

Highly enantioselective hydrogenation of enol ester phosphonates catalyzed by rhodium phosphine-phosphite complexes

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Supporting Information

General Procedures. All reactions and manipulations were performed under nitrogen or argon, either in a Braun Labmaster 100 glovebox or using standard Schlenk-type techniques. All solvents were distilled under nitrogen using the following dessicants: Sodium-benzophenone-ketyl for diethylether (Et_2O) and tetrahydrofuran (THF); sodium for *n*-hexane and toluene; CaH_2 for dichloromethane (CH_2Cl_2) and NaOMe for methanol (MeOH). NMR spectra were obtained on Bruker DPX-300, DRX-400 or DRX-500 spectrometers. $^{31}\text{P}\{^1\text{H}\}$ NMR shifts were referenced to external 85 % H_3PO_4 , while $^{13}\text{C}\{^1\text{H}\}$ and ^1H shifts were referenced to the residual signals of deuterated solvents. All data are reported in ppm downfield from Me_4Si . HPLC analyses were performed by using Waters 2690. HRMS data was obtained using a Jeol JMS-SX 102A mass spectrometer. Optical rotations were measured on a Perkin-Elmer Model 341 polarimeter.

Representative synthetic procedures

(*R*)-5,5',6,6'-tetramethyl-2,2'-bisphenoxyphosphorous chloride (6). (*R*)-5,5',6,6'-tetramethyl-2,2'-bisphenol (1.2 g, 4.95 mmol)¹ was azeotropically dried with toluene (2x30 mL), dissolved in THF and added dropwise over a mixture of PCl₃ (0.5 mL, 5.7 mmol) and pyridine (0.9 mL, 11.1 mmol) in THF. The suspension was stirred for 4 h, filtered and the solvent evaporated under vacuum to yield **6** as a white foamy solid (1.29 g, 4.2 mmol, 85%). ¹H NMR (CDCl₃, 400 MHz): δ 2.03 (s, 6H, 2 Me), 2.30 (s, 6H, 2 Me), 6.93 (d, ³*J*(H,H) = 8 Hz, 1H, H arom), 7.02 (d, ³*J*(H,H) = 8 Hz, 1H, H arom), 7.18 (d, ³*J*(H,H) = 8 Hz, 2H, 2 H arom). ³¹P{¹H} NMR (C₆D₆, 162.1 MHz): δ 169.0.

(*R*)-2-(Diphenylphosphino)phenyl-1,1'-(5,5',6,6'-tetramethyl)bisphen-2,2'-diyl phosphite (7a). A solution of (2-hydroxyphenyl)diphenyl phosphine (0.39 g, 1.58 mmol) in toluene (30 mL) was added dropwise over (*R*)-5,5',6,6'-tetramethyl-2,2'-bisphenoxyphosphorous chloride (0.484 g, 1.58 mmol) and NEt₃ (0.33 mL, 2.38 mmol) dissolved in toluene (30mL). The resulting suspension was stirred for 24 h, the mixture filtered and volatiles removed. The solid obtained was dissolved in Et₂O and passed through a short pad of neutral alumina. Solution was evaporated yielding a white solid (0.242 g, 0.42 mmol, 28%). [α]_D²⁰ = -17.5 (*c* 1.0, THF). ¹H NMR (CDCl₃, 400 MHz): δ 1.96 (s, 3H, Me), 1.98 (s, 3H, Me), 2.23 (s, 3H, Me), 2.26 (s, 3H, Me), 6.70-6.74 (m, 2H, 2 H arom), 6.86 (d, ³*J*(H,H) = 8.4 Hz, 1H, H arom), 6.95 (d, ³*J*(H,H) = 8.4 Hz, 1H, H arom), 7.02 (t, ³*J*(H,H) = 7.6 Hz, 1H, H arom), 7.11 (d, ³*J*(H,H) = 8 Hz, 1H, H arom), 7.19 (dd, ³*J*(H,H) = 8.4 Hz, 4.4 Hz, 1H, H arom), 7.27-7.40 (m, 11 H, 11 H arom). ³¹P{¹H} NMR (CDCl₃, 162.1 MHz): δ -17.1 (d, P-C), 134.5 (d, *J*(P,P) = 14 Hz, P-O).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75.5 MHz): δ 17.7 (s, Me), 17.8 (s, Me), 29.2 (s, 2 Me), 119.1 (CH arom), 120.4 (d, $J(\text{C},\text{P}) = 10$ Hz, CH arom), 124.9 (s, CH arom), 128.7 (s, CH arom), 128.8 (s, CH arom), 128.8 (s, CH arom), 128.9 (s, CH arom), 129.0 (s, CH arom), 129.2 (s, CH arom), 129.8 (s, CH arom), 130.0 (s, CH arom), 130.3 (s, C_q arom), 130.4 (s, CH arom), 130.9 (d, $J(\text{C},\text{P}) = 5$ Hz, C_q arom), 133.5 (s, 2 C_q arom), 134.2 (s, 2 CH arom), 134.4 (s, 2 CH arom), 134.7 (s, CH arom), 136.3 (dd, $J(\text{C},\text{P}) = 11, 3$ Hz, C_q arom), 136.7 (s, 2 C_q arom), 137.8 (s, 2 C_q arom), 146.5 (m, 2 C_q arom), 154.2 (m, C_q arom). HRMS (EI, direct insert): m/z 548.1673 (M^+ , exact mass calcd for $\text{C}_{34}\text{H}_{30}\text{O}_3\text{P}_2$: 548.1670).

[Rh(COD)(7a)]BF₄ (8a). A suspension of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.040 g, 0.082 mmol) and AgBF_4 in THF (5 mL) was vigorously stirred for 45 minutes in absence of light. Resulting mixture was filtered over a short pad of celite and ligand **7a** (0.090 g, 0.16 mmol) in THF (5 mL) was added dropwise. The reaction was stirred for 1 h, filtered and the solvent evaporated. The product was precipitated as an orange solid from a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ 1:2 mixture (0.09 g, 66%). ^1H NMR (CD_2Cl_2 , 400 MHz): δ 1.85-1.95 (m, 1H, CHH COD), 1.97 (s, 3H, Me), 2.05 (s, 3H, Me), 2.10-2.31 (m, 3H, 3 CHH COD), 2.33 (s, 3H, Me), 2.37 (s, 3H, Me), 2.45-2.75 (m, 4H, 4 CHH COD), 4.10 (brs, 1H, $=\text{CH COD}$), 4.76 (brs, 1H, $=\text{CH COD}$), 5.73 (brs, 2H, $=\text{CH COD}$), 7.02 (d, 1H, $^3J(\text{H},\text{H}) = 8$ Hz, H arom), 7.07-7.10 (m, 2H, 2 H arom), 7.24-7.38 (m, 6H, 6 H arom), 7.54-7.70 (m, 9H, 9 H arom). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 162.1 MHz): δ 16.4 (dd, $J(\text{P},\text{Rh}) = 136$ Hz, P-C), 132.3 (dd, $J(\text{P},\text{Rh}) = 267$ Hz, $J(\text{P},\text{P}) = 61$ Hz, P-O). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75.5 MHz): δ 17.6 (s, Me), 17.8 (s, Me), 20.6 (s, 2 Me), 27.2 (s, CHH COD), 28.4 (s, CHH COD), 32.4 (s, CHH COD), 32.9 (s, CHH COD), 100.7 (t, $J(\text{C},\text{P}) = 6$ Hz, $J(\text{C},\text{Rh}) = 6$ Hz, $=\text{CH COD}$), 106.6 (t, $J(\text{C},\text{P}) = 7$ Hz, $J(\text{C},\text{Rh}) = 7$ Hz, $=\text{CH COD}$), 112.4 (dd, $J(\text{C},\text{P})$

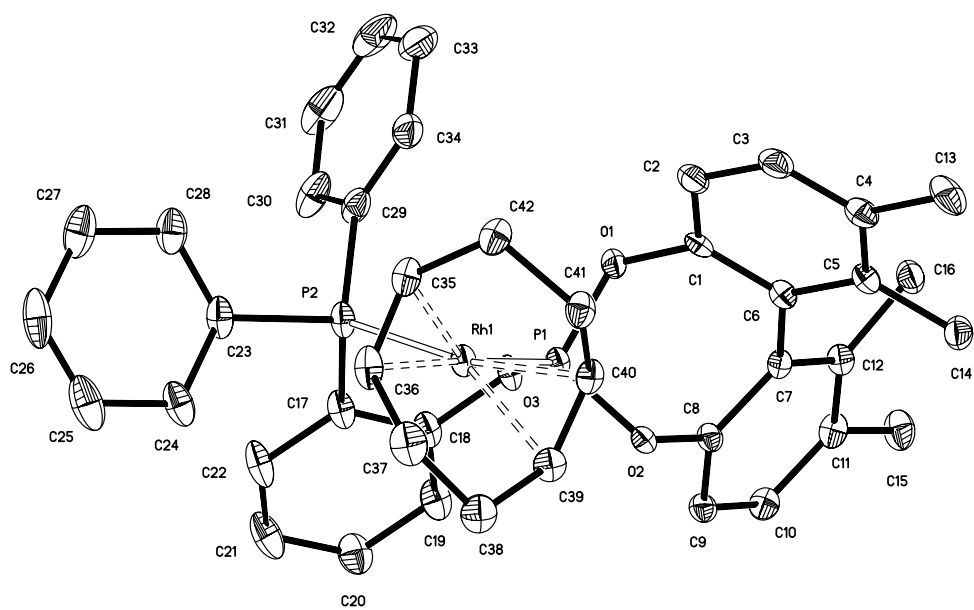
=10 Hz, $J(\text{C,Rh}) = 6$ Hz, =CH COD), 113.5 (dd, $J(\text{C,P}) = 13$ Hz, $J(\text{C,Rh}) = 5$ Hz, =CH COD), 116.5 (d, $J(\text{C,P}) = 12$ Hz, C_q arom), 117.2 (d, $J(\text{C,P}) = 12$ Hz, C_q arom), 118.4 (s, CH arom), 119.0 (s, CH arom), 122.2 (s, CH arom), 126.0 (d, $J(\text{C,P}) = 8$ Hz, CH arom), 126.7 (s, C_q arom), 127.7 (d, $J(\text{C,P}) = 10$ Hz, C_q arom), 128.3 (s, C_q arom), 129.7 (s, CH arom), 129.9 (s, CH arom), 130.1 (s, CH arom), 130.2 (s, CH arom), 130.6 (s, CH arom), 131.1 (s, CH arom), 132.4 (s, CH arom), 133.1 (s, CH arom), 133.4 (s, 2 CH arom), 133.5 (s, CH arom), 134.5 (s, CH arom), 134.7 (s, CH arom), 134.8 (s, CH arom), 135.7 (s, C_q arom), 136.2 (s, C_q arom), 138.2 (s, C_q arom), 138.6 (s, C_q arom), 145.8 (d, $J(\text{C,P}) = 5$ Hz, C_q arom), 146.2 (d, $J(\text{C,P}) = 13$ Hz, C_q arom), 155.1 (d, $J(\text{C,P}) = 10$ Hz, C_q arom). Anal. Calcd for $\text{C}_{42}\text{H}_{42}\text{O}_3\text{BF}_4\text{P}_2\text{Rh}\cdot\text{CH}_2\text{Cl}_2$: C, 55.4; H, 4.8. Found: C, 55.5; H, 4.8.

Representative procedure for Enantioselective Hydrogenation

Hydrogenations were performed as exemplified below for **2a**. In a glove box, a Fischer-Porter reactor (80 mL) was charged with **2a** (0.073 g, 0.25 mmol) and catalyst precursor **8a** (0.002 g, 0.002 mmol) in CH_2Cl_2 (5 mL). The vessel was brought outside the glove box, submitted to vacuum-hydrogen cycles and finally pressurized to 4 atm. The reaction mixture was kept on stirring for 24 hours, then the reactor was depressurized and the obtained mixture was evaporated to dryness, treated with Et_2O and passed through a short pad of silica. The resulting residue was analyzed by ^1H NMR to determine conversion and by chiral HPLC for enantiomeric excess. **1-benzoyloxy-1-dimethylphosphonylethane** (Chiralcel AD, 30°C, flow rate 1.0 mL/min, hexane/2-propanol 98.5:1.5) $t_1 = 40.8$ min (*S*), $t_2 = 47.8$ min (*R*); **1-benzoyloxy-1-dimethylphosphonylbutane** (Chiralcel AD, 30°C, flow rate 1.0 mL/min, hexane/2-

propanol 95:5) t_1 = 11.2 min (*R*), t_2 = 13.4 min (*S*); **1-benzoyloxy-1-dimethylphosphonyl-3-methylbutane** (Chiralcel AD, 30°C, flow rate 1.0 mL/min, hexane/2-propanol 95:5) t_1 = 10.1 min (*R*), t_2 = 12.5 min (*S*); **1-benzoyloxy-1-dimethylphosphonylhexane** (Chiralcel AD, 30°C, flow rate 1.0 mL/min, hexane/2-propanol 95:5) t_1 = 11.6 min (*R*), t_2 = 13.0 min (*S*); **1-benzoyloxy-1-dimethylphosphonyl-2-phenylethane** (Chiralcel AD, 30°C, flow rate 1.0 mL/min, hexane/2-propanol 95:5) t_1 = 18.9 min (*R*), t_2 = 21.0 min (*S*); **1-benzoyloxy-1-dimethylphosphonyl-2-(4-methoxyphenyl) ethane** (Chiralcel AD, 30°C, flow rate 1 mL/min, hexane/2-propanol 95:5) t_1 = 27.6 min (*R*), t_2 = 37.0 min (*S*).

[1] Z. Hua, V. C. Vassar, I. Ojima *Org. Lett.* **2003**, 5, 3831.



ORTEP view of compound **8a**. BF_4^- ion, solvent and H atoms have been omitted for clarity

Table S1. Crystal data and structure refinement for **8a·H₂O**

Empirical formula	C ₈₄ H ₈₈ B ₂ F ₈ O ₈ P ₄ Rh ₂ [C ₄₂ H ₄₂ BF ₄ O ₃ P ₂ Rh, C ₄₂ H ₄₂ BF ₄ O ₃ P ₂ Rh, 2 BF ₄ , 2 H ₂ O]	
Formula weight	1728.86	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	$a = 16.3320(12)$ Å	$\alpha = 90^\circ$
	$b = 21.0373(15)$ Å	$\beta = 90^\circ$
	$c = 23.4288(19)$ Å	$\gamma = 90^\circ$
Volume	8049.7(11) Å ³	
Z	4	
Density (calculated)	1.427 Mg/m ³	
Absorption coefficient	0.563 mm ⁻¹	
$F(000)$	3552	
Crystal size	0.50 x 0.27 x 0.12 mm ³	
θ range for data collection	2.12 to 30.94°.	
Index ranges	$-22 \leq h \leq 23$, $-28 \leq k \leq 30$, $-33 \leq l \leq 33$	
Reflections collected	88996	
Independent reflections	25153 [$R(\text{int}) = 0.0535$]	
Completeness to $\theta = 30.94^\circ$	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9355 and 0.7661	
Refinement method	Full-matrix-block least-squares on F^2	
Data / restraints / parameters	25153 / 6 / 973	
Goodness-of-fit on F^2	1.079	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0586$, $wR2 = 0.1393$	
R indices (all data)	$R1 = 0.0932$, $wR2 = 0.1630$	
Absolute structure parameter	-0.06(2)	
Largest diff. peak and hole	2.285 and -1.343 e · Å ⁻³	

Table S2. Bond lengths [Å] and angles [°] for **8a·H₂O**

Rh(1)-P(1)	2.1913(11)	C(13)-H(13A)	0.9800
Rh(1)-C(39)	2.237(5)	C(13)-H(13B)	0.9800
Rh(1)-C(40)	2.252(4)	C(13)-H(13C)	0.9800
Rh(1)-C(35)	2.265(5)	C(14)-H(14A)	0.9800
Rh(1)-P(2)	2.2835(12)	C(14)-H(14B)	0.9800
Rh(1)-C(36)	2.314(4)	C(14)-H(14C)	0.9800
P(1)-O(2)	1.602(3)	C(15)-H(15A)	0.9800
P(1)-O(3)	1.608(3)	C(15)-H(15B)	0.9800
P(1)-O(1)	1.615(3)	C(15)-H(15C)	0.9800
P(2)-C(17)	1.817(5)	C(16)-H(16A)	0.9800
P(2)-C(29)	1.822(5)	C(16)-H(16B)	0.9800
P(2)-C(23)	1.831(5)	C(16)-H(16C)	0.9800
O(1)-C(1)	1.425(5)	C(17)-C(18)	1.396(7)
O(2)-C(8)	1.414(5)	C(17)-C(22)	1.412(6)
O(3)-C(18)	1.406(5)	C(18)-C(19)	1.373(8)
C(1)-C(2)	1.381(7)	C(19)-C(20)	1.384(7)
C(1)-C(6)	1.390(7)	C(19)-H(19)	0.9500
C(2)-C(3)	1.387(7)	C(20)-C(21)	1.388(9)
C(2)-H(2)	0.9500	C(20)-H(20)	0.9500
C(3)-C(4)	1.391(8)	C(21)-C(22)	1.378(9)
C(3)-H(3)	0.9500	C(21)-H(21)	0.9500
C(4)-C(5)	1.413(7)	C(22)-H(22)	0.9500
C(4)-C(13)	1.507(7)	C(23)-C(28)	1.380(9)
C(5)-C(6)	1.422(6)	C(23)-C(24)	1.397(8)
C(5)-C(14)	1.494(7)	C(24)-C(25)	1.399(8)
C(6)-C(7)	1.485(6)	C(24)-H(24)	0.9500
C(7)-C(8)	1.404(6)	C(25)-C(26)	1.365(11)
C(7)-C(12)	1.417(6)	C(25)-H(25)	0.9500
C(8)-C(9)	1.387(6)	C(26)-C(27)	1.399(11)
C(9)-C(10)	1.359(7)	C(26)-H(26)	0.9500
C(9)-H(9)	0.9500	C(27)-C(28)	1.399(8)
C(10)-C(11)	1.400(7)	C(27)-H(27)	0.9500
C(10)-H(10)	0.9500	C(28)-H(28)	0.9500
C(11)-C(12)	1.417(7)	C(29)-C(34)	1.371(8)
C(11)-C(15)	1.498(7)	C(29)-C(30)	1.400(8)
C(12)-C(16)	1.508(6)	C(30)-C(31)	1.365(9)

C(30)-H(30)	0.9500	P(4)-C(73)	1.826(5)
C(31)-C(32)	1.378(13)	P(4)-C(79)	1.829(5)
C(31)-H(31)	0.9500	O(4)-C(51)	1.411(5)
C(32)-C(33)	1.404(13)	O(5)-C(58)	1.421(6)
C(32)-H(32)	0.9500	O(6)-C(68)	1.397(5)
C(33)-C(34)	1.401(9)	C(51)-C(52)	1.367(7)
C(33)-H(33)	0.9500	C(51)-C(56)	1.400(6)
C(34)-H(34)	0.9500	C(52)-C(53)	1.379(8)
C(35)-C(36)	1.366(8)	C(52)-H(52)	0.9500
C(35)-C(42)	1.494(7)	C(53)-C(54)	1.410(8)
C(35)-H(35)	0.9500	C(53)-H(53)	0.9500
C(36)-C(37)	1.515(8)	C(54)-C(55)	1.408(7)
C(36)-H(36)	0.9500	C(54)-C(63)	1.477(7)
C(37)-C(38)	1.540(8)	C(55)-C(56)	1.392(7)
C(37)-H(37A)	0.9900	C(55)-C(64)	1.514(7)
C(37)-H(37B)	0.9900	C(56)-C(57)	1.513(6)
C(38)-C(39)	1.507(7)	C(57)-C(58)	1.387(7)
C(38)-H(38A)	0.9900	C(57)-C(62)	1.416(6)
C(38)-H(38B)	0.9900	C(58)-C(59)	1.374(6)
C(39)-C(40)	1.353(7)	C(59)-C(60)	1.383(7)
C(39)-H(39)	0.9500	C(59)-H(59)	0.9500
C(40)-C(41)	1.494(7)	C(60)-C(61)	1.386(9)
C(40)-H(40)	0.9500	C(60)-H(60)	0.9500
C(41)-C(42)	1.558(7)	C(61)-C(62)	1.405(7)
C(41)-H(41A)	0.9900	C(61)-C(65)	1.507(7)
C(41)-H(41B)	0.9900	C(62)-C(66)	1.516(8)
C(42)-H(42A)	0.9900	C(63)-H(63A)	0.9800
C(42)-H(42B)	0.9900	C(63)-H(63B)	0.9800
Rh(2)-P(3)	2.1824(11)	C(63)-H(63C)	0.9800
Rh(2)-C(90)	2.247(5)	C(64)-H(64A)	0.9800
Rh(2)-C(89)	2.256(4)	C(64)-H(64B)	0.9800
Rh(2)-C(86)	2.286(5)	C(64)-H(64C)	0.9800
Rh(2)-P(4)	2.2900(11)	C(65)-H(65A)	0.9800
Rh(2)-C(85)	2.339(4)	C(65)-H(65B)	0.9800
P(3)-O(4)	1.607(3)	C(65)-H(65C)	0.9800
P(3)-O(5)	1.611(3)	C(66)-H(66A)	0.9800
P(3)-O(6)	1.611(3)	C(66)-H(66B)	0.9800
P(4)-C(67)	1.823(4)	C(66)-H(66C)	0.9800

C(67)-C(68)	1.396(6)	C(87)-H(87A)	0.9900
C(67)-C(72)	1.402(6)	C(87)-H(87B)	0.9900
C(68)-C(69)	1.376(6)	C(88)-C(89)	1.516(6)
C(69)-C(70)	1.391(7)	C(88)-H(88A)	0.9900
C(69)-H(69)	0.9500	C(88)-H(88B)	0.9900
C(70)-C(71)	1.375(7)	C(89)-C(90)	1.359(7)
C(70)-H(70)	0.9500	C(89)-H(89)	0.9500
C(71)-C(72)	1.396(7)	C(90)-C(91)	1.476(8)
C(71)-H(71)	0.9500	C(90)-H(90)	0.9500
C(72)-H(72)	0.9501	C(91)-C(92)	1.537(8)
C(73)-C(74)	1.389(7)	C(91)-H(91A)	0.9900
C(73)-C(78)	1.394(6)	C(91)-H(91B)	0.9900
C(74)-C(75)	1.387(7)	C(92)-H(92A)	0.9900
C(74)-H(74)	0.9500	C(92)-H(92B)	0.9900
C(75)-C(76)	1.396(7)	B(1)-F(1)	1.244(11)
C(75)-H(75)	0.9499	B(1)-F(2)	1.334(10)
C(76)-C(77)	1.361(8)	B(1)-F(3)	1.382(13)
C(76)-H(76)	0.9500	B(1)-F(4)	1.423(11)
C(77)-C(78)	1.408(7)	B(2)-F(7)	1.307(15)
C(77)-H(77)	0.9500	B(2)-F(5)	1.336(10)
C(78)-H(78)	0.9500	B(2)-F(8)	1.360(12)
C(79)-C(80)	1.390(7)	B(2)-F(6)	1.397(10)
C(79)-C(84)	1.402(7)	O(7)-H(7A)	0.8514
C(80)-C(81)	1.381(8)	O(7)-H(7B)	0.8409
C(80)-H(80)	0.9500	O(8)-H(8A)	0.9063
C(81)-C(82)	1.373(9)	O(8)-H(8B)	0.9687
C(81)-H(81)	0.9500		
C(82)-C(83)	1.370(9)	P(1)-Rh(1)-C(39)	96.56(13)
C(82)-H(82)	0.9500	P(1)-Rh(1)-C(40)	92.01(12)
C(83)-C(84)	1.394(7)	C(39)-Rh(1)-C(40)	35.08(18)
C(83)-H(83)	0.9500	P(1)-Rh(1)-C(35)	147.37(14)
C(84)-H(84)	0.9500	C(39)-Rh(1)-C(35)	94.87(18)
C(85)-C(86)	1.380(8)	C(40)-Rh(1)-C(35)	80.20(18)
C(85)-C(92)	1.527(7)	P(1)-Rh(1)-P(2)	85.69(4)
C(85)-H(85)	0.9500	C(39)-Rh(1)-P(2)	153.98(13)
C(86)-C(87)	1.489(7)	C(40)-Rh(1)-P(2)	170.87(13)
C(86)-H(86)	0.9500	C(35)-Rh(1)-P(2)	97.01(13)
C(87)-C(88)	1.539(6)	P(1)-Rh(1)-C(36)	176.34(15)

C(39)-Rh(1)-C(36)	79.87(19)	C(8)-C(7)-C(6)	118.7(4)
C(40)-Rh(1)-C(36)	85.52(17)	C(12)-C(7)-C(6)	124.5(4)
C(35)-Rh(1)-C(36)	34.7(2)	C(9)-C(8)-C(7)	123.1(4)
P(2)-Rh(1)-C(36)	97.17(13)	C(9)-C(8)-O(2)	118.7(4)
O(2)-P(1)-O(3)	104.42(18)	C(7)-C(8)-O(2)	118.1(4)
O(2)-P(1)-O(1)	102.20(16)	C(10)-C(9)-C(8)	118.7(4)
O(3)-P(1)-O(1)	93.37(17)	C(10)-C(9)-H(9)	120.6
O(2)-P(1)-Rh(1)	116.57(12)	C(8)-C(9)-H(9)	120.6
O(3)-P(1)-Rh(1)	118.84(12)	C(9)-C(10)-C(11)	122.0(4)
O(1)-P(1)-Rh(1)	117.85(13)	C(9)-C(10)-H(10)	119.0
C(17)-P(2)-C(29)	103.6(2)	C(11)-C(10)-H(10)	119.0
C(17)-P(2)-C(23)	105.9(2)	C(10)-C(11)-C(12)	118.8(4)
C(29)-P(2)-C(23)	104.9(2)	C(10)-C(11)-C(15)	119.5(5)
C(17)-P(2)-Rh(1)	107.85(17)	C(12)-C(11)-C(15)	121.6(5)
C(29)-P(2)-Rh(1)	117.00(18)	C(11)-C(12)-C(7)	120.4(4)
C(23)-P(2)-Rh(1)	116.36(15)	C(11)-C(12)-C(16)	119.2(4)
C(1)-O(1)-P(1)	115.1(3)	C(7)-C(12)-C(16)	120.4(4)
C(8)-O(2)-P(1)	117.6(3)	C(4)-C(13)-H(13A)	109.4
C(18)-O(3)-P(1)	122.6(3)	C(4)-C(13)-H(13B)	109.6
C(2)-C(1)-C(6)	123.8(4)	H(13A)-C(13)-H(13B)	109.5
C(2)-C(1)-O(1)	117.9(4)	C(4)-C(13)-H(13C)	109.3
C(6)-C(1)-O(1)	118.3(4)	H(13A)-C(13)-H(13C)	109.5
C(1)-C(2)-C(3)	117.5(5)	H(13B)-C(13)-H(13C)	109.5
C(1)-C(2)-H(2)	121.2	C(5)-C(14)-H(14A)	109.5
C(3)-C(2)-H(2)	121.2	C(5)-C(14)-H(14B)	109.4
C(2)-C(3)-C(4)	122.1(5)	H(14A)-C(14)-H(14B)	109.5
C(2)-C(3)-H(3)	119.0	C(5)-C(14)-H(14C)	109.5
C(4)-C(3)-H(3)	119.0	H(14A)-C(14)-H(14C)	109.5
C(3)-C(4)-C(5)	119.3(5)	H(14B)-C(14)-H(14C)	109.5
C(3)-C(4)-C(13)	119.6(5)	C(11)-C(15)-H(15A)	109.3
C(5)-C(4)-C(13)	121.1(5)	C(11)-C(15)-H(15B)	109.4
C(4)-C(5)-C(6)	119.6(5)	H(15A)-C(15)-H(15B)	109.5
C(4)-C(5)-C(14)	118.1(4)	C(11)-C(15)-H(15C)	109.7
C(6)-C(5)-C(14)	122.3(4)	H(15A)-C(15)-H(15C)	109.5
C(1)-C(6)-C(5)	117.6(4)	H(15B)-C(15)-H(15C)	109.5
C(1)-C(6)-C(7)	118.6(4)	C(12)-C(16)-H(16A)	109.5
C(5)-C(6)-C(7)	123.7(4)	C(12)-C(16)-H(16B)	109.3
C(8)-C(7)-C(12)	116.8(4)	H(16A)-C(16)-H(16B)	109.5

C(12)-C(16)-H(16C)	109.5	C(27)-C(28)-H(28)	120.3
H(16A)-C(16)-H(16C)	109.5	C(34)-C(29)-C(30)	119.7(5)
H(16B)-C(16)-H(16C)	109.5	C(34)-C(29)-P(2)	120.7(4)
C(18)-C(17)-C(22)	116.2(5)	C(30)-C(29)-P(2)	119.6(5)
C(18)-C(17)-P(2)	118.6(3)	C(31)-C(30)-C(29)	121.0(7)
C(22)-C(17)-P(2)	125.1(4)	C(31)-C(30)-H(30)	119.2
C(19)-C(18)-C(17)	123.6(4)	C(29)-C(30)-H(30)	119.8
C(19)-C(18)-O(3)	116.5(4)	C(30)-C(31)-C(32)	119.0(7)
C(17)-C(18)-O(3)	119.7(4)	C(30)-C(31)-H(31)	120.7
C(18)-C(19)-C(20)	118.6(5)	C(32)-C(31)-H(31)	120.3
C(18)-C(19)-H(19)	120.7	C(31)-C(32)-C(33)	121.9(6)
C(20)-C(19)-H(19)	120.7	C(31)-C(32)-H(32)	119.0
C(19)-C(20)-C(21)	120.0(5)	C(33)-C(32)-H(32)	119.1
C(19)-C(20)-H(20)	120.0	C(34)-C(33)-C(32)	117.6(8)
C(21)-C(20)-H(20)	120.0	C(34)-C(33)-H(33)	121.4
C(22)-C(21)-C(20)	120.7(5)	C(32)-C(33)-H(33)	121.0
C(22)-C(21)-H(21)	119.7	C(29)-C(34)-C(33)	120.8(7)
C(20)-C(21)-H(21)	119.7	C(29)-C(34)-H(34)	119.7
C(21)-C(22)-C(17)	120.8(5)	C(33)-C(34)-H(34)	119.5
C(21)-C(22)-H(22)	119.6	C(36)-C(35)-C(42)	127.8(5)
C(17)-C(22)-H(22)	119.6	C(36)-C(35)-Rh(1)	74.6(3)
C(28)-C(23)-C(24)	120.0(5)	C(42)-C(35)-Rh(1)	104.4(3)
C(28)-C(23)-P(2)	121.0(4)	C(36)-C(35)-H(35)	116.1
C(24)-C(23)-P(2)	118.7(4)	C(42)-C(35)-H(35)	116.1
C(23)-C(24)-C(25)	119.8(7)	Rh(1)-C(35)-H(35)	91.2
C(23)-C(24)-H(24)	120.1	C(35)-C(36)-C(37)	124.0(5)
C(25)-C(24)-H(24)	120.1	C(35)-C(36)-Rh(1)	70.7(3)
C(26)-C(25)-C(24)	120.6(7)	C(37)-C(36)-Rh(1)	109.6(3)
C(26)-C(25)-H(25)	119.8	C(35)-C(36)-H(36)	118.0
C(24)-C(25)-H(25)	119.7	C(37)-C(36)-H(36)	118.0
C(25)-C(26)-C(27)	119.6(5)	Rh(1)-C(36)-H(36)	89.7
C(25)-C(26)-H(26)	120.2	C(36)-C(37)-C(38)	112.5(4)
C(27)-C(26)-H(26)	120.3	C(36)-C(37)-H(37A)	109.1
C(28)-C(27)-C(26)	120.5(7)	C(38)-C(37)-H(37A)	109.1
C(28)-C(27)-H(27)	119.7	C(36)-C(37)-H(37B)	109.1
C(26)-C(27)-H(27)	119.7	C(38)-C(37)-H(37B)	109.1
C(23)-C(28)-C(27)	119.4(6)	H(37A)-C(37)-H(37B)	107.8
C(23)-C(28)-H(28)	120.3	C(39)-C(38)-C(37)	114.0(5)

C(39)-C(38)-H(38A)	108.8	C(86)-Rh(2)-P(4)	96.16(12)
C(37)-C(38)-H(38A)	108.7	P(3)-Rh(2)-C(85)	175.66(14)
C(39)-C(38)-H(38B)	108.8	C(90)-Rh(2)-C(85)	79.11(19)
C(37)-C(38)-H(38B)	108.7	C(89)-Rh(2)-C(85)	85.59(17)
H(38A)-C(38)-H(38B)	107.6	C(86)-Rh(2)-C(85)	34.70(19)
C(40)-C(39)-C(38)	126.3(5)	P(4)-Rh(2)-C(85)	97.03(12)
C(40)-C(39)-Rh(1)	73.1(3)	O(4)-P(3)-O(5)	102.62(17)
C(38)-C(39)-Rh(1)	106.0(3)	O(4)-P(3)-O(6)	93.81(16)
C(40)-C(39)-H(39)	116.8	O(5)-P(3)-O(6)	103.73(16)
C(38)-C(39)-H(39)	116.9	O(4)-P(3)-Rh(2)	117.60(12)
Rh(1)-C(39)-H(39)	91.1	O(5)-P(3)-Rh(2)	116.56(13)
C(39)-C(40)-C(41)	128.6(4)	O(6)-P(3)-Rh(2)	118.99(12)
C(39)-C(40)-Rh(1)	71.8(3)	C(67)-P(4)-C(73)	106.0(2)
C(41)-C(40)-Rh(1)	111.0(3)	C(67)-P(4)-C(79)	103.4(2)
C(39)-C(40)-H(40)	115.7	C(73)-P(4)-C(79)	106.2(2)
C(41)-C(40)-H(40)	115.7	C(67)-P(4)-Rh(2)	108.62(14)
Rh(1)-C(40)-H(40)	86.9	C(73)-P(4)-Rh(2)	115.29(15)
C(40)-C(41)-C(42)	113.3(4)	C(79)-P(4)-Rh(2)	116.30(16)
C(40)-C(41)-H(41A)	108.9	C(51)-O(4)-P(3)	115.0(3)
C(42)-C(41)-H(41A)	108.9	C(58)-O(5)-P(3)	117.5(3)
C(40)-C(41)-H(41B)	109.0	C(68)-O(6)-P(3)	123.0(3)
C(42)-C(41)-H(41B)	108.9	C(52)-C(51)-C(56)	121.7(4)
H(41A)-C(41)-H(41B)	107.7	C(52)-C(51)-O(4)	119.7(4)
C(35)-C(42)-C(41)	114.8(4)	C(56)-C(51)-O(4)	118.6(4)
C(35)-C(42)-H(42A)	108.6	C(51)-C(52)-C(53)	119.0(5)
C(41)-C(42)-H(42A)	108.6	C(51)-C(52)-H(52)	120.5
C(35)-C(42)-H(42B)	108.5	C(53)-C(52)-H(52)	120.5
C(41)-C(42)-H(42B)	108.5	C(52)-C(53)-C(54)	121.5(5)
H(42A)-C(42)-H(42B)	107.5	C(52)-C(53)-H(53)	119.2
P(3)-Rh(2)-C(90)	97.01(14)	C(54)-C(53)-H(53)	119.2
P(3)-Rh(2)-C(89)	92.34(13)	C(55)-C(54)-C(53)	118.5(5)
C(90)-Rh(2)-C(89)	35.14(18)	C(55)-C(54)-C(63)	122.4(5)
P(3)-Rh(2)-C(86)	148.55(14)	C(53)-C(54)-C(63)	119.1(5)
C(90)-Rh(2)-C(86)	94.13(18)	C(56)-C(55)-C(54)	119.7(5)
C(89)-Rh(2)-C(86)	80.19(17)	C(56)-C(55)-C(64)	122.5(4)
P(3)-Rh(2)-P(4)	85.69(4)	C(54)-C(55)-C(64)	117.8(5)
C(90)-Rh(2)-P(4)	155.34(14)	C(55)-C(56)-C(51)	119.5(4)
C(89)-Rh(2)-P(4)	169.52(13)	C(55)-C(56)-C(57)	123.1(4)

C(51)-C(56)-C(57)	117.4(4)	C(62)-C(66)-H(66B)	109.4
C(58)-C(57)-C(62)	117.8(4)	H(66A)-C(66)-H(66B)	109.5
C(58)-C(57)-C(56)	118.4(4)	C(62)-C(66)-H(66C)	109.5
C(62)-C(57)-C(56)	123.8(5)	H(66A)-C(66)-H(66C)	109.5
C(59)-C(58)-C(57)	123.0(4)	H(66B)-C(66)-H(66C)	109.5
C(59)-C(58)-O(5)	117.9(4)	C(68)-C(67)-C(72)	116.5(4)
C(57)-C(58)-O(5)	119.0(4)	C(68)-C(67)-P(4)	118.1(3)
C(58)-C(59)-C(60)	118.4(5)	C(72)-C(67)-P(4)	125.4(3)
C(58)-C(59)-H(59)	120.7	C(69)-C(68)-C(67)	123.3(4)
C(60)-C(59)-H(59)	120.8	C(69)-C(68)-O(6)	116.3(4)
C(59)-C(60)-C(61)	121.4(5)	C(67)-C(68)-O(6)	120.2(4)
C(59)-C(60)-H(60)	119.3	C(68)-C(69)-C(70)	118.9(4)
C(61)-C(60)-H(60)	119.3	C(68)-C(69)-H(69)	120.6
C(60)-C(61)-C(62)	119.5(5)	C(70)-C(69)-H(69)	120.4
C(60)-C(61)-C(65)	120.0(5)	C(71)-C(70)-C(69)	119.7(4)
C(62)-C(61)-C(65)	120.5(5)	C(71)-C(70)-H(70)	120.2
C(61)-C(62)-C(57)	119.7(5)	C(69)-C(70)-H(70)	120.2
C(61)-C(62)-C(66)	119.4(5)	C(70)-C(71)-C(72)	120.8(4)
C(57)-C(62)-C(66)	120.9(5)	C(70)-C(71)-H(71)	119.6
C(54)-C(63)-H(63A)	109.4	C(72)-C(71)-H(71)	119.7
C(54)-C(63)-H(63B)	109.5	C(71)-C(72)-C(67)	120.7(4)
H(63A)-C(63)-H(63B)	109.5	C(71)-C(72)-H(72)	119.6
C(54)-C(63)-H(63C)	109.5	C(67)-C(72)-H(72)	119.7
H(63A)-C(63)-H(63C)	109.5	C(74)-C(73)-C(78)	119.2(4)
H(63B)-C(63)-H(63C)	109.5	C(74)-C(73)-P(4)	119.5(4)
C(55)-C(64)-H(64A)	109.4	C(78)-C(73)-P(4)	121.0(4)
C(55)-C(64)-H(64B)	109.5	C(75)-C(74)-C(73)	120.8(5)
H(64A)-C(64)-H(64B)	109.5	C(75)-C(74)-H(74)	119.6
C(55)-C(64)-H(64C)	109.4	C(73)-C(74)-H(74)	119.6
H(64A)-C(64)-H(64C)	109.5	C(74)-C(75)-C(76)	119.6(5)
H(64B)-C(64)-H(64C)	109.5	C(74)-C(75)-H(75)	120.2
C(61)-C(65)-H(65A)	109.5	C(76)-C(75)-H(75)	120.3
C(61)-C(65)-H(65B)	109.5	C(77)-C(76)-C(75)	120.2(5)
H(65A)-C(65)-H(65B)	109.5	C(77)-C(76)-H(76)	120.0
C(61)-C(65)-H(65C)	109.4	C(75)-C(76)-H(76)	119.8
H(65A)-C(65)-H(65C)	109.5	C(76)-C(77)-C(78)	120.6(5)
H(65B)-C(65)-H(65C)	109.5	C(76)-C(77)-H(77)	119.7
C(62)-C(66)-H(66A)	109.5	C(78)-C(77)-H(77)	119.7

C(73)-C(78)-C(77)	119.5(5)	H(87A)-C(87)-H(87B)	107.3
C(73)-C(78)-H(78)	120.2	C(89)-C(88)-C(87)	113.3(4)
C(77)-C(78)-H(78)	120.3	C(89)-C(88)-H(88A)	108.9
C(80)-C(79)-C(84)	119.6(5)	C(87)-C(88)-H(88A)	108.9
C(80)-C(79)-P(4)	120.2(4)	C(89)-C(88)-H(88B)	109.0
C(84)-C(79)-P(4)	120.2(4)	C(87)-C(88)-H(88B)	108.9
C(81)-C(80)-C(79)	119.4(5)	H(88A)-C(88)-H(88B)	107.7
C(81)-C(80)-H(80)	120.4	C(90)-C(89)-C(88)	127.6(5)
C(79)-C(80)-H(80)	120.3	C(90)-C(89)-Rh(2)	72.1(3)
C(82)-C(81)-C(80)	121.4(6)	C(88)-C(89)-Rh(2)	110.7(3)
C(82)-C(81)-H(81)	119.3	C(90)-C(89)-H(89)	116.3
C(80)-C(81)-H(81)	119.3	C(88)-C(89)-H(89)	116.2
C(83)-C(82)-C(81)	119.7(5)	Rh(2)-C(89)-H(89)	87.0
C(83)-C(82)-H(82)	120.0	C(89)-C(90)-C(91)	127.1(5)
C(81)-C(82)-H(82)	120.3	C(89)-C(90)-Rh(2)	72.8(3)
C(82)-C(83)-C(84)	120.6(5)	C(91)-C(90)-Rh(2)	106.9(3)
C(82)-C(83)-H(83)	119.8	C(89)-C(90)-H(90)	116.4
C(84)-C(83)-H(83)	119.6	C(91)-C(90)-H(90)	116.5
C(83)-C(84)-C(79)	119.3(5)	Rh(2)-C(90)-H(90)	90.3
C(83)-C(84)-H(84)	120.3	C(90)-C(91)-C(92)	114.9(4)
C(79)-C(84)-H(84)	120.3	C(90)-C(91)-H(91A)	108.5
C(86)-C(85)-C(92)	122.9(5)	C(92)-C(91)-H(91A)	108.6
C(86)-C(85)-Rh(2)	70.5(3)	C(90)-C(91)-H(91B)	108.5
C(92)-C(85)-Rh(2)	109.2(3)	C(92)-C(91)-H(91B)	108.5
C(86)-C(85)-H(85)	118.5	H(91A)-C(91)-H(91B)	107.5
C(92)-C(85)-H(85)	118.5	C(85)-C(92)-C(91)	112.1(4)
Rh(2)-C(85)-H(85)	90.3	C(85)-C(92)-H(92A)	109.2
C(85)-C(86)-C(87)	127.3(5)	C(91)-C(92)-H(92A)	109.1
C(85)-C(86)-Rh(2)	74.7(3)	C(85)-C(92)-H(92B)	109.2
C(87)-C(86)-Rh(2)	103.9(3)	C(91)-C(92)-H(92B)	109.1
C(85)-C(86)-H(86)	116.3	H(92A)-C(92)-H(92B)	107.9
C(87)-C(86)-H(86)	116.3	F(1)-B(1)-F(2)	120.1(9)
Rh(2)-C(86)-H(86)	91.4	F(1)-B(1)-F(3)	106.9(11)
C(86)-C(87)-C(88)	116.3(4)	F(2)-B(1)-F(3)	103.6(9)
C(86)-C(87)-H(87A)	108.2	F(1)-B(1)-F(4)	113.3(9)
C(88)-C(87)-H(87A)	108.2	F(2)-B(1)-F(4)	108.2(8)
C(86)-C(87)-H(87B)	108.2	F(3)-B(1)-F(4)	102.9(7)
C(88)-C(87)-H(87B)	108.2	F(7)-B(2)-F(5)	107.9(9)

F(7)-B(2)-F(8)	107.0(10)	F(8)-B(2)-F(6)	108.9(8)
F(5)-B(2)-F(8)	111.0(10)	H(7A)-O(7)-H(7B)	108.4
F(7)-B(2)-F(6)	110.9(10)	H(8A)-O(8)-H(8B)	74.2
F(5)-B(2)-F(6)	111.1(8)		

Symmetry transformations used to generate equivalent atoms:

