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Asymmetric Synthesis of Diphosphine Ligands Containing Phosphorus and Carbon Stereogenic Centers by Means of a Chiral Palladium Complex Promoted Hydrophosphination Reaction

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An organopalladium complex containing ortho-metalated (*R*)-(1-(dimethylamino) ethyl)naphthalene as the chiral auxiliary has been used to promote the asymmetric hydrophosphination reaction between diphenylphosphine and phenyldi[(*Z*)-prop-1-enyl]phosphine in high regio- and stereoselectivity under mild conditions. The hydrophosphination reaction generated only two diastereomers in a ratio of 1:1. The two hydrophosphination products contained both phosphorus and carbon stereogenic centers and were subsequently isolated by fractional crystallization. Their absolute stereochemistries were analyzed by X-ray crystallography. The naphthylamine auxiliary could be removed chemoselectively from the template products by treatment with concentrated hydrochloric acid to form the corresponding optically pure neutral dichloro complexes. Subsequently, the dichloro complexes underwent ligand displacement with aqueous cyanide to generate the optically pure diphosphine ligands in high yields.

Introduction

The early development of optically active P-chiral phosphorus ligands for chiral metal catalysts can be attributed to the studies of homogeneous asymmetric hydrogenation initiated by Knowles and Sabacky[1] and Horner and co-workers[2] in the late 1960s. Although the first P-chiral disphosphine DIPAMP has proven to be a very efficient hydrogenation ligand, the development of new P-chiral diphosphines continues to offer new opportunities as well as pose considerable challenges.[3] Diphosphines with chiral carbon center(s) in the backbones, such as DIOP[4] and ChiraPhos,[5] are another group of effective phosphine ligands in asymmetric synthesis. Pioneering research showed that not only do P-chiral phosphorus ligands have the capability to achieve high enantioselectivity but phosphine ligands with backbone chirality could also provide excellent catalytic effects.[6] However, only a few diphosphines, which possess both phosphorus and carbon stereogenic centers, have been obtained by means of asymmetric synthesis.[7] We believe that they would be extremely interesting chiral ligands and deserve further examination in regard to their catalytic properties.

Our group had previously reported a series of chiral palladium template assisted asymmetric hydrophosphination reactions to synthesize optically pure phosphines with backbone chirality.[8] In pursuing our interest in the synthesis of P-stereogenic diphosphines with selected functionalities, herein we present the preparation of chiral diphosphines

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(1) Knowles, W. S.; Sabacky, M. *J. Chem. Soc., Chem. Commun.* **1968**, 1445.

(2) Horner, L.; Siegel, H.; Buthe, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 942.

(3) (a) Juge, S.; Stephan, M.; Laffitte, J. A.; Genet, J. P. *Tetrahedron Lett.* **1990**, *31*, 6357. (b) Imamoto, T.; Oshiki, T.; Onozawa, T.; K.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244. (c) Corey, E. J.; Chen, Z.; Tanoury, G. J. *J. Am. Chem. Soc.* **1993**, *115*, 11000. (d) Muci, A. R.; Campos, K. R.; Evans, D. A. *J. Am. Chem. Soc.* **1995**, *117*, 9075. (e) Aw, B. H.; Leung, P. H. *Tetrahedron: Asymmetry* **1994**, *5*, 1167. (f) Leung, P. H.; Loh, S. K.; Mok, K. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1996**, 591. (g) Selvaratnam, S.; Mok, K. F.; Leung, P. H.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **1996**, *35*, 4798.

(4) (a) Kagan, H. B.; Dang, T. P. *J. Chem. Soc., Chem. Commun.* **1971**, 481. (c) Kagan, H. B.; Dang, T. P. *J. Am. Chem. Soc.* **1972**, *94*, 6429.

(5) (a) Fryzuk, M. B.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6262. (b) Fryzuk, M. B.; Bosnich, B. *J. Am. Chem. Soc.* **1979**, *101*, 3043.

(6) Tang, W.; Zhang, X. *Chem. Rev.* **2003**, *103*, 3029.

(7) (a) Carmichael, D.; Doucet, H.; Brown, J. M. *Chem. Commun.* **1999**, 261. (b) Tang, W.; Zhang, X. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 1612. (c) Malisch, W.; Klupfel, B.; Schumacher, D.; Nieger, M. *J. Organomet. Chem.* **2002**, *661*, 95. (d) Shimizu, H.; Saito, T.; Kumobayashi, H. *Adv. Synth. Catal.* **2003**, *345*, 185. (e) Selvaratnam, S.; Mok, K. F.; Leung, P. H.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **1996**, *35*, 4798. (f) Leung, P. H.; Selvaratnam, S.; Cheng, C. R.; Mok, K. F.; Rees, N. H.; McFarlane, W. *Chem. Commun.* **1997**, 751.

(8) (a) Yeo, W. C.; Tee, S. T.; Tan, G. K.; Koh, L. L.; Leung, P. H. *Inorg. Chem.* **2004**, *43*, 8102. (b) Pullarkat, S. A.; Ding, Y.; Li, Y.; Tan, G. K.; Leung, P. H. *Inorg. Chem.* **2006**, *45*, 7455. (c) Tang, L.; Zhang, Y.; Luo, D.; Li, Y.; Mok, K. F.; Yeo, W. C.; Leung, P. H. *Tetrahedron Lett.* **2007**, *48*, 33. (d) Zhang, Y.; Tang, L.; Ding, Y.; Chua, J. H.; Li, Y.; Yuan, M.; Leung, P. H. *Tetrahedron Lett.* **2008**, *49*, 1762. (e) Yuan, M.; Pullarkat, S. A.; Ma, M.; Zhang, Y.; Huang, Y.; Li, Y.; Goel, A.; Leung, P. H. *Organometallics* **2009**, *28*, 780.

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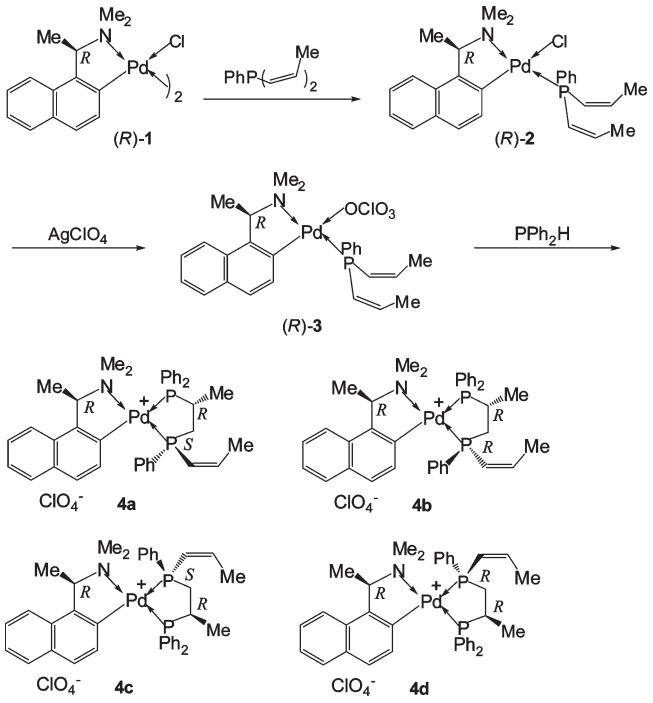
Scheme 1



which contain both phosphorus and carbon stereogenic centers by a chiral metal template promoted asymmetric hydrophosphination reaction between diphenylphosphine and phenyldi[(*Z*)-prop-1-enyl]phosphine.

Results and Discussion

In the absence of a metal ion, diphenylphosphine shows no reactivity with phenyldi[(*Z*)-prop-1-enyl]phosphine under ambient conditions. As illustrated in Scheme 1, phenyldi [(*Z*)-prop-1-enyl]phosphine was coordinated to (*R*)-**1** regioselectively to form the neutral complex (*R*)-**2**, which upon abstraction of the chloro ligand with silver perchlorate gave the perchlorato complex (*R*)-**3**. It is well-known that the chloro ligand in complex (*R*)-**2** is kinetically and thermodynamically stable. In order to provide a vacant coordination site for the reacting diphenylphosphine, (*R*)-**2** was treated with silver perchlorate prior to the introduction of diphenylphosphine into the reaction mixture.[7f] Complex (*R*)-**3** was not isolated but was subsequently treated with 1 equiv of diphenylphosphine at −78 °C to give the hydrophosphination products, **4a** and **4b** (Scheme 1). Prior to purification, the ^{31}P NMR spectrum in $CDCl_3$ exhibited two pairs of doublets at a ratio of 1:1: δ 33.6 and 49.9 (J_{PP} = 26.1 Hz) for **4a** and 29.8 and 49.0 (J_{PP} = 29.0 Hz) for **4b**. It is noteworthy that only one of the two vinyl groups in complex (*R*)-**3** reacted with diphenylphosphine, and thus the newly formed five-membered diphosphine chelate had one phosphorus and one carbon stereogenic center. Both the diphosphine chelates formed in **4a** and **4b** also adopt the same *R* absolute configuration at the newly generated carbon chiral centers. Furthermore, the hydrophosphination reaction was highly regioselective, as the diphenylphosphino groups were added to the β-carbon of the phenyldi[(*Z*)-prop-1-enyl]phosphine to form five-membered chelate rings exclusively. In addition, the newly generated stereogenic phosphorus centers within the diphosphine chelates were occupying the coordination sites trans to the NMe_2 group of the chiral metal template. It needs to be noted that **4a** and **4b** are two of the eight possible stereoisomeric products of the hydrophosphination reaction. No other products were detected by ^{31}P NMR spectroscopy in the crude solution.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **4a**

Pd(1)−P(1)	2.3680(7)	P(1)−Pd(1)−P(2)	84.57(3)
Pd(1)−P(2)	2.2473(7)	P(2)−Pd(1)−C(1)	94.06(7)
Pd(1)−N(1)	2.153(2)	N(1)−Pd(1)−P(2)	173.50(6)
Pd(1)−C(1)	2.058(3)	C(1)−Pd(1)−P(1)	176.88(8)
P(1)−C(28)	1.847(3)	Pd(1)−P(1)−C(28)	106.22(9)
P(2)−C(29)	1.849(3)	Pd(1)−P(2)−C(29)	108.59(10)
C(28)−C(29)	1.535(4)	P(1)−C(28)−C(29)	104.8(2)
C(1)−Pd(1)−N(1)	80.38(9)	P(2)−C(29)−C(28)	111.63(19)
N(1)−Pd(1)−P(1)	101.15(6)		

The coordinated ligand phenyldi[(*Z*)-prop-1-enyl]phosphine in complex (*R*)-**3** has two carbon−carbon double bonds. However, when 2 equiv of diphenylphosphine were used, no other addition products besides **4a** and **4b** were detected by ^{31}P NMR spectroscopy under similar reaction conditions, thus indicating a high selectivity in the P−H addition. One unreacted carbon−carbon double bond remained in each complex **4a** and **4b**. It is believed that the first diphenylphosphine molecule coordinates to complex (*R*)-**3** before the intramolecular hydrophosphination reaction takes place. The intermolecular hydrophosphination reaction between the phenyldi[(*Z*)-prop-1-enyl]-phosphine molecule and the second diphenylphosphine molecule does not occur or is extremely slow compared to the intramolecular one.

The two diastereomeric products could be separated into their stereoisomerically pure forms by fractional crystallization. Complex **4a** was isolated as colorless crystals from chloroform and diethyl ether in 35% yield, $[\alpha]_D$ −151 (*c* 0.5, CH_3Cl). The molecular structure and the absolute stereochemistry of **4a** were determined by X-ray crystallography. Selected bond lengths and angles of **4a** are listed in Table 1. Complex **4b** was subsequently obtained from acetonitrile and diethyl ether as colorless crystals in 42% yield, $[\alpha]_D$ +84 (*c* 1.0, CH_2Cl_2).

When complex **4a** (Figure 1) or **4b** was kept at room temperature in dichloromethane for several days, equilibrium mixtures of regioisomers were formed. When a solution of **4a** was monitored by use of its ^{31}P NMR spectrum, a new pair of

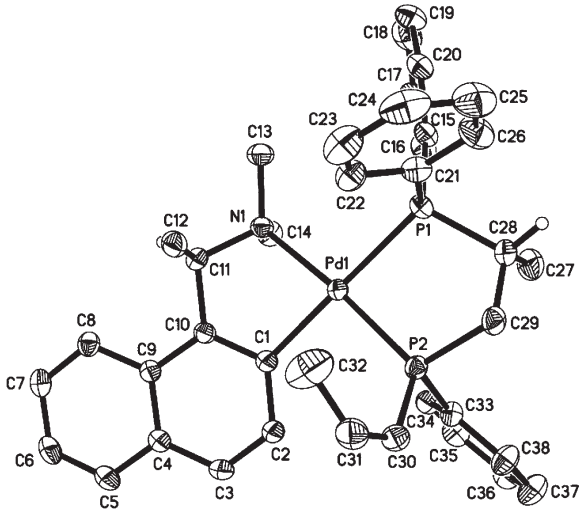


Figure 1. Molecular structure of complex **4a**.

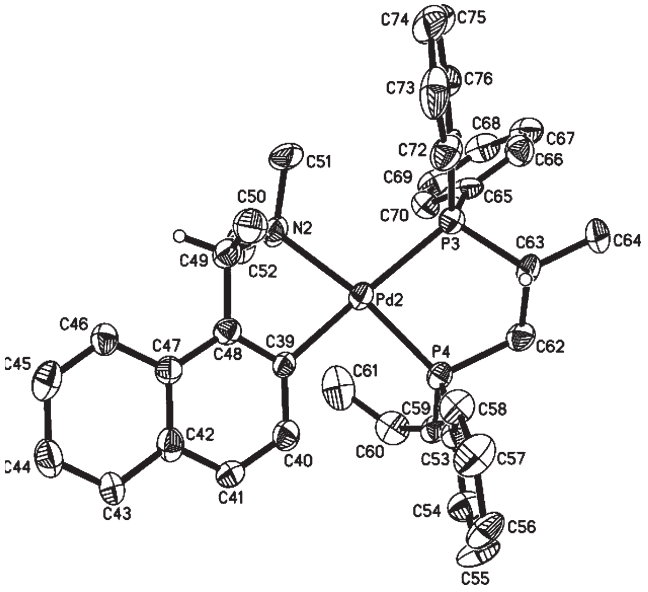


Figure 2. Molecular structure of complex **4b**.

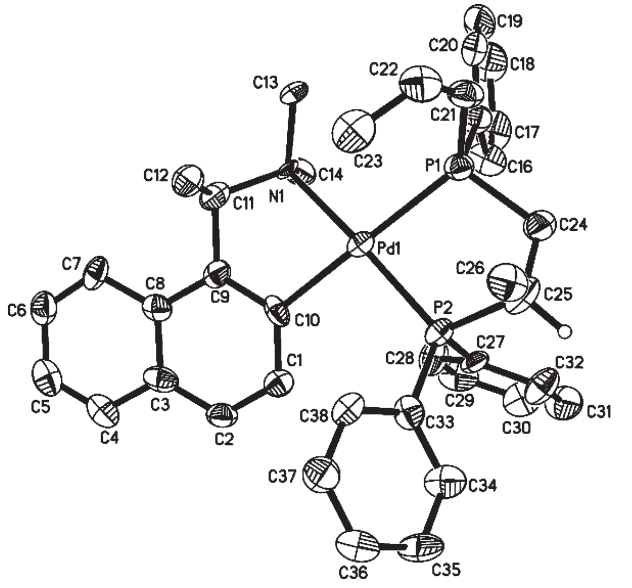


Figure 3. Molecular structure of complex **4d**.

doublets at δ 22.3 and 75.3 (J_{PP} = 21.1 Hz) was detected, which was assigned to **4c**.[8a] In the same way, **4d** was assigned as **4b**'s regioisomer: the ^{31}P NMR spectrum in $CDCl_3$ exhibited a new pair of doublets at δ 15.9 and 76.4 (J_{PP} = 22.1 Hz). Complexes **4a**, **4c**, **4b**, and **4d** are four of the eight possible stereoisomeric products of the hydrophosphination reaction. Complexes **4a** and **4c** are cis−trans regioisomers which adopt the same *R* absolute configuration at the newly generated stereogenic carbon centers and *S* absolute configuration at the newly generated chiral phosphorus centers within the diphosphine chelates but differ in the relative regio arrangement of the four nonequivalent donor atoms on the metal templates. Similarly, **4b** and **4d** are regioisomers with *R* absolute configuration at the newly generated stereogenic carbon centers and *R* absolute configuration at the newly generated chiral phosphorus centers. Upon slow recrystallization, the cis−trans regioisomers **4b** and **4d** cocrystallized in equal quantities as colorless crystals from acetonitrile and diethyl ether in 90% yield, $[\alpha]_D$ −20 (*c* 0.3, $CHCl_3$). A crystallographic analysis revealed that the two regioisomers, **4b** and **4d**, were indeed present in the same unit cell (Figures 2 and 3). Selected bond lengths and angles of **4b** and **4d** are listed in Tables 2 and 3, respectively. As expected, the five-membered diphosphine chelates were formed in these stereoisomers. The newly formed stereogenic carbon centers in complexes **4a**, **4b**, and **4d** all adopt the same *R* absolute configuration.

As shown in Scheme 2, the (*R*)-naphthylamine auxiliary can be chemoselectively removed from **4a** by treatment with concentrated hydrochloric acid to give the dichloride **5a** as yellowish crystals from acetonitrile and diethyl ether in 88% isolated yield, $[\alpha]_D$ −88 (*c* 0.6, CH_2Cl_2). The ^{31}P NMR spectrum of the dichloro complex in $CDCl_3$ showed a pair of doublets: δ 42.6 and 75.2 (J_{PP} = 6.3 Hz). Treatment of a dichloromethane solution of **5a** with aqueous potassium cyanide for 30 min liberated the optically pure diphosphine **6a** as a white solid in quantitative yield, $[\alpha]_{546}$ = +70 (*c* 0.5, $CHCl_3$). The ^{31}P NMR spectrum of the free diphosphine **6a** in $CDCl_3$ showed a pair of doublets: δ −44.8 and 2.0 (J_{PP} = 20.8 Hz). Similarly, regioisomers **4b** and **4d** were treated with concentrated hydrochloric acid to remove the chiral amine

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **4b**

Pd(2)−P(3)	2.366(3)	P(3)−Pd(2)−P(4)	84.97(11)
Pd(2)−P(4)	2.242(3)	P(4)−Pd(2)−C(39)	93.6(3)
Pd(2)−N(2)	2.135(10)	N(2)−Pd(2)−P(4)	170.9(3)
Pd(2)−C(39)	2.089(10)	C(39)−Pd(2)−P(3)	169.6(3)
P(3)−C(63)	1.869(13)	Pd(2)−P(3)−C(63)	104.2(3)
P(4)−C(62)	1.820(11)	Pd(2)−P(4)−C(62)	109.4(4)
C(63)−C(62)	1.535(14)	P(3)−C(63)−C(62)	105.4(8)
C(39)−Pd(2)−N(2)	78.9(4)	P(4)−C(62)−C(63)	111.5(7)
N(2)−Pd(2)−P(3)	103.3(3)		

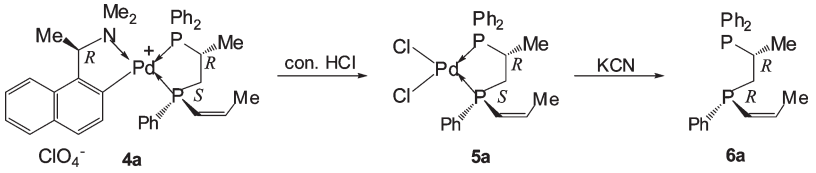
Table 3. Selected Bond Lengths (Å) and Angles (deg) for **4d**

Pd(1)−P(1)	2.348(3)	P(1)−Pd(1)−P(2)	84.35(10)
Pd(1)−P(2)	2.243(3)	P(2)−Pd(1)−C(10)	96.0(3)
Pd(1)−N(1)	2.136(8)	N(1)−Pd(1)−P(2)	172.6(2)
Pd(1)−C(10)	2.097(9)	C(10)−Pd(1)−P(1)	176.4(3)
P(1)−C(24)	1.848(12)	Pd(1)−P(1)−C(24)	106.4(4)
P(2)−C(25)	1.866(13)	Pd(1)−P(2)−C(25)	109.9(4)
C(24)−C(25)	1.525(17)	P(1)−C(24)−C(25)	111.6(8)
C(10)−Pd(1)−N(1)	80.2(4)	P(2)−C(25)−C(24)	104.7(9)
N(1)−Pd(1)−P(1)	99.1(2)		

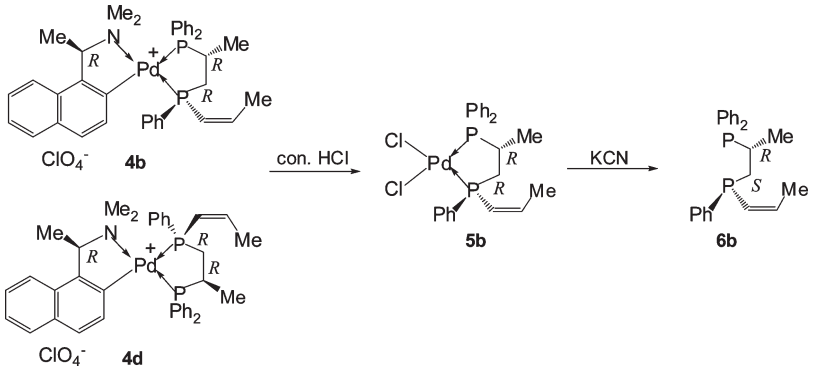
auxiliary chemoselectively (Scheme 3). The ^{31}P NMR spectrum of the dichloro complex in $CDCl_3$ showed a pair of doublets: δ 39.7 and 71.2 (J_{PP} = 5.6 Hz). The neutral dichloro complex **5b** crystallized out from acetonitrile and diethyl ether as yellowish crystals in its optically pure form, $[\alpha]_D$ −60 (*c* 0.5, CH_2Cl_2). Subsequently, the dichloro complex **5b** underwent ligand displacement with aqueous potassium cyanide at room temperature to generate **6b** in its optically pure form in high yield, $[\alpha]_D$ +246 (*c* 0.5, $CHCl_3$). The ^{31}P NMR spectrum of the free ligand in $CDCl_3$ showed a pair of doublets: δ −46.5 and 2.0 (J_{PP} = 20.5 Hz).

As illustrated in Scheme 4, in order to confirm the optical purity of the free diphosphines, the liberated optically pure **6a** was recoordinated to (*R*)-**7**. The ^{31}P NMR spectrum ($CDCl_3$) of the crude product exhibited only two pairs of doublets at δ 33.6 and 49.9 (J_{PP} = 26.1 Hz) and 22.3 and 75.3 (J_{PP} = 21.1 Hz). These signals are identical to those recorded for **4a** and **4c**. The ^{31}P NMR spectrum ($CDCl_3$) of the crude recomplexation mixture from **6b** and (*R*)-**7** exhibited two pairs of doublets at δ 29.8 and 49.0 (J_{PP} = 29.0 Hz) and 15.9 and 76.4 (J_{PP} = 22.1 Hz). These signals were identical with those observed for **4b** and **4d**. It could be confirmed that

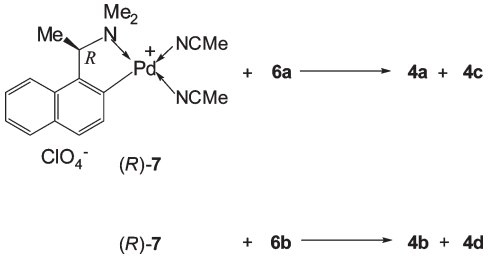
Scheme 2



Scheme 3



Scheme 4



diastereomers **4c** and **4d** were indeed regioisomers of **4a** and **4b**, respectively, and the liberated diphosphines **6a** and **6b** are therefore confirmed to be optically pure.

In conclusion, an attractive synthesis of chiral diphosphines containing both phosphorus and carbon stereogenic centers via chiral organopalladium template promoted asymmetric hydrophosphination has been demonstrated. The hydrophosphination reaction proceeds with high regio- and stereoselectivity under mild conditions. Investigations on the catalytic properties of the transition-metal complexes containing these optically active diphosphine ligands are currently in progress.

Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of purified argon. NMR spectra were recorded at 25 °C on Bruker ACF 300 and 500 MHz spectrometers. Optical rotations were measured on the specified solution in a 0.1 dm cell at 25 °C with a Perkin-Elmer model 341 polarimeter. Elemental analyses were performed by the staff at the Elemental Analysis Laboratory of the Division of Chemical and Biological Chemistry of Nanyang Technological University. Melting points were measured using the SRS Optimelt Automated Melting Point System, SRS MPA100.

All solvents used for the synthesis of ligands and reactions were deoxygenated using a positive pressure of argon. Analytical-grade chemicals were purchased from Sigma-Aldrich and Strem Chemicals. The chiral palladium complexes bis(acetonitrile) bis(acetonitrile)[(*S*)-1-[1-(dimethylamino) ethyl]-2-naphthyl-*C*,*N*]-palladium(II) perchlorate ((*R*)-**1**) were prepared according to literature methods.[9] Phenyldi[(*Z*)-prop-1-enyl]phosphine complexes (*R*)-**2** and (*R*)-**3** were prepared as previously reported by our group.[7f]

Caution! *All perchlorate salts should be handled as potentially explosive compounds. Care should be taken in handling highly toxic cyanide compounds.*

Hydrophosphination of Complex (*R*)-3. Complex (*R*)-**2** (1.20 g) in dichloromethane (30 mL) and aqueous silver perchlorate (0.80 g) were stirred vigorously at room temperature for 2 h. The mixture was filtered through Celite (to remove silver chloride), washed with water (3 × 30 mL), and dried (magnesium sulfate). The mixture was then degassed and treated with diphenylphosphine (0.35 g) at −78 °C for 12 h. By fractional crystallization, **4a** was isolated as colorless crystals from chloroform and diethyl ether: 0.56 g (35% yield). mp: 205−206 °C (dec). $[\alpha]_D$ −151 (*c* 0.5, CH_3Cl). Anal. calcd for $C_{38}H_{42}ClNO_4P_2Pd$: C, 58.5; H, 5.4; N, 1.8. Found: C, 58.4; H, 5.5; N, 1.8. ^{31}P NMR ($CDCl_3$): δ 33.6, 49.9 (J_{PP} = 26.1 Hz). ^1H NMR ($CDCl_3$): δ 0.96 (dd, 3H, $^3J_{PH}$ = 12.9 Hz, $^3J_{HH}$ = 7.0 Hz, P^1CHMe), 1.71 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 2.01 (d, 3H, $^3J_{HH}$ = 5.9 Hz, P^2CCMe), 2.09−2.23 (m, 1H, P^1CHH'), 2.43 (s, 3H, N*Meeq*), 2.44−2.56 (m, 1H, P^1CHH'), 2.95 (s, 3H, N*Meax*), 2.96−3.11 (m, 1H, P^1CHMe), 4.51 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.2 Hz, C*H*Me), 6.36 (dd, 1H, $^3J_{PH}$ = $^3J_{HH}$ = 11.7 Hz, P^2CH), 6.70 (ddq, 1H, $^3J_{PH}$ = 38.8 Hz, $^3J_{HH}$ = 11.7 Hz, $^3J_{HH}$ = 7.0 Hz, P^2CCH), 7.02−8.18 (m, 21H, aromatics). Complex **4b** was obtained from acetonitrile and diethyl ether as colorless crystals: 0.68 g (42% yield). mp: 194−196 °C (dec). $[\alpha]_D$ +84 (*c* 1.0, CH_2Cl_2). Anal. calcd for $C_{38}H_{42}ClNO_4P_2Pd$: C, 58.5; H, 5.4; N, 1.8. Found: C, 58.4; H, 5.5; N, 1.8. ^{31}P NMR ($CDCl_3$): δ 29.8, 49.0 (J_{PP} = 29.0 Hz). ^1H NMR ($CDCl_3$): δ 1.21 (dd, 3H, $^3J_{PH}$ = 12.1 Hz, $^3J_{HH}$ = 6.9 Hz, P^1CHMe), 1.71 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 1.94−2.20 (m, 2H, P^1CH_2), 2.36 (s, 3H, N*Meeq*), 2.43 (d, 3H, $^3J_{HH}$ = 7.2 Hz, P^2CCMe), 2.53−2.70 (m, 1H, P^1CHMe), 2.87 (s, 3H, N*Meax*), 4.49 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.2 Hz, C*H*Me), 6.46 (dd, 1H, $^3J_{PH}$ = $^3J_{HH}$ = 11.5 Hz, P^2CH), 6.98 (ddq, 1H, $^3J_{PH}$ = 38.1 Hz, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 7.2 Hz, P^2CCH), 7.30−7.92 (m, 21H, aromatics).

Synthesis of Regioisomers 4b and 4d. The crude product **4b** (0.40 g) was redissolved in acetonitrile (25 mL) and slowly

(9) Allen, D. G.; McLaughlin, G. M.; Robertson, G. B.; Steffen, W. L.; Salem, G.; Wild, S. B. *Inorg. Chem.* **1982**, *21*, 1007.

recrystallized from acetonitrile and diethyl ether to give the 1:1 mixture of **4b** and **4d** as colorless crystals: 0.36 g (90% yield). mp: 227 °C (dec). $[\alpha]_D$ −20 (*c* 0.3, $CHCl_3$). Anal. calcd for $C_{38}H_{42}ClNO_4P_2Pd$: C, 58.5; H, 5.4; N, 1.8. Found: C, 58.4; H, 5.5; N, 1.8. **4d**: ^{31}P NMR ($CDCl_3$): δ 15.9, 76.4 (J_{PP} = 22.1 Hz). ^1H NMR ($CDCl_3$): δ 1.21 (dd, 3H, $^3J_{PH}$ = 12.1 Hz, $^3J_{HH}$ = 6.9 Hz, P^1CHMe), 1.71 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 1.94 (d, 3H, $^3J_{HH}$ = 6.2 Hz, P^2CCMe), 1.94−2.20 (m, 2H, P^1CH_2), 2.36 (s, 3H, N*Meeq*), 2.53−2.70 (m, 1H, P^1CHMe), 2.87 (s, 3H, N*Meax*), 4.55 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.2 Hz, CHMe), 6.35 (dd, 1H, $^3J_{PH}$ = $^3J_{HH}$ = 11.5 Hz, P^2CH), 6.76−7.09 (m, 1H, P^2CCH), 7.30−8.34 (m, 21H, aromatics).

Synthesis of Complex 5a. Concentrated hydrochloric acid (10 mL) was added to a solution of **4a** (0.29 g) in dichloromethane (25 mL). The reaction mixture was stirred vigorously at room temperature for 12 h, washed with water (3 × 20 mL), and dried (magnesium sulfate). Crystallization of the crude product from acetonitrile and diethyl ether gave the dichloro complex as yellowish crystals: 0.18 g (88% yield). mp: 250 °C (dec). $[\alpha]_D$ −88 (*c* 0.6, CH_2Cl_2). Anal. calcd for $C_{24}H_{26}Cl_2P_2Pd$: C, 52.1; H, 4.7. Found: C, 52.0; H, 5.0. ^{31}P NMR ($CDCl_3$): δ 42.6, 75.2 (J_{PP} = 6.3 Hz). ^1H NMR ($CDCl_3$): δ 0.85 (dd, 3H, $^3J_{PH}$ = 14.6 Hz, $^3J_{HH}$ = 7.1 Hz, PCH*Me*), 1.98 (ddd, 3H, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.5 Hz, $^4J_{PH}$ = 3.0 Hz, PCC*Me*), 2.11−2.41 (m, 2H, PCH_2), 2.95−3.14 (m, 1H, PCHMe), 5.91 (ddd, 1H, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ = 12.1 Hz, $^4J_{HH}$ = 1.5 Hz, PC*H*), 6.74 (ddq, 1H, $^3J_{PH}$ = 41.2 Hz, $^3J_{HH}$ = 12.1 Hz, $^3J_{HH}$ = 7.1 Hz, PCC*H*), 7.40−8.13 (m, 15H, aromatics).

Synthesis of Complex 5b. Concentrated hydrochloric acid (10 mL) was added to a solution of **4b** and **4d** (0.30 g) in dichloromethane (25 mL). The reaction mixture was stirred vigorously at room temperature for 12 h, washed with water (3 × 20 mL), and dried (magnesium sulfate). Crystallization of the crude product from dichloromethane and diethyl ether gave the dichloro complex as yellowish crystals: 0.19 g (89% yield). mp: 260°C. $[\alpha]_D$: −60 (*c* 0.5, CH_2Cl_2). Anal. calcd for $C_{24}H_{26}Cl_2P_2Pd$: C, 52.1; H, 4.7. Found: C, 52.0; H, 5.0. ^{31}P NMR ($CDCl_3$): δ 39.7, 71.2 (J_{PP} = 5.6 Hz). ^1H NMR ($CDCl_3$): δ 1.14 (dd, 3H, $^3J_{PH}$ = 13.2 Hz, $^3J_{HH}$ = 6.9 Hz, PCH*Me*), 2.04 (ddd, 3H, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.3 Hz, $^4J_{PH}$ = 2.9 Hz, PCC*Me*), 2.05−2.15 (m, 1H, PCH*H*′), 2.28−2.57 (m, 1H, PC*H*H′), 2.59−2.76 (m, 1H, PC*H*Me), 6.13 (ddd, 1H, $^3J_{PH}$ = 20.1 Hz, $^3J_{HH}$ = 12.2 Hz, $^4J_{HH}$ = 1.3 Hz, PC*H*), 6.75 (ddq, 1H, $^3J_{PH}$ = 41.6 Hz, $^3J_{HH}$ = 12.2 Hz, $^3J_{HH}$ = 7.1 Hz, PCC*H*), 7.41−8.05 (m, 15H, aromatics).

Liberation of Free Ligand 6a. A solution of **5a** (0.06 g) in dichloromethane (20 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (1 g) for 30 min. The colorless organic layer was separated, washed with water (3 × 20 mL), and dried (magnesium sulfate). Upon the removal of the solvent, a white solid was obtained: 0.05 g (95% yield). $[\alpha]_{546}$ +70 (*c* 0.5, $CHCl_3$). ^{31}P NMR ($CDCl_3$): δ −44.8, 2.0 (J_{PP} = 20.8 Hz). ^1H NMR ($CDCl_3$): δ 1.21 (dd, 3H, $^3J_{PH}$ = 15.4 Hz, $^3J_{HH}$ = 6.8 Hz, PCH*Me*), 1.48−1.57 (m, 1H, PCH*H*′), 1.84 (d, 3H, $^3J_{HH}$ = 6.8 Hz, PCC*Me*), 1.96−2.19 (m, 1H, PC*H*H′), 2.19−2.32 (m, 1H, PC*H*Me), 5.94 (d, 1H, $^3J_{PH}$ = 11.5 Hz, PC*H*), 6.29 (ddq, 1H, $^3J_{PH}$ = 21.7 Hz, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 6.8 Hz, PCC*H*), 7.18−7.42 (m, 15H, aromatics).

Table 4. X-ray Crystallographic Data of **4a**, **4b**, and **4d**

	4a	**4b** and **4d**
formula	$C_{39}H_{44}Cl_3NO_4P_2Pd$	$C_{38}H_{42}ClNO_4P_2Pd$
fw	865.44	780.52
space group	*P*2(1)	*P*2(1)
cryst syst	monoclinic	monoclinic
a/Å	9.3975(5)	19.480(2)
b/Å	9.8036(6)	9.6937(11)
c/Å	20.7827(11)	20.358(2)
α/deg	90	90°
β/deg	92.841(3)	109.602(7)°
γ/deg	90	90°
V/Å^3	1912.34(19)	3621.5(7)
Z	2	4
T/K	173(2)	173(2)
D_{calcd}/g cm^{-3}	1.503	1.432
μ/mm^{-1}	0.820	0.715
λ/Å	0.71073	0.71073
Flack params	0.003(17)	−0.02(4)
R1 (obsd data)[a]	0.0379	0.0686
wR2 (obsd data)[b]	0.0485	0.0990

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP$.

Liberation of Free Ligand 6b. A solution of **5b** (0.06 g) in dichloromethane (20 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (1 g) for 30 min. The colorless organic layer was separated, washed with water (3 × 20 mL), and dried (magnesium sulfate). Upon the removal of the solvent, a white solid was obtained: 0.05 g (95% yield). $[\alpha]_D$ +246 (*c* 0.5, $CHCl_3$). ^{31}P NMR ($CDCl_3$): δ −46.5, 2.0 (J_{PP} = 20.5 Hz). ^1H NMR ($CDCl_3$): δ 1.22 (dd, 3H, $^3J_{PH}$ = 15.2 Hz, $^3J_{HH}$ = 6.7 Hz, PCH*Me*), 1.55−1.70 (m, 1H, PCH*H*′), 1.98 (d, 3H, $^3J_{HH}$ = 6.7 Hz, PCC*Me*), 1.92−2.03 (m, 1H, PC*H*H′), 2.34−2.51 (m, 1H, PC*H*Me), 5.80 (dd, 1H, $^3J_{PH}$ = 22.5 Hz, $^3J_{HH}$ = 11.3 Hz, PC*H*), 6.51 (ddq, 1H, $^3J_{PH}$ = 21.7 Hz, $^3J_{HH}$ = 11.3 Hz, $^3J_{HH}$ = 6.7 Hz, PCC*H*), 7.20−7.58 (m, 15H, aromatics).

Crystal Structure Determinations of Complexes 4a, 4b, and 4d. Crystal data and a summary of the crystallographic analyses are given in Table 4. Diffraction data were collected at the Nanyang Technological University using a Bruker X8 Apex diffractometer with Mo Kα radiation (graphite monochromator). All non-H atoms were refined anisotropically, while hydrogen atoms were introduced at a fixed distance from the carbon atoms and were assigned fixed thermal parameters. The absolute configurations of the chiral complexes were determined unambiguously using the Flack parameter.[10]

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Supporting Information Available: Crystallographic data in CIF format for complexes **4a**, **4b**, and **4d**. This material is available free of charge via the Internet at http://pubs.acs.org.

(10) Flack, H. D. *Acta Crystallogr*. **1983**, *A39*, 876.