Asymmetric syntheses, structures and co-ordination chemistry of palladium(II) complexes containing a chiral P,S hybrid bidentate ligand

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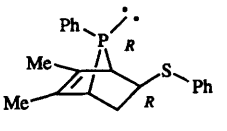
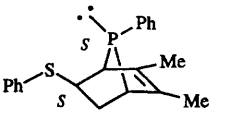
The chiral palladium complex $(+)_{589}$-di-μ-chloro-bis{(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-C^2,N}dipalladium(II) has been used successfully to promote the asymmetric [4 + 2] Diels–Alder reaction between 3,4-dimethyl-1-phenylphosphole and phenyl vinyl sulfide. The cycloaddition product (−)-(1α,4α,5α,7*R*)-2,3-dimethyl-7-phenyl-5-(phenylsulfanyl)-7-phosphabicyclo[2.2.1]hept-2-ene was formed stereoselectively on the chiral palladium template and behaves as a bidentate ligand *via* its phosphorus and sulfur donor atoms. The chiral naphthylamine auxiliary and the new P,S bidentate ligand can be selectively released with retention of chirality by treatment with hydrochloric acid or 1,2-bis(diphenylphosphino)ethane respectively. The optical purity of the liberated heterobidentate compound has been confirmed by NMR spectroscopic studies. The absolute stereochemistries and the co-ordination properties of the enantiomerically pure P,S compound and its oxidized derivative have been established by single-crystal X-ray analyses.

The stereodynamic properties of transition-metal complexes containing heterobidentate As,S and P,S ligands have received considerable attention over the past decade.[1] The primary impetus for this work has been the potential application of these molecules as supporting ligands in homogeneous catalysis.[2,3] During a transition-metal-ion catalysed reaction the arsenic or phosphorus donor atom of such an unsymmetrical bidentate pro-ligand will impart the necessary activation and stabilization to the metal ion upon co-ordination. On the other hand, the weakly bound sulfur offers a readily available catalytic site for reacting organic substrates. So far, the study of the fluxionality of metal complexes containing these heterobidentates has been the primary focus of earlier work,[1] with little attention being given to the importance of developing an analogous optically active hybrid ligand system. The availability of such chiral heterobidentates may bear heavily upon the rational development of effective catalysts in the important field of homogeneous asymmetric catalysis.

There are two basic strategies for the incorporation of stable chirality into As,S and P,S bidentates. One strategy involves the use of readily available chiral carbon skeletons as linkages for the heterodonor atoms.[3] However compounds with such structural features have not so far proved to be particularly efficient as chiral auxiliaries. The second approach involves the introduction of chirality directly onto the soft arsenic or phosphorus donor atoms. It has been demonstrated that compounds containing such asymmetric donor atoms are efficient chirality inducers in the catalytic asymmetric hydrogenation of olefins.[4] Unfortunately, this class of optically active heterosubstituted tertiary arsine and phosphine is difficult to prepare, and invariably has to be obtained by optical resolutions.[5] Indeed, due to such synthetic problems only two As,S[6,7] and one P,S[8] heterobidentates containing resolved arsenic or phosphorus stereogenic centres have been reported to date. Hence, the potential of this class of bidentate compounds as chiral auxiliaries has not been fully explored. We consider it fundamentally important to develop an easily accessible synthetic methodology for this important class of asymmetric compounds. In this paper we report the first asymmetric synthesis of a rigid, stable, P,S bidentate compound containing three carbon and one phosphorus stereogenic centres, (±)-**I**.



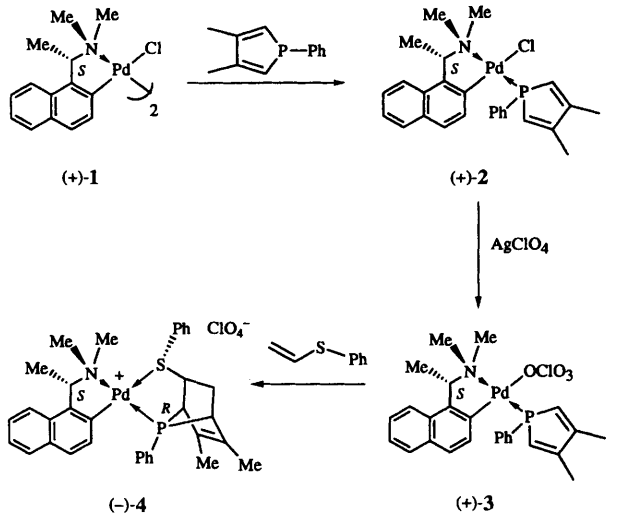
(+)-**I**



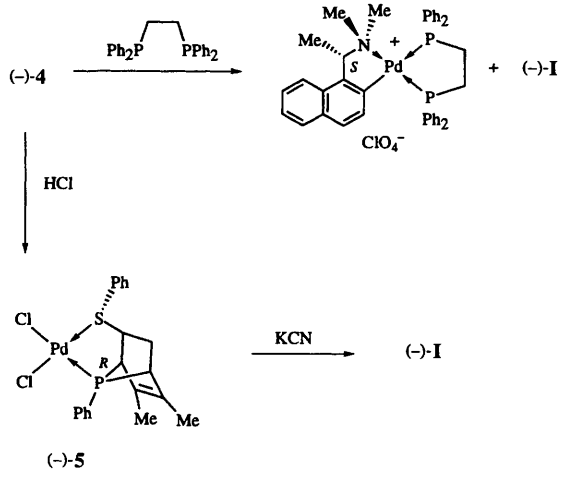
(−)-**I**

Results and Discussion

The (+) and (−) forms of the bidentate compound **I** have been prepared stereoselectively *via* asymmetric Diels–Alder reactions between phenyl vinyl sulfide and 3,4-dimethyl-1-phenylphosphole (dmpp) in the presence of 0.5 equivalent of the (+) and (−) forms, respectively, of the chiral organopalladium(II) dimer **1**, as the reaction template (Scheme 1). In using this metal template approach, dmpp was first co-ordinated regiospecifically[6–9] to (+)-**1** giving the monomeric complex (+)-**2** as bright yellow crystals in 96% isolated yield, α +335° (589 nm, dichloromethane).[9] Treatment of (+)-**2** with silver perchlorate in dichloromethane generated the non-conducting perchlorato complex (+)-**3** in essentially quantitative yield with α +285° (589 nm, dichloromethane).[10] The asymmetric [4 + 2] cycloaddition reaction was achieved by treating a 1,2-dichloroethane solution of (+)-**3** with 2 equivalents of phenyl vinyl sulfide at 75 °C. The reaction was monitored by ^{31}P NMR spectroscopy and found to be complete in 17 d, giving (−)-**4**. Prior to recrystallization, the ^{31}P NMR spectrum of the crude product (−)-**4** in $CDCl_3$ exhibited a characteristic singlet at δ 124.9 indicating that an *exo-syn* isomer had been formed on the palladium template in the Diels–Alder reaction.[11] No other ^{31}P signal was detected in this low-field region. The cycloaddition reaction product (−)-**4** was subsequently crystallized from dichloromethane–diethyl ether as fine white fibrous aggregates in 65% isolated yield, α −133.3° (589 nm, dichloromethane). The complex is stable in the solid state and in solution and behaves as a typical 1:1 electrolyte in dichloromethane and in acetone. It is noteworthy that a control reaction between dmpp and phenyl vinyl sulfide in the absence of the organopalladium promoter failed to give any Diels–Alder product under similar experimental conditions.



Scheme 1



Scheme 2

The chiral naphthylamine auxiliary can be selectively removed from compound (−)-**4** by treating an acetone solution of the latter with concentrated hydrochloric acid for 10 h at 55 °C (Scheme 2). The dichloro complex (−)-**5** thus precipitated out quantitatively from the reaction mixture was recrystallised as yellow needles from dichloromethane, α −163.4° (589 nm, dichloromethane). Its ^{31}P NMR spectrum in $CDCl_3$ exhibited a sharp singlet at δ 132.5.

The X-ray analysis of complex (−)-**5** establishes unambiguously (see Experimental section) the absolute stereochemistries at the P,S, C(7), C(10) and C(11) centres to be *R*, *S*, *R*, *R* and *S* respectively, Fig. 1. The geometry at palladium is slightly distorted square-planar with angles at Pd in the ranges 85.3(1)–95.5(1) and 173.9(1)°, Table 1, the contraction from 90° being a consequence of the bite angle of the chelating P,S ligand. There is a small pyramidalization of the palladium co-ordination plane, the Pd atom lying *ca.* 0.07 Å out of the plane of its substituents. Both the Pd–S and Pd–P bond lengths, at 2.298(3) and 2.196(2) Å, are typical, but the two Pd–Cl distances [2.303(3) and 2.364(2) Å] differ significantly, with that *trans* to phosphorus being noticeably enlarged from normal reflecting the stronger *trans* effect of phosphorus *versus* sulfur. The tetrahedral character at the sulfur centre is very pronounced, with angles ranging from 100.6(3) to 106.9(2)°.

A noticeable feature of the phosphornorbornene skeleton is a marked contraction in the C–P–C bridgehead angle to 80.7(4)° that accompanies a slight lengthening of *ca.* 0.02 Å in the P–C bonds (*cf.* those observed previously[12]). This may be a consequence of the aforementioned *trans* effect observed in the Pd–Cl bonding.

An inspection of the packing of the molecules does not reveal any notable intermolecular interactions other than weak aromatic–aromatic edge-to-face and normal van der Waals.

The free compound (−)-**I** can be liberated efficiently from (−)-**5** by treating a dichloromethane solution of the chiral dichloro-complex with aqueous cyanide. The optically active compound was obtained as a viscous colourless oil with α −22.2° (589 nm, dichloromethane). Alternatively, it can be released directly from the template complex (−)-**4** in quantitative yield by treating the latter with a stoichiometric quantity of 1,2-bis(diphenylphosphino)ethane. Significantly, the ^{31}P NMR spectrum of free **I** in $CDCl_3$ exhibited a low-field singlet at δ 97.1. This low-field signal confirms that the *exo-syn* stereochemistry is retained. It should be noted that the apparent inversion of configuration that takes place at the phosphorus

Table 1 Selected bond lengths (Å) and angles (°) for complex (−)-**5**

Pd–P	2.196(2)	Pd–S	2.298(3)
Pd–Cl(2)	2.303(3)	Pd–Cl(1)	2.364(2)
P–C(10)	1.854(9)	P–C(7)	1.866(8)
S–C(20)	1.784(5)	S–C(11)	1.839(8)
C(7)–C(8)	1.510(12)	C(7)–C(12)	1.548(10)
C(8)–C(9)	1.321(12)	C(8)–C(13)	1.481(12)
C(9)–C(14)	1.51(2)	C(9)–C(10)	1.516(11)
C(10)–C(11)	1.533(10)	C(11)–C(12)	1.568(12)
P–Pd–S	85.34(8)	P–Pd–Cl(2)	89.96(9)
S–Pd–Cl(2)	173.93(9)	P–Pd–Cl(1)	173.90(9)
S–Pd–Cl(1)	89.07(9)	Cl(2)–Pd–Cl(1)	95.45(10)
C(6)–P–C(10)	109.3(3)	C(6)–P–C(7)	111.4(3)
C(10)–P–C(7)	80.7(4)	C(6)–P–Pd	124.0(3)
C(10)–P–Pd	111.0(3)	C(7)–P–Pd	112.1(3)
C(20)–S–C(11)	102.9(4)	C(20)–S–Pd	106.9(2)
C(11)–S–Pd	100.6(3)	C(8)–C(7)–C(12)	107.2(7)
C(8)–C(7)–P	100.0(5)	C(12)–C(7)–P	99.9(5)
C(9)–C(8)–C(13)	129.3(9)	C(9)–C(8)–C(7)	110.5(7)
C(13)–C(8)–C(7)	120.1(8)	C(8)–C(9)–C(14)	128.2(8)
C(8)–C(9)–C(10)	111.6(8)	C(14)–C(9)–C(10)	120.2(8)
C(9)–C(10)–C(11)	111.0(7)	C(9)–C(10)–P	100.5(6)
C(11)–C(10)–P	96.7(6)	C(10)–C(11)–C(12)	105.4(6)
C(10)–C(11)–S	111.0(5)	C(12)–C(11)–S	105.9(6)
C(7)–C(12)–C(11)	105.8(6)		

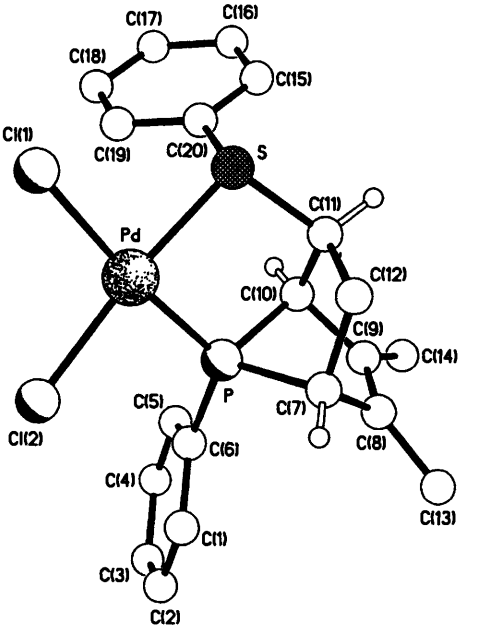
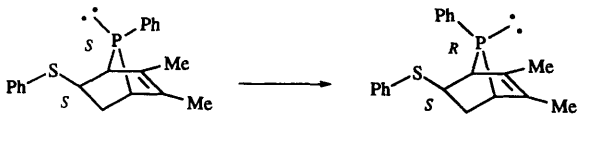
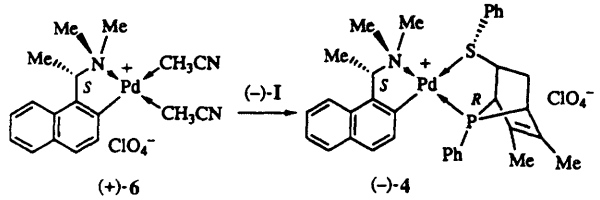


Fig. 1 The molecular structure and absolute stereochemistry of complex (−)-**5**

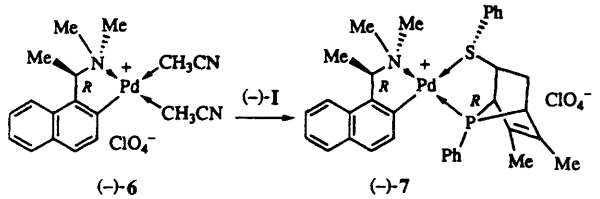


exo-syn *exo-anti*

Scheme 3

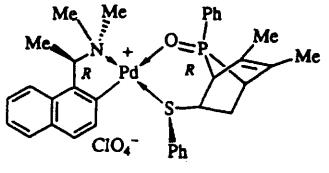


(+)-6 (−)-4



(−)-6 (−)-7

Scheme 4



(−)-8

Table 2 Selected bond lengths (Å) and angles (°) for complex (−)-**8**

Pd–C(1)	1.984(3)	Pd–N(12)	2.090(4)
Pd–O	2.138(3)	Pd–S	2.2990(10)
S–C(35)	1.770(2)	S–C(26)	1.839(4)
O–P	1.499(3)	P–C(22)	1.824(4)
P–C(25)	1.828(4)	C(22)–C(23)	1.512(7)
C(22)–C(27)	1.548(6)	C(23)–C(24)	1.342(7)
C(23)–C(28)	1.497(6)	C(24)–C(29)	1.481(7)
C(24)–C(25)	1.516(6)	C(25)–C(26)	1.540(6)
C(26)–C(27)	1.555(6)		
C(1)–Pd–N(12)	81.8(2)	C(1)–Pd–O	171.0(2)
N(12)–Pd–O	91.11(13)	C(1)–Pd–S	92.3(2)
N(12)–Pd–S	173.75(10)	O–Pd–S	94.98(9)
C(35)–S–C(26)	102.0(2)	C(35)–S–Pd	108.89(10)
C(26)–S–Pd	111.18(14)	P–O–Pd	129.0(2)
O–P–C(21)	113.4(2)	O–P–C(22)	115.9(2)
C(21)–P–C(22)	110.9(2)	O–P–C(25)	119.1(2)
C(21)–P–C(25)	110.8(2)	C(22)–P–C(25)	83.2(2)
C(23)–C(22)–C(27)	109.2(4)	C(23)–C(22)–P	97.6(3)
C(27)–C(22)–P	100.2(3)	C(24)–C(23)–C(28)	128.1(5)
C(24)–C(23)–C(22)	110.9(4)	C(28)–C(23)–C(22)	120.8(5)
C(23)–C(24)–C(29)	127.0(4)	C(23)–C(24)–C(25)	111.0(4)
C(29)–C(24)–C(25)	122.0(4)	C(24)–C(25)–C(26)	107.5(3)
C(24)–C(25)–P	97.3(3)	C(26)–C(25)–P	100.6(3)
C(25)–C(26)–C(27)	107.0(3)	C(25)–C(26)–S	115.7(3)
C(27)–C(26)–S	108.4(3)	C(22)–C(27)–C(26)	105.6(3)

stereogenic centre when phosphorus is liberated from the metal is merely a consequence of the Cahn–Ingold–Prelog (CIP) sequence rules.[13] Owing to the configurational instability of the unco-ordinated bridgehead phosphorus stereogenic centre,[11] liberated (−)-**I** quantitatively transforms into the corresponding *exo-anti* structure within 2 h (Scheme 3). The ^{31}P NMR spectrum of the free *exo-anti* isomer in $CDCl_3$ showed a characteristic singlet at δ 66.3.[11] Hence (−)-**I** cannot be stored at room temperature for longer than *ca.* 30 min and must therefore be recomplexed immediately to selected metal ions. Upon co-ordination, the *exo-syn* stereochemistry is stabilized.

The stereospecific displacement of (−)-**I** from the metal complexes was further confirmed by the quantitative repreparation of (−)-**4** from the liberated ligand and (+)-**6**:[14] the ^{31}P NMR spectrum of the crude product in $CDCl_3$ exhibited the presence of only one singlet at δ 124.9 which is identical to that recorded for the perchlorate salt directly produced from the Diels–Alder reaction. As a further check, a diastereomeric complex (−)-**7** was prepared from the liberated (−)-**I** and the equally accessible (−)-**6** (Scheme 4). The ^{31}P NMR spectrum of the crude product in $CDCl_3$ showed an entirely new singlet at δ 128.8. No resonance signal could be detected at the δ 124.9 position thus reaffirming that the liberated (−)-**I** is enantiomerically pure.

Physically, complex (−)-**7** is more soluble than its diastereomeric analogue, (−)-**4**, in most organic solvents. Indeed, the former complex could not be crystallized from a wide range of solvent systems. The two diastereomers have different chemical stabilities: whilst solutions of (−)-**4** are air-stable, those of (−)-**7** are air-sensitive. Thus the ^{31}P NMR spectrum of (−)-**4** in $CDCl_3$ remained unchanged after the sample had been kept at room temperature for 15 d, however an additional singlet was observed at δ 55.2 from a sample of (−)-**7** kept for the same period in the same solvent. This new species was crystallized from dichloromethane–diethyl ether as yellow prisms and shown by single-crystal X-ray analysis to be the oxidized complex (−)-**8**, α −270.0° (589 nm, dichloromethane). This complex is stable in the solid state and does not react or rearrange further in solution.

The X-ray analysis of complex (−)-**8** definitively established the absolute stereochemistries of the P,S, C(11), C(22), C(25) and C(26) centres to be *R,S,R,R,R* and *S* respectively, Fig. 2. This assignment is based upon both anomalous scattering (see Experimental section) and by internal reference to the known stereocentre at C(11) of the naphthylamine ligand. The directing of the stereochemistry of the O,S chelate is particularly significant in so far as the absolute stereochemistry at the potentially readily interconverting sulfur centre is controlled by the steric influence of the γ-naphthyl proton [attached to C(2)].[15] There is also ^{1}H NMR evidence for this directing effect in solution.

The distortions in the square-planar geometry at palladium seen here are greater than those in complex (−)-**5** with angles in the ranges 81.8(2)–95.0(1) and 171.0(2)–173.8(1)°. These distortions, which involve a contraction and an enlargement from 90° for the bite angles of the five- and six-membered chelate rings respectively, are accompanied by a small tetrahedral distortion, the two ligand co-ordination planes being twisted by *ca.* 6° with respect to each other. The six-membered chelate ring has a half-chair conformation, with C(26)–S–Pd–O coplanar to within 0.003 Å; the phosphorus atom and C(25) lie 0.35 and 1.11 Å above this plane respectively. The Pd–C and Pd–O distances [1.984(3) and 2.138(3) Å respectively] do not differ significantly from those observed in the related, chirally directed, amido analogue.[16] The Pd–S (*trans* to nitrogen) distance, 2.299(1) Å, is effectively unchanged from that observed in (−)-**5** (*trans* to chloride), but the Pd–N bond length is noticeably reduced to 2.090(4) Å, *cf.* values of *ca.* 2.14 Å in related palladium–naphthylamine complexes.[14–16] The pyramidalization of the sulfur centre is again particularly pronounced, with angles ranging from 102.0(2) to 111.2(1)°. The C–P–C angle within the phosphornorbornene skeleton is still acute, but enlarged relative to the values observed in (−)-**5** and related ligands.[16] There is an accompanying reduction in the associated P–C bond lengths, *ca.* 0.02 Å (see Table 2). The P–O distance of 1.499(3) Å is unremarkable.

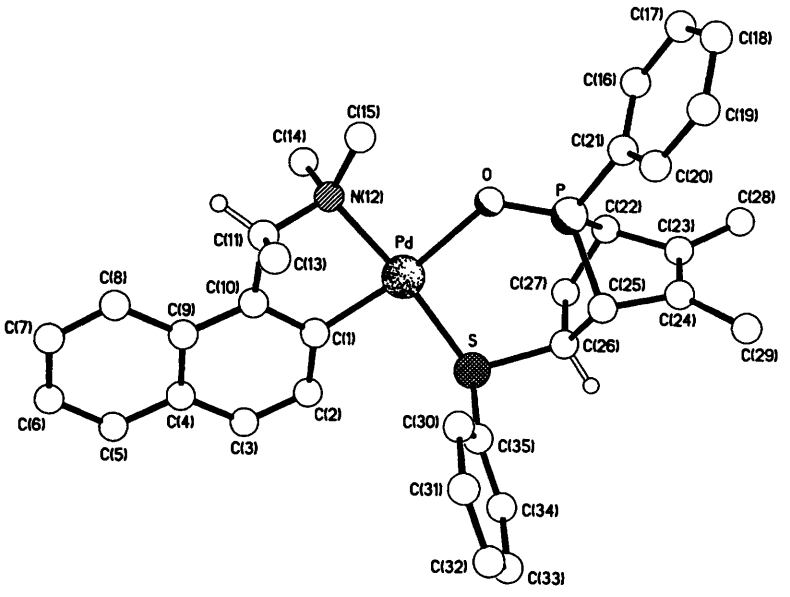


Fig. 2 The molecular structure and absolute stereochemistry of the cation in complex (−)-**8**

An inspection of the packing of the molecules reveals aromatic–aromatic edge-to-face interactions between the PPh and SPh rings of symmetry-related molecules (centroid–centroid separation 4.93 Å), but no stacking interactions involving the naphthalene rings. The closest intermolecular approach to the naphthalene rings is from the C(26) methine hydrogen atom, which is directed into the less-hindered face; the H • • • π distance of *ca.* 3.1 Å is too long for any significant C–H • • • π hydrogen bonding.

The co-ordination geometry observed for complex (−)-**8** is in accord with an interesting stereoelectronic feature invariably reported for palladium(II) complexes containing this ortho-metallated naphthylamine ligand. When heterobidentate ligands are co-ordinated to this particular metal ion the softest of the two donors always takes up a position *trans* to the σ-donating NMe_2 group in the resulting square-planar complexes.[14,17] Furthermore, the isolation of (−)-**8** indicated that the P,S chelate in the original complex (−)-**7** must be kinetically labile. However, it is interesting that in this particular labile system the oxidation process clearly occurs faster than the reported inversion of configuration at the uncoordinated bridgehead phosphorus stereogenic centre.

It is noteworthy that enantiomerically pure compound (+)-**I** is obtained with similar yield and optical purity when the equally accessible (−)-**1** was used as the chiral reaction promoter. Studies on the stereodynamic properties of optically pure (±)-**I** and the catalytic application of their metal complexes are currently in progress.

Experimental

Procedures and materials

Reactions involving air-sensitive compounds were performed under purified nitrogen using the Schlenk technique. The NMR spectra were recorded at 25 °C on Bruker ACF 300 and AMX 500 spectrometers. Optical rotations were measured on the specified solution in a 1 dm cell at 25 °C with a Perkin-Elmer model 341 polarimeter. Elemental analysis were performed by the Microanalytical Laboratory of the Department of Chemistry at the National University of Singapore.

The compounds $(+)_{589}$-di-μ-chloro-bis{(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-C^2,*N*}dipalladium(II) (+)-**1**,[18] chloro{(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-C^2,*N*}-(3,4-dimethyl-1-phenylphosphole-*P*)palladium(II) (+)-**2**[9] and the perchlorato analogue (+)-**3**,[10] and the enantiomers of bis(acetonitrile){(*R**)-1-[1-(dimethylamino)ethyl]-2-naphthyl-C^2,*N*}palladium(II) perchlorate (±)-**6**[14] were prepared by published procedures.

Syntheses

{(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-C^2,*N*}-{(1α,4α,5α,7*R*)-2,3-dimethyl-7-phenyl-5-(phenylsulfanyl)-7-phosphabicyclo[2.2.1]hept-2-ene-S^5,P^7}palladium(II) perchlorate, (−)-4. A solution of the neutral monomeric complex (+)-**2** (6.0 g, 11.4 mmol) in 1,2-dichloroethane (50 cm^3) was treated with silver perchlorate (2.4 g, 11.4 mmol) in water (2.5 cm^3) for 30 min. The resulting mixture was filtered to remove silver chloride and the yellowish organic layer was dried over anhydrous $MgSO_4$. Phenyl vinyl sulfide (3.3 cm^3, 49.0 mmol) was added and the reaction mixture was stirred for 17 d at 75 °C. The solvent was then removed under reduced pressure to give a dark purple residue. This material was chromatographed on a short silica column (silica gel 60, 10 g) with ethyl acetate–dichloromethane (1:10 v/v) as eluent giving a pale yellow solution. The solvent mixture was removed under reduced pressure and pure (−)-**4** was obtained by crystallization from dichloromethane–diethyl ether as opaque white microcrystals (5.36 g, 65%), m.p. 230–231 °C (decomp.) (Found: C, 56.0; H, 4.9; N, 1.9. Calc for $C_{34}H_{37}ClNO_4PPdS$: C, 56.1; H, 5.1; N, 1.9%). α −133.3° (589 nm, *c* 0.5 g per 100 cm^3, CH_2Cl_2). NMR ($CDCl_3$): ^1H, δ 1.37 (s, 3 H, C=C*Me*), 1.94 (d, 3 H, $^3J_{HH}$ 6.0, CH*Me*), 1.95 (s, 3 H, C=C*Me*), 2.34–2.58 (m, 2 H, CH_2), 2.70 (d, 3 H, $^4J_{PH}$ 3.7, NMe), 2.80 (d, 3 H, $^4J_{PH}$ 1.3, NMe), 3.30 (d, 1 H, $^2J_{PH}$ 1.7, PCH), 3.64 (d, 1 H, $^2J_{PH}$ 1.3, PCH), 3.85–3.99 (m, 1 H, SCH), 4.40 (qnt, 1 H, $^3J_{HH} = {}^4J_{PH}$ 6.0 Hz, C*H*Me) and 6.68–8.12 (m, 16 H, aromatics); ^{31}P-{H}, δ 124.9 (s, 1P).

Dichloro{(1α,4α,5α,7*R*)-2,3-dimethyl-7-phenyl-5-(phenylsulfanyl)-7-phosphabicyclo[2.2.1]hept-2-ene-S^5,P^7}palladium(II), (−)-5. A solution of complex (−)-**4** (0.87 g, 1.19 mmol) in acetone (20 cm^3) was treated with hydrochloric acid (12 mol dm^{-3}, 1 cm^3). The reaction mixture was then refluxed for 10 h. Yellow microcrystals of (−)-**5** precipitated during this period. The product was then filtered off and recrystallized from dichloromethane–diethyl ether (0.55 g, 93%), m.p. 243–245 °C (decomp.) (Found: C, 47.9; H, 4.2; Cl, 14.1. Calc. for

$C_{20}H_{21}Cl_2PPdS$: C, 47.9; H, 4.2; Cl, 14.1%). α −163.4° (589 nm, *c* 0.2 g per 100 cm^3, CH_2Cl_2). NMR (CD_2Cl_2): ^1H, δ 1.37 (s, 3 H, C=C*Me*), 1.65 (s, 3 H, C=C*Me*), 2.10–2.47 (m, 2 H, CH_2), 3.33 (s, 1 H, PCH), 3.52 (s, 1 H, PCH), 3.63–3.66 (m, 1 H, SCH) and 7.43–8.16 (m, 10 H, aromatics); ^{31}P-{H}, δ 132.5 (s, 1P).

Liberation of (1α,4α,5α,7*S*)-2,3-dimethyl-7-phenyl-5-(phenylsulfanyl)-7-phosphabicyclo[2.2.1]hept-2-ene, (−)-I

A solution of complex (−)-**5** (0.5 g, 1.0 mmol) in dichloromethane (20 cm^3) was stirred for 15 min in the presence of an excess of potassium cyanide (5.0 g, 80 mmol) in water (15 cm^3). The organic layer was separated, washed with water and then dried over $MgSO_4$. Removal of the solvent left a viscous oil (0.2 g, 75%). α −22.2° (589 nm, *c* 0.5 g per 100 cm^3, CH_2Cl_2). ^{31}P-{H} NMR ($CDCl_3$): δ 97.1 (s, 1P).

Alternative method. Synthesis of {(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C*^{2},*N*}{(1α,4α,5α,7*R*)-2,3-dimethyl-7-phenyl-5-(phenylsulfanyl)-7-phosphabicyclo[2.2.1]hept-2-ene-*S*^{5},*P*^{7}}palladium(II) perchlorate, (−)-7. A solution of complex (−)-**4** (0.5 g, 0.69 mmol) in dichloromethane (20 cm^3) was treated with 1,2-bis(diphenylphosphino)ethane (0.27 g, 0.69 mmol) in the same solvent (10 cm^3) for 15 min. A solution of the bis(acetonitrile) complex (−)-**6** (0.27 g, 0.69 mmol) in dichloromethane (10 cm^3) was then immediately added to the reaction mixture. After stirring for 2 h, ethyl acetate was added intermittently to crystallize the dppe side product. The reaction mixture was then filtered and removal of the solvent left a yellow glass (0.42 g, 84%) that could not be crystallized from a wide range of solvents tried. α −114.6° (589 nm, *c* 1.1 g per 100 cm^3, CH_2Cl_2). NMR ($CDCl_3$): ^1H, δ 1.38 (s, 3 H, C=C*Me*), 1.65 (d, 3 H, $^3J_{HH}$ 6.0, CH*Me*), 1.88 (s, 3 H, C=C*Me*), 2.27–2.71 (m, 2 H, CH_2), 2.62 (d, 3 H, $^4J_{PH}$ 3.7, NMe), 2.85 (d, 3 H, $^4J_{PH}$ 1.3, NMe), 3.36 (s, 1 H, PCH), 3.38 (s, 1 H, PCH), 3.80–4.00 (m, 1 H, SCH), 4.40 (qnt, 1 H, $^3J_{HH} = {}^4J_{PH}$ 6.0 Hz, C*H*Me) and 7.06–8.33 (m, 16 H, aromatics); ^{31}P-{H}, δ 128.8 (s, 1P).

Oxidation of complex (−)-7. Isolation of {(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthyl-*C*^{2},*N*}{(1α,4α,5α,7*R*)-2,3-dimethyl-7-oxo-7-phenyl-5-(phenylsulfanyl)-7-phosphabicyclo[2.2.1]-hept-2-ene-*S*^{5},*O*}palladium(II) perchlorate, (−)-8

The diastereomeric complex (−)-**7** (0.5 g, 0.69 mmol) was dissolved in dichloromethane (30 cm^3) in an ordinary round-bottomed flask. Yellow prisms formed when the solution was kept at room temperature for 15 d and diethyl ether was added at regular intervals (0.28 g, 55%), m.p. 258–260 °C (decomp.) (Found: C, 54.8; H, 4.9; N, 2.0. Calc for $C_{34}H_{37}ClNO_5PPdS$: C, 54.8; H, 5.0; N, 1.9%). α −270° (589 nm, *c* 0.2 g per 100 cm^3, CH_2Cl_2). NMR (CD_2Cl_2): ^1H, δ 1.51 (s, 3 H, C=C*Me*), 1.72 (s, 3 H, C=C*Me*), 1.92 (d, 3 H, $^3J_{HH}$ 6.4, CH*Me*), 2.24–2.63 (m, 2 H, CH_2), 2.68 (s, 3 H, NMe), 2.89–2.91 (m, 1 H, PCH), 2.93 (s, 3 H, NMe), 3.23–3.26 (m, 1 H, PCH), 3.54–3.66 (m, 1 H, SCH), 4.40 (qnt, 1 H, $^3J_{HH} = {}^4J_{PH}$ 6.4 Hz, C*H*Me) and 7.07–8.11 (m, 16 H, aromatics); ^{31}P-{H}, δ 55.2 (s, 1P).

X-Ray crystallography

Crystal data. *For complex* (−)-**5**. $C_{20}H_{21}Cl_2PPdS$, M = 501.7, monoclinic, space group $P2_1$, a = 9.499(3), b = 8.936(5), c = 11.967(4) Å, β = 92.81(2)°, U = 1014.5(8) Å^3, Z = 2, D_c = 1.64 g cm^{-3}, μ(Mo-Kα) = 13.6 cm^{-1}, $F(000)$ = 504, yellow platy needles, crystal dimensions 0.83 × 0.28 × 0.07 mm.

For complex (−)-**8**. $C_{34}H_{37}ClNO_5PPdS$, M = 744.5, monoclinic, space group $P2_1$, a = 11.135(1), b = 12.346(2), c = 12.944(1) Å, β = 113.07(1)°, U = 1637.0(3) Å^3, Z = 2, D_c = 1.51 g cm^{-3}, μ(Mo-Kα) = 8.0 cm^{-1}, $F(000)$ = 764, yellow prisms, crystal dimensions 0.47 × 0.43 × 0.30 mm.

Data collection and processing. Data for both compounds were measured on a Siemens P4/PC diffractometer with Mo-Kα radiation (λ = 0.710 73 Å, graphite monochromator) using ω scans. For **5** and **8**, 1912 and 3937 independent reflections were measured ($2\theta \leqslant 50$ and 55°) of which 1715 and 3708 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The data were corrected for Lorentz-polarization factors, and for (−)-**8** a Gaussian absorption correction (face-indexed numerical) was applied; the maximum and minimum transmission factors were 0.815 and 0.736 respectively.

Structure analysis and refinement. Both structures were solved by direct methods and the non-hydrogen atoms refined anisotropically, the phenyl rings being treated as idealized rigid bodies. The positions of the hydrogen atoms were determined from ΔF maps and subsequently optimized, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$ [$U(H) = 1.5U_{eq}(CMe)$], and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least squares based on F^2 to give (for the observed data), for (−)-**5**, R_1 = 0.039, $wR2$ = 0.093 for 202 parameters, and for (−)-**8**, $R1$ = 0.030, $wR2$ = 0.077 for 373 parameters. The maximum and minimum residual electron densities in the final ΔF maps were 0.73 and −0.98 e Å^{-3} for (−)-**5** and 0.45 and −0.29 e Å^{-3} for (−)-**8**. The mean and maximum shift/error ratios in the final refinement cycles were 0.000 and 0.000 for (−)-**5** and 0.001 and 0.012 for (−)-**8**. The absolute stereochemistries were determined unambiguously by both an *R*-factor test and the Flack parameter. For (−)-**5**, R^+ = 0.0388, R^- = 0.0394, x = 0.04(15) and for (−)-**8**, R^+ = 0.0310, R^- = 0.0321, x = −0.07(6). Computations were carried out using the SHELXTL PC program system.[19]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/241.

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