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Asymmetric synthesis of a P-chiral heteroditopic $\widehat{P\;P}$=S ligand via chiral metal template promoted cycloaddition between 3,4-dimethyl-1-phenylphosphole and its sulfonated analog

Sumod A. Pullarkat [a], Kien-Wee Tan [a], Mengtao Ma [a], Geok-Kheng Tan [b], Lip Lin Koh [b], Jagadese J. Vittal [b], Pak-Hing Leung [a,*]

[a] *Division of Chemistry and Biological Chemistry, Nanyang Technological University, Nanyang Walk 637616, Singapore*
[b] *Department of Chemistry, National University of Singapore, Kent Ridge 119260, Singapore*

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Abstract

The asymmetric [4+2] Diels-Alder reaction involving 3,4-dimethyl-1-phenylphosphole, DMPP, as the cyclic diene and its P-sulfonated analogue DMPP=S as the dienophile was carried out by utilizing the palladium(II) template complex containing *ortho*-metalated (*R*)-(1-(dimethylamino)ethyl)naphthalene as the chiral auxiliary. The reaction proceeded regiospecifically and stereoselectively to give corresponding phosphanorbornene $\widehat{P\;P}$=S ligand as the major product. Throughout the cycloaddition reaction, DMPP functions chemoselectively as the cyclic diene whilst DMPP=S assumes the role of dienophile. The absolute stereochemistry of the novel chiral heteroditopic $\widehat{P\;P}$=S ligand was established by means of single crystal X-ray diffraction analysis.

Keywords: Asymmetric cycloaddition; Chiral metal template; Heteroditopic ligand; Chiral $\widehat{P\;P}$=S ligand

1. Introduction

Heteroditopic ligands containing phosphorous along with oxygen, nitrogen or sulfur have shown promise in homogeneous catalysis and small molecule activation [1–6]. Their catalytic utility stems from the fact that they posses one weakly coordinating donor atom which can readily dissociate from the metal centre to accommodate reacting groups, but more importantly can recombine when a coordinative unsaturation develops at the metal centre therefore yielding a stable catalytic intermediate.

Literature survey reveals that ligands of the type $\widehat{P\;P}$=S, wherein the ligand chelates through P and S atoms, are less studied compared to heteroditopic ligands incorporating phosphorous along with P=NR [7–9] and P=O groups [10–12]. It is noteworthy that reports on such ligands which incorporate a chiral centre are rare [13–17]. These chiral ligands have the added advantage that they contain two non-equivalent phosphorous atoms coordinated through P and S, thus providing enhanced ligand discrimination at their *trans* coordination donor sites compared to their non-chiral counterparts.

In this paper, we report the synthesis and the spectroscopic properties of a chiral heteroditopic cycloadduct formed via an asymmetric cycloaddition reaction between 3,4-dimethyl-1-phenylphosphole (DMPP) and its sulfonated analogue (DMPP=S). This work is part of our ongoing effort to synthesize chiral systems via asymmetric transformations employing chiral cyclometalated-amine complexes, with an ultimate aim to use them as catalyst precursors and templates for organic synthesis [18].

2. Experimental

All reactions and manipulations of air-sensitive compounds were carried out under a positive pressure of dry, oxygen-free nitrogen on a high-vacuum line, or on a

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* Corresponding author. Tel.: +65 63166984.
E-mail address: pakhing@ntu.edu.sg (P.-H. Leung).

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standard Schlenk line. Solvents were dried and freshly distilled according to standard procedures and degassed prior to use when necessary. The 1-D ^{1}H and ^{31}P{^{1}H NMR spectra were measured on a Bruker ACF 300 spectrometer. Optical rotations were measured on the specified solutions in a 0.1 dm cell at 25 °C using a Perkin–Elmer model 341 polarimeter. Melting points were determined using a Büchi B-545 automatic melting point apparatus and are uncorrected. Elemental analyses were performed by the Elemental Analysis laboratory of the Department of Chemistry at the National University of Singapore.

Both enantiomers of bis(acetonitrile)[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*]palladium(II) perchlorate (R_c)-**9** and (S_c)-**9** [19], di-μ-chloro bis[1-(dimethylamino)-ethyl]-2-naphthalenyl-*C*,*N*]dipalladium(II) dichloromethane solvate (R_c)-**1** [20], chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*](3,4-dimethyl-1-phenylphosphole)palladium(II) (R_c)-**3** [21], perchlorato(R)-1-[1-(dimethylamino) ethyl]-2-naphthalenyl-*C*,*N*][3,4-dimethyl-1-phenylphosphole-*P*]palladium(II) (R_c)-**4** [22], 3,4-dimethyl-1-phenylphosphole **2** [23], 3,4-dimethyl-1-phenylphosphole-1-sulfide **5** [24], were prepared as previously reported. Solvents were distilled, dried and degassed by standard procedures where necessary. Column chromatography was performed using silica gel 60.

Caution. Perchlorate complexes are potentially explosive. They should be handled in small quantities with great care [25].

2.1. Synthesis of [(R)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-C,N] [9-thio-9-phenylphosphino-2,3,6,7-tetramethyl-6-ethylene-10-phenyl-10-phosphabicyclo[2,2,1]-hept-2-ene-$P^9(R)P^{10}(S)$]palladium(II)perchlorate, ($R_cS_pR_p$)-**6**

A solution of $(R)_c$-**4** (1.20 g, 1.8 mmol) in 1,2-dichloroethane (50 mL) was treated with DMPPS **5** (0.40 g, 1.8 mmol) and refluxed. The reaction was monitored by ^{31}P{^{1}H} NMR spectroscopy and was found to be complete in 2 days. Removal of solvent under reduced pressure gave a yellow solid (1.42 g, 97%). The ^{31}P NMR spectrum of the crude product in CD_3CN exhibited two pairs of doublets indicative of a diastereomeric mixture (1:0.3). For the major diastereomer (R_c,S_p,R_p)-**6**, the doublets were observed at δ 61.3 ($J_{P–P}$ 11.4 Hz) and 115.3 ($J_{P–P}$ 11.4 Hz). For the minor isomer the doublets occurred at δ 62.0 ($J_{P–P}$ 11.4 Hz) and 114.8 ($J_{P–P}$ 11.4 Hz). Attempted fractional crystallization yielded crystals which consist of both diastereomers but the mother liquor obtained showed presence of only the major isomer. The major isomer was subsequently purified by column chromatography on silica gel with ethyl acetate–hexane (3:1) and crystallized from acetonitrile–ether as pale yellow prisms: m.p. 238–240 °C. $[\alpha]_D = -96$ (*c* 0.3, CH_2Cl_2); 0.55 g (39% yield). $C_{38}H_{42}ClNO_4P_2PdS$ (712.9): calc. C, 56.2; H, 5.2; N, 1.7; S, 3.9; found: C, 56.6; H, 5.6; N, 1.5; S, 3.6. ^{1}H NMR ($CDCl_3$): $\delta = 1.57$ (s, 3H, =C*Me*), 1.60 (s, 3H, =C*Me*), 1.62 (d, 3H, CH*Me*, $^{3}J_{HH} = 6.8$ Hz), 2.04 (s, 3H, N*Me*$_{axial}$), 2.17 (s, 3H, C*Me*), 2.34 (s, 3H, =C*Me*), 2.65 (s , 3H, N*Me*$_{equal}$), 2.88 (d, 1H, $^{3}J_{HH} = 3$ Hz, H_1), 3.31 (m, 1H, H_4), 4.12 (dd, 1H, $^{1}J_{PH} = 14$ Hz, $^{3}J_{HH} = 7.23$ Hz, H_8), 4.23 (qn, 1H, $^{3}J_{HH} = {}^{4}J_{PH} = 6.02$ Hz, H_{10}), 6.34 (d, 1H, $^{2}J_{PH} = 28$ Hz, H_7), 7.22–7.92 (m, 16H, *aromatics*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 61.3 (d, 1P, $J_{PP} = 11.4$ Hz), 115.3 (d, 1P,$J_{PP} = 11.4$ Hz).

2.2. Preparation of dichloro[9-thio-9-phenylphosphino-2,3,6,7-tetramethyl-6-ethylene-10-phenyl-10- phosphabicyclo [2,2,1]hept-2-ene-$P^9(R)P^{10}(S)$]palladium(II)perchlorate, (S_p,R_p)-7

Complex (R_c,S_p,R$_p$)-**6** (0.40 g) was dissolved in dichloromethane (30 mL). To this solution, hydrochloric acid (4 mL, 37%) was added and the resulting solution was stirred vigorously for 1 day. The reaction mixture was then washed with distilled water (3 × 10 mL) and dried with magnesium sulfate. Removal of the solvent left the crude product as yellow powder. The dichloro complex (S_p,R_p)-**7** was then further crystallized by slow diffusion of diethyl ether into a saturated solution of the compound in acetonitrile, yellow prisms. m.p. 254–256 °C. $[\alpha]_D = -175$ (*c* 0.1, CH_2Cl_2); 0.25 g (87% yield). $C_{24}H_{26}Cl_2P_2PdS$ (585.6): calc. C, 49.2; H, 4.4; S, 5.5; found: C, 48.8; H, 4.5; S, 5.3. ^{1}H NMR (CD_2Cl_2): $\delta = 1.42$ (s, 3H, =C*Me*), 1.45 (s, 3H, =C*Me*), 2.10 (s, 3H, –C*Me*), 2.37 (s, 3H, =C*Me*), 2.59 (dd, 1H, $^{3}J_{HH} = 2.01$ Hz, H_1), 3.38 (m, 1H, H_4), 4.12 (dd, 1H, $^{1}J_{PH} = 14.25$ Hz, $^{3}J_{HH} = 7.23$ Hz, H_8), 6.79 (d, 1H, $^{2}J_{PH} = 28.5$ Hz, H_7), 7.4 1–7.83 (m, 10H, *aromatics*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 60.5 (d, 1P, $J_{PP} = 15.2$ Hz), 106.6 (d, 1P,$J_{PP} = 15.2$ Hz).

2.3. Decomplexation of 9-thio-9-phenylphosphino-2,3,6,7-tetramethyl-6-ethylene-10-phenyl-10-phosphabicyclo-[2,2,1]hept-2-ene-$P^9(R)P^{10}(S)$-biphosphole, (R_p,R_p)-**8**

To the solution of dichloro complex (S_p,R_p)-**7** (0.08 g) in dichloromethane (10 mL), an aqueous solution of potassium cyanide (0.30 g) was added and the resulting solution was stirred vigorously for 1 h. The aqueous phase was separated, and the organic layer was washed with water (3 × 5 mL) and dried over magnesium sulfate. Removal of the solvent under vacuum gave ligand (R_p,R_p)-**8** as an air-sensitive colorless oil. $[\alpha]_D = -165$ (*c* 0.1, CH_2Cl_2); 0.05 g (83% yield); ^{31}P{^{1}H} NMR ($CDCl_3$): δ 58.1 (d, 1P, $^{3}J_{PP} = 7.6$ Hz), 106.5 (d, 1P, $^{3}J_{PP} = 7.6$ Hz).

To determine the optical purity of (R_p,R_p)-**8**, the liberated ligand was recoordinated to the bis(acetonitrile) complex (R_c)-**9** to regenerate the diastereomeric complex ($R_cS_pR_p$)-**6**. In $CDCl_3$, the ^{31}P NMR spectrum of the crude recoordination product showed two doublets at δ 61.3 and 115.3. In a further check (R_p,R_p)-**8** , was recoordinated regiospecifically to (S_c)-**9** to generate the diastereomeric complex ($S_cS_pR_p$)-**6**. The ^{31}P NMR spectrum of the crude product in $CDCl_3$ showed two doublets at 61.9 and 114.8.

2.4. X-ray crystallographic study

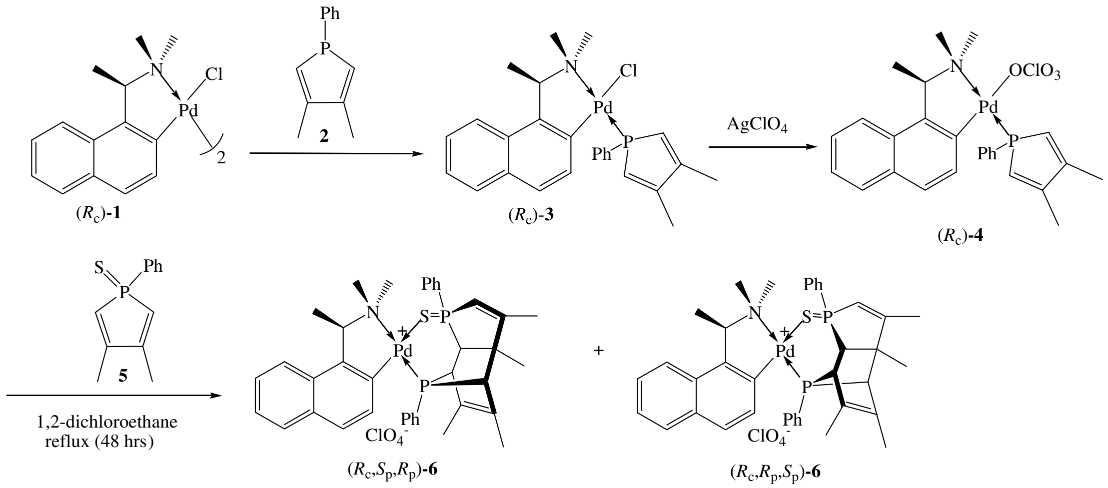
The X-ray crystallographic data for complexes (R_c,S_p,R_p)-**6** and (S_p,R_p)-**7** are given in Table 3. Crystallographic data for complexes (R_c,S_p,R_p)-**6** and (S_p,R_p)-**7** were analyzed at the National University of Singapore using a Siemens SMART CCD diffractometer with graphic monochromated Mo Kα radiation. SADABS absorption corrections were applied for both complexes. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at fixed distance from carbon atoms and were assigned fixed thermal parameters. The absolute configurations of complexes (R_c,S_p,R_p)-**6** and (S_p,R_p)-**7** were determined unambiguously using the Flack parameters [26].

3. Results and discussion

It is important to note that, in principle, both DMPP and DMPP═S may act as dienes or dienophiles, or both [18,27,28]. Alternatively each of these five membered rings may undergo self-dimerization [18,29]. These reactivity considerations, taken in conjunction with the possible *exo–endo* reaction pathways and the possible diastereomerism render the reaction between DMPP and DMPP═S a synthetically challenging process. In order to simplify the product formation, we decided to control the reaction via an intramolecular *exo*-cycloaddition pathway [30]. The Diels-Alder reaction was initiated with the palladium complex containing the *ortho*-metalated (*R*)-(1-(dimethylamino)ethyl)naphthalene, (R_c)-**1** (Scheme 1). The neutral monomer (R_c)-**3** was obtained upon coordination of 3,4-dimethyl-1-phenylphosphole **2** regiospecifically to (R_c)-**1** [21]. As evidenced from our previous studies, the coordinated phosphole in complex (R_c)-**3** can be activated towards cycloaddition reactions [18]. It should be noted that the chloro ligand in (R_c)-**3** is stable and inert and therefore cannot be replaced by incoming organic substrates. Therefore treatment of this chloro species in dichloromethane with aqueous silver perchlorate provides access to the highly labile perchlorate analogue (R_c)-**4** in quantitative yield [31].

A solution of (R_c)-**4** was subsequently refluxed with one equivalent of 3, 4-dimethyl-1-phenylphosphole-1-sulfide **5** in 1,2-dichloroethane. The reaction was monitored by means of $^{31}P\{^1H\}$ NMR spectroscopy and was found to be complete in 48 h. Prior to isolation, the 121 MHz $^{31}P\{^1H\}$ NMR spectrum of the crude product in CD_3CN exhibited two pairs of doublets, indicative of the formation of only two stereo chemically distinct products in the ratio 3:1. The doublets of the major product were observed at δ 61.3 ($J_{P–P} = 11.4$ Hz) and 115.3 ($J_{P–P} = 11.4$ Hz) and the doublets of the minor product were recorded at δ 61.9 ($J_{P–P} = 11.4$ Hz) and 114.8 ($J_{P–P} = 11.4$ Hz). The NMR signals in the low field region at δ 115.3 and 114.8 are typical for bridgehead phosphorous adopting the *exo-syn* stereochemistry [32]. According to the spectroscopic information, both products were generated from the reaction in which DMPP was reacted as cyclic diene. Therefore, a pair of diastereomeric phospha-norbornene complexes where obtained via the intramolecular [4+2] cycloaddition reaction mechanism.

Crystallization of the 3:1 diastereomeric product mixture from acetonitrile–diethyl ether yielded crystals which consisted of both diastereomers in ca. equal ratio as revealed by $^{31}P\{^1H\}$ NMR spectroscopy. The mother liquor left after the first crystallization was however found to contain the pure major isomer. The $^{31}P\{^1H\}$ NMR spectrum of these material in $CDCl_3$ showed only one pair of doublet at δ 61.3 (1P, $J_{PP} = 11.4$ Hz) and 115.3 (1P, $J_{PP} = 11.4$ Hz). The major product was subsequently purified by column chromatography on silica gel with an eluent system comprising of ethyl acetate–hexane (3:1). The pure isomer was finally crystallized from acetonitrile on slow diffusion of diethyl ether as pale yellow prisms. The single crystal X-ray diffraction analysis revealed that the major product is complex (R_c,S_p,R_p)-**6** (Fig. 1).



Scheme 1.

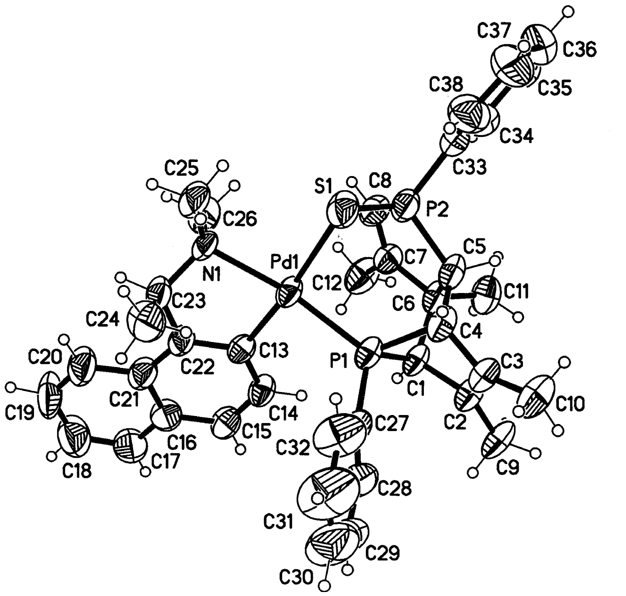


Fig. 1. Molecular structure and absolute configuration of (R_c,S_p,R_p)-**6**.

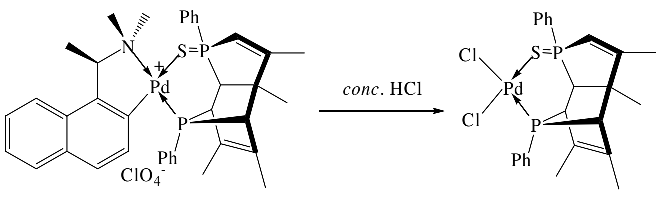
Table 1
Selected bond lengths (Å) and angles (°) for (R_c,S_p,R_p)-**6**

Pd(1)–C(13)	2.004(5)	Pd(1)–N(1)	2.146(4)
Pd(1)–P(1)	2.226(1)	Pd(1)–S(1)	2.481(1)
P(2)–S(1)	1.987(2)	P(2)–C(8)	1.768(6)
C(8)–C(7)	1.321(8)	C(6)–C(7)	1.535(8)
C(5)–C(6)	1.564(8)	P(2)–C(5)	1.832(6)
C(5)–C(4)	1.550(9)	C(1)–C(6)	1.544(8)
P(1)–C(4)	1.856(6)	P(1)–C(1)	1.874(5)
C(13)–Pd(1)–N(1)	80.7(2)	C(13)–Pd(1)–P(1)	92.0(1)
N(1)–Pd(1)–P(1)	171.3(1)	C(13)–Pd(1)–S(1)	173.9(2)
N(1)–Pd(1)–S(1)	93.4(1)	P(1)–Pd(1)–S(1)	94.0(1)
P(2)–S(1)–Pd(1)	92.4(1)	C(4)–P(1)–Pd(1)	116.7(2)
C(1)–P(1)–Pd(1)	123.9(2)	C(8)–P(2)–S(1)	113.0(2)

The X-ray structural analysis confirmed that the desired cycloadduct had formed via the *exo*-cycloaddition reaction. The desired cycloadduct coordinates to the palladium template as a bidentate chelate via the bridgehead phosphorous and the sulfur atoms of the $Ph_2P{=}S$ moiety. The sulfur atom binds to the metal centre *trans* to the C of the metal template while the softer phosphorous of the donor occupies the position *trans* to the nitrogen of the chiral palladium(II) template. This geometrical arrangement is in agreement with earlier reports involving coordination of unsymmetrical bidentates (such as As–S, P–N and P–S) to the *ortho*-metallated (*R*)-(1-(dimethylamino)ethyl)naphthalene unit wherein the softest of the two donors invariably takes up the position *trans* to the NMe_2 group in the complex [33]. The crystallographic study also revealed that the absolute configurations at P(1), P(2), C(1), C(4), C(5) and C(6) in the complex were *S*, *R*, *R*, *S*, *R* and *R*, respectively. Selected bond distances and angles are listed in Table 1. The geometry at the palladium centre is distorted square planar with angles at palladium in the range of 80.7(2)–94.0(1)° and 171.3(1)–173.9(2)°. The bite angles formed by the two chelate rings are 80.7(2)° for the organometallic naphthylamine ring and 94.01(6)° for the $\overset{\frown}{\mathrm{P}\quad\mathrm{P}}{=}\mathrm{S}$ chelate. The bond angle at the bridgehead phosphorous, C(4)–P(1)–C(1) [80.4(3)°], is in agreement with that observed for *exo* dimeric phosphole sulfides reported earlier (ca. 80°) and is indicative of the elevated levels of strain at the bridge [34]. This bridgehead angle was also similar to that observed for the cycloadduct obtained from the asymmetric dimerization of DMPP in the presence of the platinum(II) analogue of the same template [35]. The bridgehead C–P–C angle is also expectedly smaller than those seen in complexes obtained from the cycloaddition of diphenylvinylphosphine with DMPP=S (ca. 83°) and also for the *exo*-thioamide-substituted 7-phosphanorbornene P–S bidentate chelate (ca. 82°) [36,37]. The P=S bond distance is 1.987(2) Å and the Pd–S and Pd–P distances are 2.481(1) and 2.226(1) Å, respectively. It is important to note that the structural investigations reaffirmed that DMPP=S functions as a dienophile whereas DMPP functions as the cyclic diene in this cycloaddition reaction.

The chiral naphthylamine auxiliary in complex (R_c,S_p,R_p)-**6** was subsequently removed chemoselectively by treatment with concentrated hydrochloric acid at room temperature (Scheme 2). The dichloro complex (S_p,R_p)-**7** was obtained as yellow prisms from acetonitrile–diethyl ether. The $^{31}P\{^1H\}$ NMR spectrum of the complex in $CDCl_3$ showed doublet signals at δ 60.54 ($J_{PP} = 15.2$ Hz) and 106.63 ($J_{PP} = 15.2$ Hz). The molecular structure and the absolute configuration of the recrystallised (S_p,R_p)-**7** were established by single crystal X-ray crystallographic analysis (Fig. 2). The absolute configurations of the stereogenic centers were found to be retained even after reaction under acidic conditions. Selected bond parameters are given in Table 2. The stronger *trans* influence of the phosphorous atom (versus the sulfur atom) is evidenced in the difference of the Pd–Cl bond distances *trans* to the phosphorous atom (2.381(1) Å) and *trans* to the sulfur atom (2.318(1) Å) [38]. Interestingly the P=S bond distance in (S_p,R_p)-**7** [2.017(1) Å] is longer than that observed in the complex (R_c,S_p,R_p)-**6** [1.987(2) Å]. This is clearly attributed to the *trans* withdrawing effect of the coordinated aromatic carbon in the template complex.

The optically active ligand (R_p,R_p)-**8** can be stereospecifically liberated from the complex (S_p,R_p)-**7** by treatment of the dichloro complex with aqueous potassium cyanide at room temperature (Scheme 3). The liberated (R_p,R_p)-**8** was obtained as a colourless oil in 83% yield with



(R_c,S_p,R_p)-**6** (S_p,R_p)-**7**

Scheme 2.

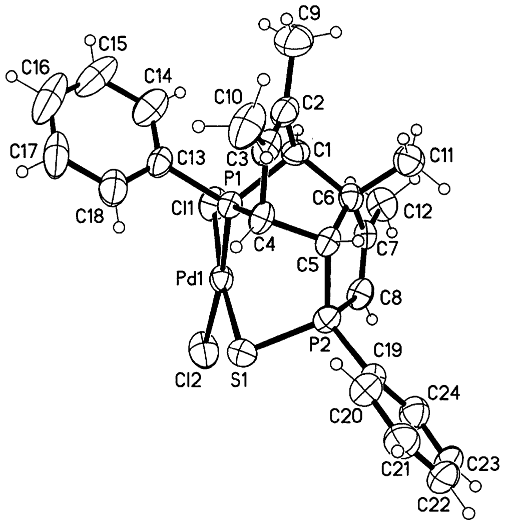


Fig. 2. Molecular structure and absolute configuration of (S_p,R_p)-**7**.

Table 2
Selected bond lengths (Å) and angles (°) for (S_p,R_p)-**7**

Pd(1)–P(1)	2.194(9)	Pd(1)–Cl(1)	2.318(1)
Pd(1)–S(1)	2.324(1)	Pd(1)–Cl(2)	2.381(1)
P(2)–S(1)	2.017(1)	C(5)–C(6)	1.559(5)
P(1)–Pd(1)–Cl(1)	83.0(4)	P(1)–Pd(1)–S(1)	91.5(4)
Cl(1)–Pd(1)–S(1)	171.8(4)	P(1)–Pd(1)–Cl(2)	174.4(3)
Cl(1)–Pd(1)–Cl(2)	94.9(4)	S(1)–Pd(1)–Cl(2)	91.1(4)
C(4)–P(1)–C(1)	81.1(2)	P(2)–S(1)–Pd(1)	93.1(5)

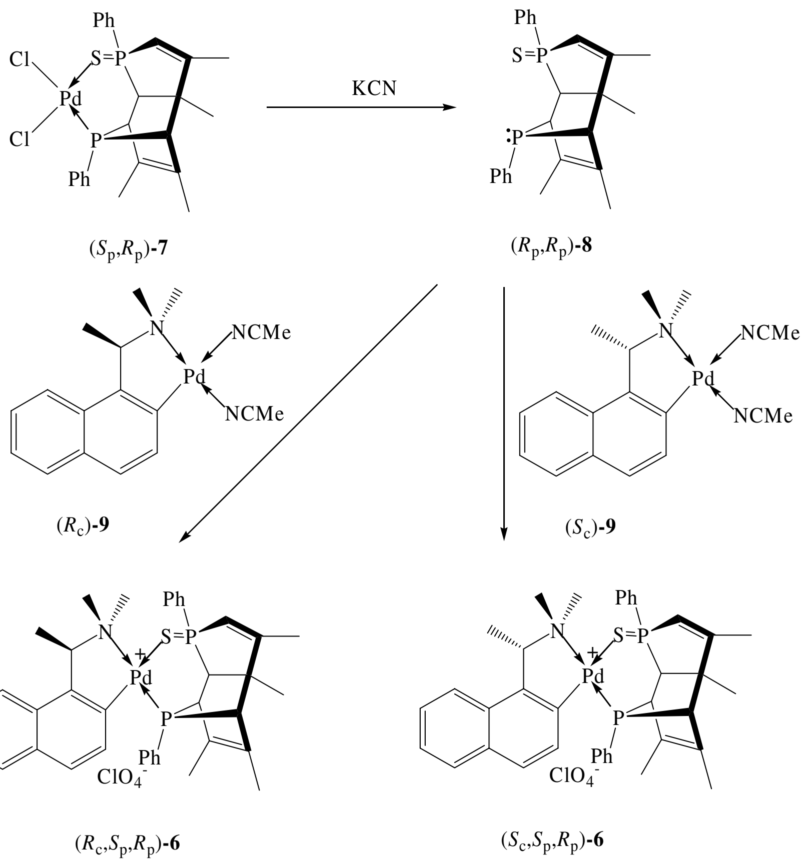
Table 3
Crystallographic data for complexes (R_c,S_p,R_p)-**6** and (S_p,R_p)-**7**

	(R_c,S_p,R_p)-**6**	(S_p,R_p)-**7**
Formula	$C_{38}H_{42}ClNO_4P_2PdS \cdot 0.5\{C_4H_{10}O\}$	$C_{24}H_{26}Cl_2P_2PdS$
Formula mass	849.64	585.75
Space group	$P2_1$	$Pna2_1$
Crystal system	Monoclinic	Orthorhombic
a (Å)	11.8816(2)	16.4405(8)
b (Å)	15.681(2)	9.4660(5)
c (Å)	22.532(3)	15.7152(8)
α (°)	90	90
β (°)	101.760(3)	90
γ (°)	90	90
V (Å^3)	4110.1(1)	2445.7(2)
Z	4	4
T (K)	223(2)	223(2)
$\rho_{\text{calc.}}$ (Mg/m^3)	1.373	1.591
λ (Å)	0.71073 (Mo)	0.71073
μ (mm^{-1})	0.686	1.204
Flack parameter	−0.01(2)	0.00(2)
R_1 (obsd data)[a]	0.0888	0.0444
wR_2 (obsd data)[b]	0.1215	0.0576

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$.

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

$[\alpha]_D = -165$ (c 0.1, CH_2Cl_2). The $^{31}P\{^1H\}$ NMR spectrum of the free ligand in $CDCl_3$exhibited two doublets at δ 58.12 (1P, $^3J_{PP} = 7.6$ Hz) and 106.50 (1P, $^3J_{PP} = 7.6$ Hz), the low field resonance signal confirms the retention of



Scheme 3.

the *exo-syn* stereochemistry [32]. It is noteworthy that the apparent inversion of configuration that occurs at the tertiary phosphorous stereogenic center when the ligand is liberated from the metal is merely a consequence of the Cahn–Ingold–Prelog (CIP) sequence rule [39]. Owing to the susceptibility of the non-coordinated bridgehead phosphorous to oxidation , the liberated (R_p,R_p)-**8** cannot be stored in its pure form. Hence the liberated ligand was re-complexed to selected metal ions to form stable metal complexes. Furthermore, in order to determine the optical purity of (R_p,R_p)-**8**, the liberated ligand was recoordinated to the bis(acetonitrile) complex (R_c)-**9** (Scheme 2.4). The recoordination procedure was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. In $CDCl_3$, the ^{31}P NMR spectrum of the crude recoordination product showed two doublets at δ 61.3 ($J_{P-P} = 11.4$ Hz) and 115.3 ($J_{P-P} = 11.4$ Hz). These NMR signals are identical with those recorded for the major diastereomer generated from the original cycloaddition reaction. No $^{31}P\{^1H\}$ signals could be detected at δ 62.0 and 114.8, thus conforming that liberated (R_p,R_p)-**8** is optically pure. In order to establish the identity of the minor product that was formed from the Diels-Alder reaction, (R_p,R_p)-**8** was recoordinated regiospecifically to (S_c)-**9** to generate the diastereomeric complex (S_c,S_p,R_p)-**6**. The $^{31}P\{^1H\}$ NMR spectrum of the crude product in $CDCl_3$ showed two doublets at 62.0 and 114.8. No $^{31}P\{^1H\}$ NMR signals could be detected for the major diastereomer thus reaffirming that liberated (R_p,R_p)-**8** is stereochemically pure.

Appendix A. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No.288010 for compound (R_c,S_p,R_p)-**6** and CCDC 288009 for compound (S_p,R_p)-**7**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax (int code) +44(1223)336 033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.03.024.

References

[1] S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169–1203.
[2] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem., Int. Ed. Engl. 38 (1999) 428–447.
[3] A. de Meijere, F.E. Meyer, Angew. Chem., Int. Ed. Engl. 33 (1994) 2379–2411.
[4] R.F. Heck, Palladium Reagents in Organic Synthesis, Academic Press, London, 1985.
[5] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457–2483.
[6] A. Suzuki, J. Organomet. Chem. 576 (1999) 147–168.
[7] K. Yonehara, T. Hashizume, K. Mori, K. Ohe, S. Uemura, Chem. Commun. (1999) 415–417.
[8] R. Pretot, A. Pfaltz, Angew. Chem., Int. Ed. Engl. 37 (1998) 323–325.
[9] K. Selvakumar, M. Valentini, M. Worle, P.S. Pregosin, A. Albinati, Organometallics 18 (1999) 4591–4597.
[10] S. Kudis, G. Helmcken, Angew. Chem., Int. Ed. Engl. 37 (1998) 3047–3050.
[11] R.W. Wegman, A.G. Abatjoglou, A.M. Harrison, J. Chem. Soc., Chem. Commun. (1987) 1891–1896.
[12] V.V. Grushin, Chem. Rev. 104 (2004) 1629–1662, and references cited therein.
[13] J.W. Faller, J.C. Wilt, J. Parr, Org. Lett. 6 (2004) 1301–1304.
[14] A. Albinati, P.S. Pregosin, K. Wick, Organometallics 15 (1996) 2419–2421.
[15] S.R. Gilbertson, P. Lan, Org. Lett. 3 (2001) 2237–2240.
[16] D.A. Evans, K.R. Campos, J.S. Tedrow, F.E. Michael, M.R. Gagne, J. Am. Chem. Soc. 122 (2000) 7905–7920.
[17] C.J. Chapman, C.G. Frost, M.P. Gill-Carey, K.K. Gabriele, M.F. Mahon, A.S. Weller, M.C. Willis, Tetrahedron: Asymmetry 14 (2003) 705–710.
[18] P.H. Leung, Acc. Chem. Res. 37 (2004) 169–177.
[19] S.Y.M. Chooi, S.Y. Siah, P.H. Leung, K.F. Mok, Inorg. Chem. 32 (1993) 4812–4818.
[20] D.G. Allen, G.M. McLaughlin, G.B. Robertson, W.L. Steffen, G. Salem, S.B. Wild, Inorg. Chem. 21 (1982) 1007–1014.
[21] S.Y. Siah, K.F. Mok, P.H. Leung, J. Chem. Soc., Chem. Commun. (1995) 1747.
[22] S.K. Loh, K.F. Mok, P.H. Leung, A.J.P. White, D.J. Williams, Tetrahedron: Asymmetry 7 (1996) 45–49.
[23] A. Breque, F. Mathey, P. Savignac, Synthesis (1981) 983–986.
[24] F. Mathey, R. Mankowski-Faveliver, Bull. Soc. Chim. Fr. (1970) 4433–4437.
[25] W.C. Wolsey, J. Chem. Ed. 50 (1973) A335.
[26] H.D. Flack, Acta Crystallogr., Sect. A 39 (1983) 876–881.
[27] Y. Kashman, I. Wagenstein, A. Rudi, Tetrahedron 32 (1976) 2427–2431.
[28] Y. Kashman, O. Awerbouch, Tetrahedron 29 (1973) 191–194.
[29] M. Gottfried, P. Ruthard, Tetrahedron Lett. 14 (1968) 1755–1758.
[30] G. He, S.K. Loh, J.J. Vittal, K.F. Mok, P.H. Leung, Organometallics 17 (1998) 3931–3936.
[31] S.Y. Loh, K.F. Mok, P.H. Leung, A.J.P. White, D.J. Williams, Tetrahedron: Asymmetry 7 (1996) 45–48.
[32] L.D. Quin, A.N. Huges, in: F.R. Hartley (Ed.), The Chemistry of Organophosphorous Compounds, vol. 1, John Wiley, New York, 1990 (Chapter 10).
[33] S.B. Wild, Coord. Chem. Rev. 166 (1997) 291–311.
[34] F. Mercier, F. Mathey, J. Fischer, J.H. Nelson, J. Am. Chem. Soc. 106 (1984) 425–426.
[35] G. He, Y. Qin, K.F. Mok, P.H. Leung, Chem. Commun. (2000) 167–168.
[36] Y. Qin, A.J.P. White, D.J. Williams, P.H. Leung, Organometallics 21 (2002) 171–174.
[37] Y. Qin, G. He, K.F. Mok, J.J. Vittal, P.H. Leung, J. Chem. Soc., Dalton Trans. (2001) 309–313.
[38] (a) T.G. Appleton, H.C. Clark, L.E. Manzer, Coord. Chem. Rev. 10 (1973) 335–343;
(b) S. Murray, F. Hartley, Chem. Rev. 81 (1981) 365–414.
[39] R.S. Cahn, C.K. Ingold, V. Prelog, Angew. Chem., Int. Ed. Engl. 5 (1966) 385–390.