Pergamon

Tetrahedron: Asymmetry Vol. 5, No. 9, pp. 1805-1814, 1994
Elsevier Science Ltd
Printed in Great Britain
0957-4166/94 $7.00+0.00

0957-4166(94)00253-3

Stereoelectronic Effects on the Chelating Properties of [2-(Methylsulfinyl)ethyl]diphenylarsine and its Phosphorus Analogue.

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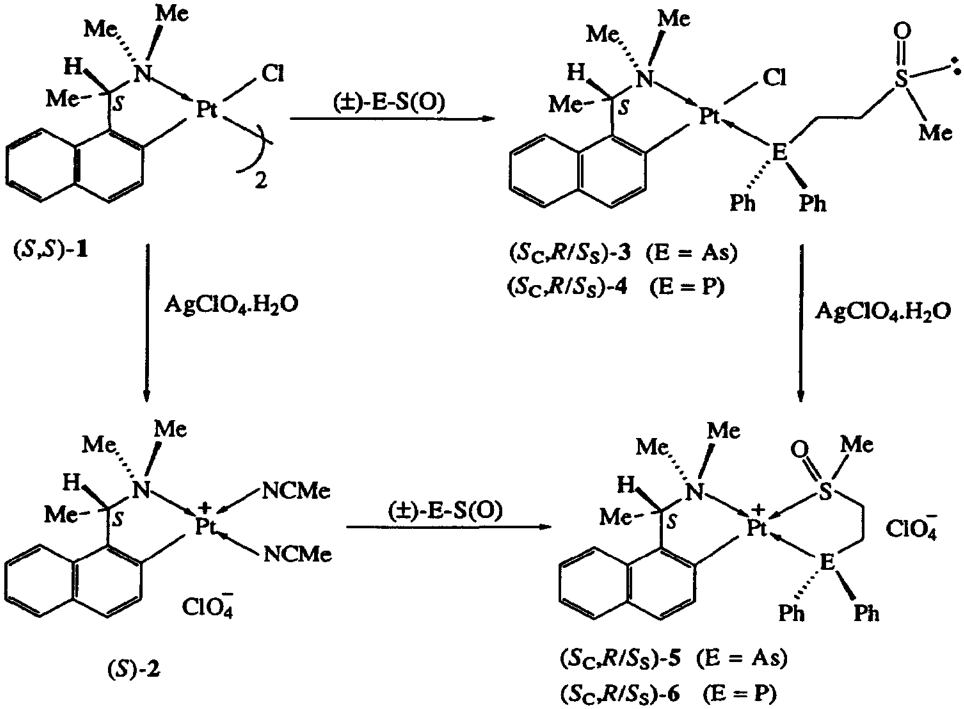
Abstract: A pair of internally diastereomeric platinum(II) complex cations containing the ortho-metalated (*S*)-(1-(dimethylamino)ethyl)naphthalene and the racemic form of the sulfinyl-substituted ligand $Ph_2ECH_2CH_2S(O)Me$ ((E-S(O), where E = As, P) has been prepared via two routes originating from (*S*)-(+)-bis(*m*-chloro)bis[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*]diplatinum(II). The crystal structure of the arsenic analogue (crystal data: triclinic, $P1$, $a = 7.950(2)$ Å, $b = 17.449(3)$ Å, $c = 21.981(4)$ Å, $\alpha = 82.67(2)°$ $\beta = 87.06(2)°$, $\gamma = 82.87(2)°$, $Z = 4$ and $R = 0.0409$) shows the ligand being coordinated to platinum(II) in both diastereomers as a bidentate chelate exclusively via arsenic and sulfur donor atoms. Proton NMR studies also indicate the retention of this As-S coordination in solution. A similar bonding mode was observed for the analogous phosphine complex. The E-S chelation appears to be governed by the electronic properties of platinum. In contrast to the previously documented palladium(II) analogues, the E-O chelation is not observed in the present series of platinum(II) compounds although there will be less severe ligand-ligand interactions if the E-S(O) ligands form six-membered chelate rings in these square-planar systems.

The study of ligand-based stereoelectronic effects in transition metal complexes containing sulfoxides is an interesting yet infrequently addressed topic. Two of the few notable representations of monodentate sulfoxide complexes come from $[Pd(R_2SO)_4]^{2+}$ complexes where steric and electronic factors interweave to produce a variety of complexes that displayed *cis-trans* isomerism and the ambidentate nature of the sulfoxide moiety,[1-3] and the $[MCl(Ph_2PCH_2CH_2PPh_2)(dmso)]^+$ (M = Pd, Pt) complexes where the sulfinyl-O coordination of the dmso ligand was brought about by the steric imposition of the diphosphine ligand.[4] In contrast, there is a dearth of such investigations for complexes with hetero-ligands incorporating a sulfoxide and a soft arsenic or phosphorus atom.[5,6] Recent complexations of the novel $Ph_2ECH_2CH_2S(O)Me$ (E = As or P, E-S(O) for short) ligands in our laboratories have nevertheless uncovered an abundant coordination chemistry that was undoubtedly influenced by stereoelectronic factors. Indeed, while the E-S(O) ligands coordinate to gold(I) in a unidentate manner through their E donors in the linear [AuCl(E-S(O))] complexes,[7] an E-S coordination mode was observed in the square-planar *cis*-$[MCl_2(E\text{-}S(O))]$ (M = Pd, Pt) complexes.[8] Interestingly, X-ray structural and solution NMR spectroscopic studies revealed an unexpected E-O coordination mode when these ligands were reacted with an optically active ortho-metalated [1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*]palladium(II) resolving unit.[9] Intrigued by this observation, we have investigated the platinum(II) analogue of the latter in an effort to gain a more intimate understanding of the subtle stereoelectronic effects operative in metal complexes containing these E-S(O) ligands.

Results and Discussion

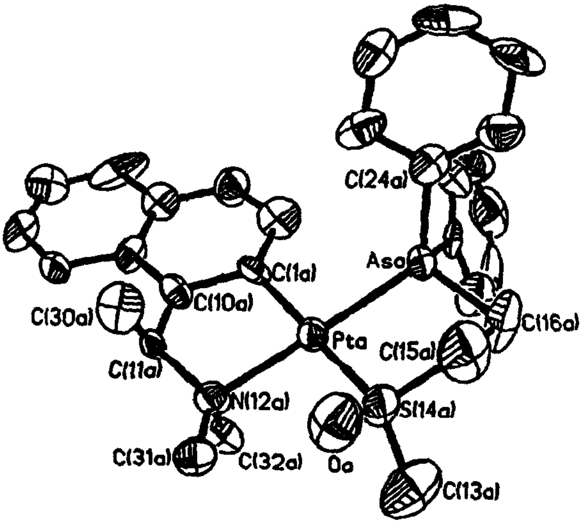
Preparation of the Complexes. The synthetic approaches for the desired diastereomeric platinum(II) complexes are outlined in Scheme I. The novel optically active starting material (*S*,*S*)-**1** has been isolated as light yellow crystals of $[\alpha]_D$ +61.5 (dichloromethane) from (*S*)-*N*,*N*-dimethyl[1-(1-naphthyl)ethyl]amine in methanol and aqueous potassium tetrachloroplatinate(II). The 300 MHz ^1H spectrum of this chloro-bridged dimer in $CDCl_3$ shows two identical set of resonances for all the non-aromatic protons, and this is attributed to the existence of symmetrical (*cis*) and anti-symmetrical (*trans*) diastereomers.[10] Metathesis of (*S*,*S*)-**1** with silver perchlorate hydrate in acetonitrile afforded the air-stable bis(acetonitrile) complex (*S*)-**2** of $[\alpha]_D$ +32.6 (dichloromethane) as pale yellow prisms in 75% yield. The two acetonitrile ligands resonate as sharp distinct singlets at δ 2.61 and 2.69 in the ^1H NMR spectrum that is indicative of their coordination to two non-equivalent positions on platinum. Treatment of (*S*)-**2** with one equiv. of the appropriate racemic E-S(O) ligand gave **5** or **6** in high yield. Alternatively, these diastereomeric salts can be prepared via a bridge-splitting reaction involving (*S*,*S*)-**1** and the sulfinyl-substituted arsine or phosphine to give the neutral complexes **3** or **4**, followed by chloride abstraction using silver perchlorate hydrate. It is pertinent to remark that no attempt was made to resolve the E-S(O) ligands using **5** and **6** in view of the costliness of the method and the recent successful resolution of these ligands on the analogous palladium(II) complexes.[9]

Scheme I



Crystal and Molecular Structures of (S_C,R_S)- and (S_C,S_S)-5. Colourless prisms of X-ray quality of the arsine analogue (S_C,R/S_S)-5 are grown by vapour diffusion of diethyl ether into a methanol solution of the complex. Crystallographic data for the complex are listed in Table 1, and selected bond distances and bond angles of the complex cations are given in Table 2. The structural analysis reveals four molecules (that

(S_C,S_S)-5



(S_C,R_S)-5

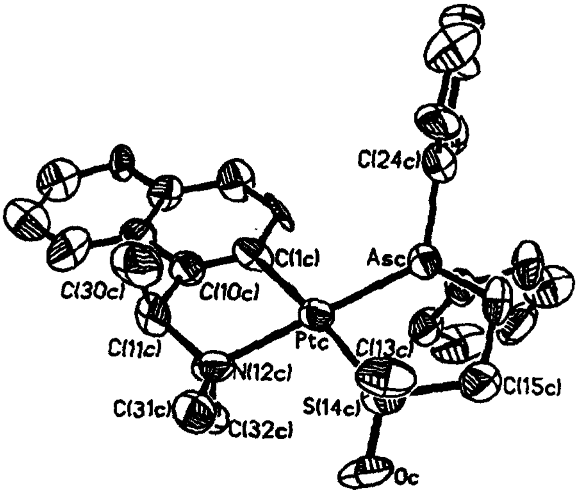


Figure 1. Molecular structures and labelling schemes for (S_C,R_S)- and (S_C,S_S)-5.

Table 1. Crystal Data for (S_C,R/S_S)-5

space group	$P1$	F(000)	1528
a, Å	7.950(2)	chem formula	$C_{29}H_{33}AsClNO_5PtS$
b, Å	17.449(3)	fw	797.0
c, Å	21.981(4)	Z	4
α, deg	82.67	abs coeff, cm^{-1}	5.970
β, deg	87.06(2)	trans coeffs	0.642-0.842
γ, deg	82.87(2)	temp, °C	25
V, Å^3	2998.9(9)	λ, Å	0.71073
D_m, g cm^{-3}	1.799	D_c, g cm^{-3}	1.765
R^a	0.0409	$R_w{}^a$	0.0455

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

are grouped into two pairs) in the unit cell. In these four molecules, the As-S(O) ligand chelates to platinum exclusively via its arsenic and sulfur donor atoms. Molecules A and D are of identical stereochemistries with the coordinated sulfur stereogenic centres of *S* absolute configuration, and differ only slightly in bond distances and angles. On the other hand, molecules B and C are also of similar structures but with the sulfur stereocentre of *R* configuration. The ortho-metalated (*S*)-naphthylamine ring in the four molecules bears the expected λ helicity as its palladium(II) counterpart.[9] However, the five-membered As-S ring adopts the δ helicity in molecules A and D (that is the (S_C,S_S)-diastereomer) and the λ conformation in molecules B and C (the (S_C,R_S)-diastereomer). Interestingly, the axial disposition of the S-Me groups in both diastereomers appears to

Table 2. Selected Bond Lengths (Å) and Angles (deg) in the four Complex Cations.

	A	B	C	D
Pt-As	2.359(1)	2.336(2)	2.345(2)	2.351(2)
Pt-C(1)	1.987(13)	1.983(15)	2.064(13)	2.071(13)
Pt-N(12)	2.139(11)	2.110(12)	2.129(11)	2.114(10)
Pt-S(14)	2.329(4)	2.311(4)	2.316(4)	2.336(5)
O-S(14)	1.526(15)	1.470(17)	1.438(14)	1.548(13)
As-Pt-C	96.4(4)	96.6(4)	98.1(4)	97.5(3)
C(1)-Pt-N(12)	80.3(5)	81.7(5)	80.3(5)	79.5(5)
N(12)-Pt-S(14)	99.3(3)	96.3(3)	94.9(3)	97.5(3)
As-Pt-S(14)	84.8(1)	85.1(1)	86.6(1)	85.7(1)

be the result of their steric interactions with the *cis*-NMe groups. Indeed, following the stereochemical argument and observations of our previous investigation of palladium(II) complexes containing the $Ph_2ECH_2CH_2SMe$ (E = As, P)[11] and $Me_2NCHMeCHMeNMe_2$ chelates,[12] the S-Me groups in molecules A and D are in sterically less favoured positions, and this seems to be justified by the significantly longer S-O distances (which at 1.526(15) and 1.548(13) Å are not within the normal 1.46-1.49 Å range for S-bonded sulfoxides[21)] and the slightly longer Pt-S bonds as compared to their B and C counterparts. Generally, the Pt-S distances in **5** are longer than the 2.21Å and the 2.193-2.237 Å range reported for S-dmso coordinated Pt-S bonds *trans* to a primary amine (NH_2)[13] and chlorine[14] respectively. The Pt-As lengths are within the 2.275-2.402 Å range encountered for the limited cases of square-planar platinum(II)-arsenic bonds in literature.[15-20]

The structural observation of the As-S chelation is consistent with the absence of the sulfinyl-O absorption[9] at *ca.* 998 cm^{-1} in the solid-state IR spectrum of **5**. Analogous behaviour in the IR spectrum is also detailed for the phosphine analogue **6**.

NMR Spectra Studies. ^1H NMR spectral studies of (S_C,*R*/S_S)-**5** in $CDCl_3$ at room temperature indicates that the platinum-sulfur bonds remain unchanged in solution. The sharp S-Me singlets at δ 3.66 and 3.69 (with indistinct satellites) are diagnostic of sulfinyl-S complexation.[8,21] The assignment of the resonances with regards to diastereomeric identities in the ^1H NMR spectrum is accomplished by comparison with the pure (S_C,S_S)-isomer (Table 3). The latter is prepared from the reaction of (*S*)-**2** with the resolved (*R*)-form[9] of the As-S(O) ligand.[22] Analogous behaviour is also ascribed to the diastereomeric mixture of **6**, where additionally, the *trans* alignment of the phosphorus to the nitrogen is inferred from the $^4J_{PH}$ coupling constant.

Table 3. Selected ^1H NMR Spectroscopic Data[a] of Sulfoxide Complexes.

Complex	δ(C-Me)	δ(N-Me)	δ(S-Me)
(S_C,*R*/S_S)-**5**	1.93 (6.2), 1.94 (6.2)	3.09, 3.13, 3.49, 3.54	3.66, 3.68
(S_C,S_S)-**5**	1.93 (6.2)	3.13, 3.54	3.68
(S_C,*R*/S_S)-**6**	1.91 (6.3), 1.92 (6.3)	3.01 (1.9), 3.06 (1.9) 3.51 (3.9), 3.63 (3.7)	3.61, 3.68
(S_C,S_S)-**6**	1.91 (6.3)	3.06 (1.9), 3.51 (3.9)	3.68

[a] Measured in $CDCl_3$ at 25°C, with chemical shifts quoted relative to Me_4Si as internal standard. Coupling constants ($^3J_{HH}$ for C-Me resonances and $^4J_{PH}$ for N-Me) in Hz are given in parentheses.

Conclusions.

The adoption of the E-O chelation in the previously studied palladium(II) analogues of **5** and **6** has been linked to the trans-withdrawing effect from the coordinated naphthalene carbon and the steric repulsion from the *cis*-NMe_2 group.[9] The present investigation of the platinum(II) complex shows conclusively the coordination mode of the sulfoxide moiety is a consequence of the relative philicity of the metal center for either oxygen or sulfur, and much less of the steric factor since the atomic radii of both palladium and platinum are very similar, and of the electronic property of the aromatic carbon. In that context, the Pd-S bonding in the solid-state and solution structures of [$PdCl_2$(E-S(O))] complexes would be attributable to the weaker trans-withdrawing effects of the chloride and the absence of steric interaction being relatively more influential than the affinity of palladium for oxygen.[8] Noteworthily, a previous study has highlighted that the transition from O-dmso in the palladium(II) complexes containing 1,10-phenanthroline or 2,2'-bipyridyl bidentates to S-bonded dmso in the platinum(II) derivatives was not due to steric factors but rather the higher electron-withdrawing ability of palladium.[24]

Acknowledgement This work has been supported by the National University of Singapore (RP 900604).

Experimental

General. Routine NMR spectra were recorded at 25°C on a Bruker ACF 300 or Bruker AMX 500 spectrometer. IR spectra were obtained with a Shimadzu IR-470 spectrometer. Optical rotations were measured on the specified solutions in a 1-dm cell at 25°C with a Perkin Elmer 241 polarimeter. Melting points were determined on an Electrothermal IA 9200 apparatus. Molar conductivites were acquired with a Horiba ES-12 conductivity meter for 10^{-3} M solutions of the complexes at 25°C. Elemental microanalyses were carried out by the Microanalytical Laboratory of the Department of Chemistry using a Perkin Elmer 2400 analyser.

Materials. Potassium tetrachloroplatinate(II) and silver perchlorate hydrate were purchased from Aldrich Chemical Company. The racemic and optically active forms of the $Ph_2ECH_2CH_2S(O)Me$ (E-S(O)) ligands were available as previously described.[8,9]

Bis(μ-chloro)bis[(*S*)-1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*]diplatinum(II) dichloromethane solvate ((*S*,*S*)-1).[25] (*S*)-*N*,*N*-dimethyl[1-(1-naphthyl)ethyl]amine (3.9 g, 19.7 mmol) in methanol (40 mL) was first added to a stirring solution of potassium tetrachloroplatinate(II) (4.1 g, 9.88 mmol) in water (50 mL). After 30 h, the mixture was filtered and the brown residual solid was extracted into boiling benzene. This was followed by a further filtration after which the solvent was evaporated under reduced pressure. Chromatography of the resulting brown residue through a silica gel 60 column with chloroform as eluent, and subsequent crystallisation of the crude product from dichloromethane-*n*-hexane afforded the complex as light yellow crystals (1.1 g, 26%), m.p. 222-223°C (dec.); $[\alpha]_D^{25}$ +61.5 (*c*, 1.0 in CH_2Cl_2); ^1H NMR (300 MHz, $CDCl_3$) δ 1.80 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CH*Me*), 1.81 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 2.91 (s, 3H, NMe), 2.97 (s, 3H, NMe), 3.08 (s, 3H, NMe), 3.11 (s, 3H, NMe), 4.21 (q, 1H, $^3J_{HH}$ = 6.3 Hz, C*H*Me), 4.22 (q, 1H, $^3J_{HH}$ = 6.3 Hz, C*H*Me), 5.30 (s, 2H, CH_2Cl_2), 7.29-7.80 (m, 12H, aromatics). Found: C, 37.1; H, 3.5; N, 3.0. $C_{28}H_{32}Cl_2N_2Pt_2.CH_2Cl_2$ requires C, 37.0; H, 3.6; N, 3.0.

[*SP*-4-3-(*S*)]-Bis(acetonitrile)[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*]-platinum(II) perchlorate ((*S*)-2). The perchlorate complex was prepared from the diplatinum(II) dimer (*S*,*S*)-**1**.CH_2Cl_2 (570 mg, 0.60 mmol) in dichloromethane (5 mL) and silver perchlorate hydrate (273 mg, 1.20 mmol) in acetonitrile (2 mL) over 1 h in the dark. Silver chloride which formed was filtered off and the filtrate was evaporated to obtain a yellow precipitate that was crystallised from acetonitrile-diethyl ether as pale yellow prisms in 75% yield (522 mg), m.p. >300°C; $[\alpha]_D^{25}$ +32.6 (*c*, 1.0 in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.76 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CH*Me*), 2.61 (s, 3H, NCMe), 2.69 (s, 3H, NCMe), 2.99 (s, 3H, NMe), 3.09 (s, 3H, NMe), 4.40 (q, 1H, $^3J_{HH}$ = 6.3 Hz, C*H*Me), 7.17-7.82 (m, 6H, aromatics); Λ_M (CH_3CN) 151.0 $cm^2\Omega^{-1}mol^{-1}$ (1:1). Found: C, 37.7; H, 3.8; N, 7.3. $C_{18}H_{22}ClN_3Pt$ requires C, 37.6; H, 3.9; N, 7.3.

[*SP*-4-3-(*R*),(*S*)]- and [SP-4-3-(*S*),(*S*)]-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*][[2-(methylsulfinyl)ethyl]diphenylarsine-*As*]platinum(II) ((*S*$_C$,*R*/*S*$_S$)-3). A solution of (*S*,*S*)-1.CH_2Cl_2 (150 mg, 0.16 mmol) in dichloromethane (10 mL) was treated with a solution of (±)-$Ph_2AsCH_2CH_2S(O)Me$ (102 mg, 0.32 mmol). Removal of solvent yielded a light yellow precipitate (glass) which was subsequently crystallised from dichloromethane-*n*-hexane as pale yellow prisms (207 mg, 87%), m.p. 199-200°C (dec.); $[\alpha]_D^{25}$ -13.3 (*c*, 1.0 in CH_2Cl_2); IR (KBr) 1043 (S=O) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.95 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CH*Me*), 1.96 (3H, $^3J_{HH}$ = 6.3 Hz, CH*Me*), 2.59 (s, 6H, 2SMe), 2.68 (AA,BB' q of d, 1H, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 11.6 Hz, $^3J_{HH}$ = 4.0 Hz, AsC*H*H'), 2.74 (AA,BB' q of d, 1H, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 3.9 Hz, AsC*H*H'), 2.76 (AA,BB' q of d, 1H, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 12.9 Hz, $^3J_{HH}$ = 3.9 Hz, AsCH*H'*), 2.93 (s, 6H, 2NMe), 2.96 (AA,BB' q of d, 1H, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 12.9 Hz, $^3J_{HH}$ = 3.9 Hz, AsCH*H'*), 3.02 (AA,BB' q of d, 1H, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 11.6 Hz, $^3J_{HH}$ = 4.0 Hz, SC*H*H'), 3.08 (AA,BB' q of d, 1H, $^2J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 3.9 Hz, SC*H*H'), 3.16-3.22 (m, 1H, SCH*H'*), 3.17 (s, 3H, NMe), 3.18 (s, 3H, NMe), 3.41 (AA,BB' q of d, 1H, $^2J_{HH}$ = 13.1 Hz, $^3J_{HH}$ = 12.9 Hz, $^3J_{HH}$ = 3.9 Hz, SCH*H'*), 4.59 (q, 2H, $^3J_{HH}$ = 6.3 Hz, C*H*Me), 6.78-8.03 (m, 32H, aromatics). Found: C, 46.6; H, 4.3; N, 1.9. $C_{29}H_{33}AsClNOPtS$ requires: C, 46.5; H, 4.4; N, 1.9. Reaction of **3** (100 mg, 0.15 mmol) in dichloromethane (5 mL) and silver perchlorate hydrate (33 mg, 0.15 mmol) in acetonitrile (1 mL) over 1 h produced **5** as a mixture of [*S*-(*R**,*R**)]- and [*R*-(*R**,*S**)]-isomers in 84% yield (91 mg) after crystallization using methanol-diethyl ether.

[*SP*-4-4-(*R*),(*S*)]- and [*SP*-4-4-(*S*),(*S*)]-Chloro[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*][[2-(methylsulfinyl)ethyl]diphenylphosphine-*P*]platinum(II) ((*S*$_C$,*R*/*S*$_S$)-4). A similar procedure using (±)-$Ph_2PCH_2CH_2S(O)Me$ afforded the complex as a light yellow precipitate, m.p. 201-202°C (dec.); $[\alpha]_D^{25}$ -31.6 (*c*, 1.0 in CH_2Cl_2); IR (KBr) 1041 (S=O) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.96 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CH*Me*), 1.97 (3H, $^3J_{HH}$ = 6.3 Hz, CH*Me*), 2.54-2.89 (m, 4H, $2PCH_2$), 2.58 (s, 3H, SMe), 2.59 (s, 3H, SMe), 2.79 (s, 6H, 2NMe), 3.14-3.35 (m, 3H, 2SC*H*H' and SCH*H'*), 3.16 (d, 3H, $^4J_{PH}$ = 4.0 Hz, NMe), 3.17 (d, 3H, $^4J_{PH}$ = 4.2 Hz, NMe), 3.53-3.60 (m, 1H, SCH*H'*), 4.16 (qn, 2H, $^3J_{HH}$ = $^4J_{PH}$ = 6.3 Hz, 2C*H*Me), 6.67-8.22 (m, 32H, aromatics); ^{31}P NMR (300 MHz, $CDCl_3$) δ 14.2 (s, $^1J_{PtP}$ = 4270 Hz), 14.7 (s, $^1J_{PtP}$ = 4272 Hz). Found: C, 49.2; H, 4.8; N, 1.9. $C_{29}H_{33}ClNOPPtS$ requires C, 49.4; H, 4.7; N, 2.0. Reaction of **4** (100 mg, 0.14 mmol) in dichloromethane (6 mL) and silver perchlorate hydrate (32 mg, 0.14 mmol) in acetonitrile (2 mL) over 1 h gave [*S*-(*R**,*R**)]- and [*R*-(*R**,*S**)]-**6** in 82% yield (89 mg) after crystallisation.

[*SP*-4-3-(*R*),(*S*)]- and [*SP*-4-3-(*S*),(*S*)]-[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*][[2-(methylsulfinyl)ethyl]diphenylarsine-*As*,*S*]platinum(II) perchlorate ((*S*$_C$,*R*/*S*$_S$)-5). A solution of (*S*)-**2** (100 mg, 0.17 mmol) in dichloromethane (5 mL) was treated with (±)-$Ph_2AsCH_2CH_2S(O)Me$ (56 mg, 0.17 mmol) in the same solvent (2 mL) at room temperature for 2 h. After removal of solvent, the light yellow precipitate (glass) was crystallised from methanol-diethyl ether as pale yellow prisms in 89% yield (126 mg), m.p. 245-246°C (dec.); $[\alpha]_D^{25}$ +16.5 (*c*, 1.0 in CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$) δ 1.93 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 1.94 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 2.57 (AA'BB' q of d, 1H, $^2J_{HH}$ = 14.1, $^3J_{HH}$ = 13.7 Hz, $^3J_{HH}$ = 5.4 Hz, AsC*H*H'), 2.60 (AA'BB' q of d, 1H, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 5.5 Hz, AsC*H*H'), 2.70 (AA'BB' q of d, 1H, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 5.7 Hz, AsCH*H'*), 2.76 (AA'BB' q of d, 1H, $^2J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 1.9 Hz, AsCH*H'*), 2.86 (AA'BB' q of d, 1H, $^2J_{HH}$ = 13.9, $^3J_{HH}$ = 13.7 Hz, $^3J_{HH}$ = 5.4 Hz, SC*H*H'), 3.09 (s, 3H, NMe), 3.13 (s, 3H,NMe), 3.25 (AA'BB' q of d, 1H, $^2J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 5.5 Hz, SC*H*H'), 3.49 (s, 3H, NMe), 3.54 (s, 3H, NMe), 3.66 (s, 3H, SMe), 3.68 (s, 3H, SMe), 3.79 (AA'BB' q of d, 1H, $^2J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 5.7 Hz, SCH*H'*), 4.17 (AA'BB' q of d, 1H, $^2J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 5.5 Hz, $^3J_{HH}$ = 1.9 Hz, SCH*H'*), 4.90 (q, 1H, $^3J_{HH}$ = 6.2 Hz, C*H*Me), 4.94 (q, 1H, $^3J_{HH}$ = 6.2 Hz, C*H*Me), 7.05-7.92 (m, 32H, aromatics); Λ_M (CH_3CN) 142.4 $cm^2\Omega^{-1}mol^{-1}$ (1:1). Found: C, 42.9; H, 4.1; N, 1.8. $C_{29}H_{33}AsClNO_5PtS$ requires C, 42.8; H, 4.1; N, 1.7.

[*SP*-4-3-(*S*),(*S*)]-[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*][[2-(methylsulfinyl)ethyl]diphenylarsine-*As*,*S*]platinum(II) perchlorate ((*S*$_C$,*S*$_S$)-5). Addition of a dichloromethane solution of the optically active (*R*)-$Ph_2AsCH_2CH_2S(O)Me$ to a stirring dichloromethane solution of (*S*)-**2** at room temperature yielded the the complex as a light yellow precipitate; ^1H NMR (500 MHz, $CDCl_3$) δ 1.93 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 2.60 (AA'BB' q of d, 1H, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 5.4 Hz, AsC*H*H'), 2.71 (AA'BB' q of d, 1H, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 5.7 Hz, AsCH*H'*), 3.13 (s, 3H, NMe), 3.25 (AA'BB' q of d, 1H, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ = 8.7 Hz, $^3J_{HH}$ = 5.4 Hz, SC*H*H'), 3.54 (s, 3H, NMe), 3.68 (s, 3H, SMe), 3.79 (AA'BB' q of d, 1H, $^2J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 5.7 Hz, SCH*H'*), 4.90 (q, 1H, $^3J_{HH}$ = 6.2 Hz, C*H*Me), 7.04-7.90 (m, 16H, aromatics).

[*SP*-4-4-(*R*),(*S*)]- and [*SP*-4-4-(*S*),(*S*)]-[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*][[2-(methylsulfinyl)ethyl]diphenylphosphine-*P*,*S*]platinum(II) perchlorate ((*S*$_C$,*R*/*S*$_C$)-6). Reaction of (*S*)-**2** (100 mg, 0.17 mmol) in dichloromethane (5 mL) and (±)-$Ph_2PCH_2CH_2S(O)Me$ (48 mg, 0.17 mmol) in dichloromethane gave a light yellow precipitate (glass) that was crystallised from methanol-diethyl ether as pale yellow prisms in 85% yield (114 mg), m.p. 249-250°C (dec.); $[\alpha]_D^{25}$ +15.2 (*c*, 1.0 in CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$) δ 1.91 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CH*Me*), 1.92 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 2.43-3.30 (m, 6H, $2PCH_2$ and 2SC*H*H'), 3.01 (d, 3H, $^4J_{PH}$ = 1.9 Hz, NMe), 3.06 (d, 3H, $^4J_{PH}$ = 1.9 Hz, NMe), 3.50-3.76 (m, 1H, SCH*H'*), 3.51 (d, 3H, $^4J_{PH}$ = 3.9 Hz, NMe), 3.61 (s, 3H, SMe), 3.63 (d, 3H, $^4J_{PH}$ = 3.7 Hz, NMe), 3.68 (s, 3H, SMe), 4.07-4.27 (m, 1H, SCH*H'*), 4.90 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.3 Hz, C*H*Me), 4.96 (qn, 1H, $^3J_{HH}$ = $^4J_{PH}$ = 6.3 Hz, C*H*Me), 6.79-8.16 (m, 32H, aromatics); ^{31}P NMR (300 MHz, $CDCl_3$) δ 38.0 (s, $^1J_{PtP}$ = 3763 Hz), 38.5 (s, $^1J_{PtP}$ = 3755 Hz); Λ_M (CH_3CN) 144.5 $cm^2\Omega^{-1}mol^{-1}$ (1:1). Found, C, 45.3; H, 4.3; N, 1.9. $C_{29}H_{33}ClNO_5PPtS$ requires C, 45.3; H, 4.3; N, 1.8.

[*SP*-4-4-(*S*),(*S*)]-[1-[1-(dimethylamino)ethyl]-2-naphthalenyl-*C*,*N*][[2-(methylsulfinyl)ethyl]diphenylphosphine-*P*,*S*]platinum(II) perchlorate ((*S*$_C$,*S*$_S$)-6). The complex was likewise acquired as a pale yellow precipitate by using (*R*)-$Ph_2PCH_2CH_2S(O)Me$ as the ligand; ^1H NMR (500 MHz, $CDCl_3$) δ 1.91 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CH*Me*), 2.54-3.30 (m, 3H, PCH_2 and SC*H*H'), 3.06 (d, 3H, $^4J_{PH}$ = 1.9 Hz, NMe), 3.50-3.76 (m, 1H, SCH*H'*), 3.51 (d, 3H, $^4J_{PH}$ = 3.9 Hz, NMe), 3.61 (s, 3H, SMe), 3.68 (s, 3H, SMe), 4.91 (qn, 1H, $^3J_{HH} = {}^4J_{PH} = 6.3$ Hz, C*H*Me), 6.79-7.95 (m, 16H, aromatics); ^{31}P NMR (300 MHz, $CDCl_3$) δ 38.0 (s, $^1J_{PtP} = 3762$ Hz).

Crystal Structural Analysis. Cell dimensions of [Pt{(*S*)-MeCH(1-$C_{10}H_6$)NMe_2-*C*,*N*}(*R*/*S*)-{$Ph_2AsCH_2CH_2S(O)Me$-*As*,*S*}]ClO_4 were determined by least-squares calculations from 48 reflections at 15° < 2θ < 30°. 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 colourless prism of approximate dimensions 0.14 X 0.17 X 0.31 mm was used. Data were collected for 3.0° ≤ 2θ ≤ 50° and index range $0 \le h \le 9, -20 \le k \le 20, -26 \le l \le 26$, with a varaible scan rate of 2.00 - 19.53° min^{-1}. A total of 11368 reflections were collected and 9638 observed reflections [$F > 3\sigma(F)$] were used in the refinement. Intensities of two standard reflections were measured after every 98 reflection data were collected; no deterioration in the intensity was detected. Semi-empirical 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 not attached to phenyl or naphthyl rings were introduced at fixed distance (0.96 Å) from carbon atoms and were assigned fixed thermal parameters. Aromatic hydrogen atoms were not included in the structure refinements since their inclusion would result in a number of parameters exceeding that allowed by the programme used. A total of 1403 parameters were refined. The function minimised during full-matrix least-squares refinement was $\sum w|F_o - F_c|^2$ (where $w^{-1} = \sigma^2(F) + 0.0007F^2$) giving $R = 0.0409$, $R_w = 0.0455$ and $S = 1.12$. All calculations were performed on a Digital Equipment Corporation Micro Vax II computer using the Siemens SHELXTL PLUS package. Details of the X-ray structural analyses for the diastereomeric complexes (including atomic coordinates, anisotropic parameters and bond distances and angles) can be obtained from the corresponding authors.

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(*Received in UK* 1 *July* 1994)