Stereochemistry of Palladium-Mediated Synthesis of PAMP-BH_3: Retention of Configuration at P in Formation of Pd-P and P-C Bonds

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SUPPORTING INFORMATION

Experimental Section

General Details Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere at room temperature in a dry box, or using standard Schlenk techniques. Petroleum ether (bp 38-53 °C), ether, THF, CH_2Cl_2 and toluene were dried and degassed using columns containing activated alumina,[1] or dried and distilled before use from Na/benzophenone (CH_2Cl_2 was distilled from CaH_2).

NMR spectra were recorded on Varian 500 or 300 MHz spectrometers. ^1H and ^{13}C NMR chemical shifts are reported relative to Me_4Si and were determined by reference to the residual ^1H or ^{13}C solvent peaks. ^{31}P NMR chemical shifts are reported relative to H_3PO_4 (85%) used as an external reference. Unless otherwise noted, peaks in NMR spectra are singlets. Infrared spectra were recorded on KBr pellets with a Perkin-Elmer 1600 series FTIR instrument and are reported in cm^{-1}. Elemental analyses were provided by Schwarzkopf Microanalytical Laboratory. Mass spectra were obtained at the University of Illinois Urbana-Champaign.

The following compounds were prepared using a previously reported procedure: (S_P)-PH(Me)(Ph)(BH_3),[2] $Pd(dba)_2$,[3] $Pd(COD)Cl_2$.[4] (R_P)-PH(Me)(Ph)(BH_3)[5] was prepared using a modification of the literature method; (–)-menthol gave (S_P)-PH(Me)(Ph)(BH_3) as the major product as reported, but

(+)-menthol yielded (R_P)-PH(Me)(Ph)(BH_3) as the major product. The ee of PH(Me)(Ph)(BH_3) was determined by chiral HPLC (Chiracel OJ-H, 10% i-PrOH/hexane, flow rate 1 mL/min, retention times are 12.1 (R) and 12.9 (S) minutes). Racemic PH(Me)(Ph)(BH_3) was prepared from BH_3-THF or BH_3-SMe_2 and PH(Me)(Ph), obtained commercially or by a literature method.[6]

Pd(TMEDA)(*o*-An)(I) To a stirred suspension of $Pd(dba)_2$ (2.03 g, 3.55 mmol) in toluene (20 mL) were added TMEDA (697 µL, 4.62 mmol) and *o*-iodoanisole (660 µL, 5.08 mmol) under N_2. The reaction mixture was heated to 55 °C at which point it turned green and became homogeneous. Once cooled back to room temperature, the reaction mixture was filtered to remove suspended Pd metal particles. The solvent was then removed from the filtrate *in vacuo* to yield an air stable yellow solid. This product was washed with diethyl ether (3 x 10 mL) and collected on a fine frit. The diethyl ether fraction was concentrated to ca. 20 mL and cooled at -25 °C. At this temperature, both dba and the product precipitated from solution. As the solution warmed to room temperature, however, the dba redissolved and more product was collected as a yellow solid. Recrystallization from CH_2Cl_2/diethyl ether afforded yellow crystals suitable for crystallographic and elemental analysis. Three crops of product were obtained (total yield: 1.21 g, 75% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21-7.18 (m, 1H, Ar), 6.88-6.83 (m, 1H, Ar), 6.82-6.64 (m, 1H, Ar), 6.52-6.49 (m, 1H, Ar), 3.85 (3H, OMe), 2.82-2.53 (m, 4H, CH_2), 2.73 (3H, Me), 2.72 (3H, Me), 2.39 (3H, Me), 2.34 (3H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 161.7 (quat, Ar), 137.4 (Ar), 130.0 (quat, Ar), 123.4 (Ar), 119.7 (Ar), 109.7 (Ar), 61.9 (CH_2), 58.3 (CH_2), 55.6 (OMe), 50.0 (Me), 49.9 (Me), 49.6 (Me), 49.1 (Me). IR: 2911, 2879, 1728, 1556, 1450, 1283, 1222, 1172, 1117, 1050, 1022, 950, 800, 750, 722, 694, 500, 472. Anal. Calcd. for $C_{13}H_{23}IN_2OPd\cdot(CH_2Cl_2)_{0.36}$: C, 32.94; H, 4.91; N, 5.75. Found: C, 32.91; H, 4.90; N, 5.70 (the presence of solvent was quantitatively confirmed by NMR).

***trans*-Pd(PPh_3)$_2$(*o*-An)(I)** This complex was prepared by a modification of a literature procedure.[7] To a bright yellow stirred suspension of $Pd(PPh_3)_4$ (2.00

g, 1.73 mmol) in toluene (10 mL) was added *o*-AnI (343 µL, 2.64 mmol, 1.5 equiv), which caused the suspension to become pale yellow. The suspension was allowed to stir under N_2 for 1 h and was then filtered. The pale yellow solid was washed with diethyl ether (3 x 15 mL) to yield 1.20 g (80%) of crude product which was used in subsequent reactions without further purification. $^{31}P\{^1H\}$ NMR (THF): δ 25.1.

Pd((S,S)-Chiraphos)(*o*-An)(I) (3) Method 1 To a solution of *trans*-$Pd(PPh_3)_2$(*o*-An)(I) (203 mg, 0.234 mmol) in toluene (6 mL) was added a solution of (S,S)-Chiraphos (100 mg, 0.234 mmol) in toluene (6 mL). The pale yellow suspension was stirred at room temperature for 72 h. The toluene was removed *in vacuo*. Petroleum ether (12 mL) was added and the suspension was allowed to stir for 24 h. The air stable, yellow solid was collected on a fine frit and dried to yield 80 mg (48%) of crude product.

Method 2 To a stirred solution of Pd(TMEDA)(*o*-An)(I) (1.000 g, 2.19 mmol) in THF (5 mL) was added, dropwise, a solution of (S,S)-Chiraphos (934 mg, 2.19 mmol) in THF (5 mL). The solution was stirred for 24 h and a yellow solid precipitated. The solid was collected on a fine frit, rinsed with THF (0.5 mL) and petroleum ether (20 mL) and dried on the frit to yield 1.212 g (72% yield) of analytically pure product. The washes were combined with the original mother liquor and a second crop precipitated at room temperature (total yield: 1.437 g, 85% yield).

NMR spectra showed two atropisomers (A and B) in a 6:1 ratio. ^1H NMR (300 MHz, CD_2Cl_2): δ 8.10-8.04 (m, 1H A and 5H B, Ar), 7.89-7.83 (m, 3H A, Ar), 7.70-7.47 (m, 11H A and 8H B, Ar), 7.37-7.32 (m, 1H A and 2H B, Ar), 7.25-7.23 (m, 3H B, Ar), 7.18-7.14 (m, 2H A, Ar), 6.99-6.94 (m, 1H A and 2H B, Ar), 6.83-6.70 (m, 3H A and 3H B, Ar), 6.50-6.45 (m, 1H A and 1H B, Ar), 6.12-6.08 (m, 1H A, Ar), 3.35 (3H B, OMe), 3.14 (3H A, OMe), 2.44-2.33 (m, 1H A and 1H B, CH), 2.19-2.04 (m, 1H A and 1H B, CH), 1.10-0.97 (m, 6H A and 6H B, Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 161.7 (Ar), 143.1 (d, J = 127, Ar, quat), 137.5 (Ar), 137.2 (d, J = 13, Ar), 136.8 (d, J = 13, Ar), 132.9 (d, J = 9, Ar), 132.3 (d, J = 3, Ar), 131.9 (d, J

= 8, Ar), 131.7 (Ar), 130.4 (d, J = 2, Ar), 130.0 (d, J = 3, Ar), 129.8 (d, J = 57, Ar, quat), 129.0 (Ar), 128.9 (Ar), 128.8 (Ar), 128.7 (d, J = 3, Ar), 128.58 (d, J = 2, Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 128.03 (Ar), 127.7 (Ar), 126.1 (d, J = 45, Ar, quat), 124.2 (Ar), 120.0 (d, J = 8, Ar), 109.9 (d, J = 5, Ar), 54.5 (OMe), 36.8 (dd, J = 27, 23, CH), 34.0 (dd, J = 24, 15, CH), 14.4-13.9 (m, Me). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 56.5 (d, J = 39, B), 55.4 (d, J = 36, A), 42.5 (d, J = 39, B), 41.8 (d, J = 36, A). IR: 3036, 2966, 2907, 1560, 1482, 1449, 1431, 1219, 1102, 1055, 1020, 743, 690, 544, 520. Anal. Calcd. for $C_{35}H_{35}IOP_2Pd$: C, 54.82; H, 4.60. Found: C, 54.83; H, 4.71.

Separation of the diastereomers of Pd((S,S-Chiraphos)(*o*-An)(P(Me)(Ph)(BH_3)) (4) and isolation of pure Pd((S,S-Chiraphos)(*o*-An)(S_P-P(Me)(Ph)(BH_3)) (4a) Pd((S,S)-Chiraphos)(*o*-An)(I) (300 mg, 0.391 mmol) was suspended in toluene (4 mL) with vigorous stirring and *rac*-PH(Me)(Ph)(BH_3) (54 mg, 0.39 mmol) was added as a solution in toluene (2 mL). $NaOSiMe_3$ (0.371 mL, 1.0 M solution in THF, 0.37 mmol) was then added slowly by syringe causing the mixture to darken somewhat, and the slurry was stirred for 30 min at room temperature. The reaction mixture was filtered through Celite on a glass-sintered frit in the glove box to remove NaI and the Celite washed with several portions of toluene (total 5 mL) giving a golden yellow solution. (Exhaustive extraction of the Celite/solid with large volumes of toluene is necessary to ensure complete extraction of all of the less soluble diastereomer). Removal of all volatiles *in vacuo* left a sticky orange solid, to which Et_2O (5 mL) was added with vigorous stirring, causing a white solid to precipitate. The mixture was stirred for 10 min and then the white solid was isolated by filtration on a glass-sintered frit, washed with Et_2O (3 mL) and dried *in vacuo*. NMR spectroscopy revealed this solid to be highly enriched in **4a** and its atropisomer **4d** (typically greater than 90% de), and it was found to be analytically pure. The Et_2O-soluble fraction was pumped down to give a sticky orange solid. NMR analysis of this material showed it contained mainly **4b** but also significant quantities of siloxy-containing byproducts. Typical yield of **4a**: 100 mg (33%, 0.131 mmol). Crystals that were suitable for X-ray

analysis were obtained by slow (11 months) diffusion of petroleum ether into a concentrated THF solution of diastereomerically pure **4a** at -25 °C.

Anal. Calcd for $C_{42}H_{46}P_3BOPd$: C, 64.93; H, 5.97. Found: C, 64.60; H, 5.78. ^{1}H NMR (THF-d_8): δ 8.12-8.08 (m, 2H, Ar), 7.95-7.91 (m, 2H, Ar), 7.63-7.50 (m, 6H, Ar), 7.35-7.17 (m, 7H, Ar), 7.15-7.11 (m, 2H, Ar), 6.83-6.82 (m, 1H, Ar), 6.77-6.72 (m, 3H, Ar), 6.70-6.64 (m, 4H, Ar), 6.48-6.45 (m, 1H, Ar), 6.21-6.18 (m, 1H, Ar), 3.23 (OMe), 2.12-2.01 (m, 2H, CH), 0.93-0.87 (m, 6H, Chiraphos Me), 0.44 (dd, J_{PH} = 9, 2, 3H, P-Me). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 161.6 (Ar), 150.0 (Ar), 149.2 (Ar), 143.1 (d, J = 26, Ar), 137.8-137.7 (m, Ar), 137.6 (d, J = 13, Ar), 137.4 (d, J = 13, Ar), 134.4-134.3 (m, Ar), 132.8 (d, J = 10, Ar), 132.2 (d, J = 2, Ar), 132.1-132.0 (m, Ar), 131.9 (Ar), 129.3 (d, J = 11, Ar), 129.2 (Ar), 128.9 (d, J = 9, Ar), 128.8 (d, J = 10, Ar), 128.5 (d, J = 9, Ar), 128.2 (Ar), 127.9 (Ar), 127.6-127.5 (m, Ar), 127.3 (Ar), 127.0 (d, J = 8, Ar), 124.3 (Ar), 120.5 (d, J = 7, Ar), 109.8 (Ar), 54.7 (OMe), 38.5-38.2 (m, CH), 33.6-33.3 (m, CH), 16.7 (d, J = 24, P-Me), 14.6-14.4 (m, Chiraphos Me), 14.0-13.8 (m, Chiraphos Me). ^{31}P{^{1}H} NMR (THF-d_8): δ 52.1 (dd, J = 291, 38), 50.9 (dd, J = 38, 16), 7.0 (broad d, J = 291). FAB-MS (Magic Bullet): m/z 775 $(M-H)^+$, 762, 685, 655, 532 $[Pd(Chiraphos)]^+$, 476, 455, 398, 371, 309, 291, 263, 243, 195, 155, 135, 119.

Purified samples of **4a**, and those formed *in situ* by reaction of **3** with **1**, contained small amounts of atropisomer **4d**, which was identified by ^{31}P{^{1}H} NMR and ^{1}H NMR. The **4a**:**4d** ratio ranged from ca. 10:1 to 40:1 and seemed to depend on conditions. Data for **4d**: ^{31}P{^{1}H} NMR (THF-d_8): δ 48.4 (dd, J = 292, 36), 45.5 (dd, J = 36, obscured by signals of **4a** so the other coupling could not be measured), –12.6 (br d, J = 292). ^{1}H NMR (THF-d_8): δ 3.29 (OMe), 0.67 (dd, J_{PH} = 8, 4, P*Me*).

Diastereoselective synthesis of Pd((S,S)-Chiraphos)(*o*-An)((R_P)-P(Me)(Ph)(BH_3)) (4b) Pd((S,S)-Chiraphos)(*o*-An)(I) (250 mg, 0.326 mmol) and (S_P)-PH(Me)(Ph)(BH_3) (45 mg, 0.33 mmol) were weighed in the glove box and transferred to a Schlenk flask with THF (total 5 mL). The flask was removed from the glove box and cooled to -78 °C and $NaOSiMe_3$ (0.326 mL, 1.0 M solution in

THF, 0.33 mmol) was added by syringe under N_2. The mixture was allowed to stir at -78 °C for 2 hours, then the cold bath was removed and the mixture allowed to warm to room temperature. All volatiles were then removed *in vacuo* to yield a pale orange sticky solid which darkened over time. The residue was washed with Et_2O (5 mL) and the washings stripped *in vacuo* to give a sticky red solid. ^{1}H NMR (THF-d_8) analysis of the solid revealed small amounts of **4b** and **4a** (in approximate ratio 92:8) and large quantities of a $OSiMe_3$-containing impurity. The Et_2O-insoluble material was then extracted with toluene (total 15 mL), filtered through Celite and reduced in volume to *ca*. 3 mL *in vacuo*. The brown/purple solution was layered with petroleum ether (10 mL) and stored at –25 °C for 24 hours. A pale pink solid was isolated by decantation, washed with petroleum ether (2 mL) and dried *in vacuo*. ^{1}H NMR spectroscopy revealed this solid to contain **4b** (and its atropisomer **4c**) in *de* >99 %. Yield: 175 mg (0.229 mmol, 70%).

Crystals that were suitable for X-ray analysis were obtained from ether at –25 °C. After the structure of **4b** was determined by X-ray crystallography, the single crystal used for the structure determination was dissolved in THF-d_8 and its ^{1}H NMR spectrum was obtained, to correlate the NMR data for **4a** and **4b** to their absolute configurations.

Anal. Calcd for $C_{42}H_{46}P_3BOPd$: C, 64.93; H, 5.97. Found: C, 64.58; H, 5.83. ^{1}H NMR (THF-d_8): δ 8.34-8.30 (m, 2H, Ar), 7.82-7.79 (m, 2H, Ar), 7.63-7.45 (m, 8H, Ar), 7.35-7.32 (m, 1H, Ar), 7.26-7.17 (m, 5H, Ar), 7.13-7.05 (m, 3H, Ar), 6.91-6.88 (m, 1H, Ar), 6.84-6.81 (m, 2H, Ar), 6.67-6.65 (m, 3H, Ar), 6.46-6.43 (m, 1H, Ar), 6.00-5.97 (m, 1H, Ar), 3.11 (OMe), 2.11-2.05 (m, 1H, CH), 1.98-1.94 (m, 1H, CH), 0.98 (dd, J = 10, 7, 3H, Me), 0.90 (dd, J = 10, 7, 3H, Me), 0.59 (dd, J_{PH} = 8, 3, P-Me). ^{31}P{^{1}H} NMR (THF-d_8): δ 54.3 (dd, J = 287, 36), 49.5 (dd, J = 36, 27), -9.1 (broad d, J = 287).

Purified samples of **4b**, and those formed *in situ* by reaction of **3** with **1**, contained small amounts of atropisomer **4c**, which was identified by ^{31}P{^{1}H} NMR and ^{1}H NMR. The **4b**:**4c** ratio was consistently ca. 30:1 in isolated samples, but

varied from ca. 10 to 20 in crude material, depending on reaction conditions for the transmetalation. Data for **4c**: $^{31}P\{^{1}H\}$ NMR (THF-d_8): δ 47.2 (dd, J = 292, 37), 45.1 (dd, J = 37, 27), –5.0 (br d, J = 292). ^{1}H NMR (THF-d_8): δ 3.41 (OMe), 1.33-1.28 (m, Me), 0.44 (dd, J_{PH} = 8, 3, PMe).

Kinetic Resolution. Synthesis of 4a. Pd((S,S)-Chiraphos)(*o*-An)(I) (139 mg, 0.181 mmol) was weighed into a vial and slurried in toluene (2 mL), and a solution of *rac*-PH(Me)(Ph)(BH_3) (50 mg, 0.36 mmol, 2 equiv) in toluene (2 mL) was added. $NaOSiMe_3$ (181 μL, 1.0 M solution in THF, 0.18 mmol) was then added via microliter syringe and the yellow slurry stirred for 30 min at room temperature. All volatiles were removed *in vacuo* to leave a sticky pale yellow residue. ^{1}H NMR spectroscopic analysis of this solid (THF-d_8) indicated a ratio of diastereomers (and accompanying atropisomers) of Pd((S,S)-Chiraphos)(*o*-An)(P(Me)(Ph)(BH_3)) **4a**/**4b** of 5.84:1 giving an overall de of 70% (the same result was obtained in a second run). The resultant solid was extracted with Et_2O (10 mL) and the yellow extracts pumped down to give a sticky yellow solid, containing **4b**, PH(Me)(Ph)(BH_3) and siloxy-containing impurities. The residual PH(Me)(Ph)(BH_3) was isolated by chromatography of this solid on silica gel eluting with hexane:CH_2Cl_2 (1:1). Chiral HPLC analysis of the isolated PH(Me)(Ph)(BH_3) showed it to be enriched in (S_P)-PH(Me)(Ph)(BH_3) with an ee of approximately 30%.

The Et_2O-insoluble material was dissolved in toluene (total 15 mL), filtered, and the solution reduced in volume to *ca.* 4 mL at which point white solid started to precipitate. The solution was layered with pentane (10 mL) and stored at -25 °C for 3 d to yield 111 mg (0.145 mmol, 80% yield) of Pd((S,S-Chiraphos)(*o*-An)((S_P)-P(Me)(Ph)(BH_3)) (**4a**) of >99% de (as shown by ^{1}H NMR in THF-d_8).

General Procedure for Transmetalation Experiments In the glove box, Pd((S,S)-Chiraphos)(*o*-An)(I) (28 mg, 0.037 mmol) was transferred to an NMR tube as a slurry in THF-d_8 (1 mL) along with a solution of enantioenriched PH(Me)(Ph)(BH_3) (5 mg, 0.036 mmol) of known ee in THF-d_8 (0.5 mL). The tube

was fitted with a rubber septum and cooled to -78 °C in a dry ice/acetone bath. $NaOSiMe_3$ (36.2 μL, 1.0 M solution in THF, 0.036 mmol) was then added by microliter syringe. After 1 minute, the tube was inverted to ensure complete mixing; the tube was kept in the bath for a further 15 min and inverted every 5 min. It was then allowed to warm to room temperature, and the ^1H and ^{31}P NMR spectra were recorded. The de of the product was calculated from integration of the OMe signals of both diastereomers and their respective atropisomers in the ^1H NMR spectrum.

General Procedure for Reductive Elimination A solution of highly diastereomerically enriched Pd((S,S)-Chiraphos)(*o*-An)(P(Me)(Ph)(BH_3)) (typical scale 50 mg) in THF-d_8 was transferred to an NMR tube, along with a solution of $FeCp_2$ (*ca*. 5 mg) and diphenylacetylene (4 equiv) in THF-d_8. (Use of a smaller excess of diphenylacetylene was found to result in lower ee's and increased OMe-containing impurities). Initial ^1H and ^{31}P NMR spectra were recorded and the initial de (ratio (**4a** + **4d**)/(**4b** + **4c**)) determined by integration of the OMe signals in the ^1H NMR spectra; similarly, the initial ratio of Pd (total OMe signals):$FeCp_2$ was also determined.

The NMR tube was then placed in an oil bath at 50 °C and monitored by NMR spectroscopy periodically. A small amount of solid was seen to deposit during the course of the reaction. Reactions were typically run for 42 hours (**4b**) and 72 hours (**4a**), since the rate of reductive elimination was different for the two diastereomers. The use of longer reaction times to effect near complete conversion generally resulted in the appearance of extra unidentified signals in the spectra, indicating decomposition by other pathways. Formation of PAMP-BH_3 was indicated by the appearance of a singlet at 3.67 ppm in the ^1H NMR spectrum (and a quartet at 10.2 ppm in the ^{31}P NMR spectrum) and of Pd((S,S-Chiraphos)(PhC≡CPh) by a singlet at 49.9 ppm in the ^{31}P NMR spectrum. Other significant byproducts observed in these reactions are detailed in Table S1.

The reaction mixture was then transferred to a vial in air, the tube washed with additional THF and the solvent removed *in vacuo*. The residue was

extracted with Et_2O in several portions (total 10 mL) and again the solvent was removed *in vacuo*. PAMP-BH_3 was then isolated by preparative TLC on silica, loading the residue as a solution in CH_2Cl_2 and eluting with hexanes/ethyl acetate (2:1). NMR yields of PAMP-BH_3 ranged from 50-70% and isolated yields were typically 20%. The identity of the product was confirmed by ^1H NMR ($CDCl_3$ or C_6D_6) and the ee was determined by chiral HPLC (Chiralpak AD, 1% *i*-PrOH/hexane, flow rate 1 mL/min, retention times are 11.8 (S) and 13.4 minutes (R)). Retention times were compared to those of the racemate and authentic (R_P)-PAMP-BH_3 prepared by the method of Livinghouse run under identical conditions.[8]

Pd((S,S)-Chiraphos)Cl_2 This compound was previously synthesized by a different method.[9] To a stirred slurry of Pd(COD)Cl_2 (150 mg, 0.52 mmol) in CH_2Cl_2 (2 mL) was added a solution of (S,S)-Chiraphos (224 mg, 0.52 mmol) in CH_2Cl_2. The mixture became homogeneous and then a white solid precipitated. The reaction mixture was stirred for 25 min. The solid was collected on a fine frit, rinsed with diethyl ether and dried on the frit to yield 240 mg of product. The ether was added to the CH_2Cl_2 mother liquor to yield a second crop of product (35 mg, total yield: 275 mg, 87%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 66.6.

Pd((S,S)-Chiraphos)(PhC≡CPh) (5) A slurry of Pd((S,S)-Chiraphos)Cl_2 (110 mg, 0.182 mmol) and diphenylacetylene (65 mg, 0.36 mmol) was stirred in dry THF (4 mL) and a solution of $NaBH(OMe)_3$ (93 mg, 0.73 mmol) in THF (3 mL) was added dropwise. During the addition the reaction mixture instantly darkened and at the end of the addition was yellow-brown. The mixture was allowed to stir for a further 20 min to give a dark brown slurry and then all volatiles were removed *in vacuo*. The residue was extracted repeatedly with toluene (total 10 mL), and the resulting solution was filtered through Celite and concentrated to *ca.* 2 mL. This solution was layered with petroleum ether (5 mL), and cooled to -25 °C for 24 h, after which time a dirty yellow solid was isolated and dried *in vacuo*. Isolated yield: 50 mg (0.07 mmol, 39%).

^{1}H NMR (THF-d_8): δ 7.89-7.75 (m, 8H, Ar), 7.49-7.34 (m, 4H, Ar), 7.31-6.97 (m, 18H, Ar), 2.62 (br, 2H, CH), 0.84 (br, 6H, Me). ^{13}C{^{1}H) NMR (THF-d_8): 137.7-137.4 (m), 136.5 (apparent t, J = 8), 135.5 (apparent t, J = 11), 135.1-134.8 (m), 134.0 (apparent t, J = 7), 131.6 (apparent t, J = 3), 130.8, 130.0, 129.8, 129.4 (apparent t, J = 4), 129.1, 128.8 (apparent t, J = 5), 128.5, 126.3, 126.2, 124.5, 123.7, 40.2 (apparent t, J = 21, CH), 17.5 (apparent t, J = 4, Me). ^{31}P{^{1}H} NMR (THF-d_8): δ 49.9. IR: 3056, 2956, 2922, 1800, 1644, 1583, 1478, 1433, 1256, 1094, 1022, 800, 750, 689, 528. Anal. Calcd for $C_{42}H_{38}P_2Pd$: C, 70.94; H, 5.39. Found: C, 70.57; H, 5.34.

Table S1. Reductive Elimination of PAMP-BH_3 (**2**) from Pd((S,S)-Chiraphos)(*o*-An)(P(Me)(Ph)(BH_3)) (**4**)[a]

Entry	Isomer de (%)[b]	Time (h)	Conversion (%)[c]	Yield (%)[d]	ee (%)[e]	Yield (%) (other MeO products)[f]	Decomp-osition (%)[g]
1	**4a** (94, S)	72	84	51 (21) *(61, 25)*	91 (93)	4, 4, 0	27
2	**4a** (94, S)	96	87	73 (20) *(83, 23)*	87 (93)	3, 3, 0	10
3	**4b** (100, R)	37	96	54 (20) *(56, 21)*	98	2, 1, 0	40
4	**4b** (88, R)	48	91	70 (21) *(78, 24)*	93 (92)	3, 5, 0	12

[a] A solution of **4**, ferrocene (internal standard), and diphenylacetylene (4 equiv) in THF-d_8 was heated at 50 °C and the progress of the reaction was monitored by ^{1}H and ^{31}P NMR. Workup: solvent was removed under vacuum and the residue was extracted with ether. PAMP-BH_3 was isolated by preparative TLC. For further details, see the experimental section.

[b] de was determined by integration of the MeO signals in the initial ^{1}H NMR spectrum, including the atropisomers **4c** and **4d**.

[c] Conversion of **4** was determined by integration of its MeO signals at the start and finish of the reaction.

[d] Yields of PAMP-BH_3 were determined by NMR integration (MeO resonance). Isolated yields are in parentheses. The figures in italics are NMR and isolated yields corrected for incomplete conversion.

[e] ee was determined by chiral HPLC (Chiralpak AD, see the experimental section). Because the diastereomers of **4** undergo reductive elimination at different rates, experiments involving incomplete conversion and in which **4** is not diastereopure are expected to lead to PAMP-BH_3 product with ee different from

the initial de of **4**. In these cases, the theoretical maximum ee of **4** is given in parentheses, as determined by NMR integration (MeO signals).

[f] Several MeO-containing products were observed. These include unknown impurities with MeO signals at δ 3.84 (X) and 3.65 (Z), and anisole (Y, δ 3.74). Their NMR yields (format: X, Y, Z) were determined by integration. In addition, $Pd(Chiraphos)_2$ was observed as a byproduct by ^{31}P NMR (ca. 4-8%, compared to **5**),[10] and unidentified impurities (^{31}P NMR singlets at 26.5 and 23.8 ppm) were observed in entry 1.

[g] The extent of decomposition was measured by comparing the integration of the initial MeO signals of **4** with the integrals of PAMP-BH_3 and the other products. The incomplete mass balance is reflected in the numbers given for % decomposition. In some cases, the sum of the yields of PAMP-BH_3 and X, Y and Z, plus the precent decomposition, is not 100%, due to rounding errors.

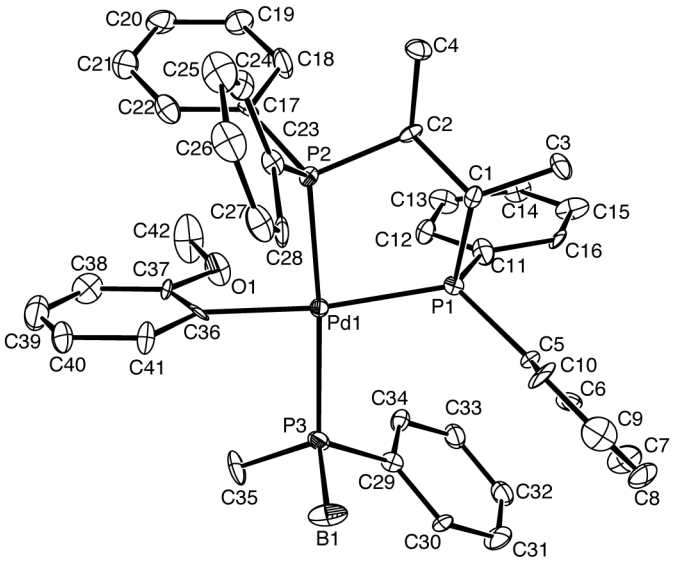

Figure S1. Complete ORTEP diagram of (S_P)-Pd((S,S)-Chiraphos)(*o*-An)(P(Me)(Ph)(BH_3)) (**4a**).

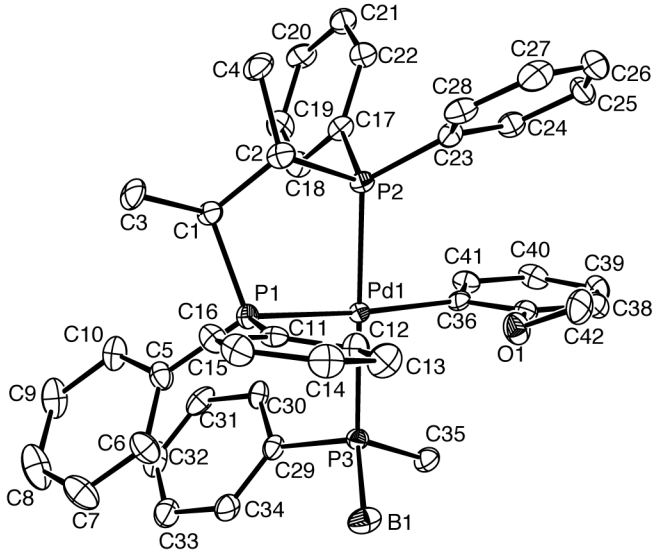

Figure S2. Complete ORTEP diagram of (R_P)-Pd((S,S)-Chiraphos)(*o*-An)(P(Me)(Ph)(BH_3)) (**4b**).

Table S2. Crystal data and structure refinement for (S_P)-Pd[(S,S)Chiraphos](*o*-An)[P(Me)(Ph)(BH_3)] (**4a**).

Identification code	glu97	
Empirical formula	$C_{42}H_{46}BOP_3Pd$	
Formula weight	776.91	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 9.9307(14) Å	α = 90°.
	b = 15.139(2) Å	β= 107.892(3)°.
	c = 13.712(2) Å	γ = 90°.
Volume	1961.7(5) $Å^3$	
Z	2	
Density (calculated)	1.315 Mg/m^3	
Absorption coefficient	0.626 mm^{-1}	
F(000)	804	
Crystal size	0.08 x 0.06 x 0.04 mm^3	
Theta range for data collection	1.56 to 28.28°.	
Index ranges	$-12\leq h\leq 13$, $-19\leq k\leq 17$, $-18\leq l\leq 13$	
Reflections collected	9833	
Independent reflections	6403 [R(int) = 0.1049]	
Completeness to theta = 28.28°	86.3 %	
Absorption correction	Empirical from SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6403 / 1 / 434	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R_1 = 0.0787, wR^2 = 0.1141	
R indices (all data)	R_1 = 0.1501, wR^2 = 0.1389	
Absolute structure parameter	0.10(4)	
Largest diff. peak and hole	1.117 and -1.226 e.$Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (S_P)-Pd[(S,S)Chiraphos](*o*-An)[P(Me)(Ph)(BH_3)]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	8802(1)	5767(1)	2516(1)	17(1)
P(1)	7043(3)	5314(2)	1065(3)	17(1)
P(2)	7117(3)	6725(2)	2735(3)	20(1)
P(3)	10699(3)	4954(2)	2323(3)	23(1)
B(1)	11660(13)	5546(8)	1467(12)	38(5)
C(35)	11994(11)	4654(8)	3523(10)	39(4)
C(1)	5746(10)	6227(6)	732(8)	18(3)
C(2)	5447(10)	6510(7)	1714(9)	19(3)
C(3)	4433(10)	6065(7)	-174(9)	29(3)
C(4)	4354(10)	7259(7)	1571(10)	27(3)
C(5)	7351(10)	5063(8)	-173(9)	22(3)
C(6)	7444(10)	4216(7)	-474(10)	28(3)
C(7)	7729(12)	4068(9)	-1390(11)	46(4)
C(8)	7902(12)	4775(9)	-1978(10)	42(4)
C(9)	7863(11)	5629(11)	-1632(10)	44(4)
C(10)	7601(10)	5770(12)	-739(8)	37(3)
C(11)	6027(9)	4411(7)	1330(10)	19(3)
C(12)	6246(12)	4199(6)	2379(10)	26(3)
C(13)	5402(12)	3572(8)	2648(11)	33(3)
C(14)	4310(12)	3142(7)	1858(10)	30(3)
C(15)	4119(12)	3339(7)	851(11)	36(4)
C(16)	4960(10)	3977(7)	580(9)	20(3)
C(17)	6700(10)	6759(8)	3937(10)	24(3)
C(18)	5515(12)	6282(8)	4058(11)	41(4)
C(19)	5273(13)	6256(8)	4974(11)	41(4)
C(20)	6179(13)	6702(9)	5808(11)	40(4)
C(21)	7315(13)	7149(9)	5700(11)	44(4)
C(22)	7580(12)	7175(8)	4782(11)	34(3)
C(23)	7496(10)	7877(7)	2493(9)	20(3)
C(24)	6853(11)	8576(7)	2812(9)	30(3)

C(25)	7077(13)	9427(8)	2506(11)	48(4)
C(26)	7948(12)	9572(8)	1927(11)	40(4)
C(27)	8619(14)	8881(10)	1642(12)	35(4)
C(28)	8405(11)	8026(8)	1918(9)	29(3)
C(29)	10176(10)	3870(7)	1814(9)	21(3)
C(30)	10526(10)	3550(7)	965(9)	24(3)
C(31)	10108(12)	2726(8)	532(11)	37(4)
C(32)	9323(11)	2189(8)	953(11)	34(3)
C(33)	8968(13)	2485(9)	1794(12)	34(4)
C(34)	9406(11)	3284(7)	2245(10)	25(3)
C(36)	10151(10)	6240(8)	3852(10)	23(3)
C(37)	10134(10)	5849(10)	4741(10)	29(3)
C(38)	10994(13)	6132(8)	5702(11)	42(4)
C(39)	11902(14)	6815(9)	5743(12)	51(4)
C(40)	11957(12)	7236(8)	4881(11)	40(4)
C(41)	11095(12)	6934(8)	3943(10)	33(3)
C(42)	9015(16)	4763(10)	5531(11)	71(5)
O(1)	9217(8)	5138(5)	4625(7)	40(2)

Table S4. Bond lengths [Å] and angles [deg] for (S_P)-Pd[(S,S)Chiraphos](*o*-An)[P(Me)(Ph)(BH_3)].

Pd(1)-C(36)	2.038(12)	C(23)-C(24)	1.375(14)
Pd(1)-P(2)	2.302(3)	C(23)-C(28)	1.387(15)
Pd(1)-P(1)	2.312(3)	C(24)-C(25)	1.394(15)
Pd(1)-P(3)	2.333(3)	C(25)-C(26)	1.358(17)
P(1)-C(11)	1.801(11)	C(26)-C(27)	1.361(18)
P(1)-C(1)	1.849(10)	C(27)-C(28)	1.382(16)
P(1)-C(5)	1.854(12)	C(29)-C(30)	1.400(14)
P(2)-C(17)	1.820(12)	C(29)-C(34)	1.413(14)
P(2)-C(23)	1.837(11)	C(30)-C(31)	1.389(14)
P(2)-C(2)	1.842(11)	C(31)-C(32)	1.370(15)
P(3)-C(29)	1.796(11)	C(32)-C(33)	1.382(18)
P(3)-C(35)	1.808(12)	C(33)-C(34)	1.366(16)
P(3)-B(1)	1.944(12)	C(36)-C(37)	1.360(17)
C(1)-C(3)	1.519(14)	C(36)-C(41)	1.388(14)
C(1)-C(2)	1.526(14)	C(37)-O(1)	1.388(15)
C(2)-C(4)	1.540(13)	C(37)-C(38)	1.400(16)
C(5)-C(6)	1.358(14)	C(38)-C(39)	1.361(16)
C(5)-C(10)	1.389(18)	C(39)-C(40)	1.358(18)
C(6)-C(7)	1.388(17)	C(40)-C(41)	1.386(17)
C(7)-C(8)	1.382(17)	C(42)-O(1)	1.435(14)
C(8)-C(9)	1.383(19)		
C(9)-C(10)	1.345(14)	C(36)-Pd(1)-P(2)	88.0(3)
C(11)-C(16)	1.394(14)	C(36)-Pd(1)-P(1)	172.7(3)
C(11)-C(12)	1.424(16)	P(2)-Pd(1)-P(1)	84.96(11)
C(12)-C(13)	1.390(14)	C(36)-Pd(1)-P(3)	87.5(3)
C(13)-C(14)	1.432(16)	P(2)-Pd(1)-P(3)	172.64(11)
C(14)-C(15)	1.367(17)	P(1)-Pd(1)-P(3)	99.71(11)
C(15)-C(16)	1.400(13)	C(11)-P(1)-C(1)	103.1(4)
C(17)-C(22)	1.371(16)	C(11)-P(1)-C(5)	106.8(6)
C(17)-C(18)	1.432(14)	C(1)-P(1)-C(5)	103.0(5)
C(18)-C(19)	1.351(17)	C(11)-P(1)-Pd(1)	112.0(4)
C(19)-C(20)	1.393(17)	C(1)-P(1)-Pd(1)	106.0(3)
C(20)-C(21)	1.362(16)	C(5)-P(1)-Pd(1)	123.7(3)
C(21)-C(22)	1.363(17)	C(17)-P(2)-C(23)	104.7(5)

C(17)-P(2)-C(2)	106.9(5)	C(19)-C(18)-C(17)	120.6(13)
C(23)-P(2)-C(2)	102.5(5)	C(18)-C(19)-C(20)	119.7(12)
C(17)-P(2)-Pd(1)	120.9(4)	C(21)-C(20)-C(19)	120.0(13)
C(23)-P(2)-Pd(1)	112.2(3)	C(20)-C(21)-C(22)	121.0(14)
C(2)-P(2)-Pd(1)	108.1(3)	C(21)-C(22)-C(17)	120.9(11)
C(29)-P(3)-C(35)	99.4(5)	C(24)-C(23)-C(28)	120.2(11)
C(29)-P(3)-B(1)	108.9(6)	C(24)-C(23)-P(2)	122.1(8)
C(35)-P(3)-B(1)	108.7(6)	C(28)-C(23)-P(2)	117.6(9)
C(29)-P(3)-Pd(1)	112.3(3)	C(23)-C(24)-C(25)	118.8(12)
C(35)-P(3)-Pd(1)	113.7(5)	C(26)-C(25)-C(24)	120.9(12)
B(1)-P(3)-Pd(1)	112.9(4)	C(25)-C(26)-C(27)	120.0(12)
C(3)-C(1)-C(2)	114.6(8)	C(26)-C(27)-C(28)	120.7(13)
C(3)-C(1)-P(1)	116.0(7)	C(27)-C(28)-C(23)	119.3(11)
C(2)-C(1)-P(1)	107.5(7)	C(30)-C(29)-C(34)	115.8(10)
C(1)-C(2)-C(4)	114.5(10)	C(30)-C(29)-P(3)	121.5(8)
C(1)-C(2)-P(2)	110.3(6)	C(34)-C(29)-P(3)	122.7(9)
C(4)-C(2)-P(2)	113.7(8)	C(31)-C(30)-C(29)	123.2(10)
C(6)-C(5)-C(10)	121.2(11)	C(32)-C(31)-C(30)	119.2(12)
C(6)-C(5)-P(1)	121.1(10)	C(31)-C(32)-C(33)	118.8(12)
C(10)-C(5)-P(1)	117.5(9)	C(34)-C(33)-C(32)	122.5(13)
C(5)-C(6)-C(7)	118.6(12)	C(33)-C(34)-C(29)	120.3(12)
C(8)-C(7)-C(6)	119.9(12)	C(37)-C(36)-C(41)	116.3(12)
C(7)-C(8)-C(9)	120.2(12)	C(37)-C(36)-Pd(1)	117.8(9)
C(10)-C(9)-C(8)	119.6(14)	C(41)-C(36)-Pd(1)	125.9(10)
C(9)-C(10)-C(5)	120.3(15)	C(36)-C(37)-O(1)	115.1(11)
C(16)-C(11)-C(12)	119.0(10)	C(36)-C(37)-C(38)	122.6(13)
C(16)-C(11)-P(1)	123.7(9)	O(1)-C(37)-C(38)	122.3(13)
C(12)-C(11)-P(1)	117.0(9)	C(39)-C(38)-C(37)	118.4(14)
C(13)-C(12)-C(11)	120.3(12)	C(40)-C(39)-C(38)	121.6(15)
C(12)-C(13)-C(14)	119.2(12)	C(39)-C(40)-C(41)	118.3(12)
C(15)-C(14)-C(13)	120.2(10)	C(40)-C(41)-C(36)	122.7(13)
C(14)-C(15)-C(16)	120.7(12)	C(37)-O(1)-C(42)	118.0(10)
C(11)-C(16)-C(15)	120.6(12)		
C(22)-C(17)-C(18)	117.9(12)		
C(22)-C(17)-P(2)	120.9(9)	Symmetry transformations used to generate equivalent atoms:	
C(18)-C(17)-P(2)	120.9(10)		

Table S5. Anisotropic displacement parameters ($Å^2$x 10^3)for (S_P)-Pd[(S,S)Chiraphos](*o*-An)[P(Me)(Ph)(BH_3)]. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	17(1)	17(1)	17(1)	0(1)	5(1)	0(1)
P(1)	17(2)	16(2)	19(2)	2(2)	6(2)	0(1)
P(2)	21(2)	22(2)	18(2)	-5(2)	7(2)	-1(1)
P(3)	15(1)	25(2)	30(2)	-3(2)	7(2)	-1(1)
B(1)	46(8)	23(11)	63(12)	9(8)	43(9)	-2(6)
C(35)	30(7)	34(8)	34(10)	0(7)	-20(7)	0(6)
C(1)	21(6)	22(6)	15(7)	-5(5)	10(6)	-11(5)
C(2)	26(6)	21(7)	16(7)	1(6)	17(6)	1(5)
C(3)	21(6)	32(8)	25(8)	4(6)	-4(6)	4(4)
C(4)	23(6)	26(7)	30(9)	4(6)	7(6)	9(5)
C(5)	20(6)	31(7)	16(7)	-7(6)	8(6)	4(5)
C(6)	17(6)	31(8)	40(9)	-6(7)	14(7)	-5(5)
C(7)	50(8)	39(9)	61(12)	-16(8)	35(9)	-22(6)
C(8)	43(8)	66(10)	27(9)	-7(8)	26(7)	-9(7)
C(9)	48(7)	49(11)	38(8)	26(9)	19(7)	0(7)
C(10)	53(7)	31(7)	34(7)	-24(10)	22(7)	4(10)
C(11)	0(5)	27(7)	25(8)	4(6)	-4(6)	13(4)
C(12)	33(6)	16(6)	27(8)	-6(6)	8(7)	-7(5)
C(13)	35(7)	31(8)	35(9)	25(7)	14(7)	10(6)
C(14)	40(7)	23(7)	35(9)	12(7)	22(8)	-5(6)
C(15)	43(7)	19(7)	61(11)	0(7)	38(8)	-9(5)
C(16)	30(6)	15(6)	17(7)	-10(6)	8(6)	4(5)
C(17)	9(5)	37(7)	24(8)	-2(7)	1(6)	9(5)
C(18)	24(7)	65(10)	29(10)	-8(8)	2(8)	-16(6)
C(19)	39(8)	60(10)	34(9)	-3(8)	23(8)	-2(7)
C(20)	42(8)	59(10)	29(9)	4(8)	23(8)	8(7)
C(21)	42(8)	56(10)	30(10)	-6(8)	7(8)	3(7)
C(22)	28(7)	30(8)	37(10)	7(7)	1(8)	-3(6)
C(23)	22(6)	21(7)	14(7)	12(6)	2(6)	0(5)
C(24)	36(7)	27(8)	23(8)	6(6)	2(7)	6(5)

C(25)	54(9)	18(8)	63(12)	6(8)	5(9)	-7(6)
C(26)	45(8)	20(8)	47(11)	17(7)	2(8)	-3(6)
C(27)	32(8)	40(10)	26(9)	15(8)	-1(7)	-8(7)
C(28)	27(6)	32(8)	20(8)	-11(6)	-5(7)	-8(5)
C(29)	20(6)	18(6)	26(8)	5(6)	8(6)	0(4)
C(30)	23(6)	36(8)	16(7)	-3(6)	12(6)	2(5)
C(31)	45(8)	26(7)	46(10)	-14(7)	21(8)	6(6)
C(32)	24(6)	31(8)	42(10)	-8(7)	2(7)	-2(5)
C(33)	27(7)	32(9)	36(11)	-7(8)	1(8)	0(6)
C(34)	30(7)	20(7)	23(8)	-5(6)	7(7)	-1(5)
C(36)	3(5)	42(8)	20(8)	0(7)	-1(6)	3(5)
C(37)	20(5)	34(8)	28(7)	-26(9)	1(6)	-3(7)
C(38)	54(9)	35(9)	37(10)	10(7)	15(9)	5(6)
C(39)	56(9)	44(10)	41(11)	-13(9)	-2(9)	5(7)
C(40)	36(8)	37(8)	42(11)	-17(8)	6(8)	-15(6)
C(41)	40(8)	29(8)	22(9)	-8(7)	0(8)	-9(6)
C(42)	100(12)	67(11)	38(11)	23(9)	7(10)	-43(9)
O(1)	42(5)	43(6)	30(6)	14(5)	4(5)	-12(4)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for (S_P)-Pd[(S,S)Chiraphos](*o*-An)[P(Me)(Ph)(BH_3)].

	x	y	z	U(eq)
H(51A)	12443	5178	1411	57
H(51B)	12027	6116	1774	57
H(51C)	10989	5644	782	57
H(35A)	12758	4316	3386	58
H(35B)	11541	4293	3927	58
H(35C)	12384	5190	3906	58
H(1A)	6250	6735	532	22
H(2A)	5017	5984	1943	23
H(3A)	3822	6588	-289	43
H(3B)	3916	5555	-30	43
H(3C)	4711	5947	-789	43
H(4A)	3498	7106	1013	40
H(4B)	4754	7808	1401	40
H(4C)	4113	7339	2207	40
H(6A)	7314	3735	-66	34
H(7A)	7807	3481	-1612	55
H(8A)	8046	4673	-2622	50
H(9A)	8022	6115	-2022	53
H(10A)	7586	6355	-494	45
H(12A)	6965	4491	2894	31
H(13A)	5549	3430	3348	40
H(14A)	3716	2720	2034	36
H(15A)	3410	3039	331	43
H(16A)	4798	4113	-124	25
H(18A)	4893	5982	3487	49
H(19A)	4488	5935	5050	50
H(20A)	6005	6695	6452	48
H(21A)	7933	7447	6274	52
H(22A)	8385	7485	4727	40
H(24A)	6267	8480	3234	36

H(25)	6613	9913	2704	58
H(26A)	8088	10155	1723	48
H(27A)	9240	8986	1249	42
H(28A)	8878	7546	1719	35
H(30A)	11075	3915	669	29
H(31A)	10364	2537	-48	45
H(32A)	9028	1622	670	41
H(33A)	8398	2120	2071	41
H(34A)	9190	3446	2849	30
H(38A)	10944	5854	6311	51
H(39A)	12511	7001	6390	61
H(40A)	12571	7725	4922	48
H(41A)	11155	7214	3337	39
H(42A)	8343	4272	5340	108
H(42B)	8642	5216	5890	108
H(42C)	9923	4546	5983	108

Table S7. Crystal data and structure refinement for (R_P)-Pd[(S,S)Chiraphos](*o*-An)[P(Me)(Ph)(BH_3)] (**4b**).

Identification code	glu99	
Empirical formula	$C_{42}H_{46}BOP_3Pd$	
Formula weight	776.91	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	*a* = 9.9565(7) Å	α= 90°.
	b = 17.8335(13) Å	β= 91.6720(10)°.
	c = 11.1574(7) Å	γ = 90°.
Volume	1980.3(2) $Å^3$	
Z	2	
Density (calculated)	1.303 g/cm^3	
Absorption coefficient	6.20 cm^{-1}	
F(000)	804	
Crystal size	0.24 x 0.20 x 0.18 mm^3	
Theta range for data collection	2.05 to 28.28°.	
Index ranges	-13≤h≤13, -23≤k≤20, -12≤l≤14	
Reflections collected	10023	
Independent reflections	6543 [R(int) = 0.0496]	
Completeness to theta = 28.28°	91.5 %	
Absorption correction	Empirical from SADABS	
Max. and min. transmission	0.8966 and 0.8654	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6543 / 1 / 433	
Goodness-of-fit on F^2	0.925	
Final R indices [I>2sigma(I)]	R_1 = 0.0528, wR^2 = 0.1109	
R indices (all data)	R_1 = 0.0764, wR^2 = 0.1260	
Absolute structure parameter	0.02(4)	
Largest diff. peak and hole	0.709 and -0.787 e.$Å^{-3}$	

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (R_P)-Pd[(S,S)Chiraphos](*o*-An)[P(Me)(Ph)(BH_3)]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	2657(1)	9460(1)	7423(1)	21(1)
P(1)	1180(2)	10458(1)	7217(2)	26(1)
P(2)	983(2)	8908(1)	8513(2)	25(1)
P(3)	4430(2)	9996(1)	6402(2)	26(1)
B(1)	4078(10)	10271(6)	4751(8)	42(3)
C(1)	20(7)	10367(4)	8479(6)	29(2)
C(2)	-501(6)	9530(7)	8504(6)	33(2)
C(3)	-1140(8)	10935(5)	8524(7)	41(2)
C(4)	-1469(7)	9371(6)	9517(6)	44(2)
C(5)	1640(7)	11447(4)	7217(7)	34(2)
C(6)	1717(8)	11850(5)	6168(8)	41(2)
C(7)	2127(10)	12588(5)	6195(9)	54(2)
C(8)	2474(9)	12935(6)	7237(10)	63(3)
C(9)	2442(9)	12536(5)	8297(9)	48(2)
C(10)	2030(8)	11800(5)	8292(8)	40(2)
C(11)	106(7)	10306(4)	5886(6)	28(2)
C(12)	311(7)	9685(4)	5202(7)	35(2)
C(13)	-542(7)	9517(7)	4221(6)	45(2)
C(14)	-1582(8)	9984(5)	3926(7)	40(2)
C(15)	-1799(7)	10627(5)	4583(7)	37(2)
C(16)	-955(7)	10795(4)	5554(7)	34(2)
C(17)	1480(7)	8829(5)	10107(6)	29(2)
C(18)	2425(7)	9349(5)	10560(6)	38(2)
C(19)	2766(8)	9327(5)	11783(6)	43(2)
C(20)	2197(8)	8812(5)	12534(7)	41(2)
C(21)	1288(9)	8301(5)	12061(7)	39(2)
C(22)	902(8)	8309(5)	10857(6)	34(2)
C(23)	339(7)	7981(5)	8119(6)	29(2)
C(24)	1121(8)	7358(5)	8395(6)	34(2)
C(25)	692(9)	6638(5)	8068(7)	39(2)

C(26)	-544(10)	6552(6)	7469(9)	54(3)
C(27)	-1292(8)	7157(6)	7176(8)	50(3)
C(28)	-866(8)	7872(5)	7510(7)	41(2)
C(29)	4988(7)	10802(5)	7312(7)	30(2)
C(30)	5180(8)	10727(5)	8539(7)	32(2)
C(31)	5609(8)	11323(6)	9234(7)	43(2)
C(32)	5870(8)	12010(5)	8713(9)	47(2)
C(33)	5691(9)	12098(6)	7494(9)	48(2)
C(34)	5235(8)	11483(5)	6787(7)	38(2)
C(35)	5972(6)	9436(8)	6435(6)	39(2)
C(36)	3723(7)	8486(5)	7540(7)	26(2)
C(37)	3473(7)	7964(4)	6632(6)	28(2)
C(38)	4143(8)	7275(5)	6592(8)	40(2)
C(39)	5067(8)	7105(5)	7478(8)	36(2)
C(40)	5322(8)	7595(5)	8429(8)	41(2)
C(41)	4661(8)	8281(5)	8467(7)	32(2)
C(42)	1778(10)	7619(5)	5157(7)	48(2)
O(1)	2507(6)	8186(3)	5765(5)	42(1)

Table S9. Bond lengths [Å] and angles [deg] for (R_P)-Pd[(S,S)Chiraphos](*o*-An)[P(Me)(Ph)(BH_3)].

Pd(1)-C(36)	2.038(8)	C(23)-C(28)	1.376(11)
Pd(1)-P(2)	2.3118(18)	C(23)-C(24)	1.386(11)
Pd(1)-P(1)	2.315(2)	C(24)-C(25)	1.398(11)
Pd(1)-P(3)	2.3338(19)	C(25)-C(26)	1.391(13)
P(1)-C(5)	1.823(8)	C(26)-C(27)	1.347(14)
P(1)-C(11)	1.825(7)	C(27)-C(28)	1.390(13)
P(1)-C(1)	1.855(7)	C(29)-C(34)	1.373(11)
P(2)-C(23)	1.823(8)	C(29)-C(30)	1.384(10)
P(2)-C(17)	1.838(7)	C(30)-C(31)	1.376(11)
P(2)-C(2)	1.847(9)	C(31)-C(32)	1.384(13)
P(3)-C(35)	1.831(9)	C(32)-C(33)	1.375(13)
P(3)-C(29)	1.837(8)	C(33)-C(34)	1.418(12)
P(3)-B(1)	1.929(9)	C(36)-C(37)	1.393(10)
C(1)-C(3)	1.538(10)	C(36)-C(41)	1.420(11)
C(1)-C(2)	1.581(13)	C(37)-C(38)	1.400(11)
C(2)-C(4)	1.533(9)	C(37)-O(1)	1.401(9)
C(5)-C(6)	1.378(11)	C(38)-C(39)	1.365(12)
C(5)-C(10)	1.399(11)	C(39)-C(40)	1.391(12)
C(6)-C(7)	1.378(12)	C(40)-C(41)	1.390(12)
C(7)-C(8)	1.353(13)	C(42)-O(1)	1.407(10)
C(8)-C(9)	1.381(14)		
C(9)-C(10)	1.376(12)	C(36)-Pd(1)-P(2)	89.2(2)
C(11)-C(12)	1.363(10)	C(36)-Pd(1)-P(1)	171.7(2)
C(11)-C(16)	1.412(10)	P(2)-Pd(1)-P(1)	85.07(7)
C(12)-C(13)	1.398(10)	C(36)-Pd(1)-P(3)	88.88(19)
C(13)-C(14)	1.361(12)	P(2)-Pd(1)-P(3)	176.91(8)
C(14)-C(15)	1.382(12)	P(1)-Pd(1)-P(3)	97.11(7)
C(15)-C(16)	1.385(10)	C(5)-P(1)-C(11)	106.6(4)
C(17)-C(22)	1.384(10)	C(5)-P(1)-C(1)	104.2(4)
C(17)-C(18)	1.405(11)	C(11)-P(1)-C(1)	104.0(3)
C(18)-C(19)	1.397(9)	C(5)-P(1)-Pd(1)	125.8(3)
C(19)-C(20)	1.376(11)	C(11)-P(1)-Pd(1)	108.8(2)
C(20)-C(21)	1.379(12)	C(1)-P(1)-Pd(1)	105.4(2)
C(21)-C(22)	1.386(10)	C(23)-P(2)-C(17)	104.3(4)

C(23)-P(2)-C(2)	105.6(4)	C(19)-C(18)-C(17)	118.3(7)
C(17)-P(2)-C(2)	104.1(3)	C(20)-C(19)-C(18)	121.4(8)
C(23)-P(2)-Pd(1)	120.9(2)	C(19)-C(20)-C(21)	119.0(7)
C(17)-P(2)-Pd(1)	111.4(2)	C(20)-C(21)-C(22)	121.6(8)
C(2)-P(2)-Pd(1)	109.3(3)	C(17)-C(22)-C(21)	119.0(8)
C(35)-P(3)-C(29)	100.2(4)	C(28)-C(23)-C(24)	118.3(8)
C(35)-P(3)-B(1)	106.6(4)	C(28)-C(23)-P(2)	122.9(7)
C(29)-P(3)-B(1)	111.9(4)	C(24)-C(23)-P(2)	118.8(6)
C(35)-P(3)-Pd(1)	114.4(4)	C(23)-C(24)-C(25)	120.8(8)
C(29)-P(3)-Pd(1)	105.8(2)	C(26)-C(25)-C(24)	119.1(8)
B(1)-P(3)-Pd(1)	116.8(3)	C(27)-C(26)-C(25)	120.3(9)
C(3)-C(1)-C(2)	112.0(6)	C(26)-C(27)-C(28)	120.5(9)
C(3)-C(1)-P(1)	116.9(5)	C(23)-C(28)-C(27)	121.1(9)
C(2)-C(1)-P(1)	107.9(5)	C(34)-C(29)-C(30)	119.1(8)
C(4)-C(2)-C(1)	113.7(8)	C(34)-C(29)-P(3)	120.7(6)
C(4)-C(2)-P(2)	113.9(7)	C(30)-C(29)-P(3)	120.1(6)
C(1)-C(2)-P(2)	107.7(5)	C(31)-C(30)-C(29)	120.9(8)
C(6)-C(5)-C(10)	118.2(8)	C(30)-C(31)-C(32)	120.4(8)
C(6)-C(5)-P(1)	121.7(6)	C(33)-C(32)-C(31)	119.7(8)
C(10)-C(5)-P(1)	119.9(6)	C(32)-C(33)-C(34)	119.5(9)
C(5)-C(6)-C(7)	120.3(8)	C(29)-C(34)-C(33)	120.3(8)
C(8)-C(7)-C(6)	121.5(9)	C(37)-C(36)-C(41)	117.2(7)
C(7)-C(8)-C(9)	119.3(9)	C(37)-C(36)-Pd(1)	116.1(6)
C(10)-C(9)-C(8)	120.2(8)	C(41)-C(36)-Pd(1)	126.6(6)
C(9)-C(10)-C(5)	120.5(8)	C(36)-C(37)-C(38)	122.3(7)
C(12)-C(11)-C(16)	118.6(7)	C(36)-C(37)-O(1)	114.7(7)
C(12)-C(11)-P(1)	118.9(6)	C(38)-C(37)-O(1)	123.0(7)
C(16)-C(11)-P(1)	122.5(6)	C(39)-C(38)-C(37)	118.9(8)
C(11)-C(12)-C(13)	121.0(8)	C(38)-C(39)-C(40)	121.2(8)
C(14)-C(13)-C(12)	119.9(9)	C(41)-C(40)-C(39)	120.0(8)
C(13)-C(14)-C(15)	120.6(8)	C(40)-C(41)-C(36)	120.4(8)
C(14)-C(15)-C(16)	119.7(7)	C(37)-O(1)-C(42)	117.6(7)
C(15)-C(16)-C(11)	120.2(7)		
C(22)-C(17)-C(18)	120.7(7)	Symmetry transformations used to generate	
C(22)-C(17)-P(2)	122.1(6)	equivalent atoms:	
C(18)-C(17)-P(2)	117.1(6)		

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (R_P)-Pd[(S,S)Chiraphos](*o*-An)[P(Me)(Ph)(BH_3)]. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	20(1)	23(1)	21(1)	0(1)	0(1)	0(1)
P(1)	25(1)	25(1)	27(1)	0(1)	-2(1)	3(1)
P(2)	22(1)	31(1)	23(1)	1(1)	1(1)	1(1)
P(3)	28(1)	26(1)	24(1)	-1(1)	2(1)	-3(1)
B(1)	38(5)	59(7)	29(5)	-5(4)	0(4)	-13(5)
C(1)	25(4)	34(4)	27(4)	6(3)	2(3)	7(3)
C(2)	25(3)	40(5)	32(3)	6(5)	-1(3)	6(5)
C(3)	36(4)	42(5)	46(5)	3(4)	8(4)	22(4)
C(4)	33(4)	51(6)	47(4)	4(5)	14(3)	12(5)
C(5)	27(4)	26(4)	47(5)	-2(4)	-1(4)	0(3)
C(6)	46(5)	33(5)	44(5)	4(4)	-11(4)	-6(4)
C(7)	52(6)	43(6)	64(6)	20(5)	-16(5)	-4(5)
C(8)	46(6)	35(5)	106(9)	-8(6)	-31(6)	-4(4)
C(9)	49(5)	39(5)	56(6)	-17(5)	-26(4)	7(4)
C(10)	36(5)	39(5)	43(5)	-11(4)	-11(4)	9(4)
C(11)	24(3)	34(4)	24(3)	9(3)	2(3)	-1(3)
C(12)	29(4)	35(5)	39(4)	0(3)	-5(3)	7(3)
C(13)	45(4)	55(6)	33(3)	-3(5)	-6(3)	2(6)
C(14)	34(4)	50(5)	36(4)	-2(4)	-10(4)	-8(4)
C(15)	22(4)	40(5)	49(5)	11(4)	-6(3)	7(3)
C(16)	33(4)	28(4)	39(4)	4(3)	-3(3)	-1(3)
C(17)	25(4)	39(5)	22(3)	2(3)	-4(3)	6(3)
C(18)	38(4)	40(6)	35(4)	-1(4)	-1(3)	-3(4)
C(19)	52(4)	45(7)	31(4)	-10(4)	-14(3)	-11(4)
C(20)	48(5)	57(6)	19(3)	8(4)	1(3)	5(4)
C(21)	50(5)	41(5)	25(4)	1(4)	2(4)	1(4)
C(22)	33(4)	39(5)	29(4)	5(3)	-3(3)	3(3)
C(23)	22(4)	36(5)	29(4)	-8(3)	1(3)	-3(3)
C(24)	31(4)	42(5)	28(4)	0(4)	0(3)	1(4)
C(25)	48(5)	25(4)	44(5)	1(4)	2(4)	-7(4)
C(26)	67(7)	38(6)	58(6)	-14(5)	19(5)	-22(5)

C(27)	27(4)	73(7)	50(5)	-23(5)	4(4)	-22(5)
C(28)	29(4)	56(6)	36(4)	1(4)	7(4)	-1(4)
C(29)	25(4)	32(4)	35(4)	-8(3)	3(3)	0(3)
C(30)	27(4)	32(5)	38(4)	-8(4)	-3(4)	9(4)
C(31)	34(4)	66(7)	29(4)	-14(4)	-1(4)	6(4)
C(32)	24(4)	48(6)	69(6)	-26(5)	-9(4)	2(4)
C(33)	40(5)	40(6)	66(6)	-15(5)	16(5)	-10(4)
C(34)	43(5)	40(5)	33(4)	-13(4)	3(4)	-9(4)
C(35)	34(3)	41(4)	43(4)	-6(6)	12(3)	-2(6)
C(36)	19(3)	30(4)	30(4)	-1(3)	7(3)	-1(3)
C(37)	28(4)	26(4)	29(4)	4(3)	3(3)	0(3)
C(38)	38(5)	29(5)	53(5)	-2(4)	10(4)	-4(4)
C(39)	24(4)	27(4)	57(5)	4(4)	1(4)	9(3)
C(40)	29(4)	42(5)	52(5)	15(4)	-4(4)	-1(4)
C(41)	28(4)	37(5)	32(4)	10(4)	-3(4)	-1(4)
C(42)	63(6)	45(6)	37(5)	-17(4)	-3(4)	-5(5)
O(1)	55(4)	35(3)	36(3)	-3(2)	-9(3)	-2(3)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for (R_P)-Pd[(S,S)Chiraphos](*o*-An)[P(Me)(Ph)(BH_3)].

	x	y	z	U(eq)
H(51A)	4890	10488	4418	63
H(51B)	3349	10640	4706	63
H(51C)	3815	9824	4290	63
H(1A)	576	10441	9231	34
H(2A)	-1009	9441	7731	39
H(3A)	-1673	10837	9232	62
H(3B)	-1713	10885	7799	62
H(3C)	-774	11445	8569	62
H(4A)	-2232	9718	9455	65
H(4B)	-999	9440	10293	65
H(4C)	-1796	8854	9452	65
H(6A)	1486	11619	5424	50
H(7A)	2167	12860	5464	64
H(8A)	2736	13447	7240	75
H(9A)	2705	12771	9031	58
H(10A)	2009	11528	9024	48
H(12A)	1044	9361	5395	42
H(13A)	-396	9078	3760	53
H(14A)	-2163	9866	3261	48
H(15A)	-2524	10951	4370	45
H(16A)	-1090	11242	5999	40
H(18A)	2822	9707	10048	45
H(19A)	3405	9674	12103	52
H(20A)	2427	8808	13367	50
H(21A)	917	7934	12572	47
H(22A)	251	7964	10551	40
H(24A)	1959	7421	8813	41
H(25A)	1237	6213	8252	47
H(26A)	-861	6064	7267	65
H(27A)	-2117	7096	6737	60

H(28A)	-1417	8292	7314	49
H(30A)	5015	10257	8908	39
H(31A)	5726	11263	10077	52
H(32A)	6171	12419	9194	57
H(33A)	5871	12567	7129	58
H(34A)	5100	11542	5946	46
H(35A)	6666	9697	5990	59
H(35B)	5791	8947	6064	59
H(35C)	6285	9364	7268	59
H(38A)	3957	6931	5958	48
H(39A)	5544	6645	7446	43
H(40A)	5949	7461	9051	49
H(41A)	4836	8614	9117	39
H(42A)	1151	7847	4570	73
H(42B)	1275	7326	5735	73
H(42C)	2402	7290	4743	73

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