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Asymmetric Synthesis of Functionalized 1,3-Diphosphines via Chiral Palladium Complex Promoted Hydrophosphination of Activated Olefins

Mingjun Yuan, Na Zhang, Sumod A. Pullarkat, Yongxin Li, Fengli Liu, Phuong-Tu Pham, and Pak-Hing Leung*

Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

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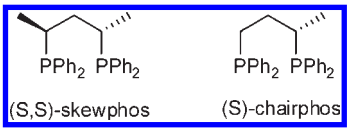
Aldehyde, ester- and keto-functionalized monophosphine palladium complexes containing the ortho-metalated (*R*)-(1-(dimethylamino)ethyl)naphthalene as the chiral auxiliary and reaction promoter were synthesized via hydrophosphination of acrolein and the subsequent Wittig reactions in a one-pot process. Under very mild conditions, the second-stage hydrophosphination of the monophosphine substrates gave the corresponding ester-, keto-, and hydroxyl-functionalized chiral 1,3-bis(diphenylphosphino)propane palladium complexes with good yields and stereoselectivities. The coordination properties and absolute configurations of the novel 1,3-diphosphine complexes were established by single crystal X-ray crystallography. The enantiomerically pure functionalized diphosphine ligands with ester and keto functionalities could be subsequently liberated stereospecifically by treatment of the corresponding dichloro palladium complexes with aqueous potassium cyanide in high yields.

Introduction

Optical pure diphosphines containing the 1,3-bis(diphenylphosphino)propane backbone, such as (*S*,*S*)-skewphos and (*S*)-chairphos, have long been proven to be powerful bidentate ligands in transition metal catalyzed asymmetric reactions.[1,2]



Compared with classical 1,2-diphosphines, the 1,3-diphosphines can form the six-membered metallacycles involving transition metals with new catalytic activity and interesting ring conformations.[3] However, literature review shows that such chiral diphosphine ligands are generally synthesized by tedious resolution or derived from chiral pools,[2] which may limit their structural diversity. To our best knowledge, there has been no report on the asymmetric synthesis of functionalized chiral 1,3-bis(diphenylphosphino)propane ligands.

In terms of synthetic value and atom economy, the addition of secondary phosphines to activated olefins such as α,β-unsaturated carbonyl derivatives, acrylonitriles, and nitroalkenes is an important process in organophosphrus chemistry,[4] since it allows to create a phosphorus−carbon bond and to introduce various functional groups into the

*To whom correspondence should be addressed. E-mail: pakhing@ntu.edu.sg.

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molecule in a single step. In general, transition metal complexes can offer better stabilization and selectivity for hydrophosphination reactions, as they can protect the reactive phosphine species from oxidation by means of coordination. Furthermore, the metal complexes will be able to provide two or more coordination sites to synthesize chiral versions of bidentate diphosphine ligands,[5] thus providing avenues for ligand activation and stereochemical control. Over the past few years, our group has established that organopalladium complexes containing (*R*)- or (*S*)-(1-(dimethylamino)ethyl)-naphthalene as the chiral auxiliary are good promoters for synthesis of various chiral phoshine ligands by means of asymmetric Diels−Alder reactions and hydrophosphination reactions.[5,6] Continuing our efforts in the development of new kinds of chiral diphosphines ligands utilizing these useful auxiliaries, we now describe a facile strategy to synthesize four monophosphine palladium complexes with aldehyde, ester- and keto-functionalities from acrolein, and their second-stage hydrophosphination reactions under mild conditions and in the absence of any protection that generate the corresponding novel chiral 1,3-diphosphine products.

Results and Discussion

Substituted α,β-unsaturated aldehydes, like cinnamaldehyde, have been known to be reactive toward diphenylphosphine and its analogues, wherein the addition reactions can occur either at the activated olefin or at the carbonyl group.[7] However, acrolein was found to be inert toward diphenylphosphine when the addition reaction was performed in a series of solvent systems in the presence of external base. Literature reports reveal that the previous synthesis of the free monophosphine ligand 3-(diphenylphosphino)propanal involves tedious organic manipulations from 3-chloropropanol or chloro-substituted dimethylacetal.[8] Interestingly, in the presence of chiral palladium complex *R*-**1** as the promoter, the Michael-type hydrophosphination reaction of acrolein proceeded chemoselectively to afford the monomeric complex *R*-**2** with the carbonyl group intact (Scheme 1). The addition process was monitored by ^{31}P NMR spectroscopy, and was found to be complete within 30 min at 0 °C in acetonitrile to afford the product *R*-**2** as a white solid in 87% yield. The 121 MHz ^{31}P NMR spectrum in $CDCl_3$ of *R*-**2** exhibited a sharp singlet at δ 35.6.

As illustrated in Scheme 1, in situ reaction of product *R*-**2** with methyl (triphenylphosphoranylidene)acetate in chloroform at room temperature for 2 h generated the ester-functionalized monophosphine palladium complex *R*-**3a** in 85% yield as indicated by a singlet resonance signal at δ 35.0 in the ^{31}P NMR spectrum ($CDCl_3$, 121 MHz). The keto-functionalized product *R*-**3b** could be obtained by using 1-(triphenylphosphoranylidene)acetone for the Wittig reaction in 81% yield. However this reaction needs to be performed at an elevated temperature (50 °C) for 24 h because of the relatively inactive nature of the employed Wittig reagent. The 121 MHz ^{31}P NMR spectrum in $CDCl_3$ of *R*-**3b** indicated a singlet resonance signal at δ 35.2. Similarly, *R*-**3c** was isolated as a pale yellow powder in 79% yield after the reaction of *R*-**2** with (phenacylidene)triphenylphosphorane in chloroform at 50 °C for 36 h and exhibited a phosphorus signal at δ 35.1 in $CDCl_3$.

Asymmetric Hydrophosphination of Ester-Functionalized Monophosphine Palladium Complex *R*-3a. It has been well established that the chloro ligand trans to the ortho-metalated aromatic carbon in *R*-**3a** is inert to displacement by any incoming phosphorus donor atoms.[5,6] Treatment of complex *R*-**3a** with aqueous silver perchlorate in dichloromethane gave the intermediate cationic perchlorate complex *R*-**4a** in essentially quantitative yield (Scheme 2). In routine synthesis, however, this highly reactive species is not isolated, and therefore upon removal of the silver chloride, the CH_3CN/CH_2Cl_2 (1:2) solution of *R*-**4a** was subsequently treated with 1 equiv of diphenylphosphine at −78 °C for the second-stage hydrophosphination reaction to generate the 1,3-diphosphine products. The process was monitored by ^{31}P NMR spectroscopy and was found to be completed within 2 h. Prior to purification, the ^{31}P NMR spectrum of the crude product in $CDCl_3$ exhibited four pairs of doublets at δ −6.1, 38.8 (J_{PP} = 55.3 Hz); 0.9, 36.2 (J_{PP} = 51.9 Hz); 8.6, 28.6 (J_{PP} = 55.3 Hz), and 10.1, 28.5 (J_{PP} = 51.7 Hz) with the intensity ratio of 15:1:9:5, respectively. The signals indicated that all the four possible isomeric products, i.e., **5a**, **6a**, **7a**, and **8a**, were formed in the hydrophosphination reaction as shown in Scheme 2. It should be noted that complexes **5a** and **6a** are regioisomers which adopt the same *R* absolute configuration at the newly formed chiral carbon centers. Similarly, complexes **7a** and **8a** are regioisomers with *S* absolute configuration at the new stereogenic centers. Apart from electronic effect, the chelate stabilization of a 6-membered ring as compared to the 7-membered analogue also contributes to the regioselectivity seen in the hydrophosphination process.

The two major products **5a** and **6a** could be isolated efficiently as equilibrium mixture by column chromatography in 66% yield.[9] The ^{31}P NMR spectrum ($CDCl_3$, 121 MHz) indicated two pairs of doublets at δ −6.1, 38.8 (J_{PP} = 55.3 Hz) and 8.6, 28.6 (J_{PP} = 55.3 Hz). Unfortunately, attempts to crystallize the isomeric complex mixtures for X-ray crytallography from various solvent systems were unsuccessful. The chiral amine auxiliary on complexes **5a** and **6a** however, could be chemoselectively removed from palladium template by treatment with concentrated hydrochloric acid (Scheme 3). The

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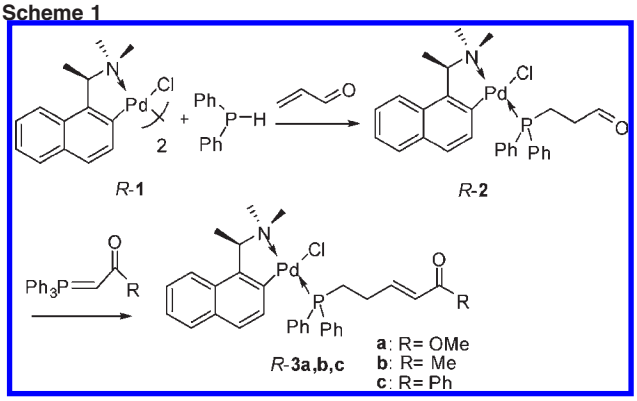
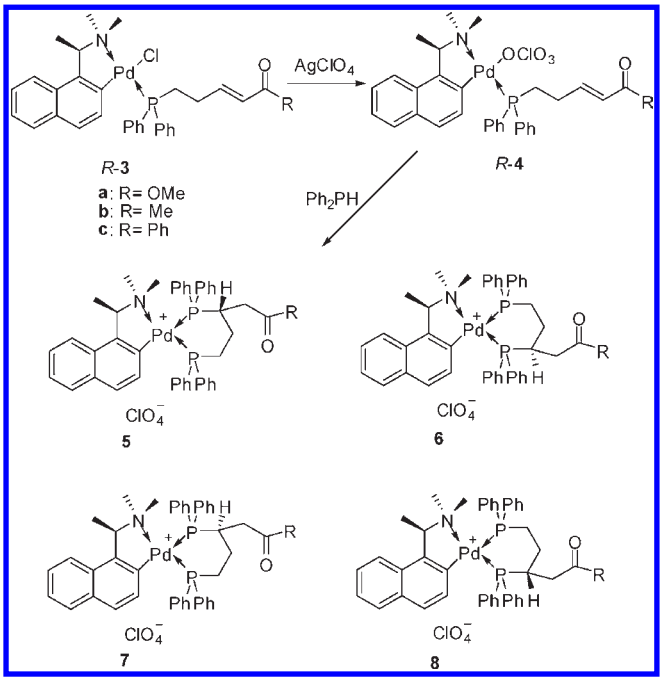
(9) The interconversion between regioisomers 5 and 6 is very fast especially in coordinating solvent, such as acetonitrile, compared with the similar 1,2-diphosphine palladium complexes (see ref 5). The equilibrium can be attained within 2 h at room temperature.

Scheme 1



Scheme 2



resultant enantiomerically pure dichloro complex **9a** was obtained as pale yellow prisms in 88% isolated yield upon crystallization from dichloromethane and diethyl ether, $[\alpha]_D = -17.5$ (*c* 1.7, CH_2Cl_2). The 121 MHz ^{31}P NMR in $CDCl_3$ of the neutral product **9a** showed a pair of doublets at δ 15.5, 21.9 (J_{PP} = 13.0 Hz).

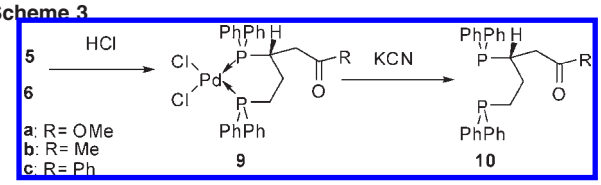
The chelating properties and the absolute stereochemistry of the coordinated ester-substituted 1,3-diphosphine complex **9a** were studied by X-ray crystallography. There are two crystallographically distinguishable molecules in the asymmetric unit with similar bond lengths, angles, and the same *R* absolute configuration at the newly formed chiral center. Figure 1 shows the ORTEP drawing of molecule 1, the selected bond, and angle parameters, and other crystallographic data are listed in Table 1 and Table 4, respectively. The Pd atom adopts the expected distorted square planar coordination geometry. The PdP_2 plane is rotated at an angle of 9.5(2)° with respect to that of $PdCl_2$, while the angles around the palladium center are in the ranges 87.3(1)−91.8(1) and 171.1(1)−175.3(1)°. Both the Pd−P bond (2.258(2), 2.249(3) Å) and the P−Pd−P bite angle (90.2(1)°) are larger than in the case of 1,2-diphosphine metallacycles previously reported.[5] The six-membered chelate ring in **9a** has a novel boat conformation with the ester functionality occupying the sterically favorable equatorial position. The phenyl rings on the phosphorus atom that is adjacent to the ester substituent are of axial (ipso atom C1) and equatorial (ipso atom C7) disposition, respectively, while the other two phenyl rings on P2 adopt bisectional orientations (see Supporting Information).

The optically pure 1,3-diphosphine ligand **10a** could be liberated stereospecifically from **9a** by treatment of the dichloro complex with aqueous potassium cyanide. The liberated diphosphine was obtained as a white solid in 95% yield, $[\alpha]_D = +19.0$ (*c* 1.0, CH_2Cl_2). The ^{31}P NMR spectrum in $CDCl_3$ of **10a** exhibited a pair of singlet at δ −15.3 and −6.4. To determine the optical purity of the diphosphine **10a**, the liberated ligand was recoordinated to the bis(acetonitrile) complex *R*-**11** (Scheme 4), the 121 MHz ^{31}P NMR of the recomplexation products in $CDCl_3$ indeed exhibited two pairs of doublets at δ −6.1, 38.8 (J_{PP} = 55.3 Hz) and 8.6, 28.6 (J_{PP} = 55.3 Hz). These resonance signals are identical with the two major products from the original hydrophosphination reaction, which indicated the formation of the regioisomers **5a** and **6a**. In a further check, the recoordination of the free ligand to equally accessible enantiomeric complex *S*-**11** generated the regioisomers **12a** and **13a** with two clearly different pairs of doublet phosphorus signals at δ 0.9, 36.2 (J_{PP} = 51.9 Hz) and 10.1, 28.5 (J_{PP} = 51.7 Hz). Note that products **13a** and **14a** are the enantiomeric forms of **7a** and **8a**, respectively. Importantly, no resonance signals were observed at δ −6.1, 38.8, 8.6, and 28.6 thus confirming that the liberated 1,3-diphosphine ligand **10a** was optically pure.

Asymmetric Hydrophosphination of Keto-Functionalized Monophosphine Palladium Complexes *R*-3b and *R*-3c. By following the similar procedure as described for the hydrophosphination of *R*-**3a**, the keto-functionalized precursor *R*-**3b** was converted to the reactive perchlorato species by treatment with silver salt. The perchlorato complex *R*-**4b** was subsequently reacted with 1 equiv of diphenylphosphine for the second-stage hydrophosphination reaction at 0 °C for 2 h in acetonitrile. The 121 MHz ^{31}P NMR spectrum of the crude product in $CDCl_3$ indicated four pairs of doublets at δ −6.7, 36.7 (J_{PP} = 55.7 Hz); 1.0, 38.8 (J_{PP} = 51.8 Hz); 8.8, 27.2 (J_{PP} = 56.3 Hz) and 10.9, 28.5 (J_{PP} = 52.0 Hz) with the intensity ratio of 17.5:1:11.2:3.1. The two major regioisomers **5b** and **6b** was subsequently isolated efficiently by column chromatography in 75% yield with two pairs of doublets at δ −6.7, 36.7 (J_{PP} = 55.7 Hz); and 8.8, 27.2 (J_{PP} = 56.3 Hz) in the ^{31}P NMR spectrum.

Upon removal of the chiral amine auxiliary of **5b** and **6b** with concentrated hydrochloric acid, the optically pure dichloro complex **9b** was crystallized as pale yellow prisms in 85% yield from dichloromethane and diethyl ether, $[\alpha]_D = -20.4$ (*c* 0.9, CH_2Cl_2). The ^{31}P NMR spectrum (121 MHz, $CDCl_3$) showed a pair of doublets at δ 16.3, 22.5 (J_{PP} = 12.7 Hz). The single-crystal X-ray crystallographic analysis clearly established its coordination mode and the absolute configuration (Figure 2). The newly formed chiral carbon center at C13 is *R*, and the novel six-membered metallacycle adopts a boat conformation with the keto-substituent occupying the sterically

Scheme 3



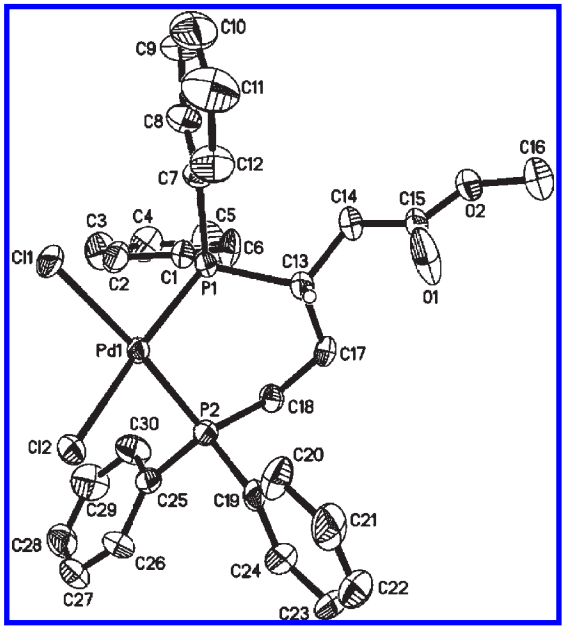


Figure 1. Molecular structure and absolute stereochemistry of complex **9a**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of **9a**

Pd1−P1	2.258(2)	Pd1−P2	2.249(3)
C13−P1	1.866(9)	C13−C17	1.514(14)
C17−C18	1.521(14)	C18−P2	1.818(9)
P2−Pd1−P1	90.2(1)	Cl2−Pd1−Cl1	91.8(1)
P1−Pd1−Cl2	175.3(1)	P2−Pd1−Cl1	171.1(1)
P1−Pd1−Cl1	91.3(1)	P2−Pd1−Cl2	87.3(1)
C17−C13−P1	116.2(7)	C17−C18−P2	114.2(7)

favorable equatorial position. Both bond lengths and angles are comparable with the analogous ester complex **9a** as showed in Table 2. Treatment of a CH_2Cl_2 solution of **9b** with aqueous potassium cyanide liberated the optical pure keto-functionalized 1,3-diphosphine ligand **10b** as a white solid in 92% yield, with $[\alpha]_{436} = +30.8$ (*c* 0.9, CH_2Cl_2). The ^{31}P NMR spectrum of the free diphosphine exhibited two singlets at δ −15.8 and −6.6. The optical purity of **10b** was confirmed by a similar recoordination process (Scheme 4). The recomplexation products involving the bis(acetonitrile) complex *R*-**11** showed two pairs of doublets at δ −6.7, 36.7 (J_{PP} = 55.7 Hz); and 8.8, 27.2 (J_{PP} = 56.3 Hz), which indicated the formation of the regioisomers **5b** and **6b**. Upon recoodination of the free ligand **10b** to complex *S*-**11**, the ^{31}P NMR of the recomplexation products gave two distinct pairs of doublets at δ 1.0, 38.8 (J_{PP} = 51.8 Hz); and 10.9, 28.5 (J_{PP} = 52.0 Hz).

The monophosphine substrate *R*-**3c**, upon abstraction of the chloro ligand with silver perchlorate, was reacted with diphenyphosphine at 0 °C for 2 h in acetonitrile. The 121 MHz ^{31}P NMR spectrum of the crude product in $CDCl_3$ showed four pairs of doublets at δ −6.3, 37.8 (J_{PP} = 56.9 Hz); 0.4, 38.6 (J_{PP} = 51.9 Hz); 8.6, 26.9 (J_{PP} = 56.3 Hz), and 10.6, 27.8 (J_{PP} = 53.0 Hz) with the intensity ratio of 12:1:7:3.5, which indicated the formation of the four isomeric hydrophosphination products **5c**, **6c**, **7c**, and **8c**. The two major regioisomers **5c** and **6c** could be isolated efficiently by column chromatography in 70% yield [δ −6.3, 37.8 (J_{PP} = 56.9 Hz); and 8.6, 26.9 (J_{PP} = 56.3 Hz)]. The regioisomers **5c** and **6c** were treated with concentrated hydrochloric acid to remove the chiral amine auxiliary chemoselectively. The resultant dichloro complex **9c** showed a pair of doublets at δ 15.8, 22.4 (J_{PP} = 13.8 Hz) in $CDCl_3$ in ^{31}P NMR spectrum, $[\alpha]_D$ = +12.6 (*c* 1.0, CH_2Cl_2). Further treatment of **9c** with aqueous potassium cyanide at room temperature liberated the chiral keto-functionalized 1,3-diphosphine ligand **10c** in quantitative yield, $[\alpha]_D = +11.4$ (*c* 0.7, CH_2Cl_2). The ^{31}P NMR spectrum of the free ligand in $CDCl_3$ exhibited a pair of singlets at δ −15.7 and −6.4. The recoordination process of the free ligand to *R*-**11** and *S*-**11** confirmed that the chiral diphosphine ligand **10c** is optically pure.

Asymmetric Hydrophosphination of *R*-2 to Synthesize Hydroxyl-Functionalized Chiral 1,3-Diphosphine Palladium Complex. Unlike the ester- and keto-functionalized monophosphine substrates *R*-**3**, the perchlorato analogue of *R*-**2** generated from abstraction of the chloro ligand with silver perchlorate is quite unstable. However, the second-stage hydrophosphination of acrolein can occur at the carbonyl group by treatment of *R*-**2** with 1 equiv diphenylphosphine in the presence of $LiClO_4$ (Scheme 5). The reaction was conducted at room temperature and was completed in 2 h to afford the hydroxyl-functionalized 1,3-phosphine products **14**, **15**, **16**, and **17**. The ^{31}P NMR spectrum (202 MHz, $CDCl_3$) of the crude reaction mixture exhibited four pairs of doublets at δ −5.1, 30.1 (J_{PP} = 56.7 Hz); 0.0, 39.3 (J_{PP} = 53.0 Hz); 5.3, 25.8 (J_{PP} = 54.1 Hz), and 13.1, 26.0 (J_{PP} = 52.5 Hz) with the intensity ratio of 1:4.1:1:6.6.

The major regioiosmers **14** and **15** could be isolated as an equilibrium mixture by column chromatography in 42% yield. The ^{31}P NMR spectrum exhibited two pairs of doublets at δ 0.0, 39.3 (J_{PP} = 53.0 Hz) and 13.1, 26.0 (J_{PP} = 52.5 Hz). Upon slow diffusion of diethyl ether into the dichloromethane solution of the isomeric mixture, the product **14** was obtained as pale yellow prisms in 40% yield, $[\alpha]_D = -90.7°$ (*c* 0.8, CH_2Cl_2). The ^{31}P NMR spectrum of crystallized **14** showed a pair of doublets at δ 13.1, 26.0 (J_{PP} = 52.5 Hz). The molecular structure was analyzed by means of single-crystal X-ray diffraction analysis (Figure 3 and Table 3). The six-membered chelating diphosphine ring has a skew conformation of δ helicity, with the hydroxyl group occupying the sterically favorable equatorial position. The newly formed stereogenic center at C27is in the *R* absolute configuration.

The addition of a secondary phosphine to an aldehyde is usually more complex, as the process has been proven to be reversible, and the corresponding adducts are prone to undergo isomerization to form phosphine oxides.[10]

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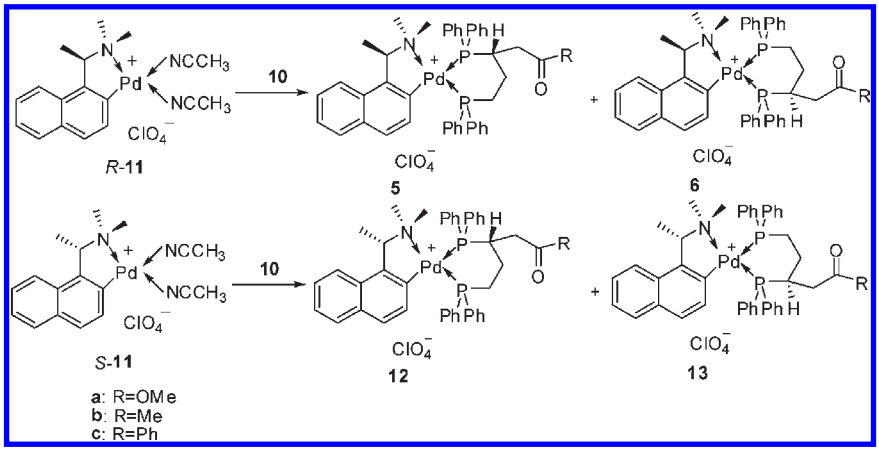
Scheme 4



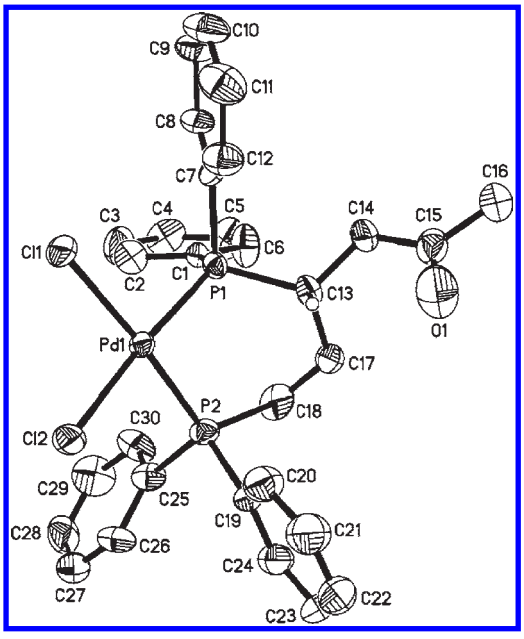


Figure 2. Molecular structure and absolute stereochemistry of complex **9b**.

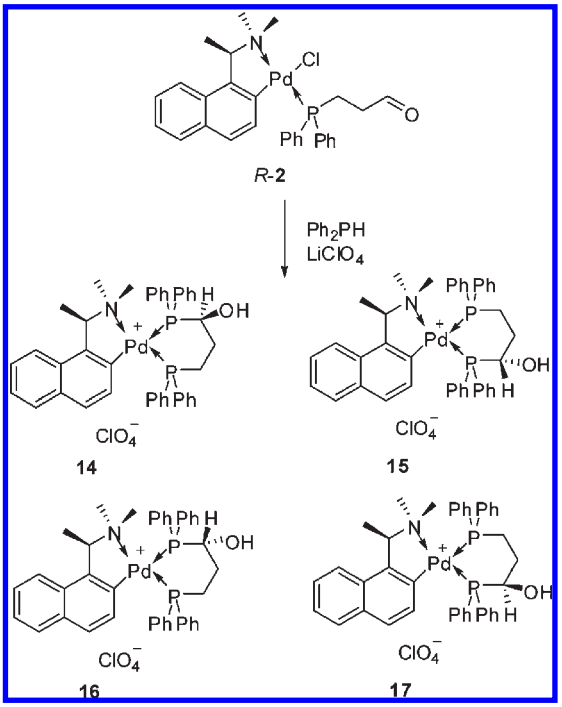
Table 2. Selected Bond Lengths (Å) and Angles (deg) of **9b**

Pd1−P1	2.245(2)	Pd1−P2	2.246(3)
C13−P1	1.869(8)	C13−C17	1.552(12)
C17−C18	1.487(14)	C18−P2	1.861(8)
P2−Pd1−P1	90.1(1)	Cl2−Pd1−Cl1	92.4(1)
P1−Pd1−Cl2	175.1(1)	P2−Pd1−Cl1	172.0(1)
P1−Pd1−Cl1	91.4(1)	P2−Pd1−Cl2	86.5(1)
C17−C13−P1	114.3(6)	C17−C18−P2	114.2(6)

Interestingly, the chiral hydroxyl group in coordinated 1,3-diphosphine palladium complexes are quite stable. The dichloromethane solution of the complex **14** can be kept for 15 d without racemization of the chiral carbon center. The subsequent liberation of the α-hydroxyl functionalized 1,3-phosphine ligand from complex **14** was unsuccessful because of its unstable nature.

In conclusion, we have demonstrated an efficicent synthesis of a new kind of ester- and keto-functionalized chiral 1,3-bis(diphenylphosphino)propane ligands, as well as hydroxyl-functionlized chiral 1,3-diphosphine palladium complex from acrolein, by means of organo-

Scheme 5



palladium complex promoted Michael-type hydrophosphination reactions. The reactions proceeded with good yields, regio- and stereoselectivities under mild conditions. Further investigations on the synthesis of a similar class of chiral diphosphines with various functionalities and the screening of transition metal catalyzed reactions are currently in progress.

Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of argon using a standard Schlenk line. NMR spectra were recorded at 25 °C on Bruker ACF 300 (^{1}H at 300 MHz, ^{13}C at 75 MHz, and ^{31}P at 121 MHz), 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz, and ^{31}P at 161 MHz) and 500 (^{1}H at 500 MHz and ^{31}P at 202 MHz) spectrometers. Chemical shifts (δ) are reported in parts per million. Proton and carbon chemical shifts are relative to the residual solvent peaks, and phosphorus chemical shifts are referenced to 85% aqueous H_3PO_4. Coupling constants are reported in hertz.

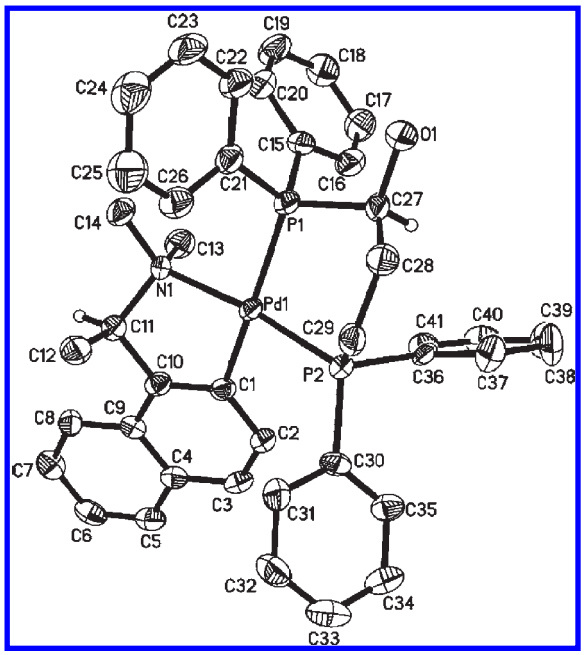


Figure 3. Molecular structure and absolute stereochemistry of complex **14**.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of **14**

Pd1−C1	2.048(5)	Pd1−N1	2.161(4)
Pd1−P1	2.377(1)	Pd1−P2	2.255(1)
C27−P1	1.845(5)	C27−C28	1.529(8)
C28−C29	1.548(8)	C29−P2	1.831(5)
C1−Pd1−N1	80.4(2)	C1−Pd1−P2	94.8(1)
N1−Pd1−P2	173.1(1)	C1−Pd1−P1	172.2(2)
N1−Pd1−P1	96.1(1)	P2−Pd1−P1	89.3(1)
C28−C27−P1	113.1(4)	C27−C28−C29	116.7(5)
C28−C29−P2	118.7(4)	P1−C27−O1	109.8(3)

Optical rotations were measured on the specified solution in a 0.1 dm cell at 20 °C with a Perkin-Elmer 341 polarimeter. Elemental analyses were performed by the Elemental Analysis Laboratory of the Division of Chemistry and Biological Chemistry at Nanyang Technological University. Melting points were measured using the SRS Optimelt Automated Melting Point System, SRS MPA100.

The chiral palladium templates *R*-**1**,[11a,b] *R*-**11**, and *S*-**11**[11c] were prepared according to literature methods.

Caution! *Perchlorate salts of metal complexes are potentially explosive compounds and should be handled with care.*

Preparation of Monophosphine Palladium Complex *R*-2. A mixture of diphenylphosphine (0.70 g, 3.76 mmol) and palladium complex *R*-**1** (1.22 g, 1.78 mmol) in acetonitrile (60 mL) was stirred at room temperature until all of *R*-**1** had dissolved (ca. 1 h). The solution was cooled to 0 °C, and fresh distilled acrolein (0.32 g, 5.71 mmol) was added in one portion. The solution was stirred at 0 °C for 30 min. The solvent was then removed via rotary evaporation, and the resultant white solid was washed with hexanes/diethyl ether (2:1, 100 mL) and subsequently dissolved in ethyl acetate/diethyl ether (1:1, 150 mL) and filtered to remove the insoluble impurity. The filtrate was collected and upon removal of the solvent yielded the product *R*-**2** as a white solid (1.82 g, 87%). Note: *R*-**2** was not stable for flash column chromatography on silica. $[\alpha]_{436} = +94.0°$ (*c* 0.8, CH_2Cl_2). Mp: 126−128 °C. Anal. Calcd for $C_{29}H_{31}ClNOPPd$: C, 59.8; H, 5.4; N, 2.4. Found: C, 59.5; H, 5.6; N, 2.5. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 35.6 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.06 (d, 3H, J_{HH} = 6.3 Hz, CH*Me*), 2.47 (m, 2H, CH_2CHO), 2.70 (d, 3H, J_{PH} = 1.3 Hz, N*Me*), 2.99 (d, 3H, J_{PH} = 3.4 Hz, N*Me*), 3.07−3.29 (m, 1H, PCH_2), 4.37 (qn, 1H, $J_{HH} = J_{PH}$ = 6.2 Hz, C*H*CH$_3$), 6.64−8.12 (m, 16H, Ar). 9.68 (br, C*H*O). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.7 (d, J_{PC} = 35.6 Hz), 23.8 (s), 39.7 (d, J_{PC} = 3.6 Hz), 48.3 (s), 51.1 (d, J_{PC} = 2.9 Hz), 72.8 (d, J_{PC} = 3.2 Hz), 123.2 (s), 124.2 (s), 124.7 (d, J_{PC} = 5.7 Hz), 125.7 (s), 128.4 (d, 2C, J_{PC} = 10.4 Hz), 128.7 (s), 128.8 (s), 128.9 (d, 2C, J_{PC} = 10.3 Hz), 129.5 (d, J_{PC} = 45.0 Hz), 130.3 (d, J_{PC} = 44.8 Hz), 130.9 (d, J_{PC} = 2.4 Hz), 131.1 (d, J_{PC} = 2.4 Hz), 131.1 (s), 133.8 (d, 2C, J_{PC} = 11.6 Hz), 134.1 (d, 2C, J_{PC} = 11.4 Hz), 135.4 (d, J_{PC} = 12.2 Hz), 149.1 (d, J_{PC} = 1.2 Hz), 149.2 (s), 200.4 (d, J_{PC} = 16.6 Hz).

Preparation of Monophosphine Palladium Complex *R*-3a. *R*-**2** was synthesized as described previously from diphenylphosphine (0.70 g, 3.76 mmol) and *R*-**1** (1.22 g, 1.78 mmol). Upon removal of the organic solvent under reduced pressure, the resulting white solid (crude *R*-**2**) was redissolved into chloroform (50 mL) before methyl (triphenylphosphoranylidene) acetate (1.88 g, 5.62 mmol) was added. The mixture was stirred for 2 h at room temperature and concentrated. Complex *R*-**3a** was isolated by column chromatography on silica (EtOAc/Hexanes = 1:2) as a pale yellow solid (*E*/*Z* > 10, 1.94 g, 85%). *R*-**3a** (*trans* isomer), $[\alpha]_D = -11.9°$ (*c* 1.4, CH_2Cl_2). Mp: 120−122 °C. Anal. Calcd for $C_{32}H_{35}ClNO_2PPd$: C, 60.2; H, 5.5; N, 2.2. Found: C, 60.5; H, 5.6; N, 2.1. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 35.0 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.05 (d, 3H, J_{HH} = 6.2 Hz, CH*Me*), 2.26 (m, 2H, PCH$_2$CH_2), 2.67 (s, 3H, N*Me*), 2.86 (m, 1H, PCH′*H*), 2.97 (d, 3H, J_{PH} = 3.0 Hz, N*Me*), 3.05 (m, 1H, PC*H*′H), 3.64 (s, 3H, CO_2*Me*), 4.34 (qn, 1H, $J_{HH} = J_{PH}$ = 6.1 Hz, C*H*CH$_3$), 5.73 (d, 1H, J_{HH} = 15.7 Hz, C*H*CO$_2$Me), 6.66−8.10 (m, 17H, Ar and CH$_2$C*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.7 (s), 27.9 (d, J_{PC} = 3.6 Hz), 29.5 (d, J_{PC} = 32.6 Hz), 48.3 (s), 51.1 (d, J_{PC} = 2.8 Hz), 51.4 (s), 72.8 (d, J_{PC} = 3.1 Hz), 121.2 (s), 123.2 (s), 124.1 (s), 124.7 (d, J_{PC} = 5.7 Hz), 125.8 (s), 128.4 (d, 2C, J_{PC} = 10.3 Hz), 128.7 (s), 128.8 (s), 128.9 (d, 2C, J_{PC} = 11.2 Hz), 129.7 (d, J_{PC} = 44.6 Hz), 130.6 (d, J_{PC} = 45.6 Hz), 130.8 (d, J_{PC} = 2.3 Hz), 131.0 (d, J_{PC} = 2.5 Hz), 131.1 (s), 133.8 (d, 2C, J_{PC} = 11.5 Hz), 134.2 (d, 2C, J_{PC} = 11.3 Hz), 135.5 (d, J_{PC} = 12.0 Hz), 148.3 (d, J_{PC} = 16.8 Hz), 149.2 (d, J_{PC} = 2.1 Hz), 149.4 (s), 166.8 (s).

Preparation of Monophosphine Palladium Complexes *R*-3b and *R*-3c. The same procedure was adopted to synthesize palladium complex *R*-**3b** from *R*-**1** (1.22 g, 1.78 mmol). After dissolving *R*-**2** into chloroform (50 mL), 1-(triphenylphosphoranylidene)-acetone (1.72 g, 5.38 mmol) was added and stirred at 50 °C for 24 h. Upon removal of the solvent, the product *R*-**3b** was isolated by column chromatography on silica (EtOAc/Hexanes = 1:2) as a pale yellow powder (1.80 g, 81%). $[\alpha]_D = -5.7°$ (*c* 1.1, CH_2Cl_2). Mp: 121−123 °C. Anal. Calcd for $C_{32}H_{35}ClNOPPd$: C, 61.7; H, 5.7; N, 2.2. Found: C, 61.5; H, 5.9; N, 2.0. ^{31}P NMR ($CDCl_3$, 121 MHz): δ 35.2 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.06 (d, 3H, J_{HH} = 6.3 Hz, CH*Me*), 2.16 (s, 3H, CO*Me*), 2.26 (m, 2H, PCH$_2$CH_2), 2.69 (d, 3H, J_{PH} = 1.5 Hz, N*Me*), 2.89 (m, 1H, PCH′*H*), 2.98 (d, 3H, J_{PH} = 3.4 Hz, N*Me*), 3.09 (m, 1H, PC*H*′H), 4.36 (qn, 1H, $J_{HH} = J_{PH}$ = 6.1 Hz, C*H*CH$_3$), 5.93 (d, 1H, J_{HH} = 16.0 Hz, C*H*COMe), 6.65−8.12 (m, 17H, Ar and CH$_2$C*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.8 (s), 26.7 (s), 28.3 (d, J_{PC} = 3.5 Hz), 29.6 (d, J_{PC} = 32.6 Hz), 48.3 (s), 51.1 (d, J_{PC} = 2.8 Hz), 72.8 (d, J_{PC} = 3.2 Hz), 123.2 (s), 124.2 (s), 124.7 (d, J_{PC} = 5.7 Hz), 125.8 (s), 128.4 (d, 2C, J_{PC} = 10.3 Hz), 128.7 (s), 128.8 (s), 128.9 (d, 2C, J_{PC} = 10.3 Hz), 129.6 (d, J_{PC} = 44.7 Hz), 130.6 (d, J_{PC} = 44.4 Hz), 130.9 (d, J_{PC} = 2.2 Hz), 131.0 (d, J_{PC} = 2.2 Hz), 131.1 (s), 131.4 (s), 133.7 (d, 2C, J_{PC} = 11.5 Hz), 134.2 (d, 2C, J_{PC} = 11.4 Hz), 135.5 (d, J_{PC} = 12.2 Hz), 147.4 (d, J_{PC} = 16.4 Hz), 149.1 (d, J_{PC} = 2.0 Hz), 149.3 (s), 198.6 (s).

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Table 4. Crystallographic Data for Complexes **9a**, **9b**, and **14**

	9a	**9b**	**14**
formula	$C_{30}H_{30}Cl_2O_2P_2Pd$	$C_{30}H_{30}Cl_2OP_2Pd$	$C_{41}H_{42}ClNO_5P_2Pd\cdot 2CH_2Cl_2$
fw	661.78	645.78	1002.40
space group	*P*1	*P*1	*P*2(1)
cryst syst	triclinic	triclinic	monoclinic
a/Å	8.6202(3)	8.5973(10)	9.6961(4)
b/Å	10.7327(4)	10.8849(12)	10.1443(4)
c/Å	16.3388(6)	16.260(2)	22.3638(9)
α/deg	96.552(2)	97.704(5)	90
β/deg	99.248(2)	99.824(5)	91.964(2)
γ/deg	106.096(2)	107.217(5)	90
V/Å^3	1413.29(9)	1404.3(3)	2198.41(15)
Z	2	2	2
T/K	223(2)	223(2)	173(2)
D_{calcd}/g cm^{-3}	1.555	1.527	1.514
λ/Å	0.71073	0.71073	0.71073
μ/mm^{-1}	0.986	0.987	0.844
F(000)	672	656	1024
Flack param	0.00(4)	0.06(3)	0.07(3)
R1 (obs data)[a]	0.0467	0.0302	0.0465
wR2(obs data)[b]	0.1372	0.0791	0.0931

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

The same procedure was used to prepare product *R*-**3c** from *R*-**1** (1.22 g, 1.78 mmol). A chloroform solution (50 mL) of *R*-**2** and (phenacylidene)triphenylphosphorane (2.05 g, 5.38 mmol) was heated at 50 °C for 36 h. The product *R*-**3c** was isolated by column chromatography on silica (EtOAc/Hexanes = 1:2) as a pale yellow powder (1.93 g, 79%). $[\alpha]_D = -20.9°$ (*c* 1.0, CH_2Cl_2). Mp: 116−119 °C. Anal. Calcd for $C_{37}H_{37}ClNOPPd$: C, 64.9; H, 5.4; N, 2.0. Found: C, 64.7; H, 5.5; N, 1.9. ^{31}P NMR ($CDCl_3$, 121 MHz): *δ* 35.1 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 2.07 (d, 3H, J_{HH} = 6.3 Hz, CH*Me*), 2.35 (m, 2H, PCH_2CH_2), 2.69 (d, 3H, J_{PH} = 1.4 Hz, N*Me*), 2.98 (d, 3H, J_{PH} = 3.4 Hz, N*Me*), 2.91−2.91 (m, 2H, PCH_2), 4.36 (qn, 1H, $J_{HH} = J_{PH}$ = 6.1 Hz, $CHCH_3$), 6.68−8.11 (m, 23H, Ar and C*H*=C*H*COPh). ^{13}C NMR ($CDCl_3$, 75 MHz): *δ* 23.7 (s), 28.4 (d, J_{PC} = 3.7 Hz), 29.6 (d, J_{PC} = 32.3 Hz), 48.3 (d, J_{PC} = 2.0 Hz), 51.1 (d, J_{PC} = 2.9 Hz), 72.9 (d, J_{PC} = 3.2 Hz), 123.2 (s), 124.1 (s), 124.7 (d, J_{PC} = 5.8 Hz), 125.7 (s), 126.3 (s), 128.4 (d, 2C, J_{PC} = 10.0 Hz), 128.5 (s, 2C), 128.6 (s, 2C), 128.7 (s), 128.8 (s), 128.9 (d, 2C, J_{PC} = 10.4 Hz), 129.7 (d, J_{PC} = 44.7 Hz), 130.7 (d, J_{PC} = 44.5 Hz), 130.9 (d, J_{PC} = 2.3 Hz), 131.0 (d, J_{PC} = 2.4 Hz), 131.1 (s), 132.6 (s), 133.8 (d, 2C, J_{PC} = 11.5 Hz), 134.2 (d, 2C, J_{PC} = 11.3 Hz), 135.5 (d, J_{PC} = 12.0 Hz), 137.8 (s), 148.3 (d, J_{PC} = 17.0 Hz), 149.2 (d, J_{PC} = 2.1 Hz), 149.4 (s), 190.8 (s).

Hydrophosphination of Complex *R*-3a. A solution of *R*-**3a** (1.0 g, 1.57 mmol) in dichloromethane (40 mL) solution was treated with $AgClO_4\cdot H_2O$ (0.53 g, 2.4 mmol) in water (3 mL), and stirred for 1 h at room temperature. The organic layer, after the removal of AgCl precipitate, was washed with H_2O (3 × 20 mL), dried over $MgSO_4$, concentrated and redissolved in dichloromethane/acetonitrile (1:1, 40 mL). The solution was allowed to cool down to −78 °C, and treated with diphenylphosphine (0.30 g, 1.57 mmol) in dichloromethane (6 mL), followed by triethylamine (0.16 g, 1.57 mmol). The mixture was stirred for 2 h, and then warmed to room temperature. Upon removal of solvent, the crude product was purified by chromatography on silica (CH_2Cl_2/Acetone/Hexanes = 2:1:3) to afford a mixture of regioisomers **5a** and **6a** as a pale yellow solid (0.92 g, 66%). ^{31}P NMR ($CDCl_3$, 121 MHz): *δ* −6.1 (d, J_{PP} = 55.3 Hz), 8.6 (d, J_{PP} = 55.3 Hz), 28.6 (d, J_{PP} = 55.3 Hz), 38.8 (d, J_{PP} = 55.3 Hz).

Hydrophosphination of Complexes *R*-3b and *R*-3c. *R*-**3b** (1.0 g, 1.61 mmol), upon abstraction of the chloro ligand with silver perchlorate, was dissolved in acetonitrile (20 mL) and cooled down to 0 °C. The solution was subsequently treated with diphenylphosphine (0.30 g, 1.57 mmol) and stirred for 2 h. The regioisomers **5b** and **6b** could be isolated by column chromatography (CH_2Cl_2/Acetone/Hexanes = 2:1:3) as a pale yellow powder (1.05 g, 75%) upon removal of solvent. ^{31}P NMR ($CDCl_3$, 121 MHz): *δ* −6.7 (d, J_{PP} = 55.7 Hz), 8.8 (d, J_{PP} = 56.3 Hz), 27.2 (d, J_{PP} = 56.3 Hz), 36.7 (J_{PP} = 55.7 Hz).

By following the same procedure as described for the hydrophsophination of *R*-**3c** (1.0 g, 1.46 mmol), the regioisomers **5c** and **6c** could be isolated by column chromatography (CH_2Cl_2/Acetone/Hexanes = 2:1:3) as a pale yellow powder (0.95 g, 70%). ^{31}P NMR ($CDCl_3$, 121 MHz): *δ* −6.3 (d, J_{PP} = 56.9 Hz), 8.6 (d, J_{PP} = 56.3 Hz), 26.9 (d, J_{PP} = 56.3 Hz), 37.8 (J_{PP} = 56.9 Hz).

Preparation of the Dichloro Palladium Complexes 9a, 9b, and 9c. A solution of regioisomers **5a** and **6a** (0.8 g, 0.90 mmol) in dichloromethane (15 mL) was treated with concentrated hydrochloric acid (8 mL) for 5 h at room temperature. The mixture was then washed with water (3 × 20 mL), dried over $MgSO_4$, and subsenquently crystallized from CH_2Cl_2-Et_2O to give the dichloro complex **9a** as pale yellow prisms (0.52 g, 88%). $[\alpha]_D$ = −17.5° (*c* 1.7, CH_2Cl_2). Mp: 275−277 °C (decomp.). Anal. Calcd for $C_{30}H_{30}Cl_2O_2P_2Pd$: C, 54.4; H, 4.6. Found: C, 54.8; H, 4.4. ^{31}P NMR ($CDCl_3$, 121 MHz): *δ* 15.5 (d, J_{PP} = 13.0 Hz), 21.9 (d, J_{PP} = 13.0 Hz). ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 1.93−2.13 (m, 2H, PCH_2CH_2), 2.22 (m, 1H, J_{HH} = 10.6 Hz, J_{HH} = 16.6 Hz, C*H*′HCO$_2$Me), 2.43−2.53 (m, 3H, CH′*H*CO$_2$Me and PCH_2), 2.96 (m, 1H, $PCHCH_2$), 3.56 (s, 3H, CO_2Me), 7.36−7.87 (m, 20H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): *δ* 24.8 (dd, J_{PC} = 8.0 Hz, J_{PC} = 31.1 Hz), 24.9 (d, J_{PC} = 4.1 Hz), 29.2 (dd, J_{PC} = 10.6 Hz, J_{PC} = 29.3 Hz), 35.3 (s), 52.3 (s), 126.3 (d, J_{PC} = 54.2 Hz), 126.8 (d, J_{PC} = 55.5 Hz), 128.4 (d, 2P, J_{PC} = 11.4 Hz), 128.6 (d, 2P, J_{PC} = 11.5 Hz), 128.7 (d, J_{PC} = 56.8 Hz), 128.9 (d, 4P, J_{PC} = 11.2 Hz), 130.1 (d, J_{PC} = 59.0 Hz), 131.3 (d, J_{PC} = 2.9 Hz), 131.6 (d, J_{PC} = 2.6 Hz), 131.7 (d, J_{PC} = 3.1 Hz), 131.9 (d, J_{PC} = 2.7 Hz), 133.3 (d, 2P, J_{PC} = 10.2 Hz), 133.7 (d, 2P, J_{PC} = 9.6 Hz), 133.8 (d, 2P, J_{PC} = 10.9 Hz), 135.3 (d, 2P, J_{PC} = 10.9 Hz), 171.1 (d, J_{PC} = 12.8 Hz).

The same procedure was used to prepare dichloro complexes **9b** and **9c**. **9b** (0.38 g, 85%) from regioisomers **5b** and **6b** (0.6 g, 0.69 mmol). $[\alpha]_D$ = −20.4° (*c* 0.9, CH_2Cl_2). Mp: 285−287 °C (decomp.). Anal. Calcd for $C_{30}H_{30}Cl_2OP_2Pd$: C, 55.8; H, 4.7. Found: C, 55.9; H, 4.5. ^{31}P NMR ($CDCl_3$, 121 MHz): *δ* 16.3 (d, J_{PP} = 12.7 Hz), 22.5 (d, J_{PP} = 12.7 Hz). ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 1.90 (s, 3H, CO*Me*), 1.91−2.06 (m, 2H, PCH_2CH_2), 2.34 (m, 1H, J_{HH} = 9.4 Hz, J_{HH} = 18.3 Hz, C*H*′HCOMe), 2.47 (m, 2H, PCH_2), 2.54 (m, 1H, CH′*H*COMe), 3.08 (m, 1H, $PCHCH_2$), 7.35−7.84 (m, 20H, Ar). ^{13}C NMR

($CDCl_3$, 100 MHz): δ 25.3 (dd, J_{PC} = 8.1 Hz, J_{PC} = 31.4 Hz), 25.4 (d, J_{PC} = 4.0 Hz), 27.6 (dd, J_{PC} = 11.0 Hz, J_{PC} = 29.8 Hz), 30.1 (s), 44.5 (d, J_{PC} = 1.9 Hz), 126.6 (d, J_{PC} = 54.0 Hz), 127.2 (d, J_{PC} = 55.6 Hz), 128.4 (d, 2P, J_{PC} = 11.4 Hz), 128.7 (d, 2P, J_{PC} = 11.5 Hz), 128.8 (d, 2P, J_{PC} = 10.9 Hz), 128.9 (d, 2P, J_{PC} = 11.4 Hz), 129.1 (d, J_{PC} = 57.3 Hz), 129.9 (d, J_{PC} = 58.4 Hz), 131.3 (d, J_{PC} = 2.8 Hz), 131.5 (d, J_{PC} = 2.8 Hz), 131.6 (d, J_{PC} = 2.7 Hz), 131.9 (d, J_{PC} = 2.7 Hz), 133.4 (d, 2P, J_{PC} = 10.3 Hz), 133.5 (d, 2P, J_{PC} = 9.3 Hz), 133.8 (d, 2P, J_{PC} = 10.8 Hz), 135.4 (d, 2P, J_{PC} = 10.6 Hz), 204.5 (d, J_{PC} = 8.8 Hz).

9c (0.39 g, 87%) was prepared from regioisomers **5c** and **6c** (0.6 g, 0.64 mmol). $[\alpha]_D$ = +12.6 (*c* 1.0, CH_2Cl_2). Mp: 160−163 °C. Anal. Calcd for $C_{35}H_{32}Cl_2OP_2Pd$: C, 59.4; H, 4.6. Found: C, 59.7; H, 4.4. ^{31}P NMR ($CDCl_3$, 161 MHz): δ 15.8 (d, J_{PP} = 13.8 Hz), 22.4 (d, J_{PP} = 13.8 Hz). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.07 (br, 2H, PCH_2CH_2), 2.53 (br, 2H, CH_2COPh), 2.90 (m, 1H, J_{HH} = 10.0 Hz, J_{HH} = 17.4 Hz, PC*H*′H), 3.01 (dd, 1H, J_{HH} = 8.8 Hz, J_{HH} = 17.4 Hz, PCH′*H*), 3.26 (br, 1H, PC*H*CH_2), 7.36−7.91 (m, 25H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 25.2 (dd, J_{PC} = 8.0 Hz, J_{PC} = 31.2 Hz), 25.3 (d, J_{PC} = 4.2 Hz), 27.8 (dd, J_{PC} = 10.9 Hz, J_{PC} = 29.8 Hz), 39.5 (s), 126.8 (d, J_{PC} = 54.3 Hz), 127.0 (d, J_{PC} = 55.0 Hz), 127.9 (s, 2C), 128.4 (d, 2C, J_{PC} = 11.4 Hz), 128.7 (d, 2C, J_{PC} = 11.5 Hz), 128.8 (s, 2C), 128.9 (d, 2C, J_{PC} = 11.3 Hz), 128.9 (d, 2C, J_{PC} = 11.0 Hz), 129.2 (d, J_{PC} = 55.0 Hz), 130.0 (d, J_{PC} = 58.4 Hz), 131.3 (d, J_{PC} = 2.8 Hz), 131.6 (d, 2C, J_{PC} = 2.7 Hz), 131.9 (d, J_{PC} = 2.7 Hz), 133.5 (d, 2C, J_{PC} = 10.2 Hz), 133.6 (d, 2C, J_{PC} = 9.3 Hz), 133.7 (d, 2C, J_{PC} = 10.7 Hz), 133.9 (s), 135.4 (d, 2C, J_{PC} = 10.6 Hz), 135.8 (s), 196.1 (d, J_{PC} = 10.0 Hz).

Liberation of Functionalized 1,3-Diphosphine Ligand 10a, 10b, and 10c. A solution of complex **9a** (0.3 g, 0.45 mmol) in dichloromethane (15 mL) was stirred vigorously with aqueous KCN (1.0 g, 15.4 mmol) for 30 min. The organic layer was separated, washed with water (3 × 15 mL), and dried with $MgSO_4$. The 1,3-diphosphine ligand **10a** was obtained as white solid upon removal of solvent under reduced pressure (0.21 g, 95%). $[\alpha]_D$ = +19.0 (*c* 1.0, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 121 MHz): δ −15.3 (s), −6.4 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.51 (m, 2H, PCH_2CH_2), 2.09−2.19 (m, 3H, CH_2CO_2Me and PC*H*′H), 2.35 (m, 1H, J_{HH} = 6.8 Hz, J_{HH} = 13.8 Hz, PCH′*H*), 2.88 (br, 1H, PC*H*CH_2), 3.47 (s, 3H, CO_2*Me*), 7.19−7.40 (m, 20H, Ar).

Similarly the keto-functionalized 1,3-diphosphine ligand **10b** (0.20 g, 92%) was achieved from **9b** (0.3 g, 0.46 mmol) as a white solid. $[\alpha]_D$ = +30.8° (*c* 0.9, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 202 MHz): δ − 15.8 (s), − 6.6 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.48 (m, 1H, PCH_2CH′*H*), 1.57 (m, 1H, PCH_2CH′H), 1.95 (s, 3H, CO*Me*), 2.14 (t, 2H, J_{HH} = J_{PH} = 8.4 Hz, CH_2COMe), 2.36 (m, 1H, J_{PH} = 8.6 Hz, J_{HH} = 17.6 Hz, PCH′*H*), 2.45 (m, 1H, J_{HH} = 17.6 Hz, PC*H*′H), 3.10 (br, 1H, PC*H*CH_2), 7.26−7.44 (m, 20H, Ar).

10c (0.21 g, 95%) was prepared from **9c** (0.3 g, 0.42 mmol) as a white solid. $[\alpha]_D$ = +11.4° (*c* 0.7, CH_2Cl_2). ^{31}P NMR ($CDCl_3$, 202 MHz): δ − 15.7 (s), − 6.4 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.64 (m, 2H, PCH_2CH_2), 2.02 (t, 2H, J_{HH} = J_{PH} = 8.5 Hz, CH_2COPh), 2.99 (m, 2H, PCH_2), 3.34 (br, 1H, PC*H*CH_2), 7.25−7.80 (m, 25H, Ar).

Hydrophosphination of Monophosphine palladium Complex *R*-2. A solution of *R*-**2** (1.0 g, 1.72 mmol) in acetonitrile (25 mL) was treated with diphenylphosphine (0.32 g, 1.72 mmol), followed by $LiClO_4 \cdot 3H_2O$ (0.68 g, 4.30 mmol) and triethylamine (0.17 g, 1.72 mmol). The mixture was stirred for 2 h at room temperature, and the solvent was removed under reduced pressure. The residue was redissolved in dichloromethane, washed with H_2O (3 × 15 mL), dried over $MgSO_4$, concentrated, and purified by column chromatography on silica (CH_2Cl_2/$C_2H_5OC_2H_5$ = 10:1) to afford a mixture of regioisomers **14** and **15** as a pale yellow solid (0.60 g, 42%). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 0.0 (d, J_{PP} = 53.0 Hz), 13.1 (d, J_{PP} = 52.5 Hz), 26.0 (d, J_{PP} = 52.5 Hz). 39.3 (d, J_{PP} = 53.0 Hz). Upon crystallization in dichloromethane-diethyl ether, product **14** was isolated as pale yellow prisms (0.57 g, 40%). $[\alpha]_D$ = −90.7° (*c* 0.8, CH_2Cl_2). Mp: 178−180 °C. Anal. Calcd for $C_{41}H_{42}ClNO_5P_2Pd$: C, 59.1; H, 5.1; N, 1.7. Found: C, 59.4; H, 5.0; N, 1.8. ^{31}P NMR ($CDCl_3$, 202 MHz): δ 13.1 (d, J_{PP} = 52.5 Hz), 26.0 (d, J_{PP} = 52.5 Hz). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.76−1.89 (m, 1H, PCH_2CH′*H*), 2.06 (d, 3H, J_{HH} = 6.2 Hz, CH*Me*), 2.16−2.28 (m, 1H, PCH_2CH′H), 2.22 (s, 3H, N*Me*), 2.44−2.55 (m, 2H, PCH_2), 2.48 (s, 3H, N*Me*), 3.47 (b, 1H, J_{HH} = 4.6 Hz, O*H*), 4.34 (qn, 1H, J_{HH} = J_{PH} = 6.0 Hz, C*H*CH_3), 4.73 (m, 1H, PC*H*OH), 6.98−8.27 (m, 26H, Ar).

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Supporting Information Available: Crystallographic data in CIF format for complexes **9a**, **9b**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.