(*R*)- and (*S*)-1,3-Bis(diphenylphosphino)-2-((diphenylphosphino)methyl)-1-phenylpropane ((*R*)- and (*S*)-heliphos): Solid-State and Solution Conformations of a Chiral, Tripodal Tris(phosphine) Ligand That Is Restrained to One Helical Conformation upon Coordination to a Rhodium(I) Metal Center

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(*R*)- and (*S*)-1,3-bis(diphenylphosphino)-2-((diphenylphosphino)methyl)-1-phenylpropane ((*R*)- and (*S*)-heliphos) were synthesized via an acid-catalyzed, diastereoselective Michael addition of diphenylphosphine to bis(1*R*,2*S*,5*R*)-(−)-menthyl) benzylidenemalonate. The crystal structure of [Rh((*R*)-heliphos)(NBD)](ClO_4) was determined by X-ray diffraction. As predicted by studies of molecular models, the framework of coordinated (*R*)-heliphos adopted a left-handed (Λ) helical conformation in the solid state, and NMR experiments indicated that it strongly favored this conformation in solution as well. The sense of helicity was controlled by the absolute configuration of the stereogenic carbon atom in the ligand.

Introduction

An essential component of asymmetric induction for many enantioselective catalytic systems is the conformation of the chiral ligand's framework. In many cases, the conformations of the framework are in themselves chiral and dictate the absolute spatial configuration of the pendant groups near the active sites on the catalyst. Control over framework conformations therefore greatly facilitates understanding the origins of enantioselection in these systems. Further, conformationally rigid or restrained ligands are common components of highly enantioselective catalysts. Approaches used to control conformational fluxionality have included use of rigid ligand frameworks (type I)[1] and use of derivatives of fluxional parent frameworks that are biased toward one conformer (type II).[2] Experimental studies of the solution framework conformation(s) of type II chiral ligands are limited in number[3] and have rarely been applied to chiral tripodal tris(phosphines).

There have been few chiral analogs of 1,1,1-tris-((diphenylphosphino)methyl)ethane (triphos) reported in the literature.[4] These ligands contain stereogenic centers either at phosphorus,[4a] at the ancillary groups attached to phosphorus,[4b,c] or at the central carbon atom of the ligand framework.[4d,e,f] There is an element of chirality in triphos and structurally equivalent tris(phosphines) that has not been directly controlled—the helical conformations they adopt upon coordination to metal centers.[4,5]

Figure 1 shows a model of the left (Λ)- and right-handed (Δ) helical conformations of coordinated triphos. The Λ and Δ conformations are enantiomers, and it is expected that interconversion between them is facile. Figure 1 also shows a model of the left (Λ)- and right-handed (Δ) helical conformations of coordinated (*R*)-1,3-bis(diphenylphosphino)-2-((diphenylphosphino)methyl)-1-phenylpropane ((*R*)-heliphos). The Λ and Δ conforma-

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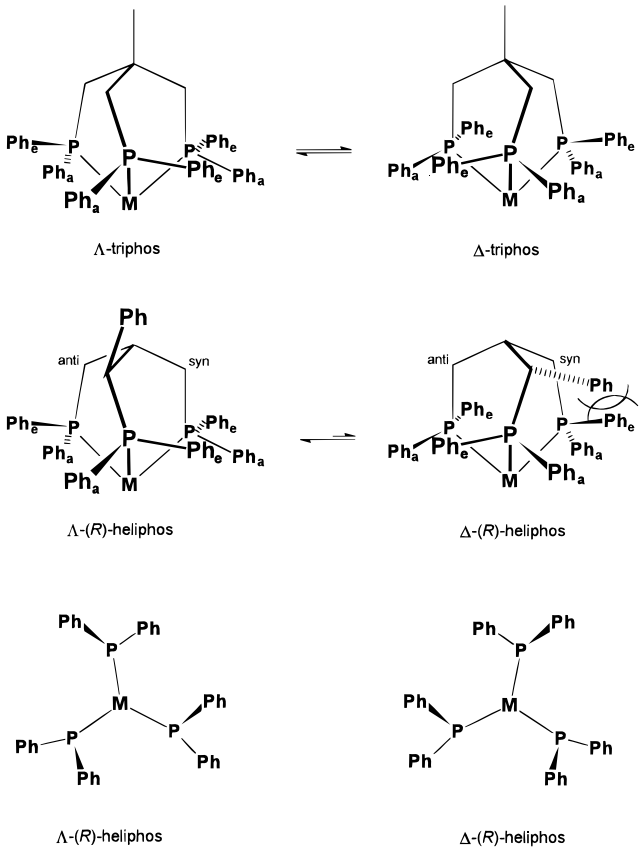

Figure 1. Schematic representations of Λ- and Δ-coordinated triphos and of (*R*)-heliphos showing the overlap of phenyl rings in the Δ-(*R*)-heliphos conformer. The chiral spatial arrangements of equatorial (e) and axial (a) phenyl rings as viewed from the perspective of the active sites on the metal center for Λ- and Δ-coordinated (*R*)-heliphos are also depicted at the bottom of the figure.

tions would be enantiomers in the absence of the phenyl substituent on the framework (as in triphos). The phenyl rings of the phosphine groups are held in chiral spatial arrangements of opposite absolute configuration by Λ- and Δ-(*R*)-heliphos. For Λ- and Δ-heliphos, one phenyl ring of each phosphine group is disposed roughly in the plane defined by the phosphorus atoms (equatorial), and the other projects toward an active site on the metal center (axial). Interconversion between the Λ and Δ conformations causes the equatorial and axial phenyl rings to exchange orientations, thereby inverting the asymmetric environment of the active sites on the catalyst.

Ligand Design

A ball and stick molecular model (HGS) of coordinated (*R*)-heliphos shows that severe steric repulsions exist between the phenyl ring on the framework and the equatorial phenyl ring of the *syn*-phosphine group in Δ-(*R*)-heliphos (Figure 1). Although we have not calculated the magnitude of this interaction, molecular models show that these phenyl rings physically overlap in the Δ configuration. This steric repulsion is absent in the Λ configuration. Conversely, models show that this severe steric repulsion occurs in Λ-(*S*)-heliphos but not in Δ-(*S*)-heliphos. We propose that these steric repulsions dictate the conformations of (*R*)- and (*S*)-heliphos, locking them into the less strained Δ-(*S*) and Λ-(*R*) conformers, respectively. Similar framework conformational arguments were recently published for the tetradentate tetraamine ligands (1-(2-pyridyl)-1-ethyl)-bis(2-(pyridylmethyl)amine and bis(2-quinolylmethyl)(1-(2-pyridyl)-1-ethyl)amine[6] while this work was in progress.[7]

Our interests are to develop several structural analogs of heliphos with various terminal phosphines, with differing substituents at the stereogenic center, and with further substitution on the backbone. Our ultimate objective is to investigate the uses of these chiral ligands in asymmetric catalysis. In this report, we describe the syntheses of the chiral tris(phosphine) ligands (*R*)- and (*S*)-heliphos as well as their helical conformations in the solid state and in solution upon coordination to rhodium in [Rh((*R*)-heliphos)(NBD)]-(ClO_4).

Experimental Section

Materials and Methods. The solvents *n*-hexane (K, Ph_2CO), methylene chloride (CaH_2), tetrahydrofuran (K, Ph_2CO), diethyl ether (K, Ph_2CO), toluene (K, Ph_2CO), triethylamine (CaH_2), tributylamine (CaH_2), and xylenes (CaH_2) were distilled from drying agents under argon gas, except methanol, which was deoxygenated by bubbling with argon gas or dinitrogen gas for 1 h. The argon and dinitrogen gases were passed through a bed of Drierite drying agent. Unless stated otherwise, commercial reagents were used without further purification and all operations were performed under an inert atmosphere of argon or dinitrogen gas.

All ^1H, ^{13}C, and ^{31}P NMR spectra were measured with a Bruker AM-400 NMR spectrometer operating at 400.13, 100.61, and 161.97 MHz, respectively. ^1H and ^{13}C NMR chemical shifts are reported in parts per million (δ) relative to tetramethylsilane using the solvent as an internal reference. ^{31}P NMR chemical shifts are reported in parts per million (δ) relative to an 85% H_3PO_4 external reference. All ^{13}C and ^{31}P NMR spectra are proton-decoupled unless stated otherwise. Mass spectra were measured using Kratos ms50 or AEI ms9 mass spectrometers. Microanalyses were performed at the University of Alberta Microanalysis Laboratory. Optical rotations were measured with a Perkin-Elmer 241 polarimeter at 589 nm (sodium D line) using 1.0 dm cells. Specific rotations, $[\alpha]_D$, are reported in degrees per decimeter at 25 °C, and the concentration (*c*) is given in grams per 100 mL. Melting points were measured with a Gallenkamp capillary melting point apparatus and are uncorrected.

$C_6H_5CH{=}C(C(O)OMenth)_2$ (2; Menth = (1*R*,2*S*,5*R*)-(−)-menthol). In air, dimenthyl malonate (**1**; 33.102 g, 87.1 mmol),[8] dissolved in benzene (120 mL), was sequentially treated with acetic acid (1.0 mL, 17.4 mmol), piperidine (0.35 mL, 3.5 mmol), and benzaldehyde (10.0 mL, 95.8 mmol) in an azeotropic distillation apparatus. The mixture was refluxed at 120 °C for 1.5 h and then at 130 °C for an additional 24 h. When the mixture was cooled to room temperature, benzene (100 mL) was added, and the resultant yellow-red solution was washed with 1 N HCl (2 × 100 mL), saturated $NaHCO_3$ (100 mL), and saturated NaCl (150 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure, affording a yellow-white solid. The solid was recrystallized from methanol to afford **2** as pure white needle-shaped crystals in 89.5% yield (36.53 g): mp

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103−104 °C; ^{1}H NMR ($CDCl_3$) δ 0.70−0.95 (m, 21 H), 1.05 (m, 3 H), 1.39 (m, 2 H), 1.50 (m, 2 H), 1.67 (br, 4 H), 1.81 (quint-d, J = 6.9, 2.6 Hz, 1 H), 1.92 (quint-d, J = 6.9, 2.6 Hz, 1 H), 2.07 (br d, J = 12.0 Hz, 1 H), 2.13 (br d, J = 12.0 Hz, 1 H), 4.85 (ddd, J = 24.4, 10.9, 4.4 Hz, 2 H), 7.25−7.40 (br, 3 H), 7.48 (m, 2 H), 7.68 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 15.87, 16.13, 20.81, 20.90, 22.00, 22.03, 22.91, 23.19, 25.35, 25.97, 31.32, 31.39, 34.07, 34.30, 40.22, 40.86, 46.70, 47.25, 75.39, 75.53, 127.31, 128.56, 129.40, 130.21, 133.02, 141.02, 163.59, 166.32; HRMS (EI) calcd for $C_{30}H_{44}O_4$ 468.3240, found 468.3224. Anal. Calcd for $C_{30}H_{44}O_4$: C, 76.94; H, 9.47. Found: C, 76.79; H, 9.62.

$C_6H_5CH(PPh_2)CH(C(O)OMenth)_2$ ((*R*)-3 and (*S*)-3). A solution of **2** (10 g, 21.3 mmol), *p*-toluenesulfonic acid hydrate (0.1 g, 0.53 mmol), and diphenylphosphine (4.05 g, 21.76 mmol) in CH_2Cl_2 (100 mL) was stirred at room temperature for 72 h. The solution was stirred over $NaHCO_3$ (1 g) for 2 h, filtered, washed with toluene (3 × 10 mL), and concentrated under reduced pressure to afford a white solid in 100% yield (13.97 g). The solid was determined to be a mixture of both **(*R*)-3** and **(*S*)-3** in a 70:30 ratio. The solid was dissolved in toluene (20 mL), and methanol was added (300 mL) under reflux. White needlelike crystals of **(*R*)-3** crystallized overnight and were isolated by filtration and washed with cold methanol (20 mL, 0 °C). The filtrate was concentrated under reduced pressure, affording a white solid which was dissolved in boiling methanol (300 mL) and concentrated to 200 mL for crystallization. Solid cubelike crystals of **(*S*)-3** were isolated by filtration and washed with cold methanol (20 mL, 0 °C). The filtrate was concentrated (~$^1/_2$ volume), and fractional crystallization afforded more **(*R*)-3** and **(*S*)-3**. The combined portions of **(*R*)-3** were recrystallized from toluene and methanol (1:20), affording white needlelike crystals of **(*R*)-3** in 80.1% yield (7.83 g): mp 96 °C; ^{1}H NMR ($CDCl_3$) δ 0.41 (d, J = 6.9 Hz, 3 H), 0.62 (q, 1 H), 0.70−0.80 (m, 10 H), 0.83−1.10 (m, 10 H), 1.18−1.35 (m, 2 H), 1.42−1.63 (m, 6 H), 1.69 (m, 2 H), 1.91 (m, 2 H), 3.94 (dd, J_{H-H} = 12.1 Hz, J_{P-H} = 6.3 Hz, 1 H), 4.39 (d, J = 12.1 Hz, 1 H), 4.45 (td, J = 4.4, 10.9 Hz, 1 H), 4.80 (td, J = 4.4, 10.9 Hz, 1 H), 6.68 (d, J = 7.2 Hz, 2 H), 6.91−7.03 (m, 3 H), 7.04−7.09 (m, 2 H), 7.13−7.18 (m, 2 H), 7.25−7.36 (m, 4 H), 7.55 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 15.69, 15.98, 20.84, 20.94, 21.98, 22.06, 22.93, 23.09, 25.50, 25.67, 31.20, 31.45, 34.12, 34.27, 40.05, 40.51, 44.93 (d, J_{P-C} = 21.6 Hz), 46.60, 47.06, 56.73 (d, J_{P-C} = 31.8 Hz), 75.38, 75.91, 126.20, 127.54, 127.82, 127.90, 128.21, 128.26, 128.36, 128.73, 129.42, 132.65, 132.82, 134.04 (d, J_{P-C} = 14.8 Hz), 135.52, 135.75, 135.88 (d, J_{P-C} = 14.8 Hz), 137.59, 166.93 (d, J_{P-C} = 19.2 Hz), 167.78; ^{31}P NMR ($CDCl_3$) δ 4.36 (s); HRMS (EI) calcd for $C_{42}H_{55}O_4P$ 654.3838, found 654.3838. Anal. Calcd for $C_{42}H_{55}O_4P$: C, 77.03; H, 8.47. Found: C, 77.04; H, 8.73.

The combined portions of **(*S*)-3** were recrystallized from pure methanol affording solid white cubes of **(*S*)-3** in 63.9% yield (2.68 g): mp 95 °C; ^{1}H NMR ($CDCl_3$) δ 0.45 (d, J = 5.9 Hz, 3 H), 0.65−1.00 (m, 20 H), 1.08 (m, 1 H), 1.25 (m, 2 H), 1.35−1.65 (m, 6 H), 1.70 (m, 2 H), 2.08 (m, 2 H), 3.92 (dd, J_{H-H} = 11.8 Hz, J_{P-H} = 8.7 Hz, 1 H), 4.39 (d, J = 11.8 Hz, 1 H), 4.51-(td, J = 4.4, 10.9 Hz, 1 H), 4.80 (td, J = 4.4, 10.9 Hz, 1 H), 6.64 (d, J = 7.3 Hz, 2 H), 6.95−7.10 (m, 5 H), 7.15 (m, 2 H), 7.25−7.36 (m, 4 H), 7.55 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 15.74, 16.49, 20.92, 21.88, 22.06, 22.92, 23.43, 25.33, 26.19, 31.20, 31.38, 34.10, 34.30, 40.26, 40.42, 45.13 (d, J_{P-C} = 23.3 Hz), 46.64, 46.97, 56.43 (d, J_{P-C} = 32.1 Hz), 75.29, 75.97, 126.23, 127.58, 127.81, 127.89, 128.12, 128.22, 128.27, 128.60, 128.62, 129.61, 132.38, 132.55, 133.64 (d, J_{P-C} = 16.3 Hz), 135.79, 136.02, 136.52 (d, J_{P-C} = 15.4 Hz), 137.51, 167.21 (d, J_{P-C} = 19.5 Hz), 167.81; ^{31}P NMR ($CDCl_3$) δ 7.92; HRMS (EI) calcd for $C_{42}H_{55}O_4P$ 654.3838, found 654.3878. Anal. Calcd for $C_{42}H_{55}O_4P$: C, 77.09; H, 8.47. Found: C, 76.99; H, 8.47.

$C_6H_5CH[P(O)Ph_2]CH(CH_2OH)_2$ ((*R*)-5 and (*S*)-5). To a stirred mixture of $LiAlH_4$ (1.08 g, 28.46 mmol) and ether (100 mL) was added dropwise a solution of **(*R*)-3** (6.5 g, 9.47 mmol) in ether (100 mL) at 0 °C over 10 min. The dropping funnel was rinsed with ether (50 mL); the reaction mixture was stirred for 20 min at 0 °C and then for 1 h at room temperature. The $LiAlH_4$ was neutralized by the dropwise addition of 1.1 mL of deoxygenated distilled water, 1.1 mL of deoxygenated 10% NaOH solution at 0 °C, and 3.3 mL of deoxygenated distilled water at room temperature. The mixture was stirred for 30 min, filtered, washed with CH_2Cl_2 (3 × 100 mL), and concentrated under reduced pressure, yielding a white solid. The solid was recrystallized from toluene (100 mL), affording white crystals of the phosphine diol (**4**). The phosphine diol was dissolved in CH_2Cl_2 (400 mL, undistilled) and oxidized by adding a solution of 10% H_2O_2 (35 mL). The reaction mixture was stirred for 5 min and then washed with a solution of saturated $Na_2S_2O_3$ (50 mL) until the excess H_2O_2 was neutralized (negative result with saturated solution of KI). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure, affording **(*R*)-5** in 77.3% yield (2.68 g), as a white powder. Further purification was unnecessary: ^{1}H NMR ($CDCl_3$) δ 2.48 (m, 1 H), 3.25 (m, 2 H), 3.50 (dd, J = 4.9, 10.7 Hz, 1 H), 3.60 (dd, J = 11.8, 8.1 Hz, 1 H), 4.29 (dd, J_{P-H} = 9.9 Hz, J_{H-H} = 3.5 Hz, 1 H), 7.10−7.35 (m, 6 H), 7.40−7.60 (m, 7 H), 7.92 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 44.06, 44.75, 60.52, 61.33 (J_{P-C} = 11.8 Hz), 127.35, 128.14, 128.25, 128.41, 128.82, 128.94, 130.92, 131.04, 131.23, 131.31, 131.36, 131.92, 132.11, 132.91 (J_{P-C} = 3.1 Hz); ^{31}P NMR ($CDCl_3$) δ 37.48; CIMS (carrier gas NH_3) calcd for $C_{22}H_{23}O_3P$ 366.3972, found 367.4 (M + H), 368.3 (M + 2H), 369.4 (M + 3H). Anal. Calcd for $C_{22}H_{23}O_3P$: C, 72.12; H, 6.33. Found: C, 72.17; H, 6.11. **(*S*)-5** was obtained by the same method.

$C_6H_5CH[P(O)Ph_2]CH(CH_2OMs)_2$ ((*R*)-6 and (*S*)-6). To a −35 °C CH_2Cl_2 (250 mL) solution of **(*R*)-5** (2.50 g, 6.82 mmol) and dry triethylamine (2.85 mL, 20.46 mmol) was added a solution of methanesulfonyl chloride (1.31 mL, 16.95 mmol) in dry CH_2Cl_2 (15 mL) over 10 min. The mixture was warmed to room temperature over 1 h and then stirred for an additional 45 min. In air, the reaction flask was placed in an ice bath and the solution was quenched by the addition of crushed ice (25 g), followed by cold water (25 g), with vigorous stirring. The ice bath was removed, and the solution was stirred until the ice melted. The organic layer was separated and the aqueous layer back-extracted with CH_2Cl_2 (50 mL). The combined organic layers were sequentially washed with cold water (2 × 60 mL), cold saturated $NaHCO_3$ (2 × 100 mL), and cold brine (2 × 60 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford a light yellow solid. The solid was recrystallized from methanol (10 mL) at −10 °C overnight, affording white crystals of **(*R*)-6** in 86.1% yield (3.07 g): mp 142−143 °C; ^{1}H NMR ($CDCl_3$) δ 2.80 (s, 3 H), 2.80 (s, 3 H), 2.95 (m, 1 H), 3.87 (m, 2 H), 4.15 (d, J = 6.1 Hz, 2 H), 4.85 (dd, J_{P-H} = 10.7 Hz, J_{H-H} = 2.9 Hz, 1 H), 7.00−7.30 (m, 6 H), 7.30−7.60 (m, 7 H), 7.95 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 36.98, 37.07, 39.19, 43.38 (d, J_{P-C} = 67.6 Hz), 67.56 (m), 128.07, 128.15, 128.26, 128.96, 129.13, 129.25, 130.37, 130.43, 130.65, 130.74, 130.95, 131.04, 131.48, 131.95, 132.27, 132.35 (br); ^{31}P NMR ($CDCl_3$) δ 31.72. Anal. Calcd for $C_{24}H_{27}O_7S_2P$: C, 55.16; H, 5.21. Found: C, 54.93; H, 5.27. **(*S*)-6** was obtained by the same method.

$C_6H_5CH[P(O)Ph_2]CH(CH_2PPh_2)_2$ ((*R*)-7 and (*S*)-7). Potassium hydride (3.25 g, 28.48 mmol, 35% mineral oil dispersion) was washed with THF (3 × 30 mL) and then suspended in THF (100 mL). Diphenylphosphine (6.23 g, 33.49 mmol) was added dropwise, resulting in a red solution. **(*R*)-6** (2.5 g, 4.78 mmol) was added at −10 °C in one portion as a powder. Stirring was continued at −10 °C for 20 min and then at room temperature for an additional 40 min. The reaction was quenched by the addition of deoxygenated saturated NH_4Cl (10 mL). The mixture was stirred until the organic layer became clear (20 min) and a white precipitate remained. The organic layer was filtered from the white precipitate, and the precipitate was washed with THF (2 × 20 mL). The combined organic fractions were then dried over deoxygenated $MgSO_4$,

filtered, and concentrated under reduced pressure in a warm water bath. The resulting oil was sonicated in the presence of hexanes (30 mL), leaving a white powder and clear solution. The mixture was filtered and the solid washed with hexanes (2 × 30 mL) and dried under reduced pressure. The solid was recrystallized from methanol, affording white crystals of **(*R*)-7** in 81.7% yield (2.57 g): mp 211−212 °C; $[\alpha]_D = -91.74°$ (toluene, *c* 0.5047); ^{1}H NMR ($CDCl_3$) δ 1.70 (m, 2 H), 2.21 (br, 1 H), 3.10 (br, 1 H), 3.80 (m, 1 H), 4.68 (m, 1 H), 7.00−7.40 (m, 29 H), 7.56 (m, 4 H), 7.71 (br, 2 H); ^{13}C NMR ($CDCl_3$) δ 32.45 (m), 32.85 (m, two carbons overlapped), 46.95 (ddd, J_{P-C} = 70.2, 10.9, 7.3 Hz), 125.38, 127.29, 128.03, 128.14, 128.23, 128.31, 128.39, 128.47, 128.54, 128.88, 129.11, 130.76, 130.84, 130.97, 131.09, 131.17, 131.56, 131.99, 132.07, 132.13, 132.20, 132.31, 132.38, 132.69 (d, J_{P-C} = 29.8 Hz), 133.49, 133.68, 133.73 (d, J_{P-C} = 10.7 Hz), 134.24, 134.45, 136.28 (d, J_{P-C} = 11.1 Hz), 136.73 (d, J_{P-C} = 13.6 Hz), 138.71 (d, J_{P-C} = 9.1 Hz), 139.25 (d, J_{P-C} = 10.3 Hz); ^{31}P NMR ($CDCl_3$) δ 32.62, −20.99, −23.97; HRMS (EI) calcd for $C_{46}H_{41}OP_3$ 702.2371, found 702.2372. Anal. Calcd for $C_{46}H_{41}OP_3$: C, 78.68; H, 5.88. Found: C, 78.37; H, 5.93. **(*S*)-7** was obtained by the same method: $[\alpha]_D = +91.93°$ (toluene, *c* 0.5058).

$C_6H_5CH(PPh_2)CH(CH_2PPh_2)_2$ ((*R*)-heliphos and (*S*)-heliphos). A high-pressure reactor was charged with a solution of **(*R*)-7** (2.5 g, 3.56 mmol) in distilled *p*-xylene (20 mL). The reactor was placed in an ice-water bath. Distilled tri-*n*-butylamine (5.04 mL, 21.2 mmol) and trichlorosilane (1.80 mL, 17.8 mmol) were added, and the reactor was sealed. The reaction mixture was warmed to room temperature and then heated to 140 °C for 96 h. The reactor was cooled to room temperature and the reaction mixture treated with 30% deoxygenated aqueous NaOH (50 mL). The reaction mixture was stirred at 60 °C for 1.5 h until both layers became transparent. The layers were separated, and the aqueous layer was back-extracted with toluene (2 × 25 mL). The combined organic layers were washed sequentially with 30% deoxygenated aqueous NaOH (50 mL), deoxygenated distilled water (50 mL), 0.1 N HCl (75 mL), and deoxygenated distilled water (50 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The remaining white solid was dried under reduced pressure for an additional 1 h and then recrystallized from methanol, affording white cube-shaped crystals of (*R*)-heliphos in 82.0% yield (2.00 g): mp 140−141 °C; $[\alpha]_D = -71.74°$ (toluene, *c* 1.0174); ^{1}H NMR ($CDCl_3$) δ 1.80 (br, 3 H), 2.99 (br, 1 H), 3.26 (br, 1 H), 4.59 (br, 1 H), 6.90−7.60 (m, 35 H); ^{13}C NMR ($CDCl_3$) δ 31.48 (m), 32.11 (m), 33.51 (m), 47.20 (dd, J_{P-C} = 8.5, 9.4 Hz), 126.64, 127.82, 127.89, 128.14, 128.24, 128.38, 128.44 (br), 128.83, 131.29, 131.38, 132.06, 132.15, 132.23, 132.33, 133.53, 133.72, 133.85, 134.05, 134.22, 136.44 (d, J_{P-C} = 14.3 Hz), 137.01 (d, J_{P-C} = 4.9 Hz), 137.14 (d, J_{P-C} = 3.2 Hz), 137.39 (d, J_{P-C} = 14.1 Hz), 137.96 (d, J_{P-C} = 9.2 Hz), 139.54 (d, J_{P-C} = 10.9 Hz); ^{31}P NMR ($CDCl_3$) δ −12.23, −21.72, −24.08; HRMS (EI) calcd for $C_{46}H_{41}P_3$ 686.2421, found 686.2437. Anal. Calcd for $C_{46}H_{41}P_3$: C, 80.51; H, 6.02. Found: C, 80.68; H, 6.09. (*S*)-heliphos was obtained by the same method: $[\alpha]_D = +72.50°$ (toluene, *c* 0.5310).

Optical Purity of (*R*)-heliphos. Crystallized (*R*)-heliphos was oxidized to the corresponding tris(phosphine oxide) by following the same experimental procedure used to oxidize **(*R*)-3** to **(*R*)-4**. A mixture of (*R*)-heliphos tris(phosphine oxide) 6 equiv of (*R*)-(+)-1,1′-bi-2-naphthol were dissolved in $CDCl_3$.[9] ^{31}P NMR (C_6D_6) δ 35.51, −21.45, −23.88.

[Rh((*R*)-heliphos)(NBD)](ClO_4). A stirred solution of [Rh($NBD)_2$](ClO_4) (98.5 mg, 0.25 mmol)[10] in CH_2Cl_2 (1.0 mL) at 0 °C was slowly treated with a solution of (*R*)-heliphos (0.1752 g, 0.25 mmol) in CH_2Cl_2 (1.0 mL). The yellow-red reaction mixture was stirred at room temperature for 1 h. The solution was concentrated under reduced pressure, and the resulting orange solid was washed with hexanes (3 × 5 mL). The solid was crystallized from methanol, affording red-orange crystals of [Rh((*R*)-heliphos)(NBD)](ClO_4) in 88.2% yield (216 mg): $[\alpha]_D = +127.18°$ (toluene, *c* 0.5032); ^{1}H NMR (CD_2Cl_2) δ 1.41 (br, 2 H), 2.37 (dd, *J* = 5.3, 16.2 Hz, 1 H), 2.67 (dd, *J* = 4.9, 15.2 Hz, 1 H), 3.35 (m, 1 H), 3.55 (m, 5 H), 3.81 (d, *J* = 9.0 Hz, 1 H), 3.87 (br, 3 H), 6.27 (m, 2 H), 6.70 (m, 8 H), 7.00−7.35 (m, 15 H), 7.50 (br, 5 H), 7.12 (m, 3 H), 7.85 (m, 2 H); ^{1}H{^{31}P} NMR (CD_2Cl_2:$CDCl_3$ = 1:1) δ 1.44 (br, 2 H), 2.42 (d, $^2J_{H-H}$ = 16.2 Hz, 1 $H^{\beta pro-S(C13)}$), 2.68 (d, $^2J_{H-H}$ = 15.6 Hz , 1 $H^{\beta pro-S(C12)}$), 3.40 (dd, $^2J_{H-H}$ = 16.2 Hz, $^3J_{H-H}$ = 7.0 Hz, 1 $H^{\beta pro-R(C13)}$), 3.49 (br, 2 H), 3.53 (br, 2 H), 3.63 (dd, $^2J_{H-H}$ = 15.6 Hz, $^3J_{H-H}$ = 7.6 Hz, 1 $H^{\beta pro-R(C12)}$), 3.82 (s, 1 $H^{\beta pro-S(C11)}$), 3.89 (br, 2 H), 3.98 (br, 1H), 6.28 (d, 2 H), 6.70 (m, 8 H), 7.00−7.35 (m, 15 H), 7.50 (br, 5 H), 7.12 (m, 3 H), 7.85 (d, 2 H); ^{13}C NMR (CD_2Cl_2) δ 25.26 (t, J_{P-C} = 17.2 Hz), 27.12 (dd, J_{P-C} = 12.6, 20.4 Hz), 37.83 (br), 44.27 (t, J_{P-C} = 13.47 Hz), 46.67, 46.91 (br), 47.42 (m), 61.82, 127.75, 127.86, 128.16, 128.61, 128.71, 129.05, 129.14, 129.53, 129.55, 129.64, 130.01, 130.10, 130.46, 130.70, 130.77, 130.88, 130.99, 131.48, 131.52, 131.59, 131.64, 132.25, 132.32, 132.43, 134.45 (d, J_{P-C} = 5.4 Hz), 134.78 (d, J_{P-C} = 5.4 Hz), 136.27, 136.59, 136.70, 136.83, 137.03 (d, J_{P-C} = 10.8 Hz), 139.95 (d, J_{P-C} = 8.9 Hz); ^{31}P NMR (CD_2Cl_2) δ −7.23 (ddd, J_{P-Rh} = 111.6, J_{P-P} = 19.3, 35.9 Hz), −0.765 (ddd, J_{P-Rh} = 113.9, J_{P-P} = 19.3, 36.7 Hz), 32.25 (pseudo-dt, J_{P-Rh} = 116.7, J_{P-P} = 36.7, 35.9 Hz). Anal. Calcd for $C_{53}H_{49}P_3RhClO_4$: C, 64.89; H, 5.04. Found: C, 64.89; H, 5.08. **[Rh((*S*)-heliphos)(NBD)](ClO_4)** was obtained by the same method: $[\alpha]_D = -128.64°$ (toluene, *c* 0.4975).

[Rh(triphos)(NBD)](ClO_4). A stirred solution of [Rh($NBD)_2$](ClO_4) (48.4 mg, 0.125 mmol)[10] in CH_2Cl_2 (2.0 mL) at 0 °C was slowly treated with a solution of triphos (78.2 mg, 0.125 mmol, Aldrich) in CH_2Cl_2 (1.0 mL). The yellow-red reaction mixture was stirred at room temperature for 1 h. The solution was concentrated under reduced pressure, and the resulting orange solid was washed with hexanes (3 × 10 mL). The solid was used without further purification: ^{1}H NMR (CD_2Cl_2) δ 1.46 (s, 2 H), 1.59 (q, 3 H), 2.42 (dd, 6 H, $(CH_2)_3CCH_3$), 3.61 (br, 4 H), 3.88 (br, 2 H), 6.89−7.25 (m, 24 H), 7.28−7.41 (t, 6 H); ^{31}P NMR (CD_2Cl_2) δ −9.59 (d, J_{P-Rh} = 113.7 Hz); ^{1}H NMR (CD_2Cl_2, −80 °C) δ 1.38 (s, 2 H), 1.50 (br, 3 H), 2.29 (br, 6 H, $(CH_2)_3CCH_3$), 3.46 (br, 4 H), 3.90 (br, 2 H), 6.92−7.02 (br, 12 H), 7.09 (t, 12 H), 7.28 (t, 6 H); ^{31}P NMR (CD_2Cl_2, −80 °C) δ 8.99 (d, J_{P-Rh} = 113.7 Hz).

Crystallographic Analysis of [Rh((*R*)-heliphos)(NBD)](ClO_4)·MeOH. Crystals suitable for an X-ray diffraction study were obtained by slow evaporation of methanol solutions of [Rh((*R*)-heliphos)(NBD)](ClO_4) under a stream of argon gas. The crystal system was monoclinic, and the space group $P2_1$ (No. 4) was consistent with an enantiomerically pure compound. Crystal data, details of data collection, and structure solution and refinement details are outlined in Table 1.

Results and Discussion

Synthesis of (*R*)- and (*S*)-heliphos. The ligands (*R*)- and (*S*)-heliphos were prepared according to Schemes 1 and 2. Knovenagel condensation of **1** with benzaldehyde in methylene chloride solution yielded bis-(1*R*,2*S*,5*R*)-(−)-menthyl) benzylidenemalonate (**2**). The most notable feature in this synthetic pathway was the acid-catalyzed, diastereoselective Michael addition of diphenylphosphine to **2** (Scheme 1). The diastereomers (*R*)-**3** and (*S*)-**3** were easily separated by fractional recrystallization from methanol/toluene solution. The separated diastereomers were then reduced with lithium

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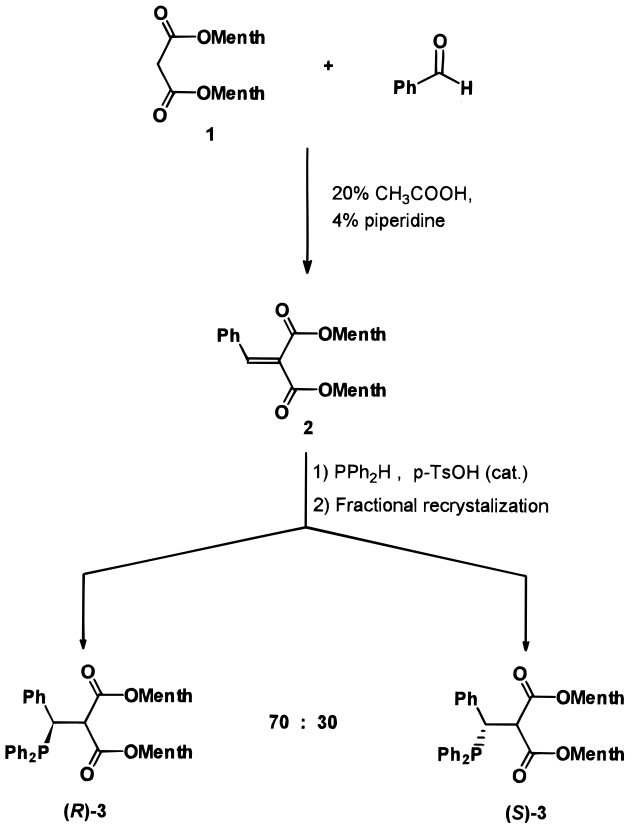
Table 1. Crystal Data and Refinement Details for [((*R*)-heliphos)Rh(NBD)](ClO$_4$)·MeOH

formula	$C_{54}H_{53}ClO_5P_3Rh$
fw	1013.23
cryst dimens (mm)	0.32 × 0.25 × 0.24
cryst syst	monoclinic
space group	$P2_1$ (No. 4)
unit cell params[a]	
a (Å)	9.5295(9)
b (Å)	18.307(2)
c (Å)	13.564(2)
β (deg)	99.362(13)
V (Å^3)	2334.9(5)
Z	2
ρ_{calcd} (g cm^{-3})	1.441
μ (mm^{-1})	0.575
diffractometer	Enraf-Nonius CAD4[b]
radiation (λ (Å))	Mo Kα (0.710 73)
monochromator	incident beam, graphite cryst
temp (°C)	−50
scan type	$\theta-2\theta$
data collection 2θ limit (deg)	50.0
total no. of data collected	8826
index ranges[c]	$-11 \le h \le 11$, $-21 \le k \le 21$, $-16 \le l \le 16$
no. of indep rflns	8169
no. of observns (NO)	7116 ($F_o^2 \ge 2\sigma(F_o^2)$)
structure soln method	direct methods/fragment search (DIRDIF-94[d])
refinement method	full-matrix least squares on F^2 (SHELXL-93[e])
abs cor method	DIFABS[f]
range of abs cor factors	1.258−0.840
no. of data/restraints/params	8169 ($F_o^2 \ge -3\sigma(F_o^2)$]/0/579
Flack absolute structure param	−0.06 (4)[g]
goodness of fit (S)[h]	1.054 ($F_o^2 \ge -3\sigma(F_o^2)$]
final R indices[i]	
$F_o^2 > 2\sigma(F_o^2)$	$R1 = 0.0579$, wR2 = 0.1567
all data	R1 = 0.0706, wR2 = 0.1715
largest diff peak and hole (e Å^{-3})	+1.488 and −0.987

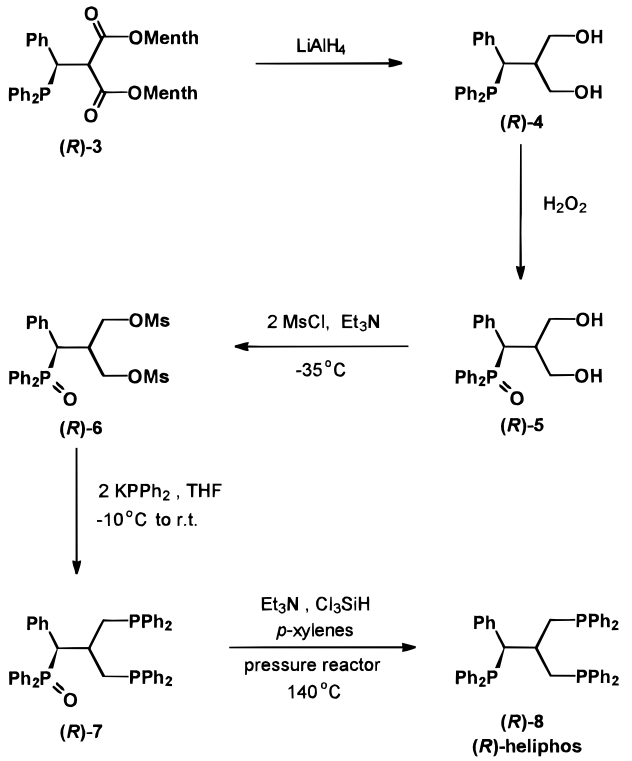
[a] Obtained from least-squares refinement of 24 reflections with 20.2° < 2θ < 25.4°. [b] Programs for diffractometer operation and data collection were those supplied by Enraf-Nonius. [c] Data in the quadrants $\pm h,+k,+l$ and $\pm h,-k,-l$ were collected. [d] Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-94 Program System; Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994. [e] Sheldrick, G. M. SHELXL-93. Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1993. Refinement was carried out on F_o^2 for all reflections (all having $F_o^2 > -3\sigma(F_o^2)$). Weighted R factors wR2 and all goodness of fit values S are based on F_o^2; conventional R factors R1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R1, and is not relevant to the choice of reflections for refinement. R factors based on F_o^2 are statistically about twice as large as those based on F_o, and R factors based on *all* data will be even larger. [f] Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158−166. [g] Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876−881. The Flack parameter will be refined to a value near 0 if the structure is in the correct configuration and will be refined to a value near 1 for the inverted configuration. [h] $S = [\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.1185P)^2 + 0.4729P]^{-1}$, where $P = [\mathrm{Max}(F_o^2,0) + 2F_c^2]/3$). [i] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^4)]^{1/2}$.

aluminum hydride to produce the phosphine diol **4** (Scheme 2). The phosphine diol **4** was oxidized with peroxide to produce **5** in 89% yield. Oxidation of **4** to the phosphine oxide **5** was necessary to prevent intramolecular displacement of a mesyl group by the phosphine in **(*R*)-6** and **(*S*)-6**. Reaction of **5** with 2 equiv of mesyl chloride in the presence of triethylamine produced the dimesylate **6**. Displacement of the mesyl

Scheme 1



Scheme 2[a]



[a] (*S*)-heliphos is prepared by starting with **(*S*)-2**.

groups with diphenylphosphine was performed by the reaction of **6** with $KPPh_2$ to produce **7**. We originally used a 10% excess of potassium hydride to ensure complete formation of $KPPh_2$ from diphenylphosphine. The resultant bis(phosphine) **7** was partially racemized (∼20%) in the process, as determined by the ^{31}P NMR

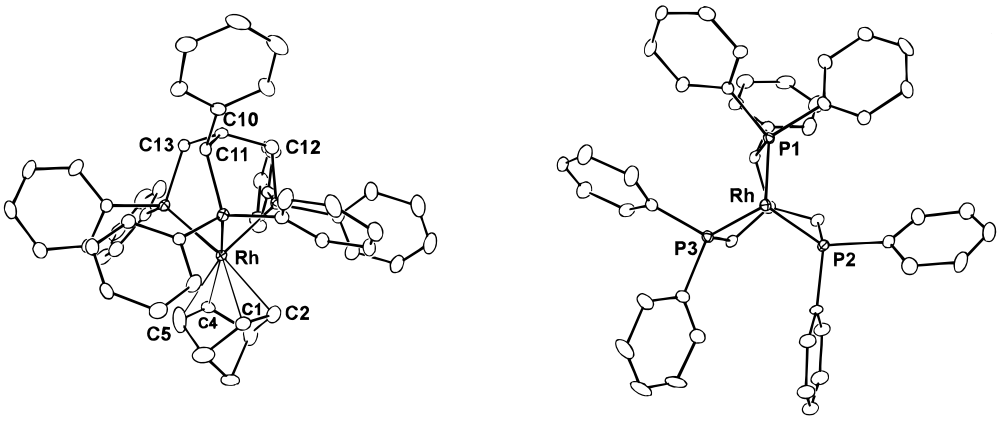


Figure 2. The crystal structure of Λ-[Rh((*R*)-heliphos)(NBD)](ClO_4), as determined by X-ray diffraction. Also shown is the arrangement of phenyl groups as viewed by the active sites on the metal (NBD is omitted for clarity). Atoms are represented at the 20% probability level. Selected bond lengths (Å) and torsional angles (deg) are as follows: Rh−P(1), 2.352(2); Rh−P(2), 2.376(2); Rh−P(3), 2.308(2); Rh−C(1), 2.216(7); Rh−C(2), 2.254(10); Rh−C(4), 2.177(7); Rh−C(5), 2.260(13); Rh−P(1)−C(11)−C(10), −30.6(6); Rh−P(2)−C(12)−C(10), −35.1(7); Rh−P(3)−C(13)−C(10), −27.9(6).

spectrum recorded in methylene chloride solution containing (*R*)-(+)-1,1′-bi-2-naphthol. The racemization of **7** was averted upon using an excess of diphenylphosphine to potassium hydride, ensuring that no free hydride was available to deprotonate **6** or **7**. Finally, both enantiomers of optically pure heliphos were obtained by reducing **7** with trichlorosilane in the presence of tributylamine in a sealed high-pressure reactor. The optical purity of (*R*)-heliphos was confirmed upon oxidation to (*R*)-heliphos tris(phosphine oxide). Addition of 6 equiv (*R*)-(+)-1,1′-bi-2-naphthol in $CDCl_3$ resulted in three peaks in the ^{31}P NMR spectrum. Addition of (*S*)-heliphos tris(phosphine oxide) resulted in three new peaks, indicating that (*S*)-heliphos was absent from the purified (*R*)-heliphos.

Rhodium(I) Norbornadiene Complexes of Triphos and Heliphos. The Rh(I) complex [Rh(triphos)(NBD)](ClO_4) was prepared by reaction of triphos with [$Rh(NBD)_2$](ClO_4). The methylene protons of Λ- and Δ-triphos ($CH_3C(CH_2PPh_2)_3$) are diastereotopic, and exchange magnetic environments upon interconversion between the Λ and Δ conformations. To determine if interconversion between coordinated Λ- and Δ-triphos was rapid, we recorded the ^1H NMR spectrum of [Rh(triphos)(NBD)](ClO_4) at −80 °C in methylene chloride solution. We were unable to separate the signals for the diastereotopic methylene protons, indicating that interconversion between Λ- and Δ-triphos was rapid on the NMR time scale.

The Rh(I) complex [Rh((*R*)-heliphos)(NBD)](ClO_4) ((*R*)-**8**) was prepared by the slow addition of (*R*)-heliphos to [$Rh(NBD)_2$](ClO_4) in methylene chloride solution. The solid-state structure of [Rh((*R*)-heliphos)(NBD)](ClO_4) was determined by X-ray diffraction. Figure 2 shows the molecular structure of (*R*)-**8**. The framework of (*R*)-**8** adopted the predicted Λ configuration in the solid state, with the Rh−P−C(methylene)−C(10) torsional angles ranging from 35.1(7) to 27.9(6)°. These values are comparable to those observed for other triphos-type ligands.[5] The distances (in Å) between the plane containing the phosphorus atoms and the ipso carbons of the axial phenyl rings are 0.474(8) (C(31)), 0.372(9) (C(61)), and 0.415(9) (C(81)). The corresponding distances for the equatorial phenyl rings are −0.21(8) (C(41)), −0.168(9) (C(61)), and −0.107(8) (C(71)) (inclinations toward the ligand framework are assigned a negative value). Figure 2 also shows the propeller-like asymmetric array of pendant phenyl rings around the rhodium center, with alternating axial and equatorial orientations.

We believe the framework of [Rh((*R*)-heliphos)(NBD)](ClO_4) also strongly favored the Λ conformer in solution for two reasons. First, the *pro-S* (assuming replacement by a phenyl ring) protons at C(12) and C(13) of Λ-(*R*)-heliphos are oriented toward an adjacent arm's equatorial phenyl ring. This orientation is similar to that of the framework phenyl ring in the unfavored Δ-(*R*)-heliphos (Figure 1). For both C(12) and C(13),[11] the $^1H\{^{31}P\}$ NMR signal for the *pro-S* proton was shifted upfield from that for the *pro-R* proton by approximately 0.9 ppm. We believe this difference in chemical shift was caused by ring current effects of the equatorial phenyl group and indicated that interconversion with appreciable amounts of Δ-(*R*)-**8** did not occur. Second, the coupling constants between the apical proton (at C(10)) and the two *pro-R* methylene protons (at C(12) and C(13)) were approximately 7 Hz, while those with the three *pro-S* methylene protons (at C(11), C(12), and C(13)) were approximately 0 Hz. According to the Karplus relationship,[12] a coupling constant of 0 Hz corresponds to $H^{\alpha(C(10))} - H^{\beta(pro-S)}$ dihedral angles of approximately 90°. These angles are supported by those obtained from molecular models (90°), and the calculated[13] hydrogen atom positions in the crystal structure of Λ-[Rh((*R*)-heliphos)(NBD)](ClO_4) ($H^{\alpha(C(10))} - H^{\beta(pro-S)(C(11))} = 87°$, $H^{\alpha(C(10))} - H^{\beta(pro-S)(C(12))} = 82°$, $H^{\alpha(C(10))} - H^{\beta(pro-S)(C(13))} = 75°$). For comparison, we note that the signals for the methylene protons in the published ^1H NMR spectrum of [$Fe(CH(CH_2PPh_2)_3)(NCCH_3)_3](BPh_4)_2$ coincided at room temperature, and the corresponding $H^{\alpha(apical)} - H^{\beta(methylene)}$ coupling constants were approximately 4 Hz.[5b] We believe the framework of [$Fe(CH(CH_2PPh_2)_3)(NCCH_3)_3](BPh_4)_2$ was conformationally fluxional and that 4 Hz is the averaged coupling constant of the two helical environments.

(11) The signals for all framework protons could be unambiguously assigned on the bases of chemical shifts, COSY, and NOE experiments.

(12) Karplus, M. J. *J. Am. Chem. Soc* **1963**, *85*, 2870.

(13) Positions were calculated assuming idealized sp^3 geometries about the carbon atoms of the framework.

Our NMR studies could not exclude a rapid equilibrium with small amounts of the Δ or some intermediate conformer in solution. We doubt, however, that the severe steric repulsions predicted by models of Δ-[Rh((*R*)-heliphos)(NBD)](ClO_4) would allow its formation.

Summary

The chiral tris(phosphines) (*R*)- and (*S*)-heliphos were easily prepared in enantiomerically pure form. It appears that the predicted locked helical conformations of (*R*)- and (*S*)-heliphos in [Rh(heliphos)(NBD)](ClO_4) were adopted in both the solution and solid state. Further, the asymmetric array of pendant phenyl rings around the metal center contains axial phenyl groups that project toward the spatial domains of the active sites. We are now determining if this projection is enantiogenic[14] in enantioselective catalytic reactions.

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Supporting Information Available: A full report on the X-ray structure of Λ-[Rh((*R*)-heliphos)(NBD)](ClO_4), including tables of experimental details, atomic coordinates, interatomic distances and angles, torsional angles, and anisotropic thermal parameters and figures giving additional views of the structure (22 pages). Ordering information is given on any current masthead page.

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(14) We define enantiogenic as the components of chirality responsible for the enantioselection during an enantioselective reaction.