Organometallics **2002,** *21,* 5301−5306

Organopalladium Complex Promoted Asymmetric Cycloaddition Reactions Involving 3,4-Dimethyl-1-phenylphosphole 1-Sulfide as the Heterocyclic Diene

Ying Qin,[1a] Selvasothi Selvaratnam,[1b] Jagadese J. Vittal,[1a] and
Pak-Hing Leung*,[1a]

Department of Chemistry and Chemical and Process Engineering Centre, National University of Singapore, Kent Ridge, Singapore, 119260

Received August 20, 2002

3,4-Dimethyl-1-phenylphosphole 1-sulfide (DMPPS) reacted as a heterocyclic diene in the asymmetric Diels−Alder reaction with diphenylvinylphosphine in the presence of an organopalladium(II) complex derived from the enantiomerically pure ortho-metalated (*R*)-(1-(dimethylamino)ethyl)naphthalene. The cycloaddition reaction proceeded at room temperature via an intramolecular mechanism in which the cyclic diene and the dienophile were coordinated simultaneously on the chiral palladium template. The (R_P)-exo cycloadduct was obtained with high stereoselectivity as a P−S bidentate chelate on the palladium template. When DMPPS was treated with the heterodienophile thiobenzophenone at 50 °C in the presence of the organopalladium(II) complex, the corresponding heterocycloaddition reaction proceeded to generate the expected cycloadduct as a rigid S−S bidentate chelate on the palladium template. However, the cyclic adduct was obtained as a racemic mixture. The low stereoselectivity in the heterocycloaddition reaction is attributed to the kinetic instability of S→Pd coordination bonds in the intermediate template complex. Both the P−S and S−S cycloadducts could be liberated from the corresponding template complexes by treatment of the template complexes with aqueous potassium cyanide.

Introduction

Recently, we have reported a series of asymmetric Diels−Alder reactions between the heterocyclic diene 3,4-dimethyl-1-phenylphosphole (DMPP) and various dienophiles with an optically pure organopalladium(II) complex acting as a reaction promoter.[2] It is commonly observed that, in the absence of the palladium reaction promoter, DMPP is inert to cycloaddition reactions. It has been established that the aromaticity within the five-membered ring deters the reactivity of phosphole as a conjugated diene in the Diels−Alder reaction.[3] Furthermore, the numerous side reactions that occur between the uncoordinated phosphorus lone pair in phosphole and the dienophiles preclude the formation of the desired cycloadducts.[3]

As analogues of DMPP, 3,4-dimethyl-1-phenylphosphole 1-sulfide (DMPPS) and 3,4-dimethyl-1-phenylphosphole 1-oxide (DMPPO) have also been subjects of much investigation. In contrast to DMPPO, which undergoes rapid dimerization at room temperature, DMPPS does not dimerize easily.[4] Therefore, it would be practically easier to control the reactivity of the phosphole dienic system in DMPPS with selected dienophiles. The potential of phosphole sulfide in cycloaddition reactions, coupled with its rich coordination chemistry,[5] has initiated much interest in this phosphorus(V) compound.[6,7] In the documented cycloaddition reactions involving DMPPS, however, prolonged and strong heating conditions were generally required. Furthermore, no asymmetric cycloaddition reaction involving DMPPS has been reported so far. The desired reactivity of DMPPS, coupled with our interest in chiral phosphanorbornene chemistry, prompted us to examine the asymmetric cycloaddition reaction of this phosphole sulfide.

Results and Discussion

Metal Template Promoted Cycloaddition of Diphenylvinylphosphine with DMPPS. The diphenylvinylphosphine palladium complex (R_C)-**1** reacted with 1 equiv of DMPPS to give a mixture of the diastereomers (R_C,R_P)- and (R_C,S_P)-**2** (Scheme 1). Prior to isolation, the ^{31}P NMR spectrum of the crude product in CDCl$_3$ exhibited four singlets at δ 53.5, 77.7 and δ 59.8, 80.0 in the ratio of 6:6:1:1. The low field signals

---

[1] (a) Department of Chemistry. (b) Chemical and Process Engineering Centre.

[2] Leung, P. H.; Lang, H.; Zhang, X.; Selvaratnam, S.; Vittal, J. J. *Tetrahedron: Asymmetry* **2000**, *11*, 2661. Leung, P. H.; He, G.; Lang, H.; Liu, A.; Loh, S.; Selvaratnam, S.; Mok, K. F.; White, A. J. P.; Williams, D. J. *Tetrahedron* **2000**, *56*, 7.

[3] Mattmann, E.; Simonutti, D.; Ricard, L.; Mercier, F.; Mathey, F. *J. Org. Chem.* **2001**, *66*, 755.

[4] Mathey, F. *Chem. Rev.* **1988**, *88*, 429.

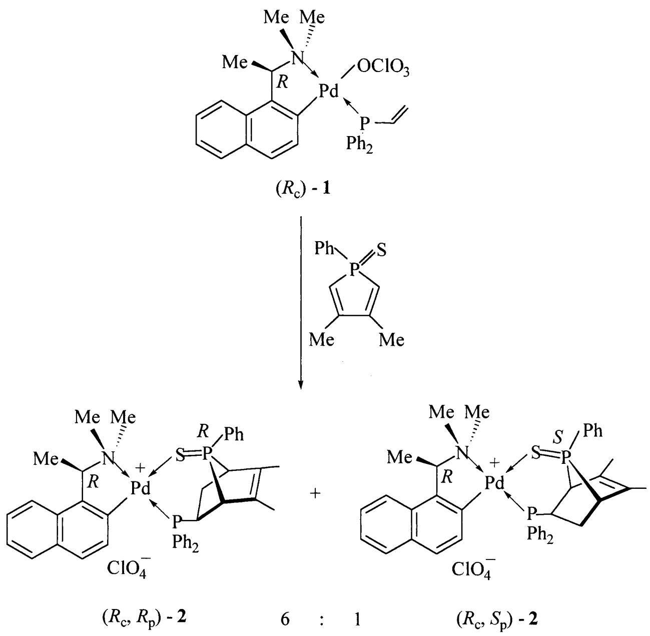
[5] Deschamps, B.; Ricard, L.; Mathey, F. *Phosphorus, Sulfur Silicon Relat. Elem.* **1997**, *123*, 119.

[6] Kashman, Y.; Awerbouch, O. *Tetrahedron* **1975**, *31*, 53. Kashman, Y.; Awerbouch, O. *Tetrahedron* **1973**, *29*, 191. Kashman, Y.; Wagenstein, I.; Rudi, A. *Tetrahedron* **1976**, *32*, 2427.

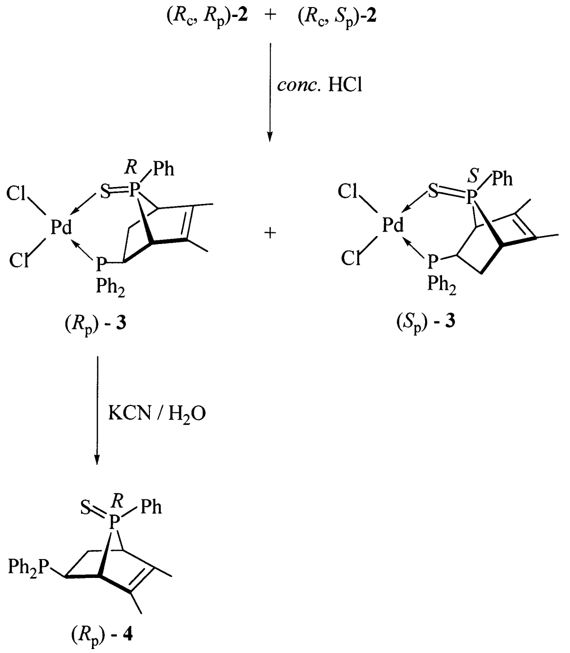
[7] Mathey, F.; Mercier, F. *Tetrahedron Lett.* **1981**, *22*, 319. Rösch, W.; Regitz, M. *Z. Naturforsch. B: Anorg. Chem., Org. Chem* **1986**, *41B*(7), 931.

10.1021/om020682u CCC: $22.00
Publication on Web 11/02/2002

Scheme 1



Scheme 2



at δ 77.7 and 80.0 are typical for a bridgehead phosphorus adopting the exo-syn stereochemistry. The ^{31}P NMR spectrum thus revealed that the two possible diastereomers were generated as a 1:6 mixture. Unfortunately, efforts to separate the two isomers directly via column chromatography or fractional crystallization were unsuccessful.

To isolate the cycloadducts in their enantiomerically pure forms, the chiral naphthylamine auxiliary in the diastereomeric mixture was then removed chemoselectively by stirring an acetone solution of the 1:6 diastereomeric mixture $(R_C,R/S_P)$-**2** with concentrated hydrochloric acid at room temperature (Scheme 2). The dichloro complex that precipitated out of solution was recrystallized twice from dichloromethane−hexane as orange prisms in 25% yield; $[\alpha]_{546} = -10.0°$ (c 0.2, CH_2Cl_2). The ^{31}P NMR spectrum of the complex in CD_2Cl_2 exhibited two sharp singlets at δ 48.9 and 77.3.

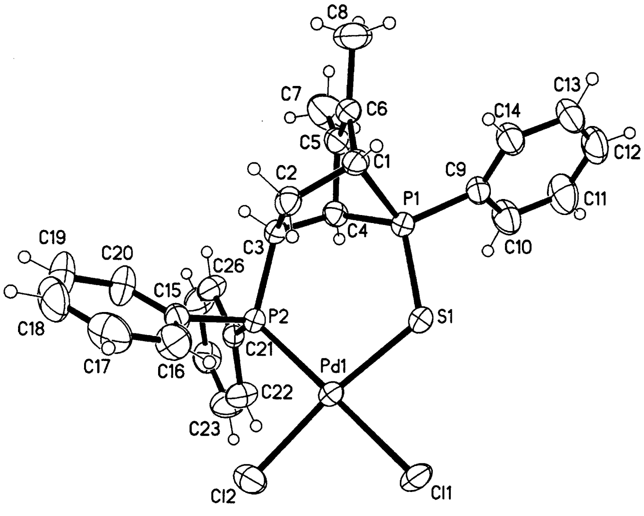


Figure 1. Molecular structure and absolute stereochemistry of (R_P)-**3**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of (R_P)-3

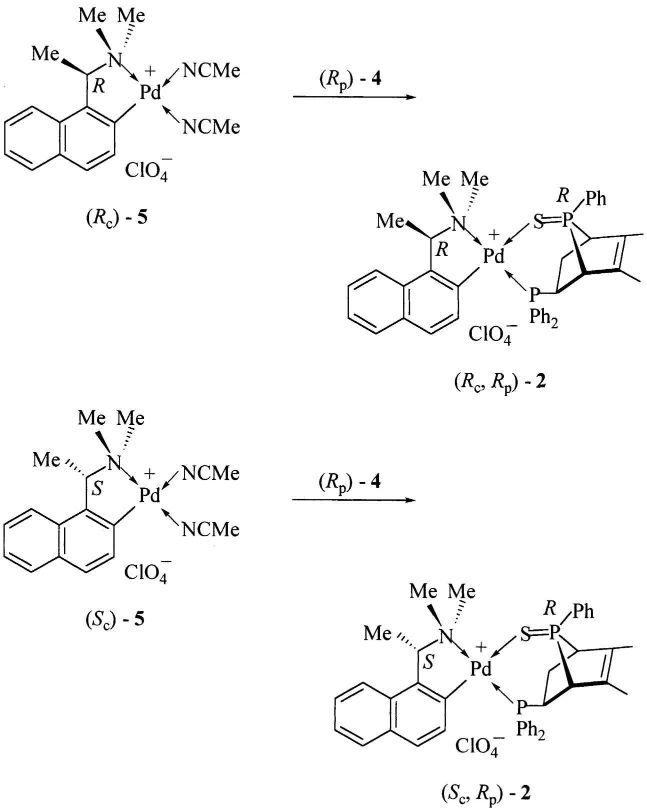
Pd(1)−P(2)	2.242(1)	Pd(1)−S(1)	2.299(1)
Pd(1)−Cl(2)	2.308(1)	Pd(1)−Cl(1)	2.374(1)
S(1)−P(1)	2.002(1)	P(1)−C(9)	1.794(2)
P(1)−C(4)	1.826(2)	P(1)−C(1)	1.827(2)
P(2)−C(15)	1.821(2)	P(2)−C(21)	1.825(2)
P(2)−C(3)	1.840(2)	C(2)−C(3)	1.560(2)
P(2)−Pd(1)−S(1)	99.3(1)	P(2)−Pd(1)−Cl(2)	89.0(1)
S(1)−Pd(1)−Cl(2)	171.0(1)	P(2)−Pd(1)−Cl(1)	176.7(1)
S(1)−Pd(1)−Cl(1)	81.7(1)	Cl(2)−Pd(1)−Cl(1)	90.2(1)
P(1)−S(1)−Pd(1)	116.8(1)	C(4)−P(1)−C(1)	83.0(1)
C(4)−P(1)−S(1)	116.5(1)	C(3)−P(2)−Pd(1)	116.9(1)
C(4)−C(3)−P(2)	116.2(1)	C(3)−C(4)−P(1)	100.5(1)

The molecular structure and the absolute configurations of the recrystallized (R_P)-**3** were established by a single-crystal X-ray crystallographic analysis. The structural analysis revealed that the diphenylphosphino group is substituted at the exo position of the phosphanorbornene skeleton. The cycloadduct is coordinated to palladium(II) as a bidentate chelate via its phosphorus and sulfur donor atoms. The geometry at palladium is distorted square planar with angles at palladium in the ranges of 81.7(1)−99.3(1) and 171.0(1)−176.7(1)°. The absolute configurations of the four newly generated stereogenic centers at P(1), C(1), C(3), and C(4) are *R*, *R*, *S*, and *R*, respectively (Figure 1). Selected bond lengths and bond angles are given in Table 1. The bond angles within the six-membered chelate PdPS ring are in the range of 99.3(1)−116.9(1)°. The bond angle at the bridgehead phosphorus, C(4)−P(1)−C(1) (83.0(1)°), is similar to that observed in a related compound containing the *exo*-thioamide-substituted 7-phosphanorbornene P−S bidentate chelate.[8] The Pd−P bonds in (R_P)-**3** (2.242(1) Å) and in the amido-substituted complex (2.203(1) Å) are similar. However, the Pd(1)−S(1) bond length (2.299(1) Å) is noticeably shorter than that (2.382(1) Å) in the six-membered thioamide P−S bidentate chelate. Apparently, the P=S→Pd coordination in (R_P)-**3** is stronger than the NC=S→Pd bonds in the amido complex.

---

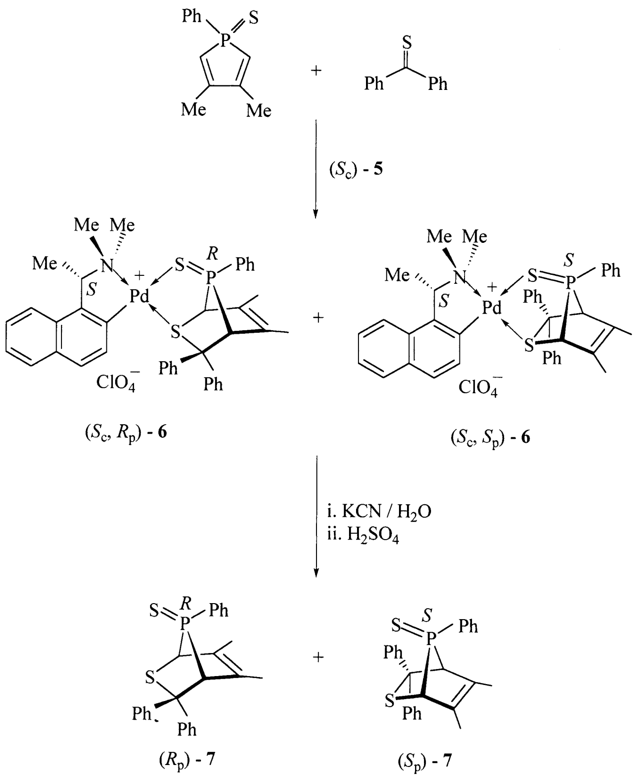
[8] Leung, P. H.; Qin, Y.; He, G.; Mok, K. F.; Vittal, J. J. *J. Chem. Soc., Dalton Trans.* **2001**, 309.

Scheme 3



Liberation and the Optical Purity of the P−S Cycloadduct ((R_P)-4. It is noteworthy that the optically active diphosphine ligand (R_P)-**4** can be stereospecifically liberated from (R_P)-**3** by treatment of the dichloro complex with aqueous potassium cyanide at room temperature (Scheme 2). Liberated (R_P)-**4** was obtained as a colorless viscous oil in 85 % yield, $[\alpha]_{546} = -4.5°$ (CH_2Cl_2). The ^{31}P NMR spectrum of the free ligand in CD_2Cl_2 exhibited two singlets at δ −14.3 and 89.1. The low-field ^{31}P resonance confirms that the exo-syn stereochemistry is retained.[9] Owing to the air sensitivity of the noncoordinated phosphorus atom, the liberated (R_P)-**4** cannot be stored in its pure form. Hence, the liberated ligand was recomplexed to selected metal ions to form stable metal complexes. To determine the optical purity of (R_P)-**4**, the liberated ligand was recoordinated to the bis(acetonitrile) complex (R_C)-**5** (Scheme 3). The recoordination process was monitored by 121 MHz ^{31}P NMR spectroscopy. In $CDCl_3$, the ^{31}P MNR spectrum of the crude recoordination product showed only two singlets at δ 53.5 and 77.7. These NMR signals are identical with those recorded for the major diastereomer generated from the original cycloaddition reaction. Thus, the diastereomer (R_C,R_P)-**2** is confirmed to be the major isomer in the Diels−Alder reaction. It is important to note that no ^{31}P NMR signals at δ 59.8 and 80.0 were observed. The absence of these signals indicated that (R_P)-**4** is enantiomerically pure. In a further check, (R_P)-**4** was recoordinated regiospecifically to (S_C)-**5** to generate the diastereomeric complex (S_C,R_P)-**2**. The ^{31}P NMR spectrum of the crude product in $CDCl_3$ showed only two singlets at δ 59.8 and 80.0. No ^{31}P NMR signals could be detected at δ 53.5 and 77.7, thus reaffirming that liberated (R_P)-**4** is stereochemically pure.

Scheme 4



Metal Template Promoted Cycloaddition of Thiobenzophenone with DMPPS. To examine whether DMPPS is able to react with a heterodienophile under the influence of the chiral palladium template, the cyclic diene was treated with thiobenzophenone in dichloromethane in the presence of a stoichiometric quantity of (S_C)-**5** (Scheme 4). The reaction was monitored by ^{31}P NMR spectroscopy and found to be complete in 12 h. Prior to purification, the ^{31}P NMR spectrum of the crude product in $CDCl_3$ exhibited two sharp singlets at δ 100.0 and δ 99.7, in the ratio of 1:1. The presence of two distinct NMR signals indicated that the two possible diastereomers of (S_C,R/S_P)-**6** were generated in similar quantities (Scheme 4). Attempts to separate the two diastereomeric products by column chromatography and by recrystallization using various solvent systems were not successful. The 1:1 mixture of (S_C,R_P)-**6** and (S_C,S_P)-**6** was subsequently crystallized from dichloromethane−diethyl ether as yellow prisms in 40% yields, $[\alpha]_D = +80°$ (c 0.3, CH_2Cl_2). Interestingly, the two diastereomers crystallized as two pairs of crystallographically independent molecules in the unit cell—two independent molecules of the diastereomer (S_C,R_P)-**6** and two of (S_C,S_P)-**6**. However, the two molecules in each pair have the same absolute stereochemistry and molecular connectivity and differ only slightly in their bond angles. For clarity, only one molecule (molecule **a**) of each diastereomer is depicted in Figures 2 and 3. Selected bond lengths and bond angles of the diastereomers are given in Table 2.

The X-ray analyses of (S_C,R_P)-**6** and (S_C,S_P)-**6** confirm that the desired diastereomeric cycloadducts were indeed produced in the heterocycloaddition reaction. The phosphanorbornene sulfides in both diastereomers co-

---

[9] Mathey, F.; Marinetti, A.; Mercier, F. *Synlett* **1992**, 385. Nelson, J. H. *Coord. Chem. Rev.* **1995**, *139*, 245.

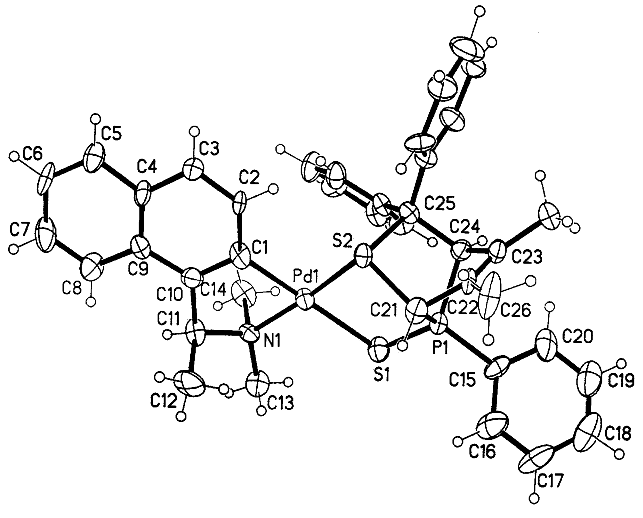


Figure 2. Molecular structure and absolute stereochemistry of (S_C,R_P)-**6**.

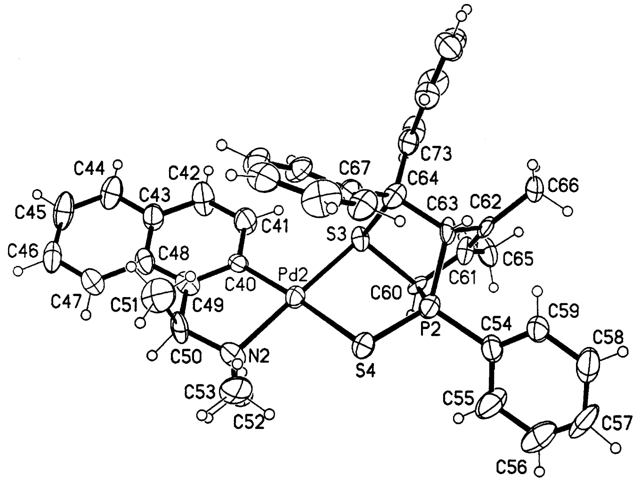


Figure 3. Molecular structure and absolute stereochemistry of (S_C,S_P)-**6**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for (S_C,R_P)-6 and (S_C,S_P)-6

(S_C,R_P)-**6** (molecule **a**)		(S_C,S_P)-**6** (molecule **a**)	
Pd(1)−C(1)	2.011(12)	Pd(2)−C(40)	2.003(12)
Pd(1)−N(1)	2.083(10)	Pd(2)−N(2)	2.093(11)
Pd(1)−S(2)	2.266(3)	Pd(2)−S(3)	2.308(3)
Pd(1)−S(1)	2.468(3)	Pd(2)−S(4)	2.445(3)
P(1)−C(21)	1.838(13)	P(2)−C(60)	1.819(14)
P(1)−C(24)	1.847(12)	P(2)−C(63)	1.840(13)
P(1)−S(1)	1.984(5)	P(2)−S(4)	1.999(5)
S(2)−C(21)	1.851(13)	S(3)−C(60)	1.855(11)
S(2)−C(25)	1.893(11)	S(3)−C(64)	1.918(12)
C(22)−C(23)	1.362(18)	C(61)−C(62)	1.231(18)
C(24)−C(25)	1.577(17)	C(63)−C(64)	1.569(17)
C(1)−Pd(1)−N(1)	83.0(4)	C(40)−Pd(2)−N(2)	81.9(5)
C(1)−Pd(1)−S(2)	91.8(4)	C(40)−Pd(2)−S(3)	93.4(4)
C(1)−Pd(1)−S(1)	176.2(4)	C(40)−Pd(2)−S(4)	174.9(4)
N(1)−Pd(1)−S(2)	174.8(3)	N(2)−Pd(2)−S(3)	170.9(3)
N(1)−Pd(1)−S(1)	94.2(3)	N(2)−Pd(2)−S(4)	93.3(3)
S(2)−Pd(1)−S(1)	91.0(1)	S(3)−Pd(2)−S(4)	91.6(1)
C(21)−P(1)−C(24)	84.4(6)	C(60)−P(2)−C(63)	84.5(6)
C(15)−P(1)−S(1)	111.3(5)	C(54)−P(2)−S(4)	110.7(5)
P(1)−S(1)−Pd(1)	97.4(1)	P(2)−S(4)−Pd(2)	96.9(1)
C(21)−S(2)−C(25)	91.6(5)	C(60)−S(3)−C(64)	93.9(5)
C(21)−S(2)−Pd(1)	105.2(5)	C(60)−S(3)−Pd(2)	102.2(4)
C(25)−S(2)−Pd(1)	105.3(4)	C(64)−S(3)−Pd(2)	108.8(4)
C(23)−C(22)−C(21)	113.4(10)	C(62)−C(61)−C(60)	114.7(12)
C(22)−C(23)−C(24)	109.2(10)	C(61)−C(62)−C(63)	111.6(11)
C(24)−C(25)−S(2)	102.9(7)	C(63)−C(64)−S(3)	104.0(7)
(S_C,R_P)-**6** (molecule **b**)		(S_C,S_P)-**6** (molecule **b**)	
Pd(4)−C(118)	2.012(13)	Pd(3)−C(79)	2.018(13)
Pd(4)−N(4)	2.087(12)	Pd(3)−N(3)	2.110(11)
Pd(4)−S(7)	2.276(3)	Pd(3)−S(5)	2.287(3)
Pd(4)−S(8)	2.456(3)	Pd(3)−S(6)	2.447(3)
P(4)−C(138)	1.859(13)	P(3)−C(99)	1.846(13)
P(4)−C(141)	1.863(13)	P(3)−C(102)	1.874(13)
P(4)−S(8)	1.972(5)	P(3)−S(6)	1.971(5)
S(7)−C(138)	1.801(12)	S(5)−C(99)	1.870(14)
S(7)−C(142)	1.889(12)	S(5)−C(103)	1.910(11)
C(139)−C(140)	1.434(18)	C(100)−C(101)	1.345(18)
C(141)−C(142)	1.482(16)	C(102)−C(103)	1.599(18)
C(118)−Pd(4)−N(4)	81.5(5)	C(79)−Pd(3)−N(3)	81.3(5)
C(118)−Pd(4)−S(7)	92.2(4)	C(79)−Pd(3)−S(5)	92.9(4)
C(118)−Pd(4)−S(8)	175.1(4)	C(79)−Pd(3)−S(6)	172.6(4)
N(4)−Pd(4)−S(7)	173.7(3)	N(3)−Pd(3)−S(5)	164.7(3)
N(4)−Pd(4)−S(8)	94.9(3)	N(3)−Pd(3)−S(6)	96.6(3)
S(7)−Pd(4)−S(8)	91.4(1)	S(5)−Pd(3)−S(6)	90.8(1)
C(138)−P(4)−C(141)	81.3(6)	C(99)−P(3)−C(102)	82.8(6)
C(132)−P(4)−S(8)	110.9(5)	C(93)−P(3)−S(6)	112.2(5)
P(4)−S(8)−Pd(4)	97.4(2)	P(3)−S(6)−Pd(3)	97.8(2)
C(138)−S(7)−C(142)	92.5(6)	C(99)−S(5)−C(103)	95.5(6)
C(138)−S(7)−Pd(4)	106.1(5)	C(99)−S(5)−Pd(3)	103.8(4)
C(142)−S(7)−Pd(4)	106.5(4)	C(103)−S(5)−Pd(3)	108.8(4)
C(140)−C(139)−C(138)	106.5(11)	C(101)−C(100)−C(99)	111.0(11)
C(139)−C(140)−C(141)	112.0(11)	C(100)−C(101)−C(102)	113.5(11)
C(141)−C(142)−S(7)	106.0(8)	C(102)−C(103)−S(5)	102.4(7)

ordinate to the palladium templates as bidentate chelates via the two sulfur atoms with the P═S→Pd sulfur coordinated regioselectively cis to the NMe_2 group. The geometry at palladium is slightly distorted square planar in both isomers. In (S_C,R_P)-**6** the absolute configurations of the four newly generated stereogenic centers at P(1), S(2), C(21), and C(24) are *R*, *R*, *R*, and *R*, respectively (Figure 2). In (S_C,S_P)-**6** the P(2), S(3), C(60), and C(63) centers are *S*, *S*, *S*, and *S*, respectively (Figure 3). It is noted that the P═S bond distances in the four independent molecules (1.984(5) and 1.972(5) Å in (S_C,R_P)-**6a** and **-6b**, respectively, and 1.999(5) and 1.971(5) Å in (S_C,S_P)-**6a** and **-6b**, respectively) are similar to that recorded in (R_P)-**3** (2.002(1) Å). The two types of S→Pd bond distances in these molecules reveal that the P═S→Pd coordination bonds (2.468(3) and 2.456(3) Å in (S_C,R_P)-**6a** and **-6b**, respectively, and 2.445(3) and 2.447(3) Å in (S_C,S_P)- **6a** and **-6b**, respectively) are remarkably longer than their corresponding phosphanorbornene S→Pd counterparts (2.266(3) and 2,276(3) Å in (S_C,R_P)-**6a** and **-6b**, respectively, and 2.308(3) and 2.287(3) Å in (S_C,S_P)-**6a** and **-6b**, respectively). The differences in these two types of S→Pd bonds are consistent with the well-established trans effects originating from the ortho-metalated naphthylamine auxiliary.[10]

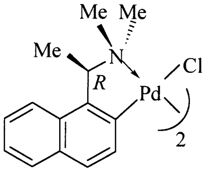
The bidentate S−S ligand can be liberated from the diastereomeric metal complexes. After treating the 1:1 diastereomeric mixture of (S_C,R_P)-**6** and (S_C,S_P)-**6** with aqueous potassium cyanide at room temperature, the racemic ligand **7** was liberated from the palladium template as an air-stable white solid in 85% yield

---

(10) Loh, S. K.; Mok, K. F.; Leung, P. H. *Tetrahedron: Asymmetry* **1996**, *7*, 45. Chooi, S. Y. M.; Tan, M. K.; Leung, P. H.; Mok, K. F. *Inorg. Chem.* **1994**, *33*, 3096. Song, Y.; Mok, K. F.; Leung, P. H. *Inorg. Chem.* **1998**, *37*, 6399. Chooi, S. Y. M.; Hor, T. S. A.; Leung, P. H.; Mok, K. F. *Inorg. Chem.* **1992**, *31*, 1494.

(Scheme 4). The ^{31}P NMR of the liberated ligand in $CDCl_3$ exhibited a sharp singlet at δ 85.0.

Interestingly, both diphenylvinylphosphine and thiobenzophenone failed to react with DMPPS when the chloro complex (R_C)-**8** was used directly to activate the cycloaddition. The *trans*-C−Pd−chloro moiety in this class of ortho-metalated naphthylamine complexes is well-known to be thermodynamically and kinetically stable. Apart from cyanide and other strong chelating agents, this chloro ligand generally cannot be displaced by other strong monodentate ligands such as tertiary phosphines and arsines.[11] Thus, only one template site is readily available on the chloro complex (R_C)-**8** at the *trans*-N−Pd−chloro position. On the other hand, when the chloro ligand on the ortho-palladated naphthylamine complex is replaced by a labile perchlorato ligand in the $AgClO_4$ treatment, as in the case of (R_C)-**1**, an additional template site becomes readily available. Evidently, the activation of the cycloaddition reactions by (R_C)-**1** involves the initial displacement of the perchlorato ligand to allow DMPPS and the reacting diphenylvinylphosphine to be coordinated simultaneously on the palladium template during the course of the intramolecular cycloaddition reaction. Thus, the resulting cycloadduct was obtained as a P−S bidentate chelate on the palladium template. In the heterocycloaddition reaction, the two labile acetonitrile ligands in (S_C)-**5** were displaced similarly by the reacting substrates to form the bidentate S−S cycloadduct. The heterobidentate cycloadducts in both reactions coordinated regiospecifically on the template complex. This regiospecificity can be attributed to the distinct electronic directing effects originating from the σ-donating nitrogen and the π-accepting aromatic carbon of the of ortho-metalated naphthylamine ring.[10] It is noteworthy that while the chiral naphthylamine auxiliary controlled the formation of the P−S cycloadduct (R_P)-**4** stereoselectively, the formation of the S−S adduct is nonstereoselective. The differences between the stereoselectivities of the two cycloaddition processes may be due to the fact that the two Pd−S bonds in the intermediate template complex in the hetero-Diels−Alder reaction containing the coordinated thiobenzophenone and DMPPS substrates are kinetically labile. Indeed, we have previously observed in similar amido-substituted palladium complexes that the C=S→Pd coordination bonds are highly labile.[8,12] On the other hand, the *trans*-N−Pd−P bonds in this class of naphthylamine complexes are known to be inert and stable. Thus, the intermediate complex in the homocycloaddition reaction containing diphenylvinylphosphine and DMPPS would be relatively more stable. As a result, a higher degree of stereoselectivity was observed when diphenylvinylphosphine was used as the dienophile. In conclusion, our current findings confirm that the activation of DMPPS can be achieved efficiently by using the ortho-palladated naphthylamine complex as the reaction activator. Investigations on the asymmetric cycloaddition reactions involving this cyclic diene are currently in progress.



(R_c) - **8**

Experimental Section

All manipulations involving air-sensitive compounds were carried out using standard Schlenk techniques. A Bruker ACF 300 spectrometer was used to record the ^1H (300 MHz) and ^{31}P (121 MHz) NMR spectra. Optical rotations were measured in the specified solutions in a 1 cm cell at specified temperatures with a Perkin-Elmer Model 341 polarimeter. Melting points were determined on an Electrothermal IA 9200 apparatus. Elemental analyses were performed by the Elemental Analysis Laboratory of the Department of Chemistry at the National University of Singapore.

The enantiomerically pure form of (R)-perchloro{1-[1-(dimethylamino)ethyl]-2-naphthalenyl-C^2,N}(diphenylvinylphosphine-P)palladium(II), (R_C)-**1**,[13] bis(acetonitrile){1-[1-(dimethylamino)ethyl]-2-naphthalenyl-C^2,N}palladium(II) perchlorate ((S_C)-**5**),[14] 3,4-dimethyl-1-phenylphosphole 1-sulfide (DMPPS),[15] and thiobenzophenone[16] were prepared according to literature methods.

Formation of {(*R*)-1-[1-(Dimethylamino)ethyl]-2-naphthyl-*C*^{2},*N*}{(1α,4α,5α,7*R*/*S*)-5-(diphenylphosphino)-2,3-dimethyl-7-phenyl-7-thio-7-phosphabicyclo[2.2.1]hept-2-ene-*S*^{7},*P*}palladium(II) Perchlorate ((R_C,R_P)-2 and (R_C,S_P)-2). Isolation of Dichloro{(1α,4α,5α,7*R*)-5-(diphenylphosphino)-2,3-dimethyl-7-phenyl-7-thio-7-phosphabicyclo [2.2.1]hept-2-ene-*S*^{7},*P*}palladium(II) ((R_P)-3). A solution of (R_c)-**1** (0.50 g, 0.82 mmol) in CH_2Cl_2 (30 mL) was treated with DMPPS (0.18 g, 0.82 mmol), and the mixture was stirred at room temperature for 2 days. Removal of solvent under reduced pressure gave a yellow residue (0.65 g, 95%). The ^{31}P NMR spectrum of the crude product in $CDCl_3$ exhibited two pairs of singlets at δ 53.5, 77.7 and δ 59.8, 80.0 in the ratio of 6:6:1:1 for the diastereomers (R_C,R_P)- and (R_C,S_P)-**2**, respectively. Efforts to separate the two diastereomers via silica gel column chromatography and fractional recrystallization were not successful. The mixture of (R_C,R_P)- and (R_C,S_P)-**2** (0.65 g, 1.78 mmol) in acetone (5 mL) was then treated with excess concentrated hydrochloric acid (0.77 g, 7.8 mmol). The reaction mixture was stirred at room temperature for 2 days. The crude product precipitated out from solution. It was filtered and then washed with acetone and diethyl ether. The product (R_P)-**3** was crystallized from dichloromethane−diethyl ether as orange prisms: yield 0.12 g (25%); $[\alpha]_{546} = -10°$ (c 0.2, CD_2Cl_2); mp 160−165 °C dec. Anal. Calcd for $C_{26}H_{26}Cl_2P_2PdS$: C, 51.2; H, 4.3; S, 5.3. Found C, 51.2; H, 4.3; S, 5.2. ^1H NMR (CD_2Cl_2): δ 1.50 (s, 3H, C=C*Me*), 1.66 (s, 3H, C=C*Me*), 1.86−2.08 (m, 1H, Ph_2PCH), 2.62−2.94 (m, 3H, Ph_2PCHCH_2 + PC*H*), 3.28 (m, 1H, PC*H*), 7.45−8.26 (m, 15H, *aromatics*). ^{31}P NMR (CD_2Cl_2): δ 48.9 (s, 1P) and 77.3 (s, 1P).

The minor isomer, (S_p)-**3**, however, could not be isolated from the reaction mixture.

---

[11] Leung, P. H.; Loh, S. K.; Vittal, J. J.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1997**, 1987. Loh, S. K.; Vittal. J. J.; Leung, P. H. *Tetrahedron: Asymmetry* **1998**, *9*, 423.

[12] Qin, Y.; White, A. J. P.; Williams, D. J.; Leung, P. H. *Organometallics* **2002**, *21*, 171.

[13] Selvaratnam, S.; Leung, P. H.; White, A. J. P.; Williams, D. J. *J. Organomet. Chem.* **1997**, *542*, 61. Aw, B. H.; Hor, T. S. A.; Selvaratnam, S.; Mok, K. F.; White, A. J. P.; Williams, D. J.; Rees, N. H.; McFarlane, W.; Leung, P. H. *Inorg. Chem.* **1997**, *36*, 2138. Liu, X.; Mok, K. F.; Vittal, J. J.; Leung, P. H. *Organometallics* **2000**, *19*, 3722.

[14] Chooi, S. Y. M.; Siah, S. Y.; Leung, P. H.; Mok, K. F. *Inorg. Chem.* **1993**, *32*, 4812.

[15] Mathey, F.; Mankowski-Faveliver, R. *Bull. Soc. Chim. Fr.* **1970**, 4433.

[16] Pedersen, B. S.; Scheibye, S.; Nilsson, N. H.; Lawesson, S. O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 223.

{(1α,4α,5α,7*R*)-5-(Diphenylphosphino)-2,3-dimethyl-7-phenyl-7-thio-7-phosphabicyclo [2.2.1]hept-2-ene ((*R*$_P$)-4). The dichloro complex (R_P)-**3** (0.11 g, 0.18 mmol) in dichloromethane (10 mL) was treated with aqueous potassium cyanide (1.2 g, 18 mmol) at room temperature for 1.5 h. The organic layer was separated, washed consecutively with water and dilute sulfuric acid (0.5 M), and dried ($MgSO_4$). After removal of solvent, pure (R_P)-**4** was obtained as a highly air-sensitive colorless oil: yield 0.07 g (85%); $[\alpha]_{546} = -4.5°$ (*c* 0.6, CH_2Cl_2). ^{31}P NMR ($CDCl_3$): δ −14.3 (s, 1P) and 89.1 (s, 1P).

{(*S*)-1-[1-(Dimethylamino)ethyl]-2-naphthyl-*C*^{2},*N*}-{(1α,4α,7*R*/*S*)-2,3-dimethyl-5-thia-6,6,7-triphenyl-7-thio-7-phosphabicyclo[2.2.1]hept-2-ene-*S*^{5},*S*^{7}}palladium(II) Perchlorate ((*S*$_C$,*R*$_P$)-6 and (*S*$_C$,*S*$_P$)-6). The bis(acetonitrile) Pd complex (S_C)-**5** (0.30 g, 0.62 mmol) in dichloromethane (40 mL) was treated with DMPPS (0.14 g, 0.62 mmol) and thiobenzophenone (0.12 g, 0.62 mmol) at room temperature for 12 h. Removal of solvent under reduced pressure gave the crude products as a black oil. The ^{31}P NMR spectrum of the crude product in $CDCl_3$ exhibited two sharp singlets at δ 99.7 and 100.0 in a ratio of ca. 1:1, indicating that the two diastereomers of **6** formed in approximately equal quantities. The crude product mixture was then purified through a silica gel column with dichloromethane−hexane (4:1 v/v) as the eluent. The 1:1 diastereomeric mixture was crystallized from dichloromethane−diethyl ether as yellow prisms: yield 0.21 g (40%). Anal. Calcd for $C_{39}H_{39}ClNO_4PPdS_2$: C, 56.9; H, 4.7; N, 1.7; S, 7.8. Found C, 56.7; H, 4.7; N, 1.7; S, 7.8. Diastereomer A: ^{1}H NMR ($CDCl_3$) δ 1.03 (s, 3H, C═C*Me*), 1.74 (s, 3H, C═C*Me*), 1.77 (d, 3H, $^3J_{HH}$ = 6.0 Hz, CH*Me*), 2.22 (s, 3H, N*Me*$_{ax}$), 2.55 (s, 3H, N*Me*$_{eq}$), 4.17 (q, 1H, $^3J_{HH}$ = 6.0 Hz, C*H*Me), 5.15 (d, 1H, $^2J_{PH}$ = 4.0 Hz, PC*H*), 5.17 (d, 1H, $^2J_{PH}$ = 5.2 Hz, PC*H*S), 6.90−8.11(m, *aromatics*). Diastereomer B: ^{1}H NMR ($CDCl_3$) δ 0.99 (s, 3H, C═C*Me*), 1.29 (d, 3H, $^3J_{HH}$ = 6.0 Hz, CH*Me*), 1.81 (s, 3H, C═C*Me*), 2.40 (s, 3H, N*Me*$_{eq}$), 2.82 (s, 3H, N*Me*$_{ax}$), 4.12 (q, 1H, $^3J_{HH}$ = 6.4 Hz, C*H*Me), 4.95 (d, 1H, $^2J_{PH}$ = 2.4 Hz, PC*H*), 5.60 (d, 1H, $^2J_{PH}$ = 5.2 Hz, PC*H*S), 6.90−8.09 (m, *aromatics*). ^{31}P NMR ($CDCl_3$): δ 99.7 (s, 1P) and 100.0 (s, 1P).

(1α,4α,7*R*/*S*)-2,3-Dimethyl-5-thia-6,6,7-triphenyl-7-thio-7-phosphabicyclo[2.2.1]hept-2-ene ((*R*$_P$)-7 and (*S*$_P$)-7). A solution of complex (S_C)-**6** (0.03 g, 0.038 mmol) in dichloromethane (8 mL) was treated with excess potassium cyanide (0.25 g, 3.8 mmol) in water (2 mL). The mixture was vigorously stirred for 2.5 h. The organic layer was separated, washed consecutively with water and dilute sulfuric acid (0.5 M), and finally dried ($MgSO_4$). After removal of solvent the mixture of (R_P)-**7** and (S_P)-**7** was obtained as an air-stable white solid (0.013 g, 85%). ^{31}P NMR ($CDCl_3$): δ 85.0 (s, 1P).

Table 3. Crystal Data and Structure Refinement for (*R*$_P$)-3 and (*S*$_C$,*R*$_P$)-/(*S*$_C$,*S*$_P$)-6

	(R_P)-**3**	(S_C,R/S_P)-**6**
formula	$C_{26}H_{26}Cl_2P_2PdS$	$C_{39}H_{39}ClNO_4PPdS_2$
fw	609.77	822.65
space group	$P2_1/c$	$P2_1$
cryst syst	monoclinic	monoclinic
a/Å	9.040(1)	24.111(3)
b/Å	16.991(1)	13.453(2)
c/Å	17.657(1)	24.153(5)
β/deg	104.307(1)	110.000(8)
V/Å^3	2628.1(3)	7362(2)
Z	4	8
T/K	223(2)	223(2)
λ/Å	0.71073	0.71073
cryst size/mm^3	0.4 × 0.3 × 0.3	0.3 × 0.2 × 0.2
ρ_{calcd}/g cm^{-3}	1.541	1.484
μ/cm^{-1}	11.24	7.75
F(000)	1232	3376
R1 (obsd data)[a]	0.0281	0.0897
wR2 (obsd data)[b]	0.0661	0.2483

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

Crystal Structure Determination of (*R*$_P$)-3 and (*S*$_C$,*R*/*S*$_P$)-6. Crystal data for (R_P)-**3** and (S_C,R/S_P)-**6** and a summary of the crystallographic analyses are given in Table 3. Diffraction data were collected on a Siemens CCD diffractometer using graphite monochromated Mo Kα radiation. SADABS absorption corrections were applied and all non-hydrogen atoms refined anisotropically.[17] Hydrogen atoms were introduced at fixed distances from carbon atoms and assigned on a Silicon Graphics workstation using programs by Siemens.

Acknowledgment. We are grateful to the National University of Singapore for support of this research and research scholarship to Y.Q.

Supporting Information Available: For (R_P)-**3** and (S_C,R_P)-/(S_C,S_P)-**6**, 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.

OM020682U

---

[17] Sheldrick, G. M. SADABS, Software for Empirical Absorption Correction; University of Göttingen, Göttingen, Germany, 1996.