Synthesis of Both Enantiomers of a P-Chirogenic 1,2-Bisphospholanoethane Ligand via Convergent Routes and Application to Rhodium Catalyzed Asymmetric Hydrogenation of CI-1008 (Pregabalin)

Garrett Hoge

Contribution from Pfizer Global Research and Development,
2800 Plymouth Road, Ann Arbor, Michigan 48105.

Supporting Information

Nuclear Magnetic Resonance. 400 MHz ^1H NMR, 100 MHz ^{13}C NMR, and 162 MHz ^{31}P 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 ^{13}C 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 Hewlett Packard (now Agilent Technologies) instrument equipped with a manual injector, quaternary pump, and a UV detector. The LC was PC controlled using HP Chemstation Plus Software. Reverse phase HPLC was performed with a 150 x 4.6mm BDS-Hypersil-C18 column supplied by Keystone Scientific Incorporated. Reverse phase chiral HPLC was performed using a Chiracel OJ-R column supplied by Chiral Technologies. Normal Phase chiral HPLC was performed using Chiracel OJ, Chiracel OD, Chiracel OD-H, Chiracel AD, and Chiracel AS columns 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 40m x 0.25mm Chiraldex G-TA or B-TA columns supplied by Advanced Separation Technologies, Incorporated or on a 25m x .25mm Coating CP Chirasil-Dex DB column supplied by Chrompack.

General procedure for asymmetric hydrogenation reactions. Pre-catalyst **36** (.01 mmole) was dissolved in 1 mL of methanol in a Griffin-Worden pressure vessel equipped with the attachments

necessary to connect to a lecture bottle. The substrate (1 mmole) was dissolved in 3 mL of the same solvent and this was delivered to the catalyst solution via syringe. The solution was freeze-pump-thaw-degassed for three cycles with N₂ and then the reaction solution was warmed to 25°C. The vessel was then sealed and pressurized to the appropriate pressure of H₂. Reaction completion times and enantiomeric excesses were monitored by chiral GC or HPLC.

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) t_1 = 10.5 min; (S) t_2 = 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.

The CI-1008 precursors, **41** and **42**, were acidified in their methanolic hydrogenation solutions with 1 N HCl. The organics were extracted into CH₂Cl₂. After drying over MgSO₄ the volatiles were removed *in vacuo*. The carboxylic acids were then converted to their corresponding methyl esters via treatment with trimethylsilyldiazomethane. The methyl esters were 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** [α]_D²⁰ = -91.7° (c 2, H₂O);¹ **(S)-N-acetylphenylalanine methyl ester** [α]_D²⁰ = +16.4° (c 2, MeOH).²

The CI-1008 precursors, **41** and **42**, were compared in terms of elution order to an authentic sample with (S) configuration via the method for enantiomeric excess determination (above).

Proof of relative and absolute stereochemistry of (1*S*,2*R*))-1-((-)-menthoxy)-2-benzylphospholaneborane (23). Although the ideal method for determining the relative and absolute stereochemistry of **23** was via x-ray crystallography, we were unsuccessful at growing crystals of this compound. We also attempted ¹H NMR NOE difference spectra to attempt to find NOE interaction between H_a and H_b (**Figure 1S**). If NOE were observed between H_a and H_b we could conclude that the benzyl substituent on the phospholane ring is cis relative to the borane group. However, we failed to see NOE between the two protons.

Figure 1S. Protons H_a and H_b of compound **23**.

There is precedent for alkylations of (1)-alkoxyphospholaneoxides to occur cis relative to the oxide when the alkoxy group attached to phosphorous is large.³ This gave us insight into the probable relative stereochemistry of **23**, but not proof.

We decided to synthesize a derivative of **23** using the same chiral alkylation method except using carbon dioxide gas as an electrophile rather than benzyl bromide (**Scheme 1S**).

Scheme 1S. Synthesis of carboxylic acid **43**.^a

^a Reagents and conditions: a) 1. *s*-BuLi, (-)-Sparteine, THF, -78°C 2. CuCl₂ 3. HCl.

This carboxylic acid derivative was a white solid and we were able to grow x-ray quality crystals for crystallography to confirm the structure. Examination of the x-ray crystal structure of **43** lead us to the stereochemical assignment of **23** by analogy.

Proof of absolute and relative stereochemistry of (1S,2R)-2-benzyl-1-methyl-phospholane (20**).**

Having assigned the relative and absolute stereochemistry of **23** and comparing the structure to that of rhodium complex **36**, the absolute and relative stereochemistry of **20** can be assigned as drawn in **Figure 2S**. This information also served as evidence that the MeLi displacement of the menthoxy group of **23** to form **20** proceeded with retention of configuration at the phosphorous atom.

Figure 2S. Relative and absolute stereochemical assignment of **20**.

In addition to this proof, we performed ¹H NMR NOE difference spectra on **20** attempting to find NOE interaction between the methyl group protons (**a**) and the methine proton (**b**) on the phospholane

ring (**Figure 3S**). We observed significant NOE between the methyl protons (**a**) and the methine proton (**b**) while irradiating at the methyl proton frequency. This experiment provided additional evidence that the methine proton is cis with respect to the methyl group on the phospholane ring of **20**.

Figure 3S. ^1H NMR NOE difference spectra for compound **20** (500 MHz, CDCl_3).

X-ray Crystal Structure Analysis: Compound 48 43

Crystal data

$C_{15}H_{20}O_3PB$

$M_r = 300.2$

Monoclinic

$P2_1$

$a = 14.36 (5) \text{ \AA}$

$b = 6.58 (5) \text{ \AA}$

$c = 20.31 (5) \text{ \AA}$

$\beta = 104.3 (2)^\circ$

$V = 1859.340 (1) \text{ \AA}^3$

$Z = 4$

$D_x = 1.07 \text{ Mg m}^{-3}$

$D_m = 1.30 \text{ Mg m}^{-3}$

X-ray radiation

$\lambda = 1.54056 \text{ \AA}$

Cell parameters from reflections

$\theta = 1.5^\circ$

$\mu = 13.34 \text{ mm}^{-1}$

$T = 298 \text{ K}$

Plate

$0.2 \times 0.2 \times 0.2 \text{ mm}$

Colourless

Crystal source: Local laboratory

Data collection: Enraf Nonius CAD-4. Cell refinement: CAD-4. Data reduction: maXus. Program(s) used to solve structure: maXus. Program(s) used to refine structure: maXus. Molecular graphics: maXus. Software used to prepare material for publication: maXus.

Absorption correction:

none

5561 measured reflections

4737 independent reflections

4430 observed reflections

$\theta_{\max} = 48.99^\circ$

$h = -15 \rightarrow 15$

$k = -6 \rightarrow 6$

$l = -22 \rightarrow 22$

Refinement

Refinement on F

$R = 0.096$

$wR = 0.183$

$S = 4.413$

4430 reflections

365 parameters

Only coordinates of H atoms refined

Count statistics

$(\Delta/\sigma)_{\max} = 9.7088$

$\Delta\rho_{\max} = 0.48 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.44 \text{ e \AA}^{-3}$

Extinction correction: None

Atomic scattering factors from

D. Waasmaier & A. Kirfel, Acta

Cryst. 1995, *A51*, 416-431

43

Figure 4S. ORTEP Diagram of **4b**. Full atom labels, BF_4^- anion and hydrogen atoms are included.

Table 1S. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for maxus (compound 43)

$$U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U_{eq}
P1	0.01278 (6)	0.18700	-0.33461 (4)	0.0469 (6)
P2	-0.48595 (6)	-0.0248 (2)	-0.33482 (4)	0.0490 (6)
O3	-0.4753 (1)	-0.1507 (4)	-0.26836 (9)	0.057 (2)
O4	0.0403 (1)	0.2755 (5)	-0.26128 (9)	0.056 (2)
O5	-0.1423 (1)	0.3396 (6)	-0.4994 (1)	0.077 (2)
O6	-0.1988 (2)	0.3821 (6)	-0.4086 (1)	0.084 (2)
C9	-0.5364 (2)	-0.2434 (6)	-0.1699 (2)	0.059 (2)
C10	-0.4944 (2)	-0.0746 (6)	-0.2063 (2)	0.055 (2)
C11	-0.0180 (2)	0.2495 (7)	-0.2113 (2)	0.058 (2)
C12	-0.1267 (2)	0.3653 (7)	-0.4401 (2)	0.053 (3)
C13	-0.5203 (2)	-0.2231 (8)	-0.3968 (1)	0.062 (3)
C14	0.0466 (3)	0.4437 (8)	-0.4306 (2)	0.077 (3)
C15	-0.6182 (2)	-0.2036 (7)	-0.4440 (2)	0.057 (3)
C16	-0.0291 (2)	0.4002 (6)	-0.3927 (2)	0.048 (2)
C17	0.1331 (3)	0.1208 (7)	-0.1253 (2)	0.081 (3)
C18	-0.4051 (2)	0.0223 (7)	-0.1601 (2)	0.068 (3)
C19	0.0474 (2)	0.2766 (6)	-0.1412 (2)	0.061 (2)
C20	-0.6266 (3)	-0.3369 (7)	-0.2159 (2)	0.068 (3)
B21	-0.0573 (4)	-0.0473 (9)	-0.3446 (2)	0.079 (4)
C22	0.1270 (2)	0.1690 (8)	-0.3568 (2)	0.070 (3)
C23	-0.4148 (3)	0.0844 (7)	-0.0918 (2)	0.076 (3)
C24	-0.0129 (3)	0.2708 (8)	-0.0875 (2)	0.077 (3)
C25	-0.1001 (3)	0.4072 (7)	-0.2285 (2)	0.077 (3)
C26	-0.1576 (3)	0.4073 (7)	-0.1732 (2)	0.085 (3)
C27	-0.7096 (2)	-0.1880 (8)	-0.2344 (2)	0.107 (3)
C28	-0.3461 (2)	-0.180 (1)	-0.3842 (2)	0.089 (3)
C29	-0.4512 (3)	-0.0880 (9)	-0.0577 (2)	0.100 (4)
C30	-0.4392 (3)	-0.2337 (9)	-0.4336 (2)	0.094 (4)
C31	0.2083 (3)	0.1736 (9)	-0.0607 (2)	0.099 (4)
C32	-0.3642 (2)	0.0019 (9)	-0.3455 (2)	0.082 (3)
C33	-0.5450 (3)	-0.1755 (8)	-0.1013 (2)	0.079 (3)
C34	0.1014 (3)	-0.0936 (8)	-0.1206 (2)	0.097 (3)
C35	0.1388 (3)	0.3700 (9)	-0.3869 (2)	0.110 (4)
C36	-0.6585 (3)	-0.5267 (8)	-0.1857 (2)	0.113 (4)
C37	-0.0944 (3)	0.4287 (8)	-0.1033 (2)	0.100 (4)
C38	-0.3214 (3)	0.1762 (9)	-0.0488 (2)	0.115 (4)

Table 1S (continued)

H9	-0.49104	-0.35308	-0.16076	0.05000
H10	-0.54260	0.02945	-0.21760	0.05000
H11	-0.04512	0.11533	-0.21623	0.05000
H13	-0.52081	-0.35019	-0.37365	0.05000
H14A	0.03472	0.36704	-0.47214	0.05000
H14B	0.05002	0.58574	-0.44064	0.05000
H16	-0.03536	0.51369	-0.36445	0.05000
H17	0.16252	0.12833	-0.16285	0.05000
H18A	-0.35175	-0.06976	-0.15423	0.05000
H18B	-0.39185	0.14234	-0.18313	0.05000
H19	0.07595	0.40891	-0.14007	0.05000
H20	-0.61141	-0.38390	-0.25684	0.05000
H22A	0.17888	0.13855	-0.31818	0.05000
H22B	0.12588	0.07075	-0.39188	0.05000
H23	-0.46453	0.18520	-0.09745	0.05000
H24A	-0.04582	0.14272	-0.09095	0.05000
H24B	0.02578	0.28852	-0.04215	0.05000
H25A	-0.07048	0.53892	-0.22445	0.05000
H25B	-0.14058	0.39102	-0.27345	0.05000
H26	-0.18527	0.27382	-0.17608	0.05000
H27A	-0.68758	-0.07358	-0.25571	0.05000
H27B	-0.76508	-0.24598	-0.26501	0.05000
H27C	-0.72618	-0.14428	-0.19371	0.05000
H28A	-0.33421	-0.29383	-0.35394	0.05000
H28B	-0.29281	-0.16233	-0.40444	0.05000
H29A	-0.40244	-0.18915	-0.04973	0.05000
H29B	-0.46204	-0.04205	-0.01513	0.05000
H30A	-0.43192	-0.35788	-0.45659	0.05000
H30B	-0.44962	-0.12318	-0.46549	0.05000
H31A	0.23026	0.31088	-0.06221	0.05000

Table 1S (continued)

H32A	-0.35813	0.11969	-0.37198	0.05000
H32B	-0.31563	0.00519	-0.30348	0.05000
H33A	-0.59422	-0.07335	-0.10835	0.05000
H33B	-0.56472	-0.29105	-0.07915	0.05000
H34A	0.05423	-0.13061	-0.16110	0.05000
H34B	0.15603	-0.18211	-0.11480	0.05000
H34C	0.07423	-0.10601	-0.08210	0.05000
H35A	0.18807	0.36557	-0.41145	0.05000
H35B	0.15747	0.46217	-0.34935	0.05000
H36A	-0.60637	-0.62240	-0.17547	0.05000
H36B	-0.67457	-0.48680	-0.14437	0.05000
H36C	-0.71337	-0.58850	-0.21567	0.05000
H37A	-0.13048	0.43758	-0.06936	0.05000
H37B	-0.06258	0.55578	-0.10586	0.05000
H38A	-0.30426	0.28838	-0.07368	0.05000
H38B	-0.33006	0.22368	-0.00598	0.05000
H38C	-0.27106	0.07638	-0.04098	0.05000
H40A	-0.28027	0.53827	-0.23373	0.05000
H40B	-0.27257	0.57737	-0.15653	0.05000
H40C	-0.20327	0.69037	-0.19303	0.05000
H21A	-0.07512	-0.09914	-0.39021	0.019 (7)
H21B	-0.02092	-0.14994	-0.31571	0.042 (9)
H21C	-0.11492	-0.01994	-0.33021	0.09 (2)
H8	-0.72457	-0.33578	-0.43254	0.12 (1)
H6	-0.23324	0.25605	-0.41768	0.16 (1)

Table 2S. FRACTIONAL ATOMIC COORDINATES & U_{iso} (compound 43)

Atom	x/a	y/b	z/c	U _{iso}
P(1)	0.01278(6)	0.18700	-0.33461(4)	0.0469(6)
P(2)	-0.48595(6)	-0.0248(2)	-0.33482(4)	0.0490(6)
O(3)	-0.4753(1)	-0.1507(4)	-0.26836(9)	0.057(2)
O(4)	0.0403(1)	0.2755(5)	-0.26128(9)	0.056(2)
O(5)	-0.1423(1)	0.3396(6)	-0.4994(1)	0.077(2)
O(6)	-0.1988(2)	0.3821(6)	-0.4086(1)	0.084(2)
O(7)	-0.6337(1)	-0.1806(5)	-0.50498(9)	0.067(2)
O(8)	-0.6872(2)	-0.2209(5)	-0.4121(1)	0.074(2)
C(9)	-0.5364(2)	-0.2434(6)	-0.1699(2)	0.059(2)
C(10)	-0.4944(2)	-0.0746(6)	-0.2063(2)	0.055(2)
C(11)	-0.0180(2)	0.2495(7)	-0.2113(2)	0.058(2)
C(12)	-0.1267(2)	0.3683(7)	-0.4401(2)	0.053(3)
C(13)	-0.5203(2)	-0.2231(8)	-0.3968(1)	0.062(3)
C(14)	0.0466(3)	0.4437(8)	-0.4306(2)	0.077(3)
C(15)	-0.6182(2)	-0.2036(7)	-0.4440(2)	0.057(3)
C(16)	-0.0291(2)	0.4002(6)	-0.3927(2)	0.048(2)
C(17)	0.1331(3)	0.1208(7)	-0.1253(2)	0.081(3)
C(18)	-0.4051(2)	0.0223(7)	-0.1601(2)	0.064(3)
C(19)	0.0474(2)	0.2766(6)	-0.1412(2)	0.061(2)
C(20)	-0.6266(3)	-0.3569(7)	-0.2159(2)	0.068(3)
B(21)	-0.0573(4)	-0.0473(9)	-0.3446(2)	0.079(4)
C(22)	0.1270(2)	0.1690(8)	-0.3568(2)	0.070(3)
C(23)	-0.4148(3)	0.0844(7)	-0.0918(2)	0.076(3)
C(24)	-0.0129(3)	0.2708(8)	-0.0875(2)	0.077(3)
C(25)	-0.1001(3)	0.4072(7)	-0.2285(2)	0.077(3)
C(26)	-0.1576(3)	0.4073(7)	-0.1732(2)	0.085(3)
C(27)	-0.7096(2)	-0.1880(8)	-0.2344(2)	0.107(3)
C(28)	-0.2461(2)	-0.180(1)	-0.3842(2)	0.089(3)
C(29)	-0.4512(3)	-0.0860(9)	-0.0577(2)	0.100(4)
C(30)	-0.4392(3)	-0.2337(9)	-0.4336(2)	0.094(4)
C(31)	0.2063(3)	0.1736(9)	-0.0607(2)	0.099(4)
C(32)	-0.3642(2)	0.0019(9)	-0.3435(2)	0.082(3)
C(33)	-0.5450(3)	-0.1755(8)	-0.1013(2)	0.079(3)
C(34)	0.1014(3)	-0.0936(8)	-0.1206(2)	0.097(3)
C(35)	0.1388(3)	0.3700(9)	-0.3869(2)	0.110(4)
C(36)	-0.6585(3)	-0.5267(8)	-0.1857(2)	0.113(4)
C(37)	-0.0944(3)	0.4287(8)	-0.1033(2)	0.100(4)
C(38)	-0.3214(3)	0.1762(9)	-0.0488(2)	0.115(4)
B(39)	-0.5561(3)	0.2290(8)	-0.3415(2)	0.073(4)
C(40)	-0.2369(3)	0.566(1)	-0.1903(2)	0.158(5)
H(9)	-0.49104	-0.35308	-0.16076	0.05000
H(10)	-0.54260	0.02945	-0.21760	0.05000
H(11)	-0.04512	0.11533	-0.21623	0.05000
H(13)	-0.52081	-0.35019	-0.37365	0.05000
H(14A)	0.03472	0.36704	-0.47214	0.05000
H(14B)	0.05002	0.58574	-0.44064	0.05000
H(16)	-0.03536	0.51369	-0.36445	0.05000
H(17)	0.16252	0.12833	-0.16285	0.05000

ORTEP

Table 2S (continued)

ccpmt				
H(18A)	-0.35175	-0.06976	-0.15423	0.05000
H(18B)	-0.39185	0.14234	-0.18313	0.05000
H(19)	0.07595	0.40891	-0.14007	0.05000
H(20)	-0.61141	-0.38390	-0.25684	0.05000
H(22A)	0.17888	0.13855	-0.31818	0.05000
H(22B)	0.12588	0.07075	-0.39188	0.05000
H(23)	-0.46453	0.18520	-0.09745	0.05000
H(24A)	-0.04582	0.14272	-0.09095	0.05000
H(24B)	0.02578	0.28852	-0.04215	0.05000
H(25A)	-0.07048	0.53892	-0.22445	0.05000
H(25B)	-0.14058	0.39102	-0.27345	0.05000
H(26)	-0.18527	0.27382	-0.17608	0.05000
H(27A)	-0.68758	-0.07358	-0.25571	0.05000
H(27B)	-0.76508	-0.24598	-0.26501	0.05000
H(27C)	-0.72618	-0.14428	-0.19371	0.05000
H(28A)	-0.33421	-0.29383	-0.35394	0.05000
H(28B)	-0.29281	-0.16233	-0.40444	0.05000
H(29A)	-0.40244	-0.18915	-0.04973	0.05000
H(29B)	-0.46204	-0.04205	-0.01513	0.05000
H(30A)	-0.43192	-0.35788	-0.45659	0.05000
H(30B)	-0.44962	-0.12318	-0.46549	0.05000
H(31A)	0.23026	0.31088	-0.06221	0.05000
H(31B)	0.17986	0.15808	-0.02291	0.05000
H(31C)	0.26166	0.08198	-0.05561	0.05000
H(32A)	-0.35813	0.11969	-0.37198	0.05000
H(32B)	-0.31563	0.00519	-0.30348	0.05000
H(33A)	-0.59422	-0.07335	-0.10835	0.05000
H(33B)	-0.56472	-0.29105	-0.07915	0.05000
H(34A)	0.05423	-0.13061	-0.16110	0.05000
H(34B)	0.15603	-0.18211	-0.11480	0.05000
H(34C)	0.07423	-0.10601	-0.08210	0.05000
H(35A)	0.18807	0.36557	-0.41145	0.05000
H(35B)	0.15747	0.46217	-0.34935	0.05000
H(36A)	-0.60637	-0.62240	-0.17547	0.05000
H(36B)	-0.67457	-0.48680	-0.14437	0.05000
H(36C)	-0.71337	-0.58850	-0.21567	0.05000
H(37A)	-0.13048	0.43758	-0.06936	0.05000
H(37B)	-0.06258	0.55578	-0.10586	0.05000
H(38A)	-0.30426	0.28838	-0.07368	0.05000
H(38B)	-0.33006	0.22368	-0.00598	0.05000
H(38C)	-0.27106	0.07638	-0.04098	0.05000
H(40A)	-0.28027	0.53827	-0.23373	0.05000
H(40B)	-0.27257	0.57737	-0.15653	0.05000
H(40C)	-0.20327	0.69037	-0.19303	0.05000
H(21A)	-0.07512	-0.09914	-0.39021	0.019(7)
H(21B)	-0.02092	-0.14994	-0.31571	0.042(9)
H(21C)	-0.11492	-0.01994	-0.33021	0.09(2)
H(8)	-0.72457	-0.33578	-0.43254	0.12(1)
H(6)	-0.23324	0.25605	-0.41768	0.16(1)

$$T = \exp[2\pi^2 U]; U = U_{\text{iso}} \text{ or } U_{\text{eq}}; U_{\text{eq}} = \frac{1}{3} \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} a_i a_j u_i u_j$$

Table 3S. ANISOTROPIC THERMAL PARAMETERS (compound 43)

Atom	U11	U22	U33	U12	U13	U23
P(1)	0.0387(5)	0.0506(7)	0.0498(5)	0.0059(6)	0.0158(4)	0.0019(6)
P(2)	0.0453(5)	0.0528(7)	0.0470(5)	-0.0037(6)	0.0148(4)	-0.0023(6)
O(3)	0.056(1)	0.069(2)	0.044(1)	0.026(1)	0.020(1)	0.005(1)
O(4)	0.044(1)	0.077(2)	0.045(1)	-0.006(1)	0.019(1)	0.010(1)
O(5)	0.047(1)	0.138(3)	0.044(1)	0.016(2)	0.013(1)	-0.003(2)
O(6)	0.049(1)	0.140(3)	0.060(1)	0.005(2)	0.022(1)	-0.010(2)
O(7)	0.041(1)	0.109(3)	0.047(1)	-0.006(2)	0.008(1)	0.000(2)
O(8)	0.059(1)	0.097(3)	0.063(1)	-0.013(2)	0.022(1)	0.006(2)
C(9)	0.056(2)	0.057(3)	0.061(2)	0.019(2)	0.016(2)	0.005(2)
C(10)	0.048(2)	0.043(3)	0.068(2)	0.012(2)	0.010(2)	-0.001(2)
C(11)	0.064(2)	0.067(3)	0.044(2)	-0.005(2)	0.027(2)	0.002(2)
C(12)	0.051(2)	0.056(3)	0.051(2)	0.012(2)	0.022(2)	0.002(2)
C(13)	0.044(2)	0.093(3)	0.045(2)	0.011(3)	0.009(2)	0.007(2)
C(14)	0.057(2)	0.078(3)	0.092(3)	-0.005(3)	0.017(2)	0.028(3)
C(15)	0.046(2)	0.066(3)	0.055(2)	-0.007(2)	0.013(2)	-0.006(2)
C(16)	0.043(2)	0.036(2)	0.064(2)	0.001(2)	0.017(2)	0.013(2)
C(17)	0.071(3)	0.092(4)	0.077(3)	0.007(3)	0.031(3)	0.012(3)
C(18)	0.053(2)	0.069(3)	0.077(2)	0.010(2)	0.018(2)	0.003(2)
C(19)	0.068(2)	0.067(3)	0.045(2)	-0.002(2)	0.019(2)	0.009(2)
C(20)	0.067(3)	0.059(3)	0.075(2)	0.006(2)	0.025(2)	0.014(2)
B(21)	0.099(4)	0.053(4)	0.077(3)	0.007(4)	0.012(3)	-0.014(3)
C(22)	0.032(2)	0.110(4)	0.068(2)	0.020(3)	0.024(2)	0.004(3)
C(23)	0.075(3)	0.099(4)	0.049(2)	-0.006(3)	0.012(2)	-0.013(3)
C(24)	0.071(3)	0.098(4)	0.061(2)	0.010(3)	0.028(2)	0.012(3)
C(25)	0.076(3)	0.087(4)	0.066(2)	0.017(3)	0.026(2)	0.013(2)
C(26)	0.080(3)	0.093(4)	0.082(3)	0.025(3)	0.040(2)	0.016(3)
C(27)	0.048(2)	0.081(3)	0.182(4)	-0.020(3)	0.019(3)	0.000(4)
C(28)	0.037(2)	0.153(5)	0.077(3)	-0.007(3)	0.023(2)	-0.007(4)
C(29)	0.106(3)	0.142(5)	0.049(2)	-0.008(4)	0.031(2)	-0.013(3)
C(30)	0.066(3)	0.142(5)	0.068(2)	0.039(3)	0.009(2)	-0.038(3)
C(31)	0.059(2)	0.143(5)	0.087(3)	0.005(3)	0.004(2)	0.028(3)
C(32)	0.043(2)	0.114(4)	0.091(3)	-0.006(3)	0.037(2)	-0.007(3)
C(33)	0.089(3)	0.104(4)	0.043(2)	-0.024(3)	0.025(2)	-0.006(3)
C(34)	0.081(3)	0.090(4)	0.112(4)	0.024(3)	0.015(3)	0.031(3)
C(35)	0.066(3)	0.138(5)	0.127(4)	-0.025(4)	0.047(3)	0.031(4)
C(36)	0.078(3)	0.096(4)	0.157(4)	-0.001(3)	0.027(3)	0.017(4)
C(37)	0.096(3)	0.112(4)	0.095(3)	0.019(3)	0.060(3)	0.002(3)
C(38)	0.122(4)	0.136(5)	0.081(3)	-0.012(4)	0.022(3)	-0.027(3)
B(39)	0.096(4)	0.051(4)	0.069(3)	0.035(3)	0.027(3)	0.010(3)
C(40)	0.108(4)	0.217(7)	0.156(4)	0.088(4)	0.085(3)	0.082(5)

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}kbl^*c^* + 2U_{13}hla^*c^*)]$$

Table 4S. INTRAMOLECULAR BOND LENGTHS (H omitted) (compound 43)

Bond length limits based on covalent radii			
P(1)-O(4)	1.557(3)	P(1)-C(16)	1.837(4)
P(1)-B(21)	1.825(6)	P(1)-C(22)	1.808(4)
P(2)-O(3)	1.559(3)	P(2)-C(13)	1.795(5)
P(2)-C(32)	1.822(4)	O(3)-C(10)	1.444(4)
O(5)-C(12)	1.183(4)	O(6)-C(12)	1.347(4)
O(7)-C(15)	1.212(4)	O(8)-C(15)	1.316(4)
C(9)-C(33)	1.497(5)	C(13)-C(15)	1.500(5)
C(14)-C(35)	1.481(6)	C(17)-C(34)	1.493(7)
C(18)-C(23)	1.485(5)	C(22)-C(35)	1.485(8)
C(23)-C(29)	1.479(7)	C(26)-C(37)	1.492(6)
C(28)-C(32)	1.488(8)		

Table 5S. INTRAMOLECULAR BOND ANGLES (H omitted) (compound 43)

Bond length limits based on covalent radii			
O(4)-P(1)-C(16)	107.3(2)	O(4)-P(1)-B(21)	115.2(2)
O(4)-P(1)-C(22)	103.3(2)	C(16)-P(1)-B(21)	119.3(2)
C(16)-P(1)-C(22)	93.6(2)	B(21)-P(1)-C(22)	115.2(3)
O(3)-P(2)-C(13)	99.9(2)	O(3)-P(2)-C(32)	105.2(2)
C(13)-P(2)-C(32)	95.3(2)	P(2)-O(3)-C(10)	125.0(3)
O(5)-C(12)-O(6)	121.2(3)	P(2)-C(13)-C(15)	116.1(4)
O(7)-C(15)-O(8)	122.9(3)	O(7)-C(15)-C(13)	124.9(3)
O(8)-C(15)-C(13)	112.2(3)	P(1)-C(22)-C(35)	104.3(4)
C(18)-C(23)-C(29)	110.8(4)	P(2)-C(32)-C(28)	106.5(4)
C(14)-C(35)-C(22)	111.3(4)		

Table 6S. INTRAMOLECULAR TORSION ANGLES (H omitted) (compound 43)

Bond length limits based on covalent radii			
O(4)-P(1)-C(22)-C(35)	-88.6(3)	C(16)-P(1)-C(22)-C(35)	20.0(3)
B(21)-P(1)-C(22)-C(35)	144.9(4)	C(13)-P(2)-O(3)-C(10)	-148.3(3)
O(3)-P(2)-C(13)-C(15)	116.9(3)	C(32)-P(2)-O(3)-C(10)	113.4(3)
O(3)-P(2)-C(32)-C(28)	87.8(4)	C(32)-P(2)-C(13)-C(15)	-136.6(4)
C(13)-P(2)-C(32)-C(28)	-14.0(4)	P(2)-C(13)-C(15)-O(7)	116.0(5)
P(2)-C(13)-C(15)-O(8)	-66.0(4)	P(1)-C(22)-C(35)-C(14)	-39.9(4)

Table 7S. INTERMOLECULAR NON-BONDED DISTANCES (H omitted) (compound 43)

non-bonded distance limits based on Van der Waal's radii											
Atom(1)-Atom(2)	dist	c.s.d.	ns	np	Ta	Tb	Tc	x(2)	y(2)	z(2)	
O(5)-O(8)	2.685	0.003	2	1	-1	0	-1	-0.31278	0.27912	-0.58790	
O(5)-C(14)	3.414	0.005	2	1	0	-1	-1	-0.04662	-0.05626	-0.56936	
O(5)-C(15)	3.358	0.004	2	1	-1	0	-1	-0.38179	0.29636	-0.55596	
O(6)-O(7)	2.637	0.003	2	1	-1	0	-1	-0.36630	0.31938	-0.49502	
O(6)-C(15)	3.507	0.004	2	1	-1	0	-1	-0.38179	0.29636	-0.55596	
O(7)-C(12)	3.360	0.004	2	1	-1	-1	-1	-0.87330	-0.13166	-0.55986	
O(7)-C(30)	3.456	0.006	2	1	-1	0	-1	-0.56078	0.26632	-0.56641	
C(12)-C(15)	3.863	0.005	2	1	-1	0	-1	-0.38179	0.29636	-0.55596	
C(13)-B(39)	3.847	0.007	1	1	0	-1	0	-0.55607	-0.77103	-0.34151	
C(16)-B(21)	3.811	0.007	1	1	0	1	0	-0.05732	0.95266	-0.34461	
C(18)-C(40)	3.997	0.007	1	1	0	-1	0	-0.23687	-0.43443	-0.19053	
C(22)-C(27)	3.785	0.006	1	1	1	0	0	0.29042	-0.18798	-0.23441	
O(5)-O(8)	2.685	0.003	2	1	-1	0	-1	-0.31278	0.27912	-0.58790	
O(5)-C(14)	3.414	0.005	2	1	0	-1	-1	-0.04662	-0.05626	-0.56936	
O(5)-C(15)	3.358	0.004	2	1	-1	0	-1	-0.38179	0.29636	-0.55596	
O(6)-O(7)	2.637	0.003	2	1	-1	0	-1	-0.36630	0.31938	-0.49502	
O(6)-C(15)	3.507	0.004	2	1	-1	0	-1	-0.38179	0.29636	-0.55596	
O(7)-C(12)	3.360	0.004	2	1	-1	-1	-1	-0.87330	-0.13166	-0.55986	
O(7)-C(30)	3.456	0.006	2	1	-1	0	-1	-0.56078	0.26632	-0.56641	
C(12)-C(15)	3.863	0.005	2	1	-1	0	-1	-0.38179	0.29636	-0.55596	
C(13)-B(39)	3.847	0.007	1	1	0	-1	0	-0.55607	-0.77103	-0.34151	
C(16)-B(21)	3.811	0.007	1	1	0	1	0	-0.05732	0.95266	-0.34461	
C(18)-C(40)	3.997	0.007	1	1	0	-1	0	-0.23687	-0.43443	-0.19053	
C(22)-C(27)	3.785	0.006	1	1	1	0	0	0.29042	-0.18798	-0.23441	

ns is the symmetry operator number - (* denotes inversion indicator)

np is the lattice point number

Ta, Tb & Tc are unit cell translations. The symmetry operations are:

1 + X, + Y, + Z

2 - X, 1/2 + Y, - Z

X-ray Crystal Structure Analysis: Compound 36

Crystal data

Empirical formula	C ₃₁ H ₄₀ BF ₄ P ₂ Rh	
Formula weight	664.29	
Temperature	299(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.9304(9) Å	α = 90°.
	b = 15.0030(14) Å	β = 90°.
	c = 19.6514(18) Å	γ = 90°.
Volume	2927.8(5) Å ³	
Z	4	
Density (calculated)	1.507 Mg/m ³	
Absorption coefficient	0.738 mm ⁻¹	
F(000)	1368	
Crystal size	0.43 x 0.14 x 0.13 mm ³	
Theta range for data collection	1.71 to 28.31°.	
Index ranges	-13 ≤ h ≤ 11, -15 ≤ k ≤ 20, -22 ≤ l ≤ 26	
Reflections collected	22163	
Independent reflections	7272 [R(int) = 0.0285]	
Completeness to theta = 28.31°	99.9 %	
Absorption correction	None	
Max. and min. transmission	0.9101 and 0.7419	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7272 / 0 / 361	
Goodness-of-fit on F ²	1.038	
Final R indices [I > 2σ(I)]	R1 = 0.0279, wR2 = 0.0698	
R indices (all data)	R1 = 0.0336, wR2 = 0.0720	
Absolute structure parameter	-0.04(2)	
Extinction coefficient	0.0087(4)	
Largest diff. peak and hole	0.498 and -0.278 e.Å ⁻³	

Table 8S. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor (compound **36**).

	x	y	z	U(eq)
Rh(1)	9159(1)	5005(1)	8773(1)	41(1)
P(15)	9813(1)	5877(1)	9680(1)	32(1)
C(16)	8735(3)	6764(2)	10005(1)	46(1)
C(18)	9158(3)	5865(2)	11013(1)	58(1)
C(19)	10153(3)	5373(2)	10535(1)	38(1)
C(20)	10099(3)	4368(2)	10598(1)	45(1)
C(17)	9020(3)	6813(2)	10767(1)	55(1)
P(12)	11256(1)	5324(1)	8378(1)	36(1)
C(27)	6930(3)	4966(2)	8777(2)	58(1)
F(36)	5668(3)	5037(2)	763(1)	108(1)
F(38)	5823(3)	6433(2)	1165(2)	116(1)
C(8)	11448(3)	6201(2)	7717(1)	44(1)
F(35)	5388(3)	6174(2)	92(2)	134(1)
C(31)	8270(3)	4340(2)	7881(1)	52(1)
F(37)	3803(2)	5897(2)	835(2)	113(1)
C(13)	12288(2)	5784(2)	9072(1)	45(1)
C(14)	11420(3)	6422(2)	9477(1)	45(1)
C(10)	12862(3)	4945(3)	7298(2)	74(1)
C(6)	8949(3)	6570(2)	7448(1)	42(1)
C(7)	10291(3)	6247(2)	7193(1)	47(1)
C(21)	11162(3)	3868(2)	10214(1)	42(1)
C(9)	12791(3)	5950(2)	7375(2)	62(1)
C(4)	6545(3)	6680(2)	7270(2)	59(1)
C(22)	10810(3)	3254(2)	9721(2)	56(1)
C(26)	12527(3)	4012(2)	10339(2)	49(1)
C(5)	7786(3)	6347(2)	7083(1)	51(1)
C(29)	7526(3)	3480(2)	8805(2)	60(1)
C(1)	8797(3)	7142(2)	8002(1)	54(1)
C(30)	8722(3)	3702(2)	8326(2)	53(1)
C(32)	6793(3)	4526(2)	8080(2)	61(1)
C(11)	12318(4)	4499(2)	7948(2)	64(1)
C(28)	7368(3)	4331(2)	9213(2)	56(1)
C(3)	6423(3)	7240(2)	7818(2)	61(1)
C(25)	13495(3)	3563(2)	9960(2)	60(1)
C(2)	7546(3)	7471(2)	8183(2)	65(1)
C(24)	13120(4)	2955(2)	9473(2)	70(1)
C(23)	11784(4)	2793(2)	9361(2)	72(1)
C(33)	6346(4)	3581(2)	8302(2)	72(1)
B(34)	5152(4)	5867(2)	735(2)	58(1)

Table 9S. Bond lengths [Å] and angles [°] (compound **36**).

Rh(1)-C(30)	2.185(3)
Rh(1)-C(31)	2.200(3)
Rh(1)-C(27)	2.215(3)
Rh(1)-C(28)	2.221(3)
Rh(1)-P(12)	2.2731(6)
Rh(1)-P(15)	2.3042(6)
P(15)-C(16)	1.823(3)
P(15)-C(14)	1.837(3)
P(15)-C(19)	1.875(2)
C(16)-C(17)	1.527(4)
C(18)-C(17)	1.508(4)
C(18)-C(19)	1.550(3)
C(19)-C(20)	1.513(4)
C(20)-C(21)	1.499(4)
P(12)-C(11)	1.832(3)
P(12)-C(13)	1.841(3)
P(12)-C(8)	1.858(3)
C(27)-C(28)	1.353(4)
C(27)-C(32)	1.527(4)
F(36)-B(34)	1.347(4)
F(38)-B(34)	1.371(4)
C(8)-C(9)	1.541(4)
C(8)-C(7)	1.543(4)
F(35)-B(34)	1.366(5)
C(31)-C(30)	1.371(4)
C(31)-C(32)	1.543(5)
F(37)-B(34)	1.354(4)
C(13)-C(14)	1.514(4)
C(10)-C(9)	1.516(6)
C(10)-C(11)	1.540(5)
C(6)-C(1)	1.394(4)
C(6)-C(5)	1.400(4)
C(6)-C(7)	1.504(4)
C(21)-C(22)	1.382(4)
C(21)-C(26)	1.394(4)
C(4)-C(3)	1.370(4)
C(4)-C(5)	1.380(5)
C(22)-C(23)	1.384(5)
C(26)-C(25)	1.390(4)
C(29)-C(28)	1.517(5)
C(29)-C(33)	1.540(4)
C(29)-C(30)	1.551(4)
C(1)-C(2)	1.383(4)
C(32)-C(33)	1.548(4)
C(3)-C(2)	1.370(5)
C(25)-C(24)	1.374(5)
C(24)-C(23)	1.366(6)
C(30)-Rh(1)-C(31)	36.44(11)
C(30)-Rh(1)-C(27)	77.25(12)

Table 9S (continued).

C(31)-Rh(1)-C(27)	65.79(12)
C(30)-Rh(1)-C(28)	65.82(12)
C(31)-Rh(1)-C(28)	77.44(11)
C(27)-Rh(1)-C(28)	35.52(11)
C(30)-Rh(1)-P(12)	103.50(8)
C(31)-Rh(1)-P(12)	101.02(8)
C(27)-Rh(1)-P(12)	157.27(8)
C(28)-Rh(1)-P(12)	164.25(9)
C(30)-Rh(1)-P(15)	150.95(8)
C(31)-Rh(1)-P(15)	170.40(9)
C(27)-Rh(1)-P(15)	107.06(8)
C(28)-Rh(1)-P(15)	100.52(8)
P(12)-Rh(1)-P(15)	83.49(2)
C(16)-P(15)-C(14)	105.12(13)
C(16)-P(15)-C(19)	94.94(12)
C(14)-P(15)-C(19)	102.55(12)
C(16)-P(15)-Rh(1)	121.35(9)
C(14)-P(15)-Rh(1)	109.26(8)
C(19)-P(15)-Rh(1)	121.04(8)
C(17)-C(16)-P(15)	105.68(18)
C(17)-C(18)-C(19)	108.3(2)
C(20)-C(19)-C(18)	113.8(2)
C(20)-C(19)-P(15)	117.9(2)
C(18)-C(19)-P(15)	103.64(17)
C(21)-C(20)-C(19)	115.6(2)
C(18)-C(17)-C(16)	106.6(2)
C(11)-P(12)-C(13)	105.93(16)
C(11)-P(12)-C(8)	95.60(14)
C(13)-P(12)-C(8)	101.29(13)
C(11)-P(12)-Rh(1)	122.81(12)
C(13)-P(12)-Rh(1)	109.60(8)
C(8)-P(12)-Rh(1)	118.81(9)
C(28)-C(27)-C(32)	107.0(3)
C(28)-C(27)-Rh(1)	72.49(16)
C(32)-C(27)-Rh(1)	95.58(18)
C(9)-C(8)-C(7)	111.4(2)
C(9)-C(8)-P(12)	102.72(19)
C(7)-C(8)-P(12)	114.87(19)
C(30)-C(31)-C(32)	106.0(3)
C(30)-C(31)-Rh(1)	71.20(16)
C(32)-C(31)-Rh(1)	95.68(19)
C(14)-C(13)-P(12)	108.03(17)
C(13)-C(14)-P(15)	109.09(17)
C(9)-C(10)-C(11)	109.5(3)
C(1)-C(6)-C(5)	117.2(3)
C(1)-C(6)-C(7)	123.6(2)
C(5)-C(6)-C(7)	118.9(2)
C(6)-C(7)-C(8)	116.9(2)
C(22)-C(21)-C(26)	118.2(3)
C(22)-C(21)-C(20)	120.5(3)
C(26)-C(21)-C(20)	121.2(2)

Table 9S (continued).

C(10)-C(9)-C(8)	109.1(2)
C(3)-C(4)-C(5)	120.7(3)
C(21)-C(22)-C(23)	121.0(3)
C(25)-C(26)-C(21)	120.2(3)
C(4)-C(5)-C(6)	120.9(3)
C(28)-C(29)-C(33)	100.2(3)
C(28)-C(29)-C(30)	102.6(2)
C(33)-C(29)-C(30)	99.9(3)
C(2)-C(1)-C(6)	121.2(3)
C(31)-C(30)-C(29)	106.6(3)
C(31)-C(30)-Rh(1)	72.36(16)
C(29)-C(30)-Rh(1)	95.83(18)
C(27)-C(32)-C(31)	102.7(2)
C(27)-C(32)-C(33)	99.7(3)
C(31)-C(32)-C(33)	100.3(3)
C(10)-C(11)-P(12)	106.9(2)
C(27)-C(28)-C(29)	106.9(2)
C(27)-C(28)-Rh(1)	71.99(16)
C(29)-C(28)-Rh(1)	95.43(17)
C(4)-C(3)-C(2)	119.7(3)
C(24)-C(25)-C(26)	120.5(3)
C(3)-C(2)-C(1)	120.3(3)
C(23)-C(24)-C(25)	119.6(3)
C(24)-C(23)-C(22)	120.5(3)
C(29)-C(33)-C(32)	93.0(2)
F(36)-B(34)-F(37)	113.7(3)
F(36)-B(34)-F(35)	106.5(3)
F(37)-B(34)-F(35)	107.0(3)
F(36)-B(34)-F(38)	111.3(3)
F(37)-B(34)-F(38)	111.8(3)
F(35)-B(34)-F(38)	106.1(3)

Table 10S. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$ (compound **36**).

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Rh(1)	38(1)	50(1)	36(1)	-11(1)	6(1)	-14(1)
P(15)	34(1)	33(1)	30(1)	-2(1)	0(1)	-4(1)
C(16)	48(1)	40(1)	49(1)	-3(1)	-5(1)	8(1)
C(18)	61(2)	81(2)	32(1)	-1(1)	4(1)	26(2)
C(19)	37(1)	45(1)	33(1)	1(1)	1(1)	7(1)
C(20)	47(2)	46(1)	42(1)	13(1)	1(1)	1(1)
C(17)	59(2)	60(2)	47(1)	-18(1)	-3(1)	17(1)
P(12)	36(1)	39(1)	34(1)	3(1)	5(1)	-1(1)
C(27)	41(1)	62(2)	72(2)	-8(2)	7(1)	-8(1)
F(36)	135(2)	59(1)	131(2)	3(1)	-4(2)	17(2)
F(38)	88(2)	109(2)	151(2)	-57(2)	-12(2)	0(1)
C(8)	47(1)	48(1)	38(1)	9(1)	6(1)	-5(1)
F(35)	136(3)	156(3)	109(2)	45(2)	34(2)	31(2)
C(31)	65(2)	54(2)	36(1)	-3(1)	-5(1)	-20(1)
F(37)	70(2)	109(2)	160(2)	-38(2)	34(2)	-23(1)
C(13)	33(1)	58(2)	43(1)	7(1)	-3(1)	-7(1)
C(14)	44(1)	49(2)	43(1)	-1(1)	-3(1)	-18(1)
C(10)	65(2)	98(3)	60(2)	1(2)	27(1)	22(2)
C(6)	50(2)	42(1)	35(1)	6(1)	-3(1)	-2(1)
C(7)	55(2)	50(1)	36(1)	5(1)	3(1)	0(1)
C(21)	50(1)	33(1)	41(1)	10(1)	-5(1)	-1(1)
C(9)	45(2)	89(2)	51(2)	15(2)	15(1)	-10(2)
C(4)	52(2)	73(2)	52(2)	-4(2)	-10(1)	-6(2)
C(22)	64(2)	49(2)	55(2)	0(1)	-9(2)	-6(1)
C(26)	51(2)	38(1)	57(2)	3(1)	-5(1)	2(1)
C(5)	63(2)	55(2)	36(1)	-2(1)	-3(1)	-7(1)
C(29)	62(2)	56(2)	61(2)	17(2)	-10(2)	-22(1)
C(1)	55(2)	59(2)	47(2)	-10(1)	-12(1)	6(1)
C(30)	63(2)	43(1)	53(2)	-7(1)	4(1)	-11(1)
C(32)	60(2)	67(2)	57(2)	14(2)	-20(2)	-16(2)
C(11)	72(2)	54(2)	66(2)	-3(2)	27(2)	14(2)
C(28)	48(2)	79(2)	43(1)	1(2)	2(1)	-25(2)
C(3)	55(2)	74(2)	54(2)	-2(2)	-4(1)	10(2)
C(25)	51(2)	49(2)	80(2)	9(2)	4(2)	4(1)
C(2)	74(2)	65(2)	55(2)	-17(2)	-9(2)	15(2)
C(24)	94(3)	53(2)	64(2)	8(2)	24(2)	23(2)
C(23)	98(3)	59(2)	60(2)	-10(2)	-6(2)	8(2)
C(33)	72(2)	72(2)	70(2)	7(2)	-19(2)	-41(2)
B(34)	62(2)	48(2)	65(2)	-3(2)	10(2)	1(2)

Table 11S. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) (compound **36**).

	x	y	z	U(eq)
H(16A)	8948	7326	9786	55
H(16B)	7795	6627	9923	55
H(18A)	8288	5571	11006	69
H(18B)	9495	5857	11476	69
H(19)	11063	5557	10668	46
H(20A)	10170	4212	11075	54
H(20B)	9224	4167	10440	54
H(17A)	9844	7142	10852	66
H(17B)	8287	7110	11002	66
H(27)	6374	5472	8921	70
H(8)	11543	6783	7939	53
H(13A)	12608	5307	9363	54
H(13B)	13062	6095	8887	54
H(14A)	11257	6958	9214	54
H(14B)	11878	6589	9894	54
H(10A)	13787	4763	7222	89
H(10B)	12331	4759	6908	89
H(7A)	10572	6634	6825	56
H(7B)	10168	5656	7003	56
H(9A)	12852	6231	6931	74
H(9B)	13538	6158	7650	74
H(4)	5783	6523	7022	71
H(22)	9905	3149	9629	67
H(26)	12791	4409	10677	58
H(5)	7851	5969	6709	62
H(29)	7579	2920	9061	72
H(1)	9550	7305	8254	64
H(30)	9424	3270	8209	64
H(11A)	13055	4320	8241	77
H(11B)	11794	3974	7833	77
H(28)	7160	4337	9700	68
H(3)	5584	7462	7941	73
H(25)	14404	3674	10037	72
H(2)	7466	7851	8555	77
H(24)	13771	2656	9220	84
H(23)	11528	2370	9040	86
H(33A)	5472	3574	8523	86
H(33B)	6372	3150	7934	86
H(32)	6210(40)	4780(20)	7761(19)	76(10)
H(31)	8680(30)	4417(18)	7447(15)	48(8)

Table 12S. Torsion angles [°] (compound **36**).

C(30)-Rh(1)-P(15)-C(16)	-122.3(2)
C(31)-Rh(1)-P(15)-C(16)	12.9(5)
C(27)-Rh(1)-P(15)-C(16)	-27.91(14)
C(28)-Rh(1)-P(15)-C(16)	-63.91(14)
P(12)-Rh(1)-P(15)-C(16)	131.49(11)
C(30)-Rh(1)-P(15)-C(14)	115.2(2)
C(31)-Rh(1)-P(15)-C(14)	-109.5(5)
C(27)-Rh(1)-P(15)-C(14)	-150.34(13)
C(28)-Rh(1)-P(15)-C(14)	173.66(13)
P(12)-Rh(1)-P(15)-C(14)	9.06(10)
C(30)-Rh(1)-P(15)-C(19)	-3.4(2)
C(31)-Rh(1)-P(15)-C(19)	131.8(5)
C(27)-Rh(1)-P(15)-C(19)	91.05(13)
C(28)-Rh(1)-P(15)-C(19)	55.05(13)
P(12)-Rh(1)-P(15)-C(19)	-109.55(10)
C(14)-P(15)-C(16)-C(17)	-87.5(2)
C(19)-P(15)-C(16)-C(17)	16.9(2)
Rh(1)-P(15)-C(16)-C(17)	148.13(17)
C(17)-C(18)-C(19)-C(20)	-164.1(3)
C(17)-C(18)-C(19)-P(15)	-34.8(3)
C(16)-P(15)-C(19)-C(20)	136.4(2)
C(14)-P(15)-C(19)-C(20)	-116.9(2)
Rh(1)-P(15)-C(19)-C(20)	5.0(3)
C(16)-P(15)-C(19)-C(18)	9.7(2)
C(14)-P(15)-C(19)-C(18)	116.4(2)
Rh(1)-P(15)-C(19)-C(18)	-121.72(18)
C(18)-C(19)-C(20)-C(21)	-172.4(2)
P(15)-C(19)-C(20)-C(21)	65.9(3)
C(19)-C(18)-C(17)-C(16)	49.7(3)
P(15)-C(16)-C(17)-C(18)	-40.0(3)
C(30)-Rh(1)-P(12)-C(11)	-11.36(17)
C(31)-Rh(1)-P(12)-C(11)	-48.60(17)
C(27)-Rh(1)-P(12)-C(11)	-100.5(3)
C(28)-Rh(1)-P(12)-C(11)	34.2(3)
P(15)-Rh(1)-P(12)-C(11)	139.98(15)
C(30)-Rh(1)-P(12)-C(13)	-136.54(13)
C(31)-Rh(1)-P(12)-C(13)	-173.78(13)
C(27)-Rh(1)-P(12)-C(13)	134.3(2)
C(28)-Rh(1)-P(12)-C(13)	-91.0(3)
P(15)-Rh(1)-P(12)-C(13)	14.80(10)
C(30)-Rh(1)-P(12)-C(8)	107.80(13)
C(31)-Rh(1)-P(12)-C(8)	70.56(13)
C(27)-Rh(1)-P(12)-C(8)	18.6(2)
C(28)-Rh(1)-P(12)-C(8)	153.3(3)
P(15)-Rh(1)-P(12)-C(8)	-100.86(10)
C(30)-Rh(1)-C(27)-C(28)	66.06(19)
C(31)-Rh(1)-C(27)-C(28)	102.7(2)
P(12)-Rh(1)-C(27)-C(28)	160.61(18)
P(15)-Rh(1)-C(27)-C(28)	-84.18(18)
C(30)-Rh(1)-C(27)-C(32)	-40.0(2)

C(31)-Rh(1)-C(27)-C(32)	-3.39(18)
C(28)-Rh(1)-C(27)-C(32)	-106.1(3)
P(12)-Rh(1)-C(27)-C(32)	54.5(3)
P(15)-Rh(1)-C(27)-C(32)	169.75(17)
C(11)-P(12)-C(8)-C(9)	-24.1(2)
C(13)-P(12)-C(8)-C(9)	83.4(2)
Rh(1)-P(12)-C(8)-C(9)	-156.56(17)
C(11)-P(12)-C(8)-C(7)	97.0(2)
C(13)-P(12)-C(8)-C(7)	-155.5(2)
Rh(1)-P(12)-C(8)-C(7)	-35.5(2)
C(27)-Rh(1)-C(31)-C(30)	-101.6(2)
C(28)-Rh(1)-C(31)-C(30)	-66.1(2)
P(12)-Rh(1)-C(31)-C(30)	97.86(18)
P(15)-Rh(1)-C(31)-C(30)	-144.8(4)
C(30)-Rh(1)-C(31)-C(32)	105.0(3)
C(27)-Rh(1)-C(31)-C(32)	3.36(18)
C(28)-Rh(1)-C(31)-C(32)	38.85(19)
P(12)-Rh(1)-C(31)-C(32)	-157.16(16)
P(15)-Rh(1)-C(31)-C(32)	-39.9(6)
C(11)-P(12)-C(13)-C(14)	-175.85(18)
C(8)-P(12)-C(13)-C(14)	84.91(19)
Rh(1)-P(12)-C(13)-C(14)	-41.44(19)
P(12)-C(13)-C(14)-P(15)	48.9(2)
C(16)-P(15)-C(14)-C(13)	-168.64(19)
C(19)-P(15)-C(14)-C(13)	92.65(19)
Rh(1)-P(15)-C(14)-C(13)	-36.9(2)
C(1)-C(6)-C(7)-C(8)	26.8(4)
C(5)-C(6)-C(7)-C(8)	-158.4(3)
C(9)-C(8)-C(7)-C(6)	-174.4(2)
P(12)-C(8)-C(7)-C(6)	69.3(3)
C(19)-C(20)-C(21)-C(22)	-120.7(3)
C(19)-C(20)-C(21)-C(26)	58.9(3)
C(11)-C(10)-C(9)-C(8)	-41.4(4)
C(7)-C(8)-C(9)-C(10)	-83.0(3)
P(12)-C(8)-C(9)-C(10)	40.4(3)
C(26)-C(21)-C(22)-C(23)	0.0(4)
C(20)-C(21)-C(22)-C(23)	179.6(3)
C(22)-C(21)-C(26)-C(25)	1.9(4)
C(20)-C(21)-C(26)-C(25)	-177.8(2)
C(3)-C(4)-C(5)-C(6)	0.2(5)
C(1)-C(6)-C(5)-C(4)	-0.3(4)
C(7)-C(6)-C(5)-C(4)	-175.4(3)
C(5)-C(6)-C(1)-C(2)	0.2(4)
C(7)-C(6)-C(1)-C(2)	175.1(3)
C(32)-C(31)-C(30)-C(29)	0.3(3)
Rh(1)-C(31)-C(30)-C(29)	90.9(2)
C(32)-C(31)-C(30)-Rh(1)	-90.6(2)
C(28)-C(29)-C(30)-C(31)	-68.2(3)
C(33)-C(29)-C(30)-C(31)	34.7(3)
C(28)-C(29)-C(30)-Rh(1)	5.1(2)
C(33)-C(29)-C(30)-Rh(1)	108.0(2)
C(27)-Rh(1)-C(30)-C(31)	66.3(2)

C(28)-Rh(1)-C(30)-C(31)	101.9(2)
P(12)-Rh(1)-C(30)-C(31)	-90.33(18)
P(15)-Rh(1)-C(30)-C(31)	168.59(15)
C(31)-Rh(1)-C(30)-C(29)	-105.6(3)
C(27)-Rh(1)-C(30)-C(29)	-39.30(18)
C(28)-Rh(1)-C(30)-C(29)	-3.71(17)
P(12)-Rh(1)-C(30)-C(29)	164.03(16)
P(15)-Rh(1)-C(30)-C(29)	62.9(3)
C(28)-C(27)-C(32)-C(31)	-68.8(3)
Rh(1)-C(27)-C(32)-C(31)	4.5(2)
C(28)-C(27)-C(32)-C(33)	34.1(3)
Rh(1)-C(27)-C(32)-C(33)	107.5(2)
C(30)-C(31)-C(32)-C(27)	67.5(3)
Rh(1)-C(31)-C(32)-C(27)	-4.6(2)
C(30)-C(31)-C(32)-C(33)	-35.1(3)
Rh(1)-C(31)-C(32)-C(33)	-107.1(2)
C(9)-C(10)-C(11)-P(12)	21.2(4)
C(13)-P(12)-C(11)-C(10)	-101.1(3)
C(8)-P(12)-C(11)-C(10)	2.3(3)
Rh(1)-P(12)-C(11)-C(10)	132.1(2)
C(32)-C(27)-C(28)-C(29)	0.3(3)
Rh(1)-C(27)-C(28)-C(29)	-90.3(2)
C(32)-C(27)-C(28)-Rh(1)	90.6(2)
C(33)-C(29)-C(28)-C(27)	-34.9(3)
C(30)-C(29)-C(28)-C(27)	67.8(3)
C(33)-C(29)-C(28)-Rh(1)	-107.7(2)
C(30)-C(29)-C(28)-Rh(1)	-5.0(2)
C(30)-Rh(1)-C(28)-C(27)	-102.3(2)
C(31)-Rh(1)-C(28)-C(27)	-65.73(19)
P(12)-Rh(1)-C(28)-C(27)	-151.8(2)
P(15)-Rh(1)-C(28)-C(27)	104.69(17)
C(30)-Rh(1)-C(28)-C(29)	3.79(18)
C(31)-Rh(1)-C(28)-C(29)	40.33(18)
C(27)-Rh(1)-C(28)-C(29)	106.1(2)
P(12)-Rh(1)-C(28)-C(29)	-45.7(4)
P(15)-Rh(1)-C(28)-C(29)	-149.25(16)
C(5)-C(4)-C(3)-C(2)	0.0(5)
C(21)-C(26)-C(25)-C(24)	-1.9(4)
C(4)-C(3)-C(2)-C(1)	0.0(5)
C(6)-C(1)-C(2)-C(3)	-0.1(5)
C(26)-C(25)-C(24)-C(23)	0.0(5)
C(25)-C(24)-C(23)-C(22)	1.8(5)
C(21)-C(22)-C(23)-C(24)	-1.8(5)
C(28)-C(29)-C(33)-C(32)	52.2(3)
C(30)-C(29)-C(33)-C(32)	-52.7(3)
C(27)-C(32)-C(33)-C(29)	-51.7(3)
C(31)-C(32)-C(33)-C(29)	53.2(3)

Figure 6S. ^1H NMR of compound **21** (400 MHz, CDCl_3).

Figure 7S. ^{13}C NMR of compound **21** (100 MHz, CDCl_3).

Figure 8S. ^1H NMR of compound **23** (400 MHz, CDCl_3).

Figure 9S. ^{13}C NMR of compound **23** (100 MHz, CDCl_3).

Figure 10S. ^1H NMR of compound **20** (400 MHz, CDCl_3).

Figure 11S. ^{13}C NMR of compound **20** (100 MHz, CDCl_3).

Figure 12S. ¹H NMR of compound **25** (400 MHz, CDCl₃).

Figure 13S. ^{13}C NMR of compound **25** (100 MHz, CDCl_3).

Figure 14S. ^1H NMR of compound **19** (400 MHz, CDCl_3).

Supporting Information References

¹ Wolf, J.P., III; Neimann, C. *Biochemistry*, **1963**, 2, 493.

² Vineyard, B.D.; Knowles, W.S.; Sabacky, M.J.; Bachman, G.L.; Weinkauff, D.J.; *J. Am. Chem. Soc.*, **1977**, 99, 5946.

³ Polniaszek, R.P.; Foster, A.L.; *J. Org. Chem.* **1991**, 56, 3137.