6)	0.140(4)	-0.043(4)	-0.011(3)	-0.065(4)
O2	0.132(7)	0.127(7)	0.090(5)	-0.007(5)	0.032(5)	0.054(5)
C1	0.044(2)	0.041(2)	0.084(3)	-0.004(2)	0.008(2)	0.012(2)
C2	0.029(2)	0.025(2)	0.035(2)	-0.004(1)	0.004(1)	0.003(1)
C3	0.035(2)	0.048(2)	0.042(2)	-0.000(2)	0.003(2)	0.003(2)
C4	0.045(2)	0.062(2)	0.042(2)	0.006(2)	0.012(2)	0.002(2)
C5	0.036(2)	0.048(2)	0.060(2)	0.009(1)	0.011(2)	0.005(2)
C6	0.037(2)	0.040(2)	0.052(2)	0.006(1)	-0.002(2)	0.007(1)
C7	0.039(2)	0.032(2)	0.038(2)	-0.001(1)	0.005(1)	0.002(1)
C8	0.053(3)	0.083(3)	0.058(3)	0.009(2)	-0.010(2)	0.019(2)
C9	0.055(3)	0.056(2)	0.088(3)	0.023(2)	-0.001(2)	0.022(2)
C10	0.069(3)	0.101(3)	0.035(2)	-0.021(2)	0.008(2)	-0.002(2)
C11	0.085(3)	0.084(3)	0.054(3)	-0.039(3)	-0.014(2)	-0.005(2)
C12	0.065(3)	0.035(2)	0.114(3)	-0.003(2)	0.026(3)	-0.024(2)
C13	0.058(3)	0.045(2)	0.117(4)	0.009(2)	0.048(3)	0.010(2)
C14	0.094(4)	0.065(3)	0.068(3)	-0.006(3)	-0.031(3)	0.033(2)
C15	0.052(3)	0.046(2)	0.107(4)	0.013(2)	-0.006(2)	0.024(2)
C16	0.052(2)	0.093(3)	0.039(2)	-0.013(2)	-0.007(2)	-0.008(2)
C17	0.061(3)	0.132(4)	0.035(2)	-0.029(3)	0.004(2)	0.017(2)
C18	0.058(3)	0.028(2)	0.118(3)	-0.005(2)	0.012(2)	-0.002(2)
C19	0.077(3)	0.039(2)	0.123(4)	0.001(2)	0.050(3)	-0.020(2)
C20	0.036(2)	0.030(2)	0.024(1)	-0.001(1)	0.001(1)	-0.004(1)
C21	0.041(2)	0.033(2)	0.034(2)	-0.003(1)	-0.002(1)	-0.002(1)
C22	0.040(2)	0.044(2)	0.035(2)	0.005(1)	-0.002(2)	-0.006(1)
C23	0.036(2)	0.059(2)	0.042(2)	-0.005(2)	0.001(2)	-0.011(2)
C24	0.045(2)	0.044(2)	0.038(2)	-0.010(2)	0.003(2)	0.001(1)
C25	0.037(2)	0.033(2)	0.031(2)	0.002(1)	0.002(1)	-0.001(1)
C26	0.039(2)	0.030(1)	0.031(2)	0.008(1)	0.008(1)	0.001(1)
C27	0.048(2)	0.052(2)	0.035(2)	-0.000(2)	0.004(2)	-0.003(2)
C28	0.064(3)	0.074(3)	0.030(2)	0.021(2)	0.003(2)	-0.000(2)
C29	0.069(3)	0.066(3)	0.042(2)	0.028(2)	0.024(2)	0.021(2)
C30	0.056(2)	0.043(2)	0.056(2)	0.013(2)	0.027(2)	0.012(2)
C31	0.042(2)	0.036(2)	0.043(2)	0.007(1)	0.014(2)	0.002(1)

Table S-10. Anisotropic Displacement Parameters for [*trans*-(dmpe)₂Ru(H)PH(Me)Ph][BPh₄] (**2-BPh₄**) (continued).

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C32	0.033(2)	0.033(2)	0.032(2)	-0.001(1)	0.005(1)	0.002(1)
C33	0.044(2)	0.041(2)	0.034(2)	0.009(1)	0.006(1)	-0.000(1)
C34	0.051(2)	0.050(2)	0.040(2)	0.006(2)	0.000(2)	0.009(2)
C35	0.050(2)	0.037(2)	0.059(2)	0.013(2)	-0.001(2)	0.005(2)
C36	0.053(2)	0.043(2)	0.050(2)	0.012(2)	-0.000(2)	-0.012(2)
C37	0.036(2)	0.037(2)	0.037(2)	0.001(1)	0.005(1)	-0.005(1)
C38	0.038(2)	0.031(2)	0.026(2)	0.000(1)	0.003(1)	0.004(1)
C39	0.042(2)	0.041(2)	0.040(2)	0.001(1)	0.003(2)	-0.003(1)
C40	0.046(2)	0.050(2)	0.049(2)	-0.010(2)	-0.009(2)	0.001(2)
C41	0.065(3)	0.039(2)	0.038(2)	-0.011(2)	0.001(2)	-0.007(1)
C42	0.061(2)	0.032(2)	0.034(2)	0.003(2)	0.007(2)	-0.005(1)
C43	0.040(2)	0.036(2)	0.029(2)	-0.001(1)	0.004(1)	-0.001(1)
C44	0.109(5)	0.078(4)	0.136(5)	0.009(3)	-0.012(4)	-0.025(4)
C45	0.110(5)	0.079(3)	0.077(3)	-0.004(3)	0.010(3)	0.009(3)
C46	0.175(9)	0.137(6)	0.166(7)	0.099(6)	0.045(6)	0.010(5)
C47	0.058(5)	0.36(2)	0.23(1)	0.015(7)	0.000(6)	-0.00(1)
C48	0.155(7)	0.219(9)	0.081(4)	-0.112(6)	-0.005(4)	0.048(5)
C49	0.086(4)	0.164(6)	0.102(5)	-0.022(4)	0.009(3)	0.040(5)

The general temperature factor expression:

$$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$

Table S-11. Bond Lengths(Å) for [*trans*-(dmpe)₂Ru(H)PH(Me)Ph][BPh₄] (**2-BPh₄**).

atom	atom	distance	atom	atom	distance
Ru1	P1	2.3423(8)	Ru1	P2	2.3173(8)
Ru1	P3	2.3158(8)	Ru1	P4	2.3118(9)
Ru1	P5	2.3219(8)	P1	C1	1.847(4)
P1	C2	1.825(3)	P2	C8	1.826(4)
P2	C10	1.815(4)	P2	C11	1.812(4)
P3	C9	1.836(4)	P3	C12	1.814(4)
P3	C13	1.816(4)	P4	C14	1.834(4)
P4	C16	1.827(4)	P4	C17	1.824(4)
P5	C15	1.844(4)	P5	C18	1.823(4)
P5	C19	1.812(4)	O1	C44	1.357(7)
O1	C47	1.47(1)	O2	C48	1.25(1)
O2	C49	1.356(10)	C2	C3	1.386(4)
C2	C7	1.399(4)	C3	C4	1.383(5)
C4	C5	1.387(5)	C5	C6	1.376(5)
C6	C7	1.381(5)	C8	C9	1.493(6)
C14	C15	1.483(6)	C20	C21	1.414(4)
C20	C25	1.391(4)	C20	B1	1.653(4)
C21	C22	1.369(4)	C22	C23	1.383(5)
C23	C24	1.375(5)	C24	C25	1.394(4)
C26	C27	1.409(4)	C26	C31	1.396(4)
C26	B1	1.645(4)	C27	C28	1.396(5)
C28	C29	1.375(6)	C29	C30	1.370(5)
C30	C31	1.386(4)	C32	C33	1.401(4)
C32	C37	1.389(4)	C32	B1	1.647(4)
C33	C34	1.387(4)	C34	C35	1.376(5)
C35	C36	1.373(4)	C36	C37	1.382(4)
C38	C39	1.403(4)	C38	C43	1.397(4)
C38	B1	1.649(4)	C39	C40	1.393(4)
C40	C41	1.373(5)	C41	C42	1.367(5)
C42	C43	1.392(4)	C44	C45	1.440(7)
C45	C46	1.486(9)	C46	C47	1.44(1)
C48	C49	1.468(7)			

Table S-11. Bond Lengths(Å) for [*trans*-(dmpe)₂Ru(H)PH(Me)Ph][BPh₄] (**2-BPh₄**) (continued).

atom	atom	distance	atom	atom	distance
Ru1	H1	1.62	P1	H2	1.61
C1	H3	0.95	C1	H4	0.95
C1	H5	0.95	C3	H6	0.95
C4	H7	0.95	C5	H8	0.95
C6	H9	0.95	C7	H10	0.95
C8	H11	0.95	C8	H12	0.95
C9	H13	0.95	C9	H14	0.95
C10	H15	0.95	C10	H16	0.95
C10	H17	0.95	C11	H18	0.95
C11	H19	0.95	C11	H20	0.95
C12	H21	0.95	C12	H22	0.95
C12	H23	0.95	C13	H24	0.95
C13	H25	0.95	C13	H26	0.95
C14	H27	0.95	C14	H28	0.95
C15	H29	0.95	C15	H30	0.95
C16	H31	0.95	C16	H32	0.95
C16	H33	0.95	C17	H34	0.95
C17	H35	0.95	C17	H36	0.95
C18	H37	0.95	C18	H38	0.95
C18	H39	0.95	C19	H40	0.95
C19	H41	0.95	C19	H42	0.95
C21	H43	0.95	C22	H44	0.95
C23	H45	0.95	C24	H46	0.95
C25	H47	0.95	C27	H48	0.95
C28	H49	0.95	C29	H50	0.95
C30	H51	0.95	C31	H52	0.95
C33	H53	0.95	C34	H54	0.95
C35	H55	0.95	C36	H56	0.95
C37	H57	0.95	C39	H58	0.95
C40	H59	0.95	C41	H60	0.95
C42	H61	0.95	C43	H62	0.95
C44	H63	0.95	C44	H64	0.95
C45	H65	0.95	C45	H66	0.95
C46	H67	0.95	C46	H68	0.95
C47	H69	0.95	C47	H70	0.95
C48	H71	0.94	C48	H72	0.95
C49	H73	0.95	C49	H74	0.95

Table S-12. Bond Angles(°) for [*trans*-(dmpe)2Ru(H)PH(Me)Ph][BPh₄] (**2-BPh₄**).

atom	atom	atom	angle	atom	atom	atom	angle
P1	Ru1	P2	99.23(3)	P1	Ru1	P3	91.91(3)
P1	Ru1	P4	96.34(3)	P1	Ru1	P5	99.84(3)
P2	Ru1	P3	83.82(3)	P2	Ru1	P4	164.43(3)
P2	Ru1	P5	94.04(3)	P3	Ru1	P4	95.24(3)
P3	Ru1	P5	168.25(3)	P4	Ru1	P5	83.71(3)
Ru1	P1	C1	121.6(1)	Ru1	P1	C2	123.85(9)
C1	P1	C2	99.0(2)	Ru1	P2	C8	108.2(1)
Ru1	P2	C10	122.7(1)	Ru1	P2	C11	119.1(1)
C8	P2	C10	103.1(2)	C8	P2	C11	100.3(2)
C10	P2	C11	100.3(2)	Ru1	P3	C9	108.2(1)
Ru1	P3	C12	121.3(1)	Ru1	P3	C13	119.5(1)
C9	P3	C12	103.7(2)	C9	P3	C13	101.4(2)
C12	P3	C13	100.1(2)	Ru1	P4	C14	108.8(1)
Ru1	P4	C16	122.4(1)	Ru1	P4	C17	119.2(1)
C14	P4	C16	102.1(2)	C14	P4	C17	100.5(2)
C16	P4	C17	100.6(2)	Ru1	P5	C15	107.4(1)
Ru1	P5	C18	117.2(1)	Ru1	P5	C19	124.4(1)
C15	P5	C18	101.0(2)	C15	P5	C19	102.7(2)
C18	P5	C19	101.0(2)	C44	O1	C47	101.9(6)
C48	O2	C49	93.5(6)	P1	C2	C3	121.6(2)
P1	C2	C7	121.2(2)	C3	C2	C7	117.2(3)
C2	C3	C4	121.2(3)	C3	C4	C5	120.3(3)
C4	C5	C6	119.6(3)	C5	C6	C7	119.6(3)
C2	C7	C6	122.0(3)	P2	C8	C9	110.9(3)
P3	C9	C8	109.0(2)	P4	C14	C15	110.7(3)
P5	C15	C14	109.1(3)	C21	C20	C25	113.9(3)
C21	C20	B1	122.2(3)	C25	C20	B1	123.9(3)
C20	C21	C22	123.6(3)	C21	C22	C23	120.2(3)
C22	C23	C24	118.9(3)	C23	C24	C25	119.9(3)
C20	C25	C24	123.5(3)	C27	C26	C31	114.3(3)
C27	C26	B1	122.0(3)	C31	C26	B1	123.7(3)
C26	C27	C28	122.3(3)	C27	C28	C29	120.5(3)
C28	C29	C30	119.0(3)	C29	C30	C31	120.1(3)
C26	C31	C30	123.7(3)	C33	C32	C37	114.9(3)
C33	C32	B1	121.2(3)	C37	C32	B1	123.7(3)
C32	C33	C34	122.9(3)	C33	C34	C35	120.2(3)
C34	C35	C36	118.2(3)	C35	C36	C37	121.3(3)
C32	C37	C36	122.4(3)	C39	C38	C43	114.7(3)
C39	C38	B1	120.8(3)	C43	C38	B1	124.4(3)

Table S-12. Bond Angles(^o) for [*trans*-(dmpe)₂Ru(H)PH(Me)Ph][BPh₄] (**2-BPh₄**) (continued).

atom	atom	atom	angle	atom	atom	atom	angle
C38	C39	C40	122.3(3)	C39	C40	C41	120.8(3)
C40	C41	C42	118.7(3)	C41	C42	C43	120.6(3)
C38	C43	C42	122.9(3)	O1	C44	C45	109.9(5)
C44	C45	C46	104.3(5)	C45	C46	C47	103.9(6)
O1	C47	C46	108.4(7)	O2	C48	C49	128.4(10)
O2	C49	C48	126.9(8)	C20	B1	C26	109.6(2)
C20	B1	C32	108.2(2)	C20	B1	C38	110.9(2)
C26	B1	C32	109.8(2)	C26	B1	C38	108.6(2)
C32	B1	C38	109.9(2)				

Table S-13. Torsion Angles(°) for [*trans*-(dmpe)₂Ru(H)PH(Me)Ph][BPh₄] (**2-BPh₄**).

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
Ru1	P1	C2	C3	90.2(3)	Ru1	P1	C2	C7	-89.2(2)
Ru1	P2	C8	C9	37.1(3)	Ru1	P3	C9	C8	40.0(3)
Ru1	P4	C14	C15	34.9(3)	Ru1	P5	C15	C14	42.6(3)
P1	Ru1	P2	C8	-100.2(1)	P1	Ru1	P2	C10	19.4(2)
P1	Ru1	P2	C11	146.3(2)	P1	Ru1	P3	C9	85.4(1)
P1	Ru1	P3	C12	-34.0(2)	P1	Ru1	P3	C13	-159.4(2)
P1	Ru1	P4	C14	-105.7(2)	P1	Ru1	P4	C16	12.9(2)
P1	Ru1	P4	C17	140.1(2)	P1	Ru1	P5	C15	78.9(2)
P1	Ru1	P5	C18	-168.4(2)	P1	Ru1	P5	C19	-40.6(2)
P1	C2	C3	C4	-178.6(3)	P1	C2	C7	C6	178.8(2)
P2	Ru1	P1	C1	39.0(2)	P2	Ru1	P1	C2	-90.3(1)
P2	Ru1	P3	C9	-13.7(1)	P2	Ru1	P3	C12	-133.1(2)
P2	Ru1	P3	C13	101.5(2)	P2	Ru1	P4	C14	76.0(2)
P2	Ru1	P4	C16	-165.4(2)	P2	Ru1	P4	C17	-38.2(2)
P2	Ru1	P5	C15	179.0(2)	P2	Ru1	P5	C18	-68.3(2)
P2	Ru1	P5	C19	59.5(2)	P2	C8	C9	P3	-49.3(4)
P3	Ru1	P1	C1	-45.0(2)	P3	Ru1	P1	C2	-174.4(1)
P3	Ru1	P2	C8	-9.3(1)	P3	Ru1	P2	C10	110.3(2)
P3	Ru1	P2	C11	-122.8(2)	P3	Ru1	P4	C14	161.8(2)
P3	Ru1	P4	C16	-79.6(2)	P3	Ru1	P4	C17	47.5(2)
P3	Ru1	P5	C15	-101.9(2)	P3	Ru1	P5	C18	10.7(3)
P3	Ru1	P5	C19	138.5(2)	P4	Ru1	P1	C1	-140.5(2)
P4	Ru1	P1	C2	90.1(1)	P4	Ru1	P2	C8	78.1(2)
P4	Ru1	P2	C10	-162.3(2)	P4	Ru1	P2	C11	-35.4(2)
P4	Ru1	P3	C9	-178.1(1)	P4	Ru1	P3	C12	62.5(2)
P4	Ru1	P3	C13	-62.9(2)	P4	Ru1	P5	C15	-16.4(2)
P4	Ru1	P5	C18	96.2(2)	P4	Ru1	P5	C19	-136.0(2)
P4	C14	C15	P5	-49.5(3)	P5	Ru1	P1	C1	134.8(2)
P5	Ru1	P1	C2	5.4(1)	P5	Ru1	P2	C8	159.1(1)
P5	Ru1	P2	C10	-81.3(2)	P5	Ru1	P2	C11	45.6(2)
P5	Ru1	P3	C9	-93.7(2)	P5	Ru1	P3	C12	146.8(2)
P5	Ru1	P3	C13	21.4(3)	P5	Ru1	P4	C14	-6.4(2)
P5	Ru1	P4	C16	112.1(2)	P5	Ru1	P4	C17	-120.7(2)
O1	C44	C45	C46	-26.4(7)	O1	C47	C46	C45	14(1)
C1	P1	C2	C3	-48.0(3)	C1	P1	C2	C7	132.6(3)
C2	C3	C4	C5	-0.7(5)	C2	C7	C6	C5	0.2(5)
C3	C2	C7	C6	-0.6(4)	C3	C4	C5	C6	0.2(5)
C4	C3	C2	C7	0.9(5)	C4	C5	C6	C7	0.1(5)
C8	C9	P3	C12	170.0(3)	C8	C9	P3	C13	-86.5(3)

Table S-13. Torsion Angles(°) for [*trans*-(dmpe)2Ru(H)PH(Me)Ph][BPh₄] (**2-BPh₄**) (continued).

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C9	C8	P2	C10	-94.2(3)	C9	C8	P2	C11	162.5(3)
C14	C15	P5	C18	-80.7(3)	C14	C15	P5	C19	175.3(3)
C15	C14	P4	C16	-95.8(3)	C15	C14	P4	C17	160.9(3)
C20	C21	C22	C23	-0.4(5)	C20	C25	C24	C23	0.2(5)
C20	B1	C26	C27	-30.1(4)	C20	B1	C26	C31	152.9(3)
C20	B1	C32	C33	-78.5(3)	C20	B1	C32	C37	95.6(3)
C20	B1	C38	C39	157.5(3)	C20	B1	C38	C43	-25.5(4)
C21	C20	C25	C24	-1.7(4)	C21	C20	B1	C26	-50.8(4)
C21	C20	B1	C32	-170.5(3)	C21	C20	B1	C38	69.0(3)
C21	C22	C23	C24	-1.3(5)	C22	C21	C20	C25	1.8(4)
C22	C21	C20	B1	-176.4(3)	C22	C23	C24	C25	1.3(5)
C24	C25	C20	B1	176.5(3)	C25	C20	B1	C26	131.1(3)
C25	C20	B1	C32	11.4(4)	C25	C20	B1	C38	-109.1(3)
C26	C27	C28	C29	0.3(5)	C26	C31	C30	C29	0.2(5)
C26	B1	C32	C33	162.0(3)	C26	B1	C32	C37	-23.9(4)
C26	B1	C38	C39	-82.0(3)	C26	B1	C38	C43	94.9(3)
C27	C26	C31	C30	0.1(5)	C27	C26	B1	C32	88.6(3)
C27	C26	B1	C38	-151.3(3)	C27	C28	C29	C30	0.0(6)
C28	C27	C26	C31	-0.4(5)	C28	C27	C26	B1	-177.7(3)
C28	C29	C30	C31	-0.3(5)	C30	C31	C26	B1	177.4(3)
C31	C26	B1	C32	-88.5(3)	C31	C26	B1	C38	31.7(4)
C32	C33	C34	C35	0.2(6)	C32	C37	C36	C35	1.4(6)
C32	B1	C38	C39	38.1(4)	C32	B1	C38	C43	-145.0(3)
C33	C32	C37	C36	-0.3(5)	C33	C32	B1	C38	42.7(4)
C33	C34	C35	C36	0.8(6)	C34	C33	C32	C37	-0.5(5)
C34	C33	C32	B1	174.1(3)	C34	C35	C36	C37	-1.6(6)
C36	C37	C32	B1	-174.7(3)	C37	C32	B1	C38	-143.3(3)
C38	C39	C40	C41	-0.3(5)	C38	C43	C42	C41	-1.0(5)
C39	C38	C43	C42	1.0(4)	C39	C40	C41	C42	0.4(5)
C40	C39	C38	C43	-0.4(4)	C40	C39	C38	B1	176.8(3)
C40	C41	C42	C43	0.2(5)	C42	C43	C38	B1	-176.1(3)
C44	O1	C47	C46	-30(1)	C44	C45	C46	C47	5.9(9)
C45	C44	O1	C47	34.6(8)					

Table S-14. Non-bonded Contacts out to 3.75 Å for [*trans*-(dmpe)₂Ru(H)PH(Me)Ph][BPh₄] (**2-BPh₄**).

atom	atom	distance	ADC	atom	atom	distance	ADC
O1	C48	3.607(9)	56501	O1	C17	3.715(6)	65502
O1	C16	3.738(6)	65502	O2	C17	3.243(9)	55404
O2	C16	3.249(9)	55404	O2	C35	3.668(9)	75503
C3	C40	3.599(5)	1	C4	C40	3.687(5)	1
C5	C12	3.628(5)	64502	C6	C22	3.700(5)	4
C7	C22	3.716(4)	4	C8	C45	3.641(7)	66503
C9	C31	3.704(5)	66503	C10	C43	3.417(5)	1
C10	C25	3.599(5)	1	C11	C36	3.537(6)	65503
C13	C30	3.629(5)	45504	C13	C37	3.636(5)	45504
C13	C29	3.666(6)	45504	C17	C48	3.593(8)	65502
C35	C48	3.576(7)	75503	C35	C49	3.695(7)	75503
C40	C45	3.708(6)	1				

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- ⁶ SMART: Area-Detector Software Package, Bruker Analytical X-ray Systems, Inc.: Madison, WI, (2001-03)
- ⁷ APEX:
- ⁸ SAINT: SAX Area-Detector Integration Program, V6.40; Bruker Analytical X-ray Systems Inc.: Madison, WI, (2003)
- ⁹ XPREF:(v 6.12) Part of the SHELXTL Crystal Structure Determination Package, Bruker Analytical X-ray Systems, Inc.: Madison, WI, (2001)
- ¹⁰ SADABS: Bruker-Nonius Area Detector Scaling and Absorption v. 2.05 Bruker Analytical X-ray Systems, Inc.: Madison, WI (2003).
- ¹¹ SIR97: Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G., & Spagna, R. SIR97: A new tool for crystal structure determination and refinement. *J. App. Cryst.* (1998)
- ¹² DIRDIF94: Beurskens, P.T., Admiraal, G., Beurskens, G., Bosman, W.P., de Gelder, R., Israel, R. and Smits, J.M.M.(1994). The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
- ¹³ Least-Squares: Function minimized $\sum w(|F_o| - |F_c|)^2$
- ¹⁴ Standard deviation of an observation of unit weight:
- $$[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$$
- where N_o = number of observations
- N_v = number of variables
- ¹⁵ Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).
- ¹⁶ Ibers, J. A. & Hamilton, W. C.; *Acta Crystallogr.*, *17*, 781 (1964).
- ¹⁷ Creagh, D. C. & McAuley, W.J. ; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

¹⁸ Creagh, D. C. & Hubbell, J.H.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

¹⁹ teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 & 1992).