has been demonstrated to be very effective in Cd-X band assignments.[1]

Conclusions

The coordinative versatility of propane-1,3-diamines toward metal ions has been demonstrated on the observation that the propane-1,3-diamine complexes in solution, owing to the less favorable entropy change in the formation of six-membered rings,[13] present lower stability than the ethylenediamine analogues. Our systematic investigations have demonstrated that, by using appropriate metal ions, it is possible to force the propane-1,3-diamines to act in unusual ways, giving rise to compounds which present uncommon and unpredictable structures.

In fact, propane-1,3-diamine and 2,2-dimethylpropane-1,3-diamine, in the presence of Cu(II), Zn(II), and Cd(II) ions, have been found to act both as chelating and as bridging (toward two metal ions) ligands, giving rise to dimeric and/or polymeric species.[2,14] This ability of propanediamines to act as bridging ambidentate ligands can play an important role in the design of ferromagnetic-like polymetallic systems.

A greater coordinative flexibility of 2,2-dimethylpropane-1,3-diamine than that of propane-1,3-diamine may be suggested by the complexity of its compounds, whose crystalline phases, as shown in this paper, can simultaneously contain monomeric and dimeric units, and by its further unique ability to act in the extended form also as monodentate ligand,[3] with the uncoordinated amino group stabilized by hydrogen bonding interactions with a water molecule of crystallization. Moreover, the apparently simple $(dmpd)MX_2$ (M = Zn, Cd; X = Cl, Br, I) compounds, in which the amine invariably acts as chelating agent, present some interesting features, since, the metal ion environment closely depending and on the metal ion and halogen dimensions, discrete monomeric or one-dimensional polymeric species are formed.

Acknowledgment. We are grateful to the Italian Consiglio Nazionale delle Ricerche (CNR) for financial support and to the "Centro CNR di Studio sulla Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione" for the use of the Coderg PHO spectrophotometer.

Registry No. 1, 139167-79-6; $Cd(dmpd)_2Cl_2$ (monomer)/$Cd(dmpd)_2Cl_2$ (dimer), 139167-77-4; $Cd(dmpd)_2Br_2$ (monomer)/$Cd(dmpd)_2Br_2$ (dimer), 139167-78-5.

Supplementary Material Available: Detailed listings of crystallographic parameters (Table S1), fractional coordinates of hydrogen atoms (Tables S2 and S3), anisotropic thermal factors (Tables S4 and S5), and "best" molecular planes formed by selected groups of atoms (Tables S6 and S7) (6 pages); listings of observed and calculated structure factor moduli (Tables S8 and S9) (19 pages). Ordering information is given on any current masthead page.

(13) Newman, M. S.; Busch, D. H.; Cheney, G. E.; Gustafson, C. R. *Inorg. Chem.* **1972**, *11*, 2890 and references therein.
(14) Vezzosi, I. M.; Saladini, M.; Battaglia, L. P.; Bonamartini Corradi, A. *Inorg. Chim. Acta* **1985**, *100*, 261.

Contribution from the Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia

Resolutions Involving Metal Complexation. Optical Resolution and Photochemical Rearrangement of (±)-(2-Mercaptoethyl)methylphenylphosphine

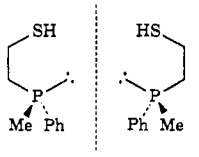
Pak Hing Leung, Anthony C. Willis, and S. Bruce Wild*

Received October 15, 1991

The asymmetric bidentate (±)-(2-mercaptoethyl)methylphenylphosphine has been resolved by the fractionial crystallization of a pair of diastereomeric thiolato-*S*-bridged dipalladium(II) complexes containing the deprotonated form of the ligand and ortho-metalated (*R*)-(1-(dimethylamino)ethyl)naphthalene. In order to recover the resolved ligand from the less soluble diastereomer of the dipalladium complex, the terminal palladium resolving unit was displaced with ethane-1,2-diamine, and the residual (thiolato)palladium(II) complex was treated with benzyl bromide; this gave a bromopalladium(II) complex containing (*S*)-(2-(benzylthio)ethyl)methylphenylphosphine bound through phosphorus only. The crystal and molecular structure of the bromopalladium complex has been determined. Crystal data: orthorhombic, $P2_12_12_1$, a = 8.774 (1) Å, b = 17.908 (3) Å, c = 18.412 (4) Å, Z = 4, and R = 0.042. The geometry around the palladium is distorted square-planar with the tertiary phosphine-*P* stereocenter of *S* absolute configuration trans to the tertiary amine-*N* of the resolving ligand of *R* absolute configuration. Optically pure (*R*)-(2-(benzylthio)ethyl)methylphenylphosphine, $[\alpha]_D$ −27.8° (*c* 1.6, dichloromethane), was displaced from the bromopalladium complex with (*R**,*R**)-(±)-1,2-phenylenebis(methylphenylphosphine) and was, in turn, converted by sodium in ammonia into a separable mixture of optically pure (*R*)-(2-mercaptoethyl)methylphenylphosphine, $[\alpha]_D$ −17.0° (*c* 3.0, dichloromethane), and optically pure (*R*)-ethylmethylphenylphosphine, $[\alpha]_D$ −7.3° (*c* 2.4, toluene). The (*R*)-(mercaptoethyl)phosphine rearranges in light with retention of configuration at phosphorus into optically pure (*S*)-ethylmethylphenylphosphine sulfide, $[\alpha]_D$ −21.6° (*c* 2.0, methanol), by an intermolecular radical chain mechanism.

Introduction

Deprotonated 2-mercaptoethyl-substituted arsines and phosphines are powerful chelating agents for a variety of transition metal ions,[1-4] giving complexes containing highly nucleophilic thiolato-*S* atoms that can be readily alkylated. Thus, with appropriate choice of ligand and alkylating agent, a *cis*-P_2S_2 macrocycle was synthesized on nickel(II),[1,4] and on palladium(II), *trans*-As_2S_2 macrocycles were prepared in diastereomerically homogeneous and optically pure forms.[5] In this paper, we describe the optical resolution of (±)-(2-mercaptoethyl)methylphenylphosphine (**1**), a model ligand for the metal-template synthesis



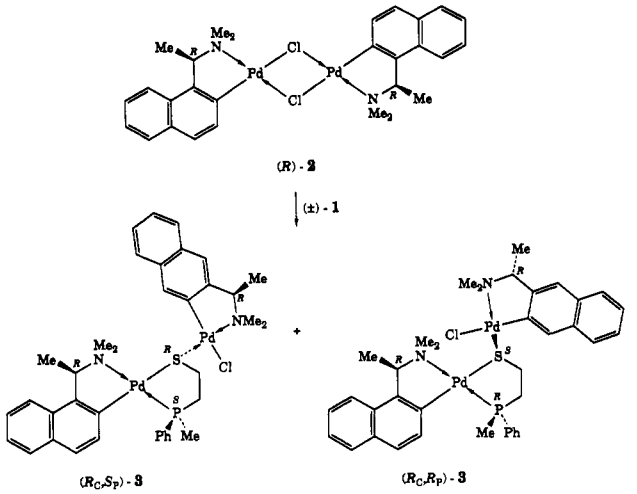
(*R*)-1 (*S*)-1

of *trans*-P_2S_2 macrocycles.[6] The resolution procedure for the phosphine–thiol, which involves the fractional crystallization of a pair of thiolato-*S*-bridged dipalladium(II) complexes containing

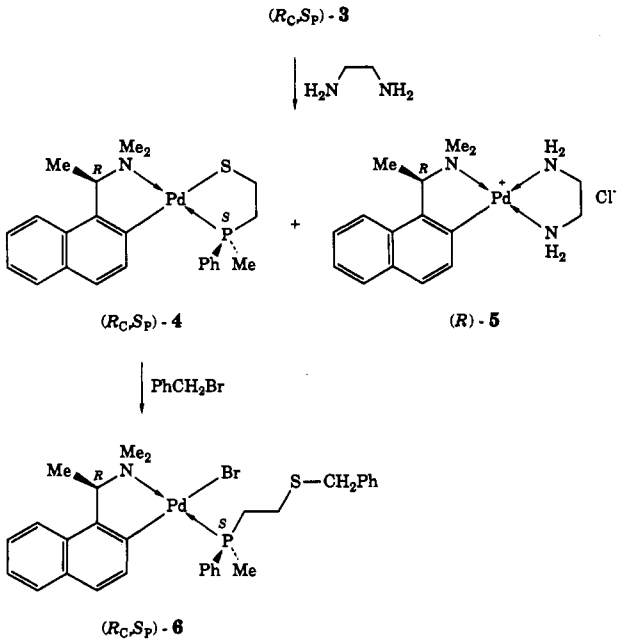
(1) Marty, W.; Schwarzenbach, G. *Chimia* **1970**, *24*, 431-433 and references cited therein.
(2) Issleib, K.; Gans, W. *Z. Anorg. Allg. Chem.* **1981**, *475*, 116-130 and references cited therein.
(3) Leung, P.-H.; Martin, J. W. L.; Wild, S. B. *Inorg. Chem.* **1986**, *25*, 3396-3400.
(4) Harris, C. M.; Livingstone, S. E. *Chelating Agents and Metal Chelates*; Dwyer, F. P., Mellor, D. P., Eds.; Academic: New York and London, 1964; Chapter 3.
(5) Kerr, P. G.; Leung, P.-H.; Wild, S. B. *J. Am. Chem. Soc.* **1987**, *109*, 4321-4328.
(6) Jones, T. L.; Willis, A. C.; Wild, S. B. *Inorg. Chem.*, following paper in this issue.

0020-1669/92/1331-1406$03.00/0

Scheme I



Scheme II



(RC,SP)-6

(*R*)-(1-dimethylamino)ethyl)naphthalene, follows closely from our earlier work on the resolution of the analogous arsine–thiol.[7] The phosphine–thiol, however, required alkylation for removal from palladium and underwent photochemical rearrangement. The various aspects of the work will be introduced in the sections that follow.

(a) Formation and Separation of Diastereomers. Phosphine–thiol (±)-**1**[3] reacts with $(+)_{589}$-bis(μ-chloro)bis[(*R*)-[1-(dimethylamino)ethyl]naphthalenyl-C^2,*N*]dipalladium(II)–0.5-dichloromethane ((*R*)-**2**·0.5CH_2Cl_2) in dichloromethane in the presence of triethylamine to give an almost quantitative yield of the diastereomers (R_C,R_P)-**3** and (R_C,S_P)-**3** (Scheme I).[8] Recrystallization of the mixture of the two compounds from dichloromethane–acetone afforded a diastereomerically homogeneous complex in 84% yield: yellow prisms, $[\alpha]_D$ −246.7° (C-H_2Cl_2). Further recrystallizations of this material, which analyzed as a monodichloromethane solvate, did not affect the optical rotation of the complex. The physical properties and ^{1}H NMR data for the complex corresponded closely to those for the analogous arsine complex for which an X-ray crystal structure determination had been carried out.[7] Accordingly, we tentatively identified the new compound as (R_C,S_P)-**3**·CH_2Cl_2. In the structure of the arsenic analogue of (R_C,S_P)-**3**, the terminal resolving unit pivots around sulfur into a conformation that places the chlorine atom 3.48 Å above the palladium of the primary resolving unit.[7] We were unable to crystallize the more soluble diastereomer of the dipalladium complex, viz. (R_C,R_P)-**3**.

(b) Liberation of Resolved Phosphine–Thiol from (R_C,S_P)-3·CH_2Cl_2. A solution of (R_C,S_P)-**3**·CH_2Cl_2 in dichloromethane was treated with a solution of diamino-1,2-ethane in water; under these conditions, the dipalladium complex was converted into (R_C,S_P)-**4**, which remained in the dichloromethane, and (*R*)-**5**, which dissolved in the water (Scheme II). (Salt (*R*)-**5** can be converted back into (*R*)-**2** by treatment with hydrochloric acid.[10]) Diastereomer (R_C,S_P)-**4** was recovered from the dichloromethane and recrystallized from dichloromethane–methanol, giving yellow needles having $[\alpha]_D$ −232° (dichloromethane). We were unable

Table I. Crystallographic Data for (R_C,S_P)-**6**

chem form	$C_{30}H_{35}BrNPPdS$	cryst dimens, mm	0.41 × 0.18 × 0.02
fw	659.0	d_{calcd}, g cm^{-3}	1.513
cryst system	orthorhombic	T, °C	21 ± 1
space group	$P2_12_12_1$	2θ range, deg	4–48
a, Å	8.774 (1)	no. of data colld	2573
b, Å	17.908 (3)	no. of data refined	1678 [$I > 3\sigma(I)$]
c, Å	18.412 (4)	no. of variables	161
V, Å^3	2893.0	R	0.042
Z	4	R_w	0.042

Table II. Final Positional and Isotropic Thermal Parameters for (R_C,S_P)-**6**

atom	x	y	z	10^3U,[a] Å^2
Pd	0.57832 (9)	0.49380 (4)	0.23430 (5)	31*
Br	0.35394 (14)	0.57172 (7)	0.27515 (10)	57*
P	0.7511 (3)	0.5733 (2)	0.2803 (2)	41*
S	0.8321 (4)	0.4355 (2)	0.4168 (2)	52*
N	0.4437 (11)	0.3980 (4)	0.2018 (5)	32 (2)
C(1)	0.3885 (16)	0.4087 (7)	0.1282 (7)	54 (4)
C(2)	0.3104 (15)	0.3822 (6)	0.2496 (7)	55 (4)
C(3)	0.5885 (15)	0.3048 (6)	0.2779 (7)	54 (4)
C(4)	0.5580 (13)	0.3342 (5)	0.2032 (5)	29 (3)
C(5)	0.6993 (13)	0.3626 (6)	0.1662 (6)	29 (3)
C(6)	0.7961 (13)	0.3162 (6)	0.1228 (6)	31 (3)
C(7)	0.7707 (14)	0.2380 (6)	0.1140 (7)	40 (3)
C(8)	0.8623 (15)	0.1977 (6)	0.0691 (7)	44 (3)
C(9)	0.9858 (15)	0.2303 (7)	0.0323 (7)	49 (4)
C(10)	1.0124 (15)	0.3051 (7)	0.0398 (7)	47 (4)
C(11)	0.9205 (14)	0.3483 (5)	0.0853 (6)	32 (3)
C(12)	0.9447 (15)	0.4259 (6)	0.0934 (6)	43 (3)
C(13)	0.8595 (14)	0.4675 (6)	0.1395 (6)	37 (3)
C(14)	0.7329 (12)	0.4371 (6)	0.1773 (6)	31 (3)
C(15)	0.6942 (15)	0.6219 (7)	0.3633 (7)	51 (4)
C(16)	0.8060 (12)	0.6493 (6)	0.2187 (6)	36 (3)
C(17)	0.9354 (15)	0.6932 (6)	0.2315 (7)	57 (3)
C(18)	0.9697 (16)	0.7500 (7)	0.1816 (8)	61 (4)
C(19)	0.8870 (17)	0.7615 (7)	0.1235 (8)	61 (4)
C(20)	0.7574 (17)	0.7193 (8)	0.1104 (8)	63 (4)
C(21)	0.7198 (16)	0.6643 (7)	0.1585 (7)	52 (4)
C(22)	0.9354 (14)	0.5318 (5)	0.3050 (6)	38 (3)
C(23)	0.9317 (16)	0.4515 (6)	0.3331 (6)	47 (3)
C(24)	0.9544 (16)	0.4824 (7)	0.4812 (7)	64 (4)
C(25)	1.1091 (14)	0.4511 (6)	0.4899 (7)	45 (3)
C(26)	1.2290 (16)	0.4722 (7)	0.4480 (8)	56 (4)
C(27)	1.3749 (16)	0.4408 (8)	0.4551 (8)	60 (4)
C(28)	1.3982 (21)	0.3891 (9)	0.5055 (9)	87 (5)
C(29)	1.2847 (20)	0.3656 (9)	0.5485 (9)	84 (5)
C(30)	1.1371 (21)	0.3948 (9)	0.5436 (9)	88 (5)

[a] Starred values denote the equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(7) Leung, P.-H.; McLaughlin, G. M.; Martin, J. W. L.; Wild, S. B. *Inorg. Chem.* **1986**, *25*, 3392–3395.

(8) For the sake of clarity, simplified descriptors have been used in the text for stereoisomers. Full stereochemical descriptors, consistent with those employed by the Chemical Abstracts Service, are given in the Experimental Section. Absolute chiralities are expressed in terms of the Cahn–Ingold–Prelog (CIP) sequence rules.[9]

(9) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385–415.

(10) Allen, D. G.; McLaughlin, G. M.; Robertson, G. B.; Steffen, W. L.; Salem, G.; Wild, S. B. *Inorg. Chem.* **1982**, *21*, 1007–1014.

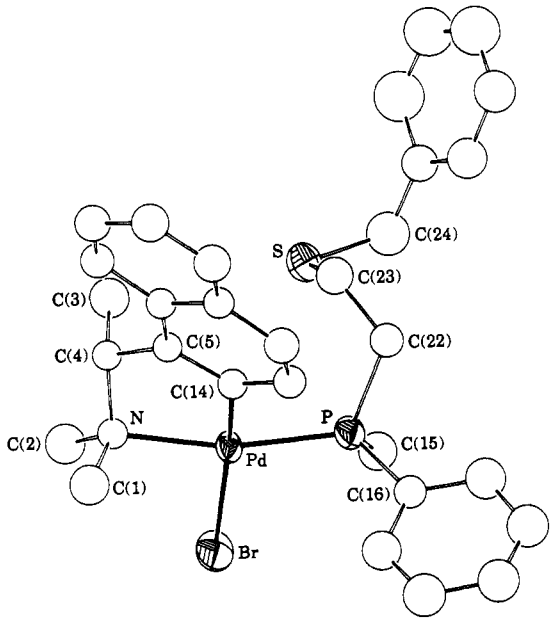


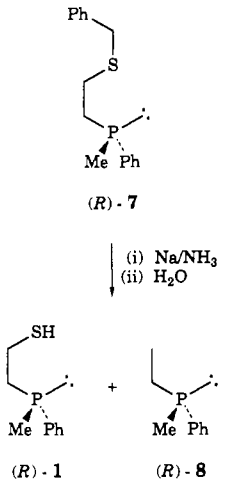
Figure 1. ORTEP view of (R_C,S_P)-**6**, showing the atom-labeling scheme for non-hydrogen atoms. Thermal ellipsoids enclose 50% probability levels.

Table III. Selected Bond Distances and Angles for (R_C,S_P)-**6**

	Bond Lengths (Å)		
Pd–Br	2.523 (2)	C(4)–C(5)	1.501 (15)
Pd–P	2.242 (3)	C(5)–C(14)	1.380 (14)
Pd–N	2.163 (8)	P–C(15)	1.824 (13)
Pd–C(14)	1.989 (1)	P–C(16)	1.833 (11)
N–C(1)	1.449 (14)	P–C(22)	1.833 (12)
N–C(2)	1.488 (15)	C(22)–C(23)	1.525 (14)
N–C(4)	1.518 (13)	S–C(23)	1.791 (13)
C(3)–C(4)	1.494 (15)	S–C(24)	1.803 (14)
	Bond Angles (deg)		
Br–Pd–P	93.64 (8)	Pd–P–C(22)	115.5 (4)
Br–Pd–N	95.4 (2)	C(15)–P–C(16)	103.6 (5)
Br–Pd–C(14)	165.5 (3)	C(15)–P–C(22)	103.1 (6)
P–Pd–N	166.9 (2)	C(16)–P–C(22)	102.8 (5)
P–Pd–C(14)	93.6 (3)	Pd–N–C(1)	109.6 (7)
N–Pd–C(14)	79.8 (4)	Pd–N–C(2)	114.5 (7)
Pd–P–C(15)	115.7 (4)	Pd–N–C(4)	103.3 (6)
Pd–P–C(16)	114.4 (4)	C(22)–S–C(24)	101.6 (6)

to remove the phosphine–thiol from (R_C,S_P)-**4** directly, so the thiolato-*S* atom in the complex was alkylated with use of benzyl bromide, giving the bromopalladium(II) complex (R_C,S_P)-**6**, which was isolated as yellow needles from acetone–dichloromethane–diethyl ether mixture, having $[\alpha]_D$ −157.1° (CH_2Cl_2). A crystal structure determination on (R_C,S_P)-**6** was carried out (Figure 1); crystal data for the complex are given in Table I, and Table II lists positional parameters employing the atom-numbering scheme of Figure 1 of the supplementary material. Table III lists most important bond distances and angles in the complex. The geometry around the palladium is square-planar with the tertiary phosphine-*P* stereocenter of *S* absolute configuration trans to the tertiary amine-*N* of the resolving ligand of *R* absolute configuration. The bond distances and angles in the puckered ortho-metalated ring are similar to those of related compounds.[7,10,11] The phosphine–thioether could now be displaced from the palladium complex; we found it convenient to use (R^*,R^*)-(±)-1,2-$C_6H_4(PMePh)_2$[12] for this purpose.[13] Optically pure (*R*)-**7** was isolated as a viscous oil that crystallized from dichloromethane–*n*-hexane as colorless needles, mp 76–78 °C, $[\alpha]_D$ −27.8° (dichloromethane).

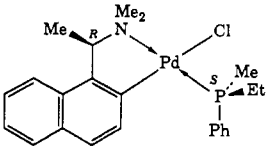
Scheme III



It now remained to convert the phosphine–thioether (*R*)-**7** into the phosphine–thiol (*R*)-**1**. Sodium in ammonia had been used previously for the regioselective cleavage of *S*-benzyl thioethers.[15] Thus, (*R*)-**7** was suspended in liquid ammonia and an excess of sodium was added to the mixture; the products were recovered and separated by HPLC on silica gel with dichloromethane–*n*-hexane as eluent. The first fraction to be eluted from the column was (*R*)-ethylmethylphenylphosphine ((*R*)-**8**), $[\alpha]_D$ −7.3 (*c* 2.4, toluene), in 20% yield, followed by the desired product (*R*)-**1**, $[\alpha]_D$ −21.6° (methanol), in 80% yield (Scheme III).

The optical purity of (*R*)-**1** obtained by this method was verified by reacting it with nickel(II) nitrate in the presence of sodium hydroxide. The corresponding *racemate* under these conditions gives a complex of the type (R^*,R^*)-(±)-*trans*-[Ni(PS)$_2$] with complete stereoselectivity; over ca. 24 h in $CDCl_3$, however, this compound rearranges with redistribution of ligands into an equilibrium mixture of itself and the corresponding meso complex, viz. (R^*,S^*)-*trans*-[Ni(PS)$_2$].[3] The reaction of (*R*)-**1** and nickel nitrate in the presence of base afforded the corresponding optically active complex (S_P,S_P)-*trans*-[Ni(PS)$_2$], $[\alpha]_D$ −102.1° (dichloromethane); the ^{1}H NMR spectrum of this compound (before recrystallization) in $CDCl_3$ showed no evidence of the corresponding meso diastereomer, even after 24 h. Thus, (*R*)-**1** having $[\alpha]_D$ −21.6° (*c* 2, methanol) is optically pure. Neither (*R*)-**1** nor (*R*)-**8** can be distilled without racemization, however.

It is appropriate here to comment upon the optical purity of (*R*)-**8** having $[\alpha]_D$ −7.3° (*c* 2.4, toluene). The highest rotation value for this phosphine in the literature is $[\alpha]_D$ +3.4° (toluene) for the *S* enantiomer; this value was considered to correspond to phosphine of 91% optical purity.[16] We have confirmed, however, that $[\alpha]_D$ −7.3° (*c* 2.4, toluene) is the correct value for optically pure (*R*)-**8**. Thus, phosphine with this rotation reacts with (*R*)-**2**·CH_2Cl_2 in dichloromethane-d_2 to give exclusively (R_C,S_P)-**9**,

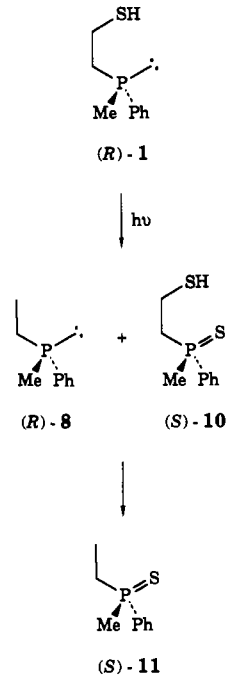


(R_C,S_P)-**9**

according to the 500-MHz ^{1}H NMR spectrum of a sample of the complex prepared in situ. A crystalline sample of (R_C,S_P)-**9**, mp 211–212 °C, was obtained subsequently by the resolution of (±)-**8**

(11) Martin, J. W. L.; Stephens, F. S.; Weerasuria, K. D. V.; Wild, S. B. *J. Am. Chem. Soc.* **1988**, *110*, 4346–4356.
(12) Roberts, N. K.; Wild, S. B. *J. Am. Chem. Soc.* **1979**, *101*, 6254–6260.
(13) Martin, J. W. L.; Palmer, J. A. L.; Wild, S. B. *Inorg. Chem.* **1984**, *23*, 2664–2668.
(14) The displacement is stereospecific with retention of configuration at phosphorus. The change in the descriptor from *S* to *R* follows as a consequence of the application of the CIP sequence rules.[9]
(15) Reed, L. J.; Niu, C.-I. *J. Am. Chem. Soc.* **1955**, *77*, 416–419.
(16) Omelanczuk, J.; Perlikowska, W.; Mikolajczyk, M. *J. Chem. Soc., Chem. Commun.* **1980**, 24–25.
(17) In ref 16, (*R*)-(+)-**11** is reported to have $[\alpha]_D$ −22.3° (MeOH).

Scheme IV



with (*R*)-**2**·CH_2Cl_2. The 500-MHz ^1H NMR spectrum of this material ($[\alpha]_D$ −85.1° (dichloromethane)) was identical to that of the sample prepared in situ, and (*R*)-**8** displaced from the pure diastereomer had $[\alpha]_D$ −7.3° (*c* 2.4, toluene).[18]

(c) Photochemical Rearrangement of Phosphine–Thiol (±)-1. Under room-lighting conditions (±)-**1** rearranges slowly into a mixture of itself with (±)-**8**, (±)-**10**, and (±)-**11** (Scheme IV).[19] In strong light (300-W UV) the conversion into phosphine sulfide (±)-**11** is complete. The rearrangement of the phosphine–thiol is not induced thermally. Thus, a sample of (±)-**1**, when heated at 100 °C for 4 days in the dark, showed no evidence of rearrangement. The rearrangement of (±)-**1** in light, together with the production of (±)-**8** and (±)-**10** as intermediates, is consistent with an intermolecular rearrangement of the phosphine–thiol according to the free radical chain mechanism indicated in Scheme V.

The photochemical conversion of (±)-**1** into (±)-**11** is highly stereoselective with retention of configuration at phosphorus. Thus, optically pure (*R*)-**1** is converted in light into optically pure (*S*)-**11** having $[\alpha]_D$ −21.6° (*c* 2.0, methanol) [lit.[16] $[\alpha]_D$ −22.3° (methanol) for the *R* enantiomer].[17] The only related work on this type of reaction appears to be the observation that tri-*n*-butylphosphine reacts with *n*-butyl mercaptan in the presence of light to produce a high yield of tri-*n*-butylphosphine sulfide and *n*-butane.[20]

Experimental Section

Preparations were carried out under an argon atmosphere, and compounds were stored in the dark. ^1H NMR spectra were recorded at 20 °C on a Jeolco FX 200 spectrometer. Optical rotations were measured on the solutions specified in a 1-dm cell at 20 °C with use of a Perkin-Elmer Model 241 polarimeter. Elemental analyses were performed by staff within the Research School of Chemistry.

$(+)_{589}$-Bis(μ-chloro)bis[(*R*)-[1-(dimethylamino)ethyl]naphthalenyl-*C*,*N*]dipalladium(II)–0.5-dichloromethane ((*R*)-**2**·0.5CH_2Cl_2) was prepared as described in ref 10. (±)-2-(Methylphenylphosphino)ethanethiol ((±)-**1**) was prepared as described in ref 3.

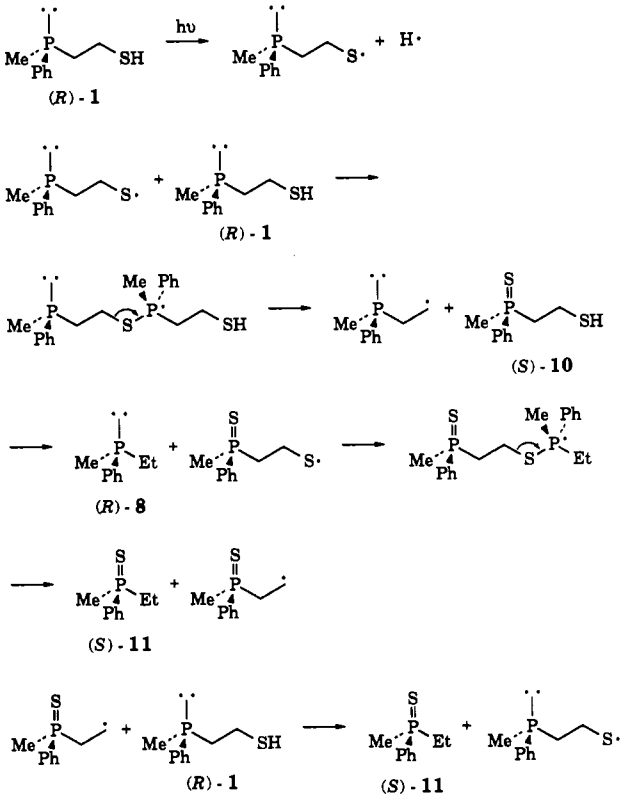
Resolution of (±)-2-(Methylphenylarsino)ethanethiol ((±)-1). Chlorobis[(*R*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*][μ-[(*S*)-2-(methylphenylphosphino)ethanethiolato-*P*,*S*]]dipalladium(II)–Dichloromethane ((*R*$_C$,*S*$_P$)-3·CH_2Cl_2). A mixture of (±)-**1** (5.0 g), (*R*)-**2**·0.5CH_2Cl_2 (20.8 g), and triethylamine (5 mL) in dichloromethane (300 mL) was stirred until all of the resolving agent had dissolved (ca. 1 h). The yellow solution was then washed with water to remove $[Et_3NH]Cl$, and the organic layer was separated and dried over $MgSO_4$. The dried solution was evaporated to dryness, leaving a yellow glass consisting of an equimolar mixture of (*R*$_C$,*R*$_P$)-**3** and (*R*$_C$,*S*$_P$)-**3**. This mixture was taken up in dichloromethane (150 mL), and the solution was diluted with acetone (50 mL). Large yellow prisms of (*R*$_C$,*S*$_P$)-**3**·CH_2Cl_2 separated from the solution after it had been concentrated to ca. 100 mL on the steam bath: mp 208–209 °C; $[\alpha]_D$ −246.7° (*c* 1.0, CH_2Cl_2); 10.4 g (84% yield). Anal. Calcd for $C_{38}H_{46}Cl_3N_2PPd_2S$: C, 50.0; H, 5.1; N, 3.1; P, 3.4; S, 3.5. Found: C, 50.3; H, 5.2; N, 2.9; P, 3.4; S, 3.4. ^1H NMR ($CDCl_3$): δ 1.84 (d, 3 H, $^3J_{HH}$ = 6.1 Hz, CH*Me*), 1.96 (d, 3 H, $^3J_{HH}$ = 6.1 Hz, CH*Me*), 2.32 (d, 3 H, $^2J_{PH}$ = 10.3 Hz, PMe), 2.40–2.91 (m, 4 H, CH_2CH_2), 2.83 (s, 3 H, NMe), 2.87 (s, 3 H, NMe), 3.12 (s, 3 H, NMe), 3.31 (d, 3 H, J_{PH} = 3.2 Hz, N*Me*), 4.17–4.42 (m, 2 H, C*H*Me), 5.27 (s, 2 H, CH_2Cl_2), 6.98–8.12 (m, 17 H, aromatics).

[*SP*-4-4-1(*R*),4(*S*)]-[1-[1-(Dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*][2-(methylphenylphosphino)ethanethiolato-*P*,*S*]palladium(II) ((*R*$_C$,*S*$_P$)-4). A solution of the dipalladium complex (*R*$_C$,*S*$_P$)-**3**·CH_2Cl_2 (10 g) in dichloromethane (100 mL) was treated with a solution of diamino-1,2-ethane (10 mL) in water (100 mL). The mixture was stirred for 1 h, and then it was separated into the two phases. The complex (*R*$_C$,*S*$_P$)-**4** was isolated from the organic phase and recrystallized from dichloromethane–methanol, forming yellow needles: mp 189–191 °C; $[\alpha]_D$ −232° (*c* 1.0, CH_2Cl_2); 4.6 g (87% yield). Anal. Calcd for $C_{23}H_{28}NPPdS$: C, 56.7; H, 5.8. Found: C, 56.4; H, 5.5. ^1H NMR ($CDCl_3$): δ 1.87 (d, 3 H $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.03 (d, 3 H, $^2J_{PH}$ = 9.5 Hz, PMe), 2.40–2.98 (m, 4 H, CH_2CH_2), 2.79 (s, 3 H, NMe), 2.91 (d, 3 H, J_{PH} = 4 Hz, NMe), 4.33 (d of q, 1 H, $^3J_{HH}$ = 6.1 Hz, J_{PH} = 6.1 Hz, C*H*Me), 7.00–7.81 (m, 11 H, aromatics).

The aqueous phase, when concentrated, gave (*R*)-**5** as colorless needles: mp 225–226 °C; $[\alpha]_D$ +98.2° (*c* 1.0, H_2O). Yield: 95%.[7]

[*SP*-4-4-1(*R*),4(*S*)]-Bromo[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*][1-(benzylthio)-2-(methylphosphino)ethane-*P*]palladium(II) ((*R*$_C$,*S*$_P$)-6). A solution of (*R*$_C$,*S*$_P$)-**5** (13.6 g) in dichloromethane (100 mL) was treated with benzyl bromide (3.3 mL). After 12 h the solvent was removed from the reaction mixture and the residue was recrystallized from acetone–dichloromethane–diethyl ether mixture, forming yellow needles: mp 192–194 °C; $[\alpha]_D$ −157.1° (*c* 0.5, CH_2Cl_2); 16.8 g (91% yield). Anal. Calcd for $C_{30}H_{35}BrNPPdS$: C, 54.7; H, 5.3. Found: C, 54.5; H, 5.3. ^1H NMR ($CDCl_3$): δ 1.89 (d, 3 H, $^3J_{HH}$ = 6.1 Hz, C*H*Me), 2.05 (d, 3 H, $^2J_{PH}$ = 10.3 Hz, PMe), 2.40–2.68 (m, 4 H, CH_2CH_2), 2.62 (s, 3 H, NMe), 4.00 (d, 3 H, J_{PH} = 4 Hz, NMe), 3.47, 3.57 (AB q, 2 H, $^2J_{HH}$ = 13.4 Hz, CH_2Ph), 4.27 (d of q, 1 H, $^3J_{HH}$ =

Scheme V



(18) Leung, P.-H.; Wild, S. B. Unpublished work.
(19) For a preliminary account of this work, see: Leung, P.-H.; Wild, S. B. *Bull. Singapore Natl. Inst. Chem.* **1989**, *17*, 37–41.
(20) Walling, C.; Basedow, O. H.; Savas, E. S. *J. Am. Chem. Soc.* **1960**, *82*, 2181–2184. Walling, C.; Pearson, M. S. *J. Am. Chem. Soc.* **1964**, *86*, 2262–2266.

6.1 Hz, C*H*Me), 6.62–7.82 (m, 16 H, aromatics).

(*R*)-1-(Benzylthio)-2-(methylphosphino)ethane ((*R*)-7). A solution of (R_C,S_P)-**6** (10 g) in dichloromethane (150 mL) was treated with a solution of (R^*,R^*)-(±)-1,2-phenylenebis(methylphenylphosphine)[12] (6.6 g) in the same solvent (50 mL). The reaction mixture was concentrated (to ca. 50 mL), and *n*-hexane (400 mL) was added slowly. The colorless palladium complex that precipitated was filtered off, and the filtrate was evaporated to dryness.[13] The residual oil was taken up in a small quantity of dichloromethane and *n*-hexane was added, whereupon the product separated as colorless needles: mp 76–78 °C; $[\alpha]_D$ −27.8° (*c* 1.6, CH_2Cl_2); 3.8 g (92% yield). Anal. Calcd for $C_{16}H_{19}PS$: C, 70.1; H, 6.9. Found: C, 70.3; H, 7.1. ^{1}H NMR ($CDCl_3$): δ 1.26 (d, 3 H, $^2J_{PH}$ = 3.2 Hz, PMe), 1.77–2.00 (m, 2 H, PCH_2), 2.34–2.96 (m, 2 H, SCH_2), 3.63 (s, 2 H, CH_2Ph), 7.13–7.48 (m, 10 H, aromatics).

(*R*)-2-(Methylphenylphosphino)ethanethiol ((*R*)-1). Sodium (1 g) was added to a suspension of (*R*)-**7** (5 g) in liquid ammonia (400 mL). The initial blue of the sodium in ammonia gave way to an orange color. After 2 h, the ammonia was allowed to evaporate off and a solution of ammonium chloride (5 g) in water (100 mL) was added. The products were then extracted into dichloromethane (2 × 100 mL), and the extract was dried ($MgSO_4$). After filtration, the extract was evaporated leaving a colorless oil (3.1 g) that was shown by ^{1}H NMR spectroscopy to be a mixture of (*R*)-**1** (80%) and (*R*)-ethylmethylphenylphosphine ((*R*)-**8**) (20%). The mixture was separated by HPLC on a silica column (Merck Si-60) at 30 psi with dichloromethane–*n*-hexane (1:4) as eluent. The first compound to be eluted from the column was (*R*)-**8**, a colorless oil: $[\alpha]_D$ −0.75° (*c* 1.33, CH_2Cl_2), −7.3° (*c* 2.4, toluene); 0.6 g (20% yield). Anal. Calcd for $C_9H_{13}P$: C, 71.0; H, 8.6. Found: C, 71.3; H, 8.9. ^{1}H NMR ($CDCl_3$): δ 0.99 (d of t, 3 H, $^3J_{HH}$ = 7.8 Hz, $^3J_{PH}$ = 15 Hz, CH_2CH_3), 1.27 (d, 3 H, $^2J_{PH}$ = 2.9 Hz, PMe), 1.48–1.78 (m, 2 H, CH_2CH_3), 7.25–7.50 (m, 5 H, aromatics). The second fraction to be eluted was the desired product (*R*)-**1**, a colorless oil: $[\alpha]_D$ −17.0 (*c* 3.0, CH_2Cl_2), 2.3 g (74% yield). Anal. Calcd for $C_9H_{13}PS$: C, 58.7; H, 7.1. Found: C, 58.6; H, 7.3. ^{1}H NMR ($CDCl_3$): identical to that of (±)-**1**.[3]

[*SP*-4-1-(*S*),(*S*)]-Bis[2-(methylphosphino)ethanethiolato-*P*,*S*)]nickel(II) ((S_P,S_P)-*trans*-9). A solution of $[Ni(H_2O)_6](NO_3)_2$ (0.73 g) in methanol (40 mL) was added slowly into a solution of (*R*)-**1** (1.4 g) in methanol (40 mL) containing 1 M NaOH (7 mL). After 30 min, the reaction mixture was evaporated to dryness and the residue was suspended in a mixture of dichloromethane (50 mL) and water (50 mL). The deep red organic layer was separated from the colorless aqueous layer, and then it was dried ($MgSO_4$), filtered, and evaporated to dryness to leave a red glassy material with a ^{1}H NMR spectrum identical to that of the crystalline complex obtained from dichloromethane–diethyl ether: $[\alpha]_D$ −102.1° (*c* 0.065, CH_2Cl_2); 1.3 g (81% yield). Anal. Calcd for $C_{18}H_{24}NiP_2S_2$: C, 50.9; H, 5.7. Found: C, 51.2; H, 5.9. ^{1}H NMR ($CDCl_3$): identical to that of corresponding racemic-trans complex.[3] There was no change in the ^{1}H NMR spectrum of the solution after storage for 5 days at 20 °C.

Photochemical Rearrangement of (±)-1. A freshly prepared sample (±)-**1** (2 g) was stored under argon for 14 days under ordinary room lighting conditions. The sample was then distilled in vacuo yielding the following compounds.

(±)-Ethylmethylphenylphosphine ((±)-8): colorless oil; bp 38–40 °C (0.03 mmHg); 0.6 g (30% yield). Anal. Calcd for $C_9H_{13}P$: C, 71.0; H, 8.6. Found: C, 70.8; H, 8.6. ^{1}H NMR ($CDCl_3$): identical to (*R*)-**8**.

(±)-1: colorless oil; bp 80–81 °C (0.03 mmHg); 0.2 g (10% yield). Anal. Calcd for $C_9H_{13}PS$: C, 58.7; H, 7.1. Found: C, 58.9; H, 6.9. ^{1}H NMR ($CDCl_3$): identical to that of initial sample.

(±)-Ethylmethylphenylphosphine Sulfide ((±)-11): colorless oil; bp 110–112 °C (0.03 mmHg); 0.4 g (20% yield). Anal. Calcd for $C_9H_{13}PS$: C, 58.7; H, 7.1. Found: C, 58.6; H, 6.9. ^{1}H NMR ($CDCl_3$): δ 1.13 (d of t, 3 H, $^3J_{HH}$ = 7.3 Hz, $^3J_{PH}$ = 20.3 Hz, CH_2CH_3), 1.95 (d, 3 H, $^2J_{PH}$ = 12.8 Hz, PMe), 2.06–2.23 (m, 2 H, CH_2CH_3), 7.46–7.98 (m, 5 H, aromatics).

(±)-(2-Mercaptoethyl)methylphenylphosphine Sulfide ((±)-10): colorless oil; bp 137–140 °C (0.03 mmHg); 0.2 g (8.5% yield). Anal. Calcd for $C_9H_{13}PS_2$: C, 50.0; H, 6.1. Found: C, 50.2; H, 6.3. ^{1}H NMR ($CDCl_3$): δ 1.74 (t, 1 H, $^3J_{HH}$ = 7.6 Hz, SH), 1.99 (d, 3 H, $^2J_{PH}$ = 12.9 Hz, PMe), 2.24–3.00 (m, 4 H, CH_2CH_2), 6.42–6.95 (m, 5 H, aromatics).

(*S*)-Ethylmethylphenylphosphine Sulfide ((*S*)-11). A sample of (*R*)-**1** (0.5 g) in an NMR tube was irradiated with UV light (300 W) for 30 min. The NMR spectrum of the sample after this exposure indicated quantitative formation of (*S*)-**11**: colorless oil, $[\alpha]_D$ −21.6° (*c* 2.0, MeOH) [lit. [16] $[\alpha]_D$ +22.3° (MeOH) for *R* enantiomer].

X-ray Crystallography. Crystals of (R_C,S_P)-**6** grew as thin plates by vapor diffusion of diethyl ether into an acetonitrile solution of the complex. One of the thicker plates was chosen, and a fragment was cleaved from it and mounted on a quartz fiber. X-ray photographs revealed *mmm* Laue symmetry, and systematic extinctions uniquely identified the space group $P2_12_12_1$. The crystallographic measurements were carried out on a Philips PW 1100/20 diffractometer employing graphite-monochromated Mo Kα radiation (0.710 69 Å). Crystallographic data are gathered together in Table I; reduction of the data and structure refinement was carried out with use of the ANUCRYS structure determination package.[21]

Registry No. (±)-**1**, 102782-08-1; (*R*)-**1**, 130932-02-4; (*R*)-**2**, 80145-77-3; (R_C,S_P)-**3**, 139493-23-5; (R_C,R_P)-**3**, 139562-13-3; (R_C,S_P)-**4**, 139461-42-0; (*R*)-**5**, 102808-70-8; (R_C,S_P)-**6**, 139461-43-1; (*R*)-**7**, 139461-41-9; (±)-**8**, 130932-00-2; (*R*)-**8**, 52119-19-4; (S_C,S_P)-*trans*-**9**, 139561-00-5; (±)-**10**, 130871-25-9; (±)-**11**, 130932-01-3; (*S*)-**11**, 62621-05-0; (R^*,R^*)-(±)-1,2-phenylenebis(methylphenylphosphine), 122331-49-1.

Supplementary Material Available: For (R_C,S_P)-**6**, a textual description of the crystal structure determination, a figure showing the atom-labeling scheme, and tables listing crystallographic parameters, bond distances and angles, anisotropic thermal parameters of non-hydrogen atoms, and calculated hydrogen atom parameters (12 pages); a table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

(21) McLaughlin, G. M.; Taylor, D.; Whimp, P. O. *The ANUCRYS Structure Determination Package*; Research School of Chemistry, Australian National University: Canberra, ACT 2601, Australia.