Optically Active Asymmetric Bidentate Ligands. Crystal and Molecular Structure of {(*R*),(S)-(−)$_{589}$-2-[1-(Dimethylamino)ethyl]phenyl-*C*^{2},*N*}[1-(diphenylphosphino)-2-(methylphenylphosphino)benzene-*P*,*P*']palladium(II) Hexafluorophosphate†

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Asymmetric bidentate (±)-1-(diphenylphosphino)-2-(methylphenylphosphino)benzene has been prepared by the reaction of sodium methylphenylphosphide with 1-chloro-2-(diphenylphosphino)-benzene in tetrahydrofuran. The chiral di(tertiary phosphine) has been resolved by fractional crystallisation of a pair of internally diastereomeric palladium(II) complexes containing the racemic ligand and an orthometallated (*S*)-dimethyl(1-phenylethyl)amine. The optically pure antipodes have α ± 51° (589 nm) in acetone. This is the first resolution of an asymmetric di(tertiary phosphine) containing a chirotopic phosphorus stereocentre. The absolute configuration of the *S* enantiomer of the ligand has been assigned by a crystal structure determination of the least-soluble diastereomeric complex {(*R*),(*S*)-(−)$_{589}$-2-[1-(dimethylamino)ethyl]phenyl-*C*^{2},*N*}[1-(diphenylphosphino)-2-(methylphenylphosphino)-benzene-*P*,*P*']palladium(II) hexafluorophosphate. Chemoselective cleavage of the diphenylphosphino moiety of the free ligand occurs in the presence of alkali metals.

Optically active di(tertiary phosphines) are arguably the most successful chiral auxiliaries in enantioselective catalysis. Essentially complete stereoselectivities have been observed for the catalytic asymmetric hydrogenation of (*Z*)-α-acetamidoacrylic acids using rhodium(I) catalysts containing such ligands as chiraphos [(2*S*,3*S*)-2,3-bis(diphenylphosphino)butane], dipamp {(*R*,*R*)-1,2-bis[(2-methoxyphenyl)phenylphosphino]-ethane}, binap [2,2'-bis(diphenylphosphino)-1,1'-binaphthyl], *etc.*[1,2] Similarly impressive results have been obtained for the catalytic asymmetric hydrogenation of α,β-unsaturated carboxylic acids, allylic alcohols and functionalised ketones using a Ru^{II}(binap) catalyst.[2,3] They play a pivotal role in a number of industrial processes: for example, in the Monsanto process for the preparation of L-dopa [3-(3,4-dihydroxyphenyl)-L-alanine], in the production of the non-nutritive sweetener aspartame and in the Takasago process for the synthesis of (−)-menthol.[3,4]

The vast majority of these optically active di(tertiary phosphines) are dissymmetric ligands containing non-stereogenic donor atoms. By comparison, there is relatively little information in the literature concerning the role of unsymmetrical bidentate ligands in enantioselective catalysis. The use of optically active bidentate ligands containing dissimilar donors has important implications in the area of asymmetric synthesis, since they are capable of exercising stereoelectronic control over the reactions of co-ordinated substrates. Certain unsymmetrical bidentate ligands such as optically active *exo*-3-dimethylamino-7,7-dimethylbicyclo[2.2.1]heptan-2-ol (daib) and some chiral oxazoline derivatives have proven to be highly successful chiral auxiliaries in enantioselective catalysis,[3,5] but the use of related ligands possessing a phosphorus donor atom has had only modest success.[6] A few asymmetric bidentates containing a chirotopic phosphorus stereocentre have been resolved: for example, (±)-methylphenyl(8-quinolyl)phosphine,[7] (±)-(2-aminoethyl)-methylphenylphosphine,[8] and (*R**,*R**)- and (*R**,*S**)-1-(methylphenylarsino)-2-(methylphenylphosphino)benzene.[9] Ligands of this type, however, are generally not suitable chiral auxiliaries for transition metal-based catalysts as they are invariably kinetically labile. Presumably the non-phosphorus donor is responsible for the kinetic lability of these complexes. The present article describes the preparation and resolution of (±)-1-(diphenylphosphino)-2-(methylphenylphosphino)benzene, an asymmetric bidentate ligand which should give rise to kinetically inert transition metal-based catalysts.

Experimental

Procedures and Materials.—Reactions were performed under argon using Schlenk techniques. Solvents were dried and purified by distillation under argon. Light petroleum was a fraction with b.p. of 40–60 °C. Proton NMR spectra were recorded at 80 MHz on a Varian CFT-20 spectrometer. All chemical shifts are reported as δ values relative to internal $SiMe_4$. Optical rotations were measured with an Optical Activity AA-10 or a Perkin Elmer model 241 polarimeter on the specified solutions in 1 dm cells at 20 °C. Elemental analyses were performed by staff within the Research School of Chemistry.

The compounds 1-chloro-2-(diphenylphosphino)benzene,[10] (±)-methylphenylphosphine[11] and (+)$_{589}$-di-μ-chloro-bis-{(*S*)-2-[1-(dimethylamino)ethyl]phenyl-*C*^{2},*N*}dipalladium(II) (*S*)-**1**,[12] were prepared by published procedures.

Synthesis of (±)-1-(*Diphenylphosphino*)-2-(*methylphenylphosphino*)*benzene*, (±)-**I**.—Sodium foil (0.99 g, 43.0 mmol) was added to a stirred solution of (±)-methylphenylphosphine (5.34 g, 43.0 mmol) in tetrahydrofuran (70 cm^3) and the solution stirred overnight. The yellow-orange solution, which contained Na[PMePh], was filtered and added dropwise to a solution of 1-chloro-2-(diphenylphosphino)benzene (12.77 g, 43.0 mmol)

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

in tetrahydrofuran (200 cm^3) at −78 °C. After the addition was complete the solution was allowed to warm to room temperature overnight. The solvent was removed under reduced pressure and the residue extracted with CH_2Cl_2 (100 cm^3) and water (100 cm^3). The aqueous layer was extracted with more CH_2Cl_2 (2 × 50 cm^3) and the combined organic layers dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give the crude product (16.07 g, 97%). The compound was purified by complexation to bivalent nickel as follows. It was dissolved in CH_2Cl_2 (80 cm^3) and the solution added to a warm ethanolic solution of $[Ni(H_2O)_6][NO_3]_2$ (6.25 g, 21.5 mmol in 70 cm^3 ethanol). More ethanol (150 cm^3) was added and the CH_2Cl_2 slowly evaporated off on a water-bath. On cooling to room temperature, diethyl ether (150 cm^3) was added to give a brown crystalline mass which was collected, washed with diethyl ether (100 cm^3) and dried *in vacuo* (14.90 g, 75%). The nickel(II) complex was dissolved in CH_2Cl_2 (300 cm^3) and treated with a five-fold excess of KCN (25.55 g, 78.4 mmol) in water (300 cm^3). The organic layer was separated off and the aqueous layer extracted with more CH_2Cl_2 (2 × 50 cm^3). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and the solvent removed under reduced pressure to give the product as a viscous oil (11.92 g, 72%). ^1H NMR (CD_2Cl_2): δ 1.44 (d, 3 H, $^2J_{PH}$ 4.5 Hz, PMe) and 6.9–7.3 (m, 19 H, aromatics). *m/z* 384 $(M)^+$, 369 $(M - Me)^+$ and 307 $(M - Ph)^+$.

Resolution of Compound (±)-**I**. *Formation and Separation of Internally Diastereomeric Complexes.* [SP-4-4-(R),(S)]-{2-[1-(*Dimethylamino*)*ethyl*]*phenyl*-C^2,N}[1-(*diphenylphosphino*)-2-(*methylphenylphosphino*)*benzene*-P,P′]*palladium*(II) *Hexafluorophosphate*, (*R*,*S*)-**2b**.—Stirring of a suspension of resolving agent (*S*)-**1** (7.38 g, 12.7 mmol) and (±)-**I** (9.78 g, 25.4 mmol) in methanol (300 cm^3) gave a colourless solution of the diastereomeric chloride salts (*R*,*S*)- and (*S*,*S*)-**2a**. An aqueous solution of NH_4PF_6 (8.28 g, 50.8 mmol in 50 cm^3 water) was added dropwise, followed by more water (50 cm^3) and the reaction mixture stirred overnight. The resulting off-white precipitate was collected, washed with diethyl ether–methanol (4:1, 120 cm^3) and diethyl ether (60 cm^3), and then dried *in vacuo* (15.33 g, 77%). α +29.2° [589 nm, *c* (g/100 dm^3) 0.890, Me_2CO]. The 1:1 diastereomeric mixture was dissolved in the minimum volume of CH_2Cl_2 (80 cm^3) and diethyl ether (70 cm^3) added to afford almost pure (*R*,*S*)-**2b**. Recrystallisation from the same solvent mixture gave the pure diastereomer (3.79 g, 49%), m.p. 196 °C (Found: C, 53.8; H, 4.9; N, 1.8. Calc. for $C_{35}H_{36}F_6NP_3Pd$: C, 53.6; H, 4.6; N, 1.8%). α −71.6° (589 nm, *c* 0.824, Me_2CO). ^1H NMR [$(CD_3)_2SO$]: δ 1.58 (d, 3 H, $^3J_{HH}$ 5.9, CMe), 2.45 (d, 3 H, $^2J_{PH}$ 11.1, PMe), 3.29 (s, 6 H, NMe_2) and 7.5–8.1 (m, 23 H, aromatics); (after 48 h) δ 1.42 (d, 3 H, $^3J_{HH}$ 6.7, CMe), 1.58 (d, 3 H, $^3J_{HH}$ 5.9, CMe), 2.40 (d, 3 H, $^2J_{PH}$ 8.6, PMe), 2.45 (d, 3 H, $^2J_{PH}$ 11.1 Hz, PMe), 3.33 (s, 6 H, NMe_2) and 7.5–8.0 (m, 46 H, aromatics).

Isolation of [SP-4-4-(S),(S)]-{2-[1-(*Dimethylamino*)*ethyl*]-*phenyl*-C^2,N}[1-(*diphenylphosphino*)-2-(*methylphenylphosphino*)*benzene*-P,P′]*palladium*(II) *Hexafluorophosphate*, (*S*,*S*)-**2b**.—After removal of the first crop of complex (*R*,*S*)-**2b**, the mother-liquor was evaporated to dryness and the residue recrystallised twice from acetone–diethyl ether to afford (*S*,*S*)-**2b** as colourless hexagonal prisms (1.82 g, 24%), m.p. 200 °C (Found: C, 54.0; H, 4.6; N, 1.9%). α +132° (589 nm, *c* 0.934, Me_2CO). ^1H NMR [$(CD_3)_2SO$]: δ 1.45 (d, 3 H, $^3J_{HH}$ 6.7, CMe), 2.43 (d, 3 H, $^2J_{PH}$ 10.4, PMe), 3.29 (s, 6 H, NMe_2) and 7.6–7.9 (m, 23 H, aromatics); (after 48 h) δ 1.45 (d, 3 H, $^3J_{HH}$ 6.7, CMe), 1.59 (d, 3 H, $^3J_{HH}$ 6.1, CMe), 2.28 (d, 3 H, $^2J_{PH}$ 11.9, PMe), 2.43 (d, 3 H, $^2J_{PH}$ 10.4 Hz, PMe), 3.30 (s, 12 H, 2 NMe_2) and 7.6–7.9 (m, 46 H, aromatics).

Preparation of [SP-4-3-(R)]-*Dichloro*[1-(*diphenylphosphino*)-2-(*methylphenylphosphino*)*benzene*-P,P′]*palladium*(II), (*R*)-**3**.—Diastereomerically pure complex (*R*,*S*)-**2b** (3.02 g, 3.85 mmol) was heated for 10 min in acetone (70 cm^3) containing hydrochloric acid (10 mol dm^{-3}, 4 cm^3). The resulting white precipitate was collected and recrystallised from a dichloromethane–methanol mixture (1.99 g, 92%), m.p. > 290 °C (Found: C, 53.4; H, 3.8. Calc. for $C_{25}H_{22}Cl_2P_2Pd$: C, 53.5; H, 4.0%). α +6.21 (589 nm) +100° (436 nm) (*c* 0.708, Me_2CO). ^1H NMR (CD_2Cl_2): δ 2.45 (d, 3 H, $^2J_{PH}$ 12.3 Hz, PMe) and 7.4–7.9 (m, 19 H, aromatics).

The [*SP*-4-3-(*S*)] enantiomer was prepared in the same way in 83% yield, m.p. > 290 °C (Found: C, 53.2; H, 3.9. Calc. for $C_{25}H_{22}Cl_2P_2Pd$: C, 53.5; H, 4.0%). α −7.30 (589 nm), −101° (436 nm) (*c* 0.740, Me_2CO).

Preparation of (S)-1-(*Diphenylphosphino*)-2-(*methylphenylphosphino*)*benzene*, (*S*)-**I**.—Enantiomer (*R*)-**3** (1.83 g, 3.26 mmol) was suspended in methanol (85 cm^3) and light petroleum (80 cm^3) and KCN (6.92 g, 106.3 mmol) added. Water (20 cm^3) was then added and the two layers separated. More water (40 cm^3) was added and the aqueous layer extracted with light petroleum (2 × 70 cm^3). The combined organic layer was dried over anhydrous $MgSO_4$, filtered and the solvent removed under reduced pressure (1.19 g, 95%). α −51° (589 nm, *c* 2.38, Me_2CO). ^1H NMR (CD_2Cl_2): identical with that of the corresponding racemic material.

The (*R*) enantiomer was prepared in the same manner in 78% yield, α +51° (589 nm, *c* 2.50, Me_2CO).

X-Ray Crystallography.—Crystal data for complex (*R*,*S*)-**2b**. $C_{35}H_{36}F_6NP_3Pd$, M = 784.0, orthorhombic, space group $P2_12_12_1$ (D_4^2, no. 19), a = 11.408(1), b = 15.422(2), c = 19.945(2) Å, U = 3509.0(3) $Å^3$ (by least-squares analysis of the setting of 25 reflections 54 < 2θ < 66°), Cu-Kα radiation λ = 1.5418 Å with a graphite monochromator, D_m = 1.467(7) g cm^{-3}, Z = 4, D_c = 1.484 g cm^{-3}, $F(000)$ = 1592, specimen: 0.33 × 0.26 × 0.21 mm, μ(Cu-Kα) = 74.3 cm^{-1}.

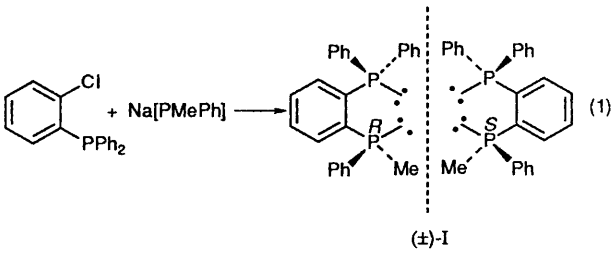
Data collection and processing. A unique data set was measured at 293(1) K in the range 2θ 4–128° using a Philips PW 1100/20 diffractometer; intensities of reflections $+h$, $+k$, $\pm l$ ($0 \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 18$, $-23 \leqslant l \leqslant 23$) were collected using θ–2θ scans of width (0.90 + 0.14 tan θ)° in θ at a rate of 1.5° min^{-1} in θ with a background count of 6 s on each side of each scan. 6375 Reflections were measured, of which 5567 [$I > 3\sigma(I)$] were accepted as significant and used in the subsequent structure solution and refinement. Measurement of standard reflections every 90 min showed a 7% decrease in intensity during data collection, therefore a correction was applied to all data.[13] A Lorentz-polarisation correction was applied. An absorption correction with transmission range 0.274–0.427 was also applied.

Structure analysis and refinement. The structure was solved by Patterson methods and refined by full-matrix least-squares techniques. Hydrogen atoms were placed in calculated positions (r_{C-H} = 0.95 Å) with isotropic thermal parameters set at 25% larger than those of the attached carbon atoms and were not refined. Anisotropic thermal parameters were refined for the non-hydrogen atoms; weights $w = [\sigma^2(F) + 0004F^2]^{-1}$ were used. Determination of the absolute configuration was achieved by the inclusion of an enantiomorph-defining X_{abs} parameter[14] with an original value of 0.5, which subsequently refined to 0.004(7) indicating the original model had the correct absolute configuration. Since $F_{obs} < F_{calc}$ for eleven low-2θ reflections, an extinction parameter was applied [final value = 0.47(4) × 10^4]. Final R and R' values were 0.029 and 0.042, respectively. All data reduction, structural solutions and refinement were performed with the XTAL 3.0 program package.[15] Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref. 16.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

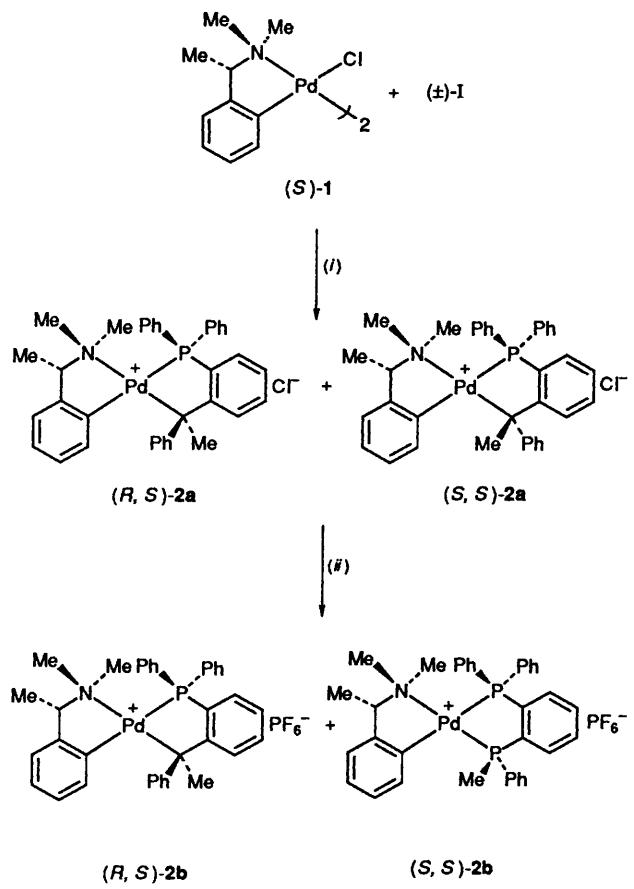
Synthesis and Resolution of Compound (±)-**I**.—The asymmetric bis(tertiary phosphine) (±)-1-(diphenylphosphino)-2-(methylphenylphosphino)benzene (±)-**I** was prepared by treating 1-chloro-2-(diphenylphosphino)benzene with sodium methylphenylphosphide in tetrahydrofuran at −78 °C [equation (1)]. The crude product was purified by complexation to



(±)-I

bivalent nickel to give a diastereomeric mixture of complexes of the type $[Ni\{(\pm)\text{-}\mathbf{I}\}_2][NO_3]_2$. The bis(tertiary phosphine) was liberated quantitatively from the diastereomeric mixture of nickel(II) complexes upon treatment with aqueous potassium cyanide. Compound (±)-**I** was isolated in 72% yield as a pale yellow viscous oil which could not be induced to crystallise.

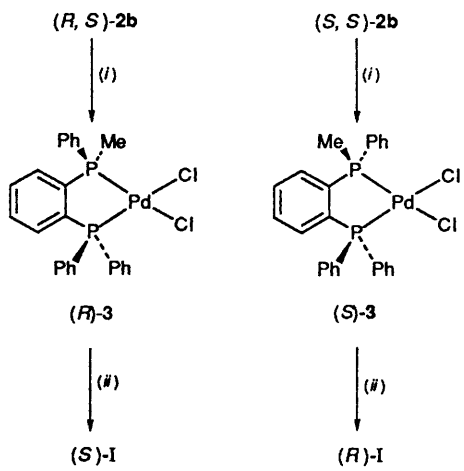
Resolution of compound (±)-**I** was achieved *via* separation by fractional crystallisation of a pair of internally diastereomeric palladium(II) complexes containing the racemic ligand and orthometallated (*S*)-$(-)_{589}$-dimethyl(1-phenylethyl)-amine. A pair of internal diastereomeric chloride salts, *viz.* (*R*,*S*)- and (*S*,*S*)-**2a**, was produced in a bridge-splitting reaction involving (±)-**I** and the dimer $(+)_{589}$-di-μ-chloro-bis{(*S*)-2-[1-(dimethylamino)ethyl]phenyl-C^2,N}dipalladium(II), (*S*)-**1**, in methanol (Scheme 1). The addition of an excess of aqueous



Scheme 1 (*i*) MeOH; (*ii*) $NH_4[PF_6]$ in water

NH_4PF_6 to this solution precipitated a 1:1 mixture of the diastereomeric hexafluorophosphate salts, (*R*,*S*)- and (*S*,*S*)-**2b**, in 77% yield. Fractional crystallisation of the diastereomeric mixture from dichloromethane by the slow addition of diethyl ether gave colourless hexagonal prisms of pure (*R*,*S*)-**2b**, α −71.6° (589 nm, acetone). Diastereomer (*S*,*S*)-**2b** was obtained by evaporating the mother-liquor to dryness and twice recrystallising the residue from an acetone–diethyl ether mixture: it crystallised as colourless hexagonal prisms, α +132° (589 nm, acetone). The liberation of the resolved bis(tertiary phosphines) from (*R*,*S*)- and (*S*,*S*)-**2b** was accomplished as shown in Scheme 2. Treatment of (*R*,*S*)- or (*S*,*S*)-**2b** in acetone with concentrated hydrochloric acid gave the respective dichloropalladium(II) complexes, (*R*)- and (*S*)-**3**, α ± 100° (436 nm, acetone). Reaction of these with aqueous potassium cyanide gave the optically pure antipodes (*S*)- and (*R*)-**I**, α ± 51° (589 nm, acetone).

Crystal Structure Determination of Complex (*R*,*S*)-**2b**.—The absolute configuration of the optically pure compound (*S*)-**I** was assigned by a crystal structure determination of the least-soluble diastereomer (*R*,*S*)-**2b**. The stereochemistry of the cation is depicted in Fig. 1. Non-hydrogen atomic coordinates are given in Table 1 and selected bond lengths and angles in Table 2. The square-planar co-ordination geometry of the palladium atom is distorted by the stereochemical constraints



Scheme 2 (*i*) Concentrated HCl in acetone; (*ii*) KCN in water

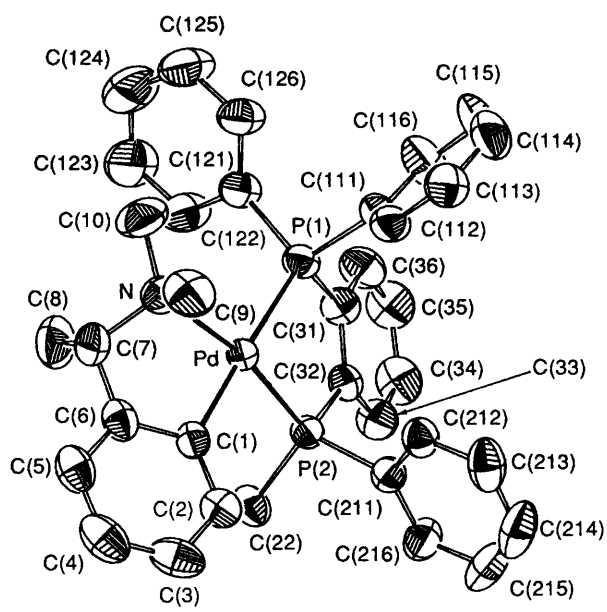


Fig. 1 Molecular structure of the cation of complex (*R*,*S*)-*2b*. Thermal ellipsoids (30%) are shown for non-hydrogen atoms

Table 1 Non-hydrogen atom coordinates for complex (*R*,*S*)-**2b**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd	0.240 44(2)	0.478 31(1)	0.638 48(1)	C(124)	0.375 0(7)	0.285 6(5)	0.879 1(3)
P(1)	0.388 14(8)	0.496 39(6)	0.719 15(5)	C(125)	0.471 6(6)	0.292 0(4)	0.838 5(3)
P(2)	0.202 25(8)	0.617 96(6)	0.656 11(4)	C(126)	0.481 7(4)	0.357 5(3)	0.793 1(2)
N	0.240 4(4)	0.339 1(2)	0.619 8(2)	C(211)	0.253 2(4)	0.690 1(2)	0.590 8(2)
C(1)	0.107 0(3)	0.469 2(2)	0.569 6(2)	C(212)	0.344 4(4)	0.661 5(3)	0.550 6(2)
C(2)	0.067 5(3)	0.526 5(3)	0.521 6(2)	C(213)	0.393 8(5)	0.717 3(4)	0.503 1(2)
C(3)	0.022 1(4)	0.503 9(4)	0.477 1(2)	C(214)	0.348 4(6)	0.798 6(4)	0.495 6(3)
C(4)	0.071 5(4)	0.423 7(4)	0.480 7(3)	C(215)	0.259 2(7)	0.827 2(3)	0.534 6(3)
C(5)	0.030 7(4)	0.362 9(3)	0.526 1(3)	C(216)	0.210 5(4)	0.773 8(3)	0.583 6(2)
C(6)	0.059 4(3)	0.385 1(3)	0.569 2(2)	C(22)	0.049 9(4)	0.642 9(3)	0.672 4(2)
C(7)	0.111 2(4)	0.320 5(3)	0.617 3(3)	C(31)	0.357 1(4)	0.598 0(3)	0.762 0(2)
C(8)	0.053 9(6)	0.326 8(4)	0.685 8(3)	C(32)	0.276 0(3)	0.653 8(2)	0.732 3(2)
C(9)	0.293 9(6)	0.323 0(4)	0.552 7(3)	C(33)	0.251 2(4)	0.733 9(3)	0.762 5(2)
C(10)	0.301 1(6)	0.282 0(3)	0.668 3(3)	C(34)	0.300 9(5)	0.755 0(3)	0.822 7(3)
C(111)	0.536 9(3)	0.503 6(3)	0.687 0(2)	C(35)	0.377 1(5)	0.697 6(3)	0.854 0(2)
C(112)	0.557 2(4)	0.484 2(3)	0.620 4(2)	C(36)	0.405 8(4)	0.620 6(3)	0.823 7(2)
C(113)	0.670 3(4)	0.485 2(3)	0.594 3(2)	P(3)	−0.030 7(2)	0.540 1(1)	0.887 2(1)
C(114)	0.762 9(4)	0.504 8(4)	0.634 4(3)	F(1)	−0.083 1(8)	0.603 2(4)	0.835 6(3)
C(115)	0.774 3(5)	0.524 9(5)	0.701 1(3)	F(2)	−0.051 9(8)	0.608 5(4)	0.942 8(3)
C(116)	0.631 7(4)	0.525 2(4)	0.727 2(3)	F(3)	−0.006(1)	0.475 1(6)	0.939 8(5)
C(121)	0.393 6(4)	0.417 3(3)	0.786 4(2)	F(4)	−0.004 4(8)	0.477 7(6)	0.833 2(5)
C(122)	0.296 2(5)	0.412 5(4)	0.827 4(3)	F(5)	−0.158 0(7)	0.512 2(7)	0.890 7(6)
C(123)	0.288 1(6)	0.347 9(5)	0.874 0(3)	F(6)	0.092 8(8)	0.567(1)	0.886 0(7)

Table 2 Selected non-hydrogen interatomic distances (Å) and interatomic angles (°)

Pd–P(1)	2.346(1)	Pd–P(2)	2.225(1)
Pd–N	2.179(3)	Pd–C(1)	2.055(4)
P(1)–Pd–P(2)	85.25(3)	P(2)–Pd–N	168.7(1)
P(1)–Pd–N	103.6(1)	P(2)–Pd–C(1)	91.5(1)
P(1)–Pd–C(1)	176.7(1)	N–Pd–C(1)	79.5(2)
Pd–N–C(9)	108.6(3)	Pd–N–C(10)	118.3(3)

of the chelating ligands and the methyl substituents on N. The atoms Pd, P(1), P(2) and C(1) are essentially coplanar [maximum deviation from the least-squares plane 0.023(4) Å], with the nitrogen atom 0.259(5) Å from the least-squares plane. The intraligand angles at the Pd atom are P(1)–Pd–P(2) 85.3(0) and N–Pd–C(1) 79.5(2)° and the interligand angles are P(2)–Pd–C(1) 91.5(1) and P(1)–Pd–N 103.6(1)°. The absolute configuration of the phosphorus stereocentre P(2) is *R* and that of the carbon C(7) stereocentre is *S*. Furthermore, the methylphenylphosphino moiety of the di(tertiary phosphine) was found to be *trans* to the nitrogen atom of the resolving agent, as indeed was observed in a related palladium(II) complex containing orthometallated (*R*)-(+)$_{589}$-dimethyl[1-(1-naphthyl)-ethyl]amine and the asymmetric bidentate (*R*)-(−)$_{589}$-methylphenyl(8-quinolyl)phosphine.[7] The two Pd–P bond distances are significantly different; Pd–P(1) [diphenylphosphino, *trans* to C(1)] 2.346(1) and Pd–P(2) (methylphenylphosphino, *trans* to N) 2.225(1) Å. The difference is likely to be due to a combination of the *trans* effect[17] and the differing basicities of the phosphorus donors, as has been observed in other similar molecules.[18]

The hexafluorophosphate anion appears to have considerable disorder. The U_{ij} values are 0.2–0.35, compared to U_{ij} < 0.1 Å^2 for the other non-hydrogen atoms. No simple modelling with multiple positions for the fluorine atoms gave a satisfactory agreement with the observed electron density. Bond distances within the anion are unreliable.

NMR Spectra.—The ^{1}H NMR spectra of the internally diastereomeric complex cations can be rationalised in terms of the solid-state structure of (*R*,*S*)-**2b**. Selected ^{1}H NMR data are presented in Table 3. Single doublet PMe and CMe resonances are observed for (*R*,*S*)- and (*S*,*S*)-**2b** in $(CD_3)_2CO$ and $(CD_3)_2SO$ which is consistent with the presence of a single diastereomer in solution in each case. This is also consistent with the solid-state structure of (*R*,*S*)-**2b** in which the methylphenylphosphino moiety is *trans* to the nitrogen atom. A similar stereochemical arrangement has been observed in solution for related palladium(II) complexes containing an optically active amine and the enantiomers of (±)-methylphenyl(8-quinolyl)phosphine, (±)-(2-aminoethyl)methylphenylphosphine, and (*R**,*R**)- and (*R**,*S**)-1-(methylphenylarsino)-2-(methylphenylphosphino)benzene.[7–9] In all of these examples, coupling of phosphorus to the NMe groups and the methine proton was observed in the respective ^{1}H NMR spectra which is only consistent with the assignment of the methylphenylphosphino moiety *trans* to the nitrogen atom of the optically active amine.

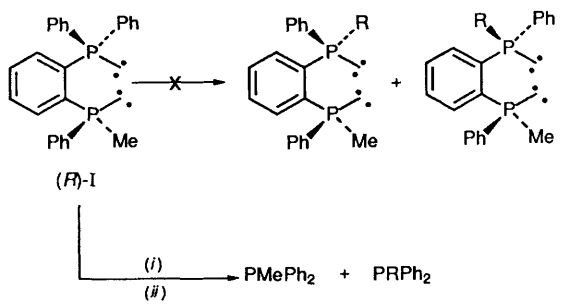
The behaviour of complexes (*R*,*S*)- and (*S*,*S*)-**2b** in $(CD_3)_2SO$, however, was not static: after standing for 48 h a second set of doublet PMe and CMe resonances was observed in the ^{1}H NMR spectra. No change was observed in $(CD_3)_2CO$ over a period of 1 week. The second set of resonances were assigned to the analogous diastereomeric complexes in which the diphenylphosphino moiety is *trans* to the nitrogen donor. Presumably facile intermolecular *cis*–*trans* isomerism is occurring in the more polar solvent and may arise as a result of labilisation of the Pd–N bond.

Chemoselective Reactions of Compound (±)-**I**.—Chemoselective cleavage of a phenyl group from the diphenylphosphino moiety of (*R*)- or (*S*)-**I**, followed by alkylation with RX, should give rise to a pair of diastereomers, the separation of which would provide a route to optically active di(tertiary phosphines) containing two chirotopic phosphorus stereocentres (Scheme 3). No evidence for the chemoselective cleavage of a phenyl group from (±)-**I**, however, has been found in tetrahydrofuran by the addition of lithium metal or in liquid ammonia in the presence of sodium metal. In both cases quenching the reaction with methyl iodide resulted in a quantitative yield of methyldiphenylphosphine which is only consistent with selective cleavage of the diphenylphosphino moiety from (±)-**I**. Cleavage of a phenyl group from the diphenylphosphino moiety of (±)-**I** by either alkali metal would have resulted in the formation of (*R**,*R**)- and (*R**,*S**)-1,2-phenylenebis(methylphenylphosphine)[11] upon reaction with methyl iodide.

Table 3 Selected ^{1}H NMR data for complexes (*R*,*S*)- and (*S*,*S*)-**2b**

		δ			
Compound	Solvent	PMe[a]	CMe[b]	CH	NMe
(*R*,*S*)-**2b**	*c*	2.50 (d, 11)	1.70 (d, 6.3)	3.78 (m)	2.75 (s)
	d	2.45 (d, 11)	1.58 (d, 5.9)		3.29 (s)
	e	2.45 (d, 11)	1.58 (d, 5.9)		3.33 (s)
		2.40 (d, 8.6)	1.42 (d, 6.7)		3.33 (s)
(*S*,*S*)-**2b**	*c*	2.49 (d, 14)	1.56 (d, 6.4)	4.07 (m)	2.54 (s), 2.76 (s)
	d	2.43 (d, 10)	1.45 (d, 6.7)		3.29 (s)
	e	2.43 (d, 10)	1.45 (d, 6.7)		3.30 (s)
		2.28 (d, 12)	1.59 (d, 6.1)		3.30 (s)

[a] $^2J_{PH}$ given in Hz in parentheses. [b] $^3J_{HH}$ given in Hz in parentheses. [c] $(CD_3)_2CO$. [d] $(CD_3)_2SO$. [e] On standing in $(CD_3)_2SO$ for 48 h.



Scheme 3 (*i*) Li in tetrahydrofuran or Na in liquid ammonia; (*ii*) RI

Conclusion

This paper describes the synthesis and resolution by metal complexation of (±)-1-(diphenylphosphino)-2-(methylphenylphosphino)benzene (±)-**I**, the first asymmetric di(tertiary phosphine) containing a chirotopic phosphorus stereocentre to be resolved. The absolute configuration of the *S* enantiomer of the di(tertiary phosphine) was established on the basis of a single-crystal X-ray analysis of an internally diastereomeric palladium(II) complex containing the optically active ligand and (*S*)-(+)$_{589}$-dimethyl(1-phenylethyl)amine. The crystal structure also showed the methylphenylphosphino moiety of the di(tertiary phosphine) to be *trans* to the nitrogen donor of the optically active amine. The same structure is retained in acetone solution, but not in dimethyl sulfoxide where facile *cis*–*trans* isomerism takes place. Indeed, the chloride-bridged dimer (+)$_{589}$-di-μ-chloro-bis{(*S*)-2-[1-(dimethylamino)ethyl]-phenyl-C^2,*N*}dipalladium(II) (*S*)-**1** is generally not suitable for the resolution of unsymmetrical bidentate ligands as both *cis* and *trans* diastereomers are invariably formed in solution. Apart from (±)-**I**, the only other asymmetric bidentate ligand to be successfully resolved using (*S*)-**1** is (*R**,*R**)-1-(methylphenylarsino)-2-(methylphenylphosphino)benzene.[9] The *R**,*S** form of the ligand and a number of other asymmetric bidentate ligands containing a single methylphenyl-phosphino or -arsino moiety and a nitrogen or sulfur donor could not be resolved using (*S*)-**1**.[7–9,19] They were all successfully resolved by the method of metal complexation, however, using the analogous chloride-bridged dimer (+)$_{589}$-di-μ-chloro-bis{(*S*)-1-[1-(dimethylamino)ethyl]naphthyl-C^2,*N*}dipalladium(II). Furthermore, the methylphenylphosphino moiety (or the methylphenylarsino group in the absence of a phosphorus donor) was found to be exclusively *trans* to the nitrogen donor of the optically active amine in the resulting internally diastereomeric palladium(II) complexes. This arrangement of donors about the palladium(II) centre can be rationalised in terms of Pearson's antisymbiosis: 'two soft ligands in mutual *trans* position will have a destabilising effect on each other when attached to class b metal atoms'.[20] Clearly, for square-planar complexes of palladium(II) containing an orthometallated amine and a bidentate ligand possessing one phosphorus/arsenic donor and a nitrogen/sulfur donor, the soft orthometallated carbon atom and the soft phosphorus/arsenic donor would be expected to adopt a *cis* disposition about the metal centre. For analogous complexes containing (*R**,*R**)- or (*R**,*S**)-1-(methylphenylarsino)-2-(methylphenylphosphino)-benzene or (±)-1-(diphenylphosphino)-2-(methylphenylphosphino)benzene the methylphenylphosphino group (being a more potent donor than either the methylphenylarsino or diphenylphosphino moieties) and the orthometallated carbon atom of the amine would be expected to adopt a mutual *cis* arrangement about the palladium(II) centre.

The ready formation of *cis* and *trans* isomers in palladium(II) complexes containing an unsymmetrical bidentate and orthometallated (*S*)-(+)$_{589}$-dimethyl(1-phenylethyl)amine presumably arises as a result of labilisation of the Pd–N bond. This does not occur in related complexes containing orthometallated (*S*)-(+)$_{589}$-dimethyl[1-(1-naphthyl)ethyl]amine due to the greater strength of the Pd–N bond in these compounds. This is reflected in the relative ease of removal of the resolving agent from these complexes: the former orthometallated amine is displaced from the metal centre upon heating of its complexes in acetone in the presence of concentrated hydrochloric acid, whereas complexes containing the latter amine must be dissolved in concentrated sulfuric acid in order to effect removal of the resolving agent.

Highly chemoselective cleavage of the diphenylphosphino moiety in compound (±)-**I** was achieved in the presence of lithium in tetrahydrofuran or sodium in ammonia. Relatively few studies on the chemoselective cleavage of alkyl or aryl groups from tertiary phosphines or arsines have been reported.[21] Nevertheless studies of this type are important as chemoselective cleavage of such groups from suitably designed optically active bidentate ligands can provide an avenue to optically active multidentate ligands.[22] Related studies by Juge[23] and Brown and co-workers[24] on the asymmetric synthesis of dissymmetric di(tertiary phosphines) containing stereogenic donor atoms are also having a significant impact on this area of research.

Future work is directed towards the utility of optically active asymmetric di(tertiary phosphines), such as (*R*)- and (*S*)-**I**, as chiral auxiliaries in enantioselective catalysis. Auxiliaries of this type should give rise to kinetically inert transition metal-based catalysts and this, coupled with the ability of such ligands to exercise stereoelectronic control over the reactions of co-ordinated substrates, has important implications in asymmetric synthesis.

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