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Stereochemical Investigations of Coordinated Sulfur Stereocenters. X-ray Structures of Diastereomers of $(-)_{589}$-[Pd{(*R*)-$CH_3CH(1\text{-}C_{10}H_6)NMe_2$-$C^2$,*N*}(*R*/*S*)-{$Ph_2PCH_2SMe$-*P*,*S*}]$PF_6$

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The reaction between bis(μ-chloro)bis[(*R*)-1-[(dimethylamino)ethyl]naphthylenyl-C^2,*N*]dipalladium(II) and 2 mol of the bidentate $Ph_2PCH_2CH_2SMe$ gave a pair of internal diastereomeric complex cations arising from the coordinated sulfur stereocenter. The hexafluorophosphate salt of the diastereomeric mixture crystallizes as a compound with $[\alpha]_D$ −35° (CH_2Cl_2) in the triclinic space group *P*1 with a = 7.8690 (10) Å, b = 17.837 (2) Å, c = 21.830 (2) Å, α = 82.86 (1)°, β = 87.19 (1)°, γ = 83.39 (1)°, and Z = 4 (R = 0.0412 and R_w = 0.0666). In solution, the complexes exhibit facile intramolecular asymmetric equilibration between diastereomers epimeric at sulfur at room temperature. A coalescence temperature of −90 °C was recorded for the interconversion by variable-temperature NMR spectroscopy. Similar behavior was observed for analogous complexes of $Ph_2AsCH_2CH_2SMe$ and $Me_2AsCH_2CH_2SMe$.

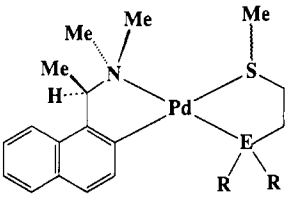
Introduction

The stereodynamics of transition metal complexes containing monodentate and bidentate thioether ligands has received considerable attention[1] and has been the subject of a recent review.[2] In particular, dynamic nuclear magnetic resonance studies of sulfur inversion in platinum(II) and palladium(II) complexes are of particular interest.[3] Most work, however, has involved dithioethanes; only a few reports have appeared concerning sulfur inversion in heterobidentate ligands possessing one sulfur donor atom.[2,4] We were interested in the stereochemistry of chelating phosphorus–sulfur and arsenic–sulfur bidentates (E–S) because of their potential use as chiral auxiliaries for homogeneous asymmetric catalysis.[5]

In general, the reactions of E–S ligands with the elements of the cobalt and nickel triads have uncovered a rich coordination chemistry.[6] So far, however, only two optically active mercaptoalkyl-substituted tertiary arsines[7,8] and one phosphine[9] have been resolved. Each of the resolved ligands contained a chiral phosphorus or arsenic stereocenter. With use of the optically active bidentates, a definitive account of the stereochemistry and dynamic behavior of square-planar complexes of bivalent nickel, palladium, and platinum was carried out.[10] We report here a stereochemical investigation of the square-planar complexes of the heterobidentate ligands $R_2ECH_2CH_2SMe$ (where E = P or As) coordinated to a (*R*)-[dimethyl(1-(2-naphthyl)ethyl)aminato-C^2,*N*]palladium unit, **1**.

Results

Stereochemistry Considerations. The square-planar palladium(II) complexes containing the thioether ligand $R_2ECH_2CH_2SMe$ and the ortho-metalated dimethyl(1-(α-naphthyl)ethyl)amine ring exhibit diastereomerism from three



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sources: (a) the relative regioarrangement of the four different donor atoms on the plane; (b) the relative configurations of the carbon and the coordinated sulfur stereocenters; (c) the relative helicities of the two nonplanar chelate rings. Thus, even with an optically pure amine, the preparation of **1** may generate mixtures of up to 16 diastereomers. A detailed literature search revealed, however, that the coordination of unsymmetrical bidentates (such as As–N,[11] As–S,[7] P–N,[11] and P–S[9]) to the ortho-metalated [dimethyl(1-(2-naphthyl)ethyl)aminato-C^2,*N*]palladium(II) unit is remarkably regiospecific: the softest of the two donors invariably takes up the position trans to the NMe_2 group in the complex. Furthermore, X-ray crystal structure determinations of such compounds indicated that the ortho-metalated *R*-naphthylamine ring adopted a particular conformation,[7-9,11] the helicity apparently being dictated by the repulsive forces between the methyl groups on the α-carbon and nitrogen centers of the organometallic ring. The five-membered ring adopts a skew configuration with the methyl substituent on the carbon center occupying an axial position. Thus the δ conformation of the ring will always be observed for the chelate ring when the absolute configuration of the carbon stereocenter is *R*. With these constraints, the number of possible diastereomers of optically active complex **1** is reduced to 4. Figure 1 shows the structures of the four possible stereomers. In these structures, the N–Me groups are oriented such that the neighboring C–Me group is axial, as found in the present and previously reported crystal structures. Structures A and D have the S–Me groups axial; B and C have the S–Me groups equatorial. Dreiding models indicated, however, that the equatorially oriented S–Me groups will experience enormous steric repulsion from the N–Me groups. We therefore deduced that isomers A and D would be favored. In structure A, the sulfur–methyl group is axial and the chelate ring has the δ conformation; in D the helicities of the E–S chelate ring and the absolute configurations of the sulfur stereocenter are enantiomorphic to the situation in A. Moreover, the axial sulfur–methyl groups in the two structures are located in distinct stereochemical environments. Model studies indicated that the S–Me group in isomer A is occupying a more sterically

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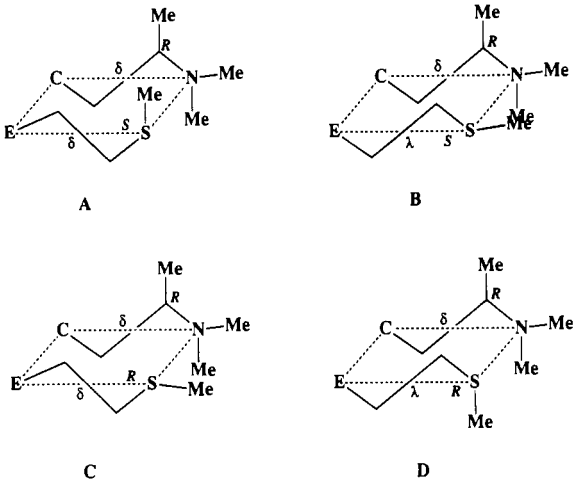
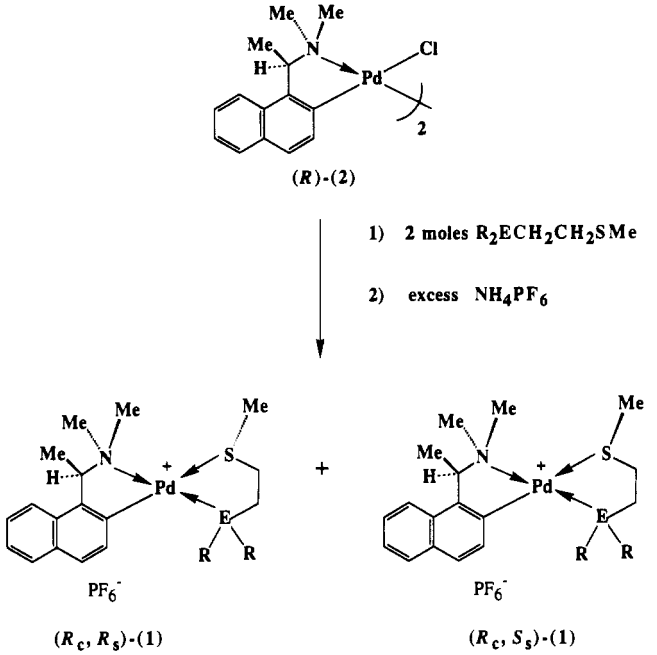


Figure 1. The four square-planar diastereomers of **1**.

Scheme I



1a R = Ph, E = P
1b R = Ph, E = As
1c R = Me, E = As

favored position than its counterpart in isomer D. The chiral array of the N–Me groups is expected to exercise a discriminating effect on the relative populations of A and D and ipso facto control the absolute configuration of the sulfur stereocenter. Structural investigations of **1** in the solid state and studies of the dynamic properties of the complexes in solution would therefore provide valuable information on the precise chiral inductive effect of alkyl substituents on nitrogen and sulfur in optically active systems. Such information is crucial for the design of catalysts suitable for metal-assisted asymmetric synthesis.[12]

Synthesis of Thioether Ligands. The methylthio-substituted phosphine and arsines were generally prepared in high yields by treating their mercapto-substituted precursors $R_2ECH_2CH_2SH$ with *n*-butyllithium and methyl iodide at −78 °C. The thioether ligands are air-sensitive, colorless, foul-smelling oils. (2-Mercaptoethyl)diphenylphosphine is light-sensitive. In light, it rearranges quantitatively into ethyldiphenylphosphine sulfide. The corresponding thioether, however, is photochemically stable. We have recently reported on the mechanism and the stereospecific nature of the analogous photochemical rearrangement of (±)-(2-mercaptoethyl)methylphenylphosphine.[9,13]

$$Ph_2PCH_2CH_2SH \xrightarrow{h\nu} Ph_2EtP(S)$$

Formation of Complexes. The diastereomers **1a–c** were prepared in high yields from reactions between the optically active dipalladium complex (*R*)-**2** and the appropriate methylthio-sub-

Scheme II

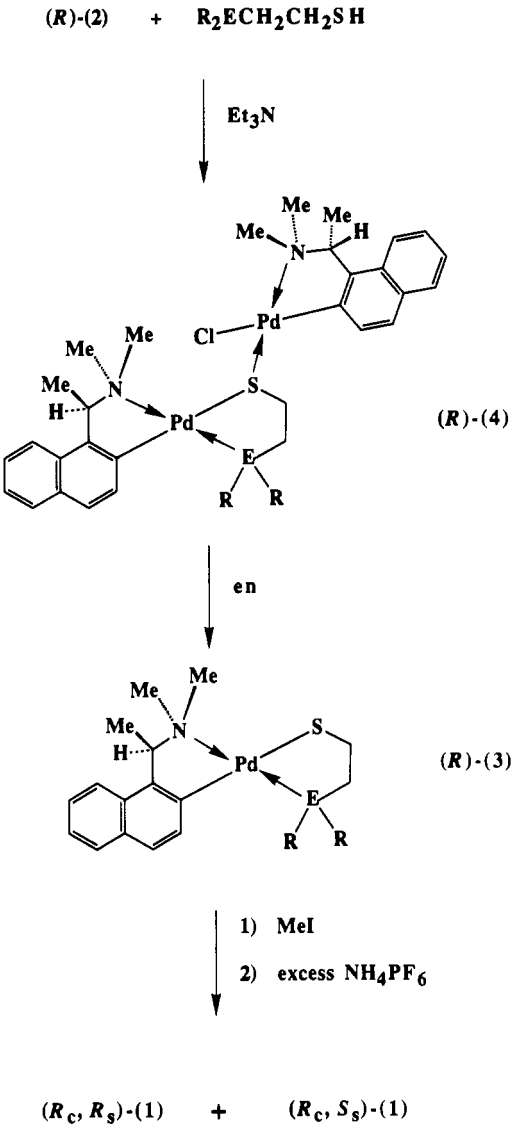


Table I. Selected Spectroscopic Properties of $(R_c,R/S_s)$-**1a–c**

	1a	1b	1c
^{1}H NMR ppm[a]			
C*Me*	1.91 d J_{HH} = 6.4 Hz	1.94 d J_{HH} = 6.3 Hz	1.88 d J_{HH} = 6.4 Hz
S*Me*	2.64 s	2.56 s	2.52 s
N*Me*	2.91 d J_{PH} = 1.3 Hz	2.97 s	2.87 s
	3.05 d J_{PH} = 3.6 Hz	3.08 s	2.98 s
E*Me*			1.69 s 1.90 s
$[\alpha]_D$ (CH_2Cl_2), deg	−35.0	−35.8	−91.7

[a] 300-MHz ^{1}H NMR spectra recorded in $CDCl_3$.

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Table II. Crysal Data for $(R_c,R_s;R_c,S_s)$-**1a**

space group	*P*1	*F*(000)	1388
a, Å	7.8690 (10)	chem formula	$C_{29}H_{33}F_6NPPdS$
b, Å	17.837 (2)	fw	696.9
c, Å	21.830 (2)	*Z*	4
α, deg	82.86 (1)	abs coeff, cm^{-1}	8.32
β, deg	87.19 (1)	trans coeff	0.273–0.309
γ, deg	83.39 (1)	temp, °C	25
V, Å^3	3018 (1)	λ, Å	0.71069
D_c, g cm^{-3}	1.534	R^a	0.0412
D_m, g cm^{-3}	1.513	Rw^a	0.0666

$^a R = \sum|F_o - F_c|/\sum(F_o)$ and $R_w = \{[\sum w|F_o - F_c|^2]/[\sum w(F_o)^2]\}^{1/2}$.

Table III. Selected Bond Lengths (Å) and Angles (deg) in the Four Complex Cations I–IV

	I	II	III	IV
Pd–C(1)	2.045 (9)	2.010 (9)	2.036 (9)	2.027 (9)
Pd–N(12)	2.160 (8)	2.149 (7)	2.117 (7)	2.136 (8)
Pd–S(14)	2.421 (3)	2.396 (3)	2.400 (3)	2.398 (5)
Pd–P(17)	2.247 (2)	2.257 (2)	2.246 (2)	2.265 (3)
S(14)–C(13)	1.774 (21)	1.857 (16)	1.796 (13)	*a*
C(1)–Pd–N(12)	80.6 (3)	81.1 (3)	81.8 (3)	81.9 (4)
N(12)–Pd–S(14)	95.0 (3)	93.8 (2)	93.5 (2)	95.0 (3)
S(14)–Pd–P(17)	86.8 (1)	87.0 (1)	86.5 (1)	86.4 (1)
P(17)–Pd–C(1)	97.7 (2)	97.9 (2)	97.9 (2)	97.1 (3)
Pd–S(14)–C(13)	107.3 (6)	109.9 (6)	108.2 (4)	*b*

^{a}C(13) is disordered. The two S(14)–C(13) distances are 1.555 (23) and 1.600 (46) Å, respectively. ^{b}The two angles are 116.2 (9) and 110.0 (14)°, respectively.

stituted ligands in dichloromethane (Scheme I). The cationic complexes can also be prepared by treating the corresponding thiolato compounds (*R*)-**3** with methyl iodide (Scheme II), but this method is relatively tedious since unusual μ-thiolato-*S* intermediates (*R*)-**4** are involved. The monomeric complexes (*R*)-**3** could not be formed directly even when 2 equiv of the thiol ligand were used. The overall yields of **1a–c** from the methylation reactions are generally lower than those of the direct synthesis (Scheme I).

In each preparation, the ^{1}H NMR spectrum of the product precipitated from the reaction mixture was recorded prior to recrystallization. Selected physical and spectroscopic properties for the recrystallized products **1a–c** are given in Table I. All three compounds are highly crystalline and air-stable. The salts behave as 1:1 electrolytes in chloroform and acetone. In solution, they are inert to most common oxidizing agents. Indeed, the complexes can be recovered unchanged after being treated with hydrogen peroxide in acetone for 7 days. In contact with aqueous cyanide, however, the complexes decompose readily, regenerating the corresponding thioether ligands.

The thiophosphine complex **1a** was subsequently found by X-ray crystallography to be an equimolar mixture of the two diastereomers: (R_c,R_s)-**1a** and (R_c,S_s)-**1a**, that is, structures A and D of Figure 1. The complexes therefore crystallized as a compound wherein each unit cell in the crystal lattice contains both diastereomeric cations. Attempts to separate the isomers by fractional crystallization of the mixture under different conditions were unsuccessful.

Crystal and Molecular Structures of (R_c,R_s)- and (R_c,S_s)-1a. Colorless needles of $(R_c,R/S_s)$-**1a** suitable for X-ray crystallography were grown by vapor diffusion of diethyl ether into an acetone solution of the complex. Crystal data for the complex are given in Table II. The structural analysis indicated four molecules in the unit cell. Selected bond distances and bond angles of the molecules are given in Table III. Of the four complex cations present, one cation of (R_c,R_s)-**1a** (molecule I) and two cations of (R_c,S_s)-**1a** (molecules II and III) were clearly identified; the fourth cation was disordered about the S14 atom resulting in half-occupancy in two diastereomers. The hexafluorophosphate anions are uncoordinated. The molecular geometries and absolute configurations of these diastereomers are represented by the ORTEP diagrams in Figure 2. Table IV gives the fractional atomic coordinates for non-hydrogen atoms. Complete lists of atomic coordinates, thermal parameters, and structure factors have been deposited as supplementary material.

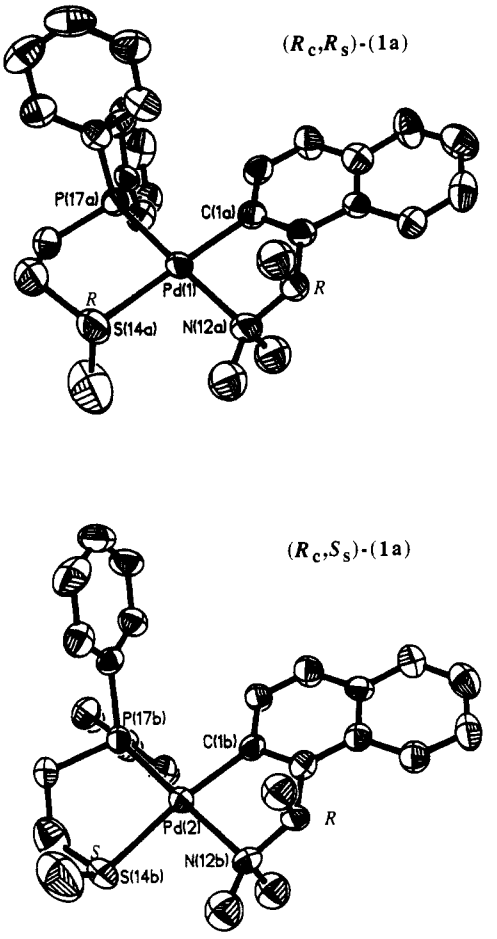

Figure 2. Molecular structures and labeling schemes for (R_c,R_s)-**1a** and (R_c,S_s)-**1a**.

Of the four diastereomeric complex cations in the crystal unit, there are no major differences in the Pd–C, Pd–N and Pd–P distances. The Pd–S distances in the R_c,S_s isomer are 2.397 and 2.400 Å with an average of 2.398 Å, which is shorter than that of the R_c,R_s isomer (2.420 Å). Interestingly, the Pd–S bond in the R_c,R_s isomer is also longer than those in an analogous palladium(II) complex incorporating the deprotonated form of $PhMeAsCH_2CH_2SH$ and ortho-metalated dimethyl(1-(α-naphthyl)ethyl)amine (2.393 Å),[7] the latter being similar to the R_c,S_s isomer. The lengthening of the Pd–S bond in the R_c,R_s isomer is due to the steric repulsion between the axially oriented S–Me and N–Me groups. Nevertheless, the Pd–C, Pd–N, Pd–S, and Pd–P distances of the four molecules are within the range of literature values. The other bond distances are also normal.

Bond angles about the palladium atom are very close to those reported for similar complex cations.[7,9,11] Thus the C1–Pd–N12 angles range from 80.6 to 81.9° in this study compared to 81.0 and 82.5° observed in [(*R*)-dimethyl(1-ethyl-α-naphthyl)-aminato-C^2,N][(*S*)-methylphenyl(quinolyl)phosphine]palladium-(II) hexafluorophosphate.[11] The S14–Pd–P17 angles are from 86.4 to 87.0°. The C1–Pd–S14 and N12–Pd–P17 angles range from 171.3 to 178.2°. With the palladium atom less than 0.1 Å from the plane defined by C1, N12, S14, and P17 atoms, the coordination geometry of the Pd atoms is square-planar. All of the other angles are unexceptional. However, the orientation of the phenyl rings in the diphenylphosphine group with respect to the plane formed by the atoms C1, N12, S14, and P17 seems to be isomer dependent. This is best illustrated by considering the torsion angles indicated in Table V. The conformations of the $Ph_2PCH_2CH_2SMe$ ligand in the R_c,R_s and R_c,S_s isomers are essentially mirror images of each other, but in the R_c,R_s cation

IV, in which C13 and C15 atoms are disordered, the torsion angles are quite different. It appears that while the (methylthio)ethyl portion of the ligand is relatively flexible, the bulky phenyl rings are locked in positions dictated by available space.

NMR Spectra of 1. The two internal diastereomers (R_c,R_s)-**1** and (R_c,S_s)-**1** are chemically distinct species in solid state (Figures 1 and 2). Thus, with use of high-field ^{1}H and ^{31}P NMR spectroscopies, it should be possible to detect and determine the relative populations of the two diastereomers in solution. At room temperature, however, each of the complexes **1a–c** exhibited one set of signals in their 300-MHz ^{1}H NMR spectra in $CDCl_3$ (Table I). Similar results were obtained with the several different NMR solvents used. Consistent with the ^{1}H NMR studies, the ^{31}P NMR spectrum of the diastereomeric mixture **1a** in $CDCl_3$ showed a singlet at δ 54.1 for the phosphorus of the complex cation and a septet centered at δ −143.8 (J_{PF} = 144 Hz) for the hexafluorophosphate ion.

The NMR spectra for **1a–c** are consistent with the following three explanations: (a) the thioether ligands are behaving as monodentates through P or As (this mode of coordination of the ligand would destroy the chirality at sulfur thus giving one isomer for each complexes); (b) the two isomeric cations are of different free energies, and only one of them is stable under the conditions employed;[14] (c) the spectra recorded are the average resonance signals of the two isomers, which are in rapid equilibration. It should be noted, however, that in the latter two considerations, the activation energies involved in the corresponding asymmetric transformations must be small since the spectra were recorded under ambient conditions.

All the examples known of a E–S ligand coordination to palladium via the E donor only contain halide or other coordinating anions.[9,15] In the absence of such species, it is unlikely that the sulfur donor will come free from the metal, especially in chloroform. Furthermore, the stabilities of **1a–c** toward strong oxidizing agents also indicate coordination of both donors of the E–S ligands (protection). Free thioethers and tertiary phosphines are oxidized to their oxides under considerably milder conditions.

Although terminal thioether-*S* stereocenters in palladium(II) complexes usually have inversion barriers[16] of 50–70 kJ mol^{-1}, the lower activation energy for this process in **1a–c** was not unexpected. Sulfur inversion barriers are dependent upon the nature and size of the chelate ring and upon the trans substituent.[2,16] Thus, a striking drop in the energy barriers was observed when the halogens in [$PtCl_2$(EtSCH$_2$CH$_2$SEt)] were replaced by phenyl groups.[17] Since the sulfur donors in **1** are coordinated trans to a similar aromatic carbon, a low activation energy for sulfur inversion is likely. Further, in the absence of major steric factors, the torsional barrier of E–CH$_2$–CH$_2$–S five-membered rings will be small.[18] Thus, the coordination of thioether ligands or the methylation of thiolato complexes (as in Schemes I and II, respectively) are kinetically nonstereospecific, the distribution of the two isomers in solution being governed by thermodynamics. Therefore, a $CDCl_3$ solution of **1** may either contain a sole stable compound or a rapid equilibrium mixture of the two diastereomers of similar energies. Variable-temperature ^{1}H NMR investigations of **1a–c** were subsequently carried out in order to unequivocably determine which of the alternatives were correct. Due to its low freezing point, acetone-d_6 was used for the low-temperature NMR experiments. At room temperature, the spectra for compounds **1a–c** were almost identical to those recorded in $CDCl_3$. The resonance signals, however, broadened as the temperature of the solution lowered and collapsed at ca. −90 °C. Thus, the spectra recorded at 25 °C in both acetone-d_6 and $CDCl_3$ represent dynamic intramolecular conversions between the two isomers of the complexes. Further, because the coalescence temperatures recorded for **1a–c** were similar, the activation energies involved in the diastereomeric equilibrations of these complexes appear to be similar also.

In the solid state, the terminal alkyl substituent of a coordinated thioether consistently occupies a sterically favored location.[3,19] It is not clear why both diastereomers are found in the present case, where crystal packing forces must be significant. In solution, a small lengthening of the metal–ligand bonds could minimize the ground-state energy differences. However, the reasons for the facile configurational and conformational interconversions observed remain unclear and will be investigated further.

Experimental Section

All reactions involving air-sensitive compounds were performed under a positive pressure of purified nitrogen. Routine ^{1}H and ^{31}P NMR spectra were recorded at 25 °C either on a Bruker ACF 300 or on a JEOL FX-90Q spectrometer. Optical rotations were measured in a 1-dm cell of 22 °C with a Perkin-Elmer Model 241 polarimeter. Melting points were determined by using a Electrothermal IA 9200 apparatus. Elemental analyses were performed by the Microanalytical Laboratory staff of the Department of Chemistry.

Bis(μ-chloro)bis[(*R*)-1-[(dimethylamino)ethyl]naphthylenyl-C^2,*N*]-dipalladium(II)—dichloromethane,[11] dimethyliodoarsine,[20] and 2-(diphenylphosphino)ethanethiol[21] were prepared as previously described. [2-(Methylthio)ethyl]diphenylphosphine[15,19] and [2-(methylthio)ethyl]-diphenylarsine[22] were prepared by modified literature methods.

2-(Dimethylarsino)ethanethiol. A solution of sodium dimethylarsenide in tetrahydrofuran (175 mL) was prepared from dimethyliodoarsine (40.0 g) and sodium (8.1 g) over 5 h with stirring. The excess sodium was filtered off, and the arsenide solution was cooled to −78 °C and then treated with ethylene sulfide (10.2 mL) in THF (50 mL). The reaction mixture was allowed to warm to room temperature with stirring being continued for another 16 h. At this stage, the solvent was removed by distillation and a solution of ammonium chloride (9.3 g) in water (175 mL) was added to the residue. The product was extracted into dichloromethane and isolated by distillation after the solution had been dried ($MgSO_4$). The product was obtained as a volatile, offensive smelling, colorless oil: bp 92–93 °C (20 mmHg); yield 11.5 g (40%). ^{1}H NMR ($CDCl_3$): δ 0.97 (s, 6 H, AsMe$_2$), 1.35–1.85 (m, 3 H, AsCH$_2$ and SH), 2.56–2.89 (m, 2 H, SCH$_2$).

[2-(Methylthio)ethyl]dimethylarsine. 2-(Dimethylarsino)ethanethiol (6.1 g) was dissolved in dry THF (100 mL). The solution was cooled to −78 °C and treated with 1.6 M *n*-butyllithium (23 mL) followed by methyl iodide (2.3 mL) in tetrahydrofuran (50 mL). The reaction mixture was then allowed to warm to room temperature, with stirring being continued for a further 16 h. At this stage, the solvent was removed by distillation, and water (80 mL) was added to the residue. The product was extracted into dichloromethane and isolated by distillation after the solution had been dried ($MgSO_4$). The tertiary arsine was thus obtained as a colorless oil: bp 97–98 °C (20 mmHg); yield 4.6 g (70%). ^{1}H NMR ($CDCl_3$): δ 0.97 (s, 6 H, AsMe), 1.62–1.80 (m, 2 H, AsCH$_2$), 2.12 (s, 3 H, SMe), 2.56–2.89 (m, 2 H, SCH$_2$).

2-(Diphenylarsino)ethanethiol. Diphenylarsine (10.0 g) was first dissolved in dry tetrahydrofuran (100 mL). The solution was cooled to −78 °C and treated with 1.6 M *n*-butyllithium (27.1 mL) followed by ethylene sulfide (2.6 mL) in tetrahydrofuran (15 mL). The reaction mixture was then allowed to warm to room temperature, with stirring being continued for a further 16 h. At this stage, the solvent was removed by distillation and a solution of ammonium chloride (2.3 g) in water (100 mL) was added to the residue. The crude product was extracted into dichloromethane and isolated by distillation after solution had been dried ($MgSO_4$). Pure (2-diphenylarsino)ethanethiol was thus obtained as a colorless oil: bp 168–170 °C (0.3 mmHg); yield 7.7 g (61%). ^{1}H NMR ($CDCl_3$): δ 1.58 (t, 1 H, $^3J_{HH}$ = 7.6 Hz, SH), 2.22–2.45 (m, 2 H, AsCH$_2$), 2.54–2.83 (m, 2 H, SCH$_2$), 7.23–7.49 (m, 10 H, aromatics).

[2-(Methylthio)ethyl]diphenylarsine. 2-(Diphenylarsino)ethanethiol (2.8 g) was dissolved in dry tetrahydrofuran (50 mL). The solution was cooled to −78 °C and treated with 1.6 M *n*-butyllithium (6.1 mL) followed by methyl iodide (0.6 mL) in tetrahydrofuran (10 mL). The

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Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$)

cation		x	y	z	U(eq)	cation		x	y	z	U(eq)
I	Pd	8209	8254	4838	43 (1)	I	S(14)	10988 (4)	7624 (2)	4570 (1)	70 (1)
	C(1)	6004 (13)	8935 (6)	5005 (4)	43 (3)		C(15)	11853 (18)	7263 (8)	5321 (6)	77 (5)
	C(2)	4883 (13)	8918 (6)	5524 (4)	49 (3)		C(16)	10471 (14)	7009 (6)	5781 (5)	53 (4)
	C(3)	3440 (13)	9425 (6)	5561 (5)	54 (4)		P(17)	8732 (3)	7782 (1)	5822 (1)	41 (1)
	C(4)	3057 (13)	9981 (5)	5058 (5)	48 (3)		C(19)	8852 (8)	9203 (3)	6211 (3)	56 (4)
	C(5)	1592 (14)	10510 (6)	5115 (6)	62 (4)		C(20)	9396	9713	6574	64 (4)
	C(6)	1220 (15)	11055 (7)	4637 (6)	68 (5)		C(21)	10645	9465	7008	72 (5)
	C(7)	2237 (15)	11065 (6)	4077 (6)	62 (4)		C(22)	11350	8707	7079	73 (5)
	C(8)	3635 (14)	10563 (5)	4023 (5)	49 (3)		C(23)	10806	8196	6715	58 (4)
	C(9)	4105 (12)	9995 (5)	4527 (4)	38 (3)		C(18)	9558	8444	6281	45 (3)
	C(10)	5598 (12)	9489 (5)	4512 (4)	42 (3)		C(25)	6213 (9)	6821 (4)	6058 (3)	58 (4)
	C(11)	6849 (13)	9508 (5)	3956 (4)	47 (3)		C(26)	4978	6452	6420	69 (5)
	C(41)	8230 (16)	10020 (7)	4057 (6)	65 (3)		C(27)	4624	6605	7027	76 (5)
	N(12)	7617 (13)	8714 (5)	3901 (4)	61 (3)		C(28)	5505	7127	7272	67 (4)
	C(42)	9062 (17)	8704 (7)	3419 (6)	69 (3)		C(29)	6740	7497	6910	56 (4)
	C(43)	6222 (18)	8282 (7)	3701 (6)	73 (3)		C(24)	7095	7344	6303	45 (3)
	C(13)	10635 (23)	6810 (10)	4223 (11)	128 (10)						
II	Pd	8064 (1)	3187 (1)	1929 (1)	37 (1)	II	S(14)	10787 (3)	2445 (3)	2060 (1)	58 (1)
	C(1)	5884 (12)	3897 (5)	1886 (4)	38 (3)		C(15)	11590 (17)	2434 (9)	1268 (7)	87 (6)
	C(2)	5089 (13)	4328 (6)	1350 (4)	48 (3)		C(16)	10148 (13)	2278 (6)	868 (5)	50 (3)
	C(3)	3699 (14)	4832 (6)	1402 (5)	54 (4)		P(17)	8410 (3)	3059 (1)	913 (1)	37 (1)
	C(4)	2924 (12)	4967 (5)	1978 (4)	44 (3)		C(19)	9709 (10)	3754 (3)	−194 (3)	57 (4)
	C(5)	1493 (14)	5506 (6)	2024 (5)	52 (3)		C(20)	10453	4324	−574	62 (4)
	C(6)	803 (14)	5666 (6)	2582 (6)	59 (4)		C(21)	10763	4985	−338	67 (4)
	C(7)	1526 (14)	5257 (6)	3149 (5)	56 (4)		C(22)	10328	5077	277	66 (4)
	C(8)	2875 (13)	4722 (6)	3080 (5)	50 (3)		C(23)	9583	4506	657	52 (4)
	C(9)	3657 (12)	4549 (5)	2507 (4)	39 (3)		C(18)	9274	3845	421	42 (3)
	C(10)	5085 (12)	4003 (5)	2456 (4)	39 (3)		C(25)	5873 (9)	3399 (3)	25 (3)	49 (3)
	C(11)	5805 (12)	3482 (5)	3002 (4)	39 (3)		C(26)	4566	3219	−322	60 (4)
	C(41)	4961 (15)	2761 (6)	3095 (5)	56 (3)		C(27)	4094	2482	−247	66 (5)
	N(12)	7734 (11)	3345 (5)	2889 (3)	46 (3)		C(28)	4929	1925	174	76 (5)
	C(42)	8510 (17)	2712 (7)	3340 (6)	69 (3)		C(29)	6237	2105	520	54 (4)
	C(43)	8538 (16)	4053 (7)	2944 (6)	67 (3)		C(24)	6709	2842	446	40 (3)
	C(13)	10479 (23)	1438 (9)	2328 (10)	112 (8)						
III	Pd	8143	2816 (1)	7105 (1)	38 (1)	III	S(14)	5395 (3)	3447 (2)	7370 (1)	52 (1)
	C(1)	10408 (12)	2189 (5)	6936 (4)	38 (3)		C(15)	4620 (13)	3872 (7)	6648 (5)	59 (4)
	C(2)	11228 (13)	2077 (6)	6356 (5)	50 (3)		C(16)	6064 (14)	4159 (25)	6226 (5)	52 (3)
	C(3)	12651 (13)	1560 (7)	6330 (5)	59 (4)		P(17)	7713 (3)	3377 (1)	6137 (1)	40 (1)
	C(4)	13289 (12)	1081 (5)	6850 (4)	44 (3)		C(19)	5662 (10)	3032 (3)	5225 (3)	62 (4)
	C(5)	14617 (15)	504 (7)	6823 (5)	64 (4)		C(20)	5044	2547	4854	71 (5)
	C(6)	15156 (15)	47 (7)	7320 (6)	73 (5)		C(21)	5590	1770	4938	61 (4)
	C(7)	14426 (15)	170 (6)	7898 (6)	67 (4)		C(22)	6754	1478	5393	66 (4)
	C(8)	13148 (14)	761 (7)	7946 (5)	62 (4)		C(23)	7371	1962	5764	53 (4)
	C(9)	12512 (12)	1216 (5)	7443 (4)	43 (3)		C(18)	6825	2739	5680	43 (3)
	C(10)	11046 (12)	1784 (5)	7470 (4)	38 (3)		C(25)	9722 (9)	3597 (4)	5052 (3)	56 (4)
	C(11)	10303 (12)	1987 (6)	8069 (4)	46 (3)		C(26)	10946	3957	4677	70 (5)
	C(41)	11137 (15)	2638 (6)	8261 (5)	59 (3)		C(27)	11835	4490	4905	61 (4)
	N(12)	8399 (11)	2176 (5)	7986 (3)	50 (3)		C(28)	11500	4662	5509	68 (5)
	C(42)	7539 (17)	2531 (7)	8503 (6)	70 (3)		C(29)	10276	4301	5884	55 (4)
	C(43)	7595 (17)	1464 (7)	7926 (6)	70 (3)		C(24)	9387	3769	5655	49 (3)
	C(13)	5728 (16)	4269 (7)	7729 (6)	66 (4)						
IV	Pd	8728 (1)	9186 (1)	10005 (1)	46 (1)	IV	S(14)	6075 (7)	8998 (3)	9877 (2)	120 (2)
	C(1)	10861 (13)	7439 (5)	10058 (4)	43 (3)		C(15)	4982 (27)	8868 (11)	10675 (9)	48 (5)
	C(2)	11891 (13)	7187 (5)	10551 (4)	48 (3)		C(15′)	6156 (26)	9513 (11)	10607 (9)	46 (4)
	C(3)	13339 (13)	6699 (6)	10501 (4)	48 (3)		C(16)	6394 (15)	8919 (6)	11154 (5)	58 (4)
	C(4)	13840 (12)	6400 (5)	9941 (4)	45 (3)		P(17)	8212 (3)	8202 (1)	11034 (1)	41 (1)
	C(5)	15319 (13)	5878 (6)	9866 (5)	53 (3)		C(19)	10665 (9)	7879 (3)	11960 (3)	54 (4)
	C(6)	15767 (13)	5618 (6)	9310 (5)	52 (3)		C(20)	11945	8059	12315	71 (5)
	C(7)	14817 (15)	5866 (6)	8831 (5)	57 (4)		C(21)	12411	8797	12237	76 (5)
	C(8)	13362 (13)	6379 (5)	8838 (4)	45 (3)		C(22)	11596	9347	11805	72 (5)
	C(9)	12828 (11)	6670 (5)	9396 (4)	35 (3)		C(23)	10315	9158	11451	58 (4)
	C(10)	11342 (11)	7187 (4)	9479 (4)	34 (3)		C(18)	9850	8420	11528	43 (3)
	C(11)	10133 (13)	7423 (5)	8950 (4)	41 (3)		C(25)	6697 (10)	7406 (3)	12051 (3)	65 (4)
	C(41)	8780 (17)	6879 (7)	8957 (6)	69 (3)		C(26)	6111	6761	12385	75 (5)
	N(12)	9344 (13)	8227 (5)	9039 (4)	59 (3)		C(27)	6276	6076	12130	83 (6)
	C(42)	8004 (20)	8495 (8)	8583 (7)	84 (4)		C(28)	7029	6035	11542	70 (5)
	C(43)	10724 (19)	8763 (8)	8884 (7)	82 (4)		C(29)	7616	6679	11207	52 (3)
	C(13)	6213 (31)	9859 (13)	9691 (11)	61 (6)		C(24)	7450	7364	11462	43 (3)
	C(13′)	4502 (58)	8499 (23)	10006 (19)	130 (13)						
anions	P(30A)	5797 (4)	699 (1)	2167 (1)	58 (1)	anions	P(30C)	801 (3)	583 (1)	−168 (1)	54 (1)
	F(31A)	6865	812	2731	88 (3)		F(31C)	1893	662	398	93 (4)
	F(32A)	4099	820	2569	179 (8)		F(32C)	746	1461	−372	111 (4)
	F(33A)	4729	587	1603	94 (4)		F(33C)	−291	504	−736	99 (4)
	F(34A)	7495	578	1766	125 (5)		F(34C)	856	−294	35	102 (4)

Table IV (Continued)

cation		x	y	z	U(eq)	cation		x	y	z	U(eq)
	F(35A)	5670	1576	1951	166 (7)		F(35C)	−885	723	236	101 (4)
	F(36A)	5924	−178	2383	134 (5)		F(36C)	2488	444	−573	156 (7)
	P(30B)	6168 (3)	5715 (2)	4387 (1)	56 (1)		P(30D)	10262 (3)	5395 (1)	7497 (1)	51 (1)
	F(31B)	4786	5697	4931	120 (5)		F(31D)	8858	5404	8034	105 (4)
	F(32B)	6292	6578	4435	133 (5)		F(32D)	11700	5263	7985	114 (4)
	F(33B)	7551	5733	3843	149 (6)		F(33D)	11666	5386	6961	88 (3)
	F(34B)	6045	4852	4340	142 (6)		F(34D)	8824	5527	7010	99 (4)
	F(35B)	7622	5488	4865	147 (6)		F(35D)	10256	4513	7518	106 (4)
	F(36B)	4715	5942	3909	154 (7)		F(36D)	10267	6278	7477	102 (4)

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

Table V. Selected Torsion Angles (deg) in the Complex Cations I–IV[a]

	I	II	III	IV
S(14)–Pd–P(17)–C(18)	97.4	−96.5	−95.6	−130.5
S(14)–Pd–P(17)–C(24)	−134.4	136.3	139.7	102.7
S(14)–C(15)–C(16)–P(17)	−55.1	60.6	56.5	−55.9[b]
				52.3
C(15)–C(16)–P(17)–C(18)	−75.9	75.0	69.8	171.2[b]
				107.1
C(15)–C(16)–P(17)–C(24)	172.9	−178.6	−178.3	−82.8[b]
				−146.9

[a] C18 and C24 are carbon atoms in the phenyl groups bonded to the phosphorus atom. [b] These are two figures when C(15) is involved since the atom is disordered.

reaction mixture was then allowed to warm to room temperature, with stirring being continued for a further 16 h. At this juncture, the solvent was removed by distillation and water (50 mL) was added to the residue. The product was extracted into dichloromethane and isolated by distillation after solution had been dried ($MgSO_4$). The product was thus obtained as a foul-smelling, colorless oil: bp 174–175 °C (0.3 mmHg); yield 2.5 g (83%). ^{1}H NMR ($CDCl_3$): δ 2.06 (s, 3 H, SMe), 2.17–2.74 (m, 4 H, SCH_2 and $AsCH_2$), 7.21–7.50 (m, 10 H, aromatics).

[2-(Methylthio)ethyl]diphenylphosphine. 2-(Diphenylphosphino)-ethanethiol (10.9 g) was dissolved in dry tetrahydrofuran (150 mL). The solution was cooled to −78 °C and treated with 1.6 M *n*-butyllithium (27.7 mL) followed by methyl iodide (2.8 mL). The reaction mixture was then allowed to warm to room temperature, with stirring being continued for a further 16 h. At this juncture, the solvent was removed by distillation and water (100 mL) was added to the residue. The product was extracted into dichloromethane and isolated by distillation after the solution had been dried ($MgSO_4$). The tertiary phosphine was thus obtained as a colorless oil: bp 150–152 °C (0.25 mmHg); yield 10.2 g (89%). ^{1}H NMR ($CDCl_3$): δ 2.07 (s, 3 H, SMe), 2.20–2.72 (m, 4 H, SCH_2 and PCH_2), 7.23–7.57 (m, 10 H, aromatics). ^{31}P NMR ($CDCl_3$): δ −17.02 (s). The ligand was previously reported to be a solid at room temperature.[15,19]

Photochemical Rearrangement of 2-(Diphenylphosphino)ethanethiol. 2-(Diphenylphosphino)ethanethiol (2 g) was sealed inside a Schlenk flask under nitrogen. After exposure to room lighting for 4 months, the tertiary phosphine had rearranged quantitatively into ethyldiphenylphosphine sulfide. ^{1}H NMR ($CDCl_3$): δ 1.19 (d of t, 3 H, $^3J_{HH}$ = 7.6 Hz, $^3J_{PH}$ = 20.3 Hz, CH_2CH_3), 2.47 (d of q, 2 H, $^3J_{HH}$ = 7.8 Hz, $^2J_{PH}$ = 11.5 Hz, CH_2CH_3), 7.27–7.95 (m, 10 H, aromatics). No rearrangement was observed after 6 months for a second sample which was kept in the dark.

Synthesis of ($R_C R/S_S$)-1a by the Direct Coordination Method: [(*R*)-1-[1-(Dimethylamino)ethyl]-2-naphthalenyl-*C*^{2},*N*][(2-(methylthio)-ethyl)diphenylphosphine-*P*,*S*]palladium(II) Chloride. A mixture of (*R*)-2·CH_2Cl_2 (3.1 g) and $Ph_2PCH_2CH_2SMe$ (2.1 g) in dichloromethane (175 mL) was stirred until the solution was homogeneous. After removal of the solvent, the product remained as a yellowish-orange glass: mp 112–113 °C dec; yield 4.5 g (96%); $[\alpha]_D$ −22.2° (*c* 1.0, CH_2Cl_2). ^{1}H NMR ($CDCl_3$): δ 2.04 (d, 3 H, $^3J_{HH}$ = 6.1 Hz, CH*Me*), 2.21 (s, 3 H, SMe), 2.42–3.26 (m, 4 H, PCH_2 and SCH_2), 2.74 (s, 3 H, NMe), 3.00 (d, 3 H, $^4J_{PH}$ = 3.4 Hz, NMe), 4.38 (qn, 1 H, $^3J_{HH}$ = $^4J_{PH}$ = 6.35 Hz, C*H*Me), 6.59–8.08 (m, 16 H, aromatics). ^{31}P NMR ($CDCl_3$): δ 36.48 (s).

[(*R*)-1-[1-(Dimethylamino)ethyl]-2-naphthalenyl-*C*^{2},*N*][(*R*/*S*)-(2-(methylthio)ethyl)diphenylphosphine-*P*,*S*]palladium(II) Hexafluorophosphate (($R_C R/S_S$)-1a). A solution of the above chloride (3.0 g) in ethanol (20 mL) was treated with excess ammonium hexafluorophosphate (1.0 g) in water (15 mL). The yellow precipitate was filtered off and washed with water, ethanol, and diethyl ether. The crude product was then recrystallized from acetone by the addition of diethyl ether: pale yellow needles; mp 199–200 °C dec; yield 3.1 g (86%); $[\alpha]_D$ −35° (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{29}H_{33}F_6NP_2PdS$: C, 49.1; H, 4.7; N, 2.0. Found: C, 49.1; H, 4.5; N, 2.1. ^{1}H NMR ($CDCl_3$): δ 1.91 (d, 3 H, $^3J_{HH}$ = 6.3 Hz, CH*Me*), 2.51–3.19 (m, 4 H, PCH_2 and SCH_2), 2.64 (s, 3 H, SMe), 2.91 (d, 3 H, $^4J_{PH}$ = 1.3 Hz, NMe), 3.05 (d, 3 H, $^4J_{PH}$ = 3.6 Hz, NMe), 4.51 (qn, 1 H, $^3J_{HH}$ = $^4J_{PH}$ = 6.2 Hz, C*H*Me), 6.63–7.92 (m, 16 H, aromatics). ^{31}P NMR ($CDCl_3$): δ 54.12 (s), −143.77 (sep, J_{PF} = 144 Hz, PF_6^-). ^{1}H NMR (acetone-d_6): δ 1.96 (d, 3 H, $^3J_{HH}$ = 6.84 Hz, CH*Me*), 2.80–3.39 (m, 4 H, PCH_2 and SCH_2), 2.87 (s, 3 H, SMe), 3.00 (d, 3 H, $^4J_{PH}$ = 1.7 Hz, NMe), 3.22 (d, 3 H, $^4J_{PH}$ = 3.7 Hz, NMe), 4.80 (qn, 1 H, $^3J_{HH}$ = $^4J_{PH}$ = 6.35 Hz, C*H*Me), 6.70–8.26 (m, 16 H, aromatics).

[(*R*)-1-[1-(Dimethylamino)ethyl]-2-naphthalenyl-*C*^{2},*N*][(*R*/*S*)-(2-(methylthio)ethyl)diphenylarsine-*As*,*S*]palladium(II) Hexafluorophosphate (($R_C R/S_S$)-1b). A mixture of (*R*)-2·CH_2Cl_2 (3.0 g) and $Ph_2AsCH_2CH_2SMe$ (2.4 g) in dichloromethane (175 mL) was stirred until the solution was homogeneous. Removal of solvent yielded a yellow glass that was dissolved in ethanol (30 mL) and treated with excess ammonium hexafluorophosphate (1.6 g) in water (20 mL). The precipitate was separated, dried, and redissolved in acetone (30 mL). Yellow needles formed when the solution was allowed to stand at room temperature and diethyl ether was added at regular intervals: mp 198–199 °C dec; yield 3.6 g (60%); $[\alpha]_D$ −35.8° (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{29}H_{33}AsF_6NPPdS$: C, 46.2; H, 4.4; N, 1.9. Found: C, 46.1; H, 4.3; N, 2.0. ^{1}H NMR ($CDCl_3$): δ 1.94 (d, 3 H, $^3J_{HH}$ = 6.3 Hz, CH*Me*), 2.56 (s, 3 H, SMe), 2.87–2.99 (m, 4 H, $AsCH_2$ and SCH_2), 2.97 (s, 3 H, NMe), 3.08 (s, 3 H, NMe), 4.53 (q, 1 H, $^3J_{HH}$ = 6.3 Hz, C*H*Me), 6.85–7.76 (m, 16 H, aromatics). ^{1}H NMR (acetone-d_6): δ 2.77 (s, 3 H, SMe), 2.92–3.28 (m, 4 H, $AsCH_2$ and SCH_2), 3.06 (s, 3 H, NMe), 3.24 (s, 3 H, NMe), 4.82 (q, 1 H, $^3J_{HH}$ = 6.3 Hz, C*H*Me), 6.93–8.06 (m, 16 H, aromatics), CH*Me* resonances obscured by the solvent.

[(*R*)-1-[1-(Dimethylamino)ethyl]-2-naphthalenyl-*C*^{2},*N*][(*R*/*S*)-(2-(methylthio)ethyl)dimethylarsine-*As*,*S*]palladium(II) Hexafluorophosphate (($R_C R/S_S$)-1c). The compound was isolated in 84% yield as pale green needles, $[\alpha]_D$ −91.7° (*c* 1.0, CH_2Cl_2), mp 161–162 °C dec, with use of $Me_2AsCH_2CH_2SMe$ as ligand. Anal. Calcd for $C_{19}H_{29}AsF_6NPPdS$: C, 36.2; H, 4.7; N, 2.2. Found: C, 36.4; H, 4.6; N, 2.1. ^{1}H NMR ($CDCl_3$): δ 1.69 (s, 3 H, As*Me*), 1.88 (d, 3 H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 1.90 (s, 3 H, AsMe), 2.37–2.66 (m, 2 H, $AsCH_2$), 2.52 (s, 3 H, SMe), 2.79–3.07 (m, 2 H, SCH_2), 2.87 (s, 3 H, NMe), 2.98 (s, 3 H, NMe), 4.42 (q, 1 H, $^3J_{HH}$ = 6.4 Hz, C*H*Me), 7.13–7.84 (m, 6 H, aromatics). ^{1}H NMR (acetone-d_6): δ 1.77 (s, 3 H, AsMe), 1.86 (d, 3 H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 1.99 (s, 3 H, AsMe), 2.65–3.29 (m, 4 H, $AsCH_2CH_2S$), 2.65 (s, 3 H, SMe), 2.90 (s, 3 H, NMe), 3.10 (s, 3 H, NMe), 4.70 (q, 1 H, $^3J_{HH}$ = 6.4 Hz, C*H*Me), 7.36–7.92 (m, 6 H, aromatics).

Synthesis of ($R_C R/S_S$)-1a by the Methylation Method: Chlorobis-[(*R*)-1-(1-(dimethylamino)ethyl]-2-naphthalenyl-*C*^{2},*N*][μ-[2-(diphenylphosphino)ethanethiolato-*P*,*S*:*S*]]dipalladium(II) ((*R*)-4). A mixture of (*R*)-2·CH_2Cl_2 (10.9 g), 2-(diphenylphosphino)ethanethiol (3.5 g) and triethylamine (2 mL) in dichloromethane (175 mL) was stirred until the solution was homogenous. The solution was then washed with water (to remove $[Et_3NH]Cl$), and the organic phase was separated and dried ($MgSO_4$). The product remained as a yellow glass after removal of solvent and was crystallized from a dichloromethane—methanol mixture: mp 196–197 °C dec. Anal. Calcd for $C_{42}H_{46}Cl_1N_2PPd_2S\cdot0.5CH_2Cl_2$: C, 54.9; H, 5.1; N, 3.0. Found: C, 54.9; H, 5.1; N, 2.8. ^{1}H NMR ($CDCl_3$): δ 1.97 (d, 3 H, $^3J_{HH}$ = 6.6 Hz, CH*Me*), 2.59–3.37 (m, 4 H, PCH_2 and SCH_2), 2.81 (s, 3 H, NMe), 2.88 (s, 3 H, NMe), 3.01 (s, 3 H, NMe), 3.35 (d, 3 H, $^4J_{PH}$ = 2.93 Hz, NMe), 4.13–4.47 (m, 4 H, C*H*Me), 6.72–8.29 (m, 22 H, aromatics). ^{31}P NMR ($CDCl_3$): δ 57.89 (s).

[(*R*)-1-[1-(Dimethylamino)ethyl]-2-naphthalenyl-*C*^{2},*N*][2-(diphenylphosphino)ethanethiolato-*P*,*S*]palladium(II) ((*R*)-3). A dichloromethane (25 mL) solution of the above-mentioned dinuclei complex (3.0 g) pre-

pared above was stirred rapidly for 10 min in contact with excess diamino-1,2-ethane (0.4 mL) in water (20 mL). The organic phase was then separated, washed several times with water, and dried ($MgSO_4$). The product remained as a yellow glass after removal of solvent: mp 183-185 °C; yield 1.6 g (86%); $[\alpha]_D$ -41.3° (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{28}H_{30}NPPdS\cdot 0.25CH_2Cl_2$: C, 59.4; H, 5.4; N, 2.5. Found: C, 59.2; H, 5.4; N, 2.3. ^1H NMR ($CDCl_3$): δ 1.87 (d, 3 H, $^3J_{HH}$ = 6.1 Hz, CH*Me*), 2.24-2.98 (m, 4 H, PCH_2 and SCH_2), 2.88 (s, 3 H, NMe), 2.97 (d, 3 H, $^4J_{PH}$ = 3.2 Hz, NMe), 4.40 (qn, 1 H, $^3J_{HH}$ = $^4J_{PH}$ = 6.35 Hz, C*H*Me), 6.74-8.11 (m, 16 H, aromatics). ^{31}P NMR ($CDCl_3$): δ 64.08 (s).

[(*R*)-1-[1-(Dimethylamino)ethyl]-2-naphthalenyl-*C*^{2},*N*][(*R*/*S*)-(2-(methylthio)ethyl)diphenylphosphine-*P*,*S*]palladium(II) Iodide. A solution of the above thiolato complex (0.8 g) in dichloromethane (15 mL) was stirred for 1 h in contact with methyl iodide (91 μL) in dichloromethane (5 mL). The product remained as an orange solid after removal of solvent: mp 197-198 °C; yield 0.9 g (90%); $[\alpha]_D$ -61.8° (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{29}H_{33}INPPdS\cdot 0.2CH_2Cl_2$: C, 49.5; H, 4.8; N, 2.0. Found: C, 49.8; H, 4.8; N, 2.0. ^1H NMR ($CDCl_3$): δ 2.02 (d, 3 H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.47-3.43 (m, 4 H, PCH_2 and SCH_2), 2.55 (s, 3 H, SMe), 2.88 (s, 3 H, NMe), 3.15 (d, 3 H, $^4J_{PH}$ = 2.8 Hz, NMe), 4.46 (qn, 1 H, $^3J_{HH}$ = $^4J_{PH}$ = 6.35 Hz, C*H*Me), 6.57-8.11 (m, 16 H, aromatics). ^{31}P NMR ($CDCl_3$): 46.17 (s). ^1H NMR (acetone-d_6): δ 2.45-3.35 (m, 4 H, PCH_2 and SCH_2), 2.53 (s, 3 H, SMe), 2.84 (s, 3 H, NMe), 3.21 (d, 3 H, $^4J_{PH}$ = 2.7 Hz, NMe), 4.47 (qn, 1 H, $^3J_{HH}$ = $^4J_{PH}$ = 6.1 Hz, C*H*Me), 6.65-8.30 (m, 16 H, aromatics) CH*Me* resonances obscured by the solvent signal. Treatment of the iodide with aqueous ammonium hexafluorophosphate gave the desired complex, (*R*$_c$,*R*/*S*$_s$)-**1a**, in 74% isolated yield. The physical and spectrochemical properties of this product were identical with those for the compound obtained by the direct coordination method.

Structural Analysis. Cell dimensions of [Pd{(*R*)-$CH_3CH(1\text{-}C_{10}H_6)$-$NMe_2$-*C*^{2},*N*}(*R*/*S*)-{$Ph_2PCH_2CH_2SMe$-*P*,*S*}]$PF_6$ were determined from 45 reflections obtained by an automated random search routine at room temperature on a Siemens R3m/v four-circle diffractometer using graphite-monochromated Mo Kα radiation. A colorless crystal of approximate dimensions 0.25 × 0.40 × 0.60 mm was used. Data were collected for 3.0° ≤ 2θ ≤ 50° and index ranges 0 ≤ *h* ≤ +9, -21 ≤ *k* ≤ +21, -25 ≤ *l* ≤ +25 with a variable scan rate of 1.50-15.0° min^{-1}. A summary of the crystallographic data is given in Table II. A total of 11 526 reflections were collected, and 10 278 of these [$F > 6\sigma(F)$] were used in the refinement. The intensities of three standard reflections were measured after every 97 reflection data were collected. Semiempirical absorption corrections were applied. The structure was solved by direct methods, and the lighter non-hydrogen atoms were located from Fourier difference maps. Non-hydrogen atoms were refined anisotropically except for methyl carbon atoms in the 1-(dimethylamino)ethylnaphthylene molecule and the disordered carbon atoms in cation IV. The function minimized during full-matrix least-squares refinement was $\sum w(F_o - F_c)^2$ where $w^{-1} = \sigma^2(F) + 0.0004F^2$, yielding R = 0.041, R_w = 0.067, and S = 2.34. Phenyl rings and the hexafluorophosphate ions were refined as rigid groups. Hydrogen atoms were introduced in calculated positions only for carbons refined anisotropically and were assigned fixed thermal parameters. All calculations were performed on a Digital Equipment Corp. MicroVax II computer using the Siemens SHELXTL PLUS package.

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Registry No. (*R*$_c$,*R*$_s$)-**1a**, 139276-65-6; (*R*$_c$,*S*$_s$)-**1a**, 139276-67-8; (*R*$_c$,*R*$_s$)-**1b**, 139276-69-0; (*R*$_c$,*S*$_s$)-**1b**, 139402-42-9; (*R*$_c$,*R*$_s$)-**1c**, 139402-44-1; (*R*$_c$,*S*$_s$)-**1c**, 139402-46-3; (*R*$_c$,*R*$_s$)-**1a** (chloride salt), 139276-70-3; (*R*$_c$,*R*$_s$)-**1a** (iodide salt), 139276-73-6; (*R*$_c$,*S*$_s$)-**1a**, 139402-47-4; (*R*)-**2**, 80145-77-3; (*R*)-**3**, 139276-72-5; (*R*)-**4**, 139276-71-4; $Me_2AsCH_2CH_2SH$, 139276-61-2; $Me_2AsCH_2CH_2Me$, 139276-62-3; $Ph_2AsCH_2CH_2SH$, 139276-63-4; $Ph_2AsCH_2CH_2Me$, 131291-87-7; $Ph_2PCH_2CH_2SH$, 3190-79-2; $Ph_2PCH_2CH_2Me$, 20859-51-2; $NaAsMe_2$, 13787-40-1; $\overline{CH_2CH_2S}$, 420-92-8; Ph_2AsH, 829-83-4; $EtPh_2P(S)$, 1017-98-7.

Supplementary Material Available: For (*R*$_c$,*R*/*S*$_s$)-**1a**, figures showing atom-labeling schemes and tables of crystallographic data, final positional parameters and equivalent isotropic thermal parameters, bond distances, bond angles, anisotropic thermal parameters of non-hydrogen atoms, and calculated hydrogen parameters (16 pages); a table of observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.

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Photochemical Behavior of Thioxophosphoranyl Diazo Compounds: Evidence for Transient λ^5-Phosphathiirenes and for Structural Isomerizations of the Diazo Group

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Photolysis of bis[bis(diisopropylamino)thioxophosphoranyl]diazomethane (**1**) in the presence of a slight excess of dimethyl acetylenedicarboxylate led to 1,3λ^5-thiaphosphole **5** in 95% yield. This compound was fully characterized including an X-ray diffraction study. Irradiation of (thioxophosphoranyl)(trimethylsilyl)diazomethane **2** gave rise to [bis(diisopropylamino)thioxophosphoranyl](trimethylsilyl)carbodiimide **6** in 60% yield. Photolysis of [bis(diisopropylamino)thioxophosphoranyl]diazomethane (**3**) quantitatively afforded 1,3,4-thiadiaza-1,6-dihydro-5λ^5-phosphinine **7** in the absence of trapping agent, while in the presence of dimethyl acetylenedicarboxylate *N*-(thioxophosphoranyl)pyrazole **8** was obtained in 70% yield. Irradiation of 1,3,4,2λ^5-thiadiazaphosphole **4** led to bis[bis(diisopropylamino)thioxophosphoranyl]carbodiimide (**9**) in 85% yield. From these results it appeared that depending on the nature of the diazo carbon substituent, the photolysis of thioxophosphoranyl diazo compounds leads to transient λ^5-phosphathiirenes with loss of nitrogen and/or to 1,3,4,2λ^5-thiadiazaphospholes which under irradiation give rise to nitrilimines which can be trapped or which rearrange into carbodiimides.

Although α-phosphoranyl diazo derivatives have been widely studied,[1] α-thioxophosphoranyl diazo compounds have attracted very little attention.[2,3] Their carbon analogues, the diazothioketones are hardly available due to their facile isomerization into 1,2,3-thiadiazoles;[4] these compounds are of special interest since they are the classical precursors of the highly unstable thiirenes A.[5] Here we report evidence for the transient formation of

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