Highly Selective Asymmetric Hydrogenation Using a Three Hindered Quadrant Bisphosphine Rhodium Catalyst

Garrett Hoge,* He-Ping Wu, William Kissel, Derek Pflum, Derek Greene, and Jian Bao

Supporting Information

Materials and Methods. All reactions and manipulations were performed under nitrogen in standard laboratory glassware. Asymmetric hydrogenation was performed in a nitrogen filled glovebox. THF (anhydrous, 99.9%), acetonitrile (anhydrous, 99.8%), ether (anhydrous, 99.8%), methyl alcohol (anhydrous, 99.8%), and dichloromethane (anyhydrous, 99.8%) were obtained from Aldrich Chemical Co. Bis(1,5-cyclooctadiene)rhodium (I) tetrafluoroborate was synthesized according to literature procedure.ⁱ Hydrogen gas was used from a lecture bottle supplied by Specialty Gas. Hydrogenations were performed in a Griffin-Worden pressure vessel supplied by Kimble/Kontes.

Nuclear Magnetic Resonance. 400 MHz ¹H NMR, 100 MHz ¹³C NMR, and 162 MHz ³¹P NMR spectra were obtained on "Barton" - a Varian Unity+400 (Inova400 after 08/15/00) spectrometer equipped with an Auto Switchable 4-Nuclei PFG probe, two RF channels, and a SMS-100 sample changer by Zymark. Spectra were generally acquired near room temperature (21°C), and standard autolock, autoshim and autogain routines were employed. Samples are usually spun at 20 Hz for 1D experiments. ¹H NMR spectra were acquired using 45-degree tip angle pulses, 1.0 second recycle delay, and 16 scans at a resolution of 0.25 Hz/point. The acquisition window was typically 8000 Hz from +18 to -2 ppm (Reference TMS at 0 ppm), and processing was with 0.2 Hz line broadening. Typical acquisition time is 80 seconds. Regular ¹³C NMR spectra were acquired using 45-degree tip angle pulses, 2.0 second recycle delay, and 2048 scans at a resolution of 1 Hz/point. Spectral width was typically 25 KHz from +235 to -15 ppm (Reference

TMS at 0 ppm). Proton decoupling was applied continuously, and 2 Hz line broadening was applied during processing. Typical acquisition time is 102 minutes. ^{31}P NMR spectra were acquired using 45-degree tip angle pulses, 1.0 second recycle delay, and 64 scans at a resolution of 2 Hz/point. Spectral width was typically 48 KHz from +200 to -100 ppm (Reference 85% Phosphoric Acid at 0 ppm). Proton decoupling was applied continuously, and 2 Hz line broadening was applied during processing. Typical acquisition time is 1.5 minutes.

Mass Spectrometry. Mass Spectrometry was performed on a Micromass Platform LC system operating under MassLynx and OpenLynx open access software. The LC was equipped with a HP1100 quaternary LC system and a Gilson 215 liquid handler as an autosampler. Data was acquired under atmospheric pressure chemical ionization with 80:20 acetonitrile/water as the solvent. Temperatures: probe was 450°C, source was 150°C. Corona discharge was 3500V for positive ion and 3200V for negative ion.

High Performance Liquid Chromatography. High Performance Liquid Chromatography (HPLC) was performed on a series 1100 Agilent Technologies instrument equipped with a manual injector, quaternary pump, and a UV detector. The LC was PC controlled using HP Chemstation Plus Software. Normal Phase chiral HPLC was performed using a Chiracel OJ column supplied by Chiral Technologies.

Gas Chromatography. Gas Chromatography (GC) was performed on a 110 volt Varian Star 3400 equipped with an FID detector with electrometer, a model 1061 packed/530 micron ID flash injector, a model 1077 split/splitless capillary injector, a relay board that monitors four

external events, and an inboard printer/plotter. Gas chromatography was performed using 40 m x 0.25 mm Chiraldex G-TA or B-TA columns supplied by Advanced Separation Technologies, Incorporated or on a 25 m x 0.25 mm Coating Chirasil-L-Val column supplied by Chrompack.

General procedure for asymmetric hydrogenation reactions. Catalyst precursor **5a** (0.01 mmole) was dissolved in 1 mL degassed methanol in a Griffin-Worden pressure vessel equipped with the attachments necessary for connection to a hydrogen cylinder. The substrate (1 mmole) was dissolved in 4 mL of the same solvent and this was delivered to the catalyst solution via syringe. The vessel was sealed and pressurized to 50 psi H₂. Reaction completion times were monitored via H₂ gas uptake and enantiomeric excesses were monitored via chiral GC or HPLC.

Procedure for 100 g asymmetric hydrogenation of 8 using 5a (27,000:1 S/C). The substrate (100 g, 442 mmole) was weighed into a hydrogenation bottle in air. The hydrogenation bottle was then transferred to a glovebox (O₂ < 5 ppm). To the substrate was added 500 mL degassed MeOH with stirring to dissolve the substrate. Catalyst precursor **5a** (9.2 mg) was then added to the substrate solution. The hydrogenation vessel was sealed and then pressurized to 50 psi H₂ and stirred vigorously with a Teflon coated magnet. Pressure of the reaction was maintained at a constant 50 psi H₂. After 40 hours H₂ uptake was complete. GC analysis showed >98% conversion to **9** and 98% e.e. (S isomer).

Enantiomeric Excess Determinations. Enantiomeric excesses of acrylic acid derivatives were determined as follows: **N-acetylalanine methyl ester** (Capillary GC, Chrompack Chiral-L-Val (25 m), 120°C, isothermal, (R) t₁ = 10.5 min; (S) t₂ = 11.0 min; **N-acetylphenylalanine methyl**

ester (HPLC, Daicel Chiralcel OJ, 1.0 mL/min, 10% isopropanol/hexane, (R) t_1 = 11.6 min; (S) t_2 = 17.7 min); **N-acetylphenylalanine** and **N-acetylalanine** were converted to their corresponding methyl esters via treatment with trimethylsilyldiazomethane and their enantiomeric excesses were analyzed as described above; **N-acetylcyclohexylglycine methyl ester** (Capillary GC, Chirasil-L-Val (25 m), 145 °C isothermal, (R) t_1 = 11.3 min; (S) t_2 = 12.0 min).

The CI-1008 precursor, **9**, was acidified in its methanolic hydrogenation solution with 1 N HCl. The organics were extracted into CH₂Cl₂. After drying over MgSO₄ the volatiles were removed invacuo. The carboxylic acid was then converted to its corresponding methyl ester via treatment with trimethylsilyldiazomethane. The methyl ester was analyzed directly (Capillary GC, Astec GTA (30 m), 140 °C, isothermal, (R) t_1 = 8.8 min; (S) t_2 = 9.5 min).

Absolute Configurations. Absolute configurations of the products of hydrogenation were determined by comparison of the signs of optical rotation with those of literature values: **(S)-N-Acetylalanine methyl ester** $[\alpha]_D^{20} = -91.7^\circ$ (c 2, H₂O),ⁱⁱ **(S)-N-acetylphenylalanine methyl ester** $[\alpha]_D^{20} = +16.4^\circ$ (c 2, MeOH),ⁱⁱⁱ **(S)-N-acetylcyclohexylglycine methyl ester** $[\alpha]_D^{20} = -4.6^\circ$ (c = 0.13, EtOH).^{iv} The CI-1008 precursor, **9**, was compared in terms of elution order to an authentic sample with (S) configuration via the method for enantiomeric excess determination (above).

Preparation of (rac)-tert-butylmethylphosphino-di-tert-butylphosphinomethane (4). A solution of **3** (20.1g, 152 mmole) in 50 mL THF was stirred at 0 °C. To the solution was added s-BuLi (104 mL, 145 mmole) while maintaining the reaction temperature below 20 °C. The addition took 20 min, after which it turned slightly cloudy and orange. The reaction was stirred

for one hour at 0 °C. The reaction solution was then transferred via cannula to a pre-cooled solution of di-tert-butylchlorophosphine (25g, 138 mmole) in 50 mL THF at 0 °C. The temperature was maintained below 20 °C. The reaction turned red immediately with addition of the first drop. The total addition took 20 min. The reaction was stirred at 0 °C for 2 h. To this solution was then added BH₃•Me₂S (14.4 mL, 152 mmole) over 10 min. while maintaining the reaction temperature <20 °C. The reaction was stirred for 1 h after which it was poured onto 100 g ice in 100 mL 1N HCl and stirred for 30 min. The aqueous solution was extracted with EtOAc (2x100 mL) and then the combined organic layers were dried over MgSO₄ and filtered. Volatiles were then removed on a rotary evaporator. The residue was recrystallized from hot heptane producing a white crystalline solid. The solid weighed 25 g (63%). mp = 150-152 °C; ¹H NMR (400 MHz, CDCl₃) δ 1.88 (t, J = 12 Hz, 2H), 1.56 (d, J = 10 Hz, 3H), 1.33 (d, J = 13 Hz, 9H), 1.27 (d, J = 13 Hz, 9H), 1.19 (d, J = 13 Hz, 9H), 0.61 (br q, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 34.29 (d, J = 25 Hz), 33.41 (d, J = 25 Hz), 30.00 (d, 25 Hz), 28.30 (s), 27.89 (s), 25.21 (s), 9.12 (dd, J = 21 and 15 Hz), 6.52 (d, J = 32 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 49.70 – 48.15 (m), 33.03 – 31.56 (m). Anal Calcd for C₁₄H₃₈B₂P₂: C, 57.98; H, 13.21. Found: C, 57.64; H, 13.01.

Preparation of (R)-tert-butylmethylphosphino-di-tert-butylphosphinomethane (2a). Both **4a** (290 mg, 1.0 mmol) and DABCO (135 mg, 1.2 mmol) were dissolved in 10 ml of degassed toluene at 20 °C. The solution was stirred for 4 h at 80 °C. The solvent was removed invacuo and then the residue was extracted with hexane (3 X 20 ml). The combined organic extracts were concentrated and dried producing **2a** (228 mg, 87%) as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 1.47-1.41 (m, 2H), 1.09 (d, J = 11 Hz, 9H), 1.03 (d, J = 11 Hz, 9H), 0.94 (d, J = 11 Hz, 9H), 0.93 (d, J = 3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 7.44 (dd, J = 19 and 6 Hz), 16.09

(dd, $J = 32$ and 25 Hz), 26.63 (d, $J = 14$ Hz), 27.95 (dd, $J = 23$ and 3 Hz), 29.73 (d, $J = 14$ Hz), 30.16 (dd, $J = 13$ and 4 Hz), 31.70 (dd, $J = 23$ and 9 Hz), 32.16 (dd, $J = 23$ and 3 Hz); ^{31}P NMR (162 MHz, CDCl_3) δ -13.66 (br m), 18.35 (br m).

Preparation of (+)-(S)-tert-butylmethylphosphino-di-tert-butylphosphinomethane)-(1,5-cyclooctadiene) rhodium(I) tetrafluoroborate (5a). A solution of **2a** (66 mg, 0.25 mmol) in 5 ml of THF was added dropwise to a solution of $[\text{Rh}(\text{COD})_2]\text{BF}_4$ (102 mg, 0.25 mmol) in 10 ml of methanol at 20°C with stirring. After addition, the reaction mixture was stirred for 1 h and solvent was removed in vacuo to provide a red solid. Recrystallization of product from warm THF provided **5a** (89 mg, 64%) as a red crystalline product. $[\alpha]_D^{24} = +52.4^\circ$ (c 0.9, MeOH); ^1H NMR (400 MHz, CDCl_3) δ 5.63 – 5.51 (m, 2H), 5.11 (br s, 2H), 3.48 – 3.328 (m, 1H), 3.14 (dt, $J = 17$ and 10 Hz, 1H), 2.49 – 2.25 (m, 4H), 2.21 – 2.09 (m, 4H), 1.69 (d, $J = 9$ Hz, 3H), 1.39 (d, $J = 14$ Hz, 9H), 1.33 (d, $J = 14$ Hz, 9H), 1.13 (d, $J = 16$ Hz, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 100.20 (dd, $J = 9$ and 6 Hz), 97.70 (dd, $J = 9$ and 6 Hz), 92.95 (t, $J = 8$ Hz), 92.27 (d, $J = 8$ Hz), 37.68 (m), 36.04 (d, $J = 9$ Hz), 32.54 (m), 31.48 (s), 30.94 (s), 30.09 (d, $J = 5$ Hz), 29.81 (d, $J = 5$ Hz), 29.32 (s), 29.16 (s), 26.57 (d, $J = 5$ Hz), 9.58 (d, $J = 21$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ -3.97 (dd, $J = 126$ and 56 Hz), -29.36 (dd, $J = 126$ and 56 Hz). Anal Calcd for $\text{C}_{21}\text{H}_{42}\text{BF}_4\text{P}_2\text{Rh}$: C, 46.18; H, 7.75. Found: C, 45.66; H, 7.19.

Chiral Preparatory HPLC Method for the Separation of the Enantiomers of 4

Column: Daicel Chiralpak AD (250x20 mm, 10 micron)
Mobile Phase: 99.25:0.75 [hexanes:isopropanol]
Flow Rate: 9 ml/minute
Detector: none (* please see note below)
Concentration: 2 mg/ml
Diluent: mobile phase
Injection Volume: 500 μ L
Run Time: 20 minutes

* A prep scale RI detector was not available. Therefore, no detection was used to monitor the retention times of the enantiomers. Solvent was fractionated via fraction collector and fractions were assayed using the analytical method provided.

Analytical Method

Column: Daicel Chiralpak AD (250x4.6 mm, 10 micron)
Mobile Phase: 99.25:0.75 [hexanes:isopropanol]
Flow Rate: 1 ml/minute
Detector: RI (35 °C)
Column Temperature: 30 °C
Concentration: 2 mg/ml
Diluent: mobile phase
Injection Volume: 25 μ L
Run Time: 13 minutes

Retention times:

4a = 6.8 minutes; $[\alpha]_D^{24} = -5.5^\circ$ (c 0.5, MeOH);

4b = 8.2 minutes

Figure 1S. ORTEP Drawing of Compound 5a.

Table 1S. Crystal data and structure refinement for compound **5a**.

Identification code	AA02	
Empirical formula	C ₂₂ H ₄₄ BF ₄ P ₂ Rh	
Formula weight	560.23	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 8.4395(4) Å	α = 90°.
	b = 16.8558(7) Å	β = 93.1200(10)°.
	c = 18.3565(8) Å	γ = 90°.
Volume	2607.4(2) Å ³	
Z	4	
Density (calculated)	1.427 Mg/m ³	
Absorption coefficient	0.814 mm ⁻¹	
F(000)	1168	
Crystal size	0.10 x 0.16 x 0.32 mm ³	
Theta range for data collection	1.64 to 26.45°.	
Index ranges	-10 ≤ h ≤ 10, -21 ≤ k ≤ 21, -22 ≤ l ≤ 22	
Reflections collected	23133	
Independent reflections	10615 [R(int) = 0.0534]	
Completeness to theta = 26.45°	99.7 %	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10615 / 1 / 542	
Goodness-of-fit on F ²	1.020	
Final R indices [I > 2σ(I)]	R1 = 0.0550, wR2 = 0.1125	
R indices (all data)	R1 = 0.0670, wR2 = 0.1181	
Absolute structure parameter	-0.04(3)	
Extinction coefficient	0.00000(17)	
Largest diff. peak and hole	0.697 and -0.569 e.Å ⁻³	

Table 2S. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **5a**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	-1951(10)	2746(5)	-838(4)	52(2)
C(2)	-472(10)	2966(6)	-553(4)	48(2)
C(3)	-207(14)	3787(5)	-243(5)	71(3)
C(4)	265(12)	4372(6)	-801(5)	66(3)
C(5)	-395(11)	4273(5)	-1564(5)	53(2)
C(6)	-1893(10)	4087(5)	-1795(4)	47(2)
C(7)	-3237(11)	3996(7)	-1310(6)	74(3)
C(8)	-3408(11)	3242(6)	-939(7)	84(4)
Rh(9)	-463(1)	2966(1)	-1763(1)	26(1)
P(10)	213(2)	2832(1)	-2975(1)	28(1)
C(11)	833(8)	1776(4)	-2877(4)	33(2)
P(12)	638(2)	1737(1)	-1881(1)	30(1)
C(13)	2022(8)	3367(5)	-3299(4)	44(2)
C(14)	2649(9)	3040(7)	-3987(4)	62(2)
C(15)	1607(11)	4261(5)	-3389(6)	67(3)
C(16)	3307(9)	3306(6)	-2674(4)	57(2)
C(17)	-1467(8)	2827(4)	-3693(4)	36(2)
C(18)	-2068(12)	3666(6)	-3848(5)	74(3)
C(19)	-1021(9)	2444(5)	-4409(4)	51(2)
C(20)	-2775(8)	2343(6)	-3380(5)	60(3)
C(21)	-321(10)	780(4)	-1643(4)	43(2)
C(22)	532(11)	84(5)	-1986(5)	58(2)
C(23)	-2089(9)	830(5)	-1956(4)	47(2)
C(24)	-307(11)	711(5)	-821(4)	55(2)
C(25)	2660(9)	1644(5)	-1483(4)	48(2)
C(51)	2624(9)	869(4)	3172(4)	37(2)
C(52)	4194(9)	675(5)	3347(4)	34(2)
C(53)	4928(10)	527(5)	4091(5)	50(2)
C(54)	4373(10)	1053(5)	4677(4)	52(2)
C(55)	4104(9)	1900(5)	4420(4)	39(2)
C(56)	2676(10)	2220(4)	4149(4)	42(2)
C(57)	1148(9)	1764(5)	4004(5)	51(2)
C(58)	1345(9)	928(5)	3713(4)	46(2)
Rh(59)	4111(1)	1988(1)	3200(1)	25(1)
P(60)	4834(2)	2134(1)	1994(1)	26(1)
C(61)	5343(8)	3196(4)	2103(4)	34(2)
P(62)	4620(2)	3301(1)	3020(1)	29(1)
C(63)	6704(8)	1626(4)	1732(4)	37(2)
C(64)	6396(11)	783(6)	1509(5)	69(3)
C(65)	7819(9)	1645(6)	2407(4)	59(3)
C(66)	7515(8)	2043(7)	1114(4)	63(3)
C(67)	3271(8)	2113(5)	1221(4)	36(2)
C(68)	1929(8)	2654(5)	1466(4)	50(2)
C(69)	3852(9)	2430(5)	503(4)	48(2)
C(70)	2585(11)	1267(5)	1112(5)	60(3)
C(71)	6048(9)	3932(4)	3562(4)	42(2)
C(72)	5483(11)	4054(5)	4329(4)	53(2)
C(73)	6193(12)	4738(5)	3199(5)	68(3)
C(74)	7672(10)	3533(6)	3604(5)	71(3)

C(75)	2841(9)	3889(4)	2943(4)	42(2)
B(81)	9172(12)	119(6)	5472(5)	45(2)
F(82)	10703(8)	310(6)	5521(6)	173(5)
F(83)	8598(12)	394(4)	6075(3)	138(3)
F(84)	8525(7)	536(4)	4894(3)	85(2)
F(85)	8927(8)	-667(4)	5410(3)	90(2)
B(91)	4915(17)	4987(11)	492(8)	89(5)
F(92)	3980(12)	4504(5)	207(9)	264(9)
F(93)	6315(10)	4874(9)	378(5)	229(7)
F(94)	5081(13)	4894(5)	1253(5)	169(4)
F(95)	4392(9)	5734(5)	447(4)	115(2)

Table 3S. Bond lengths [Å] and angles [°] for compound **5a**.

C(1)-C(2)	1.378(11)	C(52)-Rh(59)	2.230(8)
C(1)-C(8)	1.490(12)	C(53)-C(54)	1.489(11)
C(1)-Rh(9)	2.198(7)	C(54)-C(55)	1.517(11)
C(2)-C(3)	1.508(12)	C(55)-C(56)	1.387(10)
C(2)-Rh(9)	2.220(7)	C(55)-Rh(59)	2.246(7)
C(3)-C(4)	1.491(12)	C(56)-C(57)	1.513(11)
C(4)-C(5)	1.490(12)	C(56)-Rh(59)	2.211(7)
C(5)-C(6)	1.347(11)	C(57)-C(58)	1.518(11)
C(5)-Rh(9)	2.233(8)	Rh(59)-P(62)	2.2816(18)
C(6)-C(7)	1.487(12)	Rh(59)-P(60)	2.3407(17)
C(6)-Rh(9)	2.241(7)	P(60)-C(61)	1.850(7)
C(7)-C(8)	1.452(13)	P(60)-C(67)	1.884(6)
Rh(9)-P(12)	2.2867(18)	P(60)-C(63)	1.880(7)
Rh(9)-P(10)	2.3377(18)	C(61)-P(62)	1.831(7)
P(10)-C(11)	1.861(7)	P(62)-C(75)	1.799(7)
P(10)-C(17)	1.883(6)	P(62)-C(71)	1.855(7)
P(10)-C(13)	1.897(7)	C(63)-C(64)	1.497(12)
C(11)-P(12)	1.846(7)	C(63)-C(65)	1.515(10)
P(12)-C(25)	1.827(7)	C(63)-C(66)	1.527(11)
P(12)-C(21)	1.867(7)	C(67)-C(68)	1.540(10)
C(13)-C(14)	1.501(11)	C(67)-C(69)	1.529(10)
C(13)-C(16)	1.539(11)	C(67)-C(70)	1.547(10)
C(13)-C(15)	1.554(12)	C(71)-C(73)	1.520(10)
C(17)-C(18)	1.525(11)	C(71)-C(72)	1.525(10)
C(17)-C(20)	1.512(10)	C(71)-C(74)	1.525(11)
C(17)-C(19)	1.530(9)	B(81)-F(83)	1.316(11)
C(21)-C(22)	1.530(10)	B(81)-F(82)	1.330(11)
C(21)-C(24)	1.514(10)	B(81)-F(85)	1.345(11)
C(21)-C(23)	1.571(11)	B(81)-F(84)	1.361(10)
C(51)-C(52)	1.385(10)	B(91)-F(93)	1.226(14)
C(51)-C(58)	1.509(10)	B(91)-F(92)	1.231(18)
C(51)-Rh(59)	2.263(7)	B(91)-F(95)	1.336(16)
C(52)-C(53)	1.489(10)	B(91)-F(94)	1.404(16)
C(2)-C(1)-C(8)	128.3(9)	C(2)-Rh(9)-C(5)	80.7(3)
C(2)-C(1)-Rh(9)	72.7(4)	C(6)-Rh(9)-C(5)	35.1(3)
C(8)-C(1)-Rh(9)	108.1(6)	C(1)-Rh(9)-P(12)	99.9(2)
C(1)-C(2)-C(3)	120.2(9)	C(2)-Rh(9)-P(12)	96.8(3)
C(1)-C(2)-Rh(9)	70.9(4)	C(6)-Rh(9)-P(12)	169.4(2)
C(3)-C(2)-Rh(9)	111.7(6)	C(5)-Rh(9)-P(12)	154.5(2)
C(4)-C(3)-C(2)	112.8(8)	C(1)-Rh(9)-P(10)	153.9(2)
C(5)-C(4)-C(3)	118.2(8)	C(2)-Rh(9)-P(10)	164.9(2)
C(6)-C(5)-C(4)	128.1(9)	C(6)-Rh(9)-P(10)	102.5(2)
C(6)-C(5)-Rh(9)	72.8(5)	C(5)-Rh(9)-P(10)	104.2(2)
C(4)-C(5)-Rh(9)	105.6(6)	P(12)-Rh(9)-P(10)	72.55(6)
C(5)-C(6)-C(7)	124.7(8)	C(11)-P(10)-C(17)	105.1(3)
C(5)-C(6)-Rh(9)	72.2(5)	C(11)-P(10)-C(13)	105.0(3)
C(7)-C(6)-Rh(9)	108.9(6)	C(17)-P(10)-C(13)	111.7(4)
C(8)-C(7)-C(6)	118.0(8)	C(11)-P(10)-Rh(9)	94.8(2)
C(7)-C(8)-C(1)	116.6(8)	C(17)-P(10)-Rh(9)	117.0(2)
C(1)-Rh(9)-C(2)	36.3(3)	C(13)-P(10)-Rh(9)	119.7(3)
C(1)-Rh(9)-C(6)	80.4(3)	P(12)-C(11)-P(10)	95.2(3)
C(2)-Rh(9)-C(6)	89.7(3)	C(25)-P(12)-C(11)	105.5(3)
C(1)-Rh(9)-C(5)	93.0(3)	C(25)-P(12)-C(21)	103.9(4)

C(11)-P(12)-C(21)	109.0(3)	C(61)-P(60)-Rh(59)	94.1(2)
C(25)-P(12)-Rh(9)	114.5(3)	C(67)-P(60)-Rh(59)	120.1(2)
C(11)-P(12)-Rh(9)	96.9(2)	C(63)-P(60)-Rh(59)	117.4(2)
C(21)-P(12)-Rh(9)	125.3(3)	P(62)-C(61)-P(60)	96.0(3)
C(14)-C(13)-C(16)	109.6(7)	C(75)-P(62)-C(61)	107.4(3)
C(14)-C(13)-C(15)	110.8(8)	C(75)-P(62)-C(71)	103.9(4)
C(16)-C(13)-C(15)	106.9(7)	C(61)-P(62)-C(71)	108.0(3)
C(14)-C(13)-P(10)	114.6(6)	C(75)-P(62)-Rh(59)	112.6(3)
C(16)-C(13)-P(10)	106.3(5)	C(61)-P(62)-Rh(59)	96.6(2)
C(15)-C(13)-P(10)	108.4(5)	C(71)-P(62)-Rh(59)	127.0(2)
C(18)-C(17)-C(20)	109.2(7)	C(64)-C(63)-C(65)	109.5(7)
C(18)-C(17)-C(19)	109.0(7)	C(64)-C(63)-C(66)	108.2(7)
C(20)-C(17)-C(19)	108.5(7)	C(65)-C(63)-C(66)	108.3(7)
C(18)-C(17)-P(10)	110.9(5)	C(64)-C(63)-P(60)	111.5(6)
C(20)-C(17)-P(10)	105.9(5)	C(65)-C(63)-P(60)	105.9(5)
C(19)-C(17)-P(10)	113.1(5)	C(66)-C(63)-P(60)	113.4(5)
C(22)-C(21)-C(24)	111.9(7)	C(68)-C(67)-C(69)	108.6(6)
C(22)-C(21)-C(23)	110.5(6)	C(68)-C(67)-C(70)	107.9(6)
C(24)-C(21)-C(23)	108.9(7)	C(69)-C(67)-C(70)	110.3(6)
C(22)-C(21)-P(12)	110.3(6)	C(68)-C(67)-P(60)	105.4(5)
C(24)-C(21)-P(12)	108.6(5)	C(69)-C(67)-P(60)	113.5(5)
C(23)-C(21)-P(12)	106.4(5)	C(70)-C(67)-P(60)	110.9(5)
C(52)-C(51)-C(58)	124.9(6)	C(73)-C(71)-C(72)	108.7(7)
C(52)-C(51)-Rh(59)	70.7(4)	C(73)-C(71)-C(74)	108.9(7)
C(58)-C(51)-Rh(59)	110.2(5)	C(72)-C(71)-C(74)	109.8(7)
C(51)-C(52)-C(53)	126.6(7)	C(73)-C(71)-P(62)	110.1(5)
C(51)-C(52)-Rh(59)	73.4(4)	C(72)-C(71)-P(62)	110.2(5)
C(53)-C(52)-Rh(59)	106.6(5)	C(74)-C(71)-P(62)	109.2(5)
C(52)-C(53)-C(54)	115.6(7)	F(83)-B(81)-F(82)	105.0(9)
C(53)-C(54)-C(55)	112.5(7)	F(83)-B(81)-F(85)	110.8(8)
C(56)-C(55)-C(54)	126.1(7)	F(82)-B(81)-F(85)	112.9(9)
C(56)-C(55)-Rh(59)	70.5(4)	F(83)-B(81)-F(84)	108.9(9)
C(54)-C(55)-Rh(59)	111.3(5)	F(82)-B(81)-F(84)	105.9(8)
C(55)-C(56)-C(57)	125.5(8)	F(85)-B(81)-F(84)	112.9(8)
C(55)-C(56)-Rh(59)	73.2(4)	F(93)-B(91)-F(92)	115.2(15)
C(57)-C(56)-Rh(59)	105.6(5)	F(93)-B(91)-F(95)	117.0(18)
C(56)-C(57)-C(58)	115.1(6)	F(92)-B(91)-F(95)	113.3(12)
C(51)-C(58)-C(57)	112.9(6)	F(93)-B(91)-F(94)	96.2(12)
C(56)-Rh(59)-C(52)	95.5(3)	F(92)-B(91)-F(94)	112.1(17)
C(56)-Rh(59)-C(55)	36.3(3)	F(95)-B(91)-F(94)	100.5(11)
C(52)-Rh(59)-C(55)	79.4(3)		
C(56)-Rh(59)-C(51)	80.7(3)		
C(52)-Rh(59)-C(51)	35.9(2)		
C(55)-Rh(59)-C(51)	86.3(3)		
C(56)-Rh(59)-P(62)	93.3(2)		
C(52)-Rh(59)-P(62)	167.16(19)		
C(55)-Rh(59)-P(62)	102.6(2)		
C(51)-Rh(59)-P(62)	155.95(19)		
C(56)-Rh(59)-P(60)	155.4(2)		
C(52)-Rh(59)-P(60)	102.19(18)		
C(55)-Rh(59)-P(60)	164.83(18)		
C(51)-Rh(59)-P(60)	103.86(18)		
P(62)-Rh(59)-P(60)	72.58(6)		
C(61)-P(60)-C(67)	104.4(3)		
C(61)-P(60)-C(63)	106.0(3)		
C(67)-P(60)-C(63)	111.2(3)		

Table 4S. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **5a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	64(5)	60(7)	35(5)	11(4)	26(4)	-3(4)
C(2)	84(6)	38(4)	24(4)	3(4)	9(4)	-9(5)
C(3)	130(9)	43(5)	40(5)	-3(4)	-16(5)	-17(5)
C(4)	97(8)	55(6)	43(6)	-12(5)	-8(5)	-16(5)
C(5)	80(7)	23(5)	55(6)	1(4)	5(5)	-5(4)
C(6)	72(6)	29(4)	39(5)	-8(4)	-7(4)	20(4)
C(7)	57(6)	88(8)	76(8)	8(6)	-1(5)	30(5)
C(8)	63(6)	70(8)	124(10)	7(7)	54(6)	12(5)
Rh(9)	34(1)	24(1)	21(1)	-1(1)	3(1)	0(1)
P(10)	32(1)	30(1)	23(1)	2(1)	4(1)	2(1)
C(11)	38(4)	34(4)	28(4)	-8(3)	5(3)	9(3)
P(12)	39(1)	28(1)	23(1)	-1(1)	-1(1)	-2(1)
C(13)	38(4)	53(5)	41(5)	5(4)	10(3)	-7(3)
C(14)	59(5)	88(7)	43(5)	5(5)	28(4)	-1(5)
C(15)	79(7)	44(6)	78(7)	23(5)	20(5)	-24(5)
C(16)	43(5)	78(7)	51(5)	0(5)	2(4)	-18(4)
C(17)	44(4)	38(5)	24(4)	-9(3)	-6(3)	16(3)
C(18)	89(7)	71(7)	60(7)	-11(5)	-25(5)	39(6)
C(19)	65(5)	66(6)	23(4)	-5(4)	2(4)	7(4)
C(20)	29(4)	86(7)	65(6)	8(5)	-5(4)	-1(4)
C(21)	80(6)	20(3)	29(4)	5(3)	-4(4)	-5(4)
C(22)	78(6)	28(4)	69(6)	-4(4)	16(5)	3(4)
C(23)	58(5)	43(5)	41(5)	3(4)	3(4)	-18(4)
C(24)	89(6)	37(5)	38(5)	11(4)	-9(4)	-8(4)
C(25)	55(5)	47(5)	41(5)	6(4)	-8(4)	0(4)
C(51)	52(5)	34(4)	26(4)	-11(3)	3(3)	-7(3)
C(52)	60(5)	20(4)	26(4)	4(3)	22(3)	7(3)
C(53)	61(5)	34(5)	54(6)	12(4)	1(4)	11(4)
C(54)	66(5)	47(5)	41(5)	18(4)	-3(4)	8(4)
C(55)	58(4)	36(5)	24(4)	1(4)	3(3)	-14(4)
C(56)	76(6)	29(5)	24(4)	5(3)	24(4)	6(3)
C(57)	48(5)	47(6)	60(5)	4(4)	27(4)	9(4)
C(58)	47(4)	52(5)	39(5)	4(4)	8(3)	-12(4)
Rh(59)	32(1)	23(1)	21(1)	0(1)	4(1)	0(1)
P(60)	27(1)	27(1)	24(1)	-2(1)	3(1)	-1(1)
C(61)	46(4)	30(4)	25(4)	-1(3)	-1(3)	-8(3)
P(62)	40(1)	25(1)	22(1)	1(1)	-1(1)	-2(1)
C(63)	37(4)	43(5)	32(4)	-7(3)	11(3)	4(3)
C(64)	72(6)	60(6)	76(7)	-10(5)	18(5)	17(5)
C(65)	45(5)	75(7)	54(5)	-7(5)	-6(4)	29(4)
C(66)	41(4)	100(8)	50(5)	0(6)	14(3)	17(5)
C(67)	39(4)	39(5)	28(4)	-2(3)	-4(3)	0(3)
C(68)	35(4)	68(6)	46(5)	2(4)	-10(3)	8(4)
C(69)	49(5)	63(5)	30(4)	7(4)	-6(3)	-1(4)
C(70)	91(7)	45(5)	41(5)	-6(4)	-25(5)	-19(5)
C(71)	61(5)	31(4)	33(4)	-3(3)	-3(3)	-20(3)
C(72)	90(7)	36(5)	33(4)	-4(3)	-7(4)	-12(4)
C(73)	112(8)	41(5)	50(6)	3(4)	-3(5)	-32(5)
C(74)	69(6)	73(7)	70(7)	-21(5)	-20(5)	-6(5)
C(75)	65(5)	26(4)	35(4)	1(3)	3(4)	19(3)
B(81)	59(6)	43(6)	34(5)	-2(4)	3(4)	-3(4)

F(82)	56(4)	221(10)	239(11)	125(8)	-19(5)	-26(5)
F(83)	299(10)	54(4)	71(4)	-29(3)	100(5)	-45(5)
F(84)	91(4)	94(5)	67(4)	15(3)	-27(3)	0(3)
F(85)	143(6)	60(4)	66(4)	-19(3)	7(4)	2(4)
B(91)	76(9)	113(13)	76(10)	-11(9)	1(8)	49(9)
F(92)	127(7)	61(5)	580(20)	-53(9)	-154(11)	-8(5)
F(93)	94(6)	435(18)	160(9)	-181(11)	14(6)	21(9)
F(94)	270(12)	109(7)	134(8)	65(6)	56(7)	84(7)
F(95)	134(6)	111(6)	99(6)	35(5)	2(4)	-4(5)

Table 5S. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for compound **5a**.

	x	y	z	U(eq)
H(1A)	-2184	2176	-766	80
H(2A)	156	2539	-305	80
H(3A)	-1185	3969	-32	80
H(3B)	624	3763	151	80
H(4A)	-34	4901	-634	80
H(4B)	1425	4362	-810	80
H(5A)	191	4573	-1928	80
H(6A)	-2205	4277	-2292	80
H(7A)	-3140	4412	-938	80
H(7B)	-4222	4097	-1603	80
H(8A)	-4219	2931	-1214	80
H(8B)	-3806	3349	-457	80
H(11A)	107	1412	-3144	80
H(11B)	1925	1686	-3015	80
H(14A)	3578	3339	-4111	80
H(14B)	1839	3081	-4380	80
H(14C)	2936	2487	-3913	80
H(15A)	2525	4546	-3550	80
H(15B)	1309	4475	-2926	80
H(15C)	730	4322	-3749	80
H(16A)	4262	3573	-2814	80
H(16B)	3542	2752	-2575	80
H(16C)	2929	3554	-2239	80
H(18A)	-2934	3649	-4217	80
H(18B)	-1212	3988	-4022	80
H(18C)	-2439	3896	-3404	80
H(19A)	-1929	2456	-4757	80
H(19B)	-703	1898	-4320	80
H(19C)	-149	2734	-4606	80
H(20A)	-3680	2322	-3728	80
H(20B)	-3090	2587	-2931	80
H(20C)	-2396	1809	-3278	80
H(22A)	22	-409	-1860	80
H(22B)	1633	75	-1804	80
H(22C)	484	145	-2512	80
H(23A)	-2637	341	-1849	80
H(23B)	-2108	909	-2480	80
H(23C)	-2614	1272	-1731	80
H(24A)	-797	214	-689	80
H(24B)	-894	1150	-626	80
H(24C)	780	725	-620	80
H(25A)	3040	1108	-1554	80
H(25B)	2670	1759	-964	80
H(25C)	3345	2017	-1717	80
H(51A)	2237	703	2677	80
H(52A)	4719	390	2955	80
H(53A)	6080	587	4073	80
H(53B)	4718	-24	4224	80
H(54A)	5162	1050	5089	80
H(54B)	3379	841	4850	80

H(55A)	4808	2290	4679	80
H(56A)	2532	2789	4262	80
H(57A)	468	2063	3652	80
H(57B)	595	1733	4459	80
H(58A)	1606	570	4123	80
H(58B)	336	752	3478	80
H(61A)	6486	3294	2090	80
H(61B)	4763	3533	1744	80
H(64A)	7380	539	1376	80
H(64B)	5634	770	1095	80
H(64C)	5976	494	1913	80
H(65A)	8807	1384	2304	80
H(65B)	7334	1372	2803	80
H(65C)	8032	2192	2546	80
H(66A)	8458	1750	999	80
H(66B)	7810	2577	1265	80
H(66C)	6791	2067	686	80
H(68A)	1077	2667	1089	80
H(68B)	2336	3186	1548	80
H(68C)	1527	2449	1914	80
H(69A)	3002	2396	127	80
H(69B)	4749	2117	360	80
H(69C)	4175	2980	565	80
H(70A)	1791	1269	710	80
H(70B)	2103	1098	1554	80
H(70C)	3432	904	1004	80
H(72A)	6242	4381	4608	80
H(72B)	5391	3544	4567	80
H(72C)	4457	4315	4300	80
H(73A)	6936	5064	3488	80
H(73B)	5162	4994	3165	80
H(73C)	6572	4669	2714	80
H(74A)	8418	3858	3892	80
H(74B)	8040	3471	3115	80
H(74C)	7589	3015	3830	80
H(75A)	3118	4441	2868	80
H(75B)	2277	3841	3387	80
H(75C)	2170	3704	2532	80

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