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A Novel Approach toward Asymmetric Synthesis of Alcohol Functionalized C-Chiral Diphosphines via Two-Stage Hydrophosphination of Terminal Alkynols

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Alcohol functionalized diphosphine ligands with chirality residing on the carbon backbone were prepared using a novel two-stage asymmetric synthetic methodology from the corresponding terminal alkynols. Under mild conditions, the alkynols, 3-butyn-1-ol and 2-propyn-1-ol, were subjected to direct hydrophosphination to give the corresponding Markovnikov addition products. The phosphine functionalized alkenols thus obtained were subsequently subjected to a second-stage asymmetric hydrophosphination employing an organopalladium complex containing the ortho-metalated (*R*)-(1-(dimethylamino)ethyl)naphthalene as a chiral auxiliary and reaction promoter. In the reaction that involved 3-diphenylphosphanyl-but-3-en-1-ol, all four possible stereoisomeric products were generated stereoselectively in the ratio of 1:2:4:18. The major isomer was subsequently isolated in appreciable yield in its configurationally pure form and characterized by means of single-crystal X-ray crystallography. The naphthylamine auxiliary could be removed chemoselectively from the template product by treatment with concentrated hydrochloric acid to form the corresponding optically pure neutral complex. Subsequent ligand displacement from the palladium achieved using aqueous potassium cyanide generated the optically pure diphosphine ligand with chirality residing on the carbon backbone in appreciable yield. However, the similar asymmetric hydrophosphination reaction involving 2-diphenylphosphanyl-prop-2-en-1-ol did not exhibit appreciable selectivity.

Introduction

The asymmetric synthesis of functionalized optically active phosphines, mainly using natural products as chirons, has been extensively studied over many years. Among the various approaches, the asymmetric synthesis of chiral diphosphines via the addition of phosphorus−hydrogen bonds to carbon−carbon multiple bonds continues to pose considerable challenges. With free phosphines, addition onto an unsaturated C−C bond requires strong bases,[1] Brønsted acids,[2] radical initiators,[3] or transition metal catalysis.[4] However, hydrophosphination processes involving functionalized alkynes and alkenes have been reported sparingly

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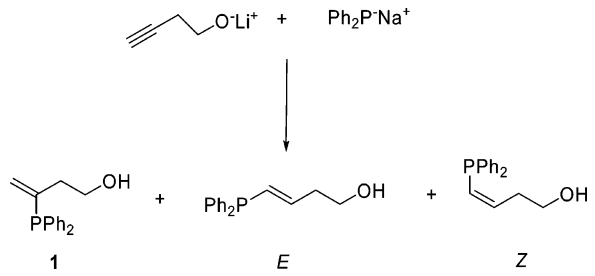
using these protocols.[1a,4c,5] This is partly because of the harsh reaction conditions employed, which do not tolerate most of the functional groups. Our group recently has reported the use of an organopalladium complex containing (*R*)- or (*S*)-(1-(dimethylamino)ethyl)naphthalene as the chiral auxiliary to promote the asymmetric hydrophosphination reactions.[6] To extend this protocol to the hydrophosphination of functionalized olefinic systems culminating in the synthesis of functionalized chiral diphosphines, the hydrophosphination of phosphine functionalized alkenols, 3-diphenylphosphanyl-but-3-en-1-ol, and 2-diphenylphosphanyl-prop-2-en-1-ol, was studied. The asymmetric hydrophosphination thus achieves an alcohol functionalized derivative of 1-2-bis(diphenylphosphino)propane (PROPHOS).[7] Literature review revealed that the previous synthesis of these compounds, which involved tedious organic manipulations extending to 14 steps as well as provided access to one enantiomer as opposed to our methodology,[8]was achieved from a chiral pool of substances such as malic or L-ascorbic acid. To our knowledge, no example of metal complex activated hydrophosphination of functionalized alkenes has been reported despite its potential for a new, direct route to a wide range of functionalized chiral diphosphine ligands. It is noteworthy that this is a second-stage hydrophosphination on the hydroxyl functionalized olefinic system, because the compounds themselves were prepared by a regioselective hydrophosphination of the parent alkynols, 3-butyn-1-ol and 2-propyn-1-ol, albeit not involving the metal template complex, which resulted in a Markovnikov addition of appreciable selectivity. This body of work assumes significance because alkenylphosphines and their functionalized derivatives, such as in the present case, are attractive candidates to control the activation of various substrates within their transition metal complexes. They also have the potential to provide access to a variety of functional ligands by modification of their carbon−carbon bond including via enantioselective catalysis.

Results and Discussion

Regioselective Hydrophosphination of Terminal Alkynols. Regioselective addition of diphenylphosphine to alkynes was previously reported under free radical, metal catalyzed, and basic addition conditions.[1d,3d,e,5f] In most cases, *E*/*Z* isomer mixtures were formed (anti-Markovnikov mode),

Scheme 1



and depending on the conditions employed, one of the isomers was predominate. Reversal of regioselectivity was achieved in the case of Pd-catalyzed hydrophosphination of alkynes using diphenylphosphane oxide in the presence of phosphonic acid and with the palladium-catalyzed addition of triphenylphosphine and methanesulfonic acid to alkynes wherein the Markovnikov product was formed as the major product.[9] For functionalized alkynes, the predominant Markovnikov product was achieved with the use of secondary phosphine−boranes as hydrophosphinating agents under metal catalyst and thermal activation conditions.[10] No reports involving reversal of regioselectivity were found in the literature involving noncatalytic addition of diphenylphosphine to functionalized alkynes under mild conditions.

The hydrophosphination product obtained by regioselective phosphine attack on the internal carbon of the terminal alkynol (Markovnikov mode) was the targeted product, because unlike the case of the anti-Markovnikov product, the newly generated chiral center was adjacent to the coordinated phosphorus of the alkenol substrate during the course of the second-stage hydrophospination reaction. This allowed us to study the directing influence of the chiral metal template on the steroselectivity of the hydrophosphination reaction in a more effective manner.

The synthetic protocol followed for the synthesis of 3-diphenylphosphanyl-but-3-en-1-ol is shown in Scheme 1. It is important to note that the hydroxyl group on the alkynol is susceptible to nucleophilic attack by the phosphide ion. Therefore, it is necessary to protect the functional group, which possesses an exchangeable proton that can quench the phosphide ion. Instead of using traditional protecting groups such as silyl ether to mask the hydroxyl group, it was deprotonated prior to the hydrophosphination so as to prevent it from quenching the phosphide ion. The recovery of the hydroxyl group from its alkoxide is technically very simple.

The $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$) of the crude reaction product showed the presence of three singlets at δ −3.4, −22.3, and −31.0 in the ratio 5:1:1.2 for the α-adduct and the *E*- and *Z*- isomers, respectively. The structural assignment for the three isomeric products could be achieved simply based on the spectroscopic principles employed for similar reactions involving free radical addition of diphenylphosphine to alkynes.[11] Purification and separation of the isomeric products were achieved by means of silica gel chromatog-

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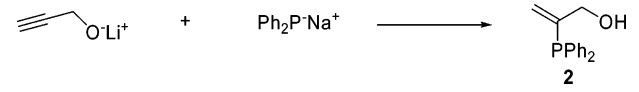
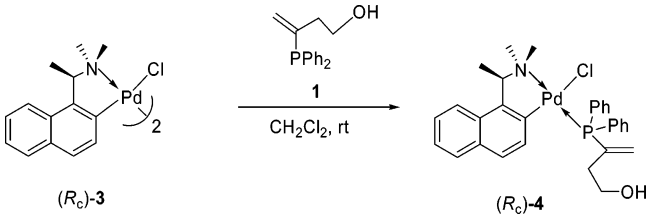
Scheme 2



Scheme 3



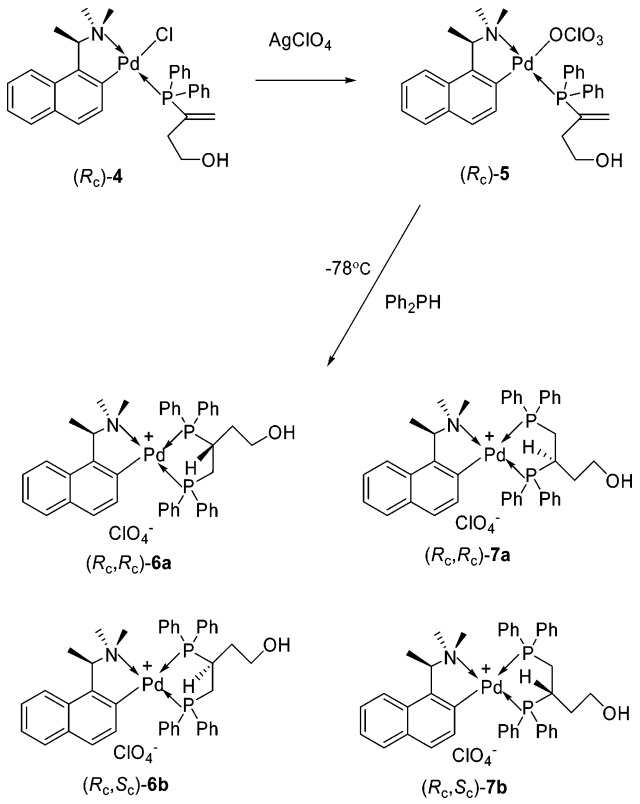
raphy under inert conditions that yielded the desired Markovnikov product **1** as a colorless oil in 43% yield. The *E*- and *Z*- isomers were formed as minor products and were not isolated.

The hydrophosphination of propargyl alcohol was carried out using the same method as that employed for 3-butyn-1-ol discussed earlier (Scheme 2). The reaction was monitored by means of $^{31}P\{^1H\}$ NMR spectroscopy and was found to be complete in 3 days. Unlike the case of 3-butyn-1-ol, only the Markovnikov product was selectively formed in the hydrophosphination reaction. The ^{31}P NMR spectrum of the crude reaction mixture in $CDCl_3$ showed only one singlet at δ −9.2. Purification of the product using silica gel column chromatography yielded pure **2** as a colorless oil in 73% yield.

Asymmetric Hydrophosphination of 3-Diphenylphosphanyl-but-3-en-1-ol. The 3-diphenylphosphanyl-but-3-en-1-ol ligand **1** was allowed to coordinate to the palladium complex (R_c)-**3** in dichloromethane yielding the neutral monomeric complex (R_c)-**4** as a yellow solid in 70% yield (Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum of the complex in $CDCl_3$ showed a singlet at δ 40.6. The coordination shift (Δ = 44.0 ppm) is consistent with the formation of (R_c)-**4**. It was well established that the chloro ligand that is trans to the ortho-metalated aromatic carbon in (R_c)-**3** is inert to displacement by incoming monodentate phosphine ligands.[12,13] Therefore, the terminal chloro ligand in (R_c)-**4** was subsequently replaced by a weakly coordinated perchlorato counterpart through treatment of (R_c)-**4** in dichloromethane with excess aqueous silver perchlorate.

The perchlorato complex (R_c)-**5** in dichloromethane then was reacted with an equivalent of diphenylphosphine at −78 °C to yield the hydrophosphination products as shown in Scheme 4. The reaction temperature was maintained at −78 °C for 10 h and subsequently stirred at room temperature for 1 day. In $CDCl_3$, the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture showed the presence of four pairs of

Scheme 4



doublets at δ (31.4, 66.4), (39.8, 77.0), (47.5, 52.6), and (48.0, 50.4) with the relative intensities of 2:18:1:4, respectively. These signals indicated that all of the four possible isomeric products were generated in the hydrophosphination reaction. Subsequently, the major isomer (R_c,R_c)-**7a** was separated by means of fractional crystallization as pale yellow crystals from dichloromethane−diethyl ether in 63% yield. The $^{31}P\{^1H\}$ NMR spectrum of pure (R_c,R_c)-**7a** in $CDCl_3$ showed a pair of doublets at δ 39.8 and 77.0 (J_{PP} = 22.7 Hz).

The single-crystal X-ray diffraction analysis of the isolated pure isomer (R_c,R_c)-**7a** revealed that the expected five-membered diphosphine chelate was formed stereoselectively (Figure 1). The newly formed stereogenic center at C(16) adopts the *R* configuration. The geometry at the Pd center is distorted square planar with angles of 80.4(2)−101.5(1)° and 173.8(1)−177.6(1)°. The five-membered diphosphine chelate adopts the λ ring configuration with the CH_2CH_2-OH substituent at C(16) in the preferred equatorial disposition.[14,6b] Selected bond lengths and angles are given in Table 1. Note that in the absence of the metal ion, the alkenol shows no reactivity with diphenylphosphine under ambient conditions. Furthermore, the four-membered ring was formed by the attack of diphenylphosphine on the α carbon of the alkenol.

A solution of (R_c,R_c)-**7a** in dichloromethane was subsequently treated with concentrated hydrochloric acid to remove the naphthylamine auxiliary chemoselectively (Scheme

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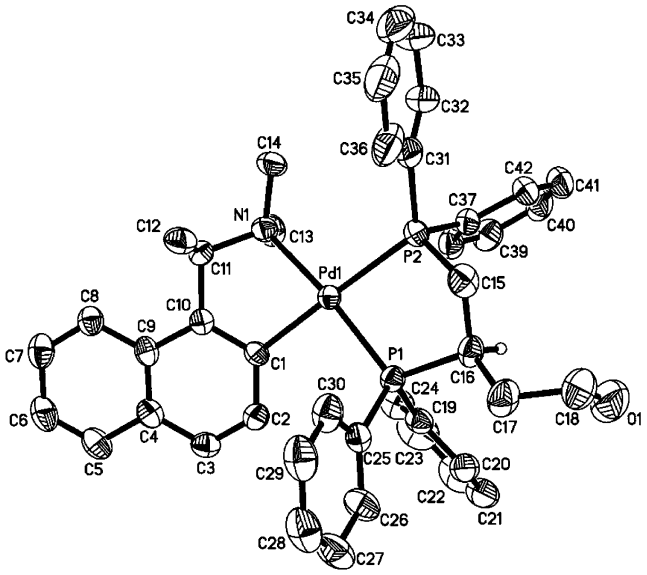


Figure 1. Molecular structure and absolute stereochemistry of (R_c,R_c)-**7a**.

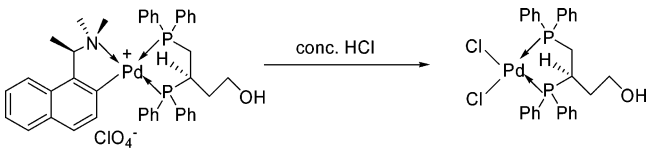
Table 1. Selected Bond Lengths (Å) and Angles (deg) for (R_c,R_c)-**7a**

Pd(1)−C(1)	2.053(4)	Pd(1)−N(1)	2.140(3)
Pd(1)−P(1)	2.250(1)	Pd(1)−P(2)	2.355(1)
P(1)−C(16)	1.862(5)	P(2)−C(15)	1.829(5)
O(1)−C(18)	1.434(10)	C(15)−C(16)	1.546(7)
C(16)−C(17)	1.536(6)	C(17)−C(18)	1.500(8)
C(1)−Pd(1)−N(1)	80.4(2)	C(1)−Pd(1)−P(1)	93.6(1)
N(1)−Pd(1)−P(1)	173.8(1)	C(1)−Pd(1)−P(2)	177.6(1)
N(1)−Pd(1)−P(2)	101.5(1)	P(1)−Pd(1)−P(2)	84.5(4)
C(16)−C(15)−P(2)	110.6(3)	C(17)−C(16)−C(15)	110.5(4)
C(17)−C(16)−P(1)	115.1(4)	C(15)−C(16)−P(1)	109.7(3)
C(18)−C(17)−C(16)	112.5(5)	O(1)−C(18)−C(17)	113.5(6)

5). The $^{31}P\{^1H\}$ NMR spectrum of the dichloro complex in $CDCl_3$ showed a pair of doublets at δ 51.1 and 71.3 (J_{PP} = 7.5 Hz). The neutral dichloro complex (R_c)-**8** crystallized from the dichloromethane−*n*-hexanes as pale yellow prisms.

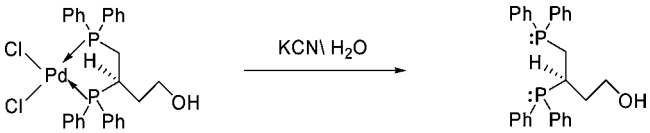
Note that the optically active diphosphine ligand (R_c)-**9** could be stereospecifically liberated from (R_c)-**8** ($[\alpha]_D$ = +37.5 (*c* 0.2, CH_2Cl_2)) by treatment of the dichloro complex with aqueous potassium cyanide at room temperature for 2 h (Scheme 6). The liberated optically pure ligand was obtained as a pale yellow oil. The $^{31}P\{^1H\}$ NMR ($CDCl_3$) spectrum of (R_c)-**9** showed a pair of doublet resonances at δ 19.31 and −0.2. Because of the potential air sensitivity of the noncoordinated phosphorus atoms, liberated (R_c)-**9** was not stored in its pure form but was recomplexed to the bis(acetonitrile) complex (R_c)-**10** (Scheme 7). The recoordination process is also a means of verifying the optical purity of the released ligand and to establish the identity of the minor isomers that were generated in the original hydrophosphination reaction.[6] The recomplexation of the released ligand (R_c)-**9** to the bis(acetonitrile) complex (R_c)-**10** was monitored by $^{31}P\{^1H\}$ NMR spectroscopy ($CDCl_3$), which exhibited doublets at δ 39.8 (J_{PP} = 22.7 Hz), 47.5 (J_{PP} = 30.4 Hz), 52.6 (J_{PP} = 30.4 Hz), and 77.0 (J_{PP} = 22.7 Hz). The resonance signals at δ 39.8 and 77.0 are identical to those observed for the major product (R_c,R_c)-**7a** in the original hydrophosphination reaction. The signals at δ 47.5 and 52.6 match signals detected in the original reaction

Scheme 5



(R_c,R_c)-**7a** (R_c)-**8**

Scheme 6



(R_c)-**8** (R_c)-**9**

mixture and are assigned to the regioisomeric product of (R_c,R_c)-**7a**, that is, (R_c,R_c)-**6a.** Formation of regioisomers during the recoordination of unsymmetrical diphosphine ligands to the naphthylamine auxiliary is well established. Previous studies on similar isomeric systems have shown that for a pair of regioisomers such as (R_c,S_c)-**6a** and (R_c,S_c)-**7a** formed on the naphthylamine chiral auxiliary system the separation in $^{31}P\{^1H\}$ resonance signals will be significantly larger than that observed for diastereomeric complexes such as (R_c,R_c)-**7a** and (R_c,S_c)-**7b**.[6,12a,15]

As further confirmation of the optical purity of (R_c)-**9**, the recomplexation reaction of the diphosphine to the equally accessible enantiomeric complex (S_c)-**10** gave distinct doublets at δ 31.4 (J_{PP} = 30.4 Hz), 47.5 (J_{PP} = 34.2 Hz), 52.6 (J_{PP} = 34.2 Hz), and 66.4 (J_{PP} = 30.4 Hz). These signals are consistent with (R_c,S_c)-**6b** and (R_c,S_c)-**7b**, which are diastereomers of (R_c,R_c)-**6a** and (R_c,R_c)-**7a**, respectively. The coupling constants of the two pairs of signals are important spectroscopic handles for pairing the resonances of the minor isomers. Comparison of the signals to those of (R_c,R_c)-**6a** and (R_c,R_c)-**7a** clearly indicates that the signals at δ 31.4 (J_{PP} = 30.4 Hz) and 66.4 (J_{PP} = 30.4 Hz) are caused by the diastereomer of (R_c,R_c)-**6a**, that is, (R_c,S_c)-**6b**. Accordingly, signals at δ 47.5 (J_{PP} = 34.2 Hz) and 52.6 (J_{PP} = 34.2 Hz) can be assigned to the diastereomer of (R_c,R_c)-**7a**, that is, (S_c, R_c)-**7b**. Thus, the recomplexation reactions identified that all four isomers, (R_c,R_c)-**6a**, (R_c,S_c)-**6b**, (R_c,R_c)-**7a**, and (R_c,S_c)-**7b**, were generated in the asymmetric hydrophosphination reaction in the ratio of 4:1:18:2, respectively.

Hydrophosphination of 2-Diphenylphosphanyl-prop-2-en-1-ol. The 2-diphenylphosphanyl-prop-2-en-1-ol ligand obtained by hydrophosphination of propargyl alcohol was coordinated to the dimeric ortho-metalated palladium complex (R_c-**3**) as shown in Scheme 8. The 121 MHz $^{31}P\{^1H\}$ NMR spectrum of the crude complex showed a singlet signal at δ 40.6 in $CDCl_3$.

Crystallization of the crude product from acetonitrile−diethyl ether gave yellow prisms of (R_c)-**13**. The monophos-

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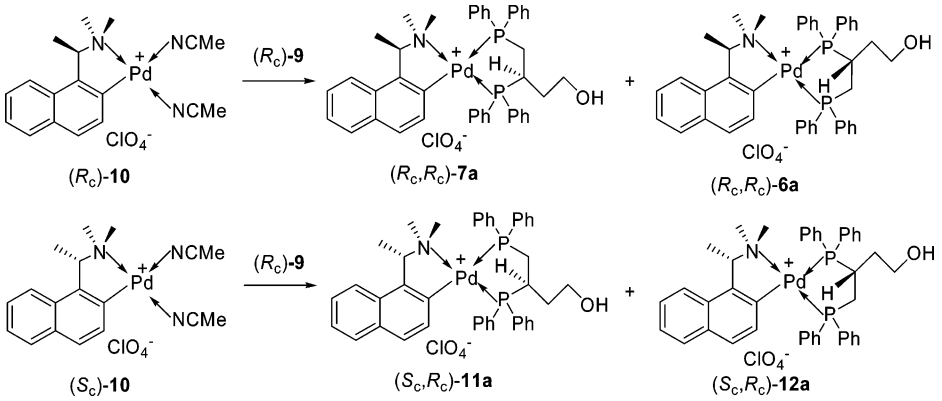
Scheme 7



Scheme 8

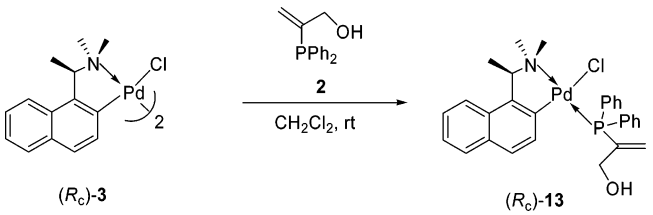


Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of (R_c)-**13**

Pd(1)−C(1)	2.005(4)	Pd(1)−N(1)	2.126(4)
Pd(1)−P(1)	2.251(1)	Pd(1)−Cl(1)	2.413(1)
O(1)−C(16)	1.380(7)	C(15)−C(17)	1.306(7)
C(15)−C(16)	1.490(8)		
C(1)−Pd(1)−N(1)	80.6(2)	C(1)−Pd(1)−P(1)	93.9(1)
N(1)−Pd(1)−P(1)	173.4(1)	C(1)−Pd(1)−Cl(1)	171.2(1)
N(1)−Pd(1)−Cl(1)	92.5(1)	P(1)−Pd(1)−Cl(1)	93.3(5)

phine complex formed was characterized by means of single-crystal X-ray diffraction analysis (Figure 2). Selected bond angles and bond lengths are given in Table 2. The X-ray structure confirmed that the monodentate phosphine was indeed the Markovnikov product obtained from the first-stage hydrophosphination reaction of propargyl alcohol. The coordination around the metal center is a distorted square planar with angles at palladium in the range of 80.6(2)−93.9(1) and 171.2(1)−173.4(1)°. The chloro complex (R_c)-**13** was subsequently converted to the perchlorato species by treatment with aqueous silver perchlorate as shown in

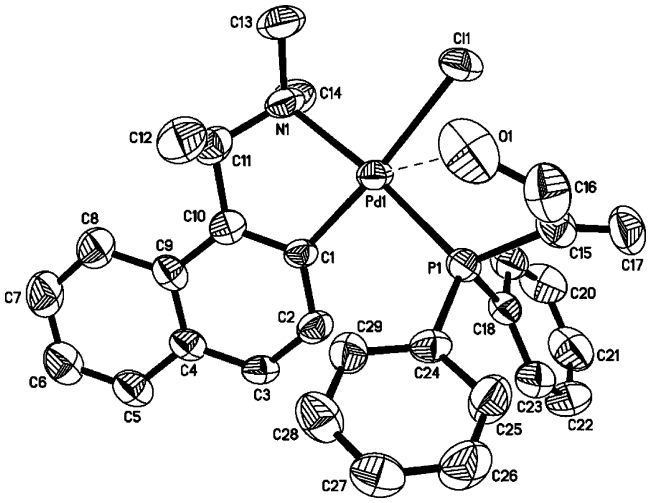
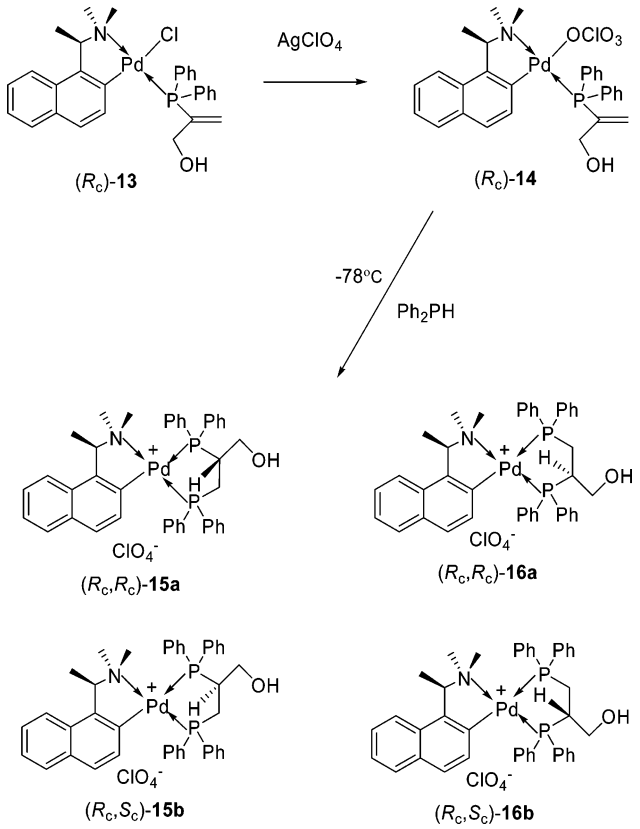


Figure 2. Molecular structure of (R_c)-**13**.

Scheme 9



Scheme 9. The perchlorato complex (R_c)-**14** was dissolved in dichloromethane and reacted with diphenylphosphine at −78 °C. The $^{31}P\{^1H\}$ spectrum ($CDCl_3$) of the crude reaction mixture exhibited four pairs of doublets in the ratio 1:2.4:5.3:7.8.

Attempted fractional crystallization using dichloromethane−*n*-hexanes gave yellow prisms suitable for single-crystal X-ray diffraction analysis. Preliminary $^{31}P\{^1H\}$ NMR (CD_2Cl_2) spectroscopic studies of the crystallized products, however, indicated the presence of two isomers because four doublet signals were observed at δ 41.6 (J_{PP} = 30.4 Hz), 42.0 (J_{PP} = 30.4 Hz), 50.0(J_{PP} = 30.4 Hz), and 51.5 (J_{PP} = 30.4 Hz).

A single-crystal X-ray diffraction analysis of the yellow prisms obtained from the hydrophosphination reaction mixture confirmed that the two diastereomers (R_c,R_c)-**15a** and

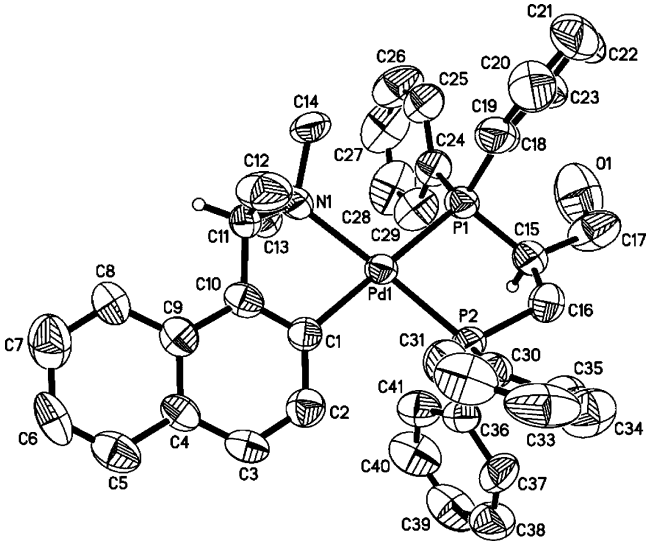


Figure 3. Molecular structure and absolute configuration of (R_c,R_c)-**15a**.

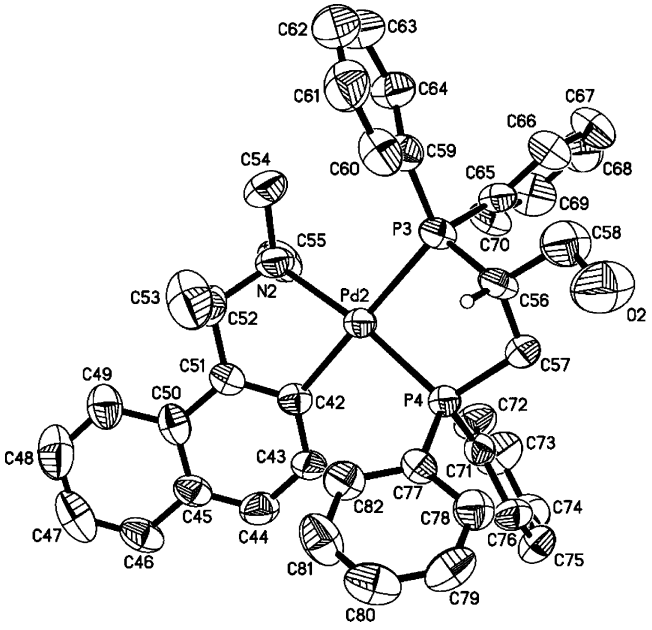


Figure 4. Molecular structure and absolute configuration of (R_c,S_c)-**15b**.

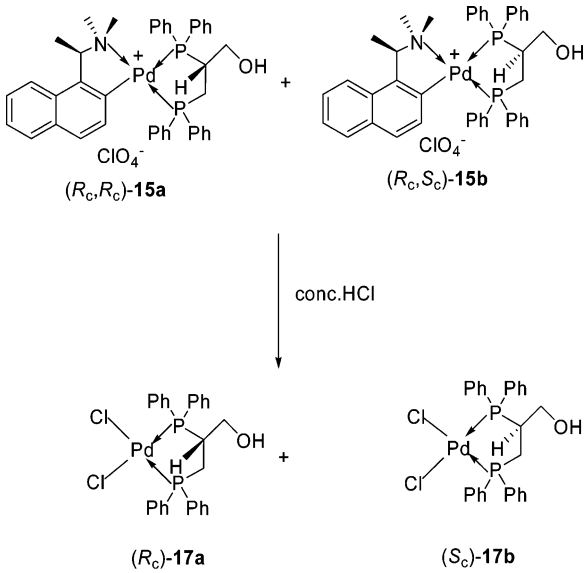
(R_c,S_c)-**15b** have co-crystallized out (Figures 3 and 4). Selected bond lengths and bond angles for the two diastereomers are given in Table 3. The single-crystal X-ray diffraction data revealed that the two diastereomers differ in the chirality at C(15) and C(56). For (R_c,S_c)-**15a** the chirality at C(15) is *S* whereas in the case of (R_c,R_c)-**15b** the chiral carbon C(56) adopts the *R* configuration. Both diastereomers show a similar coordination pattern with the geometry at the Pd metal center being distorted square planar. The angles formed by the diphosphine chelate and the naphthylamine template at the Pd metal center were in the range of 80.4(3)−99.4(2) and 174.0(2)−175.1(2)° for (R_c,R_c)-**15a**. The diastereomer (R_c,S_c)-**15b** showed a slightly elevated strain with angles at the metal center being in the range of 79.8(3)−101.7(2) and 172.9(2)−175.6(2)°.

The two diastereomers (R_c,R_c)-**15a** and (R_c,S_c)-**15b** that co-crystallized out were converted to their dichloro species (Scheme 10). The crude reaction mixture showed two doublets at δ 53.3 and 66.2 (J_{PP} = 7.6 Hz) when monitored by $^{31}P\{^1H\}$ NMR spectroscopy in CD_2Cl_2. The reaction mixture was concentrated, and diethyl ether was added that resulted in the formation of pale yellow crystals that were analyzed by means of single-crystal X-ray diffraction analysis (Figure 5). As was expected, the single-crystal X-ray diffraction analysis showed that two enantiomers (R_c)-**17a** and (S_c)-**17b** co-crystallized out in the same unit cell (Table 4).

Table 3. Selected Bond Lengths (Å) and Angles (deg) of (R_c,R_c)-**15a** and (R_c,S_c)-**15b**

(R_c,R_c)-**15a**		(R_c,S_c)-**15b**	
Pd(1)−C(1)	2.059(7)	Pd(2)−C(42)	2.059(7)
Pd(1)−N(1)	2.141(6)	Pd(2)−N(2)	2.140(6)
Pd(1)−P(2)	2.245(2)	Pd(2)−P(4)	2.257(1)
Pd(1)−P(1)	2.350(2)	Pd(2)−P(3)	2.394(1)
P(1)−C(15)	1.835(8)	P(3)−C(56)	1.853(8)
P(2)−C(16)	1.843(8)	P(4)−C(57)	1.828(8)
C(15)−C(16)	1.497(11)	C(56)−C(57)	1.537(11)
C(15)−C(17)	1.518(13)	C(56)−C(58)	1.491(12)
O(1)−C(17)	1.366(14)	O(2)−C(58)	1.447(12)
C(1)−Pd(1)−N(1)	80.4(3)	C(42)−Pd(2)−N(2)	79.8(3)
C(1)−Pd(1)−P(2)	95.7(2)	C(42)−Pd(2)−P(4)	93.3(2)
N(1)−Pd(1)−P(2)	175.1(2)	N(2)−Pd(2)−P(4)	172.8(2)
C(1)−Pd(1)−P(1)	174.0(2)	C(42)−Pd(2)−P(3)	175.6(2)
N(1)−Pd(1)−P(1)	99.4(2)	N(2)−Pd(2)−P(3)	101.7(2)
P(2)−Pd(1)−P(1)	84.8(7)	P(4)−Pd(2)−P(3)	85.1(7)

Scheme 10



Regio- and Sterochemical Observations. In principle, the hydrophosphination reaction between diphenylphosphine and alcohol functionalized alkenols may generate up to four possible stereoisomeric products. In the case of the hydrophosphination reaction involving 3-diphenylphosphanyl-but-3-en-1-ol and diphenylphosphine, the four possible isomers were formed in the ratio 1:2:4:18. The major isomer has the phosphorus of the alcohol moiety coordinated cis to the ortho-metalated aromatic carbon once the five-membered chelate is formed during the course of the hydrophosphination reaction. This was in contrast to what was observed for the hydrophosphination of 2-diphenylphosphanyl-prop-2-en-1-ol. Single-crystal X-ray analysis of the co-crystallized major isomers revealed that they were cis−trans regiosiomers

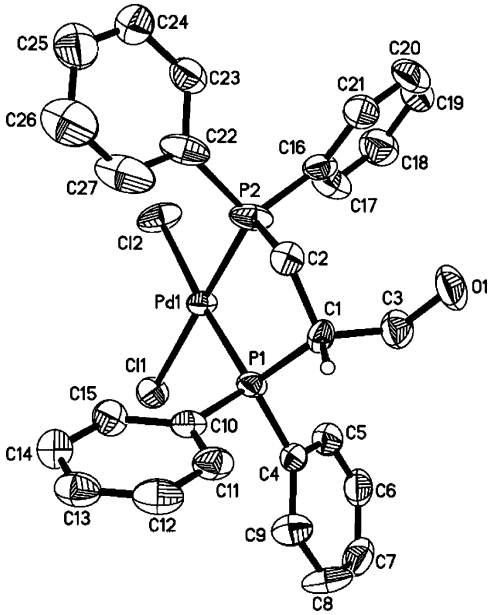


Figure 5. Molecular structure of **17**.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) of **17**

Pd(1)−P(1)	2.225(2)	Pd(1)−P(2)	2.228(2)
Pd(1)−Cl(1)	2.341(1)	Pd(1)−Cl(2)	2.364(2)
P(1)−C(1)	1.859(9)	P(2)−C(2)	1.843(6)
C(1)−C(2)	1.530(8)	C(1)−C(3)	1.520(11)
O(1)−C(3)	1.462(7)		
P(1)−Pd(1)−P(2)	86.3(6)	P(1)−Pd(1)−Cl(1)	90.3(6)
P(2)−Pd(1)−Cl(1)	175.9(6)	P(1)−Pd(1)−Cl(2)	175.7(6)
P(2)−Pd(1)−Cl(2)	90.1(6)	Cl(1)−Pd(1)−Cl(2)	93.5(6)

with the phosphorus of the alcohol moiety coordinated trans to the ortho-metalated carbon of the chiral template and differed in the chirality of the stereogenic carbon chiral center.

A possible explanation for the observed difference in stereoselectivity can be found by analyzing the structure of the complex obtained upon coordination of the phosphanylene entity of the 2-diphenylphosphanyl-prop-2-en-1-ol to the chiral template complex (R_c)-**3** (Figure 2). It was observed from the crystallographic data that the oxygen atom of the −OH group was oriented in such a way that it was in close proximity to the Pd metal center. This indicated significant Pd−O interactions, which also should exist in nonpolar solvents. In the case of 2-diphenylphosphanyl-prop-2-en-1-ol, the chelating diphosphine adduct was formed upon hydrophosphination, and the rigidity imposed by the formation of the five-membered chelate ring did not allow the Pd−O interactions to occur. Therefore, two different configurations for the newly generated carbon centers in (R_c, R_c)-**15a** and (R_c, S_c)-**15b** were allowed. In contrast, the flexibility available by virtue of the longer chain length of the CH_2CH_2OH moiety for the product formed by the hydrophosphination of 3-diphenylphosphanyl-but-3-en-1-ol allowed these interactions to occur even upon formation of the diphosphine chelate, thus influencing the chirality at the sterogenic carbon center.

The difference in regiochemistry observed for the two reactions also should be noted. In the case of 3-diphenylphosphanyl-but-3-en-1-ol, the major product was the five-membered diphosphine chelate with the phosphine functionalized alcoholic entity occupying the position trans to the NMe_2 group of the chiral template. In the major isomers (isolated as a racemic mixture) of the hydrophosphination reaction involving 2-diphenylphosphanyl-prop-2-en-1-ol, the phosphine functionalized alcohol entity occupied a position cis to the NMe_2 group. This is believed to be because of the steric factor involved in the case of 3-diphenylphosphanyl-but-3-en-1-ol in which the CH_2CH_2OH entity on the chiral carbon extends into the metal coordination sphere to have effective Pd−O interactions and, therefore, is sterically hindered by the presence of the NMe_2 group of the naphthylamine auxiliary. Therefore, the phosphine functionalized alcoholic entity prefers to occupy the position trans to the NMe_2 group. The shorter CH_2OH group of the 2-diphenylphosphanyl-prop-2-en-1-ol does not have an appreciable steric impact and, therefore, can afford to occupy the position trans to the C of the chiral metal template.

In conclusion, the synthesis of alcohol functionalized chiral diphosphines via a novel two-stage asymmetric hydrophosphination protocol was demonstrated. The hydrophosphination proceeded with high regio- and steroselectivites for the case of 3-butyn-1-ol substrate under mild conditions. Further investigations on the regio- and stereochemical considerations involved are currently underway to provide a facile method for the synthesis of P-stereogenic phosphines with selected functionalities.

Experimental Section

All reactions and manipulations of air-sensitive compounds were carried out under a positive pressure of dry, oxygen-free nitrogen on a high-vacuum line or on a standard Schlenk line. Solvents were dried and freshly distilled according to standard procedures and degassed prior to use when necessary. The 1-D ^{1}H and ^{31}P{^{1}H} NMR spectra were measured on a Bruker ACF 300 spectrometer operating at 300.1 and 121.5 MHz, respectively. Optical rotations were measured on the specified solutions in a 1-cm cell at 25 °C using a Perkin-Elmer model 341 polarimeter. Melting points were determined using a Büchi B-545 automatic melting point apparatus. Elemental analyses were performed by the Elemental Analysis laboratory of the Department of Chemistry at the National University of Singapore.

Both enantiomerically pure forms of the complexes (R_c)-**1**,[16] (R_c)-**10**, and (S_c)-**10**[17] were prepared as previously reported. Solvents were distilled, dried, and degassed by standard procedures where necessary. Column chromatography was performed using silica gel 60.

Caution: *Perchlorate salts of metal complexes are potentially explosive compounds and should be handled with care.*[18]

3-Diphenylphosphanyl-but-3-en-1-ol. Diphenylphosphide ion was generated by the addition of diphenylphosphine (2.79 g, 0.016 mol) with stirring to a Schlenk flask containing sodium metal (0.37 g, 0.016 mol) in THF (100 mL). The mixture was left to stir overnight. A solution of *n*-butyllithium in hexane (15% in hexane,

(16) (a) Allen, D. G.; McLaughlin, G. M.; Robertson, G. B.; Stefen, W. L.; Salem, G.; Wild, S. B. *Inorg. Chem.* **1982**, *21*, 1007. (b) Hockless, D. C. R.; Gugger, P. A.; Leung, P. H.; Mayadunne, R. C.; Pabel, M.; Wild, S. B. *Tetrahedron* **1997**, *53*, 4083.
(17) Chooi, S. Y. M.; Leung, P. H.; Lim, C. C.; Mok, K. F.; Quek, G. H.; Sim, K. Y.; Tan, M. K. *Tetrahedron: Asymmetry* **1992**, *3*, 529.
(18) Wolsey, W. C. *J. Chem. Educ.* **1973**, *50*, A335.

10.11 mL, 0.0162 mol) was added to 3-butyn-1-ol (1.22 mL, 0.0162 mol) in THF with stirring. The diphenylphosphide solution generated previously then was added to this solution dropwise with vigorous stirring at 0 °C. The reaction mixture was allowed to reach room temperature and was stirred for 5 days. The solvent was then distilled off to leave a dark brown slurry to which brine (150 mL) was added. The mixture was subsequently extracted with dichloromethane (3 × 100 mL). The organic layer then was dried with magnesium sulfate, and the solvent was removed by distillation to give a dark yellow oil. The crude product was purified by means of silica gel column chromatography using 20% ethyl acetate in hexane under purified nitrogen. The product was collected as the first fraction, which gave a yellow oil on removal of eluents (1.78 g, 43.2%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −3.36 (s).

2-Diphenylphosphanyl-prop-2-en-1-ol. Sodium metal (0.37 g, 0.016 mol) was placed in a 250 mL Schlenk flask containing THF (100 mL). This was followed by the addition of diphenylphosphine (2.79 g, 0.016 mol) with stirring. The mixture was stirred overnight and was observed to turn a deep,red color, which was characteristic of the diphenylphosphide ion. Propargyl alcohol (0.94 mL, 0.016 mol) then was placed in a 500 mL Schlenk flask with THF (100 mL). To this solution, *n*-butyllithium (15% solution in hexane) (0.01618 mol, 9.86 mL) was added with stirring. The sodium diphenylphosphide generated then was transferred dropwise into the Schlenk flask with stirring at 0 °C. The reaction mixture was allowed to reach room temperature and continued to be stirred over 3 days. Most of the THF then was distilled off and followed by the addition of brine (150 mL) to the residue. The mixture was extracted three times using 100 mL of dichloromethane each time. The organic layer was subsequently extracted and dried with magnesium sulfate, and the solvent was removed via distillation leaving a highly viscous dark red oil. The crude product was purified via elution through a silica gel column using 20% v/v ethyl acetate: *n*-hexanes as eluent under an inert atmosphere. The recovered product was a pale yellow oxygen-sensitive oil (2.87 g, 73.4%). ^{31}P NMR ($CDCl_3$, δ): −9.20.

Chloro[(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*]-[3-(diphenylphosphino)but-3-en-1-ol], (R_c)-4. To a solution of the complex (R_c)-**3** in dichloromethane (1.88 g, 0.003 mols), 3-diphenylphosphanyl-but-3-yn-1-ol (1.41 g, 0.005 mols) in dichloromethane was added dropwise with stirring. The reaction mixture was allowed to stir for 8 h, and then the solvent was removed under reduced pressure to give a yellow solid (1.95 g, 95.6%) m.p: 220−223 °C. Anal. Calcd for $C_{30}H_{33}NClPOPd$: C, 60.4; H, 5.5; N, 2.4. Found: C, 60.4, H, 5.9, N, 2.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 40.6 (s). ^1H NMR ($CDCl_3$, δ): 2.07 (d, 3H, $^2J_{HH}$ = 6.4 Hz, CH*Me*), 2.72 (s, 3H, N*Me*), 2.98 (s, 3H, N*Me*), 3.98 (m, 2H, CH_2CH$_2$OH), 4.09 (m, 2H, CH$_2$CH_2OH), 4.37 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.0 Hz, C*H*Me), 5.39 (d, 1H, $^3J_{PH}$ = 17.2 Hz, *cis*-PC═CH_2), 5.91 (d, 1H, $^3J_{PH}$ = 35.3 Hz, *trans*-PC═CH_2), 6.54−8.17 (m, 16H, *aromatics*).

[(*R*)-1-[1-(Dimethylamino)ethyl]-2-naphthalenyl-*C,N*][(*R*)3,4-bis(diphenylphosphino)butan-1-ol]palladium(II) Perchlorate, (R_c,R_c)-7a. A solution of the complex (R_c)-**4** (1.56 g, 0.002 mols) in dichloromethane was treated with aqueous silver perchlorate (0.63 g, 0.003 mols) for 30 min. The reaction mixture was subsequently washed with water (3 × 20 mL), and the organic layer was dried using magnesium sulfate. Upon removal of the solvent, perchlorato complex (R_c)-**5** was obtained as a yellow solid (1.39 g, 94.5%). To (R_c)-**5** (1.39 g, 0.002 mol) in dichloromethane, diphenylphosphine (0.35 g, 0.002 mol) was added with stirring at −78 °C. The temperature was maintained for 10 h then stirred at room temperature for 24 h to obtain a dark red solid upon solvent removal. Pale yellow crystals were obtained upon crystallization using dichloromethane−diethyl ether (1.2 g, 63.0%). $[\alpha]_D$ = −8.9 (*c* 1.4, CH_2Cl_2), mp 229−231 °C (decomp). Anal. Calcd for $C_{43}H_{46}Cl_3NO_5P_2Pd$: C, 55.5; H, 4.9; N, 1.5. Found: C, 55.7; H, 5.2; N, 1.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 39.8 (d, 1P, J_{PP} = 22.7 Hz), 77.0 (d, 1P, J_{PP} = 22.7 Hz). ^1H NMR ($CDCl_3$, δ): 1.15 (m, 1H, $Ph_2P^1CH'HCH$), 1.38 (m, 1H, $Ph_2P^1CH'HCH$), 2.09 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.41 (s, 3H, N*Me*), 2.71 (s, 3H, N*Me*), 2.91 (m, 1H, P^2CHCH_2), 3.07 (ddd, 2H, $^3J_{HH}$ = 3.2 Hz, $^3J_{HH}$ = 11.05, $^3J_{PH}$ = 17.55), 3.53 (m, 2H, CH$_2$CH_2OH), 4.52 (qn, 1H, $^3J_{HH}$ = 4JPH = 6.0 Hz, C*H*Me), 6.81−8.47 (m, 26H, *aromatics*).

Dichloro[(*R*)3,4-bis(diphenylphosphino)butan-1-ol]palladium-(II), (R_c)-8. A solution of the complex (R_c,R_c)-**7a** (0.99 g, 0.001 mols) in dichloromethane was stirred with concentrated hydrochloric acid (5 mL) for 8 h. The excess acid then was removed by washing with water (3 × 20 mL), and the organic layer was dried using magnesium sulfate. Upon removal of the solvent, a pale yellow solid was obtained. Crystallization from dichloromethane−*n*-hexanes yielded pale yellow needles (0.62 g, 86.1%). $[\alpha]_D$ = +37.5 (*c* 0.2, CH_2Cl_2), mp 214−217 °C. Anal. Calcd for $C_{29}H_{30}Cl_4OP_2Pd$: C, 49.4; H, 4.3. Found: C, 49.9; H, 4.7. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 51.1 (d, 1P, J_{PP} = 7.5 Hz), 71.3 (d, 1P, J_{PP} = 7.5 Hz). ^1H NMR (CD_2Cl_2, δ): 0.86 (m, 1H, P^1CHH'), 0.94 (m, 1H, P^1CHH'), 2.87 (ddd, $^3J_{HH}$ = 4.8 Hz, $^3J_{HH}$ = 12.4 Hz, $^3J_{PH}$ = 14.7 Hz).

Decomplexation of (*R*)-3,4-bis(Diphenylphosphino)butan-1-ol, (R_c)-9. A solution of the complex (R_c)-**8** (0.03 g, 0.05 mmol) in dichloromethane was stirred vigorously with aqueous potassium cyanide (0.16 g, 0.24 mmol) for 2 h. The organic layer was separated and washed with water (3 × 10 mL) and then was dried with magnesium sulfate. A pale yellow oil was obtained on removal of the solvents under reduced pressure (0.01 g, 57.2%). $[\alpha]_D$ = +64.9 (*c* 0.2, CH_2Cl_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): −19.3 (d, $^3J_{PP}$ = 19.0 Hz), −0.2 (d, $^3J_{PP}$ = 19.0 Hz).

Chloro[(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*]-[2-(diphenylphosphino)prop-2-en-1-ol], (R_c)-13. To a solution of complex (R_c)-**3** in dichloromethane (2.04 g, 0.003 mols), 2-dipenylphosphanyl-prop-2-en-1-ol (1.45 g, 0.006 mols) in dichloromethane was added dropwise with stirring. The reaction was allowed to stir for 8 h, and then the solvent was removed under reduced pressure to give a yellow solid. Crystallization using acetonitrile−diethyl ether gave yellow prisms (1.87 g, 93.0%). $[\alpha]_D$ = −38.7 (*c* 0.3, CH_2Cl_2), mp 211−213 °C. Anal. Calcd for $C_{29}H_{31}ClNOPPd$: C, 59.8; H, 5.3; N, 2.4. Found: C, 60.0; H, 4.9; N, 2.5. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 38.7 (s). ^1H NMR ($CDCl_3$, δ): 2.02 (d, 3H, $^2J_{HH}$ = 6.4 Hz, CH*Me*), 2.80 (s, 3H, N*Me*), 2.98 (s, 3H, N*Me*), 4.12 (m, 2H, CH_2OH), 4.37 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.0 Hz, C*H*Me), 5.16 (d, 1H, $^3J_{PH}$ = 16.9 Hz, *cis*-PC═CH_2), 6.02 (d, 1H, $^3J_{PH}$ = 33.7 Hz, *trans*-PC═CH_2), 6.56−8.12 (m, 16H, *aromatics*).

[(*R*)-1-[1-(Dimethylamino)ethyl]-2-naphthalenyl-*C,N*][2,3-bis-(diphenylphosphino)propan-1-ol]palladium(II) Perchlorate, (R_c,R_c)-15a and (R_c,S_c)-15b. To a solution of the complex (R_c)-**13** (1.57 g, 0.003 mols) in dichloromethane, silver perchlorate (0.83 g, 0.004 mols) in water (4 mL) was added and stirred for 30 min at room temperature. The reaction mixture then was washed with water (3 × 20 mL) and was dried with magnesium sulfate to yield the perchlorato complex (R_c)-**14** (1.82 g, 94.3%). A solution of the perchlorato complex in dichloromethane (1.82 g, 0.003 mols) was cooled to −78 °C and subsequently treated with diphenylphosphine (0.52 g, 0.003 mols). The temperature was maintained for 10 h, and then the solution was stirred at room temperature for an additional 48 h to give a dark red solid upon removal of the solvents under reduced pressure. Crystallization employing dichloromethane−*n*-hexane gave yellow prisms (0.99 g, 39%). Anal. Calcd for $C_{41}H_{42}ClNO_5P_2Pd$: C, 59.2; H, 5.0; N, 1.7. Found: C, 58.9; H, 4.9; N,

Table 5. Crystallographic Data for Complexes (R_c,R_c)-**7a**, (R_c)-**13**, **15**, and **17**

	(R_c,R_c)-**7a**	(R_c)-**13**	**15**	**17**
formula	$C_{43}H_{46}C_{l3}NO_5P_2Pd$	$C_{29}H_{31}ClNOPPd$	$C_{415}H_{43}Cl_2NO_5P_2Pd$	$C_{28}H_{28}Cl_4OP_2Pd$
M	931.50	582.37	875.01	690.64
space group	*P*2(1)2(1)2(1)	*P*2(1)2(1)2(1)	*P*1	*P*2(1)/*c*
crystal system	orthorhombic	orthorhombic	triclinic	monoclinic
a/Å	10.093(1)	12.200(5)	9.727(4)	19.514(5)
b/Å	19.017(2)	13.360(6)	10.935(5)	8.547(2)
c/Å	22.489(2)	16.791(8)	19.975(9)	17.987(4)
V/Å^3	4316.5(8)	2737.0(2)	2017.8(2)	2865.3(1)
Z	4	4	2	4
T/K	223(2)	223(2)	295(2)	223(2)
λ/Å	0.71073	0.71073	0.71073	0.71073
μ/mm^{-1}	0.734	0.855	0.716	1.154
R_1 (obs. data)[a]	0.0487	0.0523	0.0569	0.0698
wR_2 (obs. data)[b]	0.1235	0.0877	0.1238	0.1387
Flack parameter	−0.01(3)	0.03(3)	0.02(3)	

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]\}^{1/2}$, $w^{-1} = \sigma^2(F_0)^2 + (aP)^2 + bP$.

1.7. $^{31}P\{^1H\}$NMR (CD_2Cl_2, δ): 41.6 (d, 1P, $^3J_{PP}$ = 30.4 Hz), 42.0 (d, 1P, $^3J_{PP}$ = 30.4), 50.0 (d, 1P, $^3J_{PP}$ = 30.4), 51.5 (d, 1P, $^3J_{PP}$ = 30.4).

Dichloro[2,3-bis(diphenylphosphino)propan-1-ol]palladium-(II), (R_c)-17a and (R_c)-17b. A mixture of complexes (R_c,R_c)-**15a** and (R_c,S_c)-**15b** (0.85 g, 0.001 mol) in dichloromethane was treated with concentrated hydrochloric acid (4 mL) and was left to stir for 8 h. The excess acid then was removed by means of washing with water (3 × 20 mL), and the organic layer was extracted and dried using magnesium sulfate. The reaction mixture was concentrated and *n*-hexanes were added. Yellow prisms were obtained upon standing (0.52 g, 84.5%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 53.3 (d. 1P, J_{PP} = 7.6 Hz), 66.2 (d, 1P, J_{PP} = 7.6 Hz). ^1H NMR (CD_2Cl_2, δ): 2.29−2.47 (m, 2H, C*H*CH_2OH), 2.66−2.77 (m. 1H, PC*H*H′), 2.88−2.98 (m, 1H, PCH*H*′), 3.62 (dd, 2H, $^3J_{PH}$ = 10.4 Hz, $^3J_{HH}$ = 5.2 Hz, CH_2OH), 7.50−8.08 (m, 20H, *aromatics*).

Crystal Structure Determination of (R_c,R_c)-7a, (R_c)-13, (R_c,R_c)-15a, (R_c,S_c)-15b and 17. Crystal data for all four complexes and a summary of the crystallographic analyses are given in Table 5. Diffraction data were collected at the National University of Singapore using a Siemens SMART CCD diffractometer with Mo−K_α radiation (graphite monochromator) using ω-scans. SADABS absorption corrections were applied. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at a fixed distance from the carbon and nitrogen atoms and were assigned fixed thermal parameters. The absolute configurations of all chiral complexes were determined unambiguously using the Flack parameter.[19]

Supporting Information Available: For (R_c,R_c)-**7a**, (R_c)-**13**, (R_c,R_c)-**15a**, (R_c,S_c)-**15b**, and **17**. 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.

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