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Resolutions Involving Metal Complexation. Synthesis and Resolution of (±)-(2-Mercaptoethyl)methylphenylarsine. Crystal and Molecular Structure of $(-)_{589}$-[Pd{(*R*)-$CH_3CH(1\text{-}C_{10}H_6)NMe_2$-$C^2$,*N*}{(*S*)-$PhMeAsCH_2CH_2S$-*As*,*μ*-*S*}PdCl{(*R*)-$CH_3CH(1\text{-}C_{10}H_6)NMe_2$-$C^2$,*N*}]·$0.67CH_2Cl_2$

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Received January 17, 1986

The asymmetric chelating agent (±)-(2-mercaptoethyl)methylphenylarsine has been resolved into its optical antipodes by the fractional crystallization of unusual *μ*-thiolato epimers containing two ortho-metalated [(*R*)-[1-(dimethylamino)ethyl]-naphthyl-C^2,*N*]palladium(II) resolving units per bridging (methylphenylarsino)ethane-2-thiolato ligand. The least soluble epimer with $[\alpha]_D$ −283° (CH_2Cl_2) crystallizes in the space group $P2_12_12_1$, with a = 10.080 (2) Å, b = 14.157 (2) Å, c = 27.918 (4) Å, and Z = 4. The structure was solved by heavy-atom methods and refined by least-squares analysis to an R of 0.052 and R_w of 0.056 for 2347 reflections. The bridging thiolato atom and the coordinated arsenic atom both have the *S* absolute configuration in the dinuclear complex. Treatment of the dimer with diamino-1,2-ethane removes the terminal resolving unit and affords crystalline monomeric $(-)_{589}$-[(*R*)-1-[1-(dimethylamino)ethyl]naphthyl-C^2,*N*][(*S*)-(methylphenylarsino)ethanethiolato-*As*,*S*]-palladium(II) from which optically pure (*R*)-$(-)_{589}$-(2-mercaptoethyl)methylphenylarsine with $[\alpha]_D$ −16.7° (CH_2Cl_2) was liberated by treatment with cyanide. The (*S*)-$(+)_{589}$ enantiomer of the ligand was obtained in a state of 72% optical purity from the residual mixture of epimeric complexes and was subsequently brought to purity by fractional crystallization of the corresponding enantiomorphic dinuclear complexes containing (*S*)-dimethyl(1-(*α*-naphthyl)ethyl)amine.

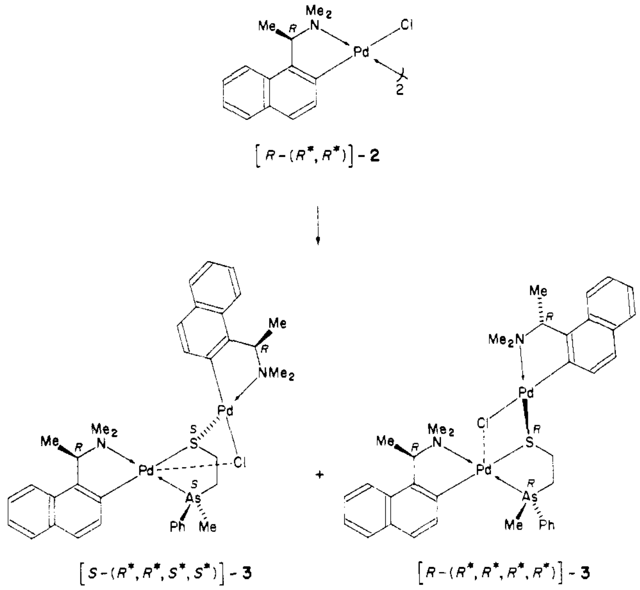
Introduction

A considerable coordination chemistry of deprotonated mercaptoalkyl-substituted primary, secondary, and tertiary phosphines and arsines has emerged in recent years, primarily due to contributions from the groups of Issleib[1] and of Schwarzenbach.[2] Although neutral complexes of the deprotonated ligands with bi- and trivalent metal ions are readily made, stereochemical considerations are complicated in such systems by diastereomerism that arises from (a) the relative arrangement of the pairs of like donor atoms of the unsymmetrical chelate rings, (b) the relative absolute configurations of the asymmetric phosphorus or arsenic donor atoms (if present), (c) the relative local helicities of nonplanar chelate rings in bis and tris bidentate or related complexes, and (d) the metal center chirality in octahedral systems. Additional asymmetric centers are created in the complexes by S-alkylation or by polymerization via *μ*-S bridges. A further compounding of difficulties may be associated with the assignment of structures to complexes that are labile with respect to redistribution of the bidentate anions between diastereomers.

In order to investigate the stability of coordination complexes of this important class of ligands, we have prepared and resolved (±)-(2-mercaptoethyl)methylphenylarsine ((±)-**1**) (Figure 1). The resolution was achieved by the fractional crystallization of dinuclear complexes that contain a *μ*-S atom of the deprotonated ligand linking two ortho-metalated [(*R*)-1-[(dimethylamino)-ethyl]naphthyl-C^2,*N*]palladium(II) resolving units.[3] The molecular structure of the least soluble dimer was confirmed by X-ray crystallography. The optically pure forms of (±)-**1** were liberated from the respective dimers in two steps: diamino-1,2-ethane removed the terminal resolving units with formation of isolable mononuclear diastereomers; in a subsequent step, cyanide was used to stereospecifically liberate the optically pure tertiary arsines from the mononuclear complexes.

In the following paper[4] a definitive account of the stereochemistry and stability of mononuclear complexes of bivalent nickel, palladium, and platinum with (±)-(2-mercaptoethyl)-methylphenylarsine and its phosphorus analogue will be presented. The work has implications for the understanding of biological reactions involving (mercaptoalkyl)amines for which model systems have already been investigated.[5] Furthermore, in subsequent work it will be shown that the isolation of pure enantiomers of asymmetric bidentates of this type was the crucial first step in the rational synthesis of optically active chelating macrocycles containing resolved asymmetric trivalent arsenic stereocenters.

Scheme I



Results and Discussion

(±)-(2-Mercaptoethyl)methylphenylarsine ((±)-**1**) was obtained in 81% yield from ethylene sulfide and sodium methylphenylarsenide in tetrahydrofuran:

$$(CH_2CH_2)_2S + Na[AsMePh] \rightarrow$$

$$PhMeAsCH_2CH_2SNa \xrightarrow{H+} \underset{(\pm)\text{-}\mathbf{1}}{PhMeAsCH_2CH_2SH} + Na^+$$

The tertiary arsine is an air-sensitive colorless oil, bp 84–85 °C (0.05 mmHg). The ^1H NMR spectrum of the compound contains a sharp AsMe singlet at δ 1.18, and, in the IR spectrum, a weak ν(SH) absorption between 2520 and 2540 cm^{-1} was observed.

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(1) Issleib, K.; Gans, W. *Z. Anorg. Allg. Chem.* **1981**, *475*, 116–130 and references therein.

(2) Marty, W.; Schwarzenbach, G. *Chimia* **1970**, *24*, 431–433 and references therein.

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

(4) Leung, P. H.; Martin, J. W. L.; Wild, S. B. *Inorg. Chem.*, following paper in this issue.

(5) Busch, D. H.; Jicha, D. C.; Thompson, M. C.; Wrathall, J. W.; Blinn, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 3642–3650. Blinn, E. L.; Busch, D. H. *Inorg. Chem.* **1968**, *7*, 820–824.

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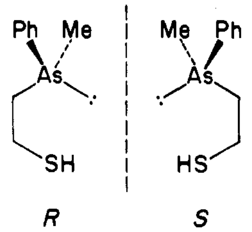


Figure 1. Enantiomers of (±)-**1**.

The resolution procedure is summarized in Scheme I. The initial mixture of dinuclear complexes was prepared from a reaction involving 2 equiv of the resolving agent $[R\text{-}(R^*,R^*)]$-**2**[3] (one dimeric unit) with 1 equiv each of (±)-**1** and triethylamine in dichloromethane. The yield of epimers was 95%. Recrystallization of the mixture from dichloromethane–acetone produced large yellow prisms of the dinuclear complex $[S\text{-}(R^*,R^*,S^*,S^*)]$-**3**[6] with $[\alpha]_D$ −283° (CH_2Cl_2). The pure epimer crystallized as a $0.67CH_2Cl_2$ solvate from the dichloromethane–acetone mixture in 85% of the theoretical yield. Further recrystallizations did not improve the optical rotation of the substance. The more soluble diastereomer could not be isolated from the mother liquor in crystalline form. It was subsequently prepared from the pure components, but again it proved impossible to crystallize. In the absence of structural data in the solid state, the soluble diastereomer has been tentatively formulated as $[R\text{-}(R^*,R^*,R^*,R^*)]$-**3** with the structure shown in Scheme I. (The dashed lines in the structures of the dinuclear complexes arise from the observation that the chlorine atom in $[S\text{-}(R^*,R^*,S^*,S^*)]$-**3** was found in an X-ray crystallographic analysis to be occupying an axial site 3.480 Å from the palladium atom indicated (vide infra). A weak interaction of the same type would lead to the structure shown for $[R\text{-}(R^*,R^*,R^*,R^*)]$-**3**.)

Crystal and Molecular Structure of $[S\text{-}(R^*,R^*,S^*,S^*)]$-3. Absolute Configuration of Coordinated (*R*)-1. Pale yellow prisms of $[S\text{-}(R^*,R^*,S^*,S^*)]$-**3**·$0.67CH_2Cl_2$ suitable for X-ray crystallography were grown by vapor diffusion of acetone into a dichloromethane solution of the complex. The compound crystallizes with four molecules per unit cell in the space group $P2_12_12_1$. The structure (R = 0.056) contains a single thiolato bridge between two nonequivalent square-planar palladium(II) moieties (S–Pd–S angle: 105°). The coordination geometry about each palladium correlates with data on a previous complex containing the ortho-metalated dimethyl(1-(α-naphthyl)ethyl)amine ring:[3] the five-membered rings containing the palladium atoms have asymmetric skew conformations of δ helicity with the methyl substituents on the asymmetric carbon stereocenters of *R* absolute configuration occupying axial sites. The As and S donor atoms are bound regiospecifically to the palladium atoms, with the softest donors taking up positions trans to the NMe_2 group in each case.

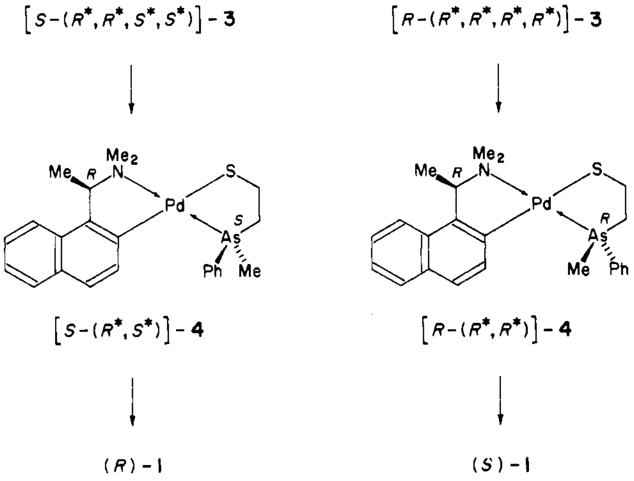
Table I. Selected Bond Distances (Å) with Estimated Standard Deviations in Parentheses

Pd(1)–As	2.320 (2)	C(11)–C(12)	1.56 (3)
–S	2.393 (5)	Pd(2)–Cl	2.438 (5)
–N(1)	2.162 (13)	–S	2.303 (5)
–C(2)	2.017 (15)	–N(2)	2.116 (15)
As–C(15)	1.92 (2)	–C(22)	2.01 (2)
–C(35)	1.97 (2)	N(2)–C(31)	1.56 (2)
–C(36)	1.90 (2)	–C(33)	1.44 (2)
S–C(37)	1.82 (3)	–C(34)	1.53 (3)
C(36)–C(37)	1.52 (3)	C(21)–C(22)	1.43 (2)
N(1)–C(11)	1.48 (2)	–C(31)	1.48 (3)
–C(13)	1.49 (2)	C(31)–C(32)	1.57 (2)
–C(14)	1.50 (2)	Pd(1)- -Pd(2)	3.726 (2)
C(1)–C(2)	1.37 (2)	- -Cl	3.476 (5)
–C(11)	1.48 (2)		

Table II. Selected Bond Angles (deg) with Estimated Standard Deviations in Parentheses

As–Pd(1)–S	85.1 (1)	As–C(36)–C(37)	109 (1)
–N(1)	176.1 (4)	S–C(37)–C(36)	111 (1)
–C(2)	96.2 (4)	S–Pd(2)–Cl	91.4 (2)
S–Pd(1)–N(1)	98.8 (4)	–N(2)	172.0 (4)
–C(2)	178.7 (4)	–C(22)	92.3 (5)
N(1)–Pd(1)–C(2)	79.9 (5)	Pd(1)–S–Pd(2)	105.0 (2)
Pd(1)–As–C(15)	119.9 (5)	–C(37)	105.9 (7)
–C(35)	115.9 (5)	Pd(2)–S–C(37)	102.8 (7)
–C(36)	106.9 (6)	Cl–Pd(2)–N(2)	94.3 (5)
C(15)–As–C(35)	105.1 (7)	–C(22)	175.8 (5)
–C(36)	104.7 (8)	N(2)–Pd(2)–C(22)	82.2 (6)
C(35)–As–C(36)	102.4 (8)	Pd(2)–N(2)–C(31)	103 (1)
Pd(1)–N(1)–C(11)	104.6 (9)	–C(33)	110 (1)
–C(13)	107.5 (10)	–C(34)	115 (1)
–C(14)	113.6 (10)	C(33)–N(2)–C(34)	110 (1)
C(13)–N(1)–C(14)	111 (1)	Pd(2)–C(22)–C(21)	112 (1)
Pd(1)–C(2)–C(1)	113 (1)	C(22)–C(21)–C(31)	116 (1)
C(2)–C(1)–C(11)	118 (1)	N(2)–C(31)–C(21)	107 (1)
N(1)–C(11)–C(1)	108 (1)	–C(32)	115 (2)
–C(12)	116 (1)		

Scheme II



We had previously observed a similar regiospecificity of coordination of unsymmetrical PN[3] and AsN[3,10] bidentates to this particular resolving unit. The five-membered ring containing the asymmetric As and S stereocenters has adopted the δ conformation in the solid state, which has apparently been dictated by the preferred equatorial disposition of the bulky phenyl group on the asymmetric arsenic stereocenter of *S* absolute configuration. The Pd(2) substituent has also taken up an equatorial position on the asymmetric μ-S stereocenter, which accordingly has the *S* absolute configuration. The orientation of the plane containing Pd(2) with respect to the one containing Pd(1) appears from molecular models

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(6) The stereochemical nomenclature adopted here is consistent with recent Chemical Abstracts Service indexing practice.[7] For clarity in the text the full stereochemical descriptors, which also contain parts defining the geometries of the square-planar palladium groups, have been omitted, although they are given in the Experimental Section. Thus, the descriptor $[S\text{-}(R^*,R^*,S^*,S^*)]$ denotes the *S* enantiomer (absolute chirality expressed in terms of the Cahn–Ingold–Prelog sequence rule symbol[9] of the most preferred or lowest numbered asymmetric stereocenter) of the diastereomer in which the relative configurations of the four asymmetric stereocenters present in decreasing order of sequence rule perference are expressed as R^*,R^*,S^*,S^*. For enantiomer $[S\text{-}(R^*,R^*,S^*,S^*)]$-**3**, the absolute configurations of the As, the S, and the two carbon stereocenters are accordingly *S*, *S*, *R*, and *R*, respectively.

(7) Blackwood, J. E.; Giles, P. M., Jr. *J. Chem. Inf. Comput. Sci.* **1975**, *15*, 67–72. *Chemical Abstracts, Index Guide to Volume 76*; Chemical Abstracts Service: Columbus, OH, 1972. *Chemical Abstracts, Ninth* Collective *Index, Index Guide to Volumes 76–85*; Chemical Abstracts Service: Columbus, OH, 1977; paragraph 203. Also see: Cahn, R. S.; Dermer, O. C. *Introduction to Chemical Nomenclature*, 5th ed.; Butterworths: London and Boston, MA, 1979; pp 140–150.

(8) The apparent inversion of configuration of the tertiary arsine that takes place when it is displaced from the metal is consistent with the specification of Cahn et al. for absolute configurations.[9]

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

(10) Martin, J. W. L.; Palmer, J. A. L.; Wild, S. B. *Inorg. Chem.* **1984**, *23*, 2664–2668.

to have been determined by the minimization of repulsive forces between the ortho-metalated naphthyl rings. The distances Pd(1)--Pd(2) and Pd(1)--Cl are also included in Table I: in neither case are they considered to be within bonding range. The Pd–S distances are within the normal range.[11]

Liberation of (R)-1. Complex [S-(R*,R*,S*,S*)]-**3** reacts with diamino-1,2-ethane under ambient conditons to give mononuclear [S-(R*,S*)]-**4** and the corresponding diamino-1,2-ethane derivative of the resolving agent, (R)-**5** (Scheme II). The latter can be converted into [R-(R*,R*)]-**2** with hydrochloric acid.[3] Diastereomer [S-(R*,S*)]-**4** was isolated in high yield as yellow crystals with $[\alpha]_D$ −262° (CH_2Cl_2) from concentrated dichloromethane–acetone solution. Complete decomposition of [S-(R*,S*)]-**4** took place when a dichloromethane solution of it was stirred with aqueous potassium cyanide for 12 h. The organic layer contained the optically active tertiary arsine as well as the optically active amine of the resolving agent. The latter was removed from the mixture by extraction into dilute sulfuric acid and was subsequently recovered from the acid by neutralization for future use. Pure (R)-(−)-**1** was then isolated from the dichloromethane by distillation. It had a boiling point of 84–85 °C (0.05 mmHg) and $[\alpha]_D$ −16.7° (CH_2Cl_2). The optical purity of (R)-(−)-**1** was confirmed by the preparation of *trans*-[Ni{(S)-**1**}$_2$] from distilled (R)-(−)-**1**: no evidence of the meso diastereomer of the complex was detected by ^1H NMR spectroscopy (see ref 4).

Partially resolved (S)-**1** with $[\alpha]_D$ +12° (CH_2Cl_2) was liberated from the noncrystalline fraction of dinuclear palladium(II) epimers remaining in the mother liquor after the isolation of [S-(R*,R*,S*,S*)]-**3**. This material was brought to optical purity by reacting it with the calculated quantity of [R-(R*,R*)]-**2** and isolating crystalline [R-(R*,R*,S*,S*)]-**3** with $[\alpha]_D$ +283° (CH_2Cl_2). Optically pure (S)-**1** with $[\alpha]_D$ +16.6° (CH_2Cl_2) was obtained from the pure [R-(R*,R*,S*,S*)]-**3** as already described. A pure sample of [R-(R*,R*,S*,S*)]-**3** with $[\alpha]_D$ −47° was subsequently prepared from optically pure (S)-**1** and [R-(R*,R*)]-**2**: it could not be induced to crystalline under any of the conditions tried. Treatment of dinuclear [R-(R*,R*,S*,S*)]-**3** with diamino-1,2-ethane gave the mononuclear complex [R-(R*,R*)]-**4**, $[\alpha]_D$ −11° (CH_2Cl_2), as a yellow glass.

The pure enantiomers of (±)-**1** with $[\alpha]_D$ ±16.6° (CH_2Cl_2) can be distilled (bp 84–85 °C (0.05 mmHg)) without loss of optical activity. Use of the pure enantiomers as ligands for bivalent nickel, palladium, and platinum is described in the following paper.[4]

Experimental Section

Reactions involving air-sensitive compounds were performed under a positive pressure of argon. Proton NMR spectra were recorded at 20 °C with use of a Jeolco FX 200 spectrometer: chemical shifts are quoted as δ values relative to internal Me_4Si. Optical rotations were measured in a 1-dm cell at 20 °C in 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]naphthyl-C^2,N]dipalladium(II)–dichloromethane solvate, [R-(R*,R*)]-**2**·CH_2Cl_2, and its enantiomorph [S-(R*,R*)]-**2**·CH_2Cl_2 were isolated as highly crystalline solids by Soxhlet extraction with dichloromethane of the material obtained by the published method.[3]

(±)-(2-Mercaptoethyl)methylphenylarsine ((±)-1). A solution of Na[AsMePh] in tetrahydrofuran was prepared from methylphenylarsine (34.2 g) and sodium (5 g) over 1 h. The excess sodium was filtered off, and the arsenide solution was cooled to −78 °C and then treated with a solution of ethylene sulfide (12.2 g) in tetrahydrofuran (50 mL). The reaction mixture was then allowed to warm to room temperature, with stirring being continued for a further 20 h. At this stage the solvent was removed by distillation, and the residue was treated with a solution of ammonium chloride (11 g) in water (400 mL). The product was then extracted into dichloromethane and isolated by distillation after the solution had been dried ($MgSO_4$). Pure (±)-**1** was thus obtained as an foul-smelling colorless oil: bp 84–85 °C (0.05 mmHg); yield 37.6 g (81%). Anal. Calcd for $C_9H_{13}AsS$: C, 47.4; H, 5.7. Found: C, 47.4; H, 5.8. ^1H NMR ($CDCl_3$): δ 1.18 (s, 3 H, AsMe), 1.49 (t, 1 H, $^3J_{HH}$ = 7.3 Hz, SH), 1.89–2.00 (m, 2 H, $AsCH_2$), 2.50–2.62 (m, 2 H, SCH_2), 7.27–7.48 (m, 5 H, aromatics).

Resolution of (±)-1. Isolation of [S-(R*,R*,S*,S*)]-3·0.67CH$_2$Cl$_2$. A mixture of (±)-**1** (5.1 g), [R-(R*,R*)]-**2**·CH_2Cl_2 (17.1 g), and triethylamine (15 mL) in dichloromethane (300 mL) was stirred until all of the resolving agent had dissolved. The yellow solution was then washed with water (to remove $[Et_3NH]Cl$), and the organic phase was separated and dried ($MgSO_4$). After removal of solvent the mixture of epimeric palladium(II) complexes remained as a yellow solid (18.5 g, 95%). Epimer [S-(R*,R*,S*,S*)]-**3** was obtained by recrystallization of this mixture from dichloromethane–acetone solution. The mixture was dissolved in dichloromethane (150 mL), and the solution was diluted with acetone (50 mL). The solution was then concentrated to ca. 100 mL on the steam bath; whereupon large yellow prisms of the product separated (8.8 g, 85%): $[\alpha]_D$ −283° (*c* 1.0, CH_2Cl_2); mp 185–187 °C. Anal. Calcd for $C_{37.67}H_{45.34}AsCl_{2.34}N_2Pd_2S$: C, 48.7; H, 4.9; N, 3.0. Found: C, 48.6; H, 5.0; N, 2.9. ^1H NMR ($CDCl_3$): δ 1.85 (d, 3 H, $^3J_{HH}$ = 6.1 Hz, CH*Me*), 1.98 (d, 3 H, $^3J_{HH}$ = 6.1 Hz, CH*Me*), 2.18 (s, 3 H, AsMe), 2.28–3.10 (m, 4 H, $AsCH_2CH_2$), 2.81 (s, 3 H, NMe), 2.85 (s, 3 H, NMe), 3.18 (s, 3 H, NMe), 3.29 (s, 3 H, NMe), 4.25 (q, 1 H, $^3J_{HH}$ = 6.3 Hz, C*H*Me), 4.39 (q, 1 H, $^3J_{HH}$ = 6.3 Hz, C*H*Me), 5.28 (s, 1.34 H, CH_2Cl_2), 7.18–8.15 (m, 17 H, aromatics). The mother liquors were retained for future use.

[SP-4-3-[S-(R*,S*)]]-[Dimethyl(1-(α-naphthyl)ethyl)aminato-C^2,N][2-(methylphenylarsino)ethanethiolato]palladium(II) ([S-(R*,S*)]-4). A solution of [S-(R*,R*,S*,S*)]-**3**·0.67CH_2Cl_2 (6.0 g) in dichloromethane (100 mL) was stirred for 1 h in contact with 1 equiv of diamino-1,2-ethane (5 mL) in water (100 mL). The organic phase was then separated, washed several times with water, and dried over $MgSO_4$. The product remained as a yellow glass after removal of solvent and was crystallized by dissolving it in dichloromethane (20 mL) and concentrating the mixture to ca. 20 mL. The pure compound formed yellow needles: mp 194–196 °C dec; yield 3.02 g (88%); $[\alpha]_D$ −262.4 (*c* 0.99, CH_2Cl_2). Anal. Calcd for $C_{23}H_{28}AsNPdS$: C, 51.9; H, 5.3; N, 2.6. Found: C, 51.8; H, 5.4; N, 2.7. ^1H NMR ($CDCl_3$): δ 1.89 (d, 3 H, ^3J_HH = 6.3 Hz, CH*Me*), 1.92 (s, 3 H, AsMe), 2.46–2.77 (m, 4 H, $AsCH_2CH_2$), 2.88 (s, 3 H, NMe), 2.96 (s, 3 H, NMe), 4.39 (q, 1 H, $^3J_{HH}$ = 6.35 Hz, C*H*Me), 7.20–7.89 (m, 11 H, aromatics).

[SP-4-(R)]-[Dimethyl(1-(α-naphthyl)ethyl)aminato-C^2,N](diamino-1,2-ethane)palladium(II) Chloride ((R)-5). The colorless aqueous fraction from the above decomposition was taken to dryness. The colorless residue was recrystallized from concentrated acetone solution giving this compound as white needles: mp 225–226 °C dec; yield 2.4 g (93%); $[\alpha]_D$ −98.2° (*c* 0.97, H_2O). Anal. Calcd for $C_{18}H_{24}ClN_3Pd$: C, 48.0; H, 6.0; N, 10.5. Found: C, 48.2; H, 6.3; N, 10.7. ^1H NMR (D_2O): δ 1.78 (d, 3 H, $^3J_{HH}$ = 6.35, CH*Me*), 2.66–2.99 (m, 4 H, CH_2CH_2), 2.76 (s, 3 H, NMe), 2.78 (s, 3 H, NMe), 4.40 (q, 1 H, $^3J_{HH}$ = 6.35 Hz, C*H*Me), 7.10–7.99 (m, 6 H, aromatics).

Compound (R)-**5** can be converted into dimer [R-(R*,R*)]-**2** with concentrated hydrochloric acid.[3]

(R)-(−)-(2-Mercaptoethyl)methylphenylarsine ((R)-1). A solution of [S-(R*,S*)]-**4** (7.2 g) in dichloromethane (400 mL) was stirred for 12 h in the presence of a solution of KCN (40 g) in water (100 mL). The almost colorless organic layer was then separated and washed thoroughly with water and then 1 M H_2SO_4 (to remove amine) and water again before finally being dried over $MgSO_4$. Distillation yielded pure (R)-**1** as a colorless oil: bp 84–85 °C (0.05 mmHg); yield 3.4 g (92%); $[\alpha]_D$ −16.7° (*c* 5.0, CH_2Cl_2). ^1H NMR ($CDCl_3$): identical with that of corresponding racemic material.

(S)-(+)-(2-Mercaptoethyl)methylphenylarsine ((S)-1). The residue from the isolation of [S-(R*,R*,S*,S*)]-**3**·0.67CH_2Cl_2 was decomposed by treatment with diamino-1,2-ethane and potassium cyanide as described above. The tertiary arsine that was obtained had $[\alpha]_D$ +12° (*c* 5.0, CH_2Cl_2), which corresponded to 72% optical purity. This material was brought to purity by reacting it with the calculated quantity of [S-(R*,S*)]-**2**·CH_2Cl_2 and isolating pure [R-(R*,R*,R*,R*)]-**3**·0.67CH_2Cl_2 with $[\alpha]_D$ +283° (*c* 1.0, CH_2Cl_2). Optically pure (S)-**1**, $[\alpha]_D$ +16.7° (*c* 5.0, CH_2Cl_2), was subsequently obtained from this complex by the usual route.

Epimer [R-(R*,R*,R*,R*)]-**3** was also prepared from [R-(R*,R*)]-**2**·CH_2Cl_2 and (S)-**1**. Although ^1H NMR spectroscopy indicated that it was pure, it could not be induced to crystallize over a wide range of conditions. Monomer [R-(R*,R*)]-**4** of high purity would not crystallize either. ^1H NMR ($CDCl_3$): δ 1.82 (s, 3 H, AsMe), 1.85 (d, 3 H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 2.19–2.77 (m, 4 H, CH_2CH_2), 2.95 (s, 3 H, NMe), 2.97 (s, 3 H, NMe), 4.40 (q, 1 H, J_{HH} = 6.35 Hz, C*H*Me), 7.08–7.95 (m, 11 H, aromatics).

Optical Purity of (R)-1. Preparation of *trans*-Bis[(S)-2-(methylphenylarsino)ethanethiolato]nickel(II). A solution of (R)-**1** (1 g) in methanol (5 mL) was added to a solution of $[Ni(H_2O)_6](NO_3)_2$ (0.64

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[11] Roundhill, D. M.; Roundhill, S. G. N.; Beaulieu, W. B.; Bagchi, U. *Inorg. Chem.* **1980**, *19*, 3365–3373 and references therein.

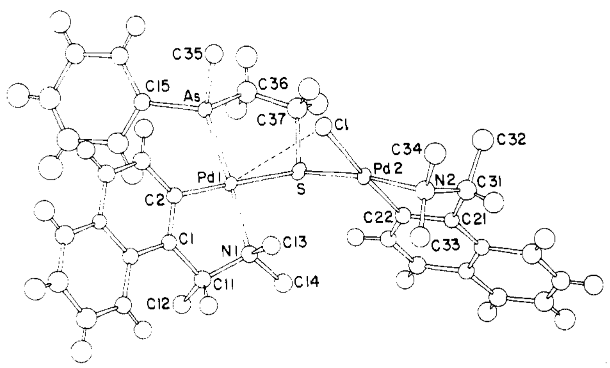

Figure 2. Molecular geometry and absolute configuration of [*S*-(*R**,*R**,*S**,*S**)]-**3**.

g) in methanol (10 mL) containing 1 M NaOH (5 mL). After 30 min, the dark green precipitate was filtered off and washed with water, methanol–water, and diethyl ether. The ^{1}H NMR spectrum of the compound in $CDCl_3$ at this stage indicated a single diastereomer. The highly soluble product was then recrystallized from a benzene–diethyl ether mixture, forming dark green crystals: mp 177–178 °C; yield 0.81 g (72%); $[\alpha]_D$ −448° (c 0.25, CH_2Cl_2). Anal. Calcd for $C_{18}H_{24}As_2NiS_2$: C, 42.1; H, 4.7. Found: C, 42.1; H, 4.7. ^{1}H NMR ($CDCl_3$): δ 1.73 (s, 6 H, AsMe), 2.06–2.37 (m, 4 H, $AsCH_2$), 2.48–2.71 (m, 4 H, SCH_2), 7.47–7.89 (m, 10 H, aromatics).

Under the same conditions (±)-**1** forms a 1:1 racemic:meso mixture of trans nickel(II) complexes with δ AsMe(racemic) = 1.73 and δ AsMe(meso) = 1.76.

Collection of X-ray Intensity Data and Solution and Refinement of the Structure of (−)$_{589}$-[*S*-(*R,*R**,*S**,*S**)]-3·0.67CH$_2$Cl$_2$.** Crystal data for ($C_{37}H_{44}AsClN_2Pd_2S$)(0.67CH_2Cl_2): M_r, 956.95; orthorhombic, space group $P2_12_12_1$ with a = 10.080 (2), b = 14.157 (2), and c = 27.918 (4) Å; V = 3984.0 Å^3; Z = 4; D_m = 1.57; D_c = 1.595 Mg m^{-3}; $F(000)$ = 1920; λ(Mo Kα) = 0.7107 Å; μ(Mo Kα) = 20.33 cm^{-1}; t = 20 ± 1 °C.

Data Collection. Clear pale yellow prisms suitable for data collection were obtained from a dichloromethane solution of the complex by diffusion of acetone vapor into it. D_m was determined by the flotation method. The crystal was a triangular prism defined by the faces 001, $\bar{1}0\bar{1}$, $10\bar{2}$, 010, and $0\bar{1}0$ with perpendicular distances of 0, 0, 0.095, 0, and 0.195 mm from a common point, respectively. Diffraction data were collected on a Picker FACS-1 four-circle diffractometer with use of graphite-monochromated Mo Kα radiation. Lattice parameters were determined by least-squares refinement of the setting angles of 12 carefully centered reflections having 2θ values between 26 and 34°. A total of 3990 unique data points were measured in the *hkl* octant to 50° (2θ) and corrected for absorption by the analytical method. Transmission factors ranged from 0.831 to 0.884. Intensities of three standard reflections (170, 601, and 0,0,14) monitored regularly throughout the data collection displayed a 4% average degradation of intensity over the time scale of the experiment. Of the 3990 reflections measured (excluding standards) 2347 had $I > 3\sigma(I)$ and were accepted as being significant above background and used in subsequent calculations.

Structural Analysis. The structure was solved by direct methods. Hydrogen atom positions (except those of methyl groups) were calculated on the basis of C–H bond length of 0.094 Å and assigned isotropic thermal parameters 10% greater than those of the carbon atoms to which they are bonded. These hydrogen atoms were then included as fixed-atom contributions in a least-squares refinement with their positions being recalculated before each cycle. In the terminal scattering model the Pd, As, and Cl atoms were refined with anisotropic thermal parameters and the N, C, and disordered solvent molecule atoms with isotropic parameters. This model was refined by full-matrix least-squares to an R of 0.052 and R_w of 0.056 with S = 1.406 (where $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o{}^2|]^{1/2}$) for 2347 observations and 222 variables. For the opposite chirality, corresponding values were 0.057, 0.063, and 1.578, respectively). According to Hamiltonian's R factor test,[12a] the probability that the original configuration is the correct one is greater than 99.5%. Atomic scattering factors and corrections for anomalous dispersion were taken from ref 12b. On the final cycle of refinement no parameter shifted by more than 0.01σ. Peaks in the final difference map for disordered solvent molecules were 0.4–0.6 e Å^{-3}. Final atomic coordinates and isotropic thermal parameters are listed in Table III. The atom nomenclature is given in Figure 2.

Table III. Final Atomic Coordinates and Isotropic Thermal Parameters for [*S*-(*R**,*R**,*S**,*S**)]-**3**

atom	x/a	y/b	z/c	B_{iso}, Å^2
Pd(1)	0.31504 (12)	0.41533 (8)	0.38639 (4)	
Pd(2)	0.26796 (13)	0.15438 (8)	0.39094 (5)	
As	0.28540 (19)	0.46415 (11)	0.46499 (6)	
Cl	0.0684 (5)	0.2477 (3)	0.4048 (2)	
S	0.4002 (5)	0.2731 (3)	0.4210 (2)	
N(1)	0.3353 (14)	0.3784 (9)	0.3116 (5)	4.1 (3)
N(2)	0.1662 (16)	0.0438 (11)	0.3556 (5)	5.4 (4)
C(1)	0.2786 (16)	0.5429 (10)	0.3085 (5)	3.6 (3)
C(2)	0.2446 (17)	0.5342 (10)	0.3557 (5)	3.7 (3)
C(3)	0.1617 (17)	0.6033 (12)	0.3769 (6)	4.4 (4)
C(4)	0.1123 (18)	0.6772 (12)	0.3507 (6)	4.5 (4)
C(5)	0.1430 (16)	0.6901 (11)	0.3023 (5)	3.3 (3)
C(6)	0.0939 (20)	0.7623 (13)	0.2756 (7)	5.4 (5)
C(7)	0.1238 (22)	0.7747 (15)	0.2278 (7)	6.5 (5)
C(8)	0.2123 (21)	0.7135 (14)	0.2057 (7)	6.3 (5)
C(9)	0.2612 (17)	0.6365 (11)	0.2326 (6)	4.4 (4)
C(10)	0.2255 (17)	0.6221 (11)	0.2809 (5)	3.7 (3)
C(11)	0.3649 (17)	0.4690 (12)	0.2873 (6)	4.1 (4)
C(12)	0.5129 (18)	0.5008 (12)	0.2883 (6)	4.7 (4)
C(13)	0.2040 (18)	0.3446 (12)	0.2947 (6)	4.8 (4)
C(14)	0.4404 (19)	0.3061 (12)	0.3022 (6)	4.9 (4)
C(15)	0.3533 (16)	0.5844 (12)	0.4854 (5)	3.9 (3)
C(16)	0.3131 (17)	0.6297 (12)	0.5259 (6)	4.7 (4)
C(17)	0.3667 (21)	0.7149 (14)	0.5385 (7)	5.7 (4)
C(18)	0.4626 (22)	0.7575 (17)	0.5088 (7)	6.5 (5)
C(19)	0.5016 (23)	0.7199 (17)	0.4705 (8)	7.8 (6)
C(20)	0.4461 (21)	0.6278 (15)	0.4566 (7)	6.5 (5)
C(21)	0.3850 (16)	−0.0251 (11)	0.3684 (5)	3.3 (3)
C(22)	0.4246 (16)	0.0689 (11)	0.3801 (6)	3.9 (4)
C(23)	0.5563 (15)	0.0877 (11)	0.3803 (5)	3.8 (3)
C(24)	0.6508 (17)	0.0233 (12)	0.3717 (6)	4.2 (4)
C(25)	0.6188 (16)	−0.0709 (11)	0.3596 (5)	3.4 (3)
C(26)	0.7117 (19)	−0.1413 (12)	0.3509 (6)	5.1 (4)
C(27)	0.6783 (20)	−0.2294 (13)	0.3401 (6)	5.7 (4)
C(28)	0.5461 (20)	−0.2543 (13)	0.3378 (6)	5.1 (4)
C(29)	0.4490 (21)	−0.1892 (13)	0.3467 (7)	5.6 (5)
C(30)	0.4803 (16)	−0.0928 (12)	0.3585 (5)	3.5 (3)
C(31)	0.2419 (20)	−0.0456 (13)	0.3731 (6)	5.5 (4)
C(32)	0.2059 (22)	−0.0791 (15)	0.4250 (7)	7.1 (5)
C(33)	0.1786 (20)	0.0541 (13)	0.3045 (7)	6.1 (5)
C(34)	0.0203 (23)	0.0332 (17)	0.3691 (8)	7.2 (6)
C(35)	0.1024 (18)	0.4597 (13)	0.4893 (6)	4.7 (4)
C(36)	0.3732 (21)	0.3743 (13)	0.5046 (7)	5.9 (5)
C(37)	0.3534 (21)	0.2765 (14)	0.4839 (6)	5.8 (5)
XS(1)[a]	0.7920 (30)	0.5322 (20)	0.4154 (11)	16.6 (9)
XS(2)	0.8504 (23)	0.5073 (15)	0.3350 (8)	15.5 (7)
XS(3)	0.8325 (24)	0.4714 (17)	0.3723 (9)	16.3 (7)
XS(4)	0.7433 (23)	0.4588 (14)	0.4561 (7)	15.1 (6)
XS(5)	0.7393 (27)	0.3890 (18)	0.4069 (9)	14.8 (8)

[a] Disordered 0.67 CH_2Cl_2 of crystallization.

Computer Programs. The ANUCRYS structure determination package[13,14] was used for all aspects of the crystal structure analysis.

Registry No. (±)-**1**, 102916-62-1; (*S*)-**1**, 102808-72-0; (*R*)-**1**, 102808-71-9; *trans*-[Ni{(*S*)-**1**}$_2$], 102850-03-3; *rac-trans*-[Ni(**1**)$_2$], 102850-06-6; *meso-trans*-[Ni(**1**)$_2$], 102850-01-1; [*R*-(*R**,*R**)]-**2**, 80145-77-3; [*S*-(*R**,*R**,*S**,*S**)]-**3**, 102808-68-4; [*R*-(*R**,*R**,*R**,*R**)]-**3**, 102916-60-9; [*S*-(*R**,*R**,*S**,*S**)]-**3**·*x*CH$_2$Cl$_2$, 102916-61-0; [*S*-(*R**,*S**)]-**4**, 102808-69-5; (*R*)-**5**, 102808-70-8; [Ni(H$_2$O)$_6$](NO$_3$)$_2$, 10171-09-2; methylphenylarsine, 53979-86-5; ethylene sulfide, 420-12-2.

Supplementary Material Available: Tables of anisotropic thermal parameters (Table IV) and calculated hydrogen atom parameters (Table V) (2 pages). Ordering information is given on any current masthead page.

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(12) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV: (a) p 288; (b) pp 99, 149.

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

(14) Ferguson, J.; Mau, A. W.-H.; Whimp, P. O. *J. Am. Chem. Soc.* **1979**, *101*, 2363–2369.