Optical Resolutions and Chelating Properties of (±)-[2-(Methylsulfinyl)ethyl]diphenylarsine and Its Phosphorus Analogue

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An optical resolution of the asymmetric chelating agents (±)-[$Ph_2ECH_2CH_2S(O)Me$] (E = As or P) has been achieved via fractional crystallization of a pair of diastereomeric palladium(II) complex cations containing the appropriate sulfinyl-substituted ligand and ortho-metalated (*S*)-(1-(dimethylamino)ethyl)naphthalene. The crystal and molecular structure of the perchlorate salt of the less soluble phosphine-palladium complex has been determined. Crystal data: monoclinic pale yellow prisms, $P2_1$, $a = 10.147(2)$ Å, $b = 10.955(2)$ Å, $c = 26.888(5)$ Å, $\beta = 97.76(2)°$, $Z = 4$, and $R = 0.0302$. The optically pure compound, $[\alpha]_D$ −16.1° (*c* 1.0, dichloromethane), crystallizes as a pair of interconvertible conformers arising from the adoption of different helicities by the nonplanar chelate rings. In both conformers, the sulfinyl-substituted phosphine coordinates to the palladium via phosphorus and oxygen with the uncoordinated sulfur stereocenter of *S* absolute configuration. Optically pure (*S*)-[2-(methylsulfinyl)ethyl]-diphenylphosphine, $[\alpha]_D$ +67.5° (*c* 1.0, dichloromethane), was displaced from the resolving palladium complex with 1,2-bis(diphenylphosphino)ethane. The (*R*)-(−)$_{589}$ enantiomer of the phosphine ligand was obtained in a state of 85% optical purity from the residual mixture of diastereomeric complexes and was subsequently brought to purity by fractional crystallization of the corresponding enantiomorphic complex containing (*R*)-(1-(dimethylamino)-ethyl)naphthalene. Enantiomerically pure forms of [2-(methylsulfinyl)ethyl]diphenylarsine are obtained similarly from the corresponding resolved palladium complexes by treatment with cyanide. The various enantiomeric forms of the sulfinyl-substituted ligands are capable of coordinating to square-planar platinum metal ions via their E, E–O, or E–S donor atoms. The mode of coordination is governed by the stereoelectronic factors of the product complexes.

Introduction

The synthetic application of enantiomerically pure sulfoxides is an important subject which has been highlighted by both organic[1] and inorganic[2,3] chemists. To date, optically active sulfoxides are conventionally obtained from Andersen's procedure involving Grignard reagents,[4] asymmetric oxidation of prochiral sulfides with titanium catalysts,[5] and optical resolution by the use of naturally existing carboxylic acids or bases for sulfoxides carrying a suitable counterpart.[6] Resolution by means of metal complexation has also been reported for several simple sulfoxides.[7] These developed methods, however, are rarely used for the preparation of asymmetric sulfoxides bearing unstable functionalities which, for example, are easily oxidized. Indeed, there has been very limited report[3] on the synthesis of optically active sulfinyl-substituted polydentates carrying donor atoms such as tertiary arsenic and phosphorus, i.e. the two most important "soft" donor centers in coordination chemistry. Due to the dual presence of a powerful donor atom and a flexible ambidentate function, this class of asymmetric E–S(O) ligands is expected to exhibit versatile coordination and stereochemistries toward transition-metal ions. The preparation of such enantiomerically pure E–S(O) chelates therefore presents a unique opportunity to probe in detail the importance of ligand-based stereoelectronic effects in determining transition-metal complex stereochemistries. Such a study may contribute to the development of genuine catalysts for asymmetric synthesis. So far, however, most inorganic work has involved symmetrical mono- or disulfoxides[8] with very little attention given to the chelating properties of asymmetrical heterodonor systems, perhaps due to the difficulties associated with the preparation and resolution of such compounds.

In this paper, we present the resolution and coordination chemistry of transition-metal complexes containing the novel asymmetric sulfinyl-substituted tertiary arsine ligand ($Ph_2AsCH_2CH_2S(O)Me$), (±)-**1**, and its phosphine analogue, (±)-**2**. Both ligands are designed to chelate to group 10 transition-metal ions utilizing their E donor atoms together with either sulfur (i.e. formation of a five-membered E–S chelate ring) or oxygen (a six-membered E–O ring) of the asymmetric sulfoxide function. In theory, the mode of sulfoxide-metal bondings in these complexes will be affected by the following concerted factors: (a) the bite angle or the ring size of the resulting metal chelates; (b) the electronic effect directed from the trans-donor atom; (c) the steric repulsion originated from the substituents on the neighboring cis donor; (d) the relative philicities of the metal ions toward sulfur and oxygen of the sulfoxide. In the presence of major stereoelectronic constraints, however, the ligands are also able to coordinate to the metal center via a sole M–E bond. We have indeed identified all three bonding modes of the E–S(O) ligands toward square-planar palladium(II) under different stereoelectronic conditions.

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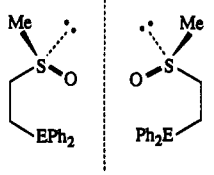


(±)-1 (E = As)

(±)-2 (E = P)

Results and Discussion

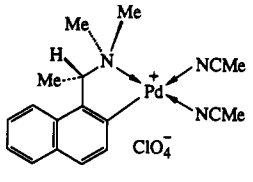
Ligand Synthesis.[9] Both racemic ligands were obtained as white needles in ca. 80% yield from the reaction between 1-chloro-2-(methylsulfinyl)ethane and $LiEPh_2$ in THF at −78 °C. In the solid state, the ligands are stable to air. In solution, NMR studies indicated that they remained unchanged after being kept for a few days under nitrogen but were oxidized to their arsine and phosphine oxides upon exposure to air. Both free ligands are, however, sensitive to heat. Indeed, they are readily decomposed thermally at 110 °C to diphenylvinylarsine and phosphine, respectively. Although not isolated, it is likely that the unstable methanesulfenic acid[10] was generated during the course of thermolysis[11] (eq 1).

$$Ph_2ECH_2CH_2S(O)Me \rightarrow Ph_2ECH{=}CH_2 + MeSOH \quad (1)$$

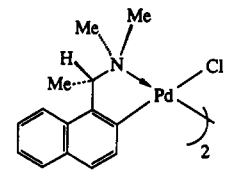
A quantitative rearrangement of both ligands to their isomeric methylthio-substituted arsine and phosphine oxides was also observed when molecular iodine was introduced into dichloromethane solutions containing the sulfoxides (eq 2). At room temperature, the isomerization of **2** was found to complete within 15 min. The process corresponded closely to a reported conversion of α-sulfinyl-substituted phosphines into their sulfide phosphine oxide.[12] In contrast, the rearrangement of the arsenic compound, **1**, to the arsine oxide was found to be relatively slow (ca. 24 h). For both ligands, the rate of rearrangement is independent of the concentration of the sample employed. These observations, taken in conjunction with the general reactivities of arsines and phosphines toward oxidation reactions, are consistent with a stronger intramolecular P–O interaction in **2** than that of As–O in **1**.

$$Ph_2ECH_2CH_2S(O)Me \rightarrow Ph_2E(O)CH_2CH_2SMe \quad (2)$$

Formation, Separation, and Structural Analysis of Diastereomers. The resolutions of (±)-**1** and (±)-**2** are based on the separation of a pair of internally diastereomeric palladium(II) salts derived from the resolving agent bis(acetonitrile)[(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*]palladium(II) perchlorate, (*S*)-**3**.[13] The latter was obtained in 85% isolated yield



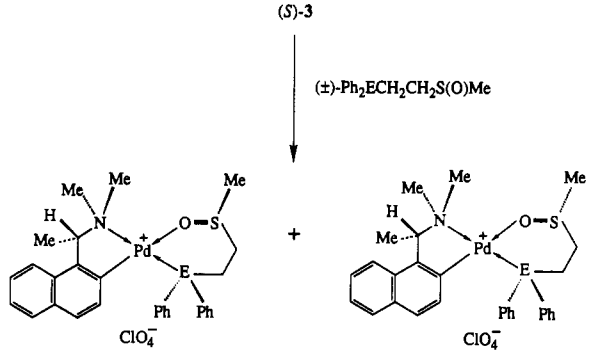
(*S*)-3



(*S*)-4

as pale yellow needles by metathesis of the corresponding optically active dichloro bridged dipalladium(II) complex (*S*)-**4**[14] with silver perchlorate in acetonitrile, $[\alpha]_D$ +104.4° (CH_2Cl_2). The initial mixture of diastereomers in each resolution process was obtained in high yields (89–98%) from 1 equiv each of (*S*)-**3** and the appropriate racemic ligand in dichloromethane (Scheme I). In each preparation, the ^1H NMR spectrum of the products obtained directly from the reaction was recorded prior to purification. In both resolutions the mixtures were separated efficiently into their diastereomeric pure forms by fractional crystallization. Recrystallization of **5** from acetone–diethyl ether produced the less soluble (S_s,S_c) isomer in 84% theoretical yield. The pure diastereomer crystallized as beautiful yellowish green needles with $[\alpha]_D$ −13.6° (CH_2Cl_2). The more soluble (R_s,S_c) isomer was crystallized from the enriched mother liquor as microcrystals, $[\alpha]_D$ −21.8° (CH_2Cl_2). The 500-MHz ^1H NMR spectrum of this material indicated, however, that it contained ca. 5% of the less soluble (S_s,S_c) isomer. The resolution procedure for the P–S(O) ligand followed closely from the analogous arsenic work. Selected physical and spectroscopic properties for the recrystallized products are given in Table I.

Scheme I



(S_s,S_c)-5 (E = As) (R_s,S_c)-5 (E = As)

(S_s,S_c)-6 (E = P) (R_s,S_c)-6 (E = P)

Table I. Selected Spectroscopic Properties of Sulfoxide Compounds

compd	δ (SMe)[a]	ν(S=O)[b]	$[\alpha]_D$,[c] deg
(*R*)-**1**	2.50 s	1030	−56.7
(*R*)-**2**	2.53 s	1031	−67.2
(R_s,S_c)-**5**	3.06 s	990	−21.8[d]
(S_s,S_c)-**5**	3.01 s	990	−13.6
(R_s,S_c)-**6**	3.12 s	987	−50.0[e]
(S_s,S_c)-**6**	3.03 s	988	−16.1
(*R*/S_s,S_c)-**7**[f]	2.58 s, 2.59 s	1035	+22.5
(*R*)-[Pd(As-S(O))Cl_2]	3.53 s[g]	1129	−119.4[h]
(*R*)-[Pd(P-S(O))Cl_2]	3.53 s[g]	1133	−108.6[h]
(*R*)-[Pt(As-S(O))Cl_2]	3.60 s[g] $^3J_{PtH}$ = 20.7 Hz	1142	−35.6[h]
(*R*)-[Pt(P-S(O))Cl_2]	3.61 s[g] $^3J_{PtH}$ = 22.8 Hz	1140	−44.0[h]

[a] 500-MHz ^1H NMR spectra chemical shift values of SMe in ppm for $CDCl_3$ solution, unless otherwise stated. [b] IR signals in cm^{-1} (KBr pellets). [c] Measured in CH_2Cl_2 unless otherwise stated. [d] 90% Optical purity. [e] 85% Optical purity. [f] A 1:1 diastereomeric mixture arising at the sulfur stereocenter. [g] Recorded in CD_3CN. [h] Measured in DMSO.

The absolute configuration of the coordinated sulfinyl-substituted phosphine and its chelating properties toward palladium(II) in the less soluble diastereomer (S_s,S_c)-**6** were studied by X-ray crystallography (Figure 1). Crystallographic data for the complex are given in Table II. Structural analysis indicated four molecules in the unit cell, consisting of two pairs of molecules which slightly differ in the ring conformation of the sulfinyl-substituted phosphine moiety of the complex cation. Selected

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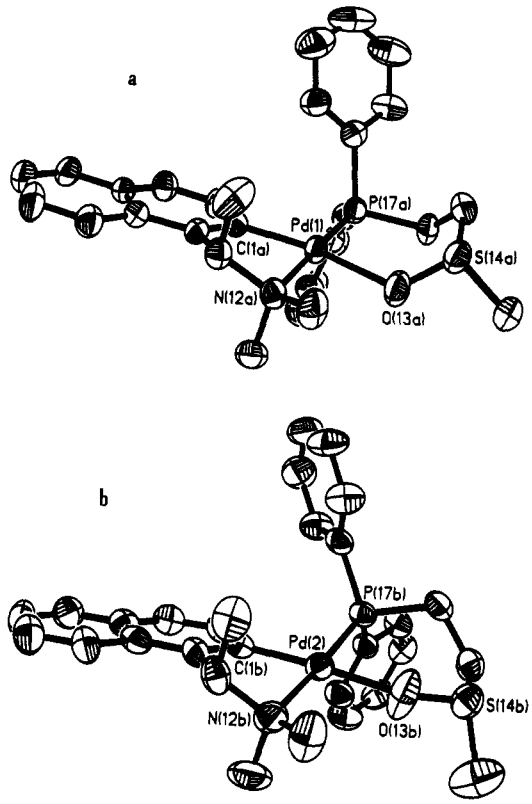

Figure 1. Molecular structures and labeling schemes for the two conformers of (S_s,S_c)-**6**.

Table II. Crystal Data for (S_s,S_c)-**6**

space group	$P2_1$	F(000)	1392
a, Å	10.147(2)	chem formula	$C_{29}H_{33}ClNO_5PPdS$
b, Å	10.955(2)	fw	680.4
c, Å	26.888(2)	Z	4
β, deg	97.76(2)	abs coeff, cm^{-1}	8.80
V, Å^3	2961(1)	trans coeffs	0.651–0.697
D_c, g cm^{-3}	1.526	temp, °C	25
D_m, g cm^{-3}	1.512	λ, Å	0.71073
R^a	0.0302	R^a_w	0.0372

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

Table III. Selected Bond Lengths (Å) and Angles (deg) in the Two Complex Conformers **a** and **b**

	a	**b**
Pd–C(1)	2.009(5)	1.987(6)
Pd–N(12)	2.117(5)	2.114(5)
Pd–O(13)	2.115(4)	2.136(5)
Pd–P(17)	2.252(2)	2.243(1)
O(13)–S(14)	1.534(5)	1.465(6)
C(1)–Pd–N(12)	81.8(2)	81.3(2)
C(1)–Pd–P(17)	98.0(2)	96.2(2)
N(12)–Pd–O(13)	90.4(2)	89.7(2)
O(13)–Pd–P(17)	89.7(1)	92.6(2)
C(1)–Pd–O(13)	171.5(2)	170.2(2)
N(12)–Pd–P(17)	178.2(1)	176.4(2)

bond distances and bond angles of the two complex cations **a** and **b** are given in Table III. 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.

In both conformers **a** and **b**, the sulfinyl-substituted phosphine coordinates to palladium via phosphorus and oxygen with the sulfur stereocenter of *S* absolute configuration. Furthermore, the five-membered organometallic rings containing the metal have the same asymmetric skew conformations of λ helicity but the six-membered P–O rings exhibit two relative configurations in the crystal structure. The six-membered ring formed between the palladium atom and the sulfinyl-substituted phosphine ligand adopts the "boat form" in both conformers **a** and **b**. The major difference between them lies in the fact that the sulfur atom is above the mean C–N–O–P plane in one case and below it in the other (+0.98(1) and –0.30(1) Å, respectively, using the axial methyl group at C(11) as reference for the positive direction). There is, however, little difference in the Pd–C, Pd–N, Pd–O, and Pd–P distances in the two conformers. Even the bond angles centered at the palladium atom are similar as shown in Table III. The palladium atom is 0.049 and 0.064 Å above the C(1)–N(12)–O(13)–P(17) mean plane in the conformers **a** and **b**, respectively. In fact the bond distances and bond angles in the five-membered organometallic ring of the complex cation are very similar to previously reported values.[14] The observed Pd–P and Pd–O bond distances are very close to values reported in the literature.

Perhaps the most significant differences between the two conformers are in the S–O distances (1.534(5) Å in conformer **a** and 1.465(6) Å in conformer **b**) and the torsion angles in the sulfinyl-substituted phosphine ligand as shown in Table V. In metal sulfoxide complexes where the coordination is through the sulfur atom the S–O bond distance is generally in the 1.46–1.49 Å range. Upon coordination through oxygen, the observed S–O distance increases to the 1.52–1.56 Å range, probably due to a decrease in double bond character between sulfur and oxygen.[3,8,15] The S–O distance in conformer **a** is in agreement with literature values for a sulfoxide coordinated through the oxygen atom while that in conformer **b** is closer to those coordinated through sulfur, although the crystal structure shows clearly that oxygen is bonded to the metal. This may be a consequence of the conformation of the sulfinyl chelate ring. The explanation for the unusually short S–O distance in conformer **b** is, however, uncertain at this stage, but the phenomenon is being investigated. Coincidentally preliminary structure determination of a related complex (*S*,*S*)-bis[[2-(methylsulfinyl)ethyl]diphenylphosphine-*O*,*P*]palladium(II) perchlorate evinced that although both ligands coordinate through the oxygen atom in the solid state, the two S–O distances in the same molecule are 1.480 and 1.488 Å.[16]

NMR studies of (S_s,S_c)-**6** at room temperature indicated that the metal–oxygen bonds remain unchanged in solution. In $CDCl_3$, the complex exhibited one set of signals in its 500-MHz ^{1}H NMR spectrum with a sharp S–Me resonance signal at δ 3.03 (Table I). The chemical shift is consistent with sulfinyl–O complexation.[8] It should be noted, however, that the presence of only one set of NMR resonance signals is diagnostic of rapid equilibration of the conformers in solution since the two conformers **a** and **b** are stereochemically distinct species.

The structure proposed for the more soluble (R_s,S_c) isomer of the phosphine complex retains the structural features of the fully characterized less soluble diastereomer (S_s,S_c)-**6**. Furthermore, because of the similarity in solubilities, optical rotations, and ^{1}H NMR spectra (apart from the absence of trans ^{31}P coupling resonance to the NMe_2 group), the (R_s,S_c) and (S_s,S_c) configurations have been assigned respectively to the more and the less soluble diastereomer of the arsenic compounds, **5**.

It is noteworthy that each resolution produced only two of the eight possible stable diastereomers (excluding the interconvertible conformational isomers). It has been well established that the coordination of unsymmetrical bidentates to the ortho-metalated [dimethyl(1-(2-naphthyl)ethyl)aminato-*C*,*N*]palladium(II) unit is remarkably regiospecific with the softer of the two donors invariably occupying the position trans to the NMe_2 group in the complex.[14,17,18] The regiospecificity of the resolving cation has

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Table IV. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³)

	x	y	z	U(eq)[a]		x	y	z	U(eq)[a]
Pd(a)	677(1)	9947	8637(1)	35(1)	C(5b)	2115(6)	675(7)	5560(3)	58(2)
C(1a)	−1223(5)	10192(5)	8331(2)	35(2)	C(6b)	1294(7)	619(8)	5109(3)	66(3)
C(2a)	−1798(5)	11259(6)	8113(2)	43(2)	C(7b)	1182(7)	1620(8)	4780(3)	66(3)
C(3a)	−3127(6)	11306(6)	7932(2)	46(2)	C(8b)	1886(6)	2644(7)	4901(2)	51(2)
C(4a)	−3937(5)	10277(5)	7939(2)	38(2)	C(9b)	2747(6)	2770(6)	5357(2)	48(2)
C(5a)	−5315(5)	10301(6)	7764(2)	50(2)	C(10b)	3482(6)	3834(6)	5500(2)	42(2)
C(6a)	−6085(6)	9298(8)	7769(2)	59(2)	C(11b)	3376(6)	4971(7)	5178(2)	51(2)
C(7a)	−5526(6)	8201(8)	7944(3)	65(3)	N(12b)	3589(6)	6023(6)	5533(2)	58(2)
C(8a)	−4196(6)	8121(6)	8128(3)	52(2)	O(13b)	5968(6)	7326(5)	6065(2)	83(2)
C(9a)	−3370(5)	9168(6)	8135(2)	39(2)	S(14b)	6874(2)	8148(2)	6376(1)	55(1)
C(10a)	−1976(5)	9149(5)	8343(2)	35(2)	C(15b)	7759(6)	7245(7)	6872(2)	52(2)
C(11a)	−1354(5)	8035(5)	8602(2)	39(2)	C(16b)	8239(6)	6050(6)	6659(2)	50(2)
N(12a)	114(5)	8089(4)	8559(2)	39(1)	P(17b)	6950(1)	4863(2)	6610(1)	39(1)
O(13a)	2653(4)	9431(4)	8907(2)	62(2)	C(18b)	6701(5)	4646(5)	7264(2)	40(2)
S(14a)	3484(2)	9772(2)	9407(1)	53(1)	C(19b)	7791(6)	4519(6)	7636(2)	45(2)
C(15a)	3399(7)	11408(7)	9455(2)	56(2)	P(20b)	7608(7)	4475(6)	8135(2)	54(2)
C(16a)	3060(5)	12016(6)	8935(2)	46(2)	C(21b)	6350(7)	4576(6)	8272(2)	58(2)
P(17a)	1286(1)	11924(1)	8694(1)	37(1)	C(22b)	5276(7)	4682(8)	7900(3)	65(3)
C(18a)	451(6)	12866(6)	9118(2)	43(2)	C(23b)	5448(6)	4752(7)	7413(2)	52(2)
C(19a)	1020(8)	13949(6)	9323(2)	57(2)	C(24b)	7814(5)	3517(6)	6433(2)	45(2)
C(20a)	401(10)	14631(7)	9658(3)	78(3)	C(25b)	7902(7)	2451(7)	6708(3)	57(2)
C(21a)	−826(10)	14277(9)	9774(3)	87(4)	C(26b)	8551(8)	1442(8)	6540(3)	76(3)
C(22a)	−1389(9)	13207(10)	9582(3)	82(4)	C(27b)	9159(7)	1497(9)	6127(3)	72(3)
C(23a)	−749(6)	12486(7)	9250(2)	56(2)	C(28b)	9086(8)	2554(9)	5858(3)	73(3)
C(24a)	1292(5)	12716(6)	8099(2)	40(2)	C(29b)	8420(7)	3546(8)	6002(2)	63(3)
C(25a)	1300(6)	12019(7)	7667(2)	57(2)	C(30b)	4368(7)	4955(8)	4810(2)	65(2)
C(26a)	1469(7)	12561(8)	7224(3)	69(3)	C(31b)	3765(9)	7193(7)	5259(3)	89(3)
C(27a)	1608(7)	13807(9)	7197(3)	68(3)	C(32b)	2414(7)	6155(10)	5803(3)	97(4)
C(28a)	1570(7)	14531(7)	7610(3)	62(2)	C(33b)	5874(11)	9038(11)	6703(4)	109(4)
C(29a)	1418(6)	13979(6)	8062(3)	50(2)	Cl(50)	4427(2)	5757(2)	9314(1)	53(1)
C(30a)	−1607(7)	7996(8)	9140(3)	69(3)	O(51)	3716(5)	5650(8)	8833(2)	109(3)
C(31a)	300(6)	7744(6)	8028(2)	53(2)	O(52)	4766(9)	4571(7)	9482(3)	140(4)
C(32a)	897(6)	7242(6)	8894(3)	57(2)	O(53)	3667(6)	6292(7)	9665(2)	100(3)
C(33a)	5118(6)	9585(9)	9271(3)	73(3)	O(54)	5620(7)	6344(9)	9314(3)	134(4)
Pd(b)	5209(1)	5509(1)	6071(1)	41(1)	Cl(60)	1170(2)	8396(2)	6679(1)	54(1)
C(1b)	4345(5)	3886(6)	5960(2)	43(2)	O(61)	1277(6)	7260(5)	6933(2)	91(2)
C(2b)	4416(6)	2861(7)	6276(2)	49(2)	O(62)	653(6)	9247(6)	7000(2)	94(2)
C(3b)	3696(6)	1841(7)	6160(2)	54(2)	O(63)	304(5)	8271(7)	6225(2)	89(2)
C(4b)	2849(6)	1750(6)	5691(2)	48(2)	O(64)	2422(5)	8772(7)	6564(2)	92(2)

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

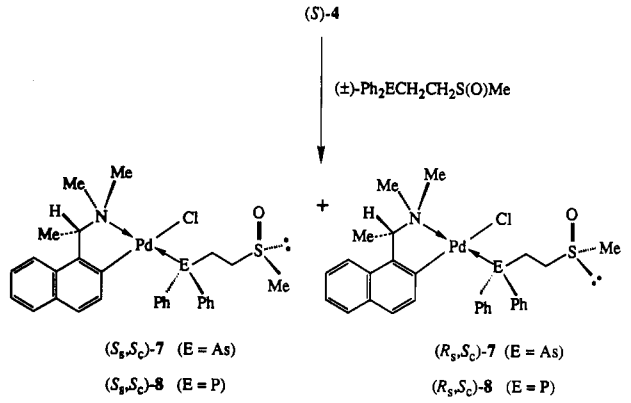
Table V. Selected Torsion Angles (deg) in the Two Complex Conformers **a** and **b**

	a	b
Pd–O(13)–S(14)–C(15)	−51.7(5)	10.6(7)
O(13)–S(14)–C(15)–C(16)	−23.0(5)	45.1(6)
S(14)–C(15)–C(16)–P(17)	−78.7(5)	−85.3(5)
O(13)–Pd–P(17)–C(16)	−0.4(3)	−11.9(3)
S(14)–O(13)–Pd–P(17)	59.0(4)	−23.1(6)

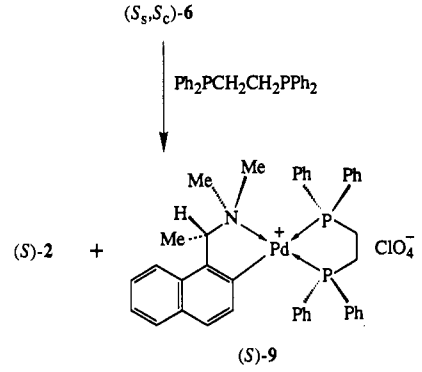
been attributed to the vast difference in the electronic-trans directing effects from the σ-donating nitrogen and π-accepting aromatic carbon atom in the five-membered organometallic ring.[18] Indeed, based on this electronic consideration alone, it is not surprising that both E–S(O) ligands are bonded to the palladium(II) resolving unit with the E donors, generally considered as π-acids, coordinated regiospecifically trans to the NMe_2 group. Spectroscopic and structural data also indicated that both E–S(O) ligands formed exclusively six-membered chelate rings with the "soft" palladium of the resolving unit via their E–O donor atoms. As intimated earlier, five-membered metal–sulfur bonding was not observed in any of these square-planar diastereomeric complexes, neither in the solid state nor in solution. The absence of metal–sulfur bonding in these diastereomeric complexes indeed exemplifies our previous stereoelectronic considerations for the chelating E–S(O) ligands. While the contribution of the high trans influence from the coordinated aromatic carbon may not necessarily be the sole cause of palladium–oxygen bonding, the enormous steric repulsion from the cis NMe_2 group will preclude the formation of a palladium–sulfur bond.

Interestingly, the formation of the E–O chelate rings on the palladium resolving agent proceeded smoothly only when (*S*)-**3** was used. With the dipalladium complex (*S*)-**4**, however, the sulfinyl groups were unable to replace the terminal chloro ligand and hence neither the E–O nor the E–S rings were formed (Scheme II). Instead, a pair of diastereomeric complexes was obtained in each resolution with only the arsenic or phosphorus donor coordinated to the resolving unit (**7**–**8**). Conductivity measurements confirmed the formation of a neutral product rather than a chloride salt. The IR and ^1H NMR studies of these complexes in $CDCl_3$ were consistent with the sulfinyl functions of both ligands being free and only the E donors being coordinated regiospecifically trans to the NMe_2 group. We have recently reported spectroscopic properties and the X-ray structure of an analogous bromo complex in which a thioether-substituted phosphine ligand was coordinated via only phosphorus to the same resolving unit with a similar geometry around palladium.[17] Efforts to resolve

Scheme II



Scheme III



the E–S(O) ligands with the internally diastereomeric complexes **7** and **8** were unsuccessful. In all attempts to separate the isomers by fractional crystallization, the complexes were repeatedly isolated as a compound containing an approximately equimolar mixture of both diastereomers. It should be noted, however, that by treatment with silver perchlorate, these neutral species **7** and **8** could be converted into the corresponding separable perchlorate salts **5** and **6**, respectively, in high yields.

Liberation of Resolved Sulfoxides. Treatment of (S_s,S_c)-**5** in dichloromethane with aqueous potassium cyanide for 0.5 h decomposed the complex efficiently. The organic layer contained the optically active sulfinyl-substituted arsine as well as the optically active amine of the resolving agent. The latter was removed from the mixture by extraction with dilute sulfuric acid. Pure (*S*)-(+)-**1** was isolated as air-stable white crystals in 91% yield, $[\alpha]_D$ +56.5° (CH_2Cl_2). Stereospecific displacement of the resolved arsenic ligand from the metal was confirmed by the quantitative repreparation of (S_s,S_c)-**5** from liberated (*S*)-**1** and (*S*)-**3**: the 500-MHz ^{1}H NMR of the crude product indicated diastereomer (S_s,S_c)-**5** only. In a further test of optical purity, the soluble diastereomer (S_s,R_c)-**5** was prepared from (*S*)-**1** and the equally accessible (*R*)-**3**; only the signals due to the (S_s,R_c) isomer were observed.

It was wasteful to isolate (R_s,S_c)-**5** in its stereoisomeric pure form from the diastereomeric mixture by recrystallizations as very poor chemical yield was obtained for this more soluble complex. It was more practical to obtain (*R*)-**1** by first liberating the optically impure (*R*)-**1** from the contaminated (R_s,S_c)-**5**. This material, with $[\alpha]_D$ –46.3° (CH_2Cl_2) which corresponded to 90% ee, was subsequently brought to optical purity by treating it with the calculated quantity of (*R*)-**3** and isolating crystalline (R_s,R_c)-**5** with $[\alpha]_D$ +13.1° (CH_2Cl_2). Optically pure (*R*)-**1** was then liberated in high yield from pure (R_s,R_c)-**5**.

For the liberation of the resolved phosphine ligand, however, treatment with aqueous cyanide did not decompose the diastereomers efficiently: the chemical yield and the purity of the ligand were not satisfactory. We found it was more convenient to treat the appropriate form of **6** with the strong chelating agent $Ph_2PCH_2CH_2PPh_2$ (Scheme III).[17] The corresponding resolved ligand **2** was liberated with formation of **9**. Optically pure (*S*)-**2** was thus obtained from (S_s,S_c)-**6** as a viscous oil that crystallized slowly upon standing as a colorless solid, mp 85–86 °C, $[\alpha]_D$ +67.5° (CH_2Cl_2). Similar to its arsenic analogue, partially resolved (*R*)-**2** obtained from (R_s,S_c)-**6** was brought to its optical purity by first treating it with (*R*)-**3**. Pure (*R*)-**2** was subsequently displaced from the pure crystalline (R_s,R_c)-**6** with the diphosphine ligand.

Square-Planar Complexes [M(E-S(O))Cl$_2$]. The reactions of $[M(CH_3CN)_2Cl_2]$ (where M = Pd and Pt) with the various forms of the sulfinyl-substituted ligands gave the neutral divalent square-planar complexes in high yields.[9] In contrast to the internal diastereomeric complexes (**5**–**6**), the E–S(O) ligands are observed by ^{1}H NMR and IR to chelate to the metal centers exclusively via their E–S donor atoms. Metal–oxygen bonds were not detected in these compounds, neither in the solid state nor in solution. We have recently reported spectroscopic studies of the racemic compounds and the X-ray structure of (±)-[Pd(P-S(O)Me)Cl$_2$]. The S–O bond distance was found to be within the range normally observed for sulfinyl-S complexation (1.469(2) Å). Similar spectroscopic properties were observed when the optically active chelating agents were used. Undoubtedly, in the absence of severe stereoelectronic misdemeanors, the $Ph_2ECH_2CH_2S(O)Me$ ligands preferred to form metal chelates with Pd(II) and Pt(II) via their "soft" donor atoms.

Both the palladium(II) and platinum(II) complexes were stable in the solid state and in solution. We were therefore surprised to find that attempts to prepare the nickel(II) derivatives were unsuccessful. Instead, the reactions between the E–S(O) ligands and $[Ni(H_2O)_6]Cl_2$ in methanol gave the corresponding methylthio-substituted arsine and phosphine oxides in quantitative yields. The isolation of these rearranged products suggests that the ligand–nickel interactions are kinetically unstable as the halide-catalyzed isomerization involved only uncoordinated tertiary phosphines and arsines. A similar facile ligand redistribution process has been reported for the nickel(II) complexes containing 2 equiv of deprotonated (±)-(2-mercaptoethyl)methylphenylarsine and its phosphorus analogue.[19] When treated with $[Ni(H_2O)_6](NO_3)_2$, however, only the free ligands were recovered quantitatively.

Experimental Section

All reactions involving air-sensitive compounds were carried out under a positive pressure of purified nitrogen. Routine NMRs were recorded at 25 °C on Bruker ACF 300 and Bruker AMX 500 spectrometers. IR spectra were obtained with a Shimadzu IR-470 instrument. Optical rotations were measured on the specified solutions in a 1-dm cell at 22 °C with a Perkin-Elmer Model 241 polarimeter. Melting points were determined on a Electrothermal IA 9200 apparatus. Mass spectra were recorded on a Micromass 7035E spectrometer. Molar conductivities were measured with a Horiba ES-12 conductivity meter for 10^{-3} M solutions of the complexes at 25 °C. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry.

Bis(μ-chloro)bis[(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*]dipalladium(II) dichloromethane solvate,[20] and (±)-1-chloro-2-(methylthio)ethane[21] were prepared as previously described; (±)-1-chloro-2-(methylsulfinyl)ethane[22] was prepared by a modified literature method.

(±)-1-Chloro-2-(methylsulfinyl)ethane. A solution of sodium metaperiodate (77.3 g) in water (720 mL) was added slowly to 1-chloro-2-(methylthio)ethane (40.0 g) in methanol (800 mL) at 0 °C. After 12 h, sodium iodate was removed by filtration and the filtrate was concentrated under vacuum. The product was extracted into dichloromethane and isolated as a colorless liquid by distillation after the solution had been dried ($MgSO_4$): bp 70–72 °C (0.2 mmHg); yield 34.3 g (75%); IR (neat, cm^{-1}) 512, 625, 660, 690, 735, 850, 942, 970, 1035 (S=O), 1123, 1292, 1405, 1640, 2900, 2960, 3000; ^{1}H NMR ($CDCl_3$) δ 2.68 (s, 3H, SMe), 3.09–3.14 (m, 2H, SCH_2), 3.87–4.02 (m, 2H, CH_2Cl); ^{13}C NMR ($CDCl_3$) δ 36.88 (SMe), 38.79 (CH_2Cl), 56.73 (SCH_2); MS, *m*/*z* 126 (M^+), 63 (100), 27 (68). Anal. Calcd for C_3H_7ClOS: C, 28.5; H, 5.6. Found: C, 28.5; H, 5.7.

(±)-[2-(Methylsulfinyl)ethyl]diphenylarsine ((±)-1).[9] A solution of diphenylarsine (24.4 g) in dried tetrahydrofuran (250 mL) was cooled to –78 °C and then treated with 1.6 M *n*-butyllithium (66.2 mL), followed by (±)-1-chloro-2-(methylsulfinyl)ethane (13.4 g) in tetrahydrofuran (50 mL). The reaction mixture was 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 (100 mL) was added to the residue. The product was extracted into dichloromethane and isolated as a white

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solid via column chromatography (silica gel 60 and a 4:1 ethyl acetate/hexane as eluent). The white solid was subsequently recrystallized as white needles from ethyl acetate by addition of *n*-hexane: mp 97–98 °C; yield 27.5 g (81%); IR (KBr, cm^{-1}) 458, 480, 610, 685, 695, 740, 880, 935, 950, 997, 1030 (S=O), 1065, 1096, 1160, 1260, 1300, 1320, 1410, 1428, 1470, 1570, 2900, 3050; ^1H NMR ($CDCl_3$) δ 2.23–2.48 (m, 2H, $AsCH_2$), 2.50 (s, 3H, SMe), 2.71–2.80 (m, 2H, CH_2S), 7.32–7.45 (m, 10H, aromatics); ^{13}C NMR ($CDCl_3$) δ 18.85 (s, $AsCH_2$), 38.04 (s, SMe), 51.30 (s, CH_2S), 128.87 (s), 132.9 (s), 138.95 (s), 139.00 (s) (aromatics); MS, *m/z* 320 (M^+). Anal. Calcd for $C_{15}H_{17}AsOS$: C, 56.2; H, 5.4. Found: C, 56.2; H, 5.4.

(±)-[2-(Methylsulfinyl)ethyl]diphenylphosphine ((±)-2).[9] The ligand was prepared as described above using diphenylphosphine as starting material, white needles from dichloromethane/*n*-hexane: mp 106–107 °C; yield 80%; IR (KBr, cm^{-1}) 424, 468, 512, 664, 697, 730, 746, 759, 900, 935, 951, 997, 1031 (S=O), 1070, 1100, 1110, 1138, 1164, 1181, 1267, 1307, 1420, 1468, 1574, 2900, 3045; ^1H NMR ($CDCl_3$) δ 2.36–2.60 (m, 2H, PCH_2), 2.53 (s, 3H, SMe), 2.68–2.76 (m, 2H, SCH_2), 7.34–7.75 (m, 10H, aromatics); ^{13}C NMR ($CDCl_3$) δ 20.41 (d, $^2J_{PC}$ = 16.1 Hz, CH_2S), 38.28 (s, SMe), 50.57 (d $^1J_{PC}$ = 18.1 Hz, PCH_2), 129.14 (s), 128.72 (d, J_{PC} = 6.5 Hz), 132.68 (d, J_{PC} = 18.9 Hz), 132.70 (d, J_{PC} = 18.9 Hz), 136.95 (d, J_{PC} = 12.2 Hz), 137.04 (d, J_{PC} = 12.2 Hz) (aromatics); ^{31}P NMR ($CDCl_3$) δ −16.2 (s); MS, *m/z* 276 (M^+). Anal. Calcd for $C_{15}H_{17}OPS$: C, 65.2; H, 6.2. Found: C, 65.3; H, 6.1.

Rearrangement of (±)-1: Isolation of [2-(Methylthio)ethyl]diphenylarsine Oxide. A solution of (±)-**1** (200 mg) in dichloromethane (10 mL) was treated with iodine (160 mg) for 24 h. Aqueous sodium thiosulfate was then added to remove the iodine. The arsine oxide was isolated as hygroscopic white crystals from dichloromethane/ether: mp 104–106 °C; yield 150 mg (75%); ^1H NMR ($CDCl_3$) δ 2.10 (s, 3H, SMe), 2.50–2.86 (m, 4H, CH_2CH_2), 7.31–7.84 (m, 10H, aromatics); ^{13}C NMR ($CDCl_3$) δ 15.43 (s, SMe), 27.06 (s, CH_2S), 30.27 (s, $AsCH_2$), 129.53 (s), 130.57 (s), 132.24 (s), 132.96 (s) (aromatics).

Rearrangement of (±)-2: Isolation of [2-(Methylthio)ethyl]diphenylphosphine Oxide. Similar treatment of (±)-**2** (500 mg) in dichloromethane (20 mL) with iodine (460 mg) for 15 min yielded the phosphine oxide as white crystals from dichloromethane/ether: mp 93–94 °C; yield 480 mg (96%); IR (KBr, cm^{-1}) 421, 509, 533, 694, 721, 738, 788, 886, 974, 994, 1007, 1026, 1070, 1100, 1120, 1172 (P=O), 1268, 1288, 1313, 1429, 1478, 1582, 2910, 3050; ^1H NMR ($CDCl_3$) δ 2.10 (s, 3H, SMe), 2.54–2.60 (m, 2H, PCH_2), 2.72–2.96 (m, 2H, SCH_2), 7.27–7.76 (m, 10H, aromatics); ^{13}C NMR ($CDCl_3$) δ 15.54 (s, SMe), 26.38 (s, CH_2S), 30.54 (d, $^1J_{PC}$ = 66.7 Hz, PCH_2), 128.81 (d, J_{PC} = 11.47 Hz), 130.78 (d, J_{PC} = 8.9 Hz), 131.98 (s), 132.57 (d, J_{PC} = 98.9 Hz) (aromatics); ^{31}P NMR ($CDCl_3$) δ 30.55; MS, *m/z* 276 (M^+). Anal. Calcd for $C_{15}H_{17}OPS$: C, 65.2; H, 6.2. Found: C, 64.9; H, 6.2.

Thermolysis of (±)-1: Isolation of Diphenylvinylarsine. A pure sample of (±)-**1** (1.5 g) was placed in a microdistillation apparatus and heated up gradually in an oil bath under high vacuum. At 110 °C, the white solid melted into a pale yellow liquid, and diphenylvinylarsine was then collected as an offensive-smelling, colorless liquid between 170 and 190 °C: bp 105–106 °C (0.1 mmHg); yield 1.1 g (92%); IR (neat, cm^{-1}) 470, 558, 585, 685, 695, 735, 942, 981, 998, 1022, 1075, 1252, 1304, 1380, 1425, 1477, 1580, 3000, 3010; ^1H NMR ($CDCl_3$) δ 5.70 (d of d, 1H, $^3J_{HH}$(*trans*) = 18.6 Hz, $^2J_{HH}$ = 1.6 Hz, C*H*H′), 6.06 (d of d, 1H, $^3J_{HH}$ = 11.3 Hz, $^2J_{HH}$ = 1.6 Hz, CH*H*′), 6.80 (d of d, 1H, $^3J_{HH}$(*trans*) = 18.6 Hz, $^2J_{HH}$(*cis*) = 11.3 Hz, AsCH), 7.27–7.43 (m, 10H, aromatics); ^{13}C NMR ($CDCl_3$) δ 128.47 (*p*-C), 128.75 (*m*-C), 129.87 (CH_2), 133.29 (*o*-C), 139.37 (AsC), 140.34 (C-1); MS, *m/z* 256 (M^+). Anal. Calcd for $C_{14}H_{13}As$: C, 65.6; H, 5.1. Found: C, 65.6; H, 5.2.

Thermolysis of (±)-2: Isolation of Diphenylvinylphosphine. A sample of (±)-**2** (2.5 g) was heated in a similar manner as described above, whereupon diphenylvinylphosphine was obtained as an offensive-smelling colorless liquid: bp 104–106 °C (0.2 mmHg); yield 1.0 g (52%); ^1H and ^{31}P NMR($CDCl_3$), identical to those reported previously.[23]

Bis(acetonitrile)[(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*]-palladium(II) Perchlorate ((*S*)-3). The perchlorate was prepared from bis(μ-chloro)bis[(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*]-dipalladium(II) dichloromethane solvate (20.9 g) in dichloromethane (600 mL) and $AgClO_4$ (11.3 g) in acetonitrile (60 mL) over 15 min. Silver chloride formed was filtered off and the filtrate was evaporated to obtain a yellow glass that was subsequently recrystallized from acetonitrile–diethyl ether as pale yellow needles (yield 23.6 g, 89%): mp 158–160 °C; $[\alpha]_D$ +104.4° (*c* 1.0, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.86 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.15 (s, 3H, NCMe), 2.48 (s, 3H, NCMe), 2.77 (s, 3H, NMe), 2.94 (s, 3H, NMe), 4.22 (q, 1H, $^3J_{HH}$ = 6.4 Hz, C*H*Me), 7.07–7.82 (m, 6H, aromatics); Λ_M 149.9 $cm^2\ \Omega^{-1}\ mol^{-1}$ (MeCN) (1:1). Anal. Calcd for $C_{18}H_{22}ClN_3O_4Pd$: C, 44.5; H, 4.6; N, 8.6. Found: C, 44.5; H, 4.5; N, 8.6.

Resolution of (±)-1: Formation and Separation of Internal Diastereomers [*SP*-4-3-(*S*),(*S*)]- and [*SP*-4-3-(*R*),(*S*)]-[1-[1-(dimethylamino)-ethyl]-2-naphthalenyl-*C,N*][2-(methylsulfinyl)ethyl]diphenylarsine-*As,O*]-palladium(II) Perchlorate. A solution of (*S*)-**3** (15.2 g) in dichloromethane (120 mL) was treated with (±)-**1** (10.1 g) in dichloromethane (30 mL) at room temperature for 3 h. Removal of solvent yielded a mixture of [*S*-(*R**,*R**)]-**5** and [*R*-(*R**,*S**)]-**5** as a light yellowish green glass (yield 15.1 g, 98%): $[\alpha]_D$ −17.8° (*c* 1.0, CH_2Cl_2). Repeated dissolution of the residue in acetone followed by addition of diethyl ether yielded pure [*S*-(*R**,*R**)]-**5** as light yellowish green needles (overall yield 6.5 g, 84%): mp 202–203 °C (dec); $[\alpha]_D$ −13.6° (*c* 1.0, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 2.01 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.78–2.91 (m, 1H, AsC*H*H′), 2.81 (s, 3H, NMe), 2.90 (s, 3H, NMe), 3.01 (s, 3H, SMe), 2.97–3.08 (m, 1H, AsCH*H*′), 3.20 (AA′BB′ q of d, 1H, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 2.5 Hz, SC*H*H′), 3.80 (AA′BB′ q of d, 1H, $^2J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 2.7 Hz, SCH*H*′), 4.43 (q, 1H, $^3J_{HH}$ = 6.4 Hz, C*H*Me), 6.57–7.95 (m, 16H, aromatics); Λ_M 140.1 $cm^2\ \Omega^{-1}\ mol^{-1}$ (MeCN) (1:1). Anal. Calcd for $C_{29}H_{33}AsClNO_5PdS$: C, 48.1; H, 4.6; N, 1.9. Found: C, 48.1; H, 4.6; N, 1.7. The more soluble diastereomer [*R*-(*R**,*S**)]-**5** was thus obtained in ca. 90% optical purity from the collected fractions of the filtrate as orange clusters of microcrystals via recrystallization using acetone–ether: mp 190–191 °C (dec); $[\alpha]_D$ −21.8° (*c* 1.0, CH_2Cl_2); overall yield 5.4 g (70%); ^1H NMR ($CDCl_3$) δ 2.00 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.75–2.92 (m, 2H, $AsCH_2$), 2.78 (s, 3H, NMe), 2.90 (s, 3H, NMe), 3.06 (s, 3H, SMe), 3.33 (AA′BB′ q of d, 1H, $^2J_{HH}$ = 14.5 Hz, $^3J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 3.1 Hz, SC*H*H′), 3.65 (AA′BB′ q of d, 1H, $^2J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 3.5 Hz, SCH*H*′), 4.43 (q, 1H, $^3J_{HH}$ = 6.4 Hz, C*H*Me), 6.56–7.85 (m, 16H, aromatics); Λ_M 141.0 $cm^2\ \Omega^{-1}\ mol^{-1}$ (MeCN) (1:1). Anal. Calcd for $C_{29}H_{33}AsClNO_5PdS$: C, 48.1; H, 4.6; N, 1.9. Found: C, 48.2; H, 4.5; N, 1.9.

(*S*)-(+)-[2-(Methylsulfinyl)ethyl]diphenylarsine ((*S*)-1). A solution of [*S*-(*R**,*R**)]-**5** (1.2 g) in dichloromethane (20 mL) was stirred for $^1/_2$ h in the presence of a solution of excess potassium cyanide (0.5 g) in water (15 mL). The colorless organic layer, after repeated washing with water, 1 M H_2SO_4 (to remove the amine) and water again, was subsequently dried ($MgSO_4$) and then subjected to column chromatography (silica gel 60 and ethyl acetate as eluent), affording a colorless liquid which crystallized upon standing as a white solid (yield 0.5 g, 91%): mp 74–75 °C; $[\alpha]_D$ +56.5° (*c* 1.0, CH_2Cl_2); ^1H NMR ($CDCl_3$) was identical with that of the corresponding racemic material. The optical purity of (*S*)-**1** was established via repreparation of [*S*-(*R**,*R**)]-**5** from (*S*)-**3** and the liberated tertiary arsine sulfoxide. The ^1H NMR spectrum and optical rotation of the reprepared compound were identical with those of the pure separated diastereomer.

(*R*)-(−)-[2-(Methylsulfinyl)ethyl]diphenylarsine ((*R*)-1). By displacement from [*R*-(*R**,*S**)]-**5** with potassium cyanide as described above, the liberated ligand had $[\alpha]_D$ −53.7° (*c* 1.0, CH_2Cl_2). Treatment with a calculated amount of (*R*)-**3** gave, after a single recrystallization, pure [*R*-(*R**,*R**)]-**5** ($[\alpha]_D$ +13.1° (*c* 1.0, CH_2Cl_2)) with a melting point and ^1H NMR spectrum similar to that of [*S*-(*R**,*R**)]-**5**. Another subjection to potassium cyanide afforded pure (*R*)-**1** white crystals in 93% yield: mp 75–76 °C; $[\alpha]_D$ −56.7° (*c* 1.0, CH_2Cl_2); ^1H NMR ($CDCl_3$) was similar with that of its enantiomer.

Resolution of (±)-2: Formation and Separation of Internal Diastereomers [*SP*-4-3-(*S*),(*S*)]- and [*SP*-4-3-(*R*),(*S*)]-[1-[1-(dimethylamino)-ethyl]-2-naphthalenyl-*C,N*][2-(methylsulfinyl)ethyl]diphenylphosphine-*O,P*]palladium(II) Perchlorate. A solution of (*S*)-**3** (17.7 g) in dichloromethane (150 mL) was treated with (±)-**2** (10.1 g) in dichloromethane (30 mL) at room temperature for 3 h. Removal of solvent yielded a mixture of [*S*-(*R**,*R**)]-**6** and [*R*-(*R**,*S**)]-**6** as a light yellowish green glass (24.0 g, 97%): $[\alpha]_D$ −27.0° (*c* 1.0, CH_2Cl_2). Repeated dissolution of the residue in acetone followed by addition of diethyl ether yielded pure [*S*-(*R**,*R**)]-**6** as pale green needles (overall yield 10.2 g, 82%): mp 205–206 °C (dec); $[\alpha]_D$ −16.1° (*c* 1.0, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.99 (d, 3H, $^3J_{HH}$ = 6.4 Hz, CH*Me*), 2.80–3.05 (m, 3H, PCH_2 and SC*H*H′), 2.84 (s, 6H, 2NMe), 3.03 (s, 3H, SMe), 3.66–3.84 (m, 1H, SCH*H*′), 4.45 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.2 Hz, C*H*Me), 6.48–8.14 (m, 16H, aromatics); ^{31}P NMR ($CDCl_3$) δ 31.61 (br s); Λ_M 141.2 $cm^2\ \Omega^{-1}$

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mol^{-1} (MeCN) (1:1). Anal. Calcd for $C_{29}H_{33}ClNO_5PPdS$: C, 51.2; H, 4.9; N, 2.1. Found: C, 51.3; H, 4.9; N, 2.1. The more soluble diastereomer [*R*-(*R**,*S**)]-**6** was recrystallized as orange clusters of microcrystals in ca. 85% optical purity using acetone–ether: mp 192–193 °C (dec); $[\alpha]_D$ −50.0° (*c* 1.0, CH_2Cl_2); combined yield 9.3 g (75%); ^1H NMR ($CDCl_3$) δ 1.97 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CH*Me*), 2.76–3.02 (m, 2H, PCH_2), 2.78 (d, 3H, $^4J_{PH}$ = 3.2 Hz, NMe), 2.83 (s, 3H, NMe), 3.12 (s, 3H, SMe), 3.33–3.43 (m, 2H, SCH_2), 4.43 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.1 Hz, C*H*Me), 6.45–8.09 (m, 16H, aromatics); ^{31}P NMR ($CDCl_3$) δ 33.23 (br s); Λ_M 141.9 $cm^2\ \Omega^{-1}\ mol^{-1}$ (MeCN) (1:1). Anal. Calcd for $C_{29}H_{33}ClNO_5PPdS$: C, 51.2; H, 4.9; N, 2.1. Found: C, 51.2; H, 4.8; N, 2.0.

(*S*)-(+)-[2-(Methylsulfinyl)ethyl]diphenylphosphine ((*S*)-2). A solution of [*S*-(*R**,*R**)]-**6** (2.7 g) in dichloromethane (25 mL) was treated with 1,2-bis(diphenylphosphino)ethane (1.6 g) in the same solvent (20 mL) for 15 min. Ethyl acetate was then added intermittently to crystallize out (*S*)-**9**. The filtrate was subjected to column chromatography (silica gel 60), affording (*S*)-**2** as a white solid (yield 1.0 g, 91%) upon standing: mp 85–86 °C; $[\alpha]_D$ +67.5° (*c* 1.0, CH_2Cl_2); $[\alpha]_D$ +74.8° (*c* 1.0, MeCN); ^1H NMR spectrum was similar with that of the corresponding racemic material. Pure [*S*-(*R**,*R**)]-**6** was reprepared from (*S*)-**3** and (*S*)-**2**, thus verifying the optical purity of the latter.

[(*S*)-1-[1-(Dimethylamino)ethyl]-2-naphthalenyl-*C,N*][1,2-ethanediylbis(diphenylphosphine)-*P,P'*]palladium(II) Perchlorate ((*S*)-9). The complex was isolated as white needles (2.8 g, yield 88%); mp 199–200 °C; $[\alpha]_D$ +86.1° (*c* 1.0, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 1.95 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 2.06–2.28 (m, 2H, PCH_2), 2.48–2.93 (m, 2H, PCH_2), 2.62 (s, 6H, 2NMe), 4.55 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.1 Hz, C*H*Me), 6.85–8.13 (m, 26H, aromatics); ^{31}P NMR ($CDCl_3$) δ 41.3 (d, $^2J_{PP}$ = 25.4 Hz), 60.5 (d, $^2J_{PP}$ = 25.9 Hz); Λ_M 139.7 $cm^2\ \Omega^{-1}\ mol^{-1}$ (MeCN) (1:1). Anal. Calcd for $C_{40}H_{40}ClNO_4P_2Pd$: C, 59.9; H, 5.0; N, 1.8. Found: C, 59.7; H, 5.0; N, 1.7.

(*R*)-(−)-[2-(Methylsulfinyl)ethyl]diphenylphosphine ((*R*)-2). The displaced ligand from [*R*-(*R**,*S**)]-**6** by the procedure described above had $[\alpha]_D$ −54.9° (*c* 1.0, CH_2Cl_2). Subsequent treatment with (*R*)-**3**, followed by two recrystallizations, yielded pure [*R*-(*R**,*R**)]-**6** of $[\alpha]_D$ +13.9° (*c* 1.0, CH_2Cl_2). A final subjection to 1,2-bis(diphenylphosphino)ethane afforded pure (*R*)-**2** as a white solid in 89% yield: mp 84–85.5 °C; $[\alpha]_D$ −67.2° (*c* 1.0, CH_2Cl_2). ^1H NMR ($CDCl_3$) was identical with its enantiomer.

Attempted Resolution of (±)-2: Formation and Separation of Internal Diastereomers [*SP*-4-4-(*S*),(*S*)]- and [*SP*-4-4-(*R*),(*S*)]-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C,N*][[2-(methylsulfinyl)ethyl]diphenylphosphine-*P*]palladium(II). A solution of (*S*)-**4**·CH_2Cl_2 (6.9 g) in dichloromethane (200 mL) was treated with a solution of (±)-**2** (5.0 g) in the same solvent. Removal of solvent after 3 h of stirring yielded a mixture of [*S*-(*R**,*R**)]-**7** and [*R*-(*R**,*S**)]-**7** as a yellow glass (5.5 g, 99% yield): mp 176–178 °C (dec); $[\alpha]_D$ +22.5° (*c* 1.0, CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 2.04 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CH*Me*), 2.04 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CH*Me*), 2.55–2.90 (m, 4H, $2PCH_2$), 2.58 (s, 3H, SMe), 2.59 (s, 3H, SMe), 2.73 (s, 6H, 2NMe), 2.96 (d, 3H, $^4J_{PH}$ = 4.3 Hz, NMe), 2.97 (d, 3H, $^4J_{PH}$ = 3.7 Hz, NMe), 3.11–3.21 (m, 2H, 2SC*H*H'), 3.25–3.33 (m, 1H, SCH*H'*), 3.50–3.57 (m, 1H, SCH*H'*), 4.37 (qn, 2H, $^3J_{HH}$ = $^4J_{PH}$ = 6.3 Hz, 2C*H*Me), 6.62–8.17 (m, 32H, aromatics); ^{31}P NMR ($CDCl_3$) δ 34.75 (s), 34.98 (s). Anal. Calcd for $C_{29}H_{33}ClNOPPdS$: C, 56.5; H, 5.4; N, 2.3. Found: C, 56.5; H, 5.3; N, 2.3. Reaction of **7** (100 mg) in dichloromethane (15 mL) and $AgClO_4$ (33 mg) in acetonitrile (5 mL) over 1 h produced **6** as a mixture of [*S*-(*R**,*R**)]- and [*R*-(*R**,*S**)]-diastereomers in 87% yield (96 mg).

Dichloro[(*R*)-[2-(methylsulfinyl)ethyl]diphenylarsine-*As,S*]palladium-(II).[24] A solution of $(CH_3CN)_2PdCl_2$ (80 mg) in acetonitrile (20 mL) was treated with (*S*)-**1** (100 mg) in the same solvent (10 mL) at room temperature for 2 h. After removal of solvent under reduced pressure, the dark yellow precipitate was recrystallized from acetonitrile/ether yielding yellow needles: mp 212.5–213.5 °C (dec); $[\alpha]_D$ −119.4° (*c* 1.0, DMSO); yield 135 mg (87%); IR (KBr, cm^{-1}) 1129 (S=O); ^1H NMR (CD_3CN) δ 2.74 (AA'BB' q of d, 1H, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 5.6 Hz, AsC*H*H'), 2.94 (AA'BB' q of d, 1H, $^2J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 5.7 Hz, $^3J_{HH}$ = 3.7 Hz, AsCH*H'*), 3.38 (AA'BB' q of d, 1H, $^2J_{HH}$ = 13.4 Hz, $^3J_{HH}$ = 13.2 Hz, $^3J_{HH}$ = 5.7 Hz, SC*H*H'), 3.53 (s, 3H, SMe), 3.90 (AA'BB' q of d, 1H, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 3.7 Hz, SCH*H'*), 7.54–7.89 (m, 10H, aromatics). Anal. Calcd for $C_{15}H_{17}AsCl_2OPdS$: C, 36.2; H, 3.5. Found: C, 36.3; H, 3.5.

Dichloro[(*R*)-[2-(methylsulfinyl)ethyl]diphenylphosphine-*P,S*]palladium-(II). The compound was obtained similarly using (*S*)-**2** (100 mg) as ligand, yellow prisms from acetonitrile–ether: mp 214–215 °C (dec); $[\alpha]_D$ −108.6° (*c* 1.0, DMSO); yield 180 mg (91%); IR (KBr, cm^{-1}) 1133 (S=O); ^1H NMR (CD_3CN) δ 2.75–2.96 (m, 2H, PCH_2), 3.38–3.65 (m, 2H, SCH_2), 3.53 (s, 3H, SMe), 7.56–7.93 (m, 10H, aromatics); ^{31}P NMR (CD_3CN) δ 70.46 (s). Anal. Calcd for $C_{15}H_{17}Cl_2OPPdS$: C, 39.7; H, 3.8. Found: C, 39.4; H, 3.7.

Dichloro[(*R*)-[2-(methylsulfinyl)ethyl]diphenylarsine-*As,S*]platinum-(II). A solution of $(CH_3CN)_2PtCl_2$ (109 mg) in acetonitrile (40 mL) was treated with (*S*)-**1** (100 mg) in acetonitrile (10 mL). After stirring for 2 h at room temperature, the solvent was removed under reduced pressure. The white precipitate was then recrystallized from acetonitrile–ether: white prisms; mp 238–239 °C (dec); $[\alpha]_D$ −35.6° (*c* 1.0, DMSO); yield 157 mg (86%); IR (KBr, cm^{-1}) 1142 (S=O); ^1H NMR (CD_3CN) δ 2.53–2.61 (m, 2H, $AsCH_2$), 3.27–3.38 (m, 1H, SC*H*H'), 3.60 (s, 3H, $^3J_{Pt-H}$ = 20.7 Hz, SMe), 3.71–3.79 (m, 1H, SCH*H'*), 7.53–7.85 (m, 10H, aromatics). Anal. Calcd for $C_{15}H_{17}AsCl_2OPtS$: C, 30.7; H, 2.9. Found: C, 30.8; H, 2.9.

Dichloro[(*R*)-[2-(methylsulfinyl)ethyl]diphenylphosphine-*P,S*]platinum-(II). The compound was prepared similarly from (*S*)-**2** (150 mg): white prisms; mp 230–231 °C (dec); yield 264 mg (88%); $[\alpha]_D$ −44.0° (*c* 1.0, DMSO); IR (KBr, cm^{-1}) 1140 (S=O); ^1H NMR (CD_3CN) δ 2.52–2.78 (m, 2H, PCH_2), 3.35–3.70 (m, 2H, SCH_2), 3.61 (s, 3H, $^3J_{Pt-H}$ = 22.8 Hz, SMe), 7.55–7.89 (m, 10H, aromatics); ^{31}P NMR (CD_3CN) δ 47.0 (s, $^1J_{Pt-P}$ = 3569 Hz). Anal. Calcd for $C_{15}H_{17}Cl_2OPPtS$: C, 33.2; H, 3.2. Found: C, 33.2; H, 3.1.

Structural Analysis. Cell dimensions of [Pd{(*S*)-CH_3CH(1-$C_{10}H_6$)-NMe_2-*C*^{2},*N*}(*S*)-{$Ph_2PCH_2CH_2S$(O)Me-*O,P*}]ClO_4 were determined by least-squares calculations from 48 reflections at $2\theta > 15°$. The reflections were obtained by an automated random search routine at room temperature on a Siemens R3m/V four-circle diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). A pale yellow crystal of approximate dimensions 0.15 × 0.20 × 0.40 mm was used. Data were collected for $3.0° \le 2\theta \le 50°$ and index range $0 \le h \le 12$, $0 \le k \le 13$, $-32 \le l \le 32$ with a variable scan rate of 1.50–15.0° min^{-1}. Table II gives a summary of the crystallographic data. A total of 5874 reflections were collected and 5079 observed reflections [$F > 3\sigma(F)$] were used in the refinement. Intensities of three standard reflections were measured after every 97 reflection data were collected; no deterioration in the intensity was detected. Semiempirical absorption corrections were applied. The structure was solved by direct methods and non-hydrogen atoms other than Pd were located from Fourier difference maps. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at fixed distance (0.960 Å) from carbon atoms and were assigned fixed thermal parameters. A total of 703 parameters were refined. The function minimized during full-matrix least-squares refinement was $\sum w|F_o - F_c|^2$ where $w^{-1} = \sigma^2(F) + 0.0006F^2$ giving R = 0.030, R_w = 0.037, and S = 1.08. All calculations were performed on a Digital Equipment Corp. MicroVax II computer using the Siemens SHELXTL PLUS package.

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Supplementary Material Available: For (S_a,S_c)-**6** tables of crystal data, data collection, solution and refinement, final positional parameters, bond distances and angles, anisotropic thermal parameters of non-hydrogen atoms, and calculated hydrogen parameters (12 pages). Ordering information is given on any current masthead page.

(24) The apparent inversion of configuration of the sulfoxide that takes place when sulfur is coordinated to the metal is consistent with the specification of Cahn–Ingold–Prelog (CIP) sequence rules.[25]

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