Optical Resolution, Configurational Stability, and Coordination Chemistry of the P-Chiral Heterocyclic Diphosphine 1,1′-Diphenyl-3,3′,4,4′-tetramethyl-2,2′-diphosphole-3,3′-diene

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The optical resolution of the C_2-symmetrical racemic ligand (R_P*S_C*)-1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-diphosphole-3,3′-diene (±)-(**1**) has been achieved efficiently via fractional crystallization of a pair of diastereomeric palladium(II) complex cations containing the appropriate form of the chelating diphosphine ligand and orthometalated (*S*)-(1-(dimethylamino)ethyl)naphthalene. The absolute stereochemistries of both diastereomeric complexes have been confirmed by single-crystal X-ray crystallography. The liberation of the optically active diphosphine ligand from the corresponding resolved complexes involved two steps: the removal of the naphthylamine ligand with concentrated hydrochloric acid followed by the decomposition of the intermediate [Pd(**1**)Cl_2] species with aqueous potassium cyanide. Thus, (R_PS_C)-(−)-(**1**) and (S_PR_C)-(+)-(**1**) were obtained in high yields with $[\alpha]_D = \pm 124.3°$ (C_6H_6). These resolved ligands are configurationally stable, as their optical purities remained unchanged upon heating at 140 °C for 48 h in benzene and in propanol. They are able to form the optically active digold complexes [Au_2(μ-**1**)Cl_2], despite the fact that the two rigid heterocyclic rings are linked with a carbon−carbon bond of restricted rotation.

Introduction

The development of heterocyclic compounds containing tertiary phosphorus donor atoms has received considerable attention and has been the subject of several recent reviews.[1] Apart from being excellent catalyst supporters,[2] the rich heterocyclic chemistry of these cyclic phosphines[3] and their interesting coordination properties[4] have also been frequently highlighted by both organic and inorganic chemists. Furthermore, the stereodynamic properties of the phosphorus atom in these heterocycles have also been discussed in many reports.[5−7] In general, it has been observed that the substituents borne on phosphorus play an important role in the rate of pyramidal inversion at the heteroatom[5] and heterocyclic rings with high aromaticities often show much lower inversion barriers[6] than their aliphatic analogues.[7] We are interested in the development of optically active ligands containing stable phosphorus stereogenic centers.[8] Here we report the optical resolution and the configurational stability of the P-chiral heterocyclic diphospholene (±)-**1**.

Results and Discussion

Resolution of the Diphosphine Ligand (±)-1. The air-sensitive diphospholene ligand (±)-**1** was prepared according to a literature method which involves the thermal dimerization of 1-phenyl-3,4-dimethylphosphole in cyclohexanol in the presence of anhydrous nickel bromide.[9] It should be noted that the diphosphine ligand contains 2 carbon and 2 phosphorus stereogenic centers and hence may exist as a mixture of up to 16 isomers.[10] Interestingly, only the C_2-symmetrical racemic form was obtained in this reported synthesis.[9] In our laboratory,

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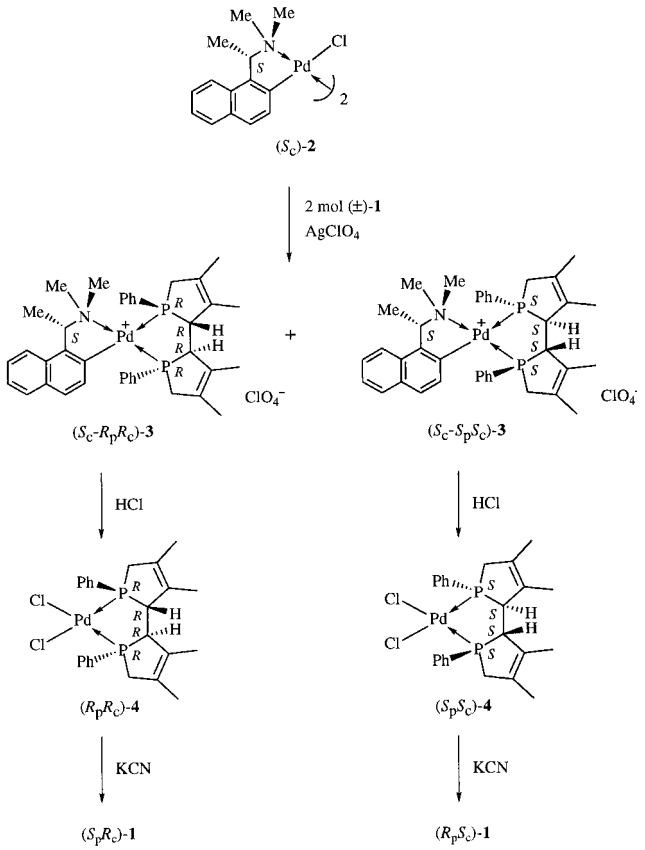
Scheme 1



(±)-**1** has been optically resolved by means of metal complexation. As illustrated in Scheme 1, the resolution process involved the use of the dimeric organopalladium complex (S_C)-**2** as the resolving agent. The initial diastereomeric mixture of cationic complexes **3** was obtained quantitatively as their chloride salts from the reaction between (±)-**1** and stoichiometric amount of (S_C)-**2** in dichloromethane. The ^{31}P NMR spectrum of the crude chloride salts in $CDCl_3$ exhibited two pairs of doublets of similar intensities at δ 54.64 (J_{PP} = 36.6 Hz), 58.07 (J_{PP} = 31.4 Hz), 74.62 (J_{PP} = 31.4 Hz), and 77.43 (J_{PP} = 36.6 Hz). However, attempts to crystallize these chloride salts were not successful, despite using many different solvent systems. Therefore, the diastereomeric complexes were converted into their perchlorate salts by treatment with silver perchlorate. As observed for many similar analogous cationic complexes,[8,11] the ^{31}P NMR spectrum of the crude perchlorate salts in $CDCl_3$ exhibited resonance signals identical with those recorded for their chloride counterparts. The less soluble diasteromer (S_C-R_PR_C)-**3** was separated from the diastereomeric mixture by fractional crystallization in dichloromethane−diethyl ether. The pure diastereomer was obtained in 82% yield with $[\alpha]_D = +83.0°$ (CH_2Cl_2). The ^{31}P NMR spectrum of (S_C-R_PR_C)-**3** in $CDCl_3$ exhibited a pair of doublets at δ 58.07 and 74.62 (J_{PP} = 31.4 Hz). The more soluble diastereomer (S_C-S_PS_C)-**3** was subsequently isolated in its optically pure form from the concentrated mother liquor as pale yellow blocks in 88% yield with $[\alpha]_D$ +25.7° (CH_2Cl_2). The ^{31}P NMR spectrum of (S_C-S_PS_C)-**3** in $CDCl_3$ exhibited the expected doublets at δ 54.64 and 77.43 (J_{PP} = 36.6 Hz). The molecular structure and absolute stereochemistry of both diastereomers were determined by X-ray structural analyses. The studies reveal that, in the less soluble (S_C-R_PR_C) isomer, the absolute stereochemistries at the five chiral centers C(11), P(1), P(2), C(15) and C(21) are *S*, *R*, *R*, *R*, and *R*, respectively (Figure 1). The X-ray analysis of diastereomer (S_C-S_PS_C)-**3** reveals the presence of two crystallographically independent molecules in the asymmetric unit (labeled **A** and **B**). Both molecules have the same absolute stereochemistry with an *S* absolute configuration at all five stereogenic centers. The coordination chemistry at palladium for the two molecules are essentially the same. There are slight differences in the bond distances and the rotations of the *P*-phenyl rings with respect to the coordination plane. For clarity, only molecule **A** of (S_C-S_PS_C)-**3** is depicted in Figure 2. The ORTEP plot of another molecule has been deposited as Supporting Information. Selected bond distances and angles of both diastereomeric complexes are given in Table 1.

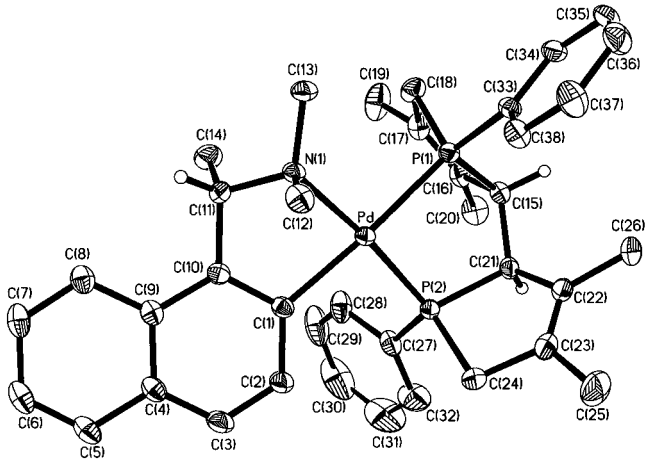


Figure 1. Molecular structure and absolute stereochemistry of (S_C-R_PR_C)-**3**.

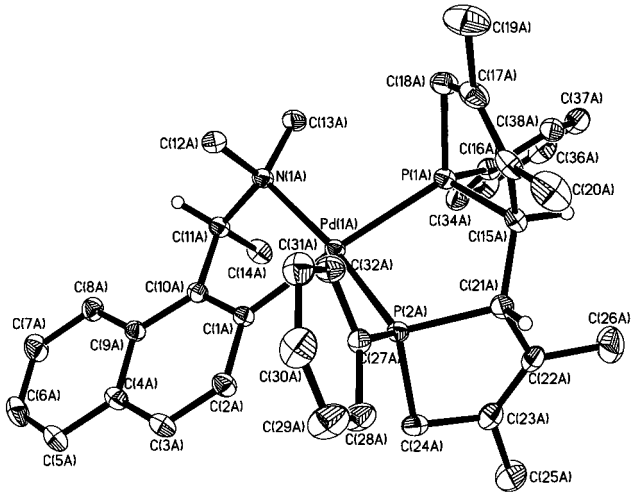


Figure 2. Molecular structure and absolute stereochemistry of (S_C-S_PS_C)-**3**.

(10) Each stereoisomeric diphosphine compound contains two phosphorus and two carbon stereogenic centers. For clarity, only two descriptors (one each for phosphorus and carbon) are used to label the chiralities of these C_2-symmetrical ligands. Full stereochemical descriptors, consistent with those employed by the Chemical Abstract Service, are given in the Experimental Section.

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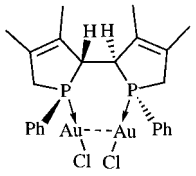
Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Diastereomeric Cationic Complexes (S_C-R_PR_C)-3 and (S_C-S_PS_C)-3

		(S_C-S_PS_C)-**3**	
	(S_C-R_PR_C)-**3**	molecule **A**	molecule **B**
Pd−C(1)	2.061(3)	2.059(3)	2.071(4)
Pd−N(1)	2.142(2)	2.154(3)	2.164(4)
Pd−P(1)	2.345(1)	2.349(1)	2.327(1)
Pd−P(2)	2.232(1)	2.233(1)	2.231(1)
P(1)−C(15)	1.854(3)	1.856(4)	1.868(5)
P(1)−C(18)	1.830(3)	1.833(4)	1.842(4)
P(2)−C(21)	1.856(3)	1.853(4)	1.862(4)
P(2)−C(24)	1.823(3)	1.828(4)	1.830(4)
C(15)−C(21)	1.525(4)	1.528(6)	1.534(6)
C(1)−Pd−N(1)	79.9(1)	80.4(1)	80.2(2)
P(1)−Pd−N(1)	101.2(1)	102.0(1)	100.3(1)
P(1)−Pd−C(1)	171.5(1)	176.1(1)	177.7(1)
P(1)−Pd−P(2)	85.3(1)	85.4(1)	85.1(4)
P(2)−Pd−C(1)	94.2(1)	92.6(1)	94.5(1)
P(2)−Pd−N(1)	172.6(1)	170.0(1)	174.1(1)
C(15)−P(1)−C(18)	93.7(1)	94.3(2)	95.1(2)
C(21)−P(2)−C(24)	93.8(1)	94.3(2)	94.4(2)

The liberation of the optically active diphosphine ligand from the corresponding resolved complexes was carried out in two steps. As illustrated in Scheme 1, the treatment of (S_C-R_PR_C)-**3** with concentrated hydrochloric acid in acetone removed the naphthylamine ligand chemoselectively. The dichloro complex (R_PR_C)-**4** was thus obtained as pale yellow plates in 94% isolated yield; $[\alpha]_D = -63.4°$ (CH_2Cl_2). The ^{31}P NMR spectrum of (R_PR_C)-**4** in $CDCl_3$ exhibited a sharp singlet at δ 88.5 for the two stereochemically equivalent phosphorus nuclei. Subsequent treatment of (R_PR_C)-**4** in dichloromethane with aqueous potassium cyanide liberated the optically active diphosphine ligand (S_PR_C)-**1** as a white solid in 90% yield; $[\alpha]_D = +124.3°$ (C_6H_6), +165.8° (EtOH). The ^{31}P NMR spectrum of (S_PR_C)-**1** in $CDCl_3$ exhibited a sharp singlet at δ −25.7. The enantiomeric ligand (R_PS_C)-**1** was obtained similarly from (S_C-S_PS_C)-**3** via the intermediate dichloro complex (S_PS_C)-**3**. It is noteworthy that the apparent inversion of configuration that takes place at the phosphorus stereogenic centers when the diphosphines are liberated from the metal is merely a consequence of the Cahn−Ingold−Prelog (CIP) sequence rule.[12] Stereospecific displacement of the resolved diphosphine ligand from the palladium resolving agent was confirmed by the quantitative repreparation of (S_C-R_PR_C)-**3** from liberated (S_PR_C)-**1** and (S_C)-**2**: the 500 MHz ^{1}H NMR spectrum of the crude product indicated a pair of doublets at δ 58.07 and 74.62 ($^3J_{PP}$ = 31.4 Hz). Similarly, when liberated (R_PS_C)-**1** was recoordinated to (S_C)-**2**, only signals due to (S_C-S_PS_C)-**3** were observed.

It is noteworthy that the configurational stabilities of tertiary phosphines have been well-documented.[6,7,13] In general, these stereogenic centers are readily racemized at elevated temperatures (E_{inv} = ca. 30 kcal mol^{-1}). Further, strikingly low barriers of inversions have been frequently observed for phosphorus centers that are located in pseudoaromatic phospholes. The configurational stability of (R_PS_C)-**1** was investigated by heating a benzene solution of the optically active diphosphine at 140 °C inside a sealed tube. After 48 h, the optical rotation and the 202 MHz ^{31}P NMR spectrum of the solution remained unchanged. Furthermore, the configurational stability was not affected by the change of solvent: there was no change in the optical rotation and ^{31}P NMR spectrum of a polar ethanolic solution of (R_PS_C)-**1** which had been heated at 140 °C for 48 h. Similar stability was observed when the optically active diphosphine was heated at 140 °C for 48 h in propanol. Undoubtedly, the air-sensitive diphosphine is configurationally stable under ambient conditions. The stability of **1** is similar to those reported for some nonconjugated five-membered cyclic monophosphines.[7] The high configurational stabilities of these cyclic phosphines have been attributed to the angle strain in the transition states. Nevertheless, no studies on optically active diphospholene have been reported previously.

Synthesis of (+)-[Au_2(1)Cl_2] ((R_PR_C)-5). Dinuclear



(R_pR_c)-**5**

gold(I) complexes containing auriophilic Au···Au interactions are important in many aspects of organometallic and structural chemistry.[14] In connection with our studies of biologically active chiral phosphine−gold(I) complexes,[15] we are interested in the coordination chemistry of (±)-**1** on this soft d^{10} metal ion. While model studies and the isolation of complexes **3** and **4** undoubtedly confirmed that the diphosphine ligand is sterically suited to form bidentate metal chelates, it was unclear if the bulky substituents on the heterocyclic phosphorus donor atoms would hinder the ligand in forming a dinuclear gold(I) complex. Unlike 1,2-bis(diphenylphosphino)ethane (dppe), which can use three rotatory single bonds within the P−P linkage to adjust the steric requirements for the accommodation of the Au···Au interaction in [Au_2(dppe)Cl_2],[16] (±)-**1** contains only one restricted rotatory 2,2′-single bond.

Interestingly, despite the above steric considerations, the diphosphine ligand coordinated efficiently as a bridging ligand to two gold centers. Thus, when (S_PR_C)-**1** was treated with sodium tetrachloroaurate in the presence of thiodiglycol, the digold complex (R_PR_C)-**5** was obtained as pale yellow prisms in 74% yield; $[\alpha]_D = +105.4°$ (CH_2Cl_2). The ^{31}P NMR spectrum of (R_PR_C)-**5** in $CDCl_3$ exhibited only one sharp singlet at δ 17.8, thus indicating that the two phosphorus donors are stereochemically equivalent. In the solid state, structural characterization of (R_PR_C)-**5** was carried out by single-crystal X-ray diffraction (Figure 3). Selected bond

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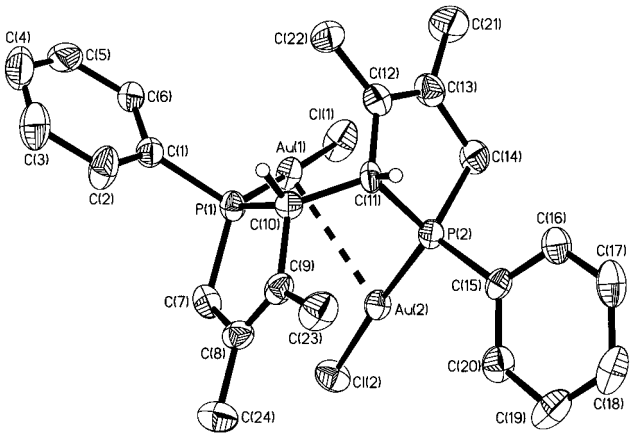

Figure 3. Molecular structure and absolute stereochemistry of (R_PR_C)-**5**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (R_PR_C)-5

Au(1)−Au(2)	3.150(1)	P(1)−C(7)	1.824(12)
Au(1)−P(1)	2.240(3)	P(1)−C(10)	1.872(10)
Au(1)−Cl(1)	2.301(3)	C(10)−C(11)	1.535(14)
Au(2)−P(2)	2.234(3)	P(2)−C(11)	1.853(11)
Au(2)−Cl(2)	2.287(3)	P(2)−C(14)	1.830(13)
Cl(1)−Au(1)−P(1)	178.3(1)	P(2)−Au(2)−Au(1)	83.0(1)
Cl(2)−Au(2)−P(2)	176.4(1)	C(7)−P(1)−C(10)	95.8(5)
Cl(1)−Au(1)−Au(2)	101.4(1)	P(1)−C(10)−C(11)	117.0(7)
P(1)−Au(1)−Au(2)	79.8(1)	C(10)−C(11)−P(2)	117.5(7)
Cl(2)−Au(2)−Au(1)	100.6(1)	C(11)−P(2)−C(14)	95.4(5)

distances and angles of the gold complex are given in Table 2. Similarly to [Au_2(dppe)Cl_2],[16] the diphosphine in (R_PR_C)-**5** coordinates as a bridging ligand to two Au−Cl moieties. The coordination geometries of both gold atoms are linear, although there are slight deviations from 180° in the Cl−Au−P bond angles. The P(1)−C(10)−C(11)−P(2) torsional angle is −65.5°, so that the two linear Cl−Au−P moieties are projecting into the space adjacent to the neighboring five-membered heterocyclic rings. Apparently, this is the only orientation that minimizes the steric repulsions between the phosphorus substituents and the Au−Cl atoms. However, the distance between the two gold atoms (3.150(1) Å) clearly indicates that there is an intramolecular Au···Au interaction in (R_PR_C)-**5**. Investigations on the asymmetric synthesis of (±)-**1** and the biological properties of the optically active gold(I) complex **5** are currently in progress.

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 AMX 500 spectrometers. Optical rotations were measured on the specified solution in a 1-dm cell at 25 °C with a Perkin-Elmer Model 341 polarimeter. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore.

The racemic ligand was prepared according to a literature method.[9] The enantiomerically pure form of bis(*μ*-chloro)bis-[(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*]dipalladium-(II) dichloromethane solvate was prepared as previously described.[17]

Resolution of 1,1′-Diphenyl-3,3′,4,4′-tetramethyl-2,2′-diphosphole-3,3′-diene ((±)-1). Isolation of {(*S*)-1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}{(1*R*,1′*R*,2*R*,2′*R*)-[1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-diphosphole-3,3′-diene-*P*^{1},*P*$^{1'}$}palladium(II) Perchlorate ((S_C-R_PR_C)-3) and Its 1*S*,1′*S*,2*S*,2′*S* Diastereomer (S_C-S_PS_C)-3. A mixture of (±)-**1** (1.97 g) and (S_C)-**2** (1.77 g) in dichloromethane (50 mL) was stirred until all of the resolving agent had dissolved (ca. 0.5 h). The solution was evaporated to dryness, leaving a yellow glass consisting of an equimolar mixture of (S_C-R_PR_C)-**3** and (S_C-S_PS_C)-**3** as their chloride salts. ^{31}P NMR ($CDCl_3$): *δ* 54.64 (d, 1 P, J_{PP} = 36.6 Hz, *P*^{1}), 58.07 (d, 1 P, J_{PP} = 31.4 Hz, *P*^{1}), 74.62 (d, 1 P, J_{PP} = 31.4 Hz, *P*$^{1'}$), 77.43 (d, 1 P, J_{PP} = 36.6 Hz, *P*$^{1'}$). This mixture was taken up in dichloromethane (100 mL), and the solution was treated vigorously with silver perchlorate (1.08 g) in water (10 mL) for 0.5 h. The resulting mixture was filtered through a layer of Celite to remove silver chloride, and the pale yellow organic layer was separated and dried over anhydrous $MgSO_4$. Removal of solvent left a pale yellow glass. Pure (S_C-R_PR_C)-**3** was subsequently obtained from dichloromethane−diethyl ether as pale yellow prisms: mp 210−212 °C dec; $[\alpha]_D$ = +83.0° (*c* 1.2, CH_2Cl_2); 1.38 g (82% yield). Anal. Calcd for $C_{38}H_{44}ClNO_4P_2Pd$: C, 58.4; H, 5.7; N, 1.8. Found: C, 58.4; H, 5.6; N, 2.0. ^{31}P NMR ($CDCl_3$): *δ* 58.07 (d, 1 P, J_{PP} = 31.4 Hz, *P*^{1}), 74.62 (d, 1 P, J_{PP} = 31.4 Hz, *P*$^{1'}$). ^{1}H NMR ($CDCl_3$): *δ* 1.23 (s, 3H, C=C*Me*), 1.44 (s, 3H, C=C*Me*), 1.84 (s, 3H, C=C*Me*), 1.44 (s, 3H, C=C*Me*), 1.96 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.66 (s, 3H, N*Me*), 2.96 (dd, 3H, $^4J_{PH(trans)}$ = 3.6 Hz, $^4J_{PH(cis)}$ = 3.2 Hz, N*Me*), 3.23 (d, 1H, $^2J_{PH}$ = 18.5 Hz, *H*^{2}), 3.42−3.50 (m, 1H, *H*$^{2'}$), 3.61−3.72 (m, 4H, 2 × C*H*$_2$), 4.56 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.1 Hz, C*H*Me), 7.08−7.80 (m, 16H, *aromatics*). The more soluble diastereomer (S_C-S_PS_C)-**3** crystallized as pale yellow blocks from the concentrated mother liquor: mp 208−212 °C dec; $[\alpha]_D$ = +25.7° (*c* 1.0, CH_2Cl_2); 1.40 g (83% yield). Anal. Calcd for $C_{38}H_{44}ClNO_4P_2Pd$: C, 58.4; H, 5.7; N, 1.8. Found: C, 58.2; H, 5.6; N, 2.0. ^{31}P NMR ($CDCl_3$): *δ* 54.51 (d, 1 P, J_{PP} = 36.6 Hz, *P*^{1}), 77.54 (d, 1 P, J_{PP} = 36.6 Hz, *P*$^{1'}$). ^{1}H NMR ($CDCl_3$): *δ* 1.00 (s, 3H, C=C*Me*), 1.23 (s, 3H, C=C*Me*), 1.71 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 1.84 (s, 6H, 2 × C=C*Me*), 2.73 (dd, 3H, $^4J_{PH(trans)}$ = 4.0 Hz, $^4J_{PH(cis)}$ = 3.2 Hz, N*Me*), 3.00 (s, 3H, N*Me*), 3.30−3.10 (m, 1H, *H*^{2}), 3.14 (d, 1H, $^2J_{PH}$ = 17.7 Hz, *H*$^{2'}$), 3.48−3.74 (m, 4H, 2 × C*H*$_2$), 4.52 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.4 Hz, C*H*Me), 7.00−7.98 (m, 16H, *aromatics*).

Dichloro{(1*R*,1′*R*,2*R*,2′*R*)-1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-diphosphole-3,3′-diene-*P*^{1},*P*$^{1'}$}palladium(II) ((R_PR_C)-4). The naphthylamine auxiliary in (S_C-R_PR_C)-**3** was removed chemoselectively by treating an acetone solution (5 mL) of the complex (0.56 g) with concentrated hydrochloric acid (5 mL, 37%) for 0.5 h. The pale yellow microcrystals of (R_PR_C)-**4** precipitated out during this period. The product was then filtered and recrystallized from ethyl acetate−hexane as yellow plates: mp 200−202 °C dec; $[\alpha]_D$ = −63.4° (*c* 0.9, CH_2Cl_2); 0.38 g (94% yield). Anal. Calcd for $C_{24}H_{28}Cl_2P_2Pd$: C, 52.0; H, 5.1. Found: C, 51.7; H, 5.0. ^{31}P NMR ($CDCl_3$): *δ* 88.50 (s, 2 P). ^{1}H NMR ($CDCl_3$): *δ* 1.15 (s, 6H, 2 × C=C*Me*), 1.75 (s, 6H, 2 × C=C*Me*), 3.21 (dd, 2H, $^2J_{PH}$ = 12.9 Hz, $^3J_{PH}$ = 17.7 Hz, *H*^{2} + *H*$^{2'}$), 3.56−3.73 (m, 4H, 2 × C*H*$_2$), 7.42−7.93 (m, 10H, *aromatics*). The S_PS_C enantiomer was prepared from optically pure (S_C-S_PS_C)-**3** under similar conditions.

(1*S*,1′*S*,2*R*,2′*R*)-1,1′-Diphenyl-3,3′,4,4′-tetramethyl-2,2′-diphosphole-3,3′-diene ((S_PR_C)-1). A solution of (R_PR_C)-**4** (0.83 g) in dichloromethane was stirred vigorously with a saturated aqueous solution of potassium cyanide (1 g) for 30 min. The resulting colorless organic layer was separated, washed with water, and then dried ($MgSO_4$). Upon the removal of solvent, a highly air-sensitive white solid was obtained: $[\alpha]_D$ = +124.3° (C_6H_6), +165.8° (EtOH); 0.51 g (90% yield). ^{31}P NMR ($CDCl_3$): *δ* −25.70 (s, 2 P).

Dichloro{*μ*-(1*R*,1′*R*,2*R*,2′*R*)-1,1′-diphenyl-3,3′,4,4′-tetramethyl-2,2′-diphosphole-3,3′-diene-*P*^{1},*P*$^{1'}$}digold(I) ((R_PR_C)-

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Table 3. Crystallographic Data for (S_C-$R_P R_C$)-3, (S_C-$S_P S_C$)-3, and ($R_P R_C$)-5

	(S_C-$R_P R_C$)-**3**	(S_C-$S_P S_C$)-**3**	($R_P R_C$)-**5**
formula	$C_{38}H_{44}ClNO_4P_2Pd$	$C_{38}H_{44}ClNO_4P_2Pd$	$C_{24}H_{28}Au_2Cl_2P_2{\cdot}2H_2O$
fw	782.53	782.53	879.27
space group	$P2_1$	$P2_1$	$P2_12_12_1$
cryst syst	monoclinic	monoclinic	orthohombic
a/Å	10.364(1)	11.094(1)	9.613(1)
b/Å	17.531(1)	18.519(1)	14.860(1)
c/Å	11.057(1)	18.503(1)	21.270(1)
V/Å^3	1884.1(1)	3708.2(1)	3030.6(1)
Z	2	4	4
T/K	293	293	293
d_{calcd}/ g cm^{-3}	1.379	1.402	1.922
λ/Å	0.710 73	0.710 73	0.710 73
μ/cm^{-1}	6.87	6.98	99.44
F(000)	808	1616	1656
R1 (obsd data)[a]	0.0235	0.0303	0.0464
wR2 (obsd data)[b]	0.0604	0.0764	0.1156

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

5). Thiodiglycol (100 mg) was first added to a stirred aqueous acetone (1:1, 4 mL) solution containing sodium tetrachloroaurate (158 mg).When the solution became colorless, a solution of ($S_P R_C$)-**1** (75 mg) was added. After 0.5 h, the reaction mixture was concentrated, and the white precipitate was filtered, washed with water, dried, and crystallized from dichloromethane−diethyl ether as pale yellow prisms: mp 200−202 °C dec; $[\alpha]_D = +105.4°$ (*c* 0.7, CH_2Cl_2); 124 mg (74% yield). Anal. Calcd for $C_{24}H_{28}Au_2Cl_2P_2$: C, 34.2; H, 3.3. Found: C, 34.0; H, 3.6. ^{31}P NMR ($CDCl_3$): δ 17.80 (s, 2 P). ^{1}H NMR ($CDCl_3$): δ 1.35 (s, 6H, 2 × C═C*Me*), 1.93 (s, 6H, 2 × C═C*Me*), 2.84 (dd, 2H, $^2J_{PH} = 4.6$ Hz, $^3J_{PH} = 18.9$ Hz, H^2 + $H^{2'}$), 3.78−3.95 (m, 4H, 2 × CH_2), 7.45−7.75 (m, 10H, *aromatics*).

Crystal Structure Determination of (S_C-$R_P R_C$)-3, (S_C-$S_P S_C$)-3, and ($R_P R_C$)-5. Crystal data for all three complexes and a summary of the crystallographic analyses are given in Table 3. Diffraction data were collected on a Siemens SMART CCD diffractometer with Mo Kα radiation (graphite monochromator) using ω-scans. The two diastereomeric palladium complexes and the gold complex were solved by direct and Patterson methods, respectively. SADABS absorption corrections were applied, and refinements by full-matrix least squares were based on SHELXL 93.[18] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at fixed distances from carbon atoms and were assigned fixed thermal parameters. The absolute configurations of all complexes were determined unambiguously by use of the Flack parameter and, in the cases of (S_C-$R_P R_C$)-**3** and (S_C-$S_P S_C$)-**3**, by internal reference to the known naphthylamine center.

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Supporting Information Available: For (S_C-$R_P R_C$)-**3**, (S_C-$S_P S_C$)-**3**, and ($R_P R_C$)-**5** tables of crystal data and data collection and solution and refinement details, 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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