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Asymmetric Synthesis of New Diphosphines and Pyridylphosphines via a Kinetic Resolution Process Promoted and Controlled by a Chiral Palladacycle

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A chiral palladacycle has been used successfully to promote the asymmetric hydrophosphination reactions between the racemic secondary phosphine ethylphenylphosphine and (*E*)/(*Z*)-diphenyl-1-propenylphosphine or 2-vinylpyridine in high regio- and stereoselectivities under mild conditions. Hydrophosphination of (*E*)-diphenyl-1-propenylphosphine with ethylphenylphosphine gave the asymmetric diphosphine chelate containing one stereogenic phosphorus donor with the *R* absolute configuration and one neighboring chiral *S*-carbon center as the major product in 60% yield. Using the same chiral metal template, the corresponding hydrophosphination reaction with (*Z*)-diphenyl-1-propenylphosphine gave the diastereomeric diphosphine in 40% yield with a chiral *R*-carbon center, but the controlled formation of the *R*-phosphorus configuration was not affected by the different stereochemistry in the carbon chain. A pair of separable diastereomeric palladium templates containing the naphthylamine auxiliary and the enantiomeric forms of (R_p/S_p)-[1-ethylphenylphosphino-2-(2-pyridine)]ethane were also generated in the ratio 1.5:1 via hydrophosphination of 2-vinylpyridine with ethylphenylphosphine. The optically pure diphosphine ligands and P, N ligands could be stereospecifically liberated from the template complexes. The coordination chemistry and the absolute stereochemistry of the template complexes and dichloro complexes were determined by X-ray crystallography.

Introduction

In recent decades chiral phosphines have attracted considerable interest, as they are important ligands in asymmetric transition metal catalysis and synthesis.[1,2] P-Stereogenic phosphine ligands can generate an asymmetric environment in close proximity to the metal center, thus enhancing the enantioselectivity of the metal-catalyzed asymmetric reaction, which makes them more attractive ligands in asymmetric synthesis. Diphosphines bearing P-stereogenic or P- and C-stereogenic centers, associated with transition metals, have been proved excellent catalysts for asymmetric hydrogenation, asymmetric hydroformylation, asymmetric hydrosilylation, and asymmetric carbon−carbon bond formation reactions with high enantioselectivity.[1] However, due to the lack of a natural pool of chirality together with configurational instability of the phosphorus stereocenters at high temperatures, only a few diphosphines containing P- and C-stereogenic centers have been reported via the asymmetric synthesis.[3−5]

Chiral pyridylphosphine ligands, which possess a combination of soft π-acceptor phosphorus and hard σ-donor

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nitrogen, have been widely used to prepare complexes of different transition metals,[6−14] some of which have been successfully applied to important catalytic asymmetric reactions, involving asymmetric allylic substitution,[8] asymmetric hydrogenation,[9] hydrosilylation,[10] asymmetric hydroboration,[11] asymmetric hydroformylation,[12] hydration of multiple bonds of unsaturated moieties,[13] and so on. More recently, catalytic ethane oligomerization using nickel and palladium complexes bearing new pyridylphosphine ligands has also been reported.[14] Although a large number of pyridylphosphine ligands with central, axial, and planar chirality have been synthesized, P-stereogenic pyridylphosphine ligands are rare, with the great majority of the pyridylphosphine ligands bearing diphenylphosphino fragments.[15]

The hydrophosphination reaction, which involves the asymmetric addition of a P−H moiety to unsaturated carbon−carbon bonds, is generally considered a straightforward and efficient approach for the synthesis of chiral phosphines containing different chemical functionalities.[16] Our group has previously reported the application of chiral cyclometalated-amine complexes as efficient chiral auxiliaries to promote the asymmetric hydrophosphination reactions involving diphenylphosphine whereby a series of chiral bidentate phosphines bearing diphenylphosphino fragments with chirality residing on the carbon backbone and incorporating various functional groups have been synthesized.[5f,17] We have also applied the methodology to the asymmetric Diels−Alder reaction between 2-vinylpyridine and DMPP to give P-stereogenic pyridylphosphines.[18] In continuation of our exploration of the synthesis of chiral phosphine ligands utilizing these efficient auxiliaries, we herein illustrate a facile strategy to synthesize diphosphines containing both P- and C-stereogenic centers and P-stereogenic pyridylphosphines via asymmetric hydrophosphination reaction promoted by chiral cyclometalated-amine complexes involving the racemic secondary phosphine (±)-PhEtPH and (*E*)/(*Z*)-diphenyl-1-propenylphosphine/2-vinylpyridine.

Results and Discussion

Asymmetric Hydrophosphination of (*E*)-Diphenyl-1-propenylphosphine. In the absence of the metal template, there is no reaction between (±)-PhEtPH and (*E*)-diphenyl-1-propenylphosphine under ambient conditions. As illustrated in Scheme 1, (*E*)-diphenyl-1-propenylphosphine was first coordinated to (R_c)-**1** regioselectively to form the neutral complex (R_c)-**2a**.[19] However, no reaction between complex (R_c)-**2a** and (±)-PhEtPH was observed. Therefore, the thermodynamically stable and kinetically inert chlorine−palladium bond was cleaved by treatment with silver perchlorate to give the kinetically labile perchlorato complex (R_c)-**3a**.[19,20] Complex (R_c)-**3a** was not isolated, but was subsequently treated with racemic (±)-PhEtPH in dichloromethane at −78 °C, and the reaction mixture was allowed to warm to room temperature. It should be noted that a ligand redistribution process between (±)-PhEtPH and (*E*)-diphenyl-1-propenylphosphine will occur prior to the hydrophosphination reaction.[17a,21] Moreover, PhEtPH is a chiral secondary phosphine, and therefore coordination to the metal center will generate two different stereocenters.[22,23] Therefore, in principle, hydrophosphination of racemic (±)-PhEtPH and (*E*)-diphenyl-1-propenylphosphine may generate eight possible stereoisomeric products (Scheme 1). Complexes **4a** and **4b** are regioisomers with the same absolute configurations at the newly generated stereogenic phosphorus and carbon centers within the diphosphine chelate but differ in the relative regioarrangement of the two nonequivalent phosphorus donor atoms on the metal

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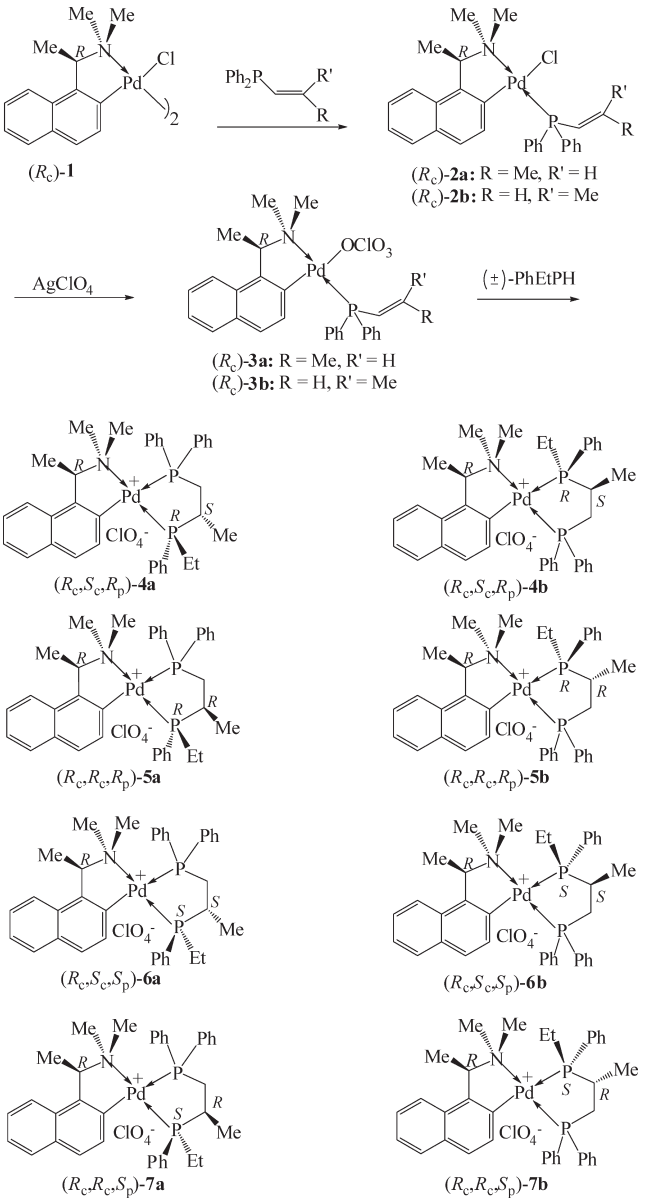
Scheme 1



template. Similarly, complexes **5a** and **5b**, **6a** and **6b**, **7a** and **7b**, and **8a** and **8b** are regioisomers with the same absolute configurations at newly generated stereogenic phosphorus and carbon centers.

Prior to purification, the $^{31}P\{^{1}H\}$ NMR spectrum of a crude hydrophosphination reaction mixture in $CDCl_3$ exhibited three pairs of doublets at δ 69.7 (d, 1P, J_{pp} = 34.2 Hz), 30.0 (d, 1P, J_{pp} = 34.2 Hz); 52.3 (d, 1P, J_{pp} = 30.4 Hz), 44.4 (d, 1P, J_{pp} = 30.4 Hz); and 53.4 (d, 1P, J_{pp} = 30.4 Hz), 42.5 (d, 1P, J_{pp} = 30.4 Hz) in the ratio 9.5:1:1, respectively. After purification by silica gel column chromatography (acetone−hexane, 1:6), only the major product, (R_c,S_c,R_p)-**4a**, was obtained. Complex (R_c,S_c,R_p)-**4a** was then crystallized from dichlomethane−diethyl ether as light yellow crystals in 60% yield (Scheme 1).

The coordination chemistry and the absolute stereochemistry of complex (R_c,S_c,R_p)-**4a** were confirmed by single-crystal X-ray diffraction analysis. The study revealed that the expected five-membered diphosphine chelate has been formed (Figure 1). Two new stereogenic centers at P(1) and

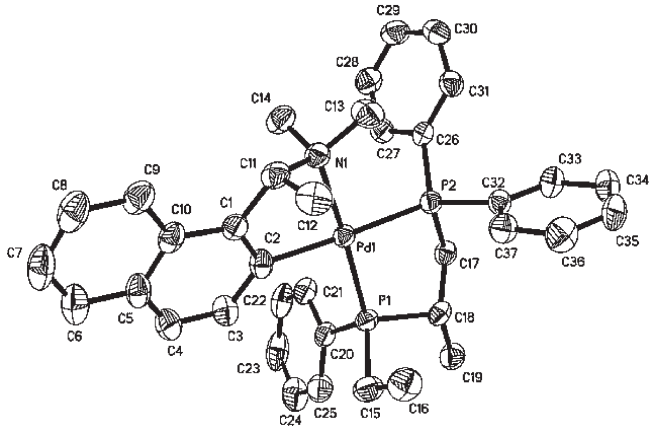
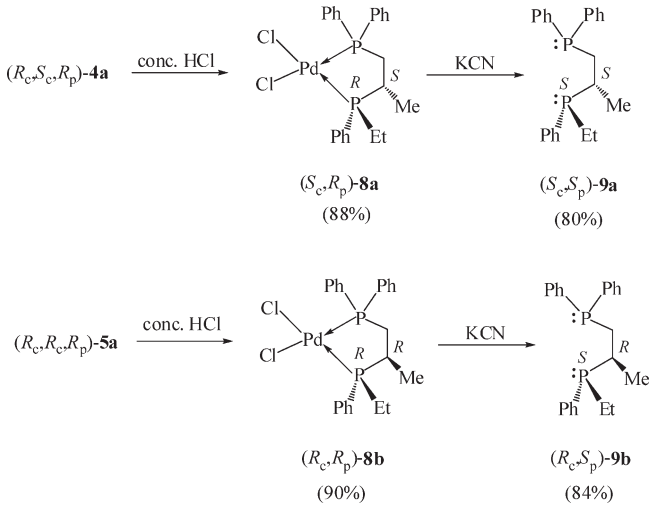


Figure 1. Molecular structure of complex (R_c,S_c,R_p)-**4a** with 50% probability ellipsoids shown.

Table 1. Selected Bond Distances (Å) and Angles (deg) of Complex (R_c,S_c,R_p)-4a

Pd(1)−C(2)	2.047(4)	C(2)−Pd(1)−P(1)	95.6 (1)
Pd(1)−N(1) p	2.134(3)	N(1)−Pd(1)−P(1)	175.5(1)
Pd(1)−P(1)	2.248 (1)	C(2)−Pd(1)−P(2)	175.3 (1)
Pd(1)−P(2)	2.340(1)	N(1)−Pd(1)−P(2)	99.0(1)
P(1)−C(18)	1.86 (4)	P(1)−Pd(1)−P(2)	85.0 (4)
P(2)−C(17)	1.83 (4)	C(18)−P(1)−Pd(1)	108.8(1)
C(17)−C(18)	1.53 (6)	C(17)−P(2)−Pd(1)	105.6 (1)
C(18)−C(19)	1.53(6)	C(17)−C(18)−P(1)	107.7(3)
C(2)−Pd(1)−N(1)	80.6(2)	C(18)−C(17)−P(2)	107.5(3)

Scheme 2



C(18) were generated, which adopt the *R* and *S* absolute configuration, respectively, while as expected, the absolute configuration of the stereocenters at C(11) remained unchanged. The X-ray analysis data taken in conjunction with the $^{31}P\{^{1}H\}$ coupling information also showed that this hydrophosphination reaction is highly regioselective, as the ethylphenylphosphino group was added preferentially to the β-carbon of the vinylphosphines to form the five-membered chelate ring exclusively.

The geometry at palladium is distorted square planar with angles at palladium in the ranges 80.6(2)−99.0(1)° and 175.3 (1)−175.5(1)°. The Pd−P(1) and Pd−P(2) bond distances are 2.248(1) and 2.340(1) Å, respectively, with the bond *trans* to the carbon of the naphthylamine auxiliary being longer by

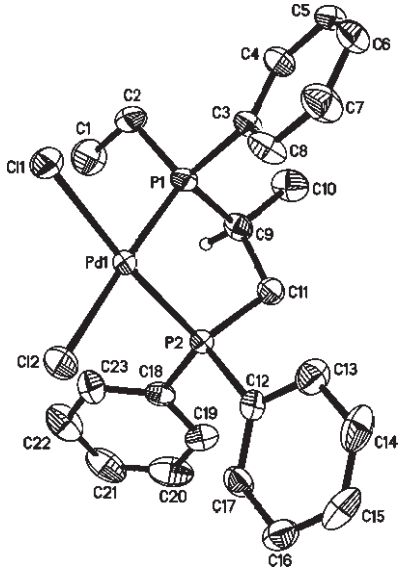


Figure 2. Molecular structure of complex (S_c,R_p)-**8a** with 50% probability ellipsoids shown.

Table 2. Selected Bond Distances (Å) and Angles (deg) of Complex (S_c,R_p)-8a

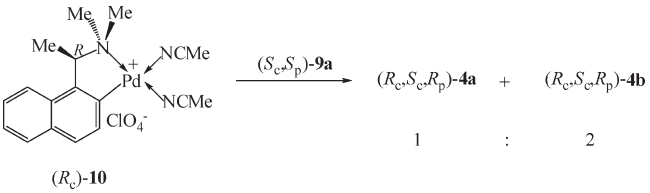
Pd(1)−Cl(1)	2.369(1)	C(9)−C(10)	1.509(7)
Pd(1)−Cl(2)	2.374(1)	P(1)−Pd(1)−Cl(1)	89.4(1)
Pd(1)−P(1)	2.246(1)	P(2)−Pd(1)−P(1)	85.8(1)
Pd(1)−P(2)	2.234(1)	P(2)−Pd(1)−Cl(2)	90.7(1)
C(9)−C(11)	1.516(7)	Cl(1)−Pd(1)−Cl(2)	94.1(1)

0.092 Å. This indicates that the two phosphorus atoms have quite different donor abilities. In the five-membered diphosphine metal chelate, the methyl substituent at the chiral carbon center, C(18), occupies an equatorial position, which is in accordance with our previous studies.[17a,g] Selected bond distances and angles of complex (R_c,S_c,R_p)-**4a** are given in Table 1.

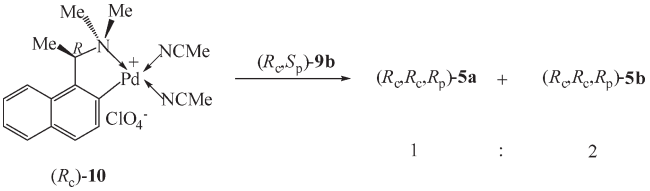
Removal of the naphthylamine auxiliary by treatment with strong acid is a standard method that leads to the formation of the corresponding neutral dichloro palladium(II) complex. As shown in Scheme 2, the chiral naphthylamine auxiliary in (R_c,S_c,R_p)-**4a** can be removed chemoselectively from the palladium template by treatment with concentrated hydrochloric acid in dichloromethane. The chiral auxiliary was recovered quantitatively from the mother liquor after treatment with base. On the other hand, the neutral dichloro complex (S_c,R_p)-**8a** was obtained efficiently as stable white crystals in 88% yield. The $^{31}P\{^1H\}$ NMR spectrum of the dichloro complex (S_c,R_p)-**8a** in $CDCl_3$ exhibited a pair of doublets at δ 80.3 (d, 1P, J_{pp} = 5.5 Hz) and 50.5 (d, 1P, J_{pp} = 5.5 Hz). The molecular structure and absolute stereochemistry of (S_c,R_p)-**8a** was established by X-ray crystallography (Figure 2). The selected bond lengths and angles are given in Table 2. The absolute configurations at C(9) and P(1) are *S* and *R*, respectively.

The optically pure diphosphine ligand (S_c,S_p)-**9a** can subsequently be liberated from the dichloro complex (S_c, R_p)-**8a** by treatment of the dichloro complex with saturated aqueous potassium cyanide in dichloromethane at room temperature for 2 h (Scheme 2). The free ligand (S_c,S_p)-**9a** was thus obtained as a white solid in 80% yield, $[\alpha]_D$ = −118.4 (*c* 0.2, CH_2Cl_2). The $^{31}P\{^1H\}$ NMR spectrum of the free diphosphine ligand (S_c,S_p)-**9a** in $CDCl_3$ exhibited a pair of doublets at δ −0.66 (d, 1P, J_{pp} = 21.2 Hz) and −19.7 (d, 1P, J_{pp} = 21.2 Hz). It is noteworthy that the apparent inversion of configuration that takes place at the phosphorus stereogenic center during the liberation reaction is merely a consequence of the Cahn−Ingold−Prelog rules.[24]

Scheme 3



Scheme 4



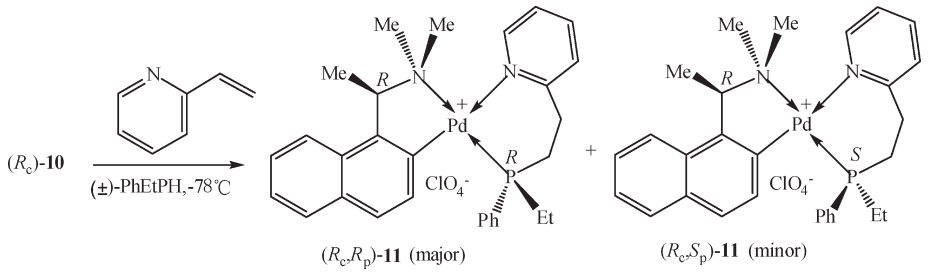
In order to confirm the optical purity of the liberated ligand and to establish the identity of the hydrophosphination product, free ligand (S_c,S_p)-**9a** was recoordinated to the bis(acetonitrile) complex (R_c)-**10**.[25] When the liberated ligand (S_c,S_p)-**9a** was recomplexed to the bis(acetonitrile) complex (R_c)-**10** (Scheme 5), the ^{31}P NMR spectrum of the crude recomplexation product mixture in $CDCl_3$ exhibited two pairs of doublets at δ 52.3 (d, 1P, J_{pp} = 30.4 Hz), 44.4 (d, 1P, J_{pp} = 30.4 Hz) and at 69.7 (d, 1P, J_{pp} = 34.2 Hz), 30.0 (d, 1P, J_{pp} = 34.2 Hz) in the ratio 2:1, respectively. The resonance signals at δ 69.7 and 30.0 are identical to those observed for the major product, (R_c,S_c,R_p)-**4a**, in the original hydrophosphination reaction, while the signals at δ 52.3 and 44.4 match one of the minor signals seen in the original reaction mixture and are assigned to the regioisomer of the major product, (R_c,S_c,R_p)-**4b**. Interestingly, in this recomplexation reaction, the regioisomer (R_c,S_c,R_p)-**4b** was the major product, while the major product, (R_c,S_c,R_p)-**4a**, in the original hydrophosphination reaction was observed to be the minor product.

Hydrophosphination of (*Z*)-Diphenyl-1-propenylphosphine. Hydrophosphination of (*Z*)-diphenyl-1-propenylphosphine was achieved by means of a similar procedure to hydrophosphination of (*E*)-diphenyl-1-propenylphosphine (Scheme 1). In principle, the hydrophosphination reaction between (*Z*)-diphenyl-1-propenylphosphine palladium complex **3b** and racemic (±)-PhEtPH may also generate the same eight possible stereoisomeric products, **4**, **5**, **6**, and **7** as that obtained from the reaction involving *E*-isomer complex **3a**.

Prior to purification, the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture in $CDCl_3$ exhibited four pairs of doublets at δ 67.7 (d, 1P, J_{pp} = 26.6 Hz), 34.9 (d, 1P, J_{pp} = 26.6 Hz); 71.1 (d, 1P, J_{pp} = 30.4 Hz), 34.4 (d, 1P, J_{pp} = 30.4 Hz); 51.7 (d, 1P, J_{pp} = 30.4 Hz), 45.6 (d, 1P, J_{pp} = 30.4 Hz); and 65.8 (d, 1P, J_{pp} = 30.4 Hz), 30.4 (d, 1P, J_{pp} = 30.4 Hz) in the ratio of 24:13:2:1, respectively. After purification by silica gel column chromatography (acetone−hexane, 1:6), only the

(24) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.
(25) Chooi, S. Y. M.; Siah, S. Y.; Leung, P. H.; Mok, K. F. *Inorg. Chem.* **1993**, *32*, 4812.

Scheme 5



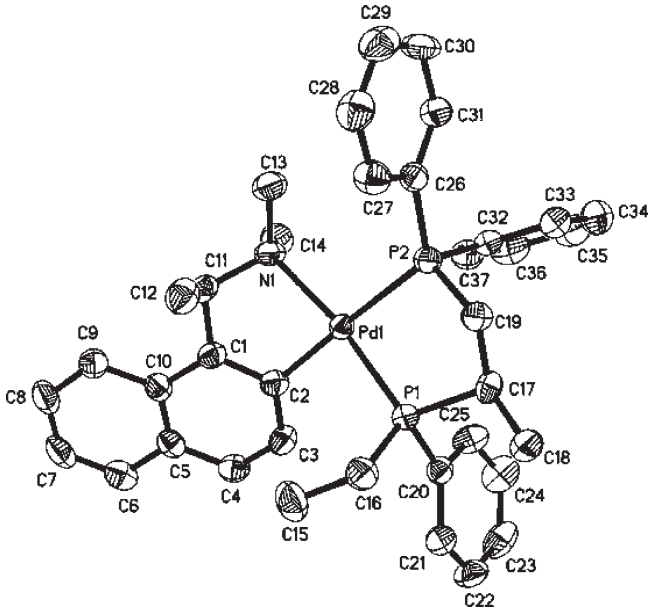


Figure 3. Molecular structure of complex (R_c,R_c,R_p)-**5a** with 50% probability ellipsoids shown.

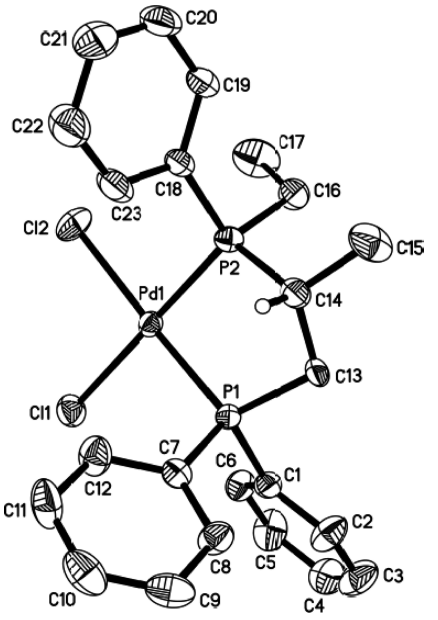


Figure 4. Molecular structure of complex (R_c,R_p)-**8b** with 50% probability ellipsoids shown.

Table 3. Selected Bond Distances (Å) and Angles (deg) of Complex (R_c,R_c,R_p)-5a

Pd(1)−C(2)	2.053(4)	C(2)−Pd(1)−P(1)	95.2 (2)
Pd(1)−N(1) p	2.139(3)	N(1)−Pd(1)−P(1)	170.3(1)
Pd(1)−P(1)	2.265(1)	C(2)−Pd(1)−P(2)	177.1(1)
Pd(1)−P(2)	2.346 (1)	N(1)−Pd(1)−P(2)	102.1(9)
P(1)−C(17)	1.857(4)	P(1)−Pd(1)−P(2)	83.9 (4)
P(2)−C(19)	1.827(4)	C(17)−P(1)−Pd(1)	110.5(1)
C(17)−C(19)	1.526(6)	C(19)−P(2)−Pd(1)	106.9(1)
C(17)−C(18)	1.537(6)	C(19)−C(17)−P(1)	109.5(3)
C(2)−Pd(1)−N(1)	79.2 (2)	C(17)−C(19)−P(2)	108.8(3)

Table 4. Selected Bond Distances (Å) and Angles (deg) of Complex (R_c,R_p)-8b

Pd(1)−Cl(1)	2.381(2)	C(14)−C(15)	1.525(11)
Pd(1)−Cl(2)	2.341(2)	P(1)−Pd(1)−Cl(1)	93.4(1)
Pd(1)−P(1)	2.249(2)	P(2)−Pd(1)−P(1)	85.8(1)
Pd(1)−P(2)	2.230(2)	P(2)−Pd(1)−Cl(2)	88.9(1)
C(13)−C(14)	1.529(10)	Cl(1)−Pd(1)−Cl(2)	91.8(1)

major product (R_c,R_c,R_p)-**5a** was obtained. Complex (R_c,R_c, R_p)-**5a** was crystallized from dichlomethane−diethyl ether as light yellow crystals in 40% yield (Scheme 1)

The single-crystal X-ray diffraction analysis of the complex (R_c,R_c,R_p)-**5a** revealed that the expected five-membered diphosphine chelate had been formed (Figure 3). Two new stereogenic centers at P(1) and C(17) were generated, both of which adopt the *R* absolute configuration, while the absolute configuration of the stereocenters at C(11) remained unchanged. The X-ray analysis also showed that this hydrophosphination reaction is also highly regioselective, as the ethylphenylphosphino group was added to the β-carbon of the vinylphosphines to form a five-membered chelate ring exclusively.

The geometry at palladium is distorted square planar with angles at palladium in the ranges 79.2 (2)−102.1(9)° and 170.3(1)−177.1(1)°. The Pd−P(1) and Pd−P(2) bond distances are 2.265(1) and 2.346 (1) Å, respectively, with the bond *trans* to the carbon of the naphthylamine auxiliary being longer by 0.081 Å. This indicates that the phosphorus atoms have quite different donor abilities. Similar to diastereomeric complex (R_c,S_c,R_p)-**4a**, in the five-membered diphosphine metal chelate, the methyl substituent at the chiral carbon center, C(17), occupies the equatorial site. Selected bond distances and angles of complex (R_c,R_c,R_p)-**5a** are given in Table 3.

As shown in Scheme 2, the chiral naphthylamine auxiliary in (R_c,R_c,R_p)-**5a** can be removed chemoselectively from the palladium template by treatment with concentrated hydrochloric acid in dichloromethane. The neutral dichloro complex (R_c,R_p)-**8b** was obtained efficiently as stable white crystals in 90% yield. The $^{31}P\{^1H\}$ NMR spectrum of the dichloro complex (R_c,R_p)-**8b** in $CDCl_3$ exhibited a pair of doublets at δ 80.8 (d, 1P, J_{pp} = 6.4 Hz) and 58.9 (d, 1P, J_{pp} = 6.4 Hz). The molecular structure and absolute stereochemistry of complex (R_c,R_p)-**8b** was established by X-ray

crystallography (Figure 4), and selected bond lengths and angles are given in Table 4. The absolute configurations at C(9) and P(1) are both *R*.

By treatment of the dichloro complex (R_c,R_p)-**8b** with saturated aqueous potassium cyanide in dichloromethane at room temperature for 2 h, the optically pure diphosphine ligand (R_c,S_p)-**9b** was liberated successfully (Scheme 4). The free ligand (R_c,S_p)-**9b** was obtained as a white solid in 84% yield, $[\alpha]_D = +92.6$ (*c* 0.2., CH_2Cl_2). The $^{31}P\{^1H\}$ NMR spectrum of the free diphosphine ligand (R_c,S_p)-**9b** in $CDCl_3$ exhibited a pair of doublets at δ −0.38 (d, 1P, J_{pp} = 18.4 Hz) and −20.5 (d, 1P, J_{pp} = 18.4 Hz).

The optical purity of the liberated ligand (R_c,S_p)-**9b** was established by subsequent recomplexation to the bis(acetonitrile) complex (R_c)-**10** (Scheme 4). The ^{31}P NMR spectrum of the crude recomplexation product mixture in $CDCl_3$ exhibited two pairs of doublets at δ 51.7 (d, 1P, J_{pp} = 30.4 Hz), 45.6 (d, 1P, J_{pp} = 30.4 Hz); 67.7 (d, 1P, J_{pp} = 26.6 Hz), 34.9 (d, 1P, J_{pp} = 26.6 Hz) in the ratio 2:1, respectively. The resonance signals at δ 67.7 and 34.9 are identical to those observed for the major product (R_c,R_c,R_p)-**5a** in the original hydrophosphination reaction, while the signals at δ 51.7 and 45.6 match one of the minor signals seen in the original reaction mixture and are assigned to the major product's regioisomer, (R_c,R_c,R_p)-**5b**.

The recoordination step therefore proves the optical purity of the liberated ligand (R_c,S_p)-**9b** and also assists in identifying the minor isomeric complexes generated directly from the hydrophosphination reaction.

Hydrophosphination of 2-Vinylpyridine. Due to the distinct electronic directing effects originating from the *ortho*-metalated [(1-(dimethylamino)ethyl)-2-naphthyl- C^2,*N*]palladium(II) unit,[26] this hydrophosphination reaction is 100% regioselective, with the soft phosphorus donor exclusively taking up the position *trans* to the NMe_2 group in the complex. As illustrated in Scheme 5, bis(acetonitrile) palladium(II) complex (R_c)-**10** was allowed to dissolve in dichloromethane first, followed by treatment with (±)-PhEtPH and 2-vinylpyridine at −78 °C. The reaction mixture was allowed to warm to ambient temperature and was found to be completed in 24 h. Prior to purification, the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture in $CDCl_3$ exhibited two singlets at δ 33.0 and 34.3 in the ratio 1.5:1. Upon fractional crystallization, the major and minor products were then crystallized from dichlomethane−diethyl ether as white crystals in 51.5% and 31.3% yield, separately. The single-crystal X-ray diffraction analysis revealed that the major product was complex (R_c,R_p)-**11**, and complex (R_c,S_p)-**11** is the minor product (Scheme 5).

The single-crystal X-ray diffraction analysis of the complex (R_c,R_p)-**11** established unambiguously that the bis(acetonitrile) palladium(II) complex (R_c)-**1** promoted hydrophosphination reaction between (±)-PhEtPH and 2-vinylpyridine had indeed occurred and the expected hydrophosphination product incorporating a six-membered P, N chelate was formed (Figure 5). As shown in Figure 5, the phosphorus donor atom is coordinated regiospecifically to the metal center in the position *trans* to the σ-donating naphthylamine-N atom, while the nitrogen atom of the pyridine binds to the position *trans* to the π-accepting aromatic carbon atom of the *ortho*-metalated naphthylamine chelate.

(26) Chooi, S. Y. M.; Hor, T. S. A.; Leung, P. H.; Mok, K. F. *Inorg. Chem.* **1992**, *31*, 1494.

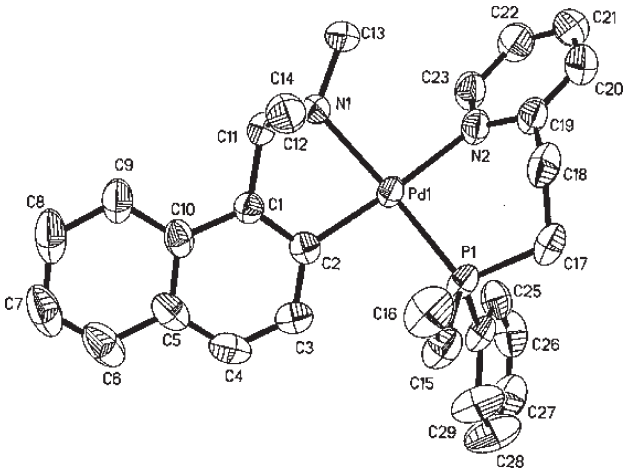


Figure 5. Molecular structure of complex (R_c,R_p)-**11** with 50% probability ellipsoids shown.

Table 5. Selected Bond Distances (Å) and Angles (deg) of Complex (R_c,R_p)-11

Pd(1)−C(2)	1.994(3)	N(2)−Pd(1)−N(1)	95.0 (1)
Pd(1)−N(1) p	2.144(3)	C(2)−Pd(1)−P(1)	93.5(1)
Pd(1)−N(2)	2.143(3)	N(2)−Pd(1)−P(1)	90.9 (8)
Pd(1)−P(1)	2.241 (8)	N(1)−Pd(1)−P(1)	167.8(9)
P(1)−C(17)	1.829(4)	C(17)−P(1)−Pd(1)	106.5(1)
C(17)−C(18)	1.552(6)	C(19)−N(2)−Pd(1)	121.5(3)
C(18)−C(19)	1.484(6)	C(18)−C(17)−P (1)	113.2(2)
C(2)−Pd(1)−N(2)	175.5(1)	C(19)−C(18)−C(17)	110.9(3)
C(2)−Pd(1)−N(1)	80.9(1)	N(2)−C(19)−C(18)	117.5(3)

A new stereogenic center adopting an *R* absolute configuration was formed at P(1), while the absolute configuration of the stereocenter at C(11) remained unchanged. The X-ray analysis also showed that this hydrophosphination reaction was highly regioselective toward the vinylic C=C bond of the vinylpyridine, as the ethylphenylphosphino group was added exclusively to the β-carbon of the vinylic C=C bond to form the six-membered chelate ring exclusively. The geometry at palladium is slightly distorted square planar with angles at palladium in the ranges 80.9(1)−95.0(1)° and 167.8(8)−175.5(1)°. The C(17)−C(18) [1.552(6) Å] and newly formed Pd(1)−N(2) [2.143(3) Å] bond lengths are typical. Table 5 shows selected bond distances and angles of complex (R_c,R_p)-**11**.

As shown in Figure 6, the minor product of this hydrophosphination reaction, complex (R_c,S_p)-**11**, has the same molecular connectivity as the major product, complex (R_c,R_p)-**11**, but differs in the absolute configuration at the newly formed stereogenic phosphorus donor, which in this instance adopts the *S* absolute configuration. The six-membered P, N chelate has also been formed with high regioselectivity toward the vinylic C=C bond of the vinylpyridine in complex (R_c,S_p)-**11**, and the absolute configuration of the stereocenter at C(11) remained unchanged. Selected bond lengths and bond angles of complex (R_c,S_p)-**11** are given in Table 6.

The chiral naphthylamine auxiliary in (R_c,R_p)-**11** and (R_c,S_p)-**11** can be removed chemoselectively by individual treatment with concentrated hydrochloric acid in dichloromethane (Scheme 6). Thus the neutral P-chiral dichloro complexes (R_p)-**12** and (S_p)-**12** were obtained efficiently as stable yellow crystals in 90% and 87% yields, respectively. The $^{31}P\{^1H\}$ NMR spectrum of the dichloro complexes (R_p)-**12** and (S_p)-**12** in $CDCl_3$ exhibited a singlet at δ 31.1. The

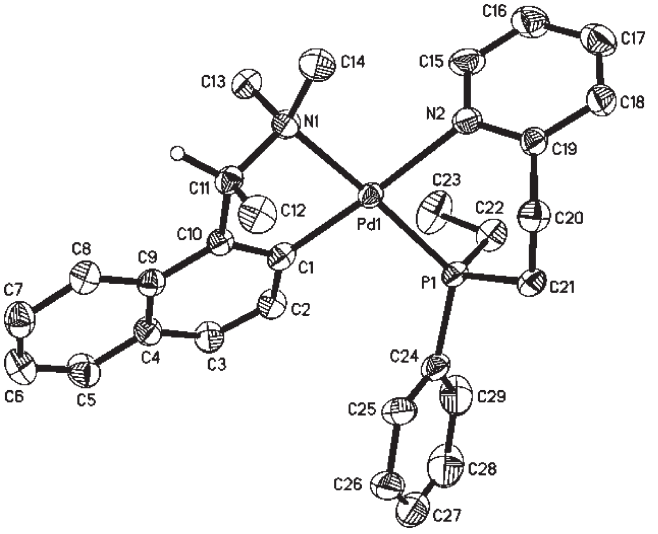


Figure 6. Molecular structure of complex (R_c,S_p)-**11** with 50% probability ellipsoids shown.

Table 6. Selected Bond Distances (Å) and Angles (deg) of Complex (R_c,S_p)-11

Pd(1)−C(1)	1.990(4)	N(2)−Pd(1)−N(1)	98.7(1)
Pd(1)−N(1)	2.132(3)	C(1)−Pd(1)−P(1)	98.3(1)
Pd(1)−N(2)	2.176(3)	N(2)−Pd(1)−P(1)	83.1(9)
Pd(1)−P(1)	2.248(1)	N(1)−Pd(1)−P(1)	173.2(1)
P(1)−C(21)	1.836(4)	C(21)−P(1)−Pd(1)	106.3(1)
C(20)−C(21)	1.537(6)	C(19)−N(2)−Pd(1)	121.3(2)
C(19)−C(20)	1.498(5)	C(20)−C(21)−P (1)	113.0(3)
C(1)−Pd(1)−N(2)	174.7(1)	C(19)−C(20)−C(21)	110.5(3)
C(1)−Pd(1)−N(1)	80.4(1)	N(2)−C(19)−C(20)	116.7(3)

molecular structure of complex (R_p)-**12** is shown in Figure 7. The geometry at palladium is regular square planar with *cis* angles ranging between 88.5(2)° and 91.2(1)°. The two Pd−Cl bond distances [2.292(2) and 2.364(1) Å] differ significantly, with the bond *trans* to the phosphorus being noticeably elongated from normal, which reflects the stronger electronic *trans* influence of the phosphorus relative to nitrogen.[17f,27] Dichloro complex (S_p)-**12** crystallized as two independent molecules in one unit cell, and both molecules have the same molecular connectivity as well as chirality and differ slightly only in the bond distances and angles involved. For clarity, only one molecule is shown Figure 8. Selected bond distances and angles of complexes (R_p)-**12** and (S_p)-**12** are given in Table 7.

The liberation of the enantiomerically pure P-chiral P, N ligands from (R_p)-**12** and (S_p)-**12** was achieved by separate treatment of the dichloro complexes with saturated aqueous potassium cyanide in dichloromethane at room temperature for 1 h (Scheme 6). Thus the optically pure P, N ligand (S_p)-**13** can be liberated successfully as an air-sensitive white solid in 81% yield, $[\alpha]_D = -26.1$ (*c* 0.2, CH_2Cl_2). The $^{31}P\{^1H\}$ NMR spectrum of the free ligand (S_p)-**13** in $CDCl_3$ exhibited a singlet at δ −18.5. The enantiomeric P, N ligand, (R_p)-**13**, with $[\alpha]_D = +26.1$ (*c* 0.2, CH_2Cl_2), could be liberated from dichloro complex (S_p)-**12** in 82% yield (Scheme 6).

To confirm the optical purity of the liberated ligands and as a confirmation of their structure and optical integrity, the free ligand (S_p)-**13** was recoordinated to bis(acetonitrile) complexes (R_c)-**10** and (S_c)-**14** separately (Scheme 7). When free ligand (S_p)-**13** was recomplexed to bis(acetonitrile) complex (R_c)-**10**, the ^{31}P NMR spectrum of the crude reaction mixture exhibited a sole sharp singlet at δ 33.0. The resonance signal at δ 33.0 is identical to that recorded for the major product (R_c,R_p)-**11** in the original hydrophosphination reaction. When the same liberated ligand (S_p)-**13**

(27) Liu, X.; Mok, K. F.; Leung, P. H. *Organometallics* **2001**, *20*, 3918.

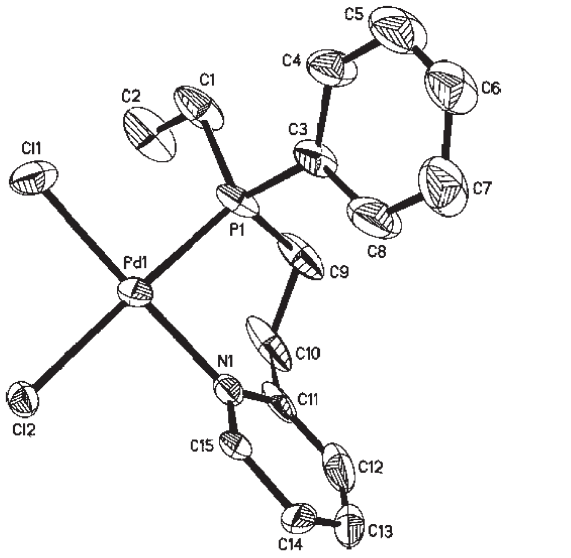
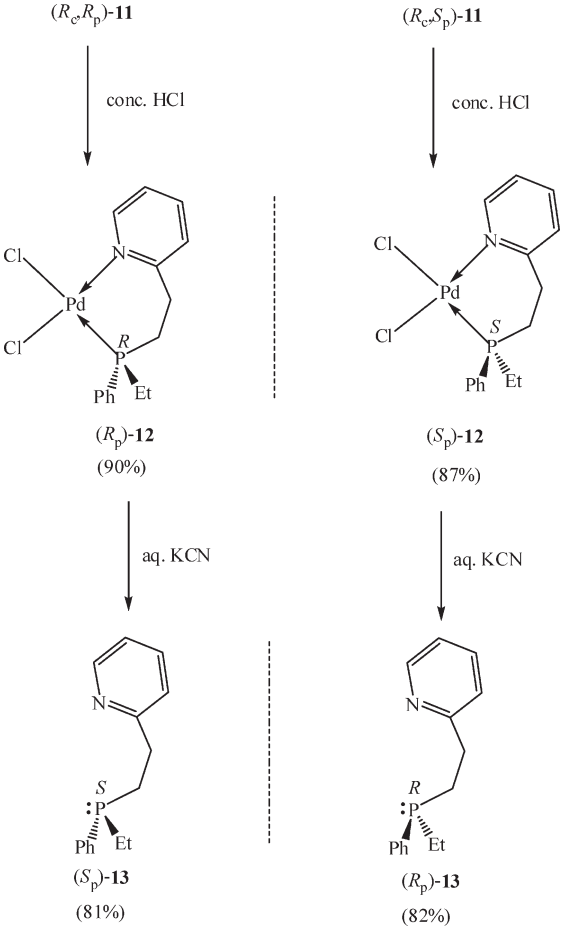


Figure 7. Molecular structure of complex (R_p)-**12** with 50% probability ellipsoids shown.

Scheme 6



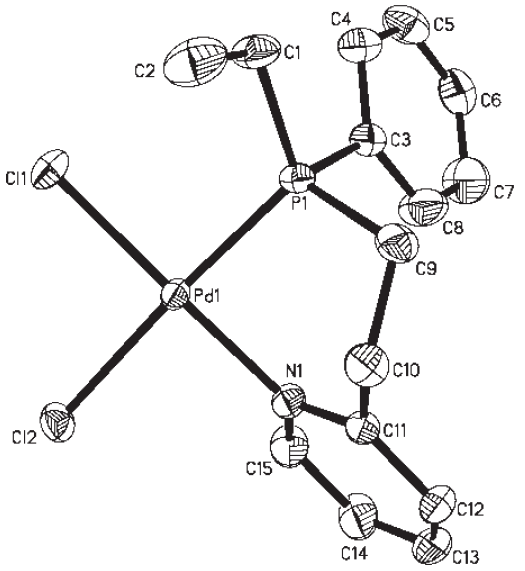
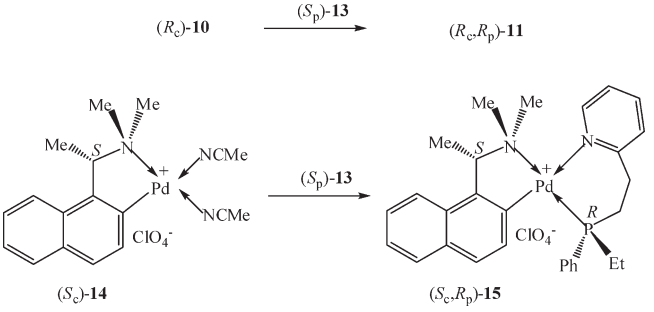


Figure 8. Molecular structure of complex (S_p)-**12** with 50% probability ellipsoids shown.

Table 7. Selected Bond Distances (Å) and Angles (deg) of Complexes (R_p)-12 and (S_p)-12

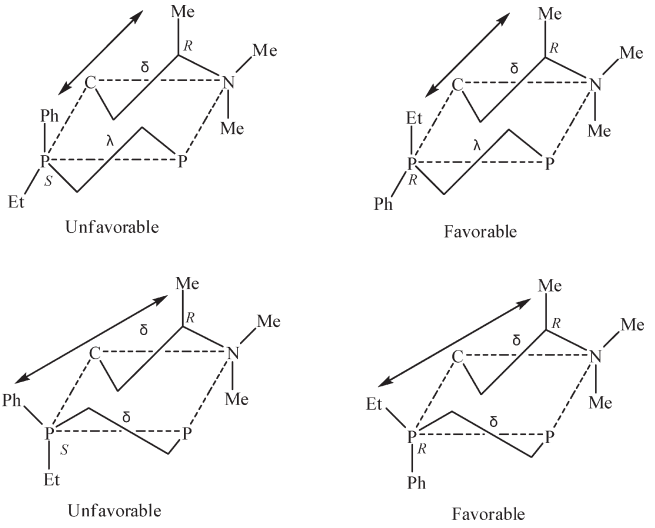
	(R_p)-**12**	(S_p)-**12**
Pd(1)−Cl(1)	2.292(2)	2.293(1)
Pd(1)−Cl(2)	2.364(1)	2.370(1)
Pd(1)−P(1)	2.229(2)	2.235(1)
Pd(1)−N(1)	2.047(5)	2.039(3)
C(9)−C(10)	1.548(10)	1.542(5)
C(10)−C(11)	1.494(13)	1.500(5)
P(1)−Pd(1)−Cl(1)	91.2(1)	91.9(1)
P(1)−Pd(1)−N(1)	88.5(2)	88.3(1)
N(1)−Pd(1)−Cl(2)	89.5(1)	88.3(1)
Cl(1)−Pd(1)−Cl(2)	91.1(1)	91.9(1)

Scheme 7



was treated with bis(acetonitrile) complex (S_c)-**14**, however, the ^{31}P NMR spectrum of the crude reaction mixture showed only one singlet at δ 34.3, which matches the resonance signal of the minor product, (R_c,S_p)-**11**, observed in the original hydrophosphination reaction. It has been well established that in the absence of any chiral NMR solvent, the NMR spectra of enantiomers exhibit identical resonance signals. Therefore, complex (S_c,R_p)-**15** should be the enantiomer of the minor product in the original hydrophosphination reaction product (R_c,S_p)-**11** (Scheme 7). The recoordination reaction thus confirmed that the free P-chiral P, N ligand (S_p)-**13** was optically pure. Subsequently, using a similar procedure, the optical purity of the liberated P-chiral P, N ligand (R_p)-**13** was also confirmed.

Scheme 8

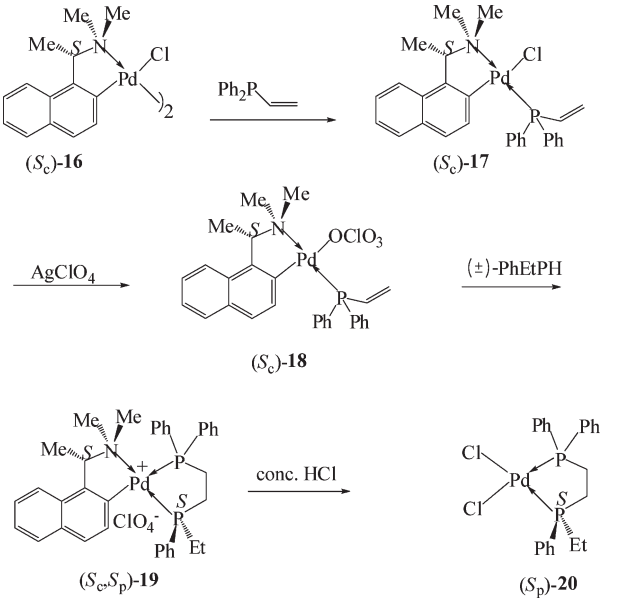


Origins of the Regio- and Stereoselectivities of the Asymmetric Hydrophosphination Reactions. Upon coordination of a secondary phosphine to the palladium, the P−H bond is relatively acidic and can undergo proton exchange with the solvents to generate a small amount of phosphido complex.[28] Therefore, the current chiral metal template promoted asymmetric hydrophosphination reactions should proceed via the simultaneous coordination of a secondary phosphine and vinylphosphines/vinylpyridine, followed by intramolecular nucleophilic addition of the phosphido complex to the coordinated vinylic C=C bond to give the product.[17a,f] The reason for the highly regioselective addition of the ethylphenylphosphino group to the β-carbon of the C=C bond of the vinylphosphines/vinylpyridine to form the five-membered diphosphine or six-membered P−N chelate ring exclusively is twofold: the coordination of the vinylphosphines/vinylpyridine on the chiral palladium template leads to the polarization of the vinylic C=C bond with the β-carbon of the C=C being partially positively charged, together with the fact that for the diphosphine chelate the five-membered chelate ring is thermodynamically more stable than a four-membered ring, and for the P−N chelate, according to a Dreiding model study, the five-membered ring has much more interchelate repulsive interactions than the six-membered ring.[19,27]

In the current hydrophosphination reactions, the absolute configuration at the stereogenic phosphorus center of the major product was *R*. It has been well established that the chiral naphthylamine chelate ring in (R_c)-**1** is locked into the static δ conformation both in the solid state and in solution with the methyl substituent on the stereogenic carbon invariably taking up the axial position above the PdCN ring (Scheme 8).[29] The Dreiding model study reveals that steric repulsion exists between the axial C-methyl group and the group of the secondary phosphine located above the PdCN ring. A correlation between the X-ray crystallography data of the current hydrophosphination products and a Dreiding model study indicates that the Ph group of the secondary

(28) (a) Waid, R. D.; Meek, D. W. *Inorg. Chem.* **1984**, *23*, 778. (b) Bartsch, R.; Hietkamp, S.; Morton, S.; Peters, H.; Stelzer, O. *Inorg. Chem.* **1983**, *22*, 3264.
(29) (a) Corey, E. J.; Bailar, J. C. *J. Am. Chem. Soc.* **1959**, *81*, 2620. (b) Roberts, N. K.; Bosnich, B. *J. Am. Chem. Soc.* **1981**, *103*, 2273.

Scheme 9



phosphine prefers to adopt the position below the PdCN ring, while the Et group occupies the position above the ring to attain the least steric repulsion arising from the axial methyl group with them (Scheme 8). As a result, the absolute configuration of the phosphorus stereogenic center of the favorable product should be *R*.

In order to confirm the influence of the axial C-methyl group of chiral palladium(II) naphthylamine on the stereoselectivity at the P-stereogenic center, one more asymmetric hydrophosphination was carried out between diphenylvinylphosphine and racemic secondary phosphine (±)PhEtPH using (S_c)-**16** (Scheme 9). As the λ configuration will always be observed for the chelate ring when the absolute configuration of the carbon stereocenter is *S*, and the axial C-methyl group projects perpendicularly below the square plane, the stereoselectivity of the major product at the P-stereogenic center will be *S*. Prior to purification, the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture showed two pairs of doublets at δ 68.4 (d, J_{PP} = 24.7 Hz), 42.7 (d, J_{PP} = 24.7 Hz) and 61.7 (d, 1P, J_{pp} = 18.4 Hz), 40.2 (d, 1P, J_{pp} = 18.4 Hz) in the ratio 14:1, respectively, indicating that a pair of diastereomeric complexes has been produced. After purifying by chromatography, only the major product (S_c,S_p)-**19** was obtained. However, good-quality single crystals of complex (S_c,S_p)-**19** suitable for X-ray structure analysis could not be obtained. The chiral naphthylamine auxiliary in (S_c,S_p)-**19** was then removed chemoselectively from palladium templates by treatment with concentrated hydrochloric acid in dichloromethane to give complex (S_p)-**20**. The $^{31}P\{^1H\}$ NMR spectrum of the dichloro complex (S_p)-**20** in $CDCl_3$ exhibited a pair of doublets at δ 73.7 (d, 1P, J_{pp} = 11.4 Hz) and 63.8 (d, 1P, J_{pp} = 11.4 Hz). The single-crystal X-ray diffraction analysis revealed that the isolated compound was the expected dichloro complex (S_p)-**20** (Figure 9). As expected, the absolute configuration of the P(1) stereogenic center was *S*. The selected bond lengths and angles are given in Table 8.

Interestingly, for hydrophosphination of *E*-isomer (R_c)-**3a**, the absolute configuration of the new stereogenic carbon center of the major product (R_c,S_c,R_p)-**4a** was *S*. On the other hand, hydrophosphination of the *Z*-isomer (R_c)-**3b**

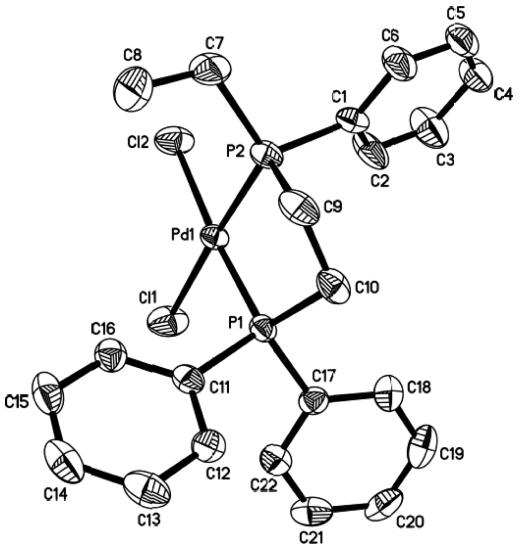


Figure 9. Molecular structure of complex (S_p)-**20** with 50% probability ellipsoids shown.

Table 8. Selected Bond Distances (Å) and Angles (deg) of Complex (S_p)-20

Pd(1)−P(1)	2.228(1)	P(2)−Pd(1)−Cl(1)	176.8(1)
Pd(1)−P(2) p	2.238(1)	P(1)−Pd(1)−Cl(1)	91.05(4)
Pd(1)−Cl(1)	2.364(1)	P(2)−Pd(1)−Cl(2)	89.1(1)
Pd(1)−Cl(2)	2.351(1)	P(1)−Pd(1)−Cl(2)	174.6(1)
P(1)−Pd(1)−P(2)	85.9(1)	Cl(1)−Pd(1)−Cl(2)	94.0(1)

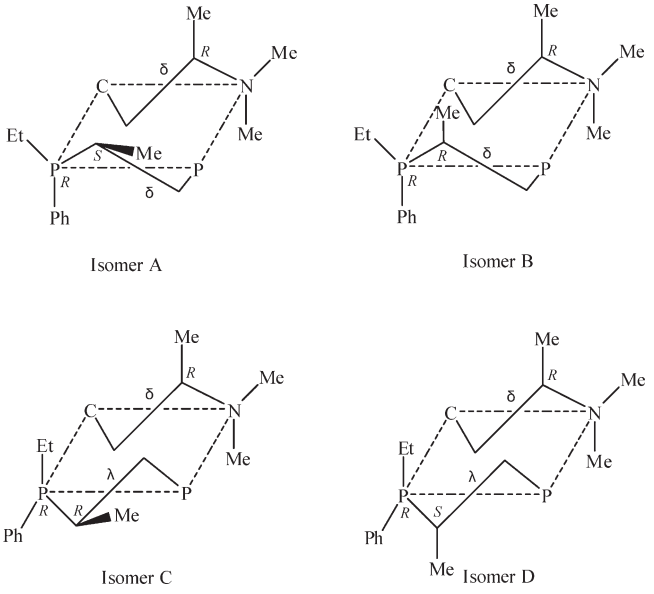
gave the major product (R_c,R_c,R_p)-**5a** in which the newly generated stereogenic carbon center had the absolute configuration *R*. On the basis of the absolute chirality of the newly formed stereogenic carbon center and the absolute conformation of the five-membered diphosphine ring, four possible stereoisomeric products are possible. As shown in Scheme 10, isomers A and B have the same δ absolute conformation of the five-membered diphosphine ring, but differ in their absolute configuration at the newly formed stereogenic carbon centers in that the absolute configuration of the carbon center in isomer A is *S*, while in isomer B it is *R*. Similarly, isomers C and D have different absolute configurations at the carbon centers but the same λ absolute conformation of the five-membered diphosphine ring. To note, the C-Me-substituted five-membered chelate ring is known to adopt a single static chiral conformation with the C-Me groups equatorially disposed.[29] Therefore, the Me group adopts an equatorial disposition in both isomers A and C, but takes up the axial disposition in isomers B and D; the favorable products should be isomers A and C, which are represented by (R_c,S_c,R_p)-**4a** and (R_c,R_c,R_p)-**5a**. This is confirmed by the X-ray crystallographic analysis that isomer A is the complex (R_c,S_c,R_p)-**4a**, while isomer B is complex (R_c,R_c,R_p)-**5a**.

Conclusion

In summary, chiral organopalladium template promoted asymmetric hydrophosphination reactions have been demonstrated. These reactions proceeded with high regio- and stereoselectivities under mild conditions. Optically pure chiral diphosphines containing both phosphorus and carbon stereogenic centers as well as P-stereogenic pyridylphosphines were obtained in high yield and optical purity.

It is important to note that PhEtPH is a chiral molecule, and as a typical secondary phosphine, the inversion barrier for PhEtPH is low at room temperature. However, the stereoselectivity at the P atom during product formation is dictated by the chiral template, in spite of the use of the racemic PhEtPH as the starting material. We are currently investigating the catalytic properties of the transition metal complexes containing these optically active phosphines.

Scheme 10



Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. NMR spectra were recorded at 25 °C on Bruker ACF 300 and AMX400 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. Melting points were determined on a Büchi melting point B-540. Elementary analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore.

The chiral palladium complexes (R_c)-**1** and (S_c)-**16**,[30] diphenylvinylphosphine,[31] the *E* and *Z* forms of diphenyl-1-propenylphosphine,[32] and the racemic ethylphenylphosphine[33] were prepared as previously described.

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

Hydrophosphination of (*E*)-Diphenyl-1-propenylphosphine. Synthesis of {(R_c)-1-[1-(Dimethylamino)ethyl]naphthyl-C^2,*N*}-[(S_c,R_p)-1-ethylphenylphosphino-1-methyl-2-diphenylphosphinoethane-P^1,P^2]palladium(II) Perchlorate, (R_c,S_c,R_p)-4a. To a

Table 9. Crystallographic Data for Complexes (R_c,S_c,R_p)-4a, (R_c,R_c,R_p)-5a, (S_c,R_p)-8a, and (R_c,R_p)-8b

	(R_c,S_c,R_p)-**4a**	(R_c,R_c,R_p)-**5a**	(S_c,R_p)-**8a**	(R_c,R_p)-**8b**
formula	$C_{38}H_{44}Cl_3NO_4P_2Pd$	$C_{39}H_{45}ClN_2O_4P_2Pd$	$C_{23}H_{26}Cl_2P_2Pd$	$C_{23}H_{26}Cl_2P_2Pd$
fw	853.43	809.56	541.68	541.68
space group	*P*2(1)2(1)2(1)	*P*2(1)2(1)2(1)	*P*2(1)	*P*2(1)
cryst syst	orthorhombic	orthorhombic	monoclinic	monoclinic
a/Å	12.5387(8)	10.5512(10)	9.0468(3)	8.9434(3)
b/Å	16.3372(10)	15.4223(16)	14.4313(6)	13.0220(4)
c/Å	18.7069(11)	23.297(2)	9.6325(4)	10.8172(4)
β/deg	90	90	111.908(2)	112.444(2)
V/Å^3	3832.1(4)	3791.0(7)	1166.77(8)	1164.36(7)
Z	4	4	2	2
T/K	223(2)	223(2)	223(2)	223(2)
ρ_{calcd}/g cm^{-3}	1.479	1.418	1.542	1.545
λ/Å	0.71073	0.71073	0.71073	0.71073
μ/mm^{-1}	0.817	0.686	1.168	1.171
Flack param	−0.01(3)	0.00(3)	0.08(4)	0.01(5)
R_1 (obsd data)[a]	0.0444	0.0497	0.0422	0.0486
wR_2 (obsd data)[b]	0.0986	0.0928	0.1318	0.1349

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Table 10. Crystallographic Data for Complexes (R_c,R_p)-11, (R_c,S_p)-11, (R_p)-12, (S_p)-12, and (S_p)-20

	(R_c,R_p)-**11**	(R_c,S_p)-**11**	(R_p)-**12**	(S_p)-**12**	(S_p)-**20**
formula	$C_{30}H_{36}Cl_3N_2O_4PPd$	$C_{29}H_{34}ClN_2O_4PPd$	$C_{15.50}H_{19}Cl_3NPPd$	$C_{15}H_{18}Cl_2NPPd$	$C_{22}H_{24}Cl_2P_2$ Pd
fw	732.33	647.40	463.04	420.57	527.65
space group	*P*2(1)	*P*2(1)2(1)2(1)	*P*4(3)2(1)2	*P*2(1)	*P*2(1)
cryst syst	monoclinic	orthorhombic	tetragonal	monoclinic	monoclinic
a/Å	9.8594(4)	10.1048(3)	8.5216(2)	10.1398(12)	8.6884(3)
b/Å	14.0726(6)	11.6626(4)	8.5216(2)	8.5738(9)	14.7236(6)
c/Å	11.7832(5)	24.2070(8)	49.3018(17)	19.062(2)	9.3534(4)
β/deg	90.2890(10)	90	90	98.478(6)	109.031(2)
V/Å^3	1634.87(12)	2852.75(16)	3580.18(17)	1639.1(3)	1131.13(8)
Z	2	2	8	4	2
T/K	223(2)	173(2)	173(2)	173(2)	223(2)
ρ_{calcd}/g cm^{-3}	1.488	1.507	1.718	1.704	1.549
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073
μ/mm^{-1}	0.898	0.837	1.567	1.545	1.203
Flack param	0.02(2)	−0.02(3)	0.06(7)	0.00(2)	0.01(3)
R_1 (obsd data)[a]	0.0332	0.0451	0.0522	0.0249	0.0378
wR_2 (obsd data)[b]	0.0864	0.0956	0.1308	0.0746	0.0903

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

solution of complex (R_c)-**2a** (0.1 g, 0.177 mmol) in dichloromethane was added silver perchlorate (0.044 g, 0.212 mmol) in water (5 mL), and the mixture was stirred vigorously at room temperature for 30 min. The reaction mixture was subsequently filtered through Celite, washed with water (3 × 20 mL), and dried with $MgSO_4$. The mixture was then degassed and cooled to −78 °C, and ethylphenylphosphine (0.025 g, 0.181 mmol) was added. The mixture was stirred overnight, during which it was allowed to gradually warm to ambient temperature. Upon completion, the solvent was removed to give a dark brown residue, which was purified by column chromatography (with an eluting gradient starting from hexane−acetone, 6:1) to give the major product as a white solid. Recrystallization of the crude product from acetone−hexane gave pure (R_c,S_c,R_p)-**4a** as pale yellow crystals: mp 239 °C; $[\alpha]_D$ −78 (*c* 0.5, CH_2Cl_2); 0.082 g (60% yield). Anal. Calcd for $C_{37}H_{42}ClNO_4P_2Pd$: C, 57.8; H, 5.5; N, 1.8. Found: C, 57.7; H, 5.3; N, 1.7. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ 69.7 (d, 1P, J_{PP} = 34.2 Hz), 30.0 (d, 1P, J_{PP} = 34.2 Hz). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.09 (dd, 3H, J_{PH} = 11.1 Hz, J_{HH} = 6.0 Hz, PCH*Me*), 1.18 (dt, 3H, J_{PH} = 13.9 Hz, J_{HH} = 7.4 Hz, CH_2*Me*), 2.03 (d, 3H, J_{HH} = 6.2 Hz, CH*Me*), 2.07−2.13 (m, 1H, C*H*H′), 2.29−2.39 (m, 1H, C*H*H′), 2.45 (d, 3H, J_{PH} = 0.81 Hz, N*Me*), 2.48−2.59 (m, 2H, *CH*$_2$Me), 2.69 (dd, 3H, J_{PH} =3.0 Hz, J_{HH} = 2.6 Hz, N*Me*), 4.51 (qn, 1H, J_{PH} = J_{HH} = 6.1 Hz, *CH*Me), 6.73−6.80 (m, 1H, P*CH*Me), 7.35−8.01 (m, 21H, aromatics). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 10.1 (d, 1C, J_{PC} = 3.7 Hz, CH_2*Me*), 15.3 (dd, 1C, J_{PC} = 20.1 Hz, J_{PC} = 5.3 Hz, CH*Me*), 15.4 (d, 1C, J_{PC} = 32.1 Hz, *CH*$_2$Me), 25.0 (s, 1C, PCH*Me*), 31.6 (dd, 1C, J_{PC} = 31.2 Hz, J_{PC} = 19.6 Hz, P*CH*Me), 36.2 (dd, 1C, J_{PC} = 29.4 Hz, J_{PC} = 11.2 Hz, P*CH*$_2$), 50.4 (d, 1C, J_{PC} = 4.1 Hz, N*Me*), 51.9 (d, 1C, J_{PC} = 2.9 Hz, N*Me*), 75.2 (dd, 1C, J_{PC} = 4.4 Hz, J_{PC} = 2.7 Hz, *C*HMe), 123.8 (s, 1C), 124.7 (d, 1C, J_{PC} = 44.3 Hz), 125.2 (s, 1C), 126.5 (s, 2C), 126.9 (s, 1C), 128.6 (d, 1C, J_{PC} = 35.5 Hz), 128.7 (s, 1C), 129.1 (d, 1C, J_{PC} = 6.6 Hz), 129.8 (d, 2C, J_{PC} = 10.5 Hz), 129.8 (d, 2C, J_{PC} = 10.5 Hz), 130.1 (d, 2C, J_{PC} = 9.7 Hz), 130.4 (d, 2C, J_{PC} = 10.2 Hz), 131.8 (d, 2C, J_{PC} = 10.7 Hz), 132.1 (s, 1C), 133.1 (d, 1C, J_{PC} = 2.1 Hz), 133.4 (d, 1C, J_{PC} = 2.3 Hz), 134.6 (d, 2C, J_{PC} = 11.1 Hz), 134.9 (d, 2C, J_{PC} = 13.5 Hz), 150.7 (s, 1C), 156.5 (s, 1C), 157.7 (s, 1C).

Synthesis of [(S_c,R_p)-Dichloro-(1-ethylphenylphosphino-1-methyl-2-diphenylphosphino)ethane-P^1,P^2]palladium(II), (S_c,R_p)-8a. A solution containing (R_c,S_c,R_p)-**4a** (0.1 g, 0.189 mmol) in dichloromethane was stirred vigorously with excess concentrated hydrochloric acid for 16 h. The reaction mixture was then washed with water (3 × 10 mL) and dried ($MgSO_4$). Crystallization of the crude product from dichloromethane−diethyl ether gave the dichloro complex (S_c,R_p)-**8a** as white crystals: mp 221 °C; $[\alpha]_D$ −100 (*c* 0.2, CH_2Cl_2); 0.091 g (88% yield). Anal. Calcd for $C_{23}H_{26}Cl_2P_2Pd$: C, 51.0; H, 4.8. Found: C, 50.9; H, 4.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ 80.3 (d, J_{PP} = 5.5 Hz), 50.5 (d, J_{PP} = 5.5 Hz). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.13 (dd, 3H, $^3J_{PH}$ = 9.2 Hz, $^3J_{HH}$ = 6.1 Hz, CH*Me*), 1.40 (dt, 3H, J_{PH} = 18.2 Hz, J_{HH} = 7.5 Hz, CH_2*Me*), 2.11−2.31 (m, 2H, *CH*$_2$Me), 2.39−2.49 (m, 1H, C*H*H′), 2.59−2.67 (m, 1H, *CH*H′), 2.76−2.93 (m, 1H, *CH*Me), 7.43−8.13 (m, 15H, aromatics). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 9.3 (s, 1C, CH_2*Me*), 14.7 (dd, 1C, J_{PC} = 22.8 Hz, J_{PC} = 5.0 Hz, CH*Me*), 17.3 (d, 1C, J_{PC} = 34.7 Hz, *CH*$_2$Me), 32.3 (dd, 1C, J_{PC} = 29.8 Hz, J_{PC} = 15.0 Hz, P*CH*Me), 37.1 (dd, 1C, J_{PC} = 35.6 Hz, J_{PC} = 14.9 Hz, P*CH*$_2$), 126.1 (d, 1C, J_{PC} = 48.3 Hz), 127.5 (d, 1C, J_{PC} = 52.8 Hz), 129.3 (d, 2C, J_{PC} = 11.6 Hz), 129.6 (d, 2C, J_{PC} = 10.7 Hz), 129.9 (d, 2C, J_{PC} = 11.3 Hz), 130.0 (d, 1C, J_{PC} = 55.8 Hz), 132.4 (d, 1C, J_{PC} = 3.1 Hz), 133.09 (d, 1C, J_{PC} = 2.6 Hz), 133.11 (d, 1C, J_{PC} = 2.3 Hz), 133.3 (d, 2C, J_{PC} = 10.6 Hz), 134.8 (d, 2C, J_{PC} = 10.6 Hz), 135.0 (d, 2C, J_{PC} = 11.6 Hz).

Liberation of (S_c,S_p)-1-Ethylphenylphosphino-1-methyl-2-diphenylphosphinoethane, (S_c,S_p)-9a. To the solution of dichloro complex (S_c,R_p)-**8a** (0.03 g, 0.055 mmol) in dichloromethane (10 mL) was added an aqueous solution of potassium cyanide (1 g), and the resulting solution was stirred vigorously for 2 h. The organic layer was separated, washed with water (3 × 20 mL), and dried ($MgSO_4$). Upon removal of solvent, white solid (S_c,S_p)-**9a** was obtained: $[\alpha]_D$ −118.4 (*c* 0.2, CH_2Cl_2); 0.016 g (80% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ −0.66 (d, 1P, J_{PP} = 21.2 Hz), −19.7 (d, 1P, J_{PP} = 21.2 Hz). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.98 (dt, 3H, J_{PH} = 15.8 Hz, J_{HH} = 7.9 Hz, CH_2*Me*), 1.09 (dd, 3H, J_{PH} = 13.2 Hz, J_{HH} = 6.8 Hz, CH*Me*), 1.68−1.95 (m, 4H, P*CH*$_2$ + *CH*$_2$Me), 2.37−2.45 (m, 1H, *CH*Me), 7.28−7.46 (m, 15H, aromatics).

Hydrophosphination of (*Z*)-Diphenyl-1-propenylphosphine. Hydrophosphination of (*Z*)-diphenyl-1-propenylphosphine was performed in a similar manner to the hydrophosphination of (*E*)-diphenyl-1-propenylphosphine.

Synthesis of {(R_c)-1-[1-(Dimethylamino)ethyl]naphthyl-C^2,*N*}-[(R_c,R_p)-1-ethylphenylphosphino-1-methyl-2-diphenylphosphinoethane-P^1,P^2]palladium(II) Perchlorate, (R_c,R_c,R_p)-5a. Pale yellow crystals: mp 243 °C; $[\alpha]_{436}$ +69.8 (*c* 0.5, CH_2Cl_2); 0.028 g (40% yield). Anal. Calcd for $C_{37}H_{42}ClNO_4P_2Pd$: C, 57.8; H, 5.5; N, 1.8. Found: C, 57.6; H, 5.2; N, 1.7. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ 67.7 (d, 1P, J_{PP} = 26.6 Hz), 34.9 (d, 1P, J_{PP} = 26.6 Hz). ^1H NMR ($CDCl_3$): δ 1.25 (dd, 3H, J_{PH} = 14.1 Hz, J_{HH} = 7.7 Hz, PCH*Me*), 1.31 (dt, 3H, J_{PH} = 15.1 Hz, J_{HH} = 7.7 Hz, CH_2*Me*), 1.87 (d, 3H, J_{HH} = 6.2 Hz, CH*Me*), 2.20−2.33 (m, 2H, P*CH*$_2$), 2.44 (dd, 3H, J_{PH} = 3.3 Hz, J_{HH} = 3.2 Hz, N*Me*), 2.56−2.72 (m, 2H, *CH*$_2$Me), 2.77 (brs, 3H, N*Me*), 4.42 (qn, 1H, $^4J_{PH}$ = $^3J_{HH}$ = 5.9 Hz, *CH*Me), 6.71−6.78 (m, 1H, P*CH*Me), 7.22−7.94 (m, 21H, aromatics). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 11.2 (d, 1C, J_{PC} = 2.5 Hz, CH_2*Me*), 14.4 (dd, 1C, J_{PC} = 15.0 Hz, J_{PC} = 4.4 Hz, CH*Me*), 15.2 (d, 1C, J_{PC} = 28.2 Hz, *CH*$_2$Me), 24.9 (s, 1C, PCH*Me*), 36.6 (dd, 1C, J_{PC} = 29.4 Hz, J_{PC} = 10.3 Hz, P*CH*$_2$), 37.6 (dd, 1C, J_{PC} = 31.6 Hz, J_{PC} = 18.8 Hz, P*CH*Me), 51.6 (dd, 1C, J_{PC} = 3.8 Hz, J_{PC} = 1.5 Hz, N*Me*), 52.9 (d, 1C, J_{PC} = 2.4 Hz, N*Me*), 74.8 (dd, 1C, J_{PC} = 6.0 Hz, J_{PC} = 2.6 Hz, *C*HMe), 123.6 (s, 1C), 125.1 (s, 1C), 126.4 (s, 1C), 127.8 (d, 1C, J_{PC} = 44.3 Hz), 128.6 (d, 1C, J_{PC} = 36.3 Hz), 128.7 (s, 1C), 129.1 (d, 1C, J_{PC} = 24.4 Hz), 129.3 (d, 1C, J_{PC} = 19.4 Hz), 129.7 (d, 2C, J_{PC} = 9.4 Hz), 130.0 (d, 2C, J_{PC} = 9.8 Hz), 130.2 (d, 2C, J_{PC} = 10.1 Hz), 131.7 (d, 1C, J_{PC} = 2.8 Hz), 132.1 (s, 1C), 132.4 (d, 1C, J_{PC} = 2.6 Hz), 132.6 (d, 2C, J_{PC} = 11.3 Hz), 132.9 (d, 2C, J_{PC} = 11.0 Hz), 133.0 (d, 2C, J_{PC} = 10.8 Hz), 134.2 (d, 2C, J_{PC} = 13.2 Hz), 150.0 (s, 1C), 155.9 (s, 1C), 157.1 (s, 1C).

Synthesis of [(R_c,R_p)-Dichloro(1-ethylphenylphosphino-1-methyl-2-diphenylphosphino)ethane-P^1,P^2]palladium(II), (R_c,R_p)-8b. White crystals: mp 220; $[\alpha]_D$ +140 (*c* 0.2, CH_2Cl_2); 0.06 g (90% yield). Anal. Calcd for $C_{23}H_{26}Cl_2P_2Pd$: C, 51.0; H, 4.8. Found: C, 50.6; H, 4.5. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ 80.8 (d, 1P, J_{PP} = 6.4 Hz) and 58.9 (d, 1P, J_{PP} = 6.4 Hz). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.22 (dd, 3H, J_{PH} = 14.6 Hz, J_{HH} = 7.1 Hz, CH*Me*), 1.41 (dt, 3H, J_{PH} = 11.3 Hz, J_{HH} = 7.7 Hz, CH_2*Me*), 2.38−2.57 (m, 2H, *CH*$_2$Me), 2.59−2.68 (m, 2H, PCH$_2$), 2.70−2.80 (m, 1H, *CH*Me), 7.38−7.99 (m, 15H, aromatics). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 10.1 (s, 1C, CH_2*Me*), 14.6 (dd, 1C, J_{PC} = 14.8 Hz, J_{PC} = 13.0 Hz, CH*Me*), 17.7 (d, 1C, J_{PC} = 29.4 Hz, *CH*$_2$Me), 35.9 (dd, 1C, J_{PC} = 30.9 Hz, J_{PC} = 14.0 Hz, P*CH*Me), 38.4 (dd, 1C, J_{PC} = 34.6 Hz, J_{PC} = 16.1 Hz, P*CH*$_2$), 128.4 (d, 1C, J_{PC} = 42.7 Hz), 129.3 (d, 2C, J_{PC} = 8.7 Hz), 129.39 (d, 1C, J_{PC} = 20.9 Hz), 129.44 (d, 1C, J_{PC} = 22.1 Hz), 129.6 (d, 2C, J_{PC} = 9.4 Hz), 129.7 (d, 2C, J_{PC} = 9.4 Hz), 132.5 (s, 2C), 132.7 (d, 1C, J_{PC} = 2.0 Hz), 133.2 (d, 2C, J_{PC} = 7.9 Hz), 134.0 (d, 2C, J_{PC} = 9.0 Hz), 134.2 (d, 2C, J_{PC} = 8.9 Hz).

Liberation of (R_c,S_p)-1-ethylphenylphosphino-1-methyl-2-diphenylphosphinoethane, (R_c,S_p)-9b. White solid: $[\alpha]_D$ +92.6 (*c* 0.2, CH_2Cl_2); 0.017 g (84% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$,

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121 MHz): δ −0.38 (d, 1P, J_{PP} = 18.4 Hz), −20.5 (d, 1P, J_{PP} = 18.4 Hz). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.94 (dt, 3H, J_{PH} = 15.3 Hz, J_{HH} = 7.7 Hz, CH_2*Me*), 1.34 (dd 3H, J_{PH} = 14.2 Hz, J_{HH} = 6.2 Hz, CH*Me*), 1.67−1.83 (m, 4H, PCH_2 + CH_2Me), 2.12−2.19 (m, 1H, *CH*Me), 7.16−7.39 (m, 15H, aromatics).

Hydrophosphination of 2-Vinylpyridine. Synthesis of {(*R*$_c$)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}[(*R*$_p$)-1-ethylphenylphosphino-2-(2-pyridine)ethane-*N*,*P*]palladium(II) Perchlorate, (*R*$_c$,*R*$_p$)-11. To the solution of (±)-PhEtPH (0.18 g, 1.30 mmol) in dichloromethane was added bis(acetonitrile) palladium complex (*R*$_c$)-**10** (0.63 g, 1.30 mmol), and the temperature was then reduced to −78 °C. Subsequently, 2-vinylpyridine (0.14 mL, 1.30 mmol) was added, and the reaction mixture was allowed to warm to room temperature with stirring for 24 h. Upon fractional crystallization, the major and minor products were then crystallized from dichlomethane−diethyl ether as white crystals, separately. (*R*$_c$,*R*$_p$)-**11**: white crystals; mp 257 °C; $[\alpha]_D$ −157.5 (*c* 0.4, CH_2Cl_2); 0.43 g (52% yield). Anal. Calcd for $C_{29}H_{34}ClN_2O_4PPd$: C, 53.8; H, 5.3; N, 4.3. Found: C, 53.5; H, 5.2; N, 4.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ 33.0. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.07 (dt, 3H, J_{PH} = 12.2 Hz, J_{HH} = 7.7 Hz, CH_2*Me*), 1.83−1.96 (m, 1H, CH*H*), 2.08 (d, 3H, J_{PH} = 6.2 Hz, CH*Me*), 2.23−2.33 (m, 2H, CH_2Me), 2.49 (d, 3H, J_{PH} = 2.8 Hz, N*Me*), 2.57−2.69 (m, 1H, *CH*H), 2.84 (s, 3H, N*Me*), 3.36−3.70 (m, 2H, PCH_2), 4.44 (qn, 1H, J_{PH} = J_{HH} = 6.2 Hz, *CH*Me), 7.04−7.98 (m, 15H, aromatics). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 8.3 (s, 1C, CH_2*Me*), 21.5 (d, 1C, J_{PC} = 32.9 Hz, CH_2Me), 23.8 (s, 1C, CH*Me*), 24.7 (d, 1C, J_{PC} = 30.9 Hz, PCH_2), 36.8 (s, 1C, CH_2), 47.2 (d, 1C, J_{PC} = 1.6 Hz, N*Me*), 51.4 (d, 1C, J_{PC} = 1.6 Hz, N*Me*), 73.6 (d, 1C, J_{PC} = 2.8 Hz, *C*HMe), 123.0 (s, 1C), 125.0 (d, 2C, J_{PC} = 13.8 Hz), 126.0 (s, 1C), 126.5 (s, 1C), 126.5 (d, 1C, J_{PC} = 5.6 Hz), 128.9 (s, 1C), 129.0 (s, 1C), 129.7 (d, 2C, J_{PC} = 10.6 Hz), 130.2 (d, 1C, J_{PC} = 44.8 Hz), 131.8 (s, 1C), 132.0 (d, 1C, J_{PC} = 2.3 Hz), 132.6 (d, 2C, J_{PC} = 12.3 Hz), 133.9 (d, 1C, J_{PC} = 11.5 Hz), 140.6 (s, 1C), 145.8 (s, 1C), 149.56 (s, 1C), 149.61 (s, 1C), 160.2 (d, 1C, J_{PC} = 2.6 Hz).

Synthesis of {(*R*$_c$)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}[(*S*$_p$)-1-ethylphenylphosphino-2-(2-pyridine)ethane-*N*,*P*]palladium(II) Perchlorate, (*R*$_c$,*S*$_p$)-11. Mp 226 °C (dec); $[\alpha]_D$ −256 (*c* 0.5, CH_2Cl_2); 0.26 g (31% yield). Anal. Calcd for $C_{29}H_{34}ClN_2O_4PPd$: C, 53.8; H, 5.3; N, 4.3. Found: C, 53.6; H, 5.2; N, 4.1. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ 34.3. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.17 (dt, 3H, J_{PH} = 20.0 Hz, J_{HH} = 7.5 Hz, CH_2*Me*), 1.85−2.02 (m, 2H, CH_2), 2.08 (d, 3H, J_{PH} = 6.3 Hz, CH*Me*), 2.16−2.40 (m, 2H, CH_2Me), 2.48 (d, 3H, J_{PH} = 3.0 Hz, N*Me*), 2.78 (s, 3H, N*Me*), 3.40−3.63 (m, 2H, PCH_2), 4.41 (qn, 1H, J_{PH} = J_{HH} = 6.1 Hz, *CH*Me), 6.52−8.84 (m, 15H, aromatics). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 9.8 (d, 1C, J_{PC} = 2.2 Hz, CH_2*Me*), 18.3 (d, 1C, J_{PC} = 28.1 Hz, CH_2Me), 24.3 (s, 1C, CH*Me*), 26.6 (d, 1C, J_{PC} = 30.9 Hz, PCH_2), 36.4 (d, 1C, J_{PC} = 2.8 Hz, CH_2), 47.3 (s, 1C, N*Me*), 51.4 (d, 1C, J_{PC} = 2.1 Hz, N*Me*), 73.2 (d, 1C, J_{PC} = 2.7 Hz, *C*HMe), 123.0 (s, 1C), 124.7 (s, 1C), 125.2 (s, 1C), 125.5 (d, 1C, J_{PC} = 5.6 Hz), 126.1 (s, 1C), 126.3 (s, 1C), 128.6 (s, 1C), 128.7 (s, 1C), 128.9 (d, 2C, J_{PC} = 10.6 Hz), 130.8 (d, 1C, J_{PC} = 49.8 Hz), 131.2 (d, 1C, J_{PC} = 2.5 Hz), 131.4 (s, 1C), 131.8 (d, 2C, J_{PC} = 10.1 Hz), 135.7 (d, 1C, J_{PC} = 12.2 Hz), 140.8 (s, 1C), 147.4 (s, 1C), 149.0 (d, 1C, J_{PC} = 1.7 Hz), 149.7 (s, 1C), 160.2 (d, 1C, J_{PC} = 3.0 Hz).

Synthesis of {(*R*$_p$)-Dichloro[1-ethylphenylphosphino-2-(2-pyridine)ethane]}palladium(II), (*R*$_p$)-12. A solution containing (*R*$_c$, *R*$_p$)-**11** (0.1 g, 0.154 mmol) in dichloromethane was stirred vigorously with excess concentrated hydrochloric acid for 16 h. The reaction mixture was then washed with water (3 × 10 mL) and dried ($MgSO_4$). Crystallization of the crude product from dichloromethane−diethyl ether gave the dichloro complex (*R*$_p$)-**12** as yellow crystals: mp 235 °C; $[\alpha]_D$ −198.0 (*c* 0.5, CH_2Cl_2); 0.059 g (90% yield). Anal. Calcd for $C_{15}H_{18}Cl_2NPPd$: C, 42.8; H, 4.3; N, 3.3. Found: C, 42.7; H, 4.3; N, 3.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ 31.1. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.34 (dt, 3H, J_{PH} = 12.4 Hz, J_{HH} = 7.2 Hz, CH_2*Me*), 1.77−1.91 (m, 1H, *CH*H′), 2.16−2.38 (m, 2H, PCH_2), 2.62−2.78 (m, 1H, *CH*H′), 3.34−3.54 (m, 2H, CH_2Me), 7.21−7.82 (m, 9H, aromatics). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 8.0 (d, 1C, J_{PC} = 3.5 Hz, CH_2*Me*), 18.9 (d, 1C, J_{PC} = 30.5 Hz, CH_2Me), 21.0 (d, 1C, J_{PC} = 36.8 Hz, PCH_2), 36.9 (d, 1C, J_{PC} = 4.3 Hz, CH_2), 123.4 (s, 1C), 125.3 (s, 1C), 129.0 (d, 2C, J_{PC} = 10.8 Hz), 129.5 (s, 1C), 131.6 (d, 1C, J_{PC} = 2.8 Hz), 131.8 (d, 2C, J_{PC} = 9.8 Hz), 140.0 (s, 1C), 155.0 (s, 1C), 158.8 (d, 1C, J_{PC} = 5.6 Hz).

Synthesis of {(*S*$_p$)-Dichloro[1-ethylphenylphosphino-2-(2-pyridine)ethane]}palladium(II), (*S*$_p$)-12. Synthesis of dichloro complex (*S*$_p$)-**3** was performed in a similar procedure to (*R*$_p$)-**12**. $[\alpha]_D$ +198.0 (*c* 0.5, CH_2Cl_2); 0.056 g (87% yield). Anal. Calcd for $C_{15}H_{18}Cl_2NPPd$: C, 42.8; H, 4.3; N, 3.3. Found: C, 42.7; H, 4.3; N, 3.4.

Liberation of (*S*$_p$)-[1-Ethylphenylphosphino-2-(2-pyridine)]-ethane, (*S*$_p$)-13. A solution of (*R*$_p$)-**12** (0.03 g, 0.071 mmol) in dichloromethane (10 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (1 g) for 2 h. The organic layer was separated, washed with water (3 × 10 mL), and dried ($MgSO_4$). Upon removal of solvent, a white solid was obtained: $[\alpha]_D$ −26.1 (*c* 0.2, CH_2Cl_2); 0.017 g (81% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ −18.5. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.05 (dt, 3H, J_{PH} = 15.5 Hz, J_{HH} = 7.5 Hz, CH_2*Me*), 1.76 (q, 2H, J_{PH} = J_{HH} = 7.5 Hz, PCH_2), 2.16 (t, 2H, J_{HH} = 8.4 Hz, CH_2), 2.79−2.93 (m, 2H, CH_2Me), 7.08−8.53 (m, 9H, aromatics). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 10.1 (d, 1C, J_{PC} = 3.7 Hz, CH_2*Me*), 15.3 (dd, 1C, J_{PC} = 20.1 Hz, J_{PC} = 5.3 Hz, CH*Me*), 15.4 (d, 1C, J_{PC} = 32.1 Hz, CH_2Me), 25.0 (s, 1C, PCH*Me*), 31.6 (dd, 1C, J_{PC} = 31.2 Hz, J_{PC} = 19.6 Hz, P*C*HMe), 36.2 (dd, 1C, J_{PC} = 29.4 Hz, J_{PC} = 11.2 Hz, PCH_2), 50.4 (d, 1C, J_{PC} = 4.1 Hz, N*Me*), 51.9 (d, 1C, J_{PC} = 2.9 Hz, N*Me*), 75.2 (dd, 1C, J_{PC} = 4.4 Hz, J_{PC} = 2.7 Hz, *C*HMe), 123.8−157.7 (m, 28C, Ar).

Liberation of (*R*$_p$)-[1-Ethylphenylphosphino-2-(2-pyridine)]-ethane, (*R*$_p$)-13. Liberation of (*S*$_p$)-[1-ethylphenylphosphino-2-(2-pyridine)]ethane to obtain free ligand (*R*$_p$)-**13** was performed in a similar procedure to the liberation of (*S*$_p$)-[1-ethylphenylphosphino-2-(2-pyridine)]ethane. (*R*$_p$)-**13**: 0.015 g (71% *P*ield); $[\alpha]_D$ +26.1 (*c* 0.2, CH_2Cl_2).

Hydrophosphination of Diphenylvinylphosphine. Synthesis of {(*S*$_c$)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}[(*S*$_p$)-1-ethylphenylphosphino-2-diphenylphosphinoethane-*P*^{1},*P*^{2}]palladium(II) Perchlorate, (*S*$_c$,*S*$_p$)-19. To a solution of complex (*S*$_c$)-**17** (0.1 g, 0.181 mmol) in dichloromethane was added silver perchlorate (0.045 g, 0.217 mmol) in water (5 mL), and the mixture was stirred vigorously at room temperature for 30 min. The mixture was filtered through Celite, washed with water, and dried with magnesium sulfate. The mixture was then degassed and cooled to −78 °C. Ethylphenylphosphine (0.025 g, 0.181 mmol) was then added, and the reaction mixture was stirred for 18 h. Upon completion, the solvent was removed to give a dark brown residue, which was purified by column chromatography (with an eluting gradient starting from hexane−acetone, 8:1) give the products as white solids. Recrystallization of the crude product from acetone−hexane gave pure (*S*$_c$,*S*$_p$)-**19** as white crystals: mp 267 °C; $[\alpha]_D$ +62 (*c* 0.5, CH_2Cl_2); 0.027 g (20% yield). Anal. Calcd for $C_{36}H_{40}ClNO_4P_2Pd$: C, 57.3; H, 5.3; N, 1.9. Found: C, 57.2; H, 5.3; N, 1.8. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ 68.4 (d, J_{PP} = 24.7 Hz), 42.7 (d, J_{PP} = 24.7 Hz). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 1.24 (dt, 3H, J_{PH} = 21.8 Hz, J_{HH} = 7.5 Hz, CH_2*Me*), 1.78−1.99 (m, 2H, PCH_2), 2.06 (d, 3H, J_{PH} = 6.2 Hz, CH*Me*), 2.28−2.50 (m, 2H, CH_2Me), 2.55 (s, 3H, N*Me*), 2.60−2.66 (m, 1H, PCH*H*′), 2.70 (s, 3H, N*Me*), 2.75−2.99 (m, 1H, PC*H*H′), 4.60 (qn, 1H, J_{PH} = 6.0 Hz, J_{HH} = 6.2 Hz, *CH*Me), 7.07−8.20 (m, 21H, aromatics). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 10.3 (d, 1C, J_{PC} = 8.2 Hz, CH_2*Me*), 19.4 (d, 1C, J_{PC} = 32.3 Hz, CH*Me*), 25.5 (s, 1C, CH_2Me), 27.6 (dd, 1C, J_{PC} = 32.3 Hz, J_{PC} = 19.5 Hz, PCH_2), 28.6 (dd, 1C, J_{PC} = 25.9 Hz, J_{PC} = 7.9 Hz, PCH_2), 51.0 (d, 1C, J_{PC} = 3.4 Hz, N*Me*), 52.3 (d, 1C, J_{PC} = 3.2 Hz, N*Me*), 75.8 (s, 1C, *C*HMe), 124.3 (d, 1C, J_{PC} = 4.7 Hz), 125.7 (s, 1C),

126.8 (dd, 2C, J_{PC} = 5.6 Hz, J_{PC} = 5.2 Hz), 127.0 (d, 2C, J_{PC} = 4.3 Hz), 128.8 (s, 1C), 129.1 (d, 2C, J_{PC} = 7.7 Hz), 129.4 (s, 1C), 129.7 (d, 1C, J_{PC} = 5.4 Hz), 130.4 (d, 2C, J_{PC} = 8.1 Hz), 130.7 (d, 1C, J_{PC} = 7.7 Hz), 132.2 (s, 1C), 132.5 (d, 2C, J_{PC} = 6.4 Hz), 132.7 (s, 1C), 133.6 (d, 2C, J_{PC} = 17.8 Hz), 134.5 (d, 2C, J_{PC} = 9.5 Hz), 134.6 (d, 1C, J_{PC} = 10.0 Hz), 135.3 (d, 2C, J_{PC} = 10.7 Hz), 151.4 (s, 1C), 157.0 (s, 1C), 157.9 (s, 1C).

Synthesis of [(S_p)-Dichloro-(1-ethylphenylphosphino-2-diphenylphosphino)ethane-P^1,P^2]palladium(II), (S_p)-20. Concentrated hydrochloric acid (5 mL) was added to a solution of (S_c,S_p)-**19** (0.1 g, 0.133 mmol) in dichloromethane (15 mL). The reaction mixture was stirred vigorously at room temperature for 16 h, washed with water (3 × 20 mL), and dried ($MgSO_4$). Crystallization of the crude product from dichloromethane−diethyl ether gave the dichloro complex as white crystals: mp 253 °C; $[\alpha]_D$ +43 (*c* 0.2, CH_2Cl_2); 0.063 g (89% yield). Anal. Calcd for $C_{22}H_{24}Cl_2P_2Pd$: C, 50.1; H, 4.6. Found: C, 50.0; H, 4.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ 73.7 (d, 1P, J_{pp} = 11.4 Hz), 63.8 (d, 1P, J_{pp} = 11.4 Hz). ^1H NMR (CDCl3): δ 1.28 (dt, 3H, $^3J_{PH}$ = 20.5 Hz, $^3J_{HH}$ = 7.4 Hz, CH_2*Me*), 1.88−2.01 (m, 1H, PhEtP-*CH*H′), 2.15−2.23 (m, 1H, PhEtP*CH*H′), 2.27−2.40 (m, 2H, *CH*$_2$Me), 2.50−2.80 (m, 2H, Ph_2PCH_2), 7.36−7.64 (m, 15H, aromatics). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 8.7 (s, 1C, CH_2*Me*), 21.7 (d, 1C, J_{PC} = 33.5 Hz, *CH*$_2$Me), 24.6 (dd, 1C, J_{PC} = 32.1 Hz, J_{PC} = 13.6 Hz, P*CH*$_2$), 29.3 (dd, 1C, J_{PC} = 34.9 Hz, J_{PC} = 12.3 Hz, P*CH*$_2$), 126.5−134.3 (m, 18C, Ar).

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Crystal Structure Determination of (R_c,S_c,R_p)-4a, (S_c,R_p)-8a, (R_c,R_c,R_p)-5a, (R_c,R_p)-8b, (R_c,R_p)-11, (R_c,S_p)-11, (R_p)-12, (S_p)-12, and (S_p)-20. X-ray crystallographic data for all nine complexes are given in Tables 9 and 10, respectively. Diffraction data for complexes (R_c,S_c,R_p)-**4a**, (R_c,R_c,R_p)-**5a**, and (R_c,R_p)-**11** were collected on SMART CCD diffractometer with graphite-monochromated Mo Kα radiation, and the other complexes on a Bruker X8 CCD diffractometer with graphite-monochromated Mo Kα radiation. For all complexes, SADABS absorption corrections were applied. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at fixed distance from carbon atoms and were assigned fixed thermal parameters. The absolute configurations of all chiral complexes were determined unambiguously using the Flack parameter.[34]

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Supporting Information Available: For complexes (R_c,S_c,R_p)-**4a**, (S_c,R_p)-**8a**, (R_c,R_c,R_p)-**5a**, (R_c,R_p)-**8b**, (R_c,R_p)-**11**, (R_c,S_p)-**11**, (R_p)-**12**, (S_p)-**12**, and (S_p)-**20**, tables of crystal data, data collection, solution and refinement, final positional parameters, bond distances and angles, thermal parameters of non-hydrogen atoms, and calculated hydrogen parameters. This material is available free of charge via the Internet at http://pubs.acs.org