

SUPPORTING INFORMATION OF THE COMMUNICATION:

Regio- and Stereoselective Ring-Opening Reactions of Chiral Substituted Spiro[2,4]hepta-4,6-dienes: A New, Simple, and Versatile Approach to the Synthesis of Optically Active Bidentate Cyclopentadienyl-Phosphine Ligands. X-Ray Crystal Structure of (S) -[Rh(η^2 -C₂H₄)(η^5 -C₅H₄CH₂CHPhPPh₂- κ P)]

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Experimental Section.

All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and deoxygenated by standard methods. NMR spectra were recorded on a Varian Mercury 200 (200MHz, ¹H; 50 MHz, ¹³C; 81 MHz, ³¹P) and a Varian Unity 500 (500 MHz, ¹H; 125 MHz, ¹³C; 202 MHz, ³¹P; 160 MHz, ¹¹B) at ambient temperature. Chemical shifts (δ) are given in ppm relative to SiMe₄. IR spectra were recorded on a Perkin-Elmer FT-IR Model 1720 X spectrometer. Mass spectra were obtained with a Finnigan MAT 95 spectrometer. Elemental analyses were obtained on a Carlo Erba Strumentazione element analyzer, Model 1106. Racemic ($\pm$)-1-phenyl-1,2-ethanediol (**1**) (Fluka), methanesulfonyl chloride (Fluka), NaNH₂ (Merck), LiⁿBu (1.6 M in hexane, Aldrich), BH₃·THF (1.0 M in THF, Aldrich), PPh₂H (Strem) and FeCl₂ (Strem) were used as purchased. Monomeric C₅H₆ was obtained from commercial dicyclopentadiene (Fluka) by dropping into hot decaline and distilling off through a Vigreux column and was stored under nitrogen at -80°C. NEt₃ (Merck) was distilled before use and stored over 4 Å molecular sieves. The compounds (*R*)-1-

phenyl-1,2-ethanediol, (*R*)-**1**¹, [Re(CO)₅Br]², [Rh(C₂H₄)₂Cl]₂³, and [ZrCl₄(THF)₂]⁴ were prepared by published methods.

(*R*)-1-Phenyl-1,2-ethanediol bis(methanesulfonate) (2). To a solution of (*R*)-**1** (10.13 g, 73.3 mmol) in 200 mL of CH₂Cl₂ was added NEt₃ (25.5 mL, 184.4 mmol). The solution was cooled to 0 °C, and methanesulfonyl chloride (12.4 mL, 160.2 mmol) in CH₂Cl₂ (50 mL) was added dropwise over 1 h. Upon complete addition, the mixture containing precipitated salts was allowed to stir at 0° C for 1 h and then at room temperature for 2 h. The mixture was then poured into 1N HCl (250 mL). The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (2 x 50 mL). The combined organic layers were washed successively with 1N HCl (50 mL), saturated NaHCO₃ (50 mL) and brine (100 mL). After drying (MgSO₄) the solution was concentrated on a rotovap to a pale yellow solid (21.24 g, 72.2 mmol, 98%). This crude product thus obtained was sufficiently pure to be used in the next step. ¹H NMR (200 MHz, CDCl₃): δ 3.03 (s, 3H, CH₃), 3.23 (s, 3H, CH₃), 4.60 (m, 2H, CH₂), 5.96 (m, 1H, CHPh), 7.59 (br, 5H, Ph). These ¹H NMR data are basically identical to those reported in the literature⁵.

(*S*)-1-Phenyl-spiro[2,4]hepta-4,6-diene (3). To a suspension of NaNH₂ (6.00 g, 153.8 mmol) in 150 ml of THF was added dropwise at room temperature freshly cracked cyclopentadiene (9.4 mL, 113.8 mmol). The addition of the diene was adjusted so as to maintain gentle reflux. (Some care needs to be exercised at this point since occasionally an induction period in the anion formation was observed). Upon complete addition, the pink mixture was stirred 1 h and then a solution of compound (*R*)-**2** (21.24 g, 72.2 mmol) in 200 mL of THF was added dropwise. This addition was accompanied by heat evolution. After the reaction mixture had cooled to room temperature overnight, 20 mL of methanol were carefully added to quench any excess of NaNH₂ or NaCp and then 300 mL of water were

added. The layers were separated and the aqueous layer was extracted with Et₂O (3 x 100 mL). The combined organic fraction was dried over MgSO₄ and then the solvent was pumped off on a rotovap. The residue was distilled (57-59 °C/6 x 10⁻² mbar, lit⁶ 63-78 °C/0.14 mm) to yield **3** as a colourless liquid (8.01 g, 47.6 mmol, 66%). [α]_D: +227.0° (c 1.5 in toluene). ¹H NMR (500 MHz, CDCl₃): δ 2.06 (m, 1H, CH₂), 2.31 (m, 1H, CH₂), 3.32 (m, 1H, CHPh), 5.88 (m, 1H, Cp), 6.20 (m, 1H, Cp), 6.43 (m, 1H, Cp), 6.47 (m, 1H, Cp), 7.18-7.29 (m, 5H, Ph). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 17.26 (CH₂), 31.05 (CHPh), 45.70 (C_{spiro}), 126.51 (CH, Ph), 128.05 (CH, Ph), 128.19 (CH, Ph), 128.70 (CH, Cp), 130.35 (CH, Cp), 135.89 (CH, Cp), 138.93 (CH, Cp), 139.39 (C_{ipso}, Ph). These analytical data are in agreement with those reported for the racemic form of **3**⁶.

(S)-[Li(C₅H₄CH₂CHPhPPh₂)] (4). A flask was charged with 40 mL of THF and cooled to -60 °C. At this temperature PPh₂H (0.54 mL, 3.1 mmol) and LiⁿBu (2.0 mL, 1.6 M in hexane, 3.1 mmol) were added. After the reaction mixture had warmed to room temperature, (*S*)-**3** (0.53 g, 3.1 mmol) was added by syringe. The mixture was stirred overnight. The solvent was removed and the product (*S*)-**4** was washed with cold hexane (3 x 20 mL) and Et₂O (2 x 20 mL) and dried in vacuum (1.00 g, 2.3 mmol, 90%) and was used immediately for the preparations described below.

(S)-[Re(CO)₃(η^5 -C₅H₄CH₂CHPhPPh₂)] (5). [Re(CO)₅Br] (618 mg, 1.52 mmol) was dissolved in 30 mL of THF and heated to reflux for 4 h. After cooling this mixture to 0 °C, (*S*)-**4** (550 mg, 1.53 mmol), dissolved in 20 mL of THF, was slowly added. The resulting solution was stirred 2 h at ambient temperature and then refluxed for 1 h. After removing of the solvent in vacuo, the yellow residue was extracted with 25 mL of toluene, and the extract was filtered over celite. The yellow filtrate was taken to dryness under reduced pressure. (*S*)-**5** was obtained by cooling a saturated hexane solution at -40 °C (693 mg, 1.11 mmol, 73%).

^{31}P NMR (202 MHz, CDCl_3): δ -0.6 (PPh_2). ^1H NMR (500 MHz, CDCl_3): δ 2.68 (m, 1H, CH_2), 2.95 (m, 1H, CH_2), 3.51 (m, 1H, CHPh), 4.73 (m, 1H, Cp), 4.84 (m, 1H, Cp), 5.01 (m, 1H, Cp), 5.04 (m, 1H, Cp), 7.07-7.68 (m, 15H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 32.28 (d, $^2J_{\text{C-P}} = 25.2$ Hz, CH_2), 48.48 (d, $^1J_{\text{C-P}} = 14.8$ Hz, CHPh), 82.93 (CH, Cp), 83.09 (CH, Cp), 84.24 (CH, Cp), 84.81 (CH, Cp), 107.82 (d, $^3J_{\text{C-P}} = 14.8$ Hz, C_{ipso} , Cp), 126.71 (d, $J_{\text{C-P}} = 2.2$ Hz, CH, Ph), 127.87 (d, $J_{\text{C-P}} = 6.6$ Hz, CH, Ph), 128.46 (CH, Ph), 128.83 (CH, Ph), 128.89 (CH, Ph), 129.18 (d, $J_{\text{C-P}} = 7.1$ Hz, CH, Ph), 129.67 (CH, Ph), 133.95 (d, $J_{\text{C-P}} = 20.2$ Hz, CH, Ph), 134.04 (d, $J_{\text{C-P}} = 20.3$ Hz, CH, Ph), 135.84 (d, $J_{\text{C-P}} = 15.9$ Hz, C_{ipso} , Ph), 136.15 (d, $J_{\text{C-P}} = 14.3$ Hz, C_{ipso} , Ph), 139.81 (d, $J_{\text{C-P}} = 8.2$ Hz, C_{ipso} , Ph), 194.31 (CO). Anal. Calcd. for $\text{C}_{28}\text{H}_{22}\text{O}_3\text{PRe}$: C, 53.92; H, 3.56. Found: C, 53.67; H, 3.57. MS: m/z [assignment, R_{int} (%]): 624 [M^+ , not observed]; 596 [$(\text{M}-\text{CO})^+$, 100]; 568 [$(\text{M}-2\text{CO})^+$, 9]; 540 [$(\text{M}-3\text{CO})^+$, 41]; 354 [$\{\text{M}-\text{Re}(\text{CO})_3\}^+$, 51]. IR (CH_2Cl_2): ν_{max} 2021, 1924 (CO) cm^{-1} .

(*S*)-[$\text{Re}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CHPhPPh}_2\text{-BH}_3)]$ (5**· BH_3).** A solution containing (*S*)-**5** (542 mg, 0.87 mmol) was treated with $\text{BH}_3\cdot\text{THF}$ (1.5 mL, 1.5 mmol, 1.0 M solution in THF). The mixture was stirred at ambient temperature overnight. The solvent was evaporated and the crude product was washed with cold hexane (2 x 20 mL) to give (*S*)-**5**· BH_3 (547 mg, 0.86 mmol, 98%) [α]_D: -37.7° (c 0.3 in toluene). ^{31}P NMR (202 MHz, CDCl_3): δ +23.8 (br, $\text{PPh}_2\text{-BH}_3$). ^{11}B NMR (160 MHz, CDCl_3): δ -41.5 (br, $\text{PPh}_2\text{-BH}_3$). ^1H NMR (500 MHz, CDCl_3): δ 0.8-1.5 (br, 3H, BH_3), 2.74 (m, 1H, CH_2), 3.36 (m, 1H, CH_2), 3.73 (m, 1H, CHPh), 4.68 (m, 1H, Cp), 4.96 (m, 2H, Cp), 5.03 (m, 1H, Cp), 7.12-7.99 (m, 15H, Ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 28.88 (d, $^2J_{\text{C-P}} = 7.4$ Hz, CH_2), 46.31 (d, $^1J_{\text{C-P}} = 29.9$ Hz, CHPh), 82.59 (CH, Cp), 82.63 (CH, Cp), 85.26 (CH, Cp), 86.16 (CH, Cp), 106.54 (d, $^3J_{\text{C-P}} = 16.4$ Hz, C_{ipso} , Cp), 127.09 (d, $J_{\text{C-P}} = 28.0$ Hz, C_{ipso} , Ph), 127.76 (d, $J_{\text{C-P}} = 2.7$ Hz, C_{ipso} , Ph), 128.24 (d, $J_{\text{C-P}} = 12.3$ Hz, CH, Ph), 128.29 (d, $J_{\text{C-P}} = 4.4$ Hz, CH, Ph), 129.01 (CH, Ph), 129.22 (d, $J_{\text{C-P}} = 9.6$ Hz, CH, Ph), 129.93 (d, $J_{\text{C-P}} = 4.4$ Hz, CH, Ph), 131.03 (d, $J_{\text{C-P}} = 2.5$ Hz, CH, Ph), 131.83 (d,

$J_{C-P} = 2.2$ Hz, CH, Ph), 132.56 (d, $J_{C-P} = 8.8$ Hz, CH, Ph), 132.98 (d, $J_{C-P} = 8.2$ Hz, CH, Ph), 134.74 (d, $J_{C-P} = 1.4$ Hz, C_{ipso} , Ph), 194.12 (CO). Anal. Calcd. for $C_{28}H_{25}BO_3PRe$: C, 52.75; H, 3.95. Found: C, 52.37; H, 4.18. MS: m/z [assignment, R_{int} (%): 638 [M^+ , not observed]; 610 [(M-CO) $^+$, 9]; 596 [(M-CO-BH $_3$) $^+$, 100]; 540 [(M-3CO-BH $_3$) $^+$, 45]; 354 [{M-Re(CO) $_3$ -BH $_3$ } $^+$, 540]. IR (CH $_2$ Cl $_2$): ν_{max} 2022, 1927 (CO) cm^{-1} .

(S)-[Rh(η^2 -C $_2$ H $_4$)(η^5 - η^1 -C $_5$ H $_4$ CH $_2$ CHPhPPh $_2$)] (6). A suspension of [Rh(C $_2$ H $_4$) $_2$ Cl] $_2$ (205 mg, 0.53 mmol) in 15 mL of Et $_2$ O was treated with (S)-4 (382 mg, 1.06 mmol) dissolved in 20 mL of THF. The reaction mixture was stirred for 1 h, leading to a red-brownish solution which was evaporated to dryness. Then the residue, dissolved in a hexane-toluene mixture (1:1) was eluted and filtered through a 5 cm pad of alumina. The solvent was evaporated and the product (S)-6 was obtained by cooling a saturated hexane solution at -40 °C (378 mg, 0.78 mmol, 74%). $[\alpha]_D^{25} +43.1^\circ$ (c 0.58 in toluene). ^{31}P NMR (202 MHz, C $_6$ D $_6$): δ +92.4 (d, $^1J_{P-Rh} = 216.7$ Hz, PPh $_2$). 1H NMR (500 MHz, C $_6$ D $_6$): δ 1.78 (br, 2H, C $_2$ H $_4$), 2.33 (m, 1H, CH $_2$), 2.43 (m, 1H, CH $_2$), 2.82 (br, 2H, C $_2$ H $_4$), 4.60 (m, 1H, CHPh), 4.99 (m, 1H, Cp), 5.34 (m, 1H, Cp), 5.80 (m, 1H, Cp), 5.83 (m, 1H, Cp), 6.48-7.61 (m, 15H, Ph). $^{13}C\{^1H\}$ NMR (125 MHz, C $_6$ D $_6$): δ 27.7 (br, C $_2$ H $_4$), 29.75 (d, $^2J_{C-P} = 7.7$ Hz, CH $_2$), 31.9 (br, C $_2$ H $_4$), 66.25 (dd, $^1J_{C-P} = 20.3$ Hz, $^2J_{C-Rh} = 2.2$ Hz, CHPh), 81.44 (CH, Cp), 85.36 (CH, Cp), 85.57 (CH, Cp), 91.60 (CH, Cp), 103.31 (C_{ipso} , Cp), 126.80 (d, $J_{C-P} = 2.2$ Hz, CH, Ph), 127.22 (d, $J_{C-P} = 9.9$ Hz, CH, Ph), 128.91 (d, $J_{C-P} = 2.2$ Hz, CH, Ph), 129.14 (dd, $^1J_{C-P} = 35.1$ Hz, $^2J_{C-Rh} = 1.7$ Hz, C_{ipso} , PPh $_2$), 130.52 (d, $J_{C-P} = 1.6$ Hz, CH, Ph), 131.95 (d, $J_{C-P} = 9.3$ Hz, CH, Ph), 133.15 (dd, $^1J_{C-P} = 34.5$ Hz, $^2J_{C-Rh} = 1.6$ Hz, C_{ipso} , PPh $_2$), 137.97 (d, $J_{C-P} = 13.2$ Hz, CH, Ph), 138.12 (C_{ipso} , CHPh), (other signals in the aryl area are overlapped by the C $_6$ D $_6$). Anal. Calcd. for C $_{27}$ H $_{26}$ PRh: C, 66.95; H, 5.41. Found: C, 67.17; H, 5.50. MS: m/z [assignment, R_{int} (%): 484 [M^+ , 18]; 456 [(M-C $_2$ H $_4$) $^+$, 100]; 270 [(M-C $_2$ H $_4$ -PPh $_2$ H) $^+$, 42].

(*S,S*)-[Fe(η^5 -C₅H₄CH₂CHPhPPh₂)₂] (7). To a suspension of FeCl₂ (110 mg, 0.87 mmol) in 20 mL of THF cooled to -40 °C was added a solution of (*S*)-4 (628 mg, 1.74 mmol) in 30 mL of THF. The resulting deep orange solution was stirred overnight without cooling and then evaporated. The residue was treated with 25 mL of toluene and filtered over celite. Evaporation of the solvent to ca. 5 mL, addition of 20 mL of hexane, and cooling during 2 days to -40 °C gave (*S,S*)-7 as a yellow microcrystalline powder (429 mg, 0.56 mmol, 65%). [α]_D: -100.2° (c 0.57 in toluene). ³¹P NMR (202 MHz, CDCl₃): δ -1.2 (PPh₂). ¹H NMR (500 MHz, CDCl₃): δ 2.60 (m, 2H, CH₂), 2.71 (m, 2H, CH₂), 3.26 (m, 2H, Cp), 3.36 (m, 2H, CHPh), 3.61 (m, 2H, Cp), 3.63 (m, 2H, Cp), 3.71 (m, 2H, Cp), 6.94-7.66 (m, 30H, Ph). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 34.02 (d, ²J_{C-P} = 23.0 Hz, CH₂), 47.78 (d, ¹J_{C-P} = 13.7 Hz, CHPh), 67.55 (CH, Cp), 67.84 (CH, Cp), 68.72 (CH, Cp), 69.54 (CH, Cp), 86.61 (d, ³J_{C-P} = 14.8 Hz, C_{ipso}, Cp), 125.99 (CH, Ph), 127.69 (d, J_{C-P} = 6.6 Hz, CH, Ph), 127.93 (CH, Ph), 128.15 (CH, Ph), 128.61 (d, J_{C-P} = 7.2 Hz, CH, Ph), 129.24 (d, J_{C-P} = 13.8 Hz, CH, Ph), 129.29 (CH, Ph), 133.08 (d, J_{C-P} = 18.1 Hz, CH, Ph), 133.98 (d, J_{C-P} = 20.3 Hz, CH, Ph), 136.85 (d, J_{C-P} = 15.4 Hz, C_{ipso}, Ph), 137.08 (d, J_{C-P} = 14.3 Hz, C_{ipso}, Ph), 140.98 (d, J_{C-P} = 8.3 Hz, C_{ipso}, Ph). Anal. Calcd. for C₅₀H₄₄P₂Fe: C, 78.74; H, 5.82. Found: C, 78.66; H, 5.91. MS: m/z [assignment, R_{int} (%): 763 [M⁺, 77]; 578 [(M-PPh₂)⁺, 28]; 566 [(M-CPPH₂)⁺, 100]; 354 [(C₅H₄CH₂CHPhPPh₂)⁺, 74].

(*S,S*)-[ZrCl₂(η^5 -C₅H₄CH₂CHPhPPh₂)₂] (8). A stirred solution of [ZrCl₄(THF)₂] (206 mg, 0.55 mmol) in 25 mL of THF cooled to -40 °C was treated dropwise with (*S*)-4 (410 mg, 1.14 mmol) dissolved in 20 mL of THF. The yellow solution was stirred 12 h at room temperature and the solvent was evaporated in vacuo. The residue was taken in 30 mL of toluene and filtered through a 3 cm bed of celite. The clear yellow solution of the zirconocene dichloride was concentrated to ca. 5 mL. Addition of 20 mL of hexane and cooling to -40 °C yielded (*S,S*)-8 as a colourless crystalline solid (290 mg, 0.33 mmol, 61%). ³¹P NMR (202

MHz, CDCl₃): δ -0.7 (PPh₂). ¹H NMR (500 MHz, CDCl₃): δ 2.91 (m, 4H, CH₂), 3.47 (m, 2H, CHPh), 5.38 (m, 2H, Cp), 5.76 (m, 2H, Cp), 5.85 (m, 2H, Cp), 5.92 (m, 2H, Cp), 6.91-7.59 (m, 30H, Ph). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 34.26 (d, ²J_{C-P} = 24.2 Hz, CH₂), 47.03 (d, ¹J_{C-P} = 14.8 Hz, CHPh), 111.34 (CH, Cp), 112.95 (d, J_{C-P} = 10.4 Hz, CH, Cp), 116.76 (d, J_{C-P} = 8.2 Hz, CH, Cp), 117.68 (d, J_{C-P} = 3.9 Hz, CH, Cp), 126.33 (d, J_{C-P} = 2.2 Hz, CH, Ph), 127.87 (d, J_{C-P} = 7.1 Hz, CH, Ph), 128.16 (CH, Ph), 128.24 (d, J_{C-P} = 10.4 Hz, CH, Ph), 128.69 (d, J_{C-P} = 7.1 Hz, CH, Ph), 129.24 (d, J_{C-P} = 7.7 Hz, CH, Ph), 129.45 (CH, Ph), 131.58 (d, ³J_{C-P} = 13.7 Hz, C_{ipso}, Cp), 133.13 (d, J_{C-P} = 18.1 Hz, CH, Ph), 134.04 (d, J_{C-P} = 20.3 Hz, CH, Ph), 136.15 (d, J_{C-P} = 15.9 Hz, C_{ipso}, Ph), 136.69 (d, J_{C-P} = 14.3 Hz, C_{ipso}, Ph), 140.27 (d, J_{C-P} = 8.8 Hz, C_{ipso}, Ph). Anal. Calcd. for C₅₀H₄₄Cl₂P₂Zr: C, 69.11; H, 5.10. Found: C, 69.28; H, 5.18.

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Table 1. Crystal data and structure refinement for (S)-6

Empirical formula	C ₂₇ H ₂₆ PRh
Formula weight	484.39
Temperature	243 K
Wavelength	.71073 Å
Crystal system	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	<i>a</i> = 9.745(13) Å <i>b</i> = 14.590(4) Å <i>c</i> = 15.777(6) Å
Volume	2244(3) Å ³
<i>Z</i>	4
Density (calculated)	1.43 Mg/m ³
Absorption coefficient	0.829 mm ⁻¹
<i>F</i> (000)	992
Crystal size	0.55 x 0.38 x 0.24 mm
Theta range for data collection	2.1 to 26.0 deg.
Index ranges	0 ≤ <i>h</i> ≤ 12, -17 ≤ <i>k</i> ≤ 0, 0 ≤ <i>l</i> ≤ 19
Reflections collected	2514
Independent reflections	2514 [<i>R</i> (int) = 0.110]
Absorption correction	None
Max. and min. transmission	0.000 and 0.000
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	2490 / 0 / 262
Goodness-of-fit on <i>F</i> ²	1.013
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0446, <i>wR</i> 2 = 0.1116
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0528, <i>wR</i> 2 = 0.1147
Absolute structure parameter	-.03(7)
Largest diff. peak and hole	1.013 and -.731 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S)-6. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Rh	9464(1)	4565(1)	2178(1)	37(1)
P	11001(2)	4764(1)	3172(1)	33(1)
C(1)	8678(8)	5926(5)	2159(7)	55(2)
C(2)	7934(7)	5379(5)	2735(5)	52(2)
C(10)	10510(10)	3965(6)	1045(5)	58(2)
C(11)	9088(10)	3928(7)	861(6)	73(3)
C(12)	8442(9)	3360(6)	1469(8)	74(3)
C(13)	9421(9)	3032(5)	2001(7)	71(3)
C(14)	10705(8)	3436(5)	1791(5)	49(2)
C(15)	12038(7)	3316(5)	2266(5)	44(2)
C(16)	11923(7)	3626(4)	3212(4)	36(1)
C(20)	13213(8)	3579(4)	3719(5)	39(2)
C(21)	13161(10)	3350(5)	4570(5)	58(2)
C(22)	14307(10)	3335(6)	5067(5)	64(2)
C(23)	15557(11)	3577(6)	4731(6)	68(3)
C(24)	15659(9)	3794(6)	3886(6)	59(2)
C(25)	14491(8)	3817(5)	3387(5)	45(2)
C(30)	10455(8)	4991(5)	4253(4)	40(1)
C(31)	10511(10)	5862(6)	4593(5)	59(2)
C(32)	9994(12)	6032(8)	5415(6)	86(3)
C(33)	9442(11)	5337(10)	5866(6)	85(3)
C(34)	9317(9)	4477(9)	5523(6)	73(3)
C(35)	9801(8)	4297(6)	4718(5)	55(2)
C(40)	12378(6)	5585(4)	2996(4)	35(1)
C(41)	12517(7)	5976(5)	2208(5)	45(2)
C(42)	13607(8)	6566(5)	2038(5)	57(2)
C(43)	14542(9)	6756(6)	2648(6)	68(2)
C(44)	14406(9)	6375(5)	3454(6)	55(2)
C(45)	13361(8)	5792(5)	3619(5)	45(2)

Table 3. Bond lengths [Å] and angles [deg] for (S)-6.

Rh-C(2)	2.098(7)
Rh-C(1)	2.127(7)
Rh-C(14)	2.133(7)
Rh-P	2.188(2)
Rh-C(10)	2.237(8)
Rh-C(13)	2.255(7)
Rh-C(11)	2.306(8)
Rh-C(12)	2.310(8)
P-C(30)	1.817(7)
P-C(40)	1.821(6)
P-C(16)	1.889(7)
C(1)-C(2)	1.410(12)
C(10)-C(11)	1.417(13)
C(10)-C(14)	1.420(12)
C(11)-C(12)	1.416(15)
C(12)-C(13)	1.358(12)
C(13)-C(14)	1.422(12)
C(14)-C(15)	1.510(10)
C(15)-C(16)	1.564(10)
C(16)-C(20)	1.492(10)
C(20)-C(21)	1.384(11)
C(20)-C(25)	1.396(10)
C(21)-C(22)	1.364(12)
C(22)-C(23)	1.374(14)
C(23)-C(24)	1.374(14)
C(24)-C(25)	1.385(11)
C(30)-C(31)	1.380(11)
C(30)-C(35)	1.403(11)
C(31)-C(32)	1.413(12)
C(32)-C(33)	1.351(16)
C(33)-C(34)	1.372(16)
C(34)-C(35)	1.381(12)
C(40)-C(41)	1.375(10)
C(40)-C(45)	1.406(10)
C(41)-C(42)	1.393(10)
C(42)-C(43)	1.354(12)
C(43)-C(44)	1.393(12)
C(44)-C(45)	1.353(11)

C(2)-Rh-C(1)	39.0(3)
C(2)-Rh-C(14)	163.7(3)
C(1)-Rh-C(14)	157.0(4)
C(2)-Rh-P	96.4(2)
C(1)-Rh-P	97.6(2)
C(14)-Rh-P	85.4(2)
C(2)-Rh-C(10)	151.7(3)
C(1)-Rh-C(10)	121.2(4)
C(14)-Rh-C(10)	37.8(3)
P-Rh-C(10)	108.2(2)
C(2)-Rh-C(13)	126.9(3)
C(1)-Rh-C(13)	156.5(3)
C(14)-Rh-C(13)	37.7(3)
P-Rh-C(13)	103.4(2)
C(10)-Rh-C(13)	61.4(4)
C(2)-Rh-C(11)	119.5(3)
C(1)-Rh-C(11)	107.8(4)
C(14)-Rh-C(11)	61.4(3)
P-Rh-C(11)	143.9(2)
C(10)-Rh-C(11)	36.3(3)
C(13)-Rh-C(11)	59.0(4)
C(2)-Rh-C(12)	109.1(3)
C(1)-Rh-C(12)	123.3(3)
C(14)-Rh-C(12)	61.2(3)
P-Rh-C(12)	138.0(2)
C(10)-Rh-C(12)	60.7(4)
C(13)-Rh-C(12)	34.6(3)
C(11)-Rh-C(12)	35.7(4)
C(30)-P-C(40)	103.8(3)
C(30)-P-C(16)	105.6(3)
C(40)-P-C(16)	103.5(3)
C(30)-P-Rh	119.8(3)
C(40)-P-Rh	118.8(2)
C(16)-P-Rh	103.5(2)
C(2)-C(1)-Rh	69.4(4)
C(1)-C(2)-Rh	71.6(4)
C(11)-C(10)-C(14)	106.3(9)
C(11)-C(10)-Rh	74.5(5)
C(14)-C(10)-Rh	67.1(4)
C(12)-C(11)-C(10)	108.5(9)
C(12)-C(11)-Rh	72.3(5)
C(10)-C(11)-Rh	69.2(5)
C(13)-C(12)-C(11)	108.2(8)
C(13)-C(12)-Rh	70.5(5)
C(11)-C(12)-Rh	72.0(5)
C(12)-C(13)-C(14)	109.2(9)
C(12)-C(13)-Rh	74.9(5)
C(14)-C(13)-Rh	66.5(4)
C(10)-C(14)-C(13)	107.5(7)
C(10)-C(14)-C(15)	126.1(8)
C(13)-C(14)-C(15)	126.4(7)
C(10)-C(14)-Rh	75.0(4)
C(13)-C(14)-Rh	75.8(4)
C(15)-C(14)-Rh	115.8(5)
C(14)-C(15)-C(16)	112.2(6)
C(20)-C(16)-C(15)	116.0(6)
C(20)-C(16)-P	117.3(5)
C(15)-C(16)-P	104.9(4)
C(21)-C(20)-C(25)	117.2(7)
C(21)-C(20)-C(16)	120.1(7)

C(25)-C(20)-C(16)	122.6(6)
C(22)-C(21)-C(20)	122.1(9)
C(21)-C(22)-C(23)	120.0(8)
C(22)-C(23)-C(24)	119.8(8)
C(23)-C(24)-C(25)	119.9(9)
C(24)-C(25)-C(20)	120.9(7)
C(31)-C(30)-C(35)	118.7(7)
C(31)-C(30)-P	121.4(6)
C(35)-C(30)-P	119.4(6)
C(30)-C(31)-C(32)	120.2(9)
C(33)-C(32)-C(31)	119.6(10)
C(32)-C(33)-C(34)	120.9(8)
C(33)-C(34)-C(35)	120.4(9)
C(34)-C(35)-C(30)	119.9(9)
C(41)-C(40)-C(45)	118.5(6)
C(41)-C(40)-P	119.0(5)
C(45)-C(40)-P	122.4(5)
C(40)-C(41)-C(42)	120.4(7)
C(43)-C(42)-C(41)	120.2(8)
C(42)-C(43)-C(44)	120.2(8)
C(45)-C(44)-C(43)	119.9(8)
C(44)-C(45)-C(40)	120.9(7)

Table 4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S)-6.

	x	y	z	U(eq)
H(1A)	9439	6215	2468	71
H(1B)	8356	5986	1577	71
H(2A)	8254	5557	3300	68
H(2B)	7160	5275	2349	68
H(10)	11217	4290	722	75
H(11)	8629	4244	392	94
H(12)	7458	3226	1501	97
H(13)	9268	2588	2457	92
H(15A)	12757	3675	1985	57
H(15B)	12310	2669	2246	57
H(16)	11284	3196	3481	47
H(21)	12274	3193	4823	75
H(22)	14238	3152	5663	83
H(23)	16373	3595	5094	89
H(24)	16557	3932	3637	77
H(25)	14563	4003	2791	59
H(31)	10912	6364	4263	77
H(32)	10036	6651	5656	112
H(33)	9127	5448	6447	111
H(34)	8881	3987	5852	95
H(35)	9688	3685	4471	71
H(41)	11846	5839	1763	59
H(42)	13698	6844	1475	74
H(43)	15316	7163	2523	88
H(44)	15068	6529	3899	71
H(45)	13288	5510	4181	59

Table 5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (S)-6.
 The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Rh	33(1)	33(1)	45(1)	-2(1)	-4(1)	-1(1)
P	29(1)	32(1)	37(1)	1(1)	3(1)	0(1)
C(1)	42(4)	44(4)	78(5)	-9(5)	-19(5)	11(3)
C(2)	29(3)	57(4)	72(5)	-15(5)	-8(4)	11(3)
C(10)	58(4)	71(5)	44(4)	-15(4)	-5(4)	0(5)
C(11)	66(6)	78(6)	74(6)	-36(5)	-34(5)	22(5)
C(12)	43(4)	49(4)	131(9)	-24(6)	-38(6)	-6(4)
C(13)	66(5)	35(3)	112(8)	-11(4)	-41(6)	-7(4)
C(14)	47(4)	37(3)	62(4)	-17(3)	-8(4)	6(3)
C(15)	38(3)	41(3)	53(4)	-7(3)	-2(4)	5(3)
C(16)	29(3)	30(3)	49(4)	2(3)	8(3)	-5(3)
C(20)	39(4)	33(3)	45(4)	-2(3)	0(3)	9(3)
C(21)	58(5)	58(5)	58(5)	9(4)	2(4)	15(4)
C(22)	68(6)	72(5)	52(4)	-6(4)	-10(5)	24(5)
C(23)	63(5)	72(6)	69(6)	-19(5)	-27(6)	20(5)
C(24)	37(4)	54(4)	85(6)	-12(4)	-6(4)	3(4)
C(25)	36(3)	47(4)	53(4)	1(3)	-7(4)	1(4)
C(30)	31(3)	49(4)	41(3)	1(3)	2(3)	11(3)
C(31)	64(5)	59(4)	55(4)	-12(4)	16(5)	13(5)
C(32)	94(8)	97(8)	68(6)	-22(6)	15(6)	27(7)
C(33)	62(5)	149(11)	45(4)	-1(6)	17(4)	28(9)
C(34)	40(5)	121(9)	57(5)	32(6)	18(4)	17(6)
C(35)	36(4)	72(5)	56(4)	16(4)	12(4)	12(4)
C(40)	30(3)	31(3)	43(4)	-1(3)	1(3)	0(3)
C(41)	48(4)	48(4)	40(3)	1(4)	1(4)	-4(3)
C(42)	53(5)	57(4)	61(5)	10(4)	9(4)	-5(4)
C(43)	45(4)	53(4)	105(7)	11(5)	4(5)	-20(4)
C(44)	43(4)	42(4)	80(5)	-1(4)	-16(5)	-8(4)
C(45)	48(4)	41(3)	47(4)	0(3)	-10(4)	2(3)