Synthesis, Resolution and Reactions of (±)-1-(Dimethylarsino)-2-(methylphenylphosphino)benzene. Crystal and Molecular Structure of [(*S*),(*S*)]-(+)$_{589}$-{2-[1-(Dimethylamino)ethyl]phenyl-*C*^{1},*N*}[1-(dimethylarsino)-2-(methylphenylphosphino)benzene-*As*,*P*]palladium(II) Hexafluorophosphate†

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Asymmetric bidentate (±)-1-(dimethylarsino)-2-(methylphenylphosphino)benzene has been prepared by the reaction of sodium dimethylarsenide with (±)-1-chloro-2-(methylphenylphosphino)benzene in tetrahydrofuran. Its resolution has been achieved by the separation by fractional crystallisation of a pair of internally diastereomeric palladium(II) complexes containing the racemic ligand and orthometallated (*S*)-dimethyl(1-phenylethyl)amine. The optically pure antipodes have α ±32° (589 nm, dichloromethane). The absolute configuration of the *R* enantiomer of the ligand has been assigned by a crystal-structure determination of the least-soluble diastereomeric complex [(*S*),(*S*)]-(+)$_{589}$-{2-[1-(dimethylamino)ethyl]phenyl-*C*^{1},*N*}[1-(dimethylarsino)-2-(methylphenylphosphino)benzene-*As*,*P*]palladium(II) hexafluorophosphate. Chemoselective cleavage of the dimethylarsino moiety of the free benzene derivative occurs in the presence of lithium metal in tetrahydrofuran.

While unsymmetrical bidentate ligands containing both an arsenic and a phosphorus donor atom are well known,[1,2] relatively few examples of chiral molecules of this type have been reported. Indeed, the four enantiomeric forms of (*R**,*R**)- and (*R**,*S**)-1-(methylphenylarsino)-2-(methylphenylphosphino)benzene are, to our knowledge, the only documented examples of this type.[3] Such compounds with a dissimilar arrangement of donor atoms have important implications in enantioselective synthesis, since they are capable of exercising stereoelectronic control over the reactions of co-ordinated substrates. Certain unsymmetrical bidentate compounds such as optically active *exo*-3-dimethylamino-7,7-dimethylbicyclo-[2.2.1]heptan-2-ol and some chiral thienyloxazolines have proven to be highly successful chiral auxiliaries in enantioselective catalysis,[4,5] but related compounds possessing a phosphorus-donor atom have, until very recently, had only modest success.[6] In the past two years there has been an upsurge of interest in the role of optically active unsymmetrical bidentate compounds containing phosphorus- and nitrogen-donor atoms as chiral auxiliaries in enantioselective catalysis. For example, the unsymmetrical tertiary phosphine (*S*)-[1-(1-isoquinolyl)naphthyl]diphenylphosphine and some optically active oxazolylphosphines have been successfully used as chiral auxiliaries in the catalytic hydroboration of vinylarenes (in up to 94% enantiomeric excess, e.e.) and the palladium(II)-catalysed allylic substitution of 1,3-diphenylprop-2-enyl acetate (in up to 99% e.e.), respectively.[7,8] In this paper we report on the synthesis and resolution of (±)-1-(dimethylarsino)-2-(methylphenylphosphino)benzene, the optically active antipodes of which are seen as potential chiral auxiliaries in enantioselective catalysis.

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: mmHg ≈ 133 Pa.

Experimental

Procedures and Materials.—Reactions were performed under argon using Schlenk techniques. Solvents were dried and purified by distillation under argon. The NMR spectra were recorded on a Varian Gemini II spectrometer operating at 300 (^{1}H) or 121 MHz (^{31}P-{^{1}H}). Chemical shifts are reported as δ values relative to $SiMe_4$ (^{1}H) or 85% H_3PO_4 (^{31}P-{^{1}H}). 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-(methylphenylphosphino)-benzene (±)-**II**,[3] iododimethylarsine,[9] (−)$_{589}$-di-μ-chloro-bis-{(*R*)-2-[1-(dimethylamino)ethyl]phenyl-*C*^{1},*N*}dipalladium(II) (*R*)-**I** and (+)$_{589}$-di-μ-chloro-bis{(*S*)-2-[1-(dimethylamino)-ethyl]phenyl-*C*^{1},*N*}dipalladium(II), (*S*)-**I**,[10] were prepared by published procedures.

Synthesis of (±)-1-(*Dimethylarsino*)-2-(*methylphenylphosphino*)*benzene* (±)-**I**.—Sodium foil (9.78 g, 0.425 mol) was added to a stirred solution of iododimethylarsine (49.3 g, 0.212 mol) in tetrahydrofuran (thf) (400 cm^3) over a period of 1 h. The solution was allowed to stir for 2 h, then filtered and added dropwise to a stirred solution of (±)-**II** (50 g, 0.213 mol) in thf (200 cm^3) at −78 °C. After the addition was complete the reaction mixture was stirred for 48 h at −20 ± 5 °C. The solvent was removed and the residue extracted with water (200 cm^3) and dichloromethane (80 cm^3). The aqueous layer was extracted with more dichloromethane (2 × 80 cm^3) and the combined organic extracts dried over anhydrous $MgSO_4$. Removal of the solvent gave a clear red liquid which contained at least five components. The crude product was distilled and two fractions were collected. Fraction 1 (b.p. 50–100 °C, 0.05 mmHg) contained tetramethyldiarsane, methyldiphenylphosphine and methylphenylphosphine. Fraction 2 (b.p. 120–

135 °C) contained a 1:1 mixture of (±)-**I** and unreacted starting material (±)-**II**. The mixture of (±)-**I** and (±)-**II** was separated by dissolving it in acetone (50 cm^3) followed by the addition of a solution of hexaaquanickel(II) perchlorate (25 g, 68 mmol) in acetone (10 cm^3). The resulting orange-brown nickel(II) complex was collected, washed with diethyl ether and dried *in vacuo* (21 g). The diethyl ether washings and the mother-liquor were combined and the solvent removed. The viscous brown residue was extracted with hot diethyl ether (3 × 50 cm^3) and the combined organic extracts dried over anhydrous $MgSO_4$. The solvent was removed and the residue distilled to give pure (±)-**II** (16.4 g, 33%), b.p. 126–128 °C. NMR ($CDCl_3$): ^1H, δ 1.57 (d, 3 H, $^2J_{PH}$ 4.6 Hz, PMe) and 7.08–7.44 (m, 9 H, aromatics); ^{31}P-{^1H}, δ −30.9 (s, 1 P). The residue from the diethyl ether extraction was dissolved in acetone (20 cm^3) and a further solution of hexaaquanickel(II) perchlorate (25 g, 68 mmol) in acetone (10 cm^3) added to give a second crop of the nickel(II) complex [10.5 g, total yield 50% based on a 67% conversion of (±) **II**], m.p. 250 °C (decomp.) (Found: C, 42.0; H, 4.1. Calc. for $C_{30}H_{36}As_2Cl_2NiP_2O_8$: C, 41.6; H, 4.2%). A solution of potassium cyanide (50 g, 0.768 mol) in water (200 cm^3) was added to a solution of the nickel(II) complex (31.5 g, 36.4 mmol) in dichloromethane (100 cm^3) and the reaction mixture stirred for 24 h. The two phases were separated and the aqueous layer extracted with dichloromethane (2 × 50 cm^3). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed by distillation under argon. Distillation of the crude product gave the asymmetric bidentate ligand (±)-**I** as a colourless, viscous liquid (21.3 g, 47.5%), b.p. 128–132 °C (0.05 mmHg) (Found: C, 59.2; H, 6.1; P, 10.4. Calc. for $C_{15}H_{18}AsP$: C, 59.2; H, 6.0; P, 10.2%). NMR ($CDCl_3$): ^1H, δ 1.04 (s, 3 H, AsMe), 1.22 (s, 3 H, AsMe), 2.16 (d, 3 H, $^2J_{PH}$ 3.9 Hz, PMe) and 7.23–7.52 (m, 9 H, aromatics); ^{31}P-{^1H}, δ −34.0 (s, 1 P).

Resolution of (±)-**I**. *Formation and Separation of Internally Diastereomeric Complexes*. [SP-4-4-(S),(S)]-{2-[1-(*Dimethylamino*)*ethyl*]*phenyl*-C^1,N}[1-(*dimethylarsino*)-2-(*methylphenylphosphino*)*benzene*-As,P]*palladium*(II) *Hexafluorophosphate*, (S,S)-**2b**.—The chloro-bridged dimer (*S*)-**1** (4.728 g, 8.15 mmol) and the racemic compound (±)-**I** (4.96 g, 16.3 mmol) were suspended in methanol (80 cm^3) and the mixture stirred for 1 h. The resulting pale yellow solution was filtered and a solution of NH_4PF_6 (0.664 g, 4.08 mmol) in water (5 cm^3) added dropwise. More water (20 cm^3) was added and the mixture stirred overnight. The white precipitate was collected, washed with methanol–water (4:1, 20 cm^3), methanol (20 cm^3) and diethyl ether (20 cm^3), and dried *in vacuo* (3.67 g, 32%). α +168° (589 nm, *c* 0.583 g per 100 cm^3, Me_2CO). The diastereomerically enriched mixture was dissolved in dichloromethane (50 cm^3) and propan-2-ol (25 cm^3) was added to give fine colourless needles of (*S*,*S*)-**2b**. These were collected, washed with chloroform (5 cm^3) and diethyl ether (20 cm^3) and dried *in vacuo* (3.40 g, 93%), m.p. 214 °C (decomp.) (Found: C, 42.6; H, 4.6; N, 2.0; P, 8.8. Calc. for $C_{25}H_{32}AsF_6NP_2Pd$: C, 42.7; H, 4.6; N, 2.0; P, 8.8%). α + 182° (589 nm, *c* 0.92 g per 100 cm^3, Me_2CO). NMR (CD_2Cl_2): ^1H, δ 1.59 (d, 3 H, $^3J_{HH}$ 6.5, CMe), 1.84 (s, 3 H, AsMe), 1.85 (s, 3 H, AsMe), 2.25 (d, 3 H, $^2J_{PH}$ 9.9, PMe), 2.90 (d, 3 H, $^4J_{PH}$ 3.2, NMe), 3.10 (d, 3 H, $^4J_{PH}$ 2.7 Hz, NMe), 4.19 (m, 1 H, C*H*Me), and 6.80–7.90 (m, 13 H, aromatics); ^{31}P-{^1H}, δ 42.81 (s, 1 P).

Isolation of [SP-4-4-(R),(R)]-{2-[1-(*Dimethylamino*)*ethyl*]-*phenyl*-C^1,N}[1-(*dimethylarsino*)-2-(*methylphenylphosphino*)-*benzene*-As,P]*palladium*(II) *Hexafluorophosphate*, (R,R)-**2b**.—To the original mother-liquor from the isolation of complex (*S*,*S*)-**2b** was added a solution of an excess of NH_4PF_6 (1.34 g, 8.2 mmol) in water (10 cm^3). The resulting white precipitate was filtered off, washed with methanol–water (4:1, 20 cm^3), methanol (20 cm^3) and diethyl ether (20 cm^3), and dried *in vacuo* (6.27 g, 55%). α +30° (589 nm, *c* 0.98 g per 100 cm^3, Me_2CO). Crude (*R*,*S*)-**2b** (5.0 g, 7.1 mmol) was heated for 15 min in acetone (80 cm^3) containing hydrochloric acid (10 mol dm^{-3}, 8 cm^3) to give a pale yellow precipitate. The mixture was cooled in ice and then the precipitate was collected, washed with acetone (20 cm^3), acetone–water (1:1, 20 cm^3) and diethyl ether (20 cm^3), and dried *in vacuo* (3.23 g, 94%). The crude dichloropalladium(II) complex (*R*)-**3** (3.23 g, 6.7 mmol) was dissolved in dichloromethane (200 cm^3) and KCN (5.0 g, 76.8 mmol) in water (80 cm^3) was added. Upon decolourisation of the organic layer, the two layers were separated and the aqueous phase extracted with dichloromethane (3 × 30 cm^3). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and the solvent removed under reduced pressure to give crude (*S*)-**I** (2.0 g, 93%). This (2.0 g, 6.58 mmol) and the chloro-bridged dimer (*R*)-**1** (1.91 g, 3.29 mmol) were suspended in methanol (60 cm^3) and the mixture stirred for 1 h. The solution was filtered and NH_4PF_6 (0.268 g, 1.64 mmol) in water (5 cm^3) was added dropwise, followed by more water (15 cm^3). The resulting white precipitate was collected, washed with methanol–water (4:1, 10 cm^3), methanol (10 cm^3) and diethyl ether (10 cm^3), and dried *in vacuo* (0.90 g, 20%). α −178° (589 nm, *c* 0.80 g per 100 cm^3, Me_2CO). An excess of NH_4PF_6 (0.52 g, 3.2 mmol) in water (5 cm^3) was added to the filtrate to give a further crop of crude (*R*,*R*)-**2b** (1.70 g, 37%). α −117° (589 nm, *c* 0.60 g per 100 cm^3, Me_2CO). Addition of water (80 cm^3) to the filtrate yielded more white precipitate (1.50 g, 32%). α −5.0° (589 nm, *c* 0.80 g per 100 cm^3, Me_2CO). The second crop of crude (*R*,*R*)-**2b** (1.70 g; α −117°) was twice recrystallised from dichloromethane–propan-2-ol to give (*R*,*R*)-**2b** as colourless plates (1.07 g, 63%). α −180° (589 nm, *c* 0.80 g per 100 cm^3, Me_2CO). This material was combined with the first crop of crude (*R*,*R*)-**2b** (1.70 g; α −178°) and the complex (2.77 g) recrystallised from dichloromethane–propan-2-ol to afford pure (*R*,*R*)-**2b** (1.86 g, 67%), m.p. 214 °C (decomp.) (Found: C, 42.4; H, 4.4; N, 2.0. Calc. for $C_{25}H_{32}AsF_6NP_2Pd$: C, 42.7; H, 4.6; N, 2.0%). α −182° (589 nm, *c* 0.90 g per 100 cm^3, Me_2CO). ^1H NMR and ^{31}P-{^1H} NMR (CD_2Cl_2): identical with those recorded for the enantiomeric complex (*S*,*S*)-**2b**.

Preparation of [SP-4-3-(S)]-*Dichloro*[1-(*dimethylarsino*)-2-(*methylphenylphosphino*)*benzene*-As,P]*palladium*(II), (S)-**3**.—The diastereomerically pure complex (*S*,*S*)-**2b** (2.17 g, 3.08 mmol) was heated for 20 min in acetone (20 cm^3) containing hydrochloric acid (10 mol dm^{-3}, 5 cm^3). The resulting pale yellow precipitate was collected, washed with acetone (10 cm^3), acetone–water (1:1, 10 cm^3) and diethyl ether (10 cm^3), and dried *in vacuo* (1.30 g, 88%), m.p. 278 °C (Found: C, 37.0; H, 3.7. Calc. for $C_{15}H_{18}AsCl_2PPd$: C, 37.4; H, 3.8%). α −31° (589 nm, *c* 0.97 g per 100 cm^3, CH_2Cl_2). NMR (CD_2Cl_2): ^1H, δ 1.97 (s, 3 H, AsMe), 2.06 (s, 3 H, AsMe), 2.38 (d, 3 H, $^2J_{PH}$ 12 Hz, PMe) and 7.45–7.86 (m, 9 H, aromatics); ^{31}P-{^1H}, δ 60.5 (s, 1 P).

The [*SP*-4-3-(*R*)] enantiomer was prepared in the same way in 85% yield, m.p. 276–278 °C (Found: C, 37.4; H, 3.7. Calc. for $C_{15}H_{18}AsCl_2PPd$: C, 37.4; H, 3.8%). α +31° (589 nm, *c* 0.80 g per 100 cm^3, CH_2Cl_2). ^1H NMR and ^{31}P-{^1H} NMR (CD_2Cl_2): identical with those recorded for the enantiomeric complex (*S*)-**3**.

Preparation of(R)-$(-)_{589}$-1-(*Dimethylarsino*)-2-(*methylphenylphosphino*)*benzene*, (R)-**I**.—A solution of KCN (2.0 g, 30.7 mmol) in water (20 cm^3) was added to a solution of the dichloropalladium(II) complex (*S*)-**3** (1.30 g, 2.7 mmol) in dichloromethane (50 cm^3) and the mixture vigorously stirred for 2 h. The organic phase was separated and the aqueous layer extracted with more dichloromethane (3 × 20 cm^3). The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to give pure (*R*)-**I** (0.68 g, 95%). α +32° (589 nm, *c* 0.80 g per 100 cm^3, CH_2Cl_2). ^1H NMR and ^{31}P-{^1H} NMR (CD_2Cl_2): identical with those recorded for the racemic compound.

The (*S*) enantiomer was prepared in the same manner in 98% yield, α −32° (589 nm, *c* 0.82 g per 100 cm^3, CH_2Cl_2).

Preparation of [SP-4-4-(R),(S)]-{2-[1-(*Dimethylamino*)*ethyl*]*phenyl*-C^1,N}[1-(*dimethylarsino*)-2-(*methylphenylphosphino*)*benzene*-As,P]*palladium*(II) *Hexafluorophosphate*, (R,S)-**2b**.—Stirring of a suspension of the chloro-bridged dimer (*S*)-**I** (0.32 g, 0.55 mmol) and (*S*)-**I** (0.34 g, 1.1 mmol) in methanol (10 cm^3) gave a colourless solution of the diastereomeric chloride salt (*R*,*S*)-**2a**. An aqueous solution of NH_4PF_6 (0.36 g, 2.2 mmol in 2 cm^3 water) was added dropwise, followed by more water (10 cm^3). The resulting white precipitate was collected, washed with methanol–water (4:1, 5 cm^3), methanol–diethyl ether (1:4, 5 cm^3) and diethyl ether (10 cm^3), and dried *in vacuo* (0.58 g, 74%), m.p. 210 °C (decomp.) (Found: C, 42.6; H, 4.6; N, 1.9. Calc. for $C_{25}H_{32}AsF_6NP_2Pd$: C, 42.7; H, 4.6; N, 2.0%). α −38° (589 nm, *c* 0.53 g per 100 cm^3, Me_2CO). NMR (CD_2Cl_2): ^1H, δ 1.76 (d, 3 H, $^3J_{HH}$ 6.4, CMe), 1.82 (s, 3 H, AsMe), 1.88 (s, 3 H, AsMe), 2.23 (d, 3 H, $^2J_{PH}$ 10.3, PMe), 2.89 (br s, 3 H, NMe), 3.14 (d, 3 H, $^4J_{PH}$ 3.0, NMe), 3.72 (m, 1 H, C*H*Me) and 6.62–7.90 (m, 13 H, aromatics); ^{31}P-{^1H}, δ 44.81 (s, 1 P).

X-Ray Crystallography for the Complex (S,S)-**2b**.—*Crystal data*. $C_{25}H_{32}AsF_6NP_2Pd$, M = 703.79, monoclinic, space group $P2_1$, a = 10.340(2), b = 11.741(3), c = 11.856(2) Å, β = 97.67(1)°, U = 1426.5(4) $Å^3$ (by least-squares analysis of the setting angles of 25 reflections 37 < 2θ < 45°), Mo-Kα radiation (λ = 0.710 69 Å) with a graphite monochromator, Z = 2, D_c = 1.638 g cm^{-3}, $F(000)$ = 704, specimen 0.17 × 0.24 × 0.19 mm, μ(Mo-Kα) = 19.7 cm^{-1}.

Data collection and processing. A unique data set was measured at 295(1) K using the ω–2θ scan technique to a maximum 2θ value of 50° on a Rigaku AFC6S diffractometer. Scans of (1.1 + 0.3 tan θ)° were made at a speed of 4.0° min^{-1} (in ω). The weak reflections [$I < 10.0\sigma(I)$] were rescanned (maximum of four scans) and the counts accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of each reflection. The ratio of peak counting time to background counting time was 4:1. The number of unique reflections was 2662. The intensities of three representative reflections were measured after every 150. These showed a decrease in intensity of 1% during data collection and hence the data were corrected accordingly. An analytical absorption correction was applied which resulted in transmission factors ranging from 0.701 to 0.793.

Structure analysis and refinement. The structure was solved by Patterson and Fourier-difference techniques. Fluorine atoms in one equatorial plane of the hexafluorophosphate anion were found to be disordered. These were refined as eight sites of half-occupancy with isotropic displacement factors constrained to be equal, with Waser restraints being imposed on distances and angles between sites.[11] All other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically generated positions but were not refined. The absolute configuration was assigned on the basis of the known chirality of the resolving agent and was confirmed by refinement of a Flack absolute-configuration parameter [final value = 0.02(2)]. Refinement was continued until all shift/error ratios were < 0.3:1. The final cycle of full-matrix least-squares refinement was based on 2164 observed reflections [$I > 3.00\sigma(I)$] and 313 parameters and converged with final R and R' values of 0.035 and 0.044, respectively. The maximum and minimum peaks on the final Fourier-difference map corresponded to 0.65(5) and −0.54(5) e $Å^{-3}$, respectively. Data reduction and refinement computations were performed with XTAL 3.2.[12] Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref. 13.

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

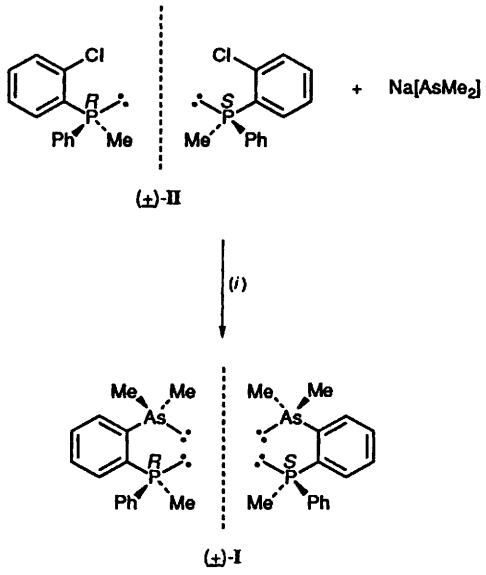
Results and Discussion

Synthesis and Resolution of Compound (±)-**I**.—The asymmetric bidentate compound (±)-1-(dimethylarsino)-2-(methylphenylphosphino)benzene (±)-**I** was prepared by the addition of sodium dimethylarsenide in thf to a solution of (±)-(2-chlorophenyl)methylphenylphosphine (±)-**II**, in the same solvent at −78 °C (Scheme 1). After the addition was completed the reaction temperature was raised to −20 ± 5 °C and maintained for 48 h in order to optimise the formation of (±)-**I**. Four major components were identified in the crude reaction mixture, namely (±)-**I**, unreacted (±)-**II**, tetramethyldiarsane and methyldiphenylphosphine. An equimolar mixture of (±)-**I** and (±)-**II** was isolated by fractional distillation of the crude product. These were separated by reaction with hexaaquanickel(II) perchlorate in acetone and gave a diastereomeric mixture of complexes of the type [Ni{(±)-**I**}$_2$]-[ClO_4]$_2$. The asymmetric bidentate ligand (±)-**I** was liberated quantitatively from the diastereomeric mixture of nickel(II) complexes upon treatment with aqueous potassium cyanide. Distillation gave pure (±)-**I** as a colourless, viscous liquid in 48% yield. Unreacted (±)-**II** was recovered from the mother-liquor of the isolated nickel(II) complexes in 33% yield, after distillation.

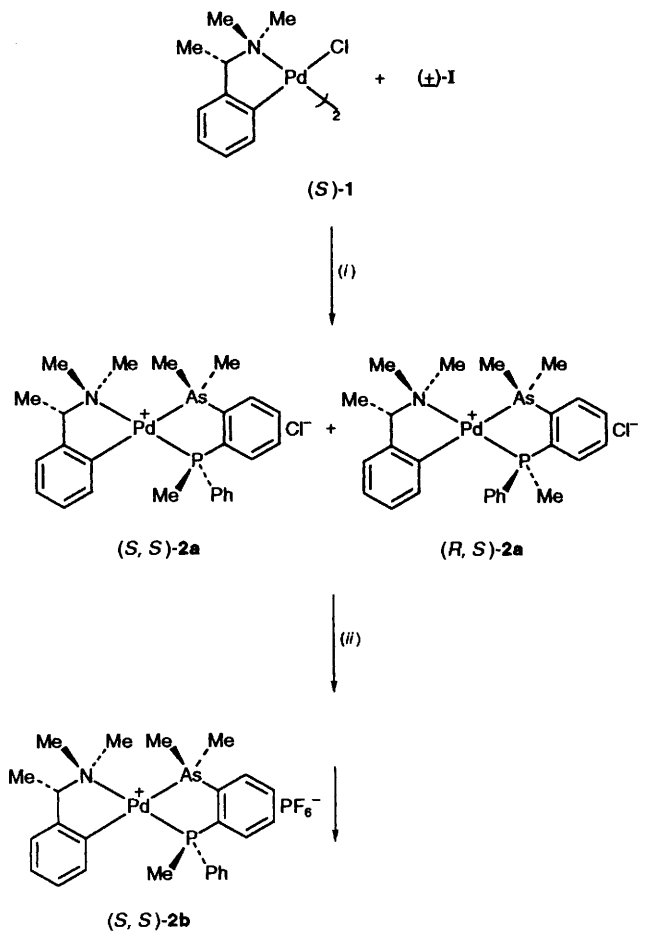
Reactions between sodium dimethylarsenide and substituted aryl halides are renowned for giving products in low yields.[2,14] Indeed, no evidence for the formation of (±)-**I** was found when the reaction between sodium dimethylarsenide and (±)-**II** in thf was carried out at 50 °C. The sole products of the reaction were tetramethyldiarsane and methyldiphenylphosphine. This is only consistent with reduction of the chloro group of (±)-**II** by sodium dimethylarsenide [equation (1)].

$$(\pm)\text{-II} + Na[AsMe_2] + H^+ \longrightarrow PMePh_2 + \tfrac{1}{2}(Me_2As)_2 + Na^+ + Cl^- \quad (1)$$

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 (*R*)- or (*S*)-dimethyl(1-phenylethyl)amine. A pair of diastereomeric chloride salts, *viz*. (*R*,*S*)- and (*S*,*S*)-**2a**, was produced in a bridge-splitting reaction involving (±)-**I** and di-μ-chloro-bis{(*S*)-2-[1-(dimethylamino)ethyl]phenyl-C^1,*N*}dipalladium(II) (*S*)-**1**, in methanol (Scheme 2). The addition of 1 equivalent of aqueous NH_4PF_6 to this solution gave a mixture of diastereomeric hexafluorophosphate salts enriched in (*S*,*S*)-**2b**. Fractional crystallisation of the dia-



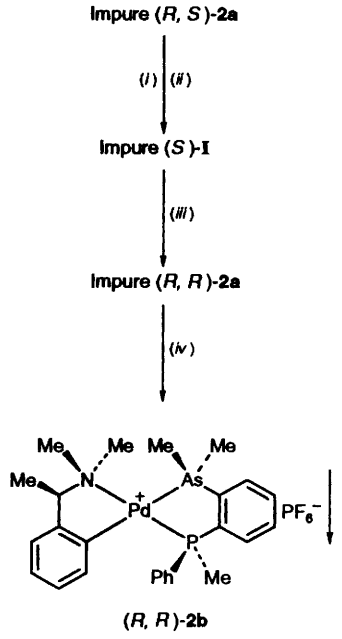
Scheme 1 (*i*) thf, −78 °C; −20 ± 5 °C, 48 h



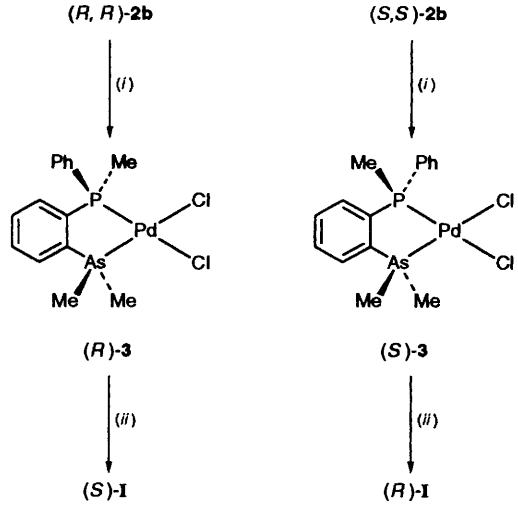
Scheme 2 (*i*) MeOH; (*ii*) NH_4PF_6 in water

stereomeric mixture from dichloromethane–propan-2-ol gave fine colourless needles of pure (*S*,*S*)-**2b**, α −182° (589 nm, acetone). The addition of an excess of aqueous NH_4PF_6 to the mother-liquor gave a mixture of diastereomeric hexafluorophosphate salts enriched in (*R*,*S*)-**2b**. Numerous attempts to separate this diastereomeric mixture by fractional crystallisation from a range of solvent systems were unsuccessful. Instead, partially resolved (±)-**I** was liberated from the mixture by reaction with concentrated hydrochloric acid in acetone followed by treatment of the isolated dichloropalladium(II) complex with aqueous potassium cyanide (Scheme 3). Resolution of the liberated ligand was achieved in a bridge-splitting reaction involving partially resolved (±)-**I** and the dimer (*R*)-**1** in methanol. The addition of an excess of aqueous NH_4PF_6 to the solution gave a mixture of diastereomeric hexafluorophosphate salts enriched in (*R*,*R*)-**2b**. The diastereomeric mixture was twice recrystallised from dichloromethane–propan-2-ol to give pure (*R*,*R*)-**2b**, α −182° (589 nm, acetone). Liberation of the optically active antipodes of (±)-**I** from (*S*,*S*)- and (*R*,*R*)-**2b** was accomplished as shown in Scheme 4. Treatment of (*R*,*R*)- or (*S*,*S*)-**2b** in acetone with concentrated hydrochloric acid gave the respective dichloropalladium(II) complexes (*R*)- and (*S*)-**3**, α ±31° (589 nm, dichloromethane). Reaction of (*R*)- or (*S*)-**3** with aqueous potassium cyanide gave the optically pure compounds (*S*)- and (*R*)-**I**, respectively, α ±32° (589 nm, dichloromethane). Diastereomerically pure (*R*,*S*)-**2b** was subsequently prepared from (*S*)-**I** and the chloro-bridged dimer (*S*)-**1** in methanol by the addition of aqueous NH_4PF_6, α −38° (589 nm, acetone).

Crystal Structure of Complex (S,S)-**2b**.—The absolute configuration of (*R*)-**I** was assigned by a crystal-structure



Scheme 3 (*i*) Acetone, concentrated HCl; (*ii*) KCN in water; (*iii*) (*R*)-**1**, MeOH; (*iv*) NH_4PF_6 in water



Scheme 4 (*i*) Acetone, concentrated HCl; (*ii*) KCN in water

determination of the internally diastereomeric complex (*S*,*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 palladium atom has a distorted square-planar co-ordination geometry with the donor atoms As, P(1), N and C(1) being essentially coplanar (maximum deviation from least-squares plane 0.0125 Å) and Pd 0.0520 Å from the least-squares plane. The angles at the Pd atom are As–Pd–P(1) 85.90(7), As–Pd–N 101.0(2), P(1)–Pd–C(1) 92.8(2) and N–Pd–C(1) 80.2(3)°. The absolute configuration of the phosphorus stereocentre P(1) is *S* and that of the carbon stereocentre C(1) is *S*. Furthermore, the methylphenylphosphino group of the asymmetric bidentate ligand was found to be *trans* to the nitrogen atom of the resolving agent. A similar arrangement was observed in related internally diastereomeric palladium(II) complexes containing an orthometallated optically active amine and the asymmetric bidentate ligands (*S*)-(+)$_{589}$-1-(diphenylphosphino)-2-(methylphenylphosphino)-ethane,[15] (*S*)-(−)$_{589}$-1-(diphenylphosphino)-2-(methylphenylphosphino)benzene[16] and (*R*)-(−)$_{589}$-methylphenyl(8-quinolyl)phosphine.[17]

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

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd	0.677 20(6)	0.500 00	0.765 92(5)	C(17)	0.971(1)	0.680(1)	0.728(1)
As	0.857 89(9)	0.559 5(1)	0.667 19(8)	C(18)	0.982(1)	0.450(1)	0.623(1)
P(1)	0.547 6(2)	0.566 5(2)	0.614 1(2)	C(19)	0.451 4(9)	0.690 0(8)	0.639 3(7)
N	0.780 4(8)	0.423 7(9)	0.916 2(7)	C(20)	0.512(1)	0.776 3(9)	0.709 1(8)
C(1)	0.523 0(9)	0.443 2(9)	0.841 7(7)	C(21)	0.444(1)	0.874(1)	0.729(1)
C(2)	0.395 6(9)	0.483(1)	0.834 6(8)	C(22)	0.317(1)	0.886(1)	0.681(1)
C(3)	0.308(1)	0.431(1)	0.898 3(9)	C(23)	0.259(1)	0.804(1)	0.613(1)
C(4)	0.346(1)	0.346(1)	0.968 3(9)	C(24)	0.323(1)	0.704(1)	0.591(1)
C(5)	0.472(1)	0.303(1)	0.977 9(8)	C(25)	0.438 7(9)	0.462 0(8)	0.541 9(8)
C(6)	0.561(1)	0.352 7(9)	0.918 6(7)	P(2)	0.863 9(3)	1.032 2(3)	0.747 0(3)
C(7)	0.703(1)	0.318(1)	0.927 6(8)	F(1)	1.002 6(7)	0.981 6(9)	0.738 7(7)
C(8)	0.747(1)	0.246(1)	1.033(1)	F(2)	0.727 3(8)	1.080 8(9)	0.751 0(9)
C(9)	0.780(1)	0.501(2)	1.014 3(8)	F(3)	0.880(1)	1.128(2)	0.655(1)
C(10)	0.919(1)	0.393(1)	0.905(1)	F(4)	0.922(1)	1.111(1)	0.847(1)
C(11)	0.777 3(9)	0.618 1(9)	0.522 8(8)	F(5)	0.849(1)	0.930(2)	0.841(1)
C(12)	0.847(1)	0.658(1)	0.438 4(9)	F(6)	0.806(1)	0.949(1)	0.649(1)
C(13)	0.783(1)	0.697(1)	0.339 3(9)	F(7)	0.849(1)	1.042(1)	0.611(1)
C(14)	0.650(1)	0.696(1)	0.317 5(9)	F(8)	0.929(1)	1.155(2)	0.757(2)
C(15)	0.577(1)	0.657 5(9)	0.401 4(7)	F(9)	0.881(1)	1.027(1)	0.877(1)
C(16)	0.639 9(9)	0.616 9(8)	0.502 0(7)	F(10)	0.798(1)	0.912(2)	0.734(1)

Atoms F(3)–F(10) have occupancy 0.5 and a common isotropic displacement factor.

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

Pd–As	2.436(1)	Pd–P(1)	2.237(2)
Pd–N	2.147(8)	Pd–C(1)	2.044(10)
As–Pd–P(1)	85.90(7)	As–Pd–N	101.0(2)
N–Pd–C(1)	80.2(3)	P(1)–Pd–N	172.7(2)
P(1)–Pd–C(1)	92.8(2)	As–Pd–C(1)	176.7(3)

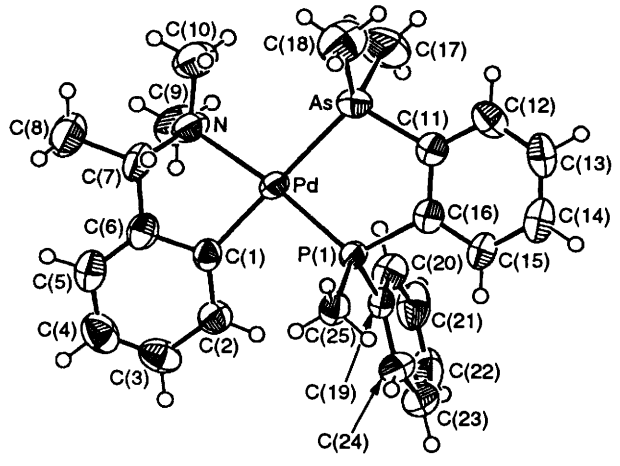
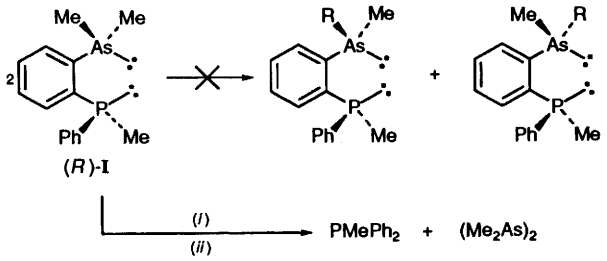


Fig. 1 Molecular structure of the cation of complex (*S*,*S*)-**2b**

NMR Spectra.—The cation in complex (*S*,*S*)-**2b** retains the same stereochemistry in solution. The ^{1}H NMR spectra of the internally diastereomeric complexes (*R*,*S*)-, (*R*,*R*)- and (*S*,*S*)-**2b** in CD_2Cl_2 were consistent with the stereogenic phosphorus centre being *trans* to the nitrogen atom of the orthometallated optically active amine. The methine proton and the non-equivalent NMe groups in these complexes are coupled to the phosphorus atom *trans* to them. A similar stereochemical arrangement has been observed in solution for related palladium(II) complexes containing the enantiomers of (*R**,*R**)- and (*R**,*S**)-1-(methylphenylarsino)-2-(methylphenylphosphino)benzene.[3]

No change was observed in the spectra recorded for complex (*S*,*S*)-**2b** in CD_2Cl_2 or $(CD_3)_2SO$ when continually monitored over 1 week. A similar result was observed for related internally diastereomeric palladium(II) complexes containing orthometallated (*R*)-dimethyl(1-phenylethyl)amine and the enantiomers of (*R**,*R**)-1-(methylphenylarsino)-2-(methylphenylphosphino)benzene.[3] In contrast, analogous compounds containing the same optically active amine (or its antipode) and the enantiomers of (*R**,*S**)-1-(methylphenylarsino)-2-(methylphenylphosphino)benzene[3] and a range of asymmetric bidentate ligands with a single arsenic or phosphorus stereocentre and a non-stereogenic N,[17–19] P[15,16] or S[20] atom underwent facile *cis-trans* isomerism in solution. Indeed, only (±)-1-(diphenylphosphino)-2-(methylphenylphosphino)-benzene could be successfully resolved using (*R*)- or (*S*)-dimethyl(1-phenylethyl)amine as the resolving agent.[16] In this case, *cis-trans* isomerism of the internally diastereomeric palladium(II) complexes was only observed in the polar solvent $(CD_3)_2SO$. The other chiral bidentate ligands, however, were successfully resolved using (*R*)-dimethyl[1-(1-naphthyl)ethyl]-amine as the resolving agent. Here, facile *cis-trans* isomerism was only observed for complexes containing the enantiomers of (±)-1-(diphenylphosphino)-2-(methylphenylphosphino)-ethane.[15] Isomerism in internally diastereomeric palladium(II) complexes containing an orthometallated optically active amine and a chiral bidentate ligand is believed to be intermolecular in nature and to proceed *via* labilisation of the Pd–N (amine) bond or the bond *trans* to the orthometallated carbon atom.[15] Furthermore, isomerism is most prevalent in complexes containing orthometallated (*R*)- or (*S*)-dimethyl-(1-phenylethyl)amine as these are invariably less kinetically inert than their counterparts containing orthometallated (*R*)-dimethyl[1-(1-naphthyl)ethyl]amine.

Chemoselective Cleavage Reactions.—Chemoselective cleavage of a methyl group from the dimethylarsino moiety of compound (*R*)- or (*S*)-**I**, followed by alkylation with RX (X = halide), should give rise to a pair of diastereomers, the separation of which would provide a general synthetic route to optically active asymmetric bidentate compounds containing two stereogenic centres (Scheme 5). Evidence for the chemoselective cleavage of a methyl group from (±)-**I** has been found in liquid ammonia in the presence of sodium metal. The secondary arsine (±)-1-(methylarsino)-2-(methylphenylphosphino)benzene was formed upon hydrolysis of the reaction mixture, however the reaction was clearly not selective as a number of other compounds including tetramethyldiarsane, methyldiphenylphosphine, methylphenylphosphine, *etc.*, were also identified amongst the reaction products. The reaction



Scheme 5 (*i*) 2 Li in thf; (*ii*) NH_4Cl in water

between (±)-**I** and lithium in tetrahydrofuran, on the other hand, was much more selective. Hydrolysis of the reaction mixture gave tetramethyldiarsane and methyldiphenylphosphine as the sole products (Scheme 5). This result, however, is only consistent with selective cleavage of the dimethylarsino group from (±)-**I**.

Conclusion

Relatively few studies on the chemoselective cleavage of alkyl or aryl groups from tertiary arsines or phosphines have been reported.[2,21] Indeed, the chemoselective cleavage of a single methyl group from 1,2-phenylenebis(dimethylarsine) by reaction with sodium in liquid ammonia is a rare example of such a reacton involving a tertiary arsine.[2] Our primary interest in studying chemoselective cleavage reactions of bidentate tertiary arsines and phosphines, in particular, lies in the role of the resulting arsenides or phosphides as potential precursors to chiral quadridentate compounds containing stereogenic arsenic- or phosphorus-donor atoms. For example, we have recently reported on the completely stereoselective synthesis of the chiral quadridentate compound (*R**,*S**)-(±)-1-[(2-aminophenyl)methylphosphino]-2-[(2-dimethylarsinophenyl)methylarsino]benzene from the reaction of (±)-(2-aminophenyl)(2-chlorophenyl)methylphosphine with sodium (2-dimethylarsinophenyl)methylarsenide.[22] Furthermore, the compound was shown to bind to cobalt(III) exclusively in the *cis*-α configuration. This result augurs well for the role of the optically active antipodes of the quadridentate compound as potential chiral auxiliaries in enantioselective synthesis. The optically active compounds (*R*)- and (*S*)-**I** are also seen as potential chiral auxiliaries in asymmetric synthesis and catalysis.

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