Resolution of a Planar-Chiral Platinum(II) Complex. Crystal and Molecular Structure of [*SP*-4-2-*A*]-(+)$_{589}$-[PtCl(achiraphos)(*R*-PMenPh$_2$)]PF$_6$ [achiraphos = (*R**,*S**)-2,3-Bis(diphenylphosphino)butane; *R*-PMenPh$_2$ = [1(*R*)-(1α,2β,5α)]-Diphenylmenthylphosphine]

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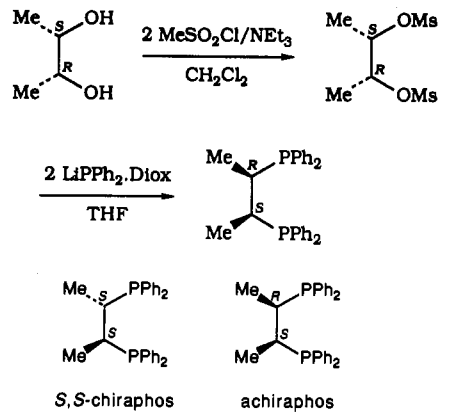
The new meso ligand (*R**,*S**)-2,3-bis(diphenylphosphino)butane (achiraphos) has been synthesized and used to prepare the prochiral square-planar meso complex [PtCl$_2$(achiraphos)]. Displacement of one or the other of the enantiotopic chlorine atoms in the complex with [1*R*-(1α,2β,5α)]-diphenylmenthylphosphine (*R*-PMenPh$_2$), and subsequent treatment of the intermediate salts with ammonium hexafluorophosphate, affords the diastereomeric complexes [*SP*-4-2-*A*]- and [*SP*-4-3-*C*]-[PtCl(achiraphos)(*R*-PMenPh$_2$)]PF$_6$, which are epimeric at planar-chiral platinum(II). The homochiral *SP*-4-2-*A* epimer, $C_{50}H_{57}ClF_6P_4Pt$, $[\alpha]_{589}$ +22.4° (*c* 0.85, acetone), crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 9.900(3) Å, b = 15.559(4) Å, c = 32.789(10) Å, Z = 4, R = 0.036, and R_w = 0.042 for 3805 unique data having $I > 3\sigma(I)$. The geometry around the platinum atom in the complex is square-planar with the *R*-PMenPh$_2$ ligand situated trans to the diphenylphosphino group attached to the *S* carbon of the achiraphos. The optically pure complex is configurationally stable in solution in the absence of chloride.

Introduction

Meso bidentates contain constitutionally equivalent ligating groups or associated stereocenters of opposite helicity.[1] Achiral (*R**,*S**)-ligands[2] of this type may be conveniently designated as C_s-bidentates. Important examples of such molecules include the diamines (*R**,*S**)-1,2-diphenyl-1,2-ethanediamine[3] and -2,3-butanediamine,[4] the bis(tertiary phosphines) (*R**,*S**)-1,2-ethanebis(methylphenylphosphine)[5] and -1,2-phenylenebis(methylphosphine),[6] and the bis(tertiary arsines) (*R**,*S**)-1,2-ethanebis(methylphenylarsine)[7] and -1,2-phenylenebis(methylphenylarsine).[8] (*R**,*S**)-Bis(tertiary phosphines and arsines), sometimes in conjunction with the corresponding *R**,*R**- or C_2-bidentates, are valuable for the synthesis of configurationally homogeneous complexes for NMR investigations of intra- and intermolecular rearrangements.[9] Because of the importance of C_2-bidentates in asymmetric synthesis,[10] in particular and of relevance to this work [*S*-(*R**,*R**)]-2,3-bis(diphenylphosphino)butane (*S*,*S*-chiraphos),[11] we have synthesized (*R**,*S**)-2,3-bis(diphenylphosphino)butane (achiraphos), an attractive C_s-bidentate for use in stereochemical analysis and for the production of planar-chiral metal complexes. The only related work on planar-chiral metal complexes appears to be the classical study of Mills and Quibell, wherein the square-planarity of a platinum(II) complex was demonstrated by the optical resolution of the planar-chiral complex (±)-(2,2-dimethyl-1,2-ethanediamine){(*R**,*S**)-1,2-diphenyl-1,2-ethanediamine)platinum(II) chloride.[12] The various aspects of the present work will be introduced in the sections that follow.

Scheme I



Results and Discussion

Synthesis. Achiraphos was prepared from (*R**,*S**)-2,3-butanediol in two steps, as indicated in Scheme I. Treatment of the crystalline bis(mesylate) with 2 equiv of lithium diphenylphosphide–1-dioxane[13] in tetrahydrofuran at 0 °C afforded the compound in 65% yield as colorless needles, mp 126–127 °C.

When reacted with [PtCl$_2$COD] (where COD = cycloocta-1,5-diene)[14] in dichloromethane, achiraphos affords in high yield the achiral meso complex [PtCl$_2$(achiraphos)]. This compound reacts with 1 equiv of silver nitrate in acetone/water to give a solution of the corresponding chloro-bridged dimer (in equilibrium

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(3) Lifschitz, I.; Bos, J. G. *Rec. Trav. Chim. Pays-Bas* **1940**, *59*, 173. Lifschitz, I.; Dijkema, K. M. *Rec. Trav. Chim. Pays-Bas* **1941**, *60*, 581. Wiliams, O. F.; Bailar, J. C. *J. Am. Chem. Soc.* **1959**, *81*, 4464.
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(10) Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581.
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(12) Mills, W. H.; Quibell, T. H. H. *J. Chem. Soc.* **1935**, 839.
(13) Issleib, K.; Tzschach, A. *Chem. Ber.* **1959**, *92*, 1118. Klein, H.-F.; Gass, M.; Zucha, U.; Eisenmann, B. *Z. Naturforsch.* **1988**, *43b*, 927.
(14) Chatt, J.; Vallarino, L. M.; Venanzi, L. M. *J. Chem. Soc.* **1957**, 2496.

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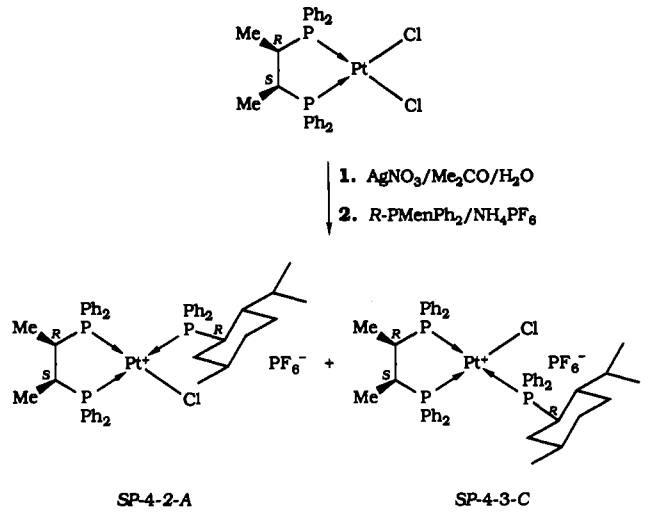
Scheme II



with (±)-[PtCl(achiraphos)(solvent)]NO_3),[15] which, after removal of silver chloride and treatment with [1(*R*)-(1α,2β,5α)]-diphenylmenthylphosphine (henceforth abbreviated to (*R*)-menthyldiphenylphosphine or *R*-PMenPh$_2$)[16] and ammonium hexafluorophosphate, yields the planar-chiral complex [PtCl(achiraphos)(*R*-PMenPh$_2$)]PF_6, which was isolated as a colorless solid and subsequently shown by $^{31}P\{^1H\}$ NMR spectroscopy to consist of a mixture of two diastereomers, epimeric at planar-chiral platinum(II), with *SP*-4-2*A*/*SP*-4-3-*C* = 2/1 (Scheme II). Recrystallization of the 2/1 mixture from hot methanol afforded a highly crystalline solid, which was found to be a 1/1 mixture of the two epimers; the mother liquor, however, when concentrated gave the kinetically stable crystalline homochiral *SP*-4-2-*A* epimer of the complex, having $[\alpha]_D$ +22.4° (*c* 0.85, acetone).

Stereochemical Notation. The stereonotation system developed for use in the Chemical Abstracts Service registry system and in the Chemical Abstracts index,[17] and endorsed by the IUPAC,[18] can be used to designate the configuration at platinum in the planar-chiral complexes. Within the stereochemical descriptor, *SP*-4 is the symmetry site term for square-planar, 4-coordinate geometry; the additional digit is the configuration number or Cahn–Ingold–Prelog (CIP) priority number[19] of the ligand atom trans to the ligand atom of highest priority attached to platinum. In the CIP system of stereonotation *R* precedes *S*.

The configuration number uniquely defines the stereochemistry around platinum, but the handedness of the molecule is more clearly indicated by adding to the descriptor the direction *C* (clockwise) or *A* (anticlockwise) of the decreasing CIP priority sequence of the two trans ligands when the molecule is viewed from the higher-priority methyl side of the C_s ligand (Figure 1). The method adopted here of constructing enantiomorphous figures for the specification of chirality in planar-chiral complexes is consistent with generally accepted proposals for specifying chirality in trigonal-planar and related systems[20] and is in accord with the IUPAC recommendation of using the symbols *C* or *A* to designate chirality in systems other than tetrahedral (*T*-4) or octahedral (*OC*-6). The ligand segment of the stereochemical descriptor, which is cumbersome when used within text, is given in the Experimental Section.

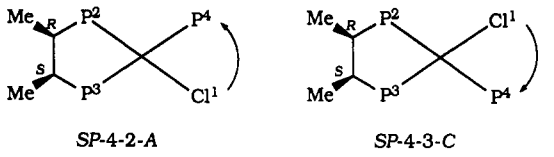


Figure 1. Diagrams indicating CIP priority numbers of ligands around platinum and showing stereochemical descriptors for epimers, which consist of a symmetry site term (*SP*-4), configuration number (2 or 3), and chirality symbol (*A* or *C*).

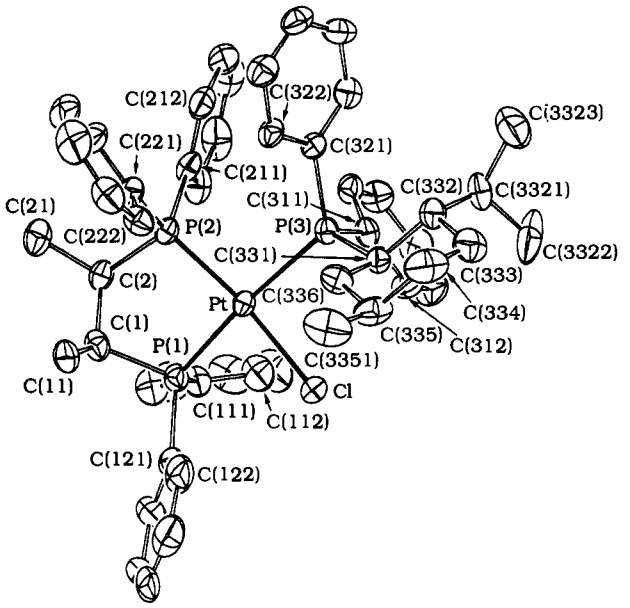


Figure 2. ORTEP view of cation of [*SP*-4-2-*A*]-(+)$_{589}$-[PtCl(achiraphos)-(*R*-PMenPh$_2$)]PF_6, showing atom-labeling for non-hydrogen atoms relevant to Table III. Thermal ellipsoids enclose 30% probability levels.

Table I. Crystallographic Data for [*SP*-4-2-*A*]-(+)$_{589}$-[PtCl(achiraphos)(*R*-PMenPh$_2$)]PF_6

$C_{50}H_{57}ClF_6P_4Pt$	fw 1126.42
a = 9.900(3) Å	space group $P2_12_12_1$
b = 15.559(4) Å	λ = 1.5418 Å
c = 32.789(10) Å	ρ_{calcd} = 1.481 g cm^{-3}
V = 5050.6 Å^3	μ = 74.3 cm^{-1}
Z = 4	R^a = 0.036
T = 20(1) °C	R_w^b = 0.042

$^a R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\{\sigma^2(|F_o|) + 0.0004(F_o)^2\}$.

Crystal and Molecular Structure of [*SP*-4-2-*A*]-[PtCl(achiraphos)(*R*-PMenPh$_2$)]PF_6. Crystal data for the complex are given in Table I. Table II gives positional parameters, and Table III lists the most important bond distances and angles in the compound. Complete data are available in the supplementary material.

The geometry around the platinum in the cation is square-planar (Figure 2). (*R*)-Diphenylmenthylphosphine is trans to the diphenylphosphino group attached to the *S* carbon of the achiraphos. In the solid state, the five-membered chelate ring in this epimer adopts a λ conformation, with one methyl group axial and the other equatorial (Figure 3). Key torsion angles within the ring are the following: Pt–P(1)–C(1)–C(2) = 46.6 (7)°, Pt–P(2)–C(2)–C(1) = 31.6 (8)°, C(11)–C(1)–C(2)–C(21) = −52(1)°. Thus, for either conformer, an unfavorable axial–axial interaction exists between a methyl group and a phenyl group in the five-membered ring of the complex. It has been argued elsewhere that this may be a source of conformational instability in coordination compounds of C_s-bidentates.[21]

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Table II. Final Positional Parameters for [*SP*-4-2-*A*]-(+)$_{589}$-[PtCl(achiraphos)(*R*-PMenPh$_2$)]PF$_6$

atom	*x/a*	*y/b*	*z/c*	U_{eq},[a] Å^2
Pt	0.57142(4)	0.50318(3)	0.60254(1)	0.0436(1)
Cl	0.8085(2)	0.5123(2)	0.60905(7)	0.068(1)
P(1)	0.5970(3)	0.5215(2)	0.53356(8)	0.0520(9)
P(2)	0.3497(2)	0.4936(2)	0.58793(7)	0.0453(7)
P(3)	0.5582(3)	0.5213(1)	0.67441(7)	0.0464(8)
C(1)	0.451(1)	0.4770(6)	0.5087(3)	0.060(4)
C(11)	0.460(1)	0.3802(7)	0.5034(3)	0.065(4)
C(2)	0.329(1)	0.5103(7)	0.5319(3)	0.052(3)
C(21)	0.192(1)	0.4766(7)	0.5161(3)	0.072(4)
C(111)	0.593(1)	0.6366(6)	0.5248(3)	0.059(4)
C(112)	0.644(2)	0.6904(8)	0.5535(4)	0.086(5)
C(113)	0.632(2)	0.7796(9)	0.5485(5)	0.115(8)
C(114)	0.568(2)	0.8134(9)	0.5169(6)	0.115(8)
C(115)	0.515(2)	0.7602(9)	0.4890(5)	0.100(6)
C(116)	0.529(1)	0.6717(8)	0.4914(4)	0.079(5)
C(121)	0.744(1)	0.4770(7)	0.5069(4)	0.065(4)
C(122)	0.801(2)	0.4021(9)	0.5195(4)	0.098(6)
C(123)	0.901(2)	0.363(1)	0.4968(6)	0.116(8)
C(124)	0.941(2)	0.402(2)	0.4605(7)	0.16(1)
C(125)	0.886(2)	0.475(2)	0.4488(5)	0.13(1)
C(126)	0.787(1)	0.515(1)	0.4706(3)	0.089(5)
C(211)	0.244(1)	0.5785(6)	0.6098(4)	0.055(4)
C(212)	0.161(1)	0.5643(8)	0.6433(4)	0.076(5)
C(213)	0.093(1)	0.636(10)	0.6599(4)	0.093(6)
C(214)	0.103(2)	0.715(1)	0.6431(6)	0.102(7)
C(215)	0.185(2)	0.7281(8)	0.6110(5)	0.094(7)
C(216)	0.258(1)	0.6610(8)	0.5943(4)	0.076(5)
C(221)	0.271(1)	0.3910(6)	0.5995(4)	0.052(4)
C(222)	0.353(1)	0.3192(6)	0.6048(4)	0.063(4)
C(223)	0.295(2)	0.2403(7)	0.6103(4)	0.079(5)
C(224)	0.163(2)	0.2315(9)	0.6122(5)	0.108(8)
C(225)	0.078(2)	0.301(1)	0.6069(4)	0.096(6)
C(226)	0.133(1)	0.3807(8)	0.5994(4)	0.072(4)
C(311)	0.577(1)	0.6364(6)	0.6775(3)	0.053(3)
C(312)	0.706(1)	0.6738(7)	0.6742(4)	0.065(4)
C(313)	0.719(1)	0.7620(8)	0.6712(4)	0.079(5)
C(314)	0.607(2)	0.8141(7)	0.6704(4)	0.083(5)
C(315)	0.483(1)	0.7796(7)	0.6724(4)	0.071(4)
C(316)	0.464(1)	0.6901(7)	0.6752(3)	0.056(4)
C(321)	0.4094(9)	0.4910(6)	0.7033(3)	0.046(3)
C(322)	0.357(1)	0.4084(6)	0.6973(3)	0.056(4)
C(323)	0.252(1)	0.3803(7)	0.7204(4)	0.073(5)
C(324)	0.199(1)	0.4306(9)	0.7504(4)	0.073(5)
C(325)	0.247(1)	0.511(1)	0.7573(3)	0.074(5)
C(326)	0.352(1)	0.5399(7)	0.7345(3)	0.063(4)
C(331)	0.695(1)	0.4670(6)	0.7017(3)	0.051(3)
C(332)	0.690(1)	0.4682(8)	0.7492(3)	0.065(4)
C(3321)	0.685(2)	0.5593(9)	0.7683(4)	0.077(5)
C(3322)	0.810(2)	0.611(1)	0.7702(5)	0.14(1)
C(3323)	0.625(2)	0.555(1)	0.8112(5)	0.124(8)
C(333)	0.809(2)	0.419(1)	0.7661(4)	0.085(6)
C(334)	0.816(2)	0.328(1)	0.7493(4)	0.110(7)
C(335)	0.822(1)	0.3218(9)	0.7035(4)	0.083(5)
C(3351)	0.819(2)	0.2285(8)	0.6875(5)	0.113(7)
C(336)	0.702(1)	0.3726(7)	0.6868(4)	0.067(4)
P(4)	0.4087(5)	0.5080(3)	0.38090(9)	0.099(2)
F(1)	0.544(1)	0.514(1)	0.4032(4)	0.214(8)
F(2)	0.467(1)	0.4453(6)	0.3487(3)	0.153(6)
F(3)	0.429(2)	0.5813(7)	0.3521(4)	0.192(8)
F(4)	0.266(1)	0.497(1)	0.3605(3)	0.186(6)
F(5)	0.345(2)	0.5663(9)	0.4131(3)	0.236(9)
F(6A)[b]	0.434(3)	0.434(2)	0.4097(8)	0.108(7)[c]
F(6B)[b]	0.348(4)	0.411(2)	0.401(1)	0.10(1)[c]
F(6C)[b]	0.346(5)	0.445(3)	0.416(1)	0.12(1)[c]

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Occupancy of disordered atoms: F(6A), 0.4; F(6B), 0.3; F(6C), 0.3. [c] Isotropic *U*.

NMR Spectra. The epimeric platinum complexes are readily distinguished by $^{31}P\{^1H\}$ NMR spectroscopy in dichloromethane-d_2. Each isomer gives rise to an ABC spin-system for the phosphorus nuclei with platinum-195 satellites (Figure 4). The C part of the spectrum in each case, which is associated with the phosphorus nucleus of the (*R*)-diphenylmenthylphosphine, is

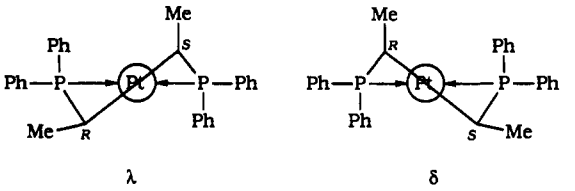


Figure 3. Isomorphous gauche conformations of the five-membered chelate ring.

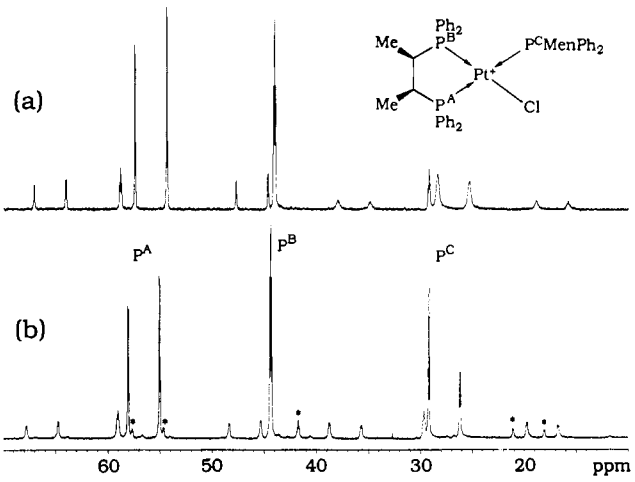


Figure 4. $^{31}P\{^1H\}$ NMR spectra of [*SP*-4-2-*A*]-(+)$_{589}$-[PtCl(achiraphos)-(*R*-PMenPh$_2$)]PF$_6$ in dichloromethane-d_2 at 296 K (a) and at 208 K (b). Peaks with asterisk have been assigned to the *SP*-4-2-*A* diastereomer with a δ conformation of the achiraphos–platinum ring.

Table III. Selected Bond Distances and Angles for [*SP*-4-2-*A*]-(+)$_{589}$-[PtCl(achiraphos)(*R*-PMenPh$_2$)]PF$_6$

Bond Lengths (Å)			
Pt–P(1)	2.294(3)	Pt–P(2)	2.251(2)
Pt–P(3)	2.377(3)	Pt–Cl	2.361(3)
P(1)–C(1)	1.799(11)	P(2)–C(2)	1.868(9)
P(1)–C(111)	1.815(10)	P(2)–C(211)	1.831(11)
P(1)–C(121)	1.829(12)	P(2)–C(221)	1.818(10)
C(1)–C(2)	1.52(1)	C(1)–C(11)	1.52(1)
C(2)–C(21)	1.54(2)		
Bond Angles (deg)			
P(1)–Pt–P(2)	84.62(9)	P(1)–Pt–Cl	88.39(9)
P(2)–Pt–P(3)	99.50(9)	P(3)–Pt–Cl	87.59(9)
P(2)–Pt–Cl	172.89(8)	P(3)–Pt–P(1)	165.71(8)
Pt–P(1)–C(1)	108.1(3)	Pt–P(2)–C(2)	108.0(3)
Pt–P(1)–C(111)	106.0(3)	Pt–P(2)–C(211)	115.2(4)
Pt–P(1)–C(121)	120.7(4)	Pt–P(2)–C(221)	115.7(4)
C(1)–P(1)–C(111)	106.9(5)	C(2)–P(2)–C(211)	102.8(5)
C(1)–P(1)–C(121)	106.1(5)	C(2)–P(2)–C(221)	106.2(5)
C(111)–P(1)–C(121)	108.3(5)	C(211)–P(2)–C(221)	107.8(5)
P(1)–C(1)–C(2)	106.4(7)	P(2)–C(2)–C(1)	110.9(7)
P(1)–C(1)–C(11)	112.7(8)	P(2)–C(2)–C(21)	112.4(7)
C(1)–C(2)–C(21)	114.6(9)	C(2)–C(1)–C(11)	116.1(9)

separated by 8.2 ppm for the two isomers. The phosphorus atom of the achiraphos trans to chlorine (P^B) is identified readily in each case by the large value of $^1J_{PtP^B}$ (3575–3576 Hz) and the small values of $^2J_{P^AP^B}$ (11.8 Hz) and $^2J_{P^BP^C}$ (ca. 11 Hz). The spectra are characterized further by large trans phosphorus–phosphorus coupling constants ($^2J_{P^AP^C}$ = 370–371 Hz) and small platinum–phosphorus couplings ($^1J_{PtP}$ = 2231–2377 Hz). The data correspond closely with those reported for other platinum(II) complexes containing bidentate and unidentate tertiary phosphines.[22]

A temperature dependence of the $^{31}P\{^1H\}$ NMR spectra of the pure *SP*-4-2-*A* complex was observed. The resonance corresponding to P^C in the *SP*-4-2-*A* isomer sharpened when the sample was cooled to 208 K, and another set of resonances appeared, which comprised ca. 10% of the intensity of the signals. We have

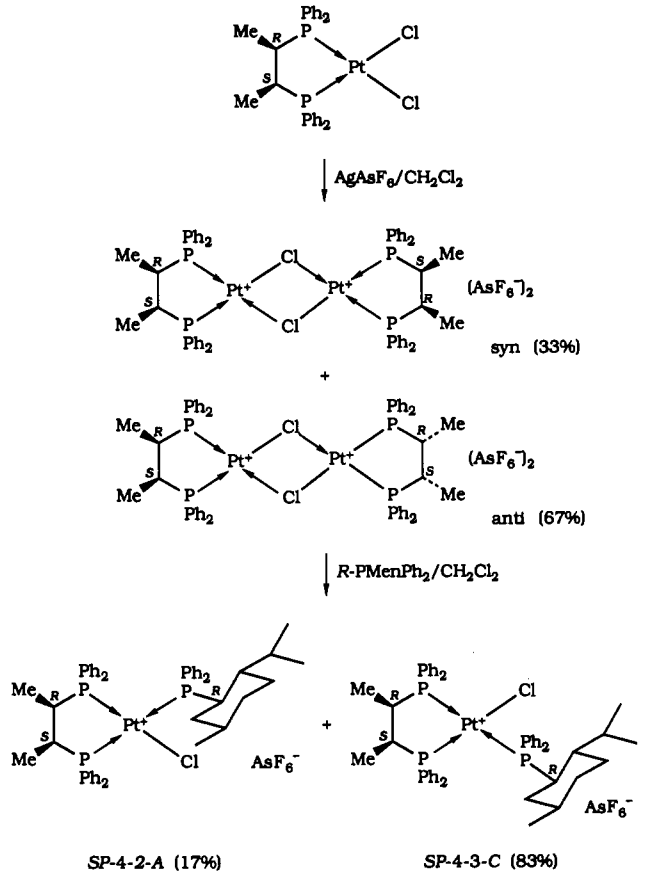
attributed the dynamic behavior observed to a freezing out of the two gauche conformations of the five-membered chelate ring in the complex. Bearing in mind that the λ conformation of the ring was observed in the solid state, this may also be the preferred conformation of the ring in solution. In five-membered chelate rings formed by C_s-bidentates, it is not possible for bulky substituents to take up simultaneously equatorial positions around the ring.[7,21] Thus, rapid axial–equatorial exchange between the methyl groups of the 2,3-butylene group is expected in these systems. In the complex [Pt(2,2′-bipyridyl)((*R**,*S**)-2,3-butanediamine)]Cl_2, the value of the platinum–methyl coupling constant ($^3J_{PtC}$ = 26 Hz), is half the value observed (51 Hz) for the corresponding *R**,*R** diastereomer in which both methyl groups are equatorial.[23,24] Support for this notion of conformational lability in rings formed by C_s-bidentates was obtained by investigating the NMR behavior of the corresponding complex of *S*,*S*-chiraphos, viz. [*SP*-4-2]-[PtCl(*S*,*S*-chiraphos)(*R*-PMenPh$_2$)]PF_6. Here too, the slightly broadened $^{31}P\{^1H\}$ NMR resonance due to P^C at 296 K sharpened up when the sample was cooled, but the slow-exchange limit indicating a single species was reached at the higher temperature of 263 K. With C_2-bidentates, such as *S*,*S*-chiraphos, both methyl groups of the 2,3-butylene group can occupy equatorial positions simultaneously, giving a more stable ring.

Pure [*SP*-4-2-*A*]-[PtCl(achiraphos)(*R*-PMenPh$_2$)]PF_6, when dissolved in dichloromethane-d_2, is configurationally stable at platinum over several days in dichloromethane, acetone, or acetone-water, even in the presence of additional *R*-PMenPh$_2$. The addition of lithium chloride to a solution of the complex in acetone-d_6, however, gives [$PtCl_2$(achiraphos)] and *R*-PMenPh$_2$. Thallium(I) phenoxide does not react with the planar-chiral complex, presumably because the bulk of the complex prevents the attack of the thallium(I) ion on the sheltered chlorine atom.

Diastereoselective Synthesis of a Planar-Chiral Platinum(II) Complex. In view of the configurational stability of the planar-chiral platinum(II) complexes in various solvents in the absence of chloride, a stereoselective synthesis of one of the epimers was attempted. For this purpose, the chloro-bridged dimer [Pt_2Cl_2(achiraphos)$_2$](AsF_6)$_2$ was prepared from [$PtCl_2$(achiraphos)] and 1 equiv of silver hexafluoroarsenate in dichloromethane. The $^{31}P\{^1H\}$ NMR spectrum of the dimer in dichloromethane-d_2 contains two singlets in the ratio 1/3 for the *syn* and *anti* diastereomers of the complex. We were unable to separate the mixture by fractional crystallization, after many attempts from different solvents. The 1/3 mixture, when treated with (*R*)-diphenylmenthylphosphine in dichloromethane, afforded the planar-chiral platinum complexes with *SP*-4-2-*A*/*SP*-4-3-*C* = 5/1 (Scheme III). When the bridge-splitting was carried out in acetone, however, *SP*-4-2-*A*/*SP*-4-3-*C* = 2/1; that is, the diastereoselectivity observed in acetone from the dimer is identical to value obtained from the original reaction between [$PtCl_2$(achiraphos)], silver nitrate, and (*R*)-diphenylmenthylphosphine in acetone–water mixture, which presumably proceeds via the intermediate solvent complex, [PtCl(achiraphos)(solvent)]NO_3.[14] Interestingly, the 1/3 mixture of diastereomers of *syn*/*anti*-[Pt_2Cl_2(achiraphos)$_2$](AsF_6)$_2$, when dissolved in acetone-d_6, transforms into a single diastereomer of the complex, which appears to be in equilibrium with the mononuclear platinum solvent complex [PtCl(achiraphos)(acetone)]AsF_6. The solvent complex exhibits an AB quartet for the phosphorus nuclei in the $^{31}P\{^1H\}$ NMR spectrum and comprises 33% of the intensity of the dimer for a 0.2 M solution in acetone-d_6. We were unable, however, to isolate from the acetone solution of the dimer a suitable crystal for X-ray structural analysis.

We are presently pursuing the resolution of less hindered chloroplatinum(II) complexes exhibiting planar-chirality in order to investigate the stereochemistry of substitution of chloride and related reactions.

Scheme III



Conclusion

Planar-chiral chloroplatinum(II) complexes containing (*R**,*S**)-bis(tertiary phosphines) can be resolved as internal diastereomers with use of appropriate homochiral phosphines as resolving ligands. The homochiral forms of the complexes are stable in organic solvents, even in the presence of additional phosphine, but chloride causes substitution of the unidentate phosphine with destruction of the chiral plane.

Experimental Section

Reactions were performed under argon using the Schlenk technique. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Gemini 300 (^1H and $^{13}C\{^1H\}$) or a Varian VXR 300s (^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) spectrometer. Samples were run in dichloromethane-d_2 at 296 K unless stated otherwise, with chemical shift values quoted relative to Me_4Si (^1H, $^{13}C\{^1H\}$) and 85% H_3PO_4 ($^{31}P\{^1H\}$). Elemental analyses were performed by staff within the Research School of Chemistry. Optical rotations were measured at the sodium-*D* line (589 nm) on the specified solutions in a 1-dm cell at 20 °C with a Perkin-Elmer Model 241 polarimeter. (*R**,*S**)-2,3-Butandiol was purchased from Aldrich.

(*R,*S**)-2,3-Butanediyl Bis(methanesulfonate).** To a solution of (*R**,*S**)-2,3-butanediol (9.0 g, 0.1 mol) and excess triethylamine (33 mL, 0.24 mol) in dichloromethane (400 mL) cooled to −10 °C (ethanol/ice bath) was added a solution of methanesulfonyl chloride (22.9 g, 0.2 mol) in dichloromethane (100 mL). The resulting mixture was stirred at −10 °C for 1 h, and then it was allowed to warm to room temperature. The mixture was then transferred to a separating funnel and washed with dilute HCl (16 mL) and water (300 mL). The organic layer was separated, dried ($MgSO_4$), filtered, and evaporated in vacuo, affording an oil that

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(23) Erickson, L.; Sarneski, J. E.; Reilley, C. N. *Inorg. Chem.* **1975**, *14*, 3007.
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crystallized on standing. The solid was isolated and recrystallized from tetrahydrofuran (35 mL) by the addition of diethyl ether (150 mL), affording the product as a colorless microcrystalline solid: mp 66–68 °C; yield 19.0 g (77%). Anal. Calcd for $C_6H_{14}O_6S_2$: C, 29.3; H, 5.7. Found: C, 29.3; H, 6.0. ^{1}H NMR ($CDCl_3$): δ 1.44 (d, $^3J_{HH}$ = 6.7 Hz, 6 H, CH*Me*), 3.09 (s, 6 H, SO_3Me), 4.90 (m, 2 H, C*H*Me). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 15.9 (CH*Me*), 38.6 (SO_3Me), 78.9 (*C*HMe).

(*R,*S**)-2,3-Bis(diphenylphosphino)butane (achiraphos).** A two-necked flask (1 L) fitted with a pressure-compensating dropping funnel and stirring bar was charged with lithium diphenyl phosphide–1-dioxane[13] (19.61 g, 0.07 mol) and tetrahydrofuran (250 mL). The orange solution was cooled to 0 °C, and a solution of (*R**,*S*)-2,3-butandiyl bis(methanesulfonate) (8.61 g, 0.035 mol) in tetrahydrofuran (100 mL) was added dropwise with stirring over 1.5 h. On completion of the addition the mixture was allowed to warm to room temperature and then it was stirred overnight. The solvent was removed in vacuo leaving an oil. The oil was dissolved in dichloromethane (500 mL) and washed with water (250 mL). The dichloromethane fraction was dried ($MgSO_4$) and filtered, and the solvent was removed to give the crude product as a clear oil. The oil, when taken up in ethanol (50 mL), deposited the pure product as colorless crystals: mp 126–127 °C; yield 14.9 g (65%). Anal. Calcd for $C_{28}H_{28}P_2$: C, 78.9; H, 6.6. Found: C, 78.8; H, 6.7. ^{1}H NMR: δ 1.09 (m, 6 H, CH*Me*), 2.62 (m, 2 H, C*H*Me), 7.24–7.54 (m, 20 H, aromatics). ^{31}P{^{1}H} NMR: δ −7.26 (s).

[*SP*-4-2-(*R,*S**)]-[2,3-Bis(diphenylphosphino)butane]dichloroplatinum(II) ([PtCl$_2$(achiraphos)]).** A solution of achiraphos (1.28 g, 3 mmol) and [$PtCl_2$(COD)][14] (1.12 g, 3 mmol) in dichloromethane (30 mL) was stirred for 0.5 h. The solvent was removed, the pale yellow residue was dissolved in dichloromethane (15 mL), and methanol (10 mL) was added. The dichloromethane was then slowly evaporated under reduced pressure to give colorless crystals of the product: mp 315–318 °C dec; yield 2.0 g (96%). Anal. Calcd for $C_{28}H_{28}Cl_2P_2Pt$: C, 48.6; H, 4.1. Found: C, 48.7; H, 4.1. ^{1}H NMR: δ_H 0.98 (d of d, 6 H, CH*Me*), 2.89 (m, 2 H, C*H*Me), 7.47–8.05 (m, 20 H, aromatics). ^{31}P{^{1}H} NMR: δ 44.2 (s, J_{PPt} = 3565 Hz).

[*SP*-4-2-*A*-[(*R,*S**),[1(*R*),1α,2β,5α]]]-(+)$_{589}$-[2,3-Bis(diphenylphosphino)butane]chloro(diphenylmenthylphosphine)platinum(II)-Hexafluorophosphate ([*SP*-4-2-*A*]-[PtCl(achiraphos)(*R*-PMenPh$_2$)]PF$_6$).** To a suspension of [$PtCl_2$(achiraphos)] (0.95 g, 1.37 mmol) in acetone (100 mL) was added a solution of $AgNO_3$ (0.24 g, 1.37 mmol) in water (10 mL). The mixture was stirred at room temperature for 2 h in the absence of light. The AgCl precipitate was then filtered off through Celite, and the filtrate was treated with *R*-$PMenPh_2$ (0.45 g, 1.37 mmol) and an excess of NH_4PF_6 (0.50 g, 3.06 mmol). The solution was stirred for a further 10 min, and the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (50 mL) and washed twice with water. The organic layer was then separated, dried over $MgSO_4$, and filtered, and the solvent was removed under reduced pressure to give the crude product as a ca. *SP*-4-2-*A*/*SP*-4-3-*C* = 2/1 mixture of diastereomers in 75% yield, $[\alpha]_D$ −4° (*c* 0.99, acetone). Recrystallization of the crude 2/1 mixture from hot methanol yielded a crystalline 1:1 mixture of the two diastereomers, which was separated. Evaporation of the mother liquor afforded a solid, which, when recrystallized from methanol, afforded the pure *SP*-4-2-*A* diastereomer: mp 252–253 °C; yield 0.2 g (13%); $[\alpha]_D$ +22.4° (*c* 0.85, acetone). Anal. Calcd for $C_{50}H_{57}ClF_6P_4Pt$: C, 53.3; H, 5.1. Found: C, 54.0; H, 5.2. ^{31}P{^{1}H} NMR: 296 K, δ 56.2 (d of d, $^1J_{PtP^A}$ = 2355 Hz, $^2J_{AB}$ = 11.8 Hz, $^2J_{AC}$ = 370 Hz, P^A), 44.4 (t, $^1J_{PtP^B}$ = 3576 Hz, P^B), 26.9 (br d, $^1J_{PtP^C}$ = 2292 Hz, P^C) (ABC spin system); 208 K, δ 27.8 (P^C), 43.4 (P^B), 56.6 (P^A) (ABC, $^1J_{PtP^A}$ = 2359 Hz, $^1J_{PtP^B}$ = 3560 Hz, $^1J_{PtP^C}$ = 2287 Hz, $^2J_{AB}$ = 11 Hz, $^2J_{BC}$ = 14 Hz, $^2J_{AC}$ = 367 Hz, major species); 19.6 (P^C), 41.7 (P^B), 56.2 (P^A) (ABC, $^1J_{PtP^A}$ = 2231 Hz, $^1J_{PtP^B}$ = 3641 Hz, $^1J_{PtP^C}$ = 2303 Hz, $^2J_{AB}$ = 13 Hz, $^2J_{BC}$ = 12 Hz, $^2J_{AC}$ = 366 Hz, minor species) (major/minor = 9/1).

The *SP*-4-3-*C* diastereomer could not be isolated in a pure state, but it has the following ^{31}P{^{1}H} NMR spectrum at 296 K: δ 56.8 (d of d, $^1J_{PtP^A}$ = 2377 Hz, $^2J_{AB}$ = 11.8 Hz, $^2J_{AC}$ = 371 Hz, P^A); 43.8 (t, $^1J_{PtP^B}$ = 3575 Hz, P^B); 18.7 (br d, $^1J_{PtP^C}$ = 2231 Hz, P^C) (ABC spin system).

[*SP*-4-2-(*R,*S**)]-*syn*/*anti*-Bis[2,3-bis(diphenylphosphino)butane]bis(μ-chloro)diplatinum(II) Hexafluoroarsenate (*syn*/*anti*-[Pt$_2$Cl$_2$(achiraphos)$_2$](AsF$_6$)$_2$).** To a solution of [$PtCl_2$(achiraphos)] (1.0 g, 1.4 mmol) in dichloromethane/acetone (2/1, 25 mL) was added $AgAsF_6$ (0.43 g, 1.4 mmol). Silver chloride precipitated immediately. The mixture was stirred overnight in the absence of light, and then it was filtered through Celite. Evaporation of the filtrate under reduced pressure left a colorless solid that was recrystallized from dichloromethane/diethyl ether, giving the colorless product as a microcrystalline solid: mp 293–295 °C; yield 1.1 g (89%). Anal. Calcd for $C_{56}H_{56}As_2Cl_2F_{12}P_4Pt_2$: C, 39.7; H, 3.0. Found: C, 39.8; H, 3.3. ^{31}P{^{1}H} NMR: δ 50.1 (s, $^1J_{PtP}$ = 3708 Hz), 50.6 (s, $^1J_{PtP}$ = 3692 Hz) (ratio = 1/3). In acetone-d_6 the complex exists as an equilibrium mixture of one diastereomer of [Pt$_2$(achiraphos)$_2$Cl$_2$](AsF$_6$)$_2$ (^{31}P{^{1}H} NMR: δ 51.9 (s, $^1J_{PtP}$ = 3699 Hz)) and the acetone complex, (*R**,*S**)-(±)-[PtCl(achiraphos)(Me$_2$CO)]AsF$_6$ (^{31}P{^{1}H} NMR: δ 39.6 (d, $^2J_{AB}$ = 11 Hz, $^1J_{PtP}$ = 3983 Hz, P trans to Cl), 49.5 (d, $^2J_{AB}$ = 11 Hz, $^1J_{PtP}$ = 3397 Hz, P trans to Me$_2$CO)).

[*SP*-4-2-*A*-[(*R,*S**),[1(*R*),1α,2β,5α]]]-(+)$_{589}$-[2,3-Bis(diphenylphosphino)butane]chloro(diphenylmenthylphosphine)platinum(II) Hexafluoroarsenate ([*SP*-4-2-*A*]-PtCl(achiraphos)(*R*-PMenPh$_2$)]AsF$_6$).** To a solution of *syn*/*anti*-[Pt$_2$Cl$_2$(achiraphos)$_2$](AsF$_6$)$_2$ (0.19 g, 0.11 mmol) (syn/anti = 1/3) in dichloromethane (15 mL) was added *R*-$PMenPh_2$ (0.075 g, 0.23 mmol) in the absence of light. The resulting solution was stirred at room temperature for 1 h, and then it was evaporated to dryness; the colorless powder remaining was shown by ^{31}P{^{1}H} NMR spectroscopy to be the desired planar-chiral product with *SP*-4-2-*A*/*SP*-4-3-*C* = 5/1. Fractional crystallization of the mixture from hot methanol afforded pure the *SP*-4-2-*A* diastereomer in 37% yield (0.05 g): mp 267 °C dec. Anal. Calcd for $C_{50}H_{57}AsClF_6P_3Pt$: C, 51.3; H, 4.9. Found: C, 51.4; H, 5.2. **[*SP*-4-2-[*S*-(*R**,*R**)]]-(+)$_{589}$-[2,3-Bis(diphenylphosphino)butane]-dichloroplatinum(II) ([PtCl$_2$(*S*,*S*-chiraphos)]).** [$PtCl_2$(COD)] (0.2 g, 0.53 mmol) and *S*,*S*-chiraphos (0.23 g, 0.54 mmol) were dissolved in dichloromethane (20 mL). After 30 min of stirring, methanol (15 mL) was added and the dichloromethane was slowly evaporated under reduced pressure affording the colorless crystalline product: mp 285 °C dec; yield 0.25 g (94%); $[\alpha]_D$ +89.0° (*c* 0.21, CH_2Cl_2). Anal. Calcd for $C_{28}H_{28}Cl_2P_2Pt$: C, 48.6; H, 4.1. Found: C, 49.0; H, 4.0. ^{31}P{^{1}H} NMR: δ 42.0 (s, $^1J_{PtP}$ = 3529 Hz).

[*SP*-4-2-[*S*-(*R,*R**),[1(*R*),1α,2β,5α]]]-(+)$_{589}$-[2,3-Bis(diphenylphosphino)butane]chloro(diphenylmenthylphosphine)platinum(II) Hexafluoroarsenate ([*SP*-4-2]-[PtCl(*S*,*S*-chiraphos)(*R*-PMenPh$_2$]AsF$_6$).** To a solution of [$PtCl_2$(*S*,*S*-chiraphos)] (0.15 g, 0.22 mmol) in dichloromethane (15 mL) was added $AgAsF_6$ (0.064 g, 0.22 mmol) in the absence of light. The resulting mixture was stirred overnight. The mixture was then filtered through Celite (to remove AgCl), and *R*-$PMenPh_2$ (0.07 g, 0.22 mmol) was added to the filtrate. The solution was stirred for 10 min, and then it was evaporated to give a pale yellow powder that when recrystallized from dichloromethane/diethyl ether afforded the pure product as a colorless microcrystalline solid: mp 265 °C dec; yield 0.21 g (83%); $[\alpha]_{589}$ −15.7° (*c* 0.29, acetone). Anal. Calcd for $C_{50}H_{57}AsClF_6P_3Pt$: C, 51.3; H, 4.9. Found: C, 50.8; H, 5.0. ^{31}P{^{1}H} NMR: 296 K, δ 19.3 (br d, $^1J_{PtP^C}$ = 2272 Hz, $^2J_{AC}$ ~ 359 Hz, P^C), 40.3 (d of d, J_{PtP^B} = 3597 Hz, P^B), 50.3 (d of d, $^1J_{PtP^A}$ = 2265 Hz, $^2J_{AB}$ = 19 Hz, $^2J_{AC}$ = 369 Hz, P^A) (ABC spin system); 268 K, δ 19.0 (P^C), 40.3 (P^B), 50.4 (P^A) (ABC, $^1J_{PtP^A}$ = 2261 Hz, $^1J_{PtP^B}$ = 3600 Hz, $^1J_{PtP^C}$ = 2267 Hz, $^2J_{AB}$ = 19 Hz, $^2J_{BC}$ = 13 Hz, $^2J_{AC}$ = 367 Hz).

Supplementary Material Available: Tables giving details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters, hydrogen atom locations, torsion angles, and selected least-squares planes (16 pages). Ordering information is given on any current masthead page.