Palladium-Complex-Promoted Asymmetric Synthesis of Stereoisomeric P-Chiral Pyridylphosphines via an Unusual Exo−Endo Stereochemically Controlled Asymmetric Diels−Alder Reaction between 2-Vinylpyridine and Coordinated 3,4-Dimethyl-1-phenylphosphole

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The organopalladium complex containing ortho-metalated (*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-vinylpyridine. The pyridyl group in the resulting phosphanorbornene cycloadducts can be located stereospecifically in the exo or endo position by controlling the electronic properties of the organopalladium promoter. In the exo-cycloaddition process, the P−N bidentate ligand (−)-2-[(1α,2α(*S*),4α,7*S*)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene-2-yl]pyridine was produced stereoselectively. In the endo-cycloaddition process, however, a pair of separable diastereomeric palladium template complexes containing the naphthylamine auxiliary and the enantiomeric forms of 2-[(1α,2β(*R*/*S*),4α,7(*R*/*S*)-5,6-dimethyl-7-phenyl-7-phosphabicyclo-[2.2.1]hept-5-ene-2-yl]pyridine were obtained. In these diastereomeric complexes, the endo-cycloadducts coordinated on palladiun as monodentate ligands via only their phosphorus donor atoms. The pyridyl-nitrogen atoms are not involved in metal complexation. The absolute configurations and the coordination properties of the exo- and endo-pyridylphosphines have been established by single-crystal X-ray analyses.

Introduction

Recently, a great deal of attention has been focused on the development of pyridyl-substituted phosphines because these ligands play important roles in many aspects of synthetic and inorganic chemistry.[1] As examples of their applications, we note the catalytic properties of uncoordinated pyridylphosphines in the chlorination of alkyl alcohols[2] and in the Mitsunobu esterification reaction between a carboxylic acid and an alcohol.[3] Their transition-metal complexes were also found to be highly efficient catalysts in carbonylation, epoxidation, and cycloaddition reactions involving a wide range of organic substrates.[4] In terms of coordination chemistry, pyridylphosphines may function either as metal chelates via both their phosphorus and nitrogen donor atoms or as monodentate ligands via the phosphorus atoms only.[5,6] These earlier studies, however, very rarely involved optically active pyridylphosphines containing resolved tertiary phosphorus stereocenters.[6] Such ligands should be important chiral auxiliaries for the analogous asymmetric catalytic processes since their P-chiral donors, which can be considered as the primary chirality inducers, are directly attached to the catalytic metal centers. Perhaps, the difficulties associated with the optical resolution and asymmetric synthesis of P-chiral phosphines have hampered the advancement of this important area of research. In this paper, we report an efficient approach to various stereoisomeric forms of the P-chiral pyridylphosphine **1** by means of an unusual exo−endo stereochemically controlled asymmetric Diels−Alder reaction between 2-vinylpyridine and 3,4-dimethyl-1-phenylphosphole in which the chiral organopalladium complex (S_c)-**2** is used as both the reaction promoter and the stereochemical controller. It is noted that the exo isomers of pyridylphosphine **1** are potential P−N metal chelates, but their endo analogues are necessarily monodentate or bridging ligands (Figure 1).

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Results and Discussion

Exo-Cycloaddition Reaction: Stereoselective Synthesis of the Exo-Cycloadduct, (R_p)-*exo*-1. Recently, we observed that the enantiomerically pure form of the naphthalenyl complex **2** is an efficient reaction promoter for the asymmetric Diels−Alder reaction

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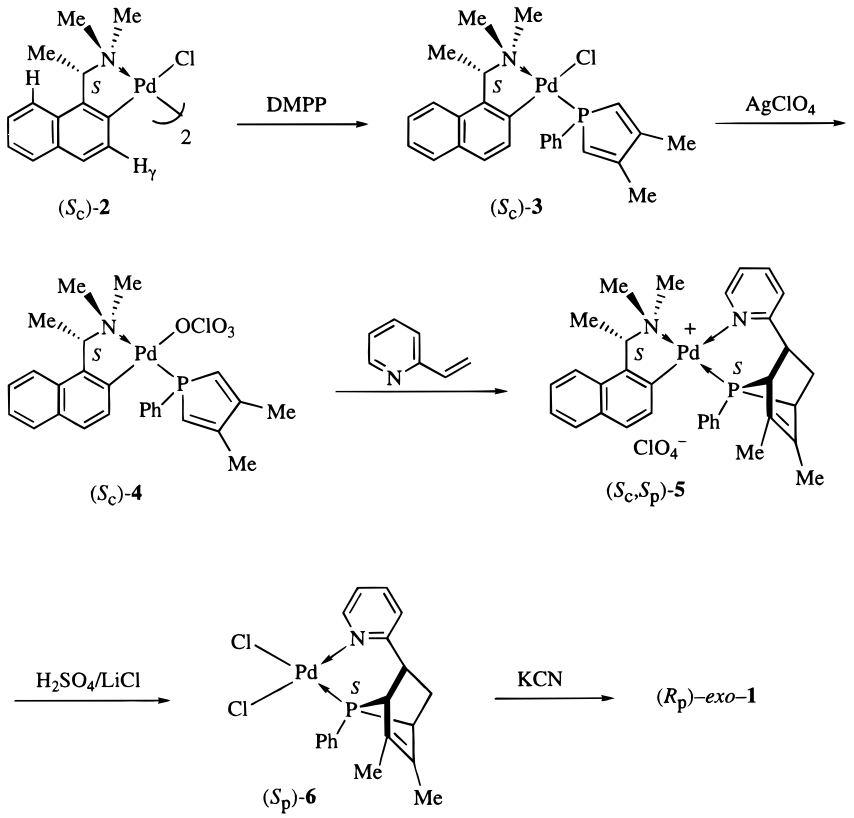
Scheme 1



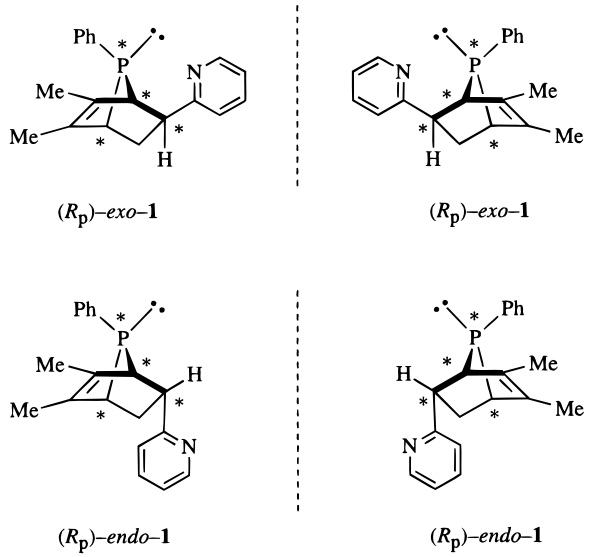


Figure 1. Syn−exo and syn−endo diastereomers of pyridylphosphine **1**.

between dimethylphenylphosphole (dmpp) and a range of dienophiles, such as vinyl-substituted arsines, phosphines, and thiols.[7] These organopalladium-complex-promoted [4 + 2] cycloaddition reactions generally give high yields of the desired P-chiral phosphanorbornene ligands in their enantiomerically pure forms. Interestingly, these palladium-complex-promoted reactions invariably produce the syn isomers in which the phosphine lone pairs and the dienophile functionalities are located on the same side of the C−P−C molecular bisector. Another noticeable feature of these asymmetric reactions is the simultaneous coordination of both the diene and the dienophile precursors on the chiral palladium template during the course of carbon−carbon bond formation. The exo-substituted phosphornorbornenes are thus generated stereospecifically via an intramolecular cycloaddition mechanism.[8,9] The stereoselectivity of the Diels−Alder reactions is attributed to the unique stereochemical features of the naphthylamine auxiliary. The rigid five-membered ortho-metalated naphthylamine ring transmits the stereochemistry of the naphthylamine auxiliary, via the sterically protruding aromatic Hγ proton and the prochiral NMe groups, to the reaction template sites in a highly efficient and predictable manner.[9,10] Following this established approach, the exo-cycloadduct (R_p)-*exo*-**1** was obtained stereoselectively by using (S_c)-**2** as the chiral template.

As illustrated in Scheme 1, the activation of dmpp toward cycloaddition reactions was achieved by the coordination of the cyclic diene to (S_c)-**2**. Due to the special electronic trans-directing effects originating from

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the σ-donating nitrogen and π-accepting aromatic carbon atom of the ortho-metalated naphthylamine chelate,[11] the chloro complex (S_c)-**3** was obtained regiospecifically in quantitative yields.[12,13] The chlorine−palladium bond in this monomeric complex is kinetically stable and, in several cases, cannot be displaced even by monodentate phosphine ligands.[13] Therefore, it is necessary to remove this chloro ligand in order to facilitate the coordination of a dienophile onto the chiral template for the subsequent intramolecular cycloaddition reaction. Treatment of a 1,2-dichloroethane solution of (S_c)-**3** with aqueous silver perchlorate generated the kinetically labile perchlorato complex (S_c)-**4** quantitatively. We have recently reported on the isolation and X-ray structural analysis of (S_c)-**4**.[12] In routine synthesis, however, the perchlorato complex was generally not isolated, and upon removal of silver chloride and drying with magnesium sulfate, the 1,2-dichloroethane solution of the perchlorato complex was treated directly with excess 2-vinylpyridine at 75 °C. The reaction was monitored by ^{31}P NMR spectroscopy and was found to be complete in 20 days. Prior to column purification, the ^{31}P NMR spectrum of the crude product in $CDCl_3$ exhibited a characteristic singlet at δ 106.2, indicating that the syn−exo isomer had been formed on the palladium template in the Diels−Alder reaction.[7,14] No other ^{31}P NMR signal was detected in this low-field region. The cycloaddition product (S_c,S_p)-**5** was subsequently purified by silica gel column chromatography as a pale yellow solid in 35% isolated yield. It is noteworthy that a control reaction between dmpp and 2-vinylpyridine in the absence of the organopalladium template failed to give any Diels−Alder product under similar experimental conditions.

Although (S_c,S_p)-**5** is stable both in the solid and in solution, it is highly soluble in most organic solvents and could not be induced to crystallize. Treatment of the perchlorate salt with concentrated sulfuric acid at room temperature removed the naphthylamine auxiliary chemoselectively. Upon additon of excess lithium chloride into the acidic solution, the dichloro complex (S_p)-**6** was obtained as pale yellow prisms in 58% yield, $[\alpha]_D = +59.4°$ ($c = 0.2$, CH_2Cl_2). In agreement with its syn−exo stereochemistry, the ^{31}P NMR spectrum of (S_p)-**6** in $CDCl_3$ exhibited a sharp singlet at δ 99.5.[7,14] The chelating properties and the absolute configuration of the coordinated pyridine-substituted phosphine ligand in complex (S_p)-**6** were studied by X-ray crystallography (Figure 2). Selected bond distances and angles of the complex are given in Table 1. The structure analysis establishes the absolute stereochemistries at the newly generated P(1), C(7), C(10), and C(11) centers to be *S*, *S*, *R*, and *S*, respectively. The geometry at palladium is slightly distorted square planar with angles at Pd(1) in the ranges 85.2(1)−92.1(2)° and 173.9(1)−197.6(2)°. The small C−P−C bridgehead angle (81.9(3)°) is a characteristic feature of this class of phosphornorbornene chelates. Both the Pd−P and Pd−N bond lengths, 2.205(2) and 2.066(5) Å, are typical, but the two Pd−Cl distances (2.281(2) and 2.394(2) Å) differ significantly, with the bond trans to the phosphorus being noticeably larger than normal. This reflects the stronger electronic trans effect of the phosphorus relative to the aromatic nitrogen donor.

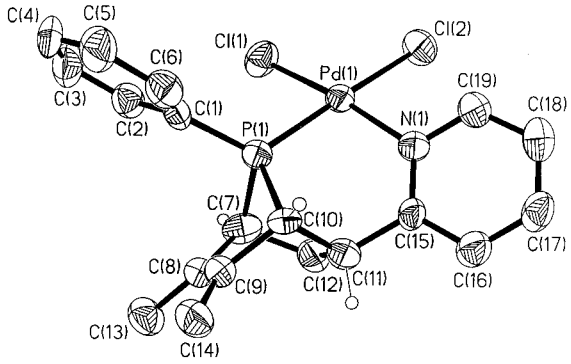

Figure 2. Molecular structure and absolute configuration of (S_p)-**6**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for (S_p)-6

Pd(1)−P(1)	2.205(2)	Pd(1)−N(1)	2.066(5)
Pd(1)−Cl(1)	2.281(2)	Pd(1)−Cl(2)	2.394(2)
P(1)−C(1)	1.800(7)	P(1)−C(7)	1.841(7)
P(1)−C(10)	1.844(6)	C(8)−C(9)	1.311(9)
C(11)−C(12)	1.539(10)	C(11)−C(15)	1.511(9)
N(1)−C(15)	1.342(8)	N(1)−C(19)	1.361(9)
P(1)−Pd(1)−N(1)	90.8(2)	P(1)−Pd(1)−Cl(1)	85.2(1)
P(1)−Pd(1)−Cl(2)	173.9(1)	N(1)−Pd(1)−Cl(1)	174.6(2)
N(1)−Pd(1)−Cl(2)	92.1(2)	C(7)−P(1)−C(10)	81.9(3)
C(7)−C(8)−C(9)	112.1(7)	C(8)−C(9)−C(10)	110.6(6)
C(10)−C(11)−C(12)	106.2(6)	C(11)−C(12)−C(7)	106.4(6)
N(1)−C(15)−C(11)	120.9(6)	C(10)−C(11)−C(15)	109.4(5)
C(12)−C(11)−C(15)	117.7(6)	C(15)−N(1)−C(19)	118.8(6)

The liberation of free (R_p)-*exo*-**1** from (S_p)-**6** was achieved by the treatment of the dichloro complex with aqueous potassium cyanide. Thus, the pyridylphosphine was obtained as a highly air-sensitive white solid in 81%, $[\alpha]_D = -52.5°$ ($c = 2.6$, CH_2Cl_2). The ^{31}P NMR spectrum of the free pyridylphosphine in $CDCl_3$ exhibited a sharp singlet at δ 90.7. The low-field ^{31}P resonance indicates that the syn−exo stereochemistry is retained. It is noteworthy that the apparent inversion of configuration that takes place at the bridgehead phosphorus stereogenic center during the liberation process is merely a consequence of the Cahn−Ingold−Prelog (CIP) rules.[15] Stereospecific displacement of (R_p)-*exo*-**1** from (S_p)-**6** was confirmed by the quantitative repreparation of (S_c,S_p)-**5** from the liberated pyridylphosphine with (S_c)-**2**. The 202 MHz ^{31}P NMR spectrum of the crude product indicated the presence of (S_c,S_p)-**5** only.

Endo-Cycloaddition Reaction: Synthesis of (R_p)-*endo*- and (S_p)-*endo*-1. As intimated earlier, the palladium- and platinum-complex-promoted cycloaddition reactions between dmpp and various dienophiles invariably produce the corresponding exo-cycloadducts. Thus far, no endo-cycloadducts have been produced by these organopalladium-complex-catalyzed reactions. We were, therefore, surprised to find that the coordinated cyclic diene in the chloro complex (S_c)-**3** reacted smoothly

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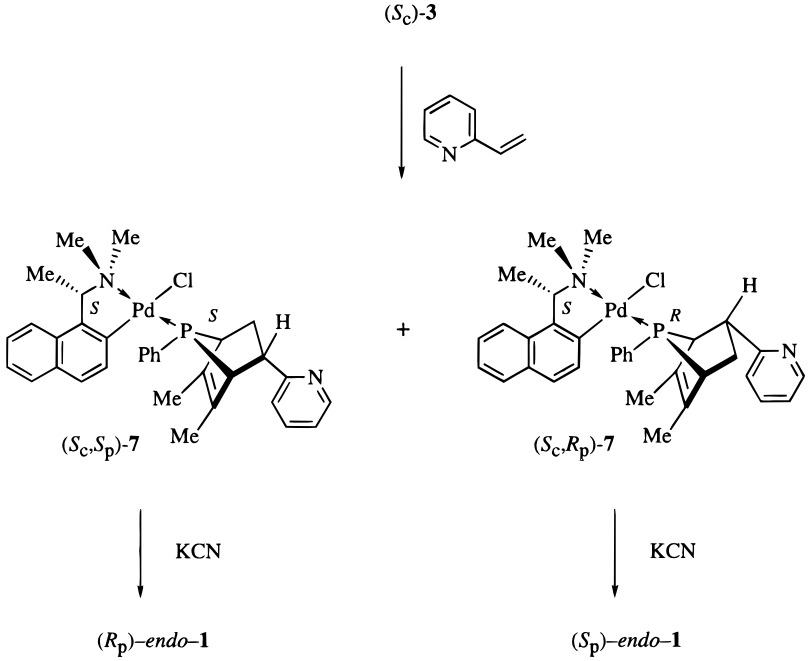
Scheme 2



with 2-vinylpyridine to give a 1:1 diastereomeric mixture of two endo-cycloaddition products (S_c,R_p)- and (S_c,S_p)-**7** (Scheme 2). A further dramatic observation was the relatively fast reaction rate associated with the endo-cycloaddition process: the reaction was found to be complete in 4 days as compared with the lengthy 20 days period required for the exo-cycloaddition reaction under similar reaction conditions. Prior to purification, the ^{31}P NMR spectrum of the crude endo-cycloaddition products in $CDCl_3$ exhibited two sharp singlets of about equal intensities at δ 122.0 and 123.8. Importantly, no ^{31}P NMR signal due to the exo-cycloadduct (S_c,S_p)-**5** was detected.

The endo diasteromer (S_c,S_p)-**7** was isolated efficiently as pale yellow prisms in 94% yield by fractional crystallization from acetone−diethyl ether, $[\alpha]_{436} = -93.1°$ (c = 3.0, CH_2Cl_2). The diastereomeric analogue (S_c,R_p)-**7** was highly soluble in most organic solvents and could not be induced to crystallize. The ^{31}P NMR spectrum of the crystalline (S_c,S_p)-**7** in $CDCl_3$ exhibited a characteristic sharp singlet at δ 122.0. The single-crystal X-ray analysis of (S_c,S_p)-**7** unambiguously established the coordination chemistry of the endo-substituted pyridylphosphine ligand (Figure 3). The analysis reaffirms that, as described, the pyridyl-functional group is attached at the endo position of the newly generated phosphornorbornene skeleton and the endo cycloadduct is coordinated to palladium as a monodentate ligand via its phosphorus donor atom only. The aromatic nitrogen donor is not involved in metal complexation. The absolute stereochemistries at the five chiral centers C(11), P(14), C(15), C(18), and C(20) are *S*, *S*, *R*, *S*, and *R*, respectively. As expected from a monodentate ligand, the Pd−P(14) bond (2.228(1) Å) in (S_c,S_p)-**7** is longer than its counterpart in (S_p)-**6** (2.205(2) Å) (Tables 1 and 2). The Pd−N bond distance (2.156(3) Å) in the orthometalated naphthylamine chelate in (S_c,S_p)-**7** is also longer than its counterpart (2.066(5) Å) in the chelating ligand in complex (S_p)-**6**. It is noteworthy that the

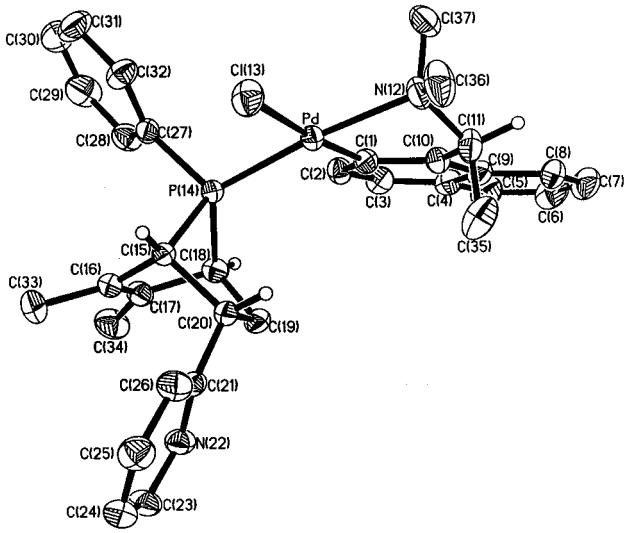


Figure 3. Molecular structure and absolute configuration of (S_c,S_p)-**7**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (S_c,S_p)-7

Pd−P(14)	2.228(1)	Pd−N(12)	2.155(3)
Pd−Cl(13)	2.403(1)	Pd−C(1)	2.008(3)
P(14)−C(15)	1.845(3)	P(14)−C(18)	1.854(3)
P(14)−C(27)	1.817(3)	C(16)−C(17)	1.334(3)
C(19)−C(20)	1.552(5)	C(20)−C(21)	1.513(5)
N(22)−C(21)	1.333(4)	N(22)−C(23)	1.343(5)

P(14)−Pd−N(12)	174.1(1)	P(14)−Pd−Cl(13)	89.9(1)
P(14)−Pd−C(1)	94.7(1)	N(12)−Pd−Cl(13)	95.0(1)
N(12)−Pd−Cl(13)	95.0(1)	N(12)−Pd−C(1)	80.5(1)
Cl(13)−Pd−C(1)	175.1(1)	C(15)−P(14)−C(18)	81.2(2)
C(15)−C(16)−C(17)	111.2(3)	C(16)−C(17)−C(18)	110.2(3)
C(15)−C(20)−C(21)	109.1(3)	C(18)−C(19)−C(20)	106.5(3)
C(15)−C(20)−C(19)	105.1(3)	C(21)−C(20)−C(19)	117.2(3)
N(22)−C(21)−C(20)	118.9(3)	C(21)−N(22)−C(23)	117.0(4)

C−P−C angles in both palladium complexes are similar (81.9(3)° in (S_p)-**6** and 81.2(2)° in (S_c,S_p)-**7**). The structural analyses reveal that these contraced bond angles are the unique features of the phosphornorbornene

framework and they are not affected significantly by metal chelation.

The free endo-pyridylphosphine ligand (R_p)-*endo*-**1** can be liberated directly from (S_c,S_p)-**7** by treating a dichloromethane solution of the chloro complex with aqueous cyanide. After the removal of the naphthylamine auxiliary with dilute sulfuric acid, the optically active cycloadduct was obtained as an air-sensitive pale yellow solid with $[\alpha]_D = -7.0°$ (c = 1.0, CH_2Cl_2). Significantly, the ^{31}P NMR spectrum of the free (R_p)-*endo*-**1** in $CDCl_3$ exhibited the expected low-field sharp singlet at δ 107.6, which reaffirms the syn−endo stereochemistry of the liberated cycloadduct.

The stereospecific displacement of (R_p)-*endo*-**1** from the organopalladium reaction promoter was established by the quantitative repreparation of (S_c,S_p)-**7** from the liberated ligand and (S_c)-**2**: the ^{31}P NMR spectrum of the crude product in $CDCl_3$ exhibited the presence of only one singlet at δ 122.0. As a further check, a diastereomeric complex (R_c,S_p)-**7** was prepared from liberated (R_p)-*endo*-**1** and the equally accessible (R_c)-**2**. The ^{31}P NMR spectrum of the crude product in $CDCl_3$ showed an entirely different signal at δ 128.8, which is identical to that recorded for the soluble (S_c,R_p)-**7** diastereomer produced directly from the Diels−Alder reaction. No resonance signal could be detected at the δ 122.0 position, thus reaffirming that the liberated (R_p)-*endo*-**1** is enantiomerically pure. Partially resolved (S_p)-*endo*-**1** was liberated similarly from (S_c,R_p)-**7** by treatment with aqueous cyanide. The free ligand was purified by recoordination to (R_c)-**2**, forming the highly crystalline complex (R_c,R_p)-**7** from which pure (S_p)-*endo*-**1** was liberated, $[\alpha]_D = +7.0°$ (c = 1.0, CH_2Cl_2). Alternatively, the pure (+)-endo cycloadduct was obtained directly from the Diels−Alder reaction between dmpp and 2-vinylpyridine by using (R_c)-**2** as the chiral rection promoter.

Conclusion

In view of the stereochemistry of (S_c,S_p)-**5**, it is clear that this exo cycloadduct was generated via an intramolecular cycloaddition mechanism in which both the cyclic diene and the dienophile were coordinated simultaneously to the palladium template during the course of the cycloaddition reaction. Due to the close interaction of both of the reaction precursors with the chiral template, the optically exo cycloadduct (S_c,S_p)-**5** was obtained in a highly stereoselective manner. On the other hand, the endo cycloadducts (S_c,R_p)- and (S_c,S_p)-**7** were generated via an intermolecular mechanism in which only the dmpp was coordinated to the metallic reaction promoter during the course of reaction. Despite the fact that the pyridyl function is a potential ligand for palladium(II), the geometrical restrictions associated within the two diasteromeric endo complexes precluded any possible metal complexation of 2-vinylpyridine in the reaction transition state. Clearly, the kinetic stability of the chloro ligand in (S_c)-**3** dictates the intermolecular mechanism and hence discriminates the formation of the exo cycloadducts. Furthermore, the lack of dienophile−template interaction in the endo cycloaddition process causes the nondiscriminative formation of the two nonequivalent endo cycloadducts. Due to the electron deficiency in the cationic transition state of the exo-cycloaddition reaction, however, the cyclic diene is poorly activated and, hence, a very slow reaction rate is observed.[16] Such a low degree of activation also precludes the dmpp from undergoing the potential competing intermolecular endo-cyloaddition reaction. In contrast, during the course of the endo-cycloaddition reaction, dmpp received a higher degree of activation from the neutral template and, hence, a faster reaction rate was observed. Recently, we found that these electronic and steric designs can be extended to the controlled formation of the exo and endo cycloadducts from the analogous reaction between dmpp and ethyl vinyl ketone.[17] Studies on other dienophiles containing various types of donor atoms and different functional groups are currently in progress.

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 enantiomerically pure forms of bis(μ-chloro)bis-[(*R*/*S*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*]dipalladium(II) dichloromethane solvate,[18] **2**, chloro(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*][3,4-dimethyl-1-phenylphosphole-*P*]palladium(II),[12] (S_c)-**3**, and perchlorato(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*][3,4-dimethyl-1-phenylphosphole-*P*]palladium (II),[12] (S_c)-**4**, were prepared according to literature methods. 2-Vinylpyridine and silica gel-60 were used as obtained from commercial sources.

Dichloro{2-[(1α,2α(S),4α,7*S*)-5,6-dimethyl-7-phenyl-7-phosphabicyclo [2.2.1]-hept-5-ene-2-yl]pyridine-*N*^{1},*P*^{2}}-palladium(II), [(S_p)-6]. A solution of the chloro complex (S_c)-**3** (3.0 g) in 1,2-dichloroethane (20 mL) was treated with silver perchlorate (1.3 g) in water (1 mL) for 30 min. The resulting mixture was filtered through a layer of Celite to remove silver chloride, and the pale yellow organic layer was dried over anhydrous $MgSO_4$. Excess 2-vinylpyridine (2.5 g) was added to the dried complex solution, and the reaction mixture was stirred for 20 days at 75 °C. The solvent was removed under reduced pressure to give a black residue. This material was chromatographed on a silica gel column (50 g, Merck, 40−63 μm) with dichloromethane−ethyl acetate (4:1 v/v) as eluant, giving the perchlorate salt (S_c,S_p)-**5** as a pale yellow glass (1.4 g, 35%) that could not be crystallized from any of the solvents tried: ^{31}P NMR ($CDCl_3$) δ 106.2 (s). The cationic complex (0.4 g) was treated with concentrated sulfuric acid (70%, 3 mL) for 0.5 h, and the acidic solution was poured onto ice (ca. 4 g). Lithium chloride (0.8 g) was then added, and the mixture was stirred for 1 h. Addition of dichloromethane (20 mL) gave a clear yellow organic layer, which was subsequently separated, and the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with water and then dried over anhydrous $MgSO_4$. Removal of solvent and recrystallization from methanol gave the dichloro complex (S_p)-**6** as pale yellow prisms: mp 234−236 °C (dec); $[\alpha]_D = +59.4°$ (c = 0.2, CH_2Cl_2); 0.16 g (57.4%

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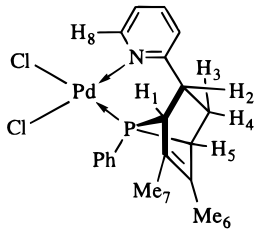
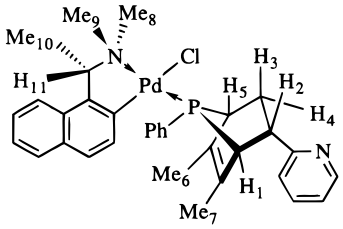
yield). Anal. Calcd for $C_{19}H_{20}Cl_2NPPd$: C, 48.6; H, 4.3; N, 3.0. Found: C, 48.8; H, 4.4; N, 3.3. ^{31}P NMR ($CDCl_3$) δ 99.5 (s); ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 3H, *Me*$_7$), 1.74 (s, 3H, *Me*$_6$), 2.39 (ddd, 1H, $^3J_{PH} = 36.5$, $^3J_{HH} = {}^2J_{H'H} = 12.0$ Hz, H_4), 2.59 (m, 1H, H_1), 3.34 (ddd, 1H, $^3J_{PH} = 23.7$, $^3J_{HH} = 9.4$, $^3J_{H'H} = 4.3$ Hz, H_2), 3.70 (m, 1H, H_5), 3.88 (bd, 1H, $^2J_{H'H} = 12.0$ Hz, H_3), 7.30−7.85 (m, 8H, *aromatics*), 9.70 (d, 1H, $^2J_{HH} = 5.2$ Hz, H_8). It is noteworthy that upon isolating (S_p)-**6**, the naphthylamine auxiliary could be recovered from the aqueous layer by neutralization for future use.[19]



Chloro{(*S*)-1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},*N*}-{2-[(1α,2*β*(*R*), 4α,7*S*)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]-hept-5-ene-2-yl]pyridine-*N*^{1},*P*^{2}}palladium-(II), [(S_c,S_p)-7]. A mixture of the chloro complex (S_c)-**3** (1.3 g) and 2-vinylpyridine (1 g) in 1,2-dichloroethane (20 mL) was then stirred for 4 days at 75 °C. Removal of the solvent gave the crude diastereomeric product mixture (S_c,R_p)- and (S_c,S_p)-**7** as a pale yellow glass: ^{31}P NMR ($CDCl_3$) δ 122.0 (s), 123.8 (s). Repeated dissolution of the crude product in acetone followed by slow addition of diethyl ether yielded pure (S_c,S_p)-**7** as pale yellow prisms: mp 158−159 °C; $[\alpha]_{436} = -93.1°$ ($c = 3.0$, CH_2Cl_2); 0.64 g (94% yield). Anal. Calcd for $C_{33}H_{36}ClN_2PPd\cdot 0.5$ diethyl ether: C, 62.6; H, 5.7; N, 4.4; P, 4.9. Found: C, 62.3; H, 6.1; N, 4.4; P, 4.9. ^{31}P NMR ($CDCl_3$) δ 122.0 (s); ^{1}H NMR ($CDCl_3$) δ 0.92 (s, 3H, *Me*$_7$), 1.80 (s, 3H, *Me*$_6$), 1.93 (d, 3H, $^3J_{HH} = 6.4$ Hz, *Me*$_{10}$), 2.40 (dddd, 1H, $^3J_{PH} = 34.0$, $^2J_{HH} = 12.3$, $^3J_{H'H} = 5.0$, $^3J_{H''H} = 1.5$ Hz, H_4), 2.53 (m, 1H, H_3), 2.57 (d, 3H, $^4J_{PH} = 1.1$ Hz, *Me*$_9$), 2.91 (d, 3H, $^4J_{PH} = 3.0$ Hz, *Me*$_8$), 3.14 (s, 1H, H_1), 3.85 (m, 1H, H_5), 4.27 (qn, 1H, $^3J_{HH} = {}^4J_{PH} = 6.1$ Hz, H_{11}), 5.09−5.10 (m, 1H, H_2), 7.04−8.43 (m, 15H, *aromatics*).



2-[(1α,2α(*S*),4α,7*R*)-5,6-Dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]-hept-5-ene-2-yl]pyridine, [(R_p)-*exo*-1]. A solution of (S_p)-**6** (0.8 g) in dichloromethane (100 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (2 g) for 30 min. The resulting colorless organic layer was separated, washed with water and then dried ($MgSO_4$). Upon removal of solvent, a highly air-sensitive low-melting solid was obtained: $[\alpha]_D = -52.5°$ ($c = 2.6$, CH_2Cl_2); 0.42 g (81% yield). ^{31}P NMR ($CDCl_3$) δ 90.7 (s). Due to its stereodynamic instability, the free ligand was not isolated and was immediately used for recomplexation reactions.[20]

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Table 3. Crystallographic Data for Complexes (S_p)-6 and (S_c,S_p)-7

	(S_p)-**6**	(S_c,S_p)-**7**
formula	$C_{19}H_{20}Cl_2NPPd$	$C_{33}H_{36}ClN_2PPd\cdot 0.5Et_2O$
fw	470.63	670.52
space group	$P2_12_12_1$	$P2_12_12_1$
cryst syst	orthorhombic	orthorhombic
a/Å	8.111(1)	11.896(2)
b/Å	11.591(1)	14.154(1)
c/Å	20.622(1)	21.398(4)
V/Å^3	1938.8(1)	3594.6(9)
Z	4	4
T/K	293	293
ρ_{calcd}/g cm^{-3}	1.612	1.239
λ/Å	0.710 73 (Mo)	0.710 73 (Mo)
μ/cm^{-1}	13.16	6.6
R_1 (obsd data)[a]	0.0580	0.0316
wR_2 (obsd data)[b]	0.0992	0.0978

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

2-[(1α,2*β*(*R*),4α,7*S*)-5,6-Dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]-hept-5-ene-2-yl]pyridine, [(R_p)-*endo*-1]. A solution of (S_c,S_p)-**7** (0.5 g) in dichloromethane (10 mL) was stirred vigorously with a saturated aqueous solution of potassium cyanide (5.0 g) for 2 h. The resulting colorless organic layer was separated, washed successively with water (4 × 20 mL), dilute sulfuric acid (0.5M, 20 mL), and water (2 × 20 mL), and then dried ($MgSO_4$). Upon removal of solvent, a highly air-sensitive low-melting solid was obtained: $[\alpha]_D = -7.0°$ ($c = 0.3$, CH_2Cl_2); 0.14 g (60% yield); ^{31}P NMR ($CDCl_3$) δ 107.6 (s).

Crystal Structure Determination of (S_p)-6 and (S_c,S_p)-7. Crystal data and a summary of the crystallographic analyses for (S_p)-**6** and (S_c,S_p)-**7** are given in Table 3. For both complexes, independent reflections were measured on a Siemens SMART CCD diffractometer with Mo Kα radiation (graphite monochromator) using ω-scans. For (S_p)-**6**, a yellow prism with dimensions 0.20 × 0.10 × 0.05 mm was selected. A total of 4772 [$R = 0.0861$] independent reflections were collected. All non-hydrogen atoms were refined anisotropically. Full-matrix least-squares refinement on F^2 with absorption corrected data gave $R_1 = 0.0580$, $wR_2 = 0.0992$ for 4772 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$, $1.98 \le \theta \le 29.38°$] and 218 parameters. The absolute stereochemistry was determined unambiguously by refining the Flack parameter [$x = -0.03(5)$]. For (S_c,S_p)-**7**, a pale yellow block with dimensions 0.50 × 0.50 × 0.33 mm was used. There were 7358 unique reflections measured ($2\theta \le 54°$), and the stucture was solved by direct methods with all the non-hydrogen atoms refined anisotropically. Refinements were by full-matrix least squares based on F^2. The absolute stereochemistry was determined by use of the Flack parameter [$x = 0.02(3)$].

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Supporting Information Available: 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 for (S_p)-**6** and (S_c,S_p)-**7** (14 pages). Ordering information is given on any current masthead page.

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