Molecular Recognition in a Palladium Complex Promoted Asymmetric Synthesis of a *P*-Chiral Heterodifunctionalized Bidentate Phosphine Ligand

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The organopalladium complex containing orthometalated (*S*)-(1-(dimethylamino)ethyl)-naphthalene as the chiral auxiliary has been used successfully to promote the asymmetric [4+2] Diels−Alder reaction between 3,4-dimethyl-1-phenylphosphole and 2-methylene-3-quinuclidinone. In this reaction, the organopalladium template exhibited remarkable stereochemical and electronic directing effects such that the quinuclidinone-nitrogen atom in the resulting phosphanorbornene cycloadduct is located stereospecifically in the exo position. Only one enantiomerically pure P−N bidentate ligand was obtained, although four diastereomeric products are possible. The absolute configuration and the coordination properties of the *P*-chiral cycloadduct have been established by single-crystal X-ray analyses.

Introduction

Recently, a great deal of attention has been focused on the development of enantiomerically pure cyclopalladated complexes because these compounds play important roles in many aspects of synthetic stereochemistry.[2] As examples of their applications, we note their high efficiency in the optical resolution of chiral ligands,[3] their unique structural features that can be used as reliable internal references for the absolute stereochemistry assignments using solution NMR spectroscopy,[4] their sensitivity in chiral environments which allows them to be used routinely as diamagnetic chiral shift reagents in the NMR determination of enantiomerical purities,[5] their special dynamic properties in solution which are ideal for chiral recognition reactions,[6] and their stereoelectronic peculiarities which have been used in the asymmetric synthesis of optically active organic molecules.[7] Recently, we used the organopalladium complex containing the optically active forms of orthopalladated (1-(dimethylamino)ethyl)naphthalene as the chiral template to promote the asymmetric [4+2] Diels−Alder reaction between 3,4-dimethyl-1-phenylphosphole and various organic dienophiles.[8] Hence, a number of functionalized *P*-chiral phosphine ligands have been produced enantioselectively. Furthermore, we observed that it is possible to select either the exo or the endo cycloaddition reaction pathways in these asymmetric syntheses simply by controlling the number of coordination sites on the organopalladium template.[9−11] In this

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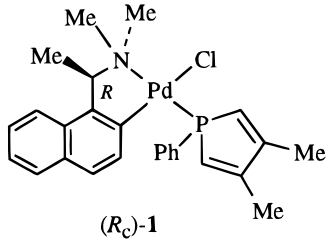
paper, we show that in the cycloaddition reaction with the heterofunctionalized dienophile, 2-methylene-3-quinuclidinone, the orthopalladated template displays an interesting selectivity toward the amine and keto groups on this dienophile.

Results and Discussion

Stereoelectronic Considerations and Cycloaddition Reaction. In the past decade, the activation of 3,4-dimethyl-1-phenylphosphole (DMPP) toward cycloaddition reactions via metal complexation has been established by the groups of Mathey[12] and Nelson.[13] Recently, we found that the coordinated DMPP in the chloro complex (R_c)-**1** undergoes intermolecular Diels−Alder reaction with dienophiles to give the corresponding endo-cycloadducts exclusively. However, when the kinetically stable chloro ligand is replaced by a labile perchlorato counterpart, the resulting chiral template (R_c)-**2** produces exo-cycloadducts stereospecifically via an intramolecular mechanism in which both DMPP and the reacting dienophile are coordinated simultaneously onto the chiral template during the course of reaction. These exo-cycloadducts are obtained as bidentate ligands in which the bridgehead phosphorus and a donor atom from the vinyllic functional groups are coordinated to the palladium template. Thus stable P−O bidentate ligands were synthesized from the reactions between (R_c)-**2** and *N*,*N*-dimethylacrylamide, ethyl vinyl ketone, and vinyl sulfoxides, respectively.[8,9] Similarly, an optically pure P−N bidentate was obtained when (R_c)-**2** was treated with 2-vinylpyridine.[11] It is important to note that, due to the distinct electronic directing effects originating from the σ-donating nitrogen and π-accepting aromatic carbon of the organometallic ring in (R_c)-**1** and (R_c)-**2**,[3,14] all monodentate and heterobidentate cycloadducts are coordinated on the chiral template in a regiospecific manner.



(R_c)-**1**

In extending the synthetic application of the orthometalated naphthylamine ring in (R_c)-**2**, especially in its ability to differentiate between nitrogen and oxygen donor atoms, we herein report the reaction between (R_c)-**2** and 2-methylene-3-quinuclidinone. In principle, this cycloaddition reaction may produce a pair each of stereochemically distinct diastereomeric P−N and P−O cycloadducts,[15] even though it is predictable that the softest phosphorus donor will coordinate to the template in the position trans to NMe_2 (Scheme 1). It is noted that thermodynamically stable P−N and P−O chelates are commonly found among the analogous cyclopalladated complexes.

The cycloaddition reaction between (R_c)-**2** and excess 2-methylene-3-quinuclidinone was conducted at room temperature in dichloromethane. The reaction was monitored by ^{31}P NMR spectroscopy. After 1 day, the ^{31}P NMR spectrum of the reaction mixture in CD_2Cl_2 showed a strong sharp singlet at δ 35.4 for unreacted (R_c)-**2** together with a new sharp singlet at δ 133.4 for the cycloaddition adduct. No other ^{31}P resonance signal was detected in the 202 MHz NMR spectrum. On the second day, colorless prisms of the cycloadduct were formed inside the reaction flask. However, these colorless crystals could not be redissolved in dichloromethane. Subsequent monitoring of the mother liquor of the reaction mixture showed a relative weakening of the signal pertaining to (R_c)-**2** and a stronger low-field signal. After 5 days, the ^{31}P NMR signal due to the starting material (R_c)-**2** could no longer be detected in the reaction mixture, thus indicating the completion of the reaction. It should be reiterated that only one low-field ^{31}P signal was detected throughout the cycloaddition process. Furthermore the ^{31}P NMR spectrum of the colorless product crystals in Me_2SO-d_6 showed only one sharp singlet at δ 132.5, thus confirming that only one diastereomer was formed in the Diels−Alder reaction. The cycloadduct was obtained in 75% isolated yield with $[\alpha]_D$ −155.0° (*c* 1.0, DMSO). Interestingly, the crystallized perchlorate salt is only soluble in dimethyl sulfoxide and is highly insoluble in acetonitrile, chloroform, and dichloromethane. It is noteworthy that the low-field ^{31}P NMR resonance signal is typical for phosphanorbornenes that bear the syn orientation with respect to the phosphorus lone pair locations.[8−13,16] The IR spectrum (KBr) of the cycloadduct shows a strong ν(C=O) at 1736 cm^{-1}. This IR signal is consistent with the structural assignments in which the carbonyl group is not involved in carbonyl-O metal complexation.[17]

The X-ray crystallographic determination of the complex reaffirms that an enantiomerically pure cycloadduct has been formed in which the chiral phosphanorbornene ligand created indeed coordinates to palladium as a bidentate chelate via the bridgehead phosphorus and the exo-substituted nitrogen atom (Figure 1). Furthermore, the structure analysis unambiguously establishes the *S* absolute stereochemistry at all four newly generated P(1), C(21), C(23), and C(26) centers. Accordingly, the sole diastereomer obtained from the cycloaddition reaction is (R_c,S_p,S_c)-**3**, as depicted in Scheme 1. The geometry at palladium is distorted square-planar with angles at Pd in the ranges 80.8(1)−103.6(1)° and 170.6(2)−174.1(2)° (Table 1). These distortions involve contractions from 90° for the bite angles of both chelate rings and the drastic enlargement of the

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(15) In this series of compounds, each possible diastereomeric cycloadduct contains four carbon and one phosphorus stereocenters. For clarity, the first descriptor always refers to the absolute configuration at the carbon center in the organometallic ring. The second and third refer to the chiralities at phosphorus and the disubstituted carbon in the phosphanorbornene skeleton.
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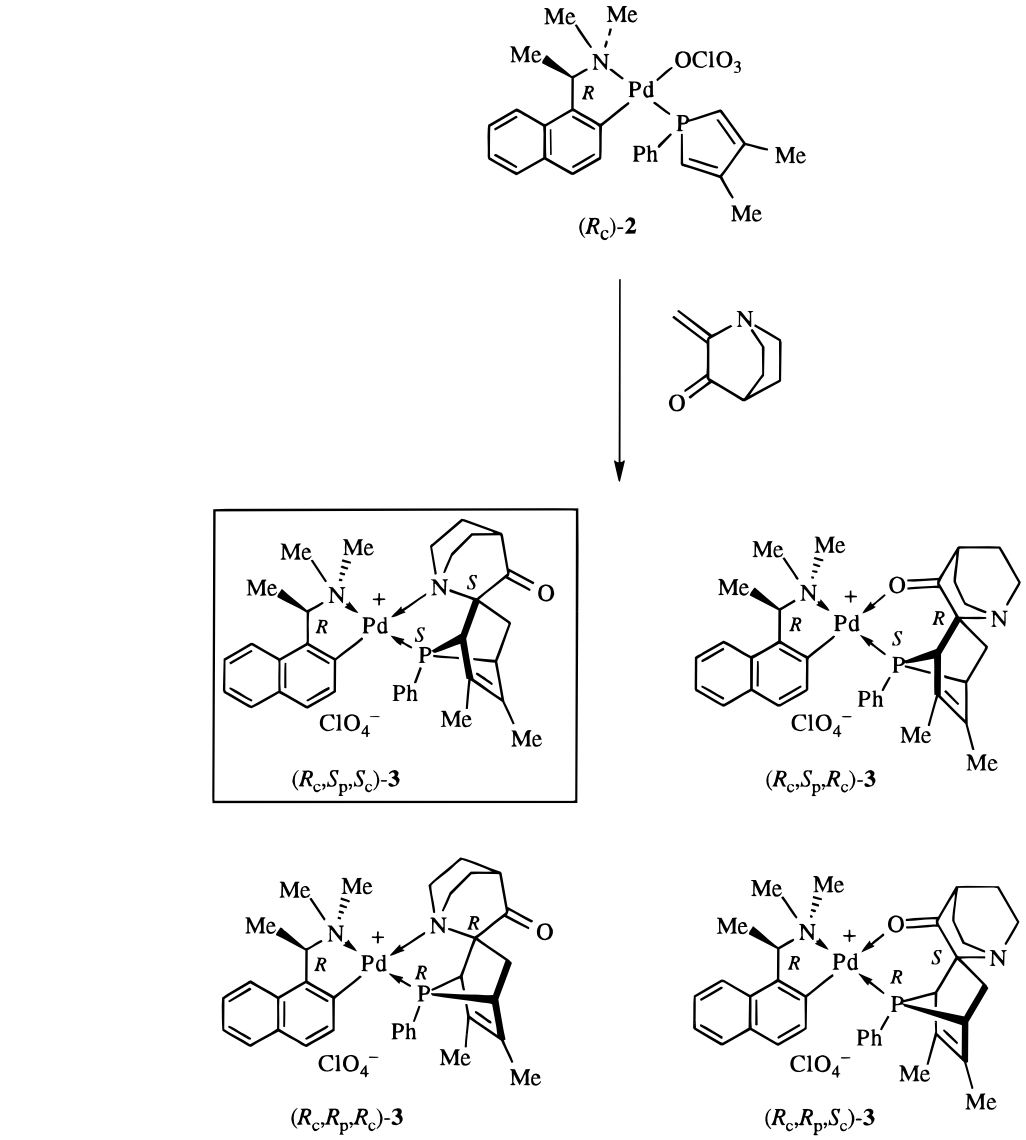
Scheme 1. Diels–Alder Reaction and the Four Possible Diastereomeric Cycloadducts



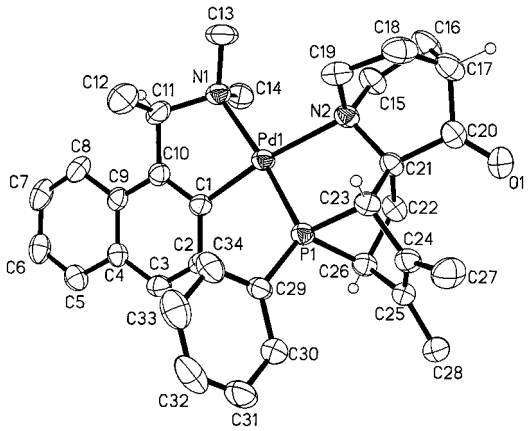


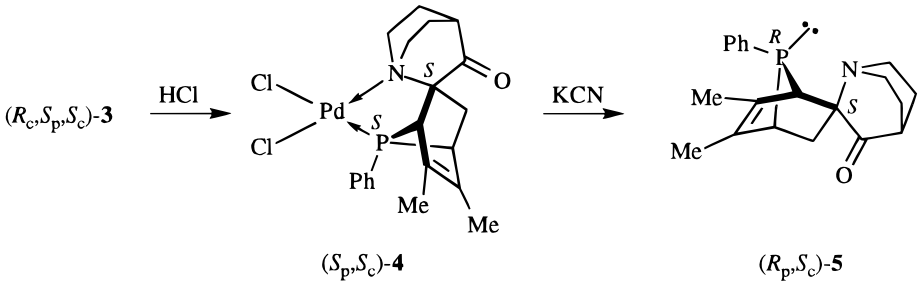
Figure 1. Molecular structure and absolute configuration of (R_c,S_p,S_c)-**3**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for (R_c,S_p,S_c)-3

Pd(1)−P(1)	2.222(1)	Pd(1)−N(1)	2.188(3)
Pd(1)−C(1)	1.996(4)	Pd(1)−N(2)	2.240(3)
P(1)−C(29)	1.793(3)	P(1)−C(23)	1.860(4)
P(1)−C(26)	1.837(5)	C(23)−C(24)	1.518(5)
C(24)−C(25)	1.329(6)	C(25)−C(26)	1.514(6)
C(26)−C(22)	1.549(6)	C(22)−C(21)	1.558(6)
C(21)−C(23)	1.572(5)	C(21)−C(20)	1.537(5)
N(2)−C(21)	1.522(5)	N(2)−C(19)	1.503(5)
N(2)−C(15)	1.504(5)	C(20)−O(1)	1.211(6)
C(17)−C(18)	1.542(7)	C(17)−C(20)	1.490(6)
N(1)−C(11)	1.502(7)	N(1)−C(13)	1.482(4)
P(1)−Pd(1)−N(1)	174.1(2)	P(1)−Pd(1)−C(1)	95.2(1)
P(1)−Pd(1)−N(2)	80.8(1)	N(1)−Pd(1)−C(1)	81.0(1)
N(1)−Pd(1)−N(2)	103.6(1)	C(23)−P(1)−C(26)	81.0(2)
C(22)−C(21)−C(23)	103.5(3)	C(22)−C(21)−N(2)	111.8(3)
C(20)−C(21)−C(22)	112.9(3)	C(17)−C(20)−C(21)	113.1(4)
C(21)−N(2)−C(19)	110.9(3)	C(21)−N(2)−C(15)	107.1(3)
C(20)−C(17)−C(18)	108.4(4)	C(20)−C(17)−C(16)	107.3(4)
C(21)−C(20)−O(1)	122.2(4)	C(17)−C(20)−O(1)	124.7(4)
N(1)−C(11)−C(10)	107.4(3)	Pd(1)−N(1)−C(11)	105.0(3)

N(1)−Pd−N(2) and C(1)−Pd−P(1) interchelate bond angles. In addition, there is also a small tetrahedral distortion at palladium: the two ligand coordination planes are twisted by ca. 10.1° with respect to each other. The tetrahedral distortion and the enlargement of the interchelate angles, particularly the large N(1)−Pd−N(2) angle [103.6(1)°], are clearly due to the ligand−ligand repulsions. The Pd−P(1), Pd−C(1), and Pd−N(1) distances [2.222(1), 1.996(4), and 2.188(3) Å, respectively] are similar to the related, chirally directed,

Scheme 2



ketophosphine-*P*,*O* analogue.[9] Possibly due to the combined effects arising from the interchelate steric and electronic interactions, the Pd−N(2) distance [2.240(3) Å] is significantly longer than its Pd−N(1) counterpart within the same complex. Another noticeable feature of the P−N chelate is a marked lengthening of the C(21)−C(23) distance [1.572(5) Å], which is clearly attributed to the intrachelate repulsive interactions between the bridgehead moiety and the cyclic amine rings. As a unique feature of phosphanorbornenes, the C(23)−P(1)−C(26) bridgehead angle is acute [81.0(2)°].

Removal of Chiral Auxiliary and Liberation of Phosphine. Presumably due to its high thermodynamic and kinetic stabilities, the *P*-chiral cycloadduct could not be liberated directly from the template complex (R_c,S_p,S_c)-**3** in a single step, despite the strong reaction conditions used. However, stereospecific liberation of the optically pure P−N bidentate ligand could be achieved in two steps, i.e., via treatment with concentrated hydrochloric acid to remove the chiral auxiliary from the template complex followed by the displacement of the phosphine ligand from palladium with cyanide (Scheme 2). In the first step, the naphthylamine ligand was removed chemoselectively by treating (R_c,S_p,S_c)-**3** with concentrated hydrochloric acid in dimethyl sulfoxide at 60 °C for 12 h to give the corresponding dichloro complex (S_p,S_c)-**4** as bright yellow prisms in 50% yield, $[\alpha]_D$ −36.1° (*c* 1.0, DMSO). Dimethyl sulfoxide was used as the solvent as it is the only solvent that could dissolve the template complex efficiently. Nevertheless, the low isolated yield of (S_p,S_c)-**4** is attributed to the presence of this high-boiling polar solvent, as it somewhat impairs the dichloromethane extraction of the dichloro product complex from the acidic reaction mixture. The ^{31}P NMR spectrum of (S_p,S_c)-**4** in Me_2SO-d_6 showed a characteristic low-field sharp singlet at δ 131.3. Similarly to (R_c,S_p,S_c)-**3**, the IR spectrum (KBr) of (S_p,S_c)-**4** shows a strong ν(C═O) at 1732 cm^{-1}, indicating that the carbonyl group is not involved in carbonyl-O metal complexation.

The X-ray analysis of (S_p,S_c)-**4** reaffirms that while the orthometalated naphthylamine has been displaced by two chloro ligands in the acid treatment of the template complex, the five-membered P−N chelate ring remains intact (Figure 2). As desired, the *S* absolute configuration at all carbon and phosphorus stereogenic centers in (S_p,S_c)-**4** has not been disrupted. The geometry at palladium is slightly distorted square-planar with angles at Pd in the ranges 82.6(1)−93.9(1)° and 173.8(1)− 76.0(1)° (Table 2). The bite angle of the P−N chelate ring [82.6(1)°] is somewhat enlarged relative to the value observed in (R_c,S_p,S_c)-**3**. Both the Pd−P and Pd−N lengths [2.208(1) and 2.127(2) Å, respectively] in

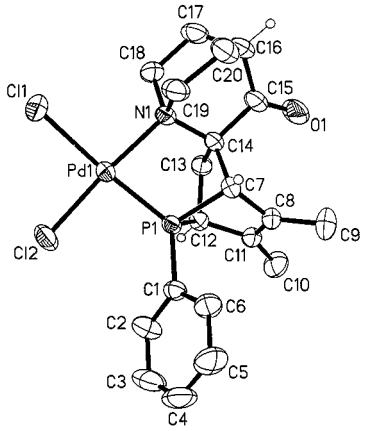


Figure 2. Molecular structure and absolute configuration of (S_p,S_c)-**4**.

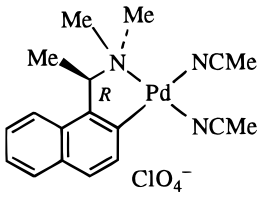
Table 2. Selected Bond Lengths (Å) and Angles (deg) for (S_p,S_c)-4

Pd(1)−P(1)	2.208(1)	Pd(1)−N(1)	2.127(2)
Pd(1)−Cl(1)	2.387(1)	Pd(1)−Cl(2)	2.295(1)
P(1)−C(1)	1.801(3)	P(1)−C(7)	1.850(3)
P(1)−C(12)	1.846(3)	C(7)−C(8)	1.523(4)
C(8)−C(11)	1.335(4)	C(11)−C(12)	1.520(3)
C(12)−C(13)	1.550(4)	C(13)−C(14)	1.546(4)
C(14)−C(7)	1.575(4)	C(14)−C(15)	1.533(4)
N(1)−C(14)	1.526(3)	N(1)−C(18)	1.510(4)
N(1)−C(19)	1.504(4)	C(15)−O(1)	1.211(4)
C(16)−C(20)	1.531(5)	C(15)−C(16)	1.494(5)
P(1)−Pd(1)−N(1)	82.6(1)	P(1)−Pd(1)−Cl(1)	176.0(1)
P(1)−Pd(1)−Cl(2)	92.4(1)	N(1)−Pd(1)−Cl(1)	93.9(1)
N(1)−Pd(1)−Cl(2)	173.8(1)	C(7)−P(1)−C(12)	81.8(1)
C(7)−C(14)−C(13)	105.0(2)	C(7)−C(14)−N(1)	109.3(2)
C(7)−C(14)−C(15)	111.5(2)	C(14)−C(15)−C(16)	113.9(3)
C(14)−N(1)−C(18)	109.1(2)	C(14)−N(1)−C(19)	110.4(2)
C(18)−N(1)−C(19)	106.1(2)	C(14)−C(15)−O(1)	120.9(3)
C(15)−C(16)−C(17)	106.4(3)	C(15)−C(16)−C(20)	108.1(3)

(S_p,S_c)-**4** are shorter than their counterparts in the cationic template complex. However, the C(7)−C(14) distance [1.575(4) Å] is elongated noticably by the intrachelate replusive interactions. The two Pd−Cl distances [2.295(1) and 2.387(1) Å] differ significantly, with the bond trans to phosphorus being noticeably enlarged from normal, reflecting the stronger trans effect of phosphorus versus nitrogen. The bridgehead C−P−C angle [81.8(1)°] within the phosphanorbornene skeleton is still acute, but enlarged relative to the value observed in (R_c,S_p,S_c)-**3**.

Treatment of a dichloromethane solution of (S_p,S_c)-**4** with aqueous potassium cyanide liberates the enantiomerically pure bidentate ligand (R_p,S_c)-**5** as an air-sensitive white solid in 70% isolated yield: $[\alpha]_D$ −130.2° (*c* 1.0, CH_2Cl_2). Significantly, the ^{31}P NMR spectrum of the liberated ligand in CD_2Cl_2 showed a low-field sharp

singlet at δ 118.8. This low-field signal confirms that the syn stereochemical orientation is retained. It should be noted that the seeming inversion of configuration that takes place at the phosphorus stereogenic center when phosphorus is liberated from the metal is merely a consequence of the Cahn−Ingold−Prelog (CIP) sequence rules.[18] The enantiomeric purity of (R_p,S_c)-**5** was established by the quantitative repreparation of (R_c,S_p,S_c)-**3** from the reaction between the liberated (R_p,S_c)-**5** and the bis-(acetonitrile) complex (R_c)-**6**: the 202 MHz ^{31}P NMR spectrum of the crude product indicated the presence of (R_c,S_p,S_c)-**3** only. In a further test of enantiomeric purity, the diastereomeric complex (S_c,S_p,S_c)-**3** was prepared from (R_p,S_c)-**5** and the equally accessible (S_c)-**6**: no NMR signal was detected at δ 132.5, but a new sharp singlet was observed at δ 139.1 due to the presence of (S_c,S_p,S_c)-**3**. Finally, it should be noted that (S_p,R_c)-**5** has been prepared similarily from (S_c)-**2** and 2-methylene-3-quinuclidinone. We are currently investigating the biological properties of gold(I) complexes containing these optically active aminophosphines.



(R_c)-**6**

Conclusion

A correlation between the X-ray crystallography data of the cycloaddition product (R_c,S_p,S_c)-**3** and a Dreiding model study of all the four possible isomers of **3** depicted in Scheme 1 confirmed that there are more severe interchelate steric constraints within the two P−N isomers. The formation of the P−O cycloadducts, however, would markedly relieve the interchelate repulsive interactions. Therefore, the formation of a P−N isomer in this Diels−Alder reaction cannot be due to steric reasons and must be due to the electronic directing factors originated from the coordinated aromatic carbon in the organometallic ring. On the other hand, the well-documented stereochemistry of the projecting H_γ and N-Me groups of the chiral naphthylamine auxiliary can be used to explain the stereospecific generation of (R_c,S_p,S_c)-**3** but not its (R_c,R_p,R_c) diastereomer.[3−6] Model studies confirmed that, of the two P−N diastereomers, more severe repulsive forces exist between the cycloadduct and the chiral auxiliary in (R_c,R_p,R_c)-**3**. The present asymmetric synthesis of the heterofunctionalized *P*-chiral phosphine therefore clearly demonstrates that the chiral orthopalladated naphthylamine unit is indeed a versatile reagent for asymmteric synthesis since its electronic directing and chiral inductive effects operate coherently. With all these desirable stereoelectronic features, undoubtedly, we can expect to see an increasing use of the chiral cyclopalladated complexes in all aspects of synthetic stereochemistry.

(18) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. Proton NMR spectra were recorded at 500.14 MHz and ^{31}P spectra at 202.46 MHz on a Brucker AMX500 NMR spectrometer. Optical rotations were measured on the specified solutions in a 1 dm cell at 25 °C with a Perkin-Elmer model 341 polarimeter. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry at the National University of Singapore.

Both of the enantiomeric pure forms of perchlorato(*R*/*S*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*][3,4-dimethyl-1-phenyl-phosphole-*P*]palladium(II),[9] **2**, and bis(acetonitrile)-[(*R*/*S*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*]-palladium(II) perchlorate,[14] **6**, were prepared according to literature methods.

Template Synthesis of (R_c,S_p,S_c)-3. 2-Methylene-3-quinuclidinone hydrochloride dihydrate (2.1 g) was added slowly into a solution of sodium hydroxide (0.4 g) in ethanol (50 mL) at 0 °C. The reaction mixture was allowed to stir for 1 h at room temperature and then evaporated to dryness under reduced pressure. Dichloromethane (20 mL) was added to extract 2-ethylene-3-quinuclidinone. The organic solution was filtered (to remove sodium chloride) and then added into a dichloromethane (20 mL) solution of the perchlorato complex (R_c)-**2** (1.2 g). Upon standing at room temperature for 5 days, pure (R_c,S_p,S_c)-**3** crystallized from the reaction mixture as colorless prisms, mp 233−236 °C (dec); $[\alpha]_D$ −155° (*c* 1.0, DMSO); 1.1 g (75.0% yield). Anal. Calcd for $C_{34}H_{40}ClN_2O_5PPd$: C, 56.0; H, 5.5; N, 3.8. Found C, 56.3; H, 5.7; N, 3.7. ^{31}P NMR (Me_2SO-d_6): δ 132.5 (s). ^{1}H NMR (Me_2SO-d_6): δ 1.35 (s, 3H, C=C*Me*), 1.83 (d, 3H, $^3J_{HH}$ = 6.1 Hz, CH*Me*), 1.91 (s, 3H, C=C*Me*), 1.93−2.35 (m, 4H, *alicyclics*), 2.50 (d, 3H, $^4J_{HH}$ = 1.3 Hz, N*Me*), 2.62 (bs, 1H, PC*H*), 2.97 (d, 3H, $^4J_{HH}$ = 3.6 Hz, N*Me*), 3.09−4.05 (m, 8H, *alicyclics*), 4.43 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.1 Hz, C*H*Me), 6.80−7.80 (m, 11H, *aromatics*).

Removal of Chiral Auxiliary and Isolation of (S_p,S_c)-4. The template complex (R_c,S_p,S_c)-**3** (0.36 g) was dissolved in dimethyl sulfoxide (10 mL). Concentrated hydrochloric acid (3 mL) was added, and the acidic solution was heated at 60 °C for 12 h and then cooled to room temperature. The solution was diluted with water (100 mL) and extracted with dichloromethane (3 × 100 mL). The combined extracts were washed with water (3 × 50 mL) and dried ($MgSO_4$). Removal of solvent and recrystallization from dichloromethane/diethyl ether gave the dichloro complex (S_p,S_c)-**4** as yellow prisms, mp 264−267 °C (dec); $[\alpha]_D$ −36° (*c* 0.5, DMSO); 0.12 g (50.0% yield). Anal. Calcd for $C_{20}H_{24}Cl_2NOPPd$: C, 47.8; H, 4.8; N, 2.8. Found: C, 47.9; H, 4.7; N, 2.7.^{31}P NMR (Me_2SO-d_6): δ 131.3 (s). ^{1}H NMR (Me_2SO-d_6): δ 1.44 (s, 3H, C=C*Me*), 1.66 (s, 3H, C=C*Me*), 1.77−2.32 (m, 4H, *alicyclics*), 2.62 (bs, 1H, PC*H*), 2.89−2.96 (m, 1H, *alicyclics*), 3.39−3.73 (m, 2H, *alicyclics*), 3.79 (bs, 1H, PC*H*), 4.04−4.24 (m, 4H, *alicyclics*), 7.43−7.82 (m, 5H, *aromatics*).

Removal of Palladium and Isolation of (R_p,S_c)-5. A solution of (S_p,S_c)-**4** (0.1 g) in dichloromethane (20 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (2.0 g) for 0.5 h. The resulting colorless organic layer was separated, washed successively with water (4 × 20 mL), and then dried ($MgSO_4$). Upon removal of solvent, a highly air-sensitive low-melting solid was obtained: $[\alpha]_D$ −130.2° (*c* 1.0, CH_2Cl_2); 48 mg (70% yield). ^{31}P NMR (CD_2Cl_2): δ 118.8 (s).

Crystal Structure Determination of (R_c,S_p,S_c)-3 and (S_p,S_c)-4. Crystal data and a summary of the crystallographic analyses for (R_c,S_p,S_c)-**3** and (S_p,S_c)-**4** are given in Table 3. For both complexes, independent reflections were measured on a Bruker AXS SMART CCD diffractometer with Mo Kα radiation (graphite monochromator) using frames. The data were processed using SAINT programs, and the structure solution

Table 3. Crystallographic Data for Complexes (R_c,S_p,S_c)-3 and (S_p,S_c)-4

	(R_c,S_p,S_c)-**3**	(S_p,S_c)-**4**
formula	$C_{34}H_{40}ClN_2O_5PPd$	$C_{20}H_{24}Cl_2NOPPd$
fw	729.50	502.67
space group	$P2_1$	$P2_12_12_1$
cryst syst	monoclinic	orthorhombic
a, Å	9.850(1)	7.454(1)
b, Å	13.859(1)	14.435(1)
c, Å	12.093(1)	19.005(1)
β, deg	106.139(1)	90
V, Å^3	1585.8(1)	2044.8(1)
Z	2	4
T, K	293	293
d(calcd), g cm^{-3}	1.528	1.633
λ, Å	0.710 73 (Mo)	0.710 73 (Mo)
μ, cm^{-1}	7.65	12.56
R_1 (obs data)[a]	0.0369	0.0242
wR_2 (obs data)[b]	0.0937	0.0626

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

and refinement were done using SHELXTL (version 5.0) programs. Empirical absorption corrections were applied to the data using the program SADABS. For (R_c,S_p,S_c)-**3**, a colorless prism with dimensions 0.37 × 0.33 × 0.13 mm was selected. A total of 9607 independent reflections were collected, of which 6106 were unique. All the non-hydrogen atoms were refined anisotropically. Full-matrix least-squares refinement on F^2 with absorption corrected data gave $R_1 = 0.0369$, $wR_2 = 0.0937$ for 5753 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, 1.75° ≤ θ ≤ 29.36°] and 401 parameters. The absolute stereochemistry was determined unambiguously by refining the Flack parameter [$x = -0.04(3)$]. For (S_p,S_c)-**4**, a pale yellow block with dimensions 0.38 × 0.28 × 0.23 mm was used. A total of 13 181 reflections were measured in the θ range 1.77−29.15°, of which 4927 were unique reflections ($R_{(int)} = 0.0185$). Anisotopic thermal parameters were refined for all the non-hydrogen atoms. In the final least-squares cycles, the model converged at $R_1 = 0.0242$, $wR_2 = 0.0626$ for 4718 reflections with $|F_o| > 4\sigma(|F_o|$ and 235 parameters. The absolute stereochemistry was determined by use of the Flack parameter [$x = 0.02(2)$].

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Supporting Information Available: For (R_c,S_p,S_c)-**3** and (S_p,S_c)-**4** 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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