Optically Active Asymmetric Bidentate Ligands. Crystal and Molecular Structure of [*SP*-4-4-(*R*),(*R*)]-$(-)_{589}$-{1-[1-(Dimethylamino)ethyl]naphthyl-*C*^{2},*N*}[1-(diphenylphosphino)-2-(methylphenylphosphino)ethane-*P*,*P*′]-palladium(II) Hexafluorophosphate†

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Asymmetric bidentate (±)-1-(diphenylphosphino)-2-(methylphenylphosphino)ethane has been resolved by the separation by fractional crystallisation of internally diastereomeric palladium(II) complexes containing the racemic ligand and orthometallated (*R*)-dimethyl[1-(1-naphthyl)ethyl]amine. The absolute configuration of the *S* enantiomer of the ligand has been assigned by a crystal structure determination of the least-soluble diastereomeric palladium(II) complex (*R*,*R*)-$(-)_{589}$-{1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},*N*}[1-(diphenylphosphino)-2-(methylphenylphosphino)ethane-*P*,*P*′]-palladium(II) hexafluorophosphate. The X-ray analysis also showed the methylphenylphosphino group of the di(tertiary phosphine) to be *trans* to the amino group of the resolving agent. This *trans* arrangement is retained in dichloromethane but facile intermolecular *cis–trans* isomerisation occurs in more polar solvents. Chemoselective cleavage of a phenyl group from the diphenylphosphino moiety of the free diphosphine occurred in the presence of lithium in tetrahydrofuran to give a separable 1 : 1 diastereomeric mixture of (*R**,*R**)- and (*R**,*S**)-1-(ethylphenylphosphino)-2-(methylphenylphosphino)ethane upon further reaction with bromoethane.

Optically active di(tertiary phosphines) have been highly successful as chiral auxiliaries in enantioselective catalysis.[1] Numerous compounds of this type have been synthesised the majority of which have diphenylphosphino donor groups, the chirality residing in the backbone. Indeed, (*R*,*R*)-1,2-bis-[(2-methoxyphenyl)phenylphosphino]ethane, L^1,[2] and its analogues[3] and (*R*,*R*)-1,2-phenylenebis(methylphenylphosphine), L^2,[4] are amongst the few examples of optically active di(tertiary phosphines) containing stereogenic phosphorus donor atoms to have been successfully used as chiral auxiliaries in asymmetric catalysis. Synthetic routes to L^1 and its analogues rely on the coupling of enantiomerically pure tertiary phosphine oxides[2,3] or phosphinoboranes.[5,6] In recent times significant advances in the synthesis of such precursors have been made by Brown,[7] Juge[6,8] and Imamoto[3,5,9] and their co-workers, allowing much easier access to compounds of this type. The di(tertiary phosphine), L^2, on the other hand, was prepared in an enantiomerically pure form *via* the separation by fractional crystallisation of a pair of internally diastereomeric palladium(II) complexes containing the racemic ligand and an optically active orthometallated amine.[10]

The role of asymmetric di(tertiary phosphines) containing dissimilar phosphorus donor atoms in enantioselective catalysis has received far less attention. Indeed, the only report of such a ligand being used in this manner was the reduction of prochiral enamides using a rhodium(I) catalyst incorporating diastereomerically pure 1-(diphenylphosphino)-2-(menthylphenylphosphino)ethane.[11] We recently reported on the synthesis and resolution of (±)-1-(diphenylphosphino)-2-(methylphenylphosphino)benzene, the first example of an enantiomerically pure asymmetric di(tertiary phosphine) containing a single stereogenic phosphorus donor atom.[12] The use of optically active bidentate compounds containing dissimilar donors has important implications in asymmetric catalysis since such compounds are capable of exercising stereoelectronic control over the reactions of co-ordinated substrates. Compounds containing a single phosphorus donor atom have, until very recently, had only modest success as chiral auxiliaries in asymmetric catalysis presumably as a result of the kinetic lability of the resulting transition metal-based catalysts.[13] The unsymmetrical tertiary phosphine (*S*)-[(1-isoquinolyl)naphthyl]diphenylphosphine[14] and certain optically active oxazolylphosphines[15] have been successfully used as chiral auxiliaries in the catalytic hydroboration of vinylarenes and the palladium(II)-catalysed substitution of allylic acetates, respectively. The present article describes the resolution and chemoselective cleavage reactions of (±)-1-(diphenylphosphino)-2-(methylphenylphosphino)ethane, an asymmetric di(tertiary phosphine) that should give rise to kinetically inert transition metal-based catalysts.

Experimental

Procedures and Materials.—Reactions involving air-sensitive reagents 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 diphenylvinylphosphine,[16] methylphenyl-

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† *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.

phosphine,[10] (−)$_{589}$-di-μ-chloro-bis{(*R*)-1-[1-(dimethylamino)ethyl]naphthyl-C^2,*N*}dipalladium(II), (*R*)-**1**,[17] and di-μ-chloro-bis{2-[(dimethylamino)methyl]phenyl-C^1,*N*}dipalladium(II)[18] were prepared by published procedures.

Synthesis of (±)-1-(*Diphenylphosphino*)-2-(*methylphenylphosphino*)*ethane*, (±)-dpmpe.—This was based on a modified literature procedure.[19] To a solution of methylphenylphosphine (5.90 g, 47.5 mmol) in benzene (200 cm^3) was added diphenylvinylphosphine (10.09 g, 47.5 mmol) and potassium *tert*-butoxide (*ca.* 2 g). The resulting orange solution was refluxed for 15 h. The reaction mixture was washed with water (2 × 100 cm^3) and the washings extracted with benzene (2 × 100 cm^3). The combined organic layers were dried over anhydrous MgSO$_4$, filtered and the solvent removed under reduced pressure. Distillation of the crude product gave (±)-dpmpe as a colourless, viscous liquid which slowly crystallised on standing (12.5 g, 78%), b.p. 160 °C at 0.05 mmHg, m.p. 37 °C. NMR (CDCl$_3$): ^{1}H, δ 1.29 (d, 3 H, $^2J_{PH}$ 3.0 Hz, PMe), 1.71 (m, 2 H, CH$_2$PMePh), 2.03 (m, 2 H, CH$_2$PPh$_2$) and 7.25–7.45 (m, 15 H, aromatics); ^{31}P-{^{1}H}, δ −30.2 (d, 1 P, $^3J_{PP}$ 26.0, PMePh) and −12.1 (d, 1 P, $^3J_{PP}$ 26.0 Hz, PPh$_2$). *m*/*z* 336, *M*$^+$; and 321, [*M* − Me]$^+$.

Resolution of (±)-*dpmpe. Formation and Separation of Internally Diastereomeric Complexes.* [SP-4-4-(R),(R)]- *and* [SP-4-3-(R),(R)]-{1-[1-(*Dimethylamino*)*ethyl*]*naphthyl*-C^2,N}-[1-(*diphenylphosphino*)-2-(*methylphenylphosphino*)*ethane*-P,P′]*palladium*(II) *Hexafluorophosphate*, (*R*,*R*)-**2a** *and* **-2b**.—A mixture of (±)-dpmpe (5.33 g, 15.8 mmol) and complex (*R*)-**1** (5.54 g, 7.92 mmol) in methanol (100 cm^3) was stirred until all the solids had dissolved. The reaction mixture was filtered and 1 equivalent of NH$_4$PF$_6$ (1.29 g, 7.92 mmol) in water (10 cm^3) was added dropwise. More water (50 cm^3) was added. The resulting white precipitate was filtered off, washed with methanol–water (1:1, 50 cm^3), diethyl ether–methanol (4:1, 75 cm^3) and diethyl ether (50 cm^3), and then dried *in vacuo* (6.0 g, 51%), α −49.7° (589 nm, *c* 1.00 g per 100 dm^3, Me$_2$CO). Recrystallisation from acetone (40 cm^3) by dropwise addition of diethyl ether gave a 2:1 diastereomeric mixture of complexes (*R*,*R*)-**2a** and **-2b** (4.2 g, 70%), α −2.9° (589 nm, *c* 1.00 g per 100 dm^3, Me$_2$CO). NMR [(CD$_3$)$_2$CO]: ^{1}H, δ 1.88 (d, 3 H, $^3J_{HH}$ 6.3, CMe of **2b**), 1.97 (d, 3 H, $^3J_{HH}$ 6.3, CMe of **2a**), 2.28 (d, 3 H, $^2J_{PH}$ 11.0, PMe of **2b**), 2.28 (m, 2 H, CH$_2$ of **2b**), 2.29 (d, 3 H, $^2J_{PH}$ 11.2 Hz, PMe of **2a**), 2.29 (m, 2 H, CH$_2$ of **2a**), 2.68 (m, 2 H, CH$_2$ of **2b**), 2.69 (br s, 3 H, NMe of **2a**), 2.70 (br s, 3 H, NMe of **2b**), 2.71 (m, 2 H, CH$_2$ of **2a**), 2.84 (br s, 3 H, NMe of **2a**), 2.84 (s, 3 H, NMe of **2b**), 4.75 (m, 1 H, C*H*Me of **2a**), 4.75 (m, 1 H, C*H*Me of **2b**) and 6.90–8.45 (m, 42 H, aromatics of **2a** and **2b**); ^{31}P-{^{1}H}, δ 31.3 (d, 1 P, $^2J_{PP}$ 25.8, P of **2b**), 44.7 (d, 1 P, $^2J_{PP}$ 25.2, P of **2a**), 54.1 (d, 1 P, $^2J_{PP}$ 25.2, P of **2a**) and 63.2 (d, 1 P, $^2J_{PP}$ 25.8 Hz, P of **2b**). Recrystallisation of the 2:1 diastereomeric mixture of (*R*,*R*)-**2a** and **-2b** from acetone–propan-2-ol gave white fibrous needles of (*R*,*R*)-**2a** (0.57 g, 14%), m.p. 240 °C (Found: C, 53.9; H, 4.9; N, 1.8. Calc. for C$_{35}$H$_{38}$F$_6$NP$_3$Pd: C, 53.5; H, 4.9; N, 1.8%). α −29.0° (589 nm, *c* 100 g per 100 dm^3, Me$_2$CO). NMR: ^{1}H [(CD$_3$)$_2$CO], δ 1.97 (d, 3 H, $^3J_{HH}$ 6.3, CMe), 2.29 (d, 3 H, $^2J_{PH}$ 11.2, PMe), 2.29 (m, 2 H, C*H*$_2$PMePh), 2.69 (br s, 3 H, NMe), 2.71 (m, 2 H, C*H*$_2$PPh$_2$), 2.84 (s, 3 H, NMe), 4.75 (m, 1 H, C*H*Me) and 7.08–8.15 (m, 21 H, aromatics); (CD$_2$Cl$_2$), δ 1.82 (m, 1 H, CH*H*PMePh), 1.96 (d, 3 H, $^3J_{HH}$ 6.3, CMe), 2.05 (m, 1 H, C*H*HPMePh), 2.13 (d, 3 H, $^2J_{PH}$ 10.7, PMe), 2.48 (m, 2 H, C*H*$_2$PPh$_2$), 2.55 (d, 3 H, $^4J_{PH}$ 1.6 Hz, NMe), 2.61 (br s, 3 H, NMe), 4.49 (m, 1 H, C*H*Me) and 7.05–8.15 (m, 21 H, aromatics); ^{31}P-{^{1}H} [(CD$_3$)$_2$CO], δ 44.7 (d, 1 P, $^2J_{PP}$ 25.2, P) and 54.1 (d, 1 P, $^2J_{PP}$ 25.2 Hz, P).

Attempted Isolation of [SP-4-4-(S),(R)]- *and* [SP-4-3-(S),(R)]-{1-[1-(*Dimethylamino*)*ethyl*]*naphthyl*-C^2,N}[1-(*diphenylphosphino*)-2-(*methylphenylphosphino*)*ethane*-P,P′]*palladium*(II) *Hexafluorophosphate*, (*S*,*R*)-**2a** *and* **-2b**.—Addition of an excess of aqueous ammonium hexafluorophosphate (2.6 g, 15.8 mmol in 20 cm^3 of water) to the original filtrate from the isolation of complexes (*R*,*R*)-**2a** and **-2b** gave a white precipitate which was filtered off, washed with methanol–water (1:1, 50 cm^3), diethyl ether–methanol (4:1, 75 cm^3) and diethyl ether (50 cm^3), and then dried *in vacuo* (5.8 g, 49%). Several recrystallisations from acetone–propan-2-ol gave a 60:30:7:3 diasteromeric mixture of (*S*,*R*)-**2b**, (*S*,*R*)-**2a**, (*R*,*R*)-**2a** and (*R*,*R*)-**2b**, respectively, which could not be further separated by fractional crystallisation from a range of solvent systems (2.0 g, 35%). α +12.9° (589 nm, *c* 1.00 g per 100 dm^3, Me$_2$CO). ^{31}P-{^{1}H} NMR [(CD$_3$)$_2$CO]: δ 29.6 [d, 1 P, $^2J_{PP}$ 24.2, (*S*,*R*)-**2b**], 31.3 [d, 1 P, $^2J_{PP}$ 25.8, (*R*,*R*)-**2b**], 44.5 [d, 1 P, $^2J_{PP}$ 24.0, (*S*,*R*)-**2a**], 44.7 [d, 1 P, $^2J_{PP}$ 25.2, (*R*,*R*)-**2a**], 48.3 [d, 1 P, $^2J_{PP}$ 24.0, (*S*,*R*)-**2a**], 54.1 [d, 1 P, $^2J_{PP}$ 25.2, (*R*,*R*)-**2a**], 63.2 [d, 1 P, $^2J_{PP}$ 25.8, (*R*,*R*)-**2b**] and 63.4 [d, 1 P, $^2J_{PP}$ 24.2 Hz, (*S*,*R*)-**2b**].

Preparation of [SP-4-3-(R)]-*Dichloro*[1-(*diphenylphosphino*)-2-(*methylphenylphosphino*)*ethane*-P,P′]*palladium*(II), (*R*)-**3**.—A 2:1 diastereomeric mixture of complexes (*R*,*R*)-**2a** and **-2b** (0.7 g, 0.891 mmol) was dissolved in concentrated sulfuric acid (10 cm^3) and the resulting yellow solution poured onto ice (10 g). Lithium chloride (1.13 g, 163 mmol) was added and the reaction mixture was extracted with dichloromethane (50 cm^3). The aqueous layer was extracted with more dichloromethane (3 × 20 cm^3) and the combined organic extracts dried (anhydrous MgSO$_4$) and filtered. The volume of the solution was reduced to *ca.* 10 cm^3 and methanol was added to give pale yellow prisms of complex (*R*)-**3** (0.342 g, 77%), m.p. > 250 °C (Found: C, 48.8; H, 4.3. Calc. for C$_{21}$H$_{22}$Cl$_2$P$_2$Pd: C, 49.1; H, 4.3%). α −40° (589 nm, *c* 1.00 g per 100 dm^3, CH$_2$Cl$_2$). NMR (CD$_2$Cl$_2$): ^{1}H, δ 1.58 (m, 1 H, C*H*HPMePh), 2.05 (m, 1 H, CH*H*PMePh), 2.15 (d, 3 H, $^2J_{PH}$ 12.4 Hz, PMe), 2.25 (m, 1 H, C*H*HPPh$_2$), 2.58 (m, 1 H, CH*H*PPh$_2$) and 7.40–8.12 (m, 15 H, aromatics); ^{31}P-{^{1}H}, δ 63.5 (d, 1 P, $^3J_{PP}$ 10.5, P) and 65.5 (d, 1 P, $^3J_{PP}$ 10.5 Hz, P).

Preparation of (S)-(+)$_{589}$-1-(*Diphenylphosphino*)-2-(*methylphenylphosphino*)*ethane*, (*S*)-dpmpe.—Enantiomerically pure complex (*R*)-**3** (0.31 g, 0.62 mmol) was suspended in methanol (20 cm^3) and light petroleum (b.p. 40–60 °C) (40 cm^3) and KCN (1.21 g, 18.6 mmol) added. The mixture was vigorously shaken, water (10 cm^3) added and the two layers separated. The aqueous layer was extracted with more light petroleum (2 × 25 cm^3) and the combined organic extracts dried over anhydrous MgSO$_4$. Removal of the solvent gave (*S*)-dpmpe as a colourless liquid (0.17 g, 85%). α +10° (589 nm, *c* 0.50 g per 100 dm^3, CH$_2$Cl$_2$). ^{1}H NMR (CDCl$_3$): identical with that of the corresponding racemic material.

Synthesis of (R*,R*)- *and* (R*,S*)-1-(*Ethylphenylphosphino*)-2-(*methylphenylphosphino*)*ethane*, (*R**,*R**)- *and* (*R**,*S**)-epmpe.—Lithium (0.326 g, 22.3 mmol) was added to a stirred solution of (±)-dpmpe (3.58 g, 10.6 mmol) in tetrahydrofuran (80 cm^3) and the mixture stirred overnight. The dark orange solution was filtered and added dropwise to a stirred solution of ethyl bromide (1.16 g, 10.6 mmol) in tetrahydrofuran at −78 °C. After the addition was complete the solution was allowed to warm to room temperature overnight. The solvent was removed and the residue extracted with dichloromethane (2 × 80 cm^3) and water (2 × 50 cm^3). The organic extracts were dried (MgSO$_4$), filtered and the solvent removed under reduced pressure. Distillation gave the product as a colourless oil (2.67 g, 87%), b.p. 165–170 °C at 0.05 mmHg. NMR (CDCl$_3$): ^{1}H, δ 0.87 [d of t, 3 H, $^3J_{HH}$ 7.7, $^3J_{PH}$ 15.3, PCH$_2$*Me*-(*R**,*S**)], 0.88 [d of t, 3 H, $^3J_{HH}$ 7.7, $^3J_{PH}$ 15.3, PCH$_2$*Me*-(*R**,*R**)], 1.28 [d, 3 H, $^2J_{PH}$ 2.1, PMe-(*R**,*R**)], 1.29 [d, 3 H, $^2J_{PH}$ 2.1 Hz, PMe-(*R**,*S**)], 1.68 (m, 12 H, 6CH$_2$) and 7.25–7.65 (m, 20 H, aromatics); ^{31}P-{^{1}H}, δ −30.9 [d, 1 P, $^3J_{PP}$ 25.0, PMePh-(*R**,*R**)], −30.7 [d, 1 P, $^3J_{PP}$ 23.0, PMePh-(*R**,*S**)], −15.4 [d, 1 P, $^3J_{PP}$

25.0, PEtPh-(R^*,R^*)] and −15.3 [d, 1 P, $^3J_{PP}$ 23.0 Hz, PEtPh-(R^*,S^*)].

Separation of the 1:1 *Diastereomeric Mixture of Compounds* (R^*,R^*)- *and* (R^*,S^*)-epmpe.—The 1:1 diastereomeric mixture of compounds (R^*,R^*)- and (R^*,S^*)-epmpe (1.12 g, 3.88 mmol) was dissolved in dichloromethane (10 cm^3) and a solution of [Ni(H_2O)$_6$]Cl_2 (0.46 g, 1.94 mmol) in water (10 cm^3) and of KSCN (0.372 g, 3.82 mmol) in water (1 cm^3) added. The two phases were separated and the aqueous phase extracted with more dichloromethane (2 × 10 cm^3). The combined organic extracts were dried ($MgSO_4$), the solution filtered and the solvent removed under reduced pressure. The residue was redissolved in hot ethanol (6 cm^3) to give [Ni(NCS){(R^*,S^*)-epmpe}$_2$]SCN as deep orange microcrystals upon cooling (0.20 g, 14%). The nickel(II) complex was dissolved in dichloromethane (10 cm^3) and treated with a ten-fold excess of KCN (0.173 g, 266 mmol) in water (5 cm^3). The organic layer was separated and the aqueous layer extracted with more dichloromethane (2 × 10 cm^3). The combined organic layers were dried ($MgSO_4$), the solution filtered and the solvent removed under reduced pressure to give pure compound (R^*,S^*)-epmpe (0.153 g, 100%). NMR ($CDCl_3$): ^{1}H, δ 0.87 (d of t, 3 H, $^3J_{HH}$ 7.7, $^3J_{PH}$ 15.3, PCH$_2$*Me*), 1.29 (d, 3 H, $^2J_{PH}$ 2.1 Hz, PMe), 1.68 (m, 6 H, 6CH$_2$) and 7.25–7.65 (m, 10 H, aromatics); ^{31}P-{^{1}H}, δ −30.7 (d, 1 P, $^3J_{PP}$ 23.0, PMePh) and −15.3 (d, 1 P, $^3J_{PP}$ 23.0 Hz, PEtPh). The filtrate from the isolation of [Ni(NCS){(R^*,S^*)-epmpe}$_2$]SCN was evaporated to dryness and the residue recrystallised from dichloromethane–diethyl ether to give more product (0.73 g, 51%). Liberation of the asymmetric di(tertiary phosphine) from the nickel(II) complex was achieved following the above procedure to give a *ca.* 3:1 diastereomeric mixture of (R^*,R^*)- and (R^*,S^*)-epmpe, respectively.

Preparation of [SP-4-4-(R*,S*)]- *and* [SP-4-3-(R*,S*)]-{2-[(*Dimethylamino*)*methyl*]*phenyl*-C^1,N}[1-(*ethylphenylphosphino*)-2-(*methylphenylphosphino*)*ethane*-P,P′]*palladium*(II) *Hexafluorophosphate*, (R^*,S^*)-**4a** *and* -**4b**.—To a stirred suspension of di-μ-chloro-bis{2-[(dimethylamino)methyl]-phenyl-C^1,N}dipalladium(II) (0.147 g, 0.266 mmol) in methanol (10 cm^3) was added a solution of compound (R^*,S^*)-epmpe (0.153 g, 0.53 mmol). The mixture was stirred for 2 h. The pale yellow solution was filtered and a solution of NH_4PF_6 (0.173 g, 1.06 mmol) in water (5 cm^3) added. The resulting white precipitate was collected, washed with methanol–water (1:1, 20 cm^3), methanol–diethyl ether (1:4, 20 cm^3) and diethyl ether (20 cm^3) and then dried *in vacuo* (0.32 g, 89%). NMR [$(CD_3)_2CO$]: ^{1}H, δ 1.29 (d of t, 3 H, $^3J_{HH}$ 7.8, $^3J_{PH}$ 21.4, PCH$_2$*Me* of **4b**), 1.50 (d of t, 3 H, $^3J_{HH}$ 7.8, $^3J_{PH}$ 17.5, PCH$_2$*Me* of **4a**), 1.68 (m, 1 H, C*H*HP), 2.12 (d, 3 H, $^2J_{PH}$ 12.8, PMe of **4b**), 2.13 (m, 1 H, CH*H*P), 2.25 (d, 3 H, $^2J_{PH}$ 11.0, PMe of **4a**), 2.49 (d, 3 H, $^4J_{PH}$ 1.8, NMe$_2$ of **4b**), 2.50 (m, 4 H, 2CH$_2$P), 2.58 (d, 3 H, $^4J_{PH}$ 2.2, NMe$_2$ of **4a**), 2.80 (m, 6 H, 3CH$_2$P), 2.82 (br s, 3 H, NMe$_2$ of **4a**), 2.92 (br s, 3 H, NMe$_2$ of **4b**), 3.74 (m, 1 H, C*H*HNMe$_2$ of **4b**), 3.95 (m, 1 H, C*H*HNMe$_2$ of **4a**), 4.50 (d, 1 H, $^2J_{HH}$ 8.0, CH*H*NMe$_2$ of **4a**), 4.76 (d, 1 H, $^2J_{HH}$ 8.0 Hz, CH*H*NMe$_2$ of **4b**) and 6.74–8.31 (m, 40 H, aromatics); ^{31}P-{^{1}H}, δ 31.6 (d, 1 P, $^2J_{PP}$ 24.0, P of **4b**), 43.1 (d, 1 P, $^2J_{PP}$ 22.4, P of **4a**), 55.4 (d, 1 P, $^2J_{PP}$ 22.4, P of **4a**) and 70.8 (d, 1 P, $^2J_{PP}$ 24.0 Hz, P of **4b**). Reaction of the 3:1 diastereomeric mixture of (R^*,R^*)- and (R^*,S^*)-epmpe (0.537 g, 0.972 mmol) with di-μ-chloro-bis{2-[(dimethylamino)-methyl]phenyl-C^1,N}dipalladium(II) (0.537 g, 0.972 mmol) under similar reaction conditions gave a mixture of four diastereomers, *viz.* (R^*,R^*)-**4a** and -**4b** and (R^*,S^*)-**4a** and -**4b**, in 90% yield. ^{31}P-{^{1}H} NMR [$(CD_3)_2CO$]: δ 31.6 [d, 1 P, $^2J_{PP}$ 24.0, P of (R^*,S^*)-**4b**], 33.1 [d, 1 P, $^2J_{PP}$ 23.0, P of (R^*,R^*)-**4b**], 43.1 [d, 1 P, $^2J_{PP}$ 22.4, P of (R^*,S^*)-**4a**], 44.5 [d, 1 P, $^2J_{PP}$ 25.5, P of (R^*,R^*)-**4a**], 55.4 [d, 1 P, $^2J_{PP}$ 22.4, P of (R^*,S^*)-**4a**], 56.3 [d, 1 P, $^2J_{PP}$ 25.5, P of (R^*,R^*)-**4a**], 70.2 [d, 1 P, $^2J_{PP}$ 23.0, P of (R^*,R^*)-**4b**] and 70.8 [d, 1 P, $^2J_{PP}$ 24.0 Hz, P of (R^*,S^*)-**4b**].

X-Ray Crystallography.—*Crystal data for complex* (*R*, *R*)-**2a**. $C_{35}H_{38}F_6NP_3Pd$, M = 786.0, monoclinic, space group $P2_1$ (no. 4), a = 10.256(1), b = 17.605(3), c = 19.772(2) Å, β = 102.340(8)°, U = 3487.4(8) Å^3 (by least-squares analysis of the setting of 25 reflections having 86.89 < 2θ < 99.94°), Cu-Kα radiation (λ = 1.541 78 Å) with a graphite monochromator, Z = 4, D_c = 1.497 g cm^{-3}, $F(000)$ = 1600, specimen 0.28 × 0.10 × 0.04 mm, μ(Cu-Kα) = 61.0 cm^{-1}.

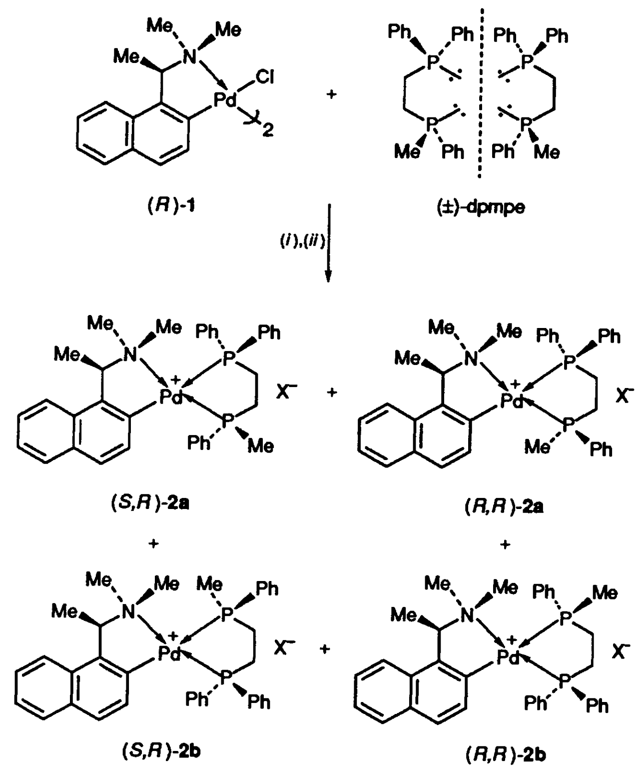
Data collection and processing. A unique data set was measured at 296(1) K using the ω–2θ scan technique to a maximum range 2θ value of 120.1° on a Rigaku AFC6R diffractometer. Scans of (1.30 + 0.30 tan θ)° were made at a speed of 8.0° min^{-1} (in omega). The weak reflections [I < 1.0σ(I)] were rescanned (maximum of four scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak to background counting times was 2:1. Of the 5727 reflections collected, 5390 were unique (R_{int} = 0.034). The intensities of three representative reflections were measured after every 150. No decay correction was applied. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.77 to 1.00. The data were corrected for Lorentz and polarisation effects.

Structure analysis and refinement. The structure was solved by Patterson methods[20] and expanded using Fourier techniques.[21] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and held fixed. The absolute configuration was assigned by refinement in each enantiomorph. The final cycle of full-matrix least-squares refinement was based on 4706 observed reflections [I > 3.00σ(I)] and 827 variable parameters and converged (largest parameter shift < 0.01 times its e.s.d.) with final R and R' values of 0.036 and 0.028, respectively. The standard deviation of an observation of unit weight was 2.30. The weighting scheme was based on counting statistics and included a factor (p = 0.003) to downweight the intense reflections. The maximum and minimum peaks on the final Fourier-difference map corresponded to 0.39 and −0.41 e Å^{-3}, respectively. Neutral atom scattering factors were taken from ref. 22. Anomalous dispersion effects were included in F_c;[23] the values for Δf' and Δf'' were those of Creagh and McAuley.[24] The values for the mass attenuation coefficients were those of Creagh and Hubbell.[25] All calculations were performed using the TEXSAN[26] crystallographic software package.

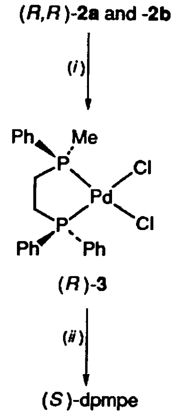
Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis and Resolution of (±)-dpmpe.—The asymmetric di(tertiary phosphine) (±)-1-(diphenylphosphino)-2-(methylphenylphosphino)ethane, (±)-dpmpe, was prepared *via* the base-catalysed addition of methylphenylphosphine to diphenylvinylphosphine following the procedure of King and Kapoor.[19] Its resolution was achieved *via* the separation by fractional crystallisation of internally diastereomeric palladium(II) complexes containing the racemic ligand and orthometallated (*R*)-(+)$_{589}$-dimethyl[1-(1-naphthyl)ethyl]amine. Reaction of (±)-dpmpe with the dimer (−)$_{589}$-di-μ-chloro-bis{(*R*)-1-[1-(dimethylamino)ethyl]naphthyl-C^2,N}dipalladium(II), (*R*)-**1**, in methanol produced four diastereomeric chloride salts (Scheme 1). Addition of 1 equivalent of aqueous NH_4PF_6 to the solution precipitated a mixture of hexafluorophosphate salts enriched in (*R*,*R*)-**2a** and -**2b** (X = PF$_6$). Indeed, one recrystallisation of the diastereomeric mixture from acetone–diethyl ether gave a 2:1 mixture of (*R*,*R*)-**2a** and -**2b** (X = PF$_6$), respectively. Several recrystallisations of the 2:1 diastereomeric mixture of (*R*,*R*)-**2a** and -**2b** (X = PF$_6$) from acetone–propan-2-ol gave pure (*R*,*R*)-**2a** (X = PF$_6$), α −29.0° (589 nm, acetone),



Scheme 1 (*i*) MeOH; (*ii*) NH_4PF_6 in water



Scheme 2 (*i*) Concentrated H_2SO_4; anhydrous LiCl; (*ii*) KCN in water

albeit in low yield. It should be noted, however, that separation of the 2:1 mixture of (*R*,*R*)-**2a** and -**2b** ($X = PF_6$) is not required in order to effect the resolution of (±)-dpmpe as both diastereomers contain the *S* form of the ligand. The addition of an excess of aqueous NH_4PF_6 to the remaining solution containing diastereomeric chloride salts gave a precipitate enriched in (*S*,*R*)-**2a** and -**2b** ($X = PF_6$). After several recrystallisations of the mixture from acetone–propan-2-ol a 60:30:7:3 diastereomeric mixture of (*S*,*R*)-**2b**, (*S*,*R*)-**2a**, (*R*,*R*)-**2a** and (*R*,*R*)-**2b**, respectively, was produced. Attempts further to separate the mixture by fractional crystallisation from a range of solvent systems were not successful. The liberation of the resolved di(tertiary phosphine) from (*R*,*R*)-**2a** and -**2b** ($X = PF_6$) was accomplished as shown in Scheme 2. Dissolution of the diastereomeric mixture of (*R*,*R*)-**2a** and -**2b** ($X = PF_6$) in concentrated sulfuric acid followed by the addition of LiCl gave the dichloro complex (*R*)-**3**, α −40.0° (589 nm, dichloromethane). Reaction of (*R*)-**3** with aqueous KCN gave optically pure (*S*)-dpmpe, α +10° (589 nm, dichloromethane).

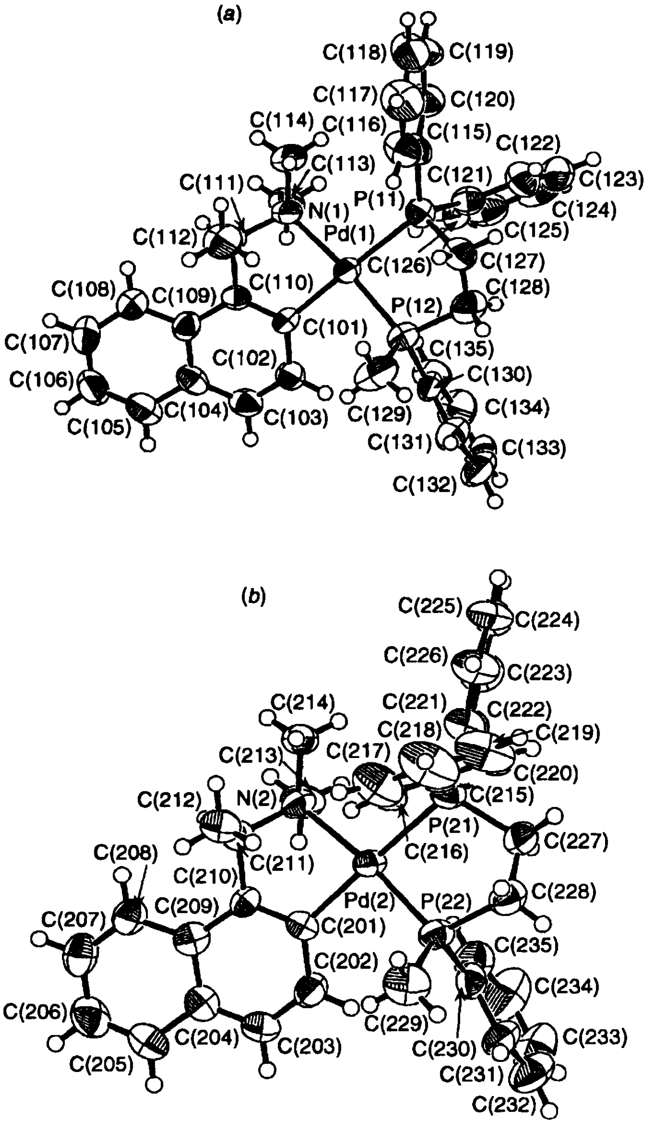


Fig. 1 Molecular structure of the cation of complex (*R*,*R*)-**2a** in which the ethano backbone of the co-ordinated di(tertiary phosphine) has adopted (*a*) a λ conformation and (*b*) a δ conformation

Crystal Structure of Complex (*R*,*R*)-**2a**.—The absolute configuration of the optically pure ligand (*S*)-dpmpe was assigned by a crystal structure determination of the internally diastereomeric complex (*R*,*R*)-**2a**. Two cations were present in the unit cell as a result of the ethano backbone of the co-ordinated di(tertiary phosphine) adopting λ and δ conformations. The stereochemistries of the two cations are shown in Fig. 1(*a*) and (*b*). Non-hydrogen atomic coordinates are given in Table 1 and selected bond lengths and angles in Table 2. The palladium atoms in the two cations have approximately square-planar geometries with the metal atom and the four donor atoms (2P, C and N) being essentially coplanar (maximum deviation from the least-squares plane 0.098 and 0.038 Å for the λ and δ conformers, respectively). The angles at Pd(1) are P(11)–Pd(1)–P(12) 83.6(1), P(12)–Pd(1)–C(101) 94.9(3), P(11)–Pd(1)–N(1) 101.4(2) and N(1)–Pd(1)–C(101) 80.2(3)°, while those at Pd(2) are P(21)–Pd(2)–P(22) 83.47(9), P(22)–Pd(2)–C(201) 93.9(3), P(21)–Pd(2)–N(2) 103.3(2) and N(2)–Pd(2)–C(201) 79.3(3)°. The phosphorus stereocentre P(12) [and P(22)] and the carbon stereocentre C(111) [and C(211)] have the same *R* absolute configuration in the two cations. Furthermore, the methylphenylphosphino group of the asymmetric di(tertiary phosphine) was found to be *trans* to the nitrogen atom of the

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

Atom	*x*	*y*	*z*
Pd(1)	0.122 79(6)	−0.4803	−0.267 64(3)
Pd(2)	0.104 07(6)	0.4973	0.233 23(3)
P(1)	0.097 1(3)	0.298 6(2)	0.531 5(2)
P(2)	0.838 9(3)	0.242 9(2)	0.950 4(2)
P(11)	−0.074 7(3)	−0.545 8(2)	−0.257 4(1)
P(12)	0.224 5(3)	−0.571 3(2)	−0.195 7(1)
P(21)	−0.080 7(2)	0.561 3(2)	0.260 5(1)
P(22)	0.212 1(2)	0.543 2(2)	0.336 1(1)
F(11)	0.240 4(7)	0.330 7(6)	0.541 5(5)
F(12)	−0.045 1(7)	0.264 7(5)	0.519 7(5)
F(13)	0.089 8(8)	0.290 6(6)	0.453 5(4)
F(14)	0.103 3(9)	0.304 1(6)	0.609 1(4)
F(15)	0.040 8(7)	0.378 9(4)	0.519 2(4)
F(16)	0.150 9(8)	0.214 5(6)	0.543 1(5)
F(21)	0.975 0(9)	0.208 0(8)	0.972 1(5)
F(22)	0.704 9(9)	0.272 9(8)	0.924 0(8)
F(23)	0.862(1)	0.253 8(7)	0.876 9(5)
F(24)	0.825(1)	0.233(1)	1.022 2(5)
F(25)	0.783(1)	0.165 7(6)	0.929 2(6)
F(26)	0.889(1)	0.321 1(6)	0.967 8(6)
N(1)	0.044 9(7)	−0.395 8(5)	−0.341 8(4)
N(2)	0.022 2(7)	0.445 4(5)	0.136 0(4)
C(101)	0.295 2(8)	−0.424 6(6)	−0.273 1(4)
C(102)	0.420 0(9)	−0.424 1(7)	−0.223 4(4)
C(103)	0.523 0(9)	−0.382 3(7)	−0.234 4(5)
C(104)	0.517 1(9)	−0.337 1(6)	−0.294 6(5)
C(105)	0.625 7(10)	−0.294 6(8)	−0.307 4(6)
C(106)	0.619(1)	−0.256 6(8)	−0.366 3(7)
C(107)	0.503(1)	−0.257 9(9)	−0.417 4(7)
C(108)	0.390 8(10)	−0.297 0(7)	−0.406 7(6)
C(109)	0.396 2(9)	−0.337 5(6)	−0.345 4(5)
C(110)	0.284 9(8)	−0.383 4(5)	−0.331 8(4)
C(111)	0.155 4(9)	−0.385 6(6)	−0.383 8(5)
C(112)	0.157(1)	−0.450 6(8)	−0.433 4(5)
C(113)	0.032 8(10)	−0.322 9(7)	−0.305 8(6)
C(114)	−0.083 0(10)	−0.411 3(8)	−0.390 9(6)
C(115)	−0.222 1(9)	−0.565 6(7)	−0.324 7(5)
C(116)	−0.217(1)	−0.619 6(8)	−0.374 3(6)
C(117)	−0.331(1)	−0.635 8(9)	−0.422 7(7)
C(118)	−0.446(1)	−0.594 8(10)	−0.427 2(6)
C(119)	−0.451(1)	−0.539 6(8)	−0.380 2(6)
C(120)	−0.338(1)	−0.524 4(7)	−0.328 5(5)
C(121)	−0.135 1(9)	−0.506 3(7)	−0.183 5(5)
C(122)	−0.231(1)	−0.545 7(7)	−0.154 8(6)
C(123)	−0.267(1)	−0.514 5(10)	−0.097 5(6)
C(124)	−0.211(1)	−0.449 1(9)	−0.069 1(6)
C(125)	−0.118(1)	−0.409 4(8)	−0.095 5(6)
C(126)	−0.081 2(10)	−0.440 6(7)	−0.154 1(5)
C(127)	−0.020 4(9)	−0.641 3(6)	−0.231 1(5)
C(128)	0.097(1)	−0.637 5(6)	−0.175 6(6)
C(129)	0.325(1)	−0.630 9(9)	−0.236 3(6)
C(130)	0.320 8(9)	−0.549 5(6)	−0.109 5(4)
C(131)	0.409(1)	−0.601 8(7)	−0.073 4(5)
C(132)	0.471(1)	−0.589 4(8)	−0.005 7(6)
C(133)	0.446(1)	−0.524 2(9)	0.025 1(5)
C(134)	0.362(1)	−0.468 5(8)	−0.009 1(5)
C(135)	0.299 5(9)	−0.484 1(8)	−0.077 6(5)
C(201)	0.266 0(8)	0.438 4(6)	0.216 6(5)
C(202)	0.404 5(9)	0.453 3(7)	0.246 9(5)
C(203)	0.503 0(8)	0.409 0(7)	0.229 4(5)
C(204)	0.475 0(9)	0.351 2(7)	0.182 4(5)
C(205)	0.577 2(10)	0.303 9(7)	0.164 5(6)
C(206)	0.545(1)	0.247 1(8)	0.119 2(6)
C(207)	0.414(1)	0.232 0(7)	0.087 9(5)
C(208)	0.314(1)	0.275 8(6)	0.101 6(5)
C(209)	0.339 4(9)	0.336 2(6)	0.149 0(4)
C(210)	0.237 7(8)	0.383 6(6)	0.167 9(4)
C(211)	0.093 6(9)	0.370 1(6)	0.136 0(5)
C(212)	0.036 7(9)	0.309 1(7)	0.178 5(5)
C(213)	0.058 2(9)	0.493 2(7)	0.080 4(4)
C(214)	−0.125 7(9)	0.436 1(7)	0.117 3(5)
C(215)	−0.161 9(8)	0.501 2(7)	0.314 7(4)
C(216)	−0.134 4(10)	0.424 9(7)	0.319 5(5)
C(217)	−0.189(1)	0.378 2(8)	0.362 3(7)
C(218)	−0.265(1)	0.410 7(9)	0.404 5(7)
C(219)	−0.292(1)	0.486(1)	0.402 3(6)
C(220)	−0.241 5(10)	0.534 7(7)	0.357 5(5)
C(221)	−0.204 3(9)	0.605 6(7)	0.196 3(4)
C(222)	−0.164 7(9)	0.649 2(7)	0.147 0(5)
C(223)	−0.256(1)	0.686 3(7)	0.095 3(5)
C(224)	−0.390(1)	0.681 0(7)	0.093 0(5)
C(225)	−0.432 5(9)	0.638 4(7)	0.141 9(5)
C(226)	−0.344 3(9)	0.600 5(7)	0.192 3(5)
C(227)	−0.007 4(9)	0.636 6(6)	0.319 2(5)
C(228)	0.096 0(9)	0.598 3(6)	0.376 0(5)
C(229)	0.284(1)	0.472 0(7)	0.399 5(5)
C(230)	0.334 1(9)	0.613 9(6)	0.332 4(5)
C(231)	0.432 3(10)	0.632 8(7)	0.392 8(5)
C(232)	0.521(1)	0.690 7(9)	0.391 2(6)
C(233)	0.511(1)	0.733 3(8)	0.331 7(7)
C(234)	0.415(1)	0.716 2(8)	0.273 0(6)
C(235)	0.329(1)	0.654 7(9)	0.274 1(6)

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

Pd(1)–P(11)	2.376(3)	Pd(2)–P(21)	2.364(3)
Pd(1)–N(1)	2.122(8)	Pd(2)–N(2)	2.132(7)
Pd(1)–P(12)	2.245(3)	Pd(2)–P(22)	2.249(2)
Pd(1)–C(101)	2.045(9)	Pd(2)–C(201)	2.043(9)
P(11)–Pd(1)–P(12)	83.6(1)	P(21)–Pd(2)–P(22)	83.47(9)
P(11)–Pd(1)–N(1)	101.4(2)	P(21)–Pd(2)–N(2)	103.3(2)
P(11)–Pd(1)–C(101)	178.1(2)	P(21)–Pd(2)–C(201)	175.8(3)
P(12)–Pd(1)–N(1)	173.3(2)	P(22)–Pd(2)–N(2)	173.1(2)
P(12)–Pd(1)–C(101)	94.9(3)	P(22)–Pd(2)–C(201)	93.9(3)
N(1)–Pd(1)–C(101)	80.2(3)	N(2)–Pd(2)–C(201)	79.3(3)
Pd(1)–P(11)–C(115)	128.3(3)	Pd(2)–P(21)–C(215)	110.2(4)
Pd(1)–P(11)–C(127)	105.1(3)	Pd(2)–P(21)–C(227)	103.1(5)
Pd(1)–P(11)–C(121)	108.8(4)	Pd(2)–P(21)–C(221)	122.2(3)
Pd(1)–P(12)–C(128)	109.3(3)	Pd(2)–P(22)–C(228)	109.8(3)
Pd(1)–P(12)–C(130)	121.9(3)	Pd(2)–P(22)–C(230)	115.5(3)
Pd(1)–P(12)–C(129)	111.8(4)	Pd(2)–P(22)–C(229)	115.2(4)
Pd(1)–N(1)–C(111)	103.9(5)	Pd(2)–N(2)–C(211)	106.1(5)
Pd(1)–N(1)–C(114)	118.3(7)	Pd(2)–N(2)–C(214)	117.0(6)
Pd(1)–N(1)–C(113)	109.4(6)	Pd(2)–N(2)–C(213)	108.1(6)
Pd(1)–C(101)–C(102)	128.3(7)	Pd(2)–C(201)–C(202)	127.1(8)
Pd(1)–C(101)–C(110)	113.1(6)	Pd(2)–C(201)–C(210)	114.7(7)

resolving agent. A similar arrangement was observed in related palladium(II) complexes containing an orthometallated optically active amine and the asymmetric bidentate ligands (*R*)-$(-)_{589}$-methylphenyl(8-quinolyl)phosphine and (*S*)-$(-)_{589}$-1-(diphenylphosphino)-2-(methylphenylphosphino)-benzene.[12,17] The two Pd–P bond lengths in each of the two cations are also significantly different. For the diphenylphosphino group *trans* to C(111) or C(211), bond distances of Pd(1)–P(11) 2.376 or Pd(2)–P(21) 2.364 Å were found, while Pd(1)–P(12) 2.245 and Pd(2)–P(22) 2.249 Å were observed for the methylphenylphosphino moiety *trans* to N(1) and N(2), respectively. A similar difference has been observed in a related palladium(II) complex containing orthometallated (*S*)-$(-)_{589}$-dimethyl(1-phenylethyl)amine and the asymmetric di(tertiary phosphine) (*S*)-$(-)_{589}$-1-(diphenylphosphino)-2-(methylphenylphosphino)benzene, and was attributed to a combination of the *trans* effect[27] and the differing basicities of the phosphorus donors.[12]

NMR Spectra.—The ^{1}H and ^{31}P-{^{1}H} NMR spectra of the internally diastereomeric complex (*R*,*R*)-**2a** in CD_2Cl_2 or $(CD_3)_2CO$ were consistent with the presence of a single diastereomer in solution. Single doublet PMe and CMe

Table 3 Selected ^{1}H and ^{31}P-{^{1}H} NMR data for complexes **2a**, **2b**, **4a** and **4b** in $(CD_3)_2CO$

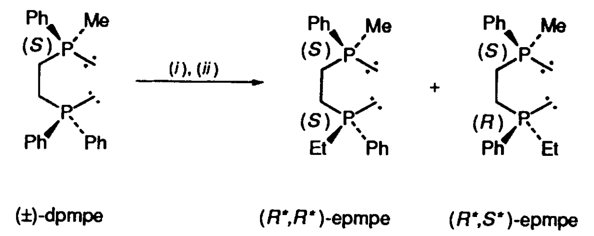
	^{1}H			^{31}P-{^{1}H}
Compound	δ(CMe)	δ(PMe)	δ(NMe_2)	δ(P)
(*R*,*R*)-**2a**	1.97 (d)	2.29 (d)	2.69 (br s), 2.84 (br s)	44.7 (d), 54.1 (d)
(*S*,*R*)-**2a**	1.95 (d)	2.56 (d)	2.66 (br s), 3.02 (d)	44.5 (d), 48.3 (d)
(*R*,*R*)-**2b**	1.88 (d)	2.28 (d)	2.70 (br s), 2.86 (br s)	31.3 (d), 63.2 (d)
(*S*,*R*)-**2b**	2.01 (d)	2.57 (d)	2.67 (br s), 2.98 (t)	29.6 (d), 63.4 (d)
(*R**,*S**)-**4a**	—	2.25 (d)	2.58 (d), 2.82 (br s)	43.1 (d), 55.4 (d)
(*R**,*S**)-**4b**	—	2.12 (d)	2.49 (d), 2.92 (br s)	31.6 (d), 70.8 (d)
(*R**,*R**)-**4a**	—	2.23 (d)	2.51 (br s), 2.93 (d)	44.5 (d), 56.3 (d)
(*R**,*R**)-**4b**	—	2.27 (d)	2.50 (br s), 2.79 (br s)	33.1 (d), 70.2 (d)

resonances and a pair of doublet P resonances were observed in the respective ^{1}H and ^{31}P-{^{1}H} NMR spectra. Selected ^{1}H and ^{31}P-{^{1}H} NMR data for (*R*,*R*)-**2a** [and for the related diastereomeric complexes (*R*,*R*)-**2b**, (*S*,*R*)-**2a** and (*S*,*R*)-**2b**] are given in Table 3. Presumably, the diastereomeric complex (*R*,*R*)-**2a** had the same stereochemistry in solution as that which was observed in the solid state, *i.e.* the methylphenylphosphino group was *trans* to the nitrogen-donor atom. A similar stereochemical arrangement has been observed in solution for related palladium(II) complexes containing an orthometallated optically active amine and the enantiomers of (±)-methylphenyl(8-quinolyl)phosphine,[17] (±)-(2-aminoethyl)methylphenylphosphine,[28] (±)-(2-aminophenyl)methylphenylphosphine[29] and (*R**,*R**)- and (*R**,*S**)-1-(methylphenylarsino)-2-(methylphenylphosphino)benzene.[30] For all of these complexes, 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. Stereoisomerism arising from the ethano backbone of the co-ordinated di(tertiary phosphine) adopting λ or δ conformations was not apparent for (*R*,*R*)-**2a** in solution. Presumably, rapid interconversion between these two conformers occurs in solution, as has been observed for numerous chiral transition-metal complexes containing 1,2-diaminoethane.[31]

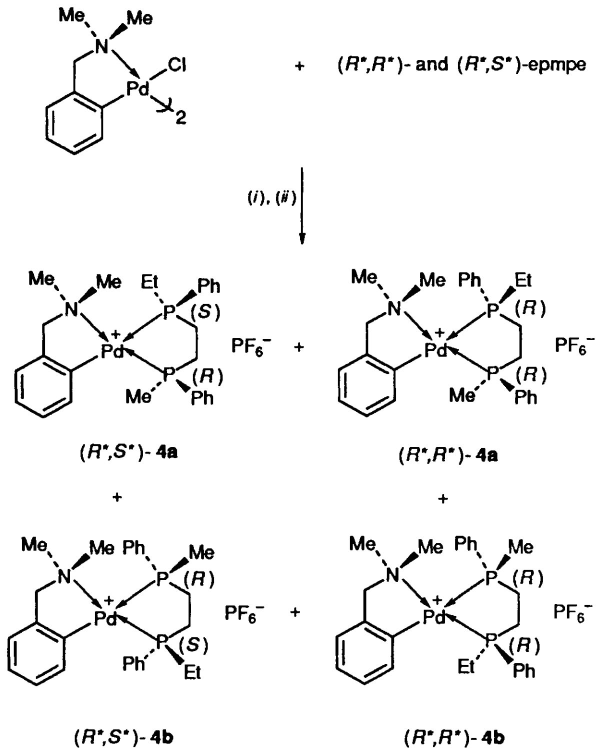
No change was observed in the spectra recorded for complex (*R*,*R*)-**2a** in CD_2Cl_2 when continually monitored over a period of 1 week. In $(CD_3)_2CO$, however, the complex was observed to undergo facile *cis–trans* isomerism, as shown by the appearance of a second set of doublet phosphorus resonances in the ^{31}P-{^{1}H} NMR spectrum. A 2:1 equilibrium mixture of (*R*,*R*)-**2a** and -**2b** was established over 48 h. The observed isomerism of (*R*,*R*)-**2a** in $(CD_3)_2CO$ readily accounts for the presence of four diastereomers, *viz.* (*R*,*R*)-**2a**, -**2b**, (*S*,*R*)-**2a** and -**2b**, in the resolution procedure as interconversion between (*S*,*R*)-**2a** and -**2b** *via cis–trans* isomerism would be expected to occur under similar conditions. The NMR assignments for (*S*,*R*)-**2a** and -**2b** were made by comparing ^{1}H and ^{31}P-{^{1}H} NMR data for the 60:30:7:3 diastereomeric mixture of (*S*,*R*)-**2a**, -**2b**, (*R*,*R*)-**2a** and -**2b**, with those for (*R*,*R*)-**2a** and -**2b**, and were based on the notion that diastereomers having the same arrangement of donor groups about the same central metal ion should give rise to similar NMR spectra. ^{31}P-{^{1}H} NMR spectroscopy was expected, and indeed found, to be the most diagnostic tool in this regard since the phosphorus atoms were directly attached to the palladium centre. The ^{31}P-{^{1}H} NMR spectrum of the 60:30:7:3 diastereomeric mixture in $(CD_3)_2CO$ contained a pair of doublet phosphorus resonances at δ 44.7 and 54.1, and at δ 31.3 and 63.2, for (*R*,*R*)-**2a** and -**2b**, respectively, and hence the corresponding signals at δ 44.5 and 48.3, and at δ 29.6 and 63.4, were assigned to (*S*,*R*)-**2a** and -**2b**, respectively.

The observation of isomerism for complex (*R*,*R*)-**2a** in acetone but not in dichloromethane suggests the process is intermolecular in nature and may occur as a result of labilisation of the Pd–PPh$_2$ or Pd–N bonds in the more polar solvent. Support for the former was provided by the crystal structure determination of (*R*,*R*)-**2a** which clearly showed a significantly longer Pd–P distance for the diphenylphosphino moiety compared with that for the methylphenylphosphino group. The latter, however, seems less likely as no evidence of lability (or *cis–trans* isomerism) has been found in related internally diastereomeric palladium(II) complexes containing orthometallated (*R*)- or (*S*)-dimethyl[1-(1-naphthyl)ethyl]-amine, (*R*)- or (*S*)-**1**, and asymmetric bidentate ligands with As, P or N donor atoms.[17,28–30] Furthermore, the Pd–N bond distances in (*R*,*R*)-**2a** (2.122 and 2.132 Å for the λ and δ conformers, respectively) are amongst the shortest hitherto reported for complexes of this type (they typically lie between 2.13 and 2.20 Å).[12,17,32] *cis–trans* Isomerism, however, has been observed in analogous palladium(II) complexes containing (*R*)- or (*S*)-dimethyl(1-phenylethyl)amine. For example, related internally diastereomeric palladium(II) complexes containing (*S*)-dimethyl(1-phenylethyl)amine and the enantiomers of (±)-1-(diphenylphosphino)-2-(methylphenylphosphino)benzene underwent facile *cis–trans* isomerism over a period of 48 h in $(CD_3)_2SO$.[12] No isomerism was observed for these complexes in $(CD_3)_2CO$. Isomerisation here can be rationalised in terms of labilisation of the Pd–PPh$_2$ or Pd–N bonds in the more polar solvent. Furthermore, attempts to resolve a number of unsymmetrical bidentate compounds, including (*R**,*S**)-1-(methylphenylarsino)-2-(methylphenylphosphino)benzene[30] and (±)-methylphenyl(8-quinolyl)phosphine,[17] by reaction with the dimer $(-)_{589}$-di-μ-chloro-bis{(*S*)-2-[1-(dimethylamino)ethyl]phenyl-*C*^{1},*N*}dipalladium(II) in methanol, resulted in the formation of an inseparable mixture of *cis* and *trans* isomers. In both of these cases facile *cis–trans* isomerism was presumed to arise as a result of labilisation of the Pd–N bond. They were successfully resolved by the method of metal complexation, however, using the analogous chloride-bridged dimer (*R*)- or (*S*)-**1**. The greater kinetic inertness of complexes containing (*R*)- or (*S*)-dimethyl[1-(1-naphthyl)ethyl]amine compared to those containing (*R*)- or (*S*)-dimethyl(1-phenylethyl)amine is reflected in the relative ease of removal of the resolving agent from these complexes: the latter 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 former amine must be dissolved in concentrated sulfuric acid in order to effect removal of the resolving agent.

Chemoselective Cleavage of a Phenyl Group from Compound (±)-dpmpe.—Completely selective cleavage of a phenyl group from the diphenylphosphino moiety of (±)-dpmpe occurred in tetrahydrofuran upon the addition of 2 equivalents of lithium (Scheme 3). Treatment of the intermediate lithium (2-methylphenylphosphinoethyl)phenylphosphide with bromoethane gave a 1:1 diasteromeric mixture of (*R**,*R**)- and (*R**,*S**)-1-(ethylphenylphosphino)-2-(methylphenylphosphino)ethane, (*R**,*R**)- and (*R**,*S**)-epmpe. Separation of



Scheme 3 (*i*) 2Li in tetrahydrofuran; (*ii*) EtBr in tetrahydrofuran. Only one enantiomer of each of the chiral di(tertiary phosphines) is depicted



Scheme 4 (*i*) MeOH; (*ii*) NH_4PF_6 in water. Only one enantiomer of each of the chiral diasteromeric complexes is shown

these was achieved by reaction of the di(tertiary phosphine) with an aqueous solution of $[Ni(H_2O)_6]Cl_2$ and KSCN, followed by fractional crystallisation of the resulting diastereomeric mixture of nickel(II) complexes from ethanol. Complexes of the type $[NiNCS\{(R^*,S^*)\text{-epmpe}\}_2]SCN$ precipitated preferentially from solution and gave pure (*R**,*S**)-epmpe upon further reaction with aqueous KCN. The purity of the asymmetric di(tertiary phosphine) was determined by its reaction with di-μ-chloro-bis{2-[(dimethylamino)methyl]-phenyl-C^1,*N*}dipalladium(II) in methanol to give a 2:1 diastereomeric mixture of complexes (*R**,*S**)-**4a** and -**4b** upon addition of aqueous NH_4PF_6. Two pairs of doublet phosphorus resonances were observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of (*R**,*S**)-**4a** and -**4b** in $(CD_3)_2CO$ (Table 3). The NMR assignments were made by comparing the spectra of (*R**,*S**)-**4a** and -**4b** with those recorded for the related complexes (*S*,*R*)-**2a**, -**2b**, (*R*,*R*)-**2a** and -**2b**. Reaction of (*R**,*R**)- and (*R**,*S**)-epmpe with the same chloride-bridged dimer under similar reaction conditions gave rise to a mixture of four complexes, *viz.* (*R**,*S**)-**4a**, -**4b**, (*R**,*R**)-**4a** and -**4b** (Scheme 4).

Conclusion

Relatively few studies on the chemoselective cleavage of alkyl or aryl groups from tertiary phosphines have been reported.[29,33] Nevertheless studies of this type are important as chemoselective cleavage of such groups from suitably designed bidentates can provide an avenue to chiral multidentate compounds. For example, we have recently shown that chemoselective cleavage of a phenyl group from (±)-(2-aminophenyl)methylphenylphosphine occurs in the presence of lithium in tetrahydrofuran and provides a route to the chiral quadridentate (*R**,*S**)-1-[(2-aminophenyl)methylphosphino]-2-[(2-dimethylarsinophenyl)-methylarsino]benzene.[34] Importantly, this compound was synthesised with complete stereoselectivity which augurs well for the role of the optically active forms as chiral auxiliaries in enantioselective synthesis. Furthermore, chemoselective cleavage of a phenyl group from (*S*)-1-(diphenylphosphino)-2-(methylphenylphosphino)ethane, (*S*)-dpmpe, followed by alkylation of the intermediate lithium (2-methylphenylphosphinoethyl)phenylphosphide and separation of the resulting pair of diastereomers, should provide a general synthetic route to optically active asymmetric di(tertiary phosphines) containing two chirotopic phosphorus stereocentres. Future work will be directed towards the utility of the optically active asymmetric di(tertiary phosphine) (*S*)-dpmpe as a precursor to such compounds, and their role as chiral auxiliaries in enantioselective catalysis. Auxiliaries of this type should give rise to kinetically inert transition metal-based catalysts and this, coupled with their ability to exercise stereoelectronic control over the reactions of co-ordinated substrates, has important implications in asymmetric synthesis.

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