Synthesis, Resolution and Reactions of (±)-(2-Aminophenyl)methylphenylphosphine. Crystal and Molecular Structure of (*R**,*R**,*S**,*R**)-(±)-(1,3-Bis{[2-(methylphenylphosphino)phenyl]amino}propane)nickel(II) Perchlorate†

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Asymmetric bidentate (±)-(2-aminophenyl)methylphenylphosphine has been prepared in 80% yield from (2-aminophenyl)diphenylphosphine *via* the secondary phosphine (±)-(2-aminophenyl)phenylphosphine. The chiral tertiary phosphine has been resolved by the method of metal complexation *via* the separation by fractional crystallisation of a pair of internally diastereomeric palladium(II) complexes containing the racemic ligand and (*S*)-[1-(1-ethyl)naphthyl]dimethylamine. The optically pure antipodes of the phosphine have α ± 160° (589 nm, CH_2Cl_2). A number of square-planar bis(bidentate ligand) complexes of bivalent nickel, palladium and platinum containing the various forms of the ligand have been prepared and their solution behaviour studied by ^1H and ^{31}P-{^1H} NMR spectroscopy. Monodeprotonation of the co-ordinated amino groups in the complexes has also been achieved by reaction with anhydrous sodium carbonate in acetone. The palladium(II) and platinum(II) complexes form *cis* diastereomers exclusively, whereas *trans* diastereomers were observed for the nickel(II) analogues. Furthermore, most of the complexes are kinetically labile. Reaction of (±)-(2-aminophenyl)methylphenylphosphine with *n*-butyllithium and *N,N,N',N'*-tetramethylethylenediamine in tetrahydrofuran followed by the addition of 1,3-bis(*p*-tolylsulfonyloxy)propane gave the quadridentate ligand (*R**,*R**)- and (*R**,*S**)-1,3-bis{[2-(methylphenylphosphino)phenyl]amino}propane. The (*R**,*R**) and (*R**,*S**) forms of the quadridentate ligand have been separated by complexation to nickel(II). The structure of the nickel(II) complex containing the (*R**,*R**) form of the quadridentate ligand, *viz.* (*R**,*R**,*S**,*R**)-(1,3-bis{[2-(methylphenylphosphino)phenyl]amino}propane)nickel(II) perchlorate, has been determined by X-ray crystallography.

Over the past decade we have carried out a number of investigations concerning the dynamic behaviour in solution of bis(bidentate ligand) complexes of bivalent nickel, palladium and platinum containing ligands bearing at least one chirotopic arsenic or phosphorus stereogenic donor atom.[1–5] The impetus for the work has been the paucity of information in the literature concerning dynamic processes of complexes of this type in solution, and our belief that a detailed knowledge of such behaviour must precede any rational approach towards the design and synthesis of related transition metal-based chiral auxiliaries that can be successfully used in enantioselective synthesis and catalysis.

Early work on complexes containing the diastereomers and enantiomers of 1,2-phenylenebis(methylphenylarsine), dias, and its phosphorus analogue, diph, provided the first direct evidence of ligand exchange in square-pyramidal complexes containing bis(tertiary arsines).[1,2] Ligand redistribution was also observed for square-planar bis(tertiary arsine)nickel(II) complexes but not for the palladium(II) and platinum(II) analogues. No evidence for intermolecular bidentate ligand exchange was observed for any of the complexes containing the bis(tertiary phosphine). Redistribution of the bidentate ligands between different metal centres in complexes of this type is readily monitored by ^1H NMR spectroscopy as interconversion between racemic and *meso* diastereomers is only compatible with ligand exchange as these internally diastereomeric cations are not related by an internal axis of rotation. The earlier work also confirmed the presence of axial-halogeno ligand exchange in square-pyramidal cations of the type [MX(bidentate ligand)$_2$]$^+$ (X = Cl, Br or I; bidentate ligand = diph or dias) with the rate of exchange increasing in the order Ni ≪ Pd < Pt. Hitherto, the only related work concerned the lability of the axial-halogeno bond in the square-pyramidal cations [MX(diars)$_2$]$^+$ [M = Ni,[6] Pd[7] or Pt;[6] diars = 1,2-phenylenebis(dimethylarsine)] and [MX(tetars)]$^+$ (M = Ni, Pd or Pt; tetars = 1,2-bis{[3-(dimethylarsino)propyl]phenylarsino}ethane[8]). Of particular significance, however, was the discovery of facile intramolecular isomerisation of the chelate rings in square-planar and square-pyramidal complexes of Ni^{II}, Pd^{II} and Pt^{II} containing di(tertiary arsines) and di(tertiary phosphines). The process proceeded in a stepwise manner *via* five-co-ordinate intermediates and hence only occurred for square-planar cations in the presence of a catalytic amount of halide ion.[1,2,9] Furthermore, the rate of isomerisation appeared to be invariant of the nature of the metal centre.

Later work focused on related complexes of bivalent nickel, palladium and platinum containing the diastereomers and enantiomers of the asymmetric bidentate ligand 1-(methylphenylarsino)-2-(methylphenylphosphino)benzene, phas.[3] All possible stereoisomers of the different species were detected and unambiguously identified. Axial-halogeno exchange and

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Non-SI unit employed: mmHg ≈ 13.6 × 9.8 Pa.

redistribution of the bidentate ligands in the presence of free ligand was observed for all of the square-pyramidal complexes. No evidence of ligand exchange was observed for any of the square-planar derivatives, although facile intramolecular *cis–trans* isomerism was observed for $[Ni\{(R^*,S^*)\text{-phas}\}_2][ClO_4]_2$ in CD_3CN. Presumably the isomerisation proceeded *via* a five-co-ordinate species involving co-ordinated CD_3CN. Square-planar bis(bidentate ligand) complexes of Ni^{II}, Pd^{II} and Pt^{II} containing the racemic and optically active forms of the deprotonated asymmetric bidentate ligands methylphenyl(2-sulfanylethyl)arsine, L, and its phosphorus analogue, L′, were also investigated.[4] Ligand redistribution was rife in solutions of these complexes under ambient conditions, especially for the nickel and palladium derivatives of the tertiary arsine. Furthermore, *trans* diastereomers were observed exclusively for the nickel(II) complexes and *cis* diastereomers for $[Pt(L')_2]$. Both *cis* and *trans* isomers were detected for the analogous palladium(II) compounds and $[Pt(L)_2]$. More recent work was concerned with related complexes containing asymmetric bidentate ligands bearing both soft and hard donor atoms rather than two soft donor atoms. Square-planar and square-pyramidal bis(bidentate ligand) complexes of Pd^{II} and Pt^{II} containing (±)-methylphenyl(8-quinolyl)arsine and its phosphorus analogue were prepared in enantiomerically and diastereomerically homogeneous forms and their behaviour in solution was investigated by variable-temperature NMR spectroscopy.[5] All of the cations had the *cis* co-ordination geometry and underwent facile intermolecular ligand redistribution (As > P) for both metals (Pd > Pt). The square-pyramidal cations showed, in addition, even more rapid axial-chloro site exchange. The exclusive formation of *cis* diastereomers is in accordance with 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.'[10]

We describe herein the synthesis and resolution of (±)-(2-aminophenyl)methylphenylphosphine and the dynamic behaviour in solution of square-planar bis(bidentate ligand) complexes of bivalent nickel, palladium and platinum containing the enantiomeric forms of the ligand. Studies of this type have important implications in the area of asymmetric synthesis since optically active bidentate ligands containing dissimilar donors are capable of exercising stereoelectronic control over the reactions of co-ordinated substrates. The synthesis of the quadridentate ligand (*R**,*R**)- and (*R**,*S**)-1,3-bis{[2-(methylphenylphosphino)phenyl]amino}propane using (±)-(2-aminophenyl)methylphenylphosphine as a precursor is also presented. Although a number of acyclic quadridentate ligands with PN_2P donor atoms have been reported in the literature,[11–13] this is the first example of a ligand incorporating two 1,2-phenylene linkages and having stereogenic phosphorus donor atoms.

Experimental

Procedures and Materials.—Reactions involving air-sensitive compounds were performed under argon using the Schlenk technique. Solvents were dried and purified by distillation under argon. The NMR spectra were recorded on a Varian Gemini 300 spectrometer (^1H at 300 MHz and $^{31}P\text{-}\{^1H\}$ at 121.5 MHz); chemical shifts are reported as δ values relative to internal $SiMe_4$(^1H) and external 85% H_3PO_4 ($^{31}P\text{-}\{^1H\}$). 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 (2-aminophenyl)diphenylphosphine,[14] $(+)_{589}$-di-μ-chloro-bis{(*S*)-1-[1-(dimethylamino)ethyl]naphthyl-C^2,N}dipalladium(II) (*S*)-**1**,[15] (*R**,*R**)-1,2-phenylene-bis(methylphenylphosphine),[16] di-μ-chloro-bis{2-[(dimethylamino)methyl]phenyl-C^2,N}dipalladium(II)[17] and dichloro-(cycloocta-1,5-diene)platinum(II)[18] were prepared by published procedures.

Synthesis of (±)-(2-*Aminophenyl*)*phenylphosphine*, (±)-L^1.—Lithium foil (4.40 g, 634 mmol) was added to a solution of (2-aminophenyl)diphenylphosphine (58.6 g, 211 mmol) in tetrahydrofuran (thf) (400 cm^3) and the reaction mixture stirred overnight. Water (50 cm^3) was added dropwise to the deep orange solution and the thf removed by distillation. The residue was extracted with dichloromethane (3 × 50 cm^3), dried over anhydrous $MgSO_4$, filtered and the solvent removed by evaporation. Distillation of the crude product gave the secondary phosphine as a colourless, air-sensitive liquid (35.8 g, 84%), b.p. 108–110 °C (0.05 mmHg); ^1H NMR ($CDCl_3$) δ 3.84 (br s, 2 H, NH_2), 5.08 (d, 1 H, $^1J_{PH}$ 222 Hz, PH), 6.58–7.42 (m, 9 H, aromatics); *m*/*z* 201 $(M)^+$, 123 $(M - PhH)^+$.

Synthesis of (±)-(2-*Aminophenyl*)*methylphenylphosphine*, (±)-L^2.—Sodium foil (3.34 g, 146 mmol) was added to a solution of (±)-L^1 (29.3 g, 146 mmol) in thf (250 cm^3) and the mixture stirred for 3 h. The resulting clear yellow solution was added dropwise to a stirred solution of methyl iodide (20.66 g, 146 mmol) in thf (150 cm^3) at −78 °C. After the addition was complete the reaction mixture was allowed to warm to room temperature overnight. The solvent was removed and the residue extracted with dichloromethane (50 cm^3) and water (50 cm^3). The aqueous layer was extracted with more dichloromethane (2 × 50 cm^3) and the combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the crude product purified by distillation to give the tertiary phosphine as a colourless, air-sensitive liquid (28.2 g, 90%), b.p. 124–126 °C (0.05 mmHg) (Found: C, 72.7; H, 6.8. Calc. for $C_{13}H_{14}NP$: C, 72.6; H, 6.5%); ^1H NMR ($CDCl_3$) δ 1.58 (d, 3 H, $^2J_{PH}$ 3.3 Hz, PMe), 4.07 (br s, 2 H, NH_2), 6.50–7.39 (m, 9 H, aromatics); $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$) δ −42.8 (s, 1 P); *m*/*z* 215 $(M)^+$, 200 $(M - Me)^+$, 122 $(M - C_6H_5NH_2)^+$.

Resolution of (±)-L^2. *Formation and Separation of Internally Diastereomeric Complexes.* [SP-4-2-(S),(S)]-[(2-*Aminophenyl*)-*methylphenylphosphine*-N,P]{1-[1-(*dimethylamino*)*ethyl*]*naphthyl*-C^2,N}*palladium*(II) *Hexafluorophosphate*, (S,S)-**2b**.— To a suspension of the resolving agent (*S*)-**1** (13.95 g, 20.5 mmol) in methanol (150 cm^3) was slowly added a solution of (±)-L^2 (8.83 g, 41.0 mmol) in methanol (50 cm^3) with stirring. To the resulting pale yellow solution of diastereomeric chloride salts (*S*,*S*)-**2a** and (*R*,*S*)-**2a**, an aqueous solution of NH_4PF_6 (20.2 g, 124 mmol in 50 cm^3 of water) was added dropwise, followed by a further 50 cm^3 of water. The resulting white precipitate was collected, washed with water (200 cm^3), diethyl ether–methanol (4:1, 100 cm^3) and diethyl ether (100 cm^3), and then dried *in vacuo* (25.0 g, 92%). α +34.7° (589 nm, *c* 1.013 g per 100 cm^3, Me_2CO). The 1:1 diastereomeric mixture was dissolved in dichloromethane (100 cm^3) and propan-2-ol (50 cm^3) added to give almost pure (*S*,*S*)-**2b**. Recrystallisation of this material from the same solvent mixture gave the pure diastereomer as colourless rosettes (8.13 g, 33%), m.p. 252–256 °C (Found: C, 49.0; H, 4.7; N, 4.1. Calc. for $C_{27}H_{30}F_6N_2P_2Pd$: C, 48.8; H, 4.6; N, 4.2%). α +163° (589 nm, *c* 1.02 g, per 100 cm^3, Me_2CO). ^1H NMR [$(CD_3)_2CO$]: δ 1.93 (d, 3 H, $^3J_{HH}$ 6.4, CH*Me*), 2.52 (d, 3 H, $^3J_{PH}$ 10.2, PMe), 2.97 (d, 3 H, $^3J_{PH}$ 1.5, NMe), 3.22 (d, 3 H, $^3J_{PH}$ 3.4 Hz, NMe), 4.74 (m, 1 H, C*H*Me), 6.35 (br s, 1 H, NH), 6.65 (br s, 1 H, NH), 7.30–8.06 (m, 15 H, aromatics).

Isolation of [SP-4-2-(R),(S)]-[(2-*Aminophenyl*)*methylphenylphosphine*-N,P]{1-[1-(*dimethylamino*)*ethyl*]*naphthyl*-C^2,N}-*palladium*(II) *Hexafluorophosphate*, (R,S)-**2b**.—After removal of the first crop of (*S*,*S*)-**2b**, the mother-liquor was evaporated to dryness and the residue recrystallised twice from acetone–diethyl ether to afford (*R*,*S*)-**2b** as colourless needles (6.88 g, 28%), m.p. 201–205 °C (Found: C, 48.5; H, 4.6; N, 4.1. Calc. for $C_{27}H_{30}F_6N_2P_2Pd$: C, 48.8; H, 4.5; N, 4.2%). α −101.6° (589 nm, *c* 1.12 g per 100 cm^3, Me_2CO). ^1H NMR

$[(CD_3)_2CO]$: δ 1.93 (d, 3 H, $^3J_{HH}$ 6.3, CH*Me*), 2.29 (d, 3 H, $^2J_{PH}$ 10.5, PMe), 2.98 (d, 3 H, $^3J_{PH}$ 1.7, NMe), 3.20 (d, 3 H, $^3J_{PH}$ 3.4 Hz, NMe), 4.73 (m, 1 H, C*H*Me), 6.20 (br s, 1 H, NH), 6.83 (br s, 1 H, NH), 6.91–8.26 (m, 15 H, aromatics).

Preparation of [SP-4-2-(R)]-[(2-*Aminophenyl*)*methylphenylphosphine*-N,P]*dichloropalladium*(II), (R)-**3**.—Diastereomerically pure (*R,S*)-**2b** (2.6 g, 3.9 mmol) was dissolved in concentrated sulfuric acid (15 cm^3) and the solution poured onto ice (100 g). Lithium chloride (3.8 g, 90 mmol) was added and the mixture extracted with dichloromethane (250 cm^3). The aqueous layer was washed with more dichloromethane (3 × 20 cm^3) and the combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed and the residue recrystallised from hot methanol to give pure (*R*)-**3** as fine yellow needles (1.4 g, 91%), m.p. 225 °C (decomp.) (Found: C, 39.2; H, 3.3; N, 3.4. Calc. for $C_{13}H_{14}Cl_2NPPd$: C, 39.8; H, 3.6; N, 3.6%). α −42° (589 nm, *c* 1.05 g per 100 cm^3, Me_2SO). ^1H NMR $[(CD_3)_2SO]$: δ 2.26 (d, 3 H, $^2J_{PH}$ 12.6 Hz, PMe), 7.43–7.87 (m, 11 H, NH_2 and aromatics). ^{31}P-{^1H} NMR $[(CD_3)_2SO]$: δ 41.1 (s, 1 P).

Preparation of [SP-4-2-(S)]-[(2-*Aminophenyl*)*methylphenylphosphine*-N,P]*dichloropalladium*(II) *Hemihydrate*, (S)-**3**.—This compound was prepared in the same way as its enantiomer in 88% yield, m.p. 225 °C (decomp.) (Found: C, 39.0; H, 3.2; N, 3.3. Calc. for $C_{13}H_{15}Cl_2NO_{0.5}PPd$: C, 38.9; H, 3.8; N, 3.5%). α +42° (589 nm, *c* 0.93 g per 100 cm^3, Me_2SO). ^1H NMR $[(CD_3)_2SO]$: identical to the spectrum recorded for (*R*)-**3**.

Preparation of (S)-(−)$_{589}$-(2-*Aminophenyl*)*methylphenylphosphine*, (S)-L^2.—*Method A*. A solution of potassium cyanide (2 g, 31 mmol) in water (20 cm^3) was added to a solution of enantiomerically pure (*R*)-**3** (2.1 g, 5.4 mmol) in dichloromethane (100 cm^3) and the mixture shaken vigorously for a few minutes to give an almost colourless organic phase. The organic layer was separated off and the aqueous layer washed with more dichloromethane (3 × 20 cm^3). The combined organic layers were dried over anhydrous $MgSO_4$, filtered and the solvent removed under reduced pressure to give optically pure (*S*)-L^2 as a colourless, viscous oil (1.06 g, 92%). α −160° (589 nm, *c* 0.92 g per 100 cm^3, Me_2CO). ^1H ($CDCl_3$) and ^{31}P-{^1H} NMR ($CDCl_3$): identical to the spectra recorded for the racemic compound (±)-L^2.

Method B. A solution of the complex (*R,S*)-**2b** (5.02 g, 7.55 mmol) in dichloromethane (200 cm^3) was treated with a solution of (*R*,R**)-1,2-phenylenebis(methylphenylphosphine) (2.41 g, 7.47 mmol) in dichloromethane (100 cm^3). The mixture was stirred for 1 h and then concentrated to *ca.* 25 cm^3 under reduced pressure. *n*-Hexane (250 cm^3) was added to the solution to afford a white precipitate which was collected, washed with *n*-hexane (3 × 30 cm^3) and dried *in vacuo* (5.65 g, 98%). [This by-product consisted of the internally diastereomeric palladium(II) complexes, (*SS,S*)- and (*RR,S*)-**4**.] The mother-liquor was evaporated to dryness to give optically pure (*S*)-L^2 (1.56 g, 97%).

Preparation of (R)-(+)$_{589}$-(2-*Aminophenyl*)*methylphenylphosphine*, (R)-L^2.—This compound was prepared in the same manner as its enantiomer in yields of 76 and 98% using methods A and B, respectively. α +160° (589 nm, *c* 1.03 g per 100 cm^3, Me_2CO).

Mono(bidentate ligand) Complexes. Preparation of (±)-[SP-4-2]-[(2-*Aminophenyl*)*methylphenylphosphine*-N,P]*dichloropalladium*(II), (±)-**3**.—A solution of (±)-L^2 (2.06 g, 9.6 mmol) in methanol (5 cm^3) was slowly added to a stirred suspension of the dimer di-μ-chloro-bis{2-[(dimethylamino)methyl]phenyl-C^2,*N*}dipalladium(II) (2.66 g, 4.8 mmol) in methanol (65 cm^3). An aqueous solution of NH_4PF_6 (3.12 g, 19.1 mmol in 10 cm^3 of water) was added to the solution to give a yellow precipitate which was collected and dried *in vacuo*. The precipitate was dissolved in the minimum amount of acetone and hydrochloric acid (10 mol dm^{-3}, 15 cm^3) added to afford the dichloro complex (±)-**3**. The complex was recrystallised from hot methanol as fine yellow needles (2.90 g, 77%), m.p. 224 °C (decomp.) (Found: C, 39.6; H, 3.5; N, 3.5. Calc. for $C_{13}H_{14}Cl_2NPPd$: C, 39.8; H, 3.6; N, 3.6%). ^1H $[(CD_3)_2SO]$ and ^{31}P-{^1H} NMR $[(CD_3)_2SO]$ identical to the spectra recorded for the optically active analogues.

Preparation of (±)-[SP-4-2]-[(2-*Aminophenyl*)*methylphenylphosphine*-N,P]*dichloroplatinum*(II), (±)-**5**.—Anhydrous sodium carbonate (0.5 g, 4.7 mmol) and dichloro(cycloocta-1,5-diene)platinum(II) (1.25 g, 3.4 mmol) were suspended in methanol (70 cm^3) and the mixture boiled for 5 min. The hot solution was filtered and (±)-L^2 (0.72 g, 3.4 mmol) added to the stirred solution. Hydrochloric acid (10 mol dm^{-3}, 20 cm^3) was added and the volume of the solution reduced to *ca.* 35 cm^3 to give an off-white precipitate. The solid was collected and recrystallised from dichloromethane–methanol to give fine white needles of (±)-**5** (0.9 g, 56%), m.p. 248 °C (decomp.). ^1H NMR $[(CD_3)_2SO]$: δ 2.19 (d, 3 H, $^2J_{PH}$ 12.2 Hz, PMe), 7.37–8.45 (m, 11 H, NH_2 and aromatics). ^{31}P-{^1H} NMR $[(CD_3)_2SO]$: δ 11.16 (s, 1 P, $^1J_{PtP}$ 3837 Hz).

Bis(bidentate ligand) Complexes. Preparation of (±)-[SP-4-1-(*R*,R**)]-*Bis*[(2-*aminophenyl*)*methylphenylphosphine*]*nickel*(II) *Perchlorate*, (R*,R*)-**6**.—A solution of (±)-L^2 (2.13 g, 9.9 mmol) in acetone (50 cm^3) was added to a solution of hexaaquanickel(II) perchlorate (1.81 g, 5.0 mmol) in acetone (50 cm^3) and the mixture stirred for 1 h. The volume of the solution was reduced to *ca.* 20 cm^3 and diethyl ether added to give deep orange prisms of (*R*,R**)-**6** (2.86 g, 84%), m.p. 305 °C (decomp.) (Found: C, 45.2; H, 4.0; N, 4.0. Calc. for $C_{26}H_{28}Cl_2N_2NiO_8P_2$: C, 45.4; H, 4.1; N, 4.1%). ^1H NMR $[(CD_3)_2CO]$: δ 1.50 (t, 6 H, $|^2J_{PH} + {}^4J_{P'H}|$ 12.7 Hz, PMe), 6.69 (br s, 4 H, NH_2), 7.40–7.81 (m, 18 H, aromatics). ^1H NMR $[(CD_3)_2CO$ after 6 h]: δ 1.49 (t, 3.7 H, $|^2J_{PH} + {}^4J_{P'H}|$ 12.7, PMe *rac*), 2.42 (t, 2.3 H, $|^2J_{PH} + {}^4J_{P'H}|$ 11.3 Hz, PMe *meso*), 6.69 (br s, 2.5 H, NH_2 *rac*), 6.70 (br s, 1.5 H, NH_2 *meso*), 7.14–7.81 (m, 18 H, aromatics). ^{31}P-{^1H} NMR $[(CD_3)_2CO]$: δ 31.77 (s, 2 P). ^{31}P-{^1H} NMR $[(CD_3)_2CO$ after 6 h]: δ 31.77 (s, 1.2 P, *rac*), 32.01 (s, 0.8 P, *meso*).

Preparation of [SP-4-1-(S,S)]-*Bis*[(2-*aminophenyl*)*methylphenylphosphine*]*nickel*(II) *Perchlorate*, (S,S)-**6**.—This compound was prepared in a similar manner to the racemic analogue (*R*,R**)-**6** in 85% yield, m.p. 298 °C (decomp.) (Found: C, 45.2; H, 3.8; N, 3.7. Calc. for $C_{26}H_{28}Cl_2N_2NiO_8P_2$: C, 45.5; H, 4.1; N, 4.1%). α +258° (589 nm, *c* 0.334 g per 100 cm^3, Me_2CO). ^1H NMR $[(CD_3)_2CO]$ and ^{31}P-{^1H} NMR $[(CD_3)_2CO]$: identical to the spectra of pure (*R*,R**)-**6**.

Preparation of (±)-[SP-4-2-(R*,R*)]-*Bis*[(2-*aminophenyl*)-*methylphenylphosphine*]*palladium*(II) *Hexafluorophosphate*, (R*,R*)-**7**.—A solution of (±)-L^2 (0.62 g, 2.9 mmol) in ethanol (5 cm^3) was added to a solution of the dichloro complex (±)-**3** (1.13 g, 2.9 mmol) in ethanol (135 cm^3). The resulting yellow solution was filtered and the solvent removed by evaporation. The residue was dissolved in hot water (100 cm^3) and a solution of NH_4PF_6 (0.93 g, 57.6 mmol) in water (5 cm^3) added dropwise to give a white precipitate of (*R*,R**)-**7**–(*R*,S**)-**7** (1.49 g, 73%). ^1H NMR $[(CD_3)_2CO]$: δ 1.80 (d, 3.7 H, $^2J_{PH}$ 10.8, PMe *rac*), 2.62 (d, 2.3 H, $^2J_{PH}$ 10.3 Hz, PMe *meso*), 7.21–7.90 (m, 22 H, NH_2 and aromatics). ^{31}P-{^1H} NMR $[(CD_3)_2CO]$: δ 36.28 (s, 1.2, P, *rac*), 36.70 (s, 0.8 P, *meso*). Recrystallisation of the white precipitate from acetone–diethyl ether gave pure (*R*,R**)-**7** (0.6 g, 29%), m.p. 290 °C (decomp.) (Found: C, 37.6; H, 3.1; N, 3.1. Calc. for $C_{26}H_{28}F_{12}N_2P_4Pd$: C, 37.8; H, 3.4; N, 3.4%). ^1H NMR $[(CD_3)_2CO]$: δ 1.80 (d, 6 H, $^2J_{PH}$ 10.8 Hz, PMe), 7.36 (br s, 4 H, NH_2), 7.41–7.90 (m, 18 H, aromatics). ^{31}P-{^1H} NMR $[(CD_3)_2CO]$: δ 36.28 (s, 2 P).

Preparation of [SP-4-1-(S,S)]-*Bis*[(2-*aminophenyl*]*methylphenylphosphine*]*palladium*(II) *Hexafluorophosphate*, (S,S)-**7**.—This compound was prepared in a similar manner to its racemic analogue (*R**,*R**)-**7** in 77% yield, m.p. 285 °C (Found: C, 37.8; H, 3.3; N, 3.0. Calc. for $C_{26}H_{28}F_{12}N_2P_4Pd$: C, 37.8; H, 3.4; N, 3.4%). α +343° (589 nm, *c* 0.867 g per 100 cm^3, Me_2CO). ^1H NMR [$(CD_3)_2CO$] and ^{31}P-{^1H} NMR [$(CD_3)_2CO$]: identical to the spectra of pure (*R**,*R**)-**7**.

Preparation of [SP-5-13-(R*,R*),(R*,S*)]-*Bis*[(2-*aminophenyl*)*methylphenylphosphine*]*chloroplatinum*(II) *Chloride Dihydrate*, (R*,R*),(R*,S*)-**8a**.—The racemic ligand (±)-L^2 (0.25 g, 1.2 mmol) and the dichloro complex (±)-**5** (0.56 g, 1.2 mmol) were suspended in ethanol (70 cm^3) and the mixture stirred until the solution became clear. The solvent was then removed by evaporation and the residue recrystallised from dichloromethane–diethyl ether to give (*R**,*R**),(*R**,*S**)-**8a** (0.8 g, 99%), m.p. 235 °C (decomp.) (Found: C, 42.4; H, 4.5; N, 3.5. Calc. for $C_{26}H_{32}Cl_2N_2O_2P_2Pt$: C, 42.6; H, 4.4; N, 3.8%). ^1H NMR [$(CD_3)_2SO$]: δ 1.97 (d, 3 H, $^2J_{PH}$ 12, PMe *rac*), 2.21 (d, 3 H, $^2J_{PH}$ 12 Hz, PMe *meso*), 7.21–7.73 (m, 22 H, NH_2 and aromatics).

Preparation of [SP-4-2-(R*,R*),(R*,S*)]-*Bis*[(2-*aminophenyl*)*methylphenylphosphine*]*platinum*(II) *Hexafluorophosphate*, (R*,R*),(R*,S*)-**8b**.—The mixture of diastereomeric chloride salts (R*,R*),(R*,S*)-**8a** (0.40 g, 0.58 mmol) was dissolved in hot water (25 cm^3) and a solution of NH_4PF_6 (0.2 g, 1.2 mmol) in water (5 cm^3) added dropwise to give a white precipitate. The precipitate was collected and recrystallised from acetone to afford (*R**,*R**),(*R**,*S**)-**8b** (0.5 g, 94%), m.p. 262 °C (decomp.) (Found: C, 34.0; H, 3.4; N, 3.0. Calc. for $C_{26}H_{28}F_{12}N_2P_4Pt$: C, 34.1; H, 3.1; N, 3.1%). ^1H NMR [$(CD_3)_2SO$]: δ 1.93 (d, 3 H, $^2J_{PH}$ 11.5, PMe *rac*), 2.65 (d, 3 H, $^2J_{PH}$ 11.5 Hz, PMe *meso*), 7.20–7.91 (m, 22 H, NH_2 and aromatics).

Deprotonation of Bis(*bidentate ligand*) *Complexes*.—These reactions were carried out for all of the bis(bidentate ligand) complexes of bivalent nickel and palladium. The procedure involved suspension of the appropriate complex in acetone, thf or dichloromethane followed by the addition of excess anhydrous sodium carbonate. The deprotonated complexes were characterised by ^1H NMR spectroscopy (Table 2).

Synthesis and Separation of (R*,R*)- *and* (R*,S*)-1,3-*Bis*{[2-(*methylphenylphosphino*)*phenyl*]*amino*}*propane*, (R*,R*)- *and* (R*,S*)-L^3.—To a mixture of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.62 g, 5.30 mmol) and *n*-butyllithium (2.88 cm^3 of a 1.6 mol dm^{-3} solution in *n*-hexane, 5.29 mmol) was added a solution of the ligand (±)-L^2 (0.95 g, 4.41 mmol) in thf (10 cm^3) at 0 °C. The resulting yellow solution was added dropwise to a solution of 1,3-bis(*p*-tolylsulfonyloxy)propane (0.85 g, 2.21 mmol) in thf (20 cm^3) at −78 °C. The reaction mixture was stirred at room temperature for 2 h and the solvent then removed by evaporation. The residue was dissolved in dichloromethane (20 cm^3), the extract dried over magnesium sulfate, filtered and the solvent removed by evaporation to afford a yellow oil. The crude product was a mixture of unreacted (±)-L^2, and (*R**,*R**)- and (*R**,*S**)-L^3. ^1H NMR ($CDCl_3$): δ 1.54 (d, 6 H, $^2J_{PH}$ 4.8 Hz, PMe, L^3), 1.58 (d, 3 H, $^2J_{PH}$ 3.3, PMe, L^2), 1.60 (d, 6 H, $^2J_{PH}$ 3.9, PMe, L^3), 2.23 (m, 4 H, CH_2), 4.03 (m, 8 H, NCH_2), 4.64 (br s, 2 H, NH), 6.50–7.44 (m, aromatics). The remaining NH resonances were obscured by the other resonances. ^{31}P-{^1H} NMR ($CDCl_3$): δ −44.2 (s, 2 P, L^3), −42.8 (s, 1 P, L^2), −36.7 (s, 2 P, L^3). The mixture of (±)-L^2, and (*R**,*R**)- and (*R**,*S**)-L^3 was dissolved in acetone (30 cm^3) and added dropwise to a solution of hexaaquanickel(II) perchlorate (0.99 g, 2.71 mmol) in acetone (10 cm^3). The solvent was removed by evaporation and the residue dissolved in hot methanol (20 cm^3). Bright orange prisms of (*R**,*R**,*S**,*R**)-[NiL^3][ClO_4]$_2$·0.5MeOH (0.21 g, 13%) formed on cooling the solution to room temperature, m.p. 308 °C (decomp.) (Found: C, 47.4; H, 4.3; Cl, 9.6; N, 3.7. Calc. for $C_{29.5}H_{34}Cl_2N_2NiO_{8.5}P_2$: C, 47.6; H, 4.6; Cl, 9.5; N, 3.7%). ^1H NMR (CD_3CN): δ 1.10 (d, 3 H, $^2J_{PH}$ 12.2, PMe), 1.35 (d, 3 H, $^2J_{PH}$ 11.8 Hz, PMe), 2.28 (m, 2 H, CH_2), 3.62 (m, 4 H, NCH_2), 6.91–7.83 (m, 18 H, aromatics). The NH resonances were obscured by other resonances. ^{31}P-{^1H} NMR (CD_3CN): δ 28.9, 31.7 (AB quartet, 2 P, $^2J_{PP}$ 108 Hz).

X-Ray Crystallography.—*Crystal data for* (*R**,*R**,*S**,*R**)-[NiL^3][ClO_4]$_2$. $C_{29}H_{32}Cl_2N_2NiO_8P_2$, *M* = 728.13, monoclinic, space group $P2_1/c$ (no. 14), *a* = 15.993(3), *b* = 10.421(2), *c* = 19.588(2) Å, *U* = 3189.8(9) $Å^3$ (by least-squares analysis of the setting of 25 reflections 27.3 < 2θ < 33.7°), Mo-Kα radiation (λ = 0.710 69 Å with a graphite monochromator), *Z* = 4, D_c = 1.516 g cm^{-3}, *F*(000) = 1504, specimen 0.14 × 0.18 × 0.29 mm, μ(Mo-Kα) = 9.27 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 2θ value of 50° on a Rigaku AFC6S diffractometer. Scans of (1.10 + 0.34 tan θ)° were made at a speed of 2.0° min^{-1} (in ω). The weak reflections [$I < 10.0\sigma(I)$] were rescanned (maximum of 4 scans) and the counts accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. Of the 6213 reflections which were collected, 5988 were unique (R_{int} = 0.023). The intensities of three representative reflections were measured after every 150 reflections. No decay correction was required. An analytical absorption correction was applied which resulted in transmission factors ranging from 0.86 to 0.90. The data were corrected for Lorentz and polarisation effects.

Structure analysis and refinement. The structure was solved by Patterson methods[19] with anisotropic displacement factors and expanded using Fourier techniques.[20] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically generated positions but were not refined. The final cycle of full-matrix least-squares refinement was based on 3345 observed reflections [$I > 3.00\sigma(I)$] and 397 variable parameters and converged (largest parameter shift was 0.09 times its e.s.d.) with final *R* and *R*′ values of 0.058 and 0.038, respectively. The standard deviation of an observation of unit weight was 3.13. The weighting scheme was based on counting statistics and included a factor (*p* = 0.002) to downweight the intense reflections. The maximum and minimum peaks on the final Fourier difference map corresponded to 0.69 and −0.61 e $Å^{-3}$, respectively. Neutral-atom scattering factors were taken from Cromer and Waber.[21] Anomalous dispersion effects were included in F_c;[22] the values for Δ*f*′ and Δ*f*″ were those of Creagh and McAuley.[23] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[24] All calculations were performed using the TEXSAN[25] software package.

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

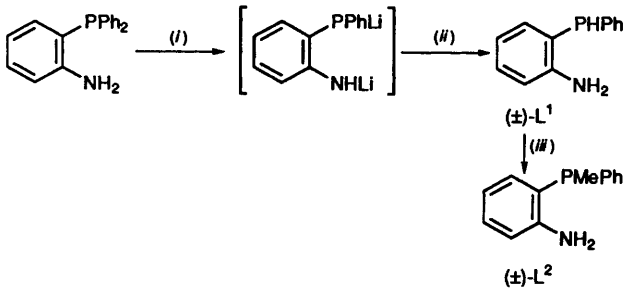
Results and Discussion

Synthesis and Resolution of (±)-L^2.—The asymmetric bidentate ligand (±)-(2-aminophenyl)methylphenylphosphine, (±)-L^2, was prepared from (2-aminophenyl)diphenylphosphine[14] in a two-step synthesis (Scheme 1). In the first step, (2-aminophenyl)diphenylphosphine was treated with 3 equivalents of lithium in thf, followed by hydrolysis with water to give the chiral secondary phosphine (±)-(2-aminophenyl)phenylphosphine, (±)-L^1, in 84% yield. When less than three equivalents of lithium were used some unreacted starting material was recovered from the reaction. Presumably deprotonation of the amino group accompanied the chemoselective cleavage of a phenyl moiety from (2-aminophenyl)-

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

	δ				
Compound[a]	CMe[b]	PMe[c]	NMe[d]	CH	H$^{\gamma}$
(*S*,*S*)-**2b**	1.93 (d, 6.4)	2.52 (d, 10.2)	2.97 (d, 1.5), 3.22 (d, 3.4)	4.74 (m)	*e*
(*R*,*S*)-**2b**	1.93 (d, 6.3)	2.29 (d, 10.5)	2.98 (d, 1.7), 3.20 (d, 3.4)	4.73 (m)	6.95 (dd)[f]

[a] In $(CD_3)_2CO$. [b] $^3J_{HH}$ given in Hz in parentheses. [c] $^2J_{PH}$ given in Hz in parentheses. [d] $^4J_{PH}$ given in Hz in parentheses. [e] Obscured by the aromatic resonances. [f] $^3J_{HH}$ 9 and J_{PH} 6 Hz.

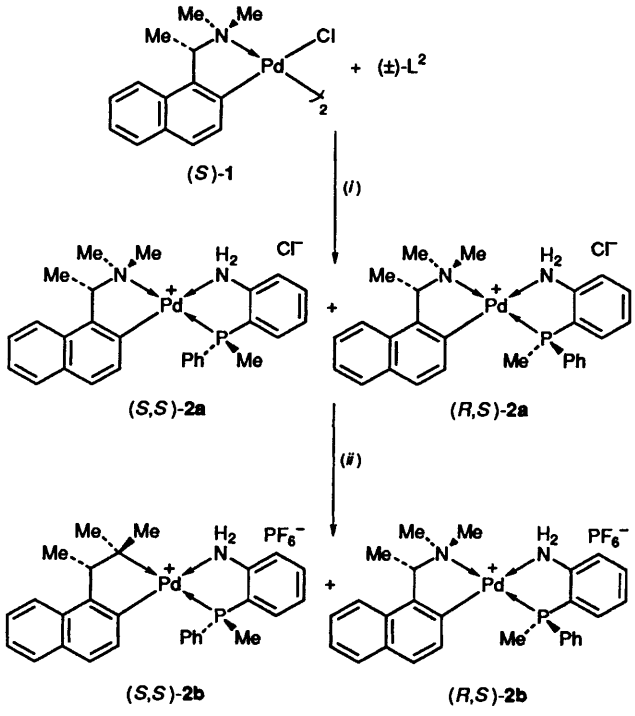


Scheme 1 (*i*) 3Li in thf; (*ii*) H_2O; (*iii*) Na in thf, MeI in thf

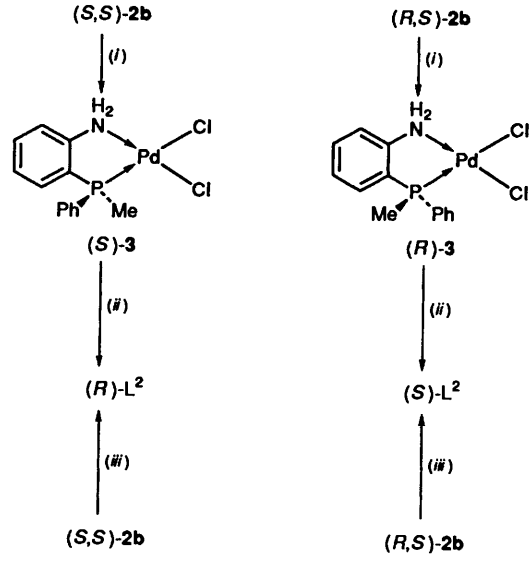
diphenylphosphine.† Subsequent treatment of (±)-L^1 with 1 equivalent of sodium in thf followed by the addition of a solution of methyl iodide in the same solvent at −78 °C gave (±)-L^2 in 90% yield.

The resolution of (±)-L^2 was achieved by the separation by fractional crystallisation of a pair of internally diastereomeric palladium(II) complexes containing the racemic ligand and orthometallated (*S*)-[1-(1-ethyl)naphthyl]dimethylamine. A pair of diastereomeric chloride salts, *viz.* (*S*,*S*)- and (*R*,*S*)-**2a**, was produced in a bridge-splitting reaction involving (±)-L^2 and (+)$_{589}$-di-μ-chloro-bis{(*S*)-1-[1-(dimethylamino)ethyl]-naphthyl-C^2,N}dipalladium(II), (*S*)-**1**, in methanol (Scheme 2). The addition of an excess of aqueous ammonium hexafluorophosphate to the solution precipitated a 1:1 mixture of the diastereomeric hexafluorophosphate salts (*S*,*S*)- and (*R*,*S*)-**2b** in 92% yield. Fractional crystallisation of the diastereomeric mixture from dichloromethane by the addition of propan-2-ol gave colourless rosettes of (*S*,*S*)-**2b**, α +163° (589 nm, acetone). Diastereomer (*R*,*S*)-**2b** was obtained by evaporating the mother-liquor to dryness and twice recrystallising the residue from acetone–diethyl ether. Pure (*R*,*S*)-**2b** was isolated as colourless needles, α −101.6° (589 nm, acetone). Two different procedures were employed to liberate the resolved tertiary phosphines from (*S*,*S*)- and (*R*,*S*)-**2b**. The first method involved dissolution of diastereomerically pure (*S*,*S*)- or (*R*,*S*)-**2b** in concentrated sulfuric acid followed by the addition of lithium chloride to give the respective dichloropalladium(II) complexes (*S*)- and (*R*)-**3**, α ±42° (589 nm, Me_2SO) (Scheme 3). Subsequent treatment of (*S*)- or (*R*)-**3** with aqueous potassium cyanide gave the respective optically pure antipodes (*R*)- and (*S*)-L^2, α ±160° (589 nm, acetone). Alternatively, treatment of (*S*,*S*)- or (*R*,*S*)-**2b** with (*R**,*R**)-1,2-phenylenebis(methylphenylphosphine), (*R**,*R**)-diph,[16] in dichloromethane gave the optically pure enantiomers (*R*)- and (*S*)-L^1 directly after removal by filtration of the internally diastereomeric palladium(II) complexes (*SS*,*S*)- and (*RR*,*S*)-**4** (Scheme 3).

The ^{1}H NMR spectra of the internally diastereomeric complexes (*S*,*S*)- and (*R*,*S*)-**2b** in $(CD_3)_2CO$ were consistent with the two nitrogen donor atoms being *cis* to one another. The NMe groups are non-equivalent in both (*S*,*S*)- and



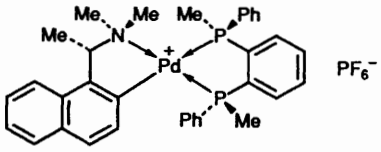
Scheme 2 (*i*) MeOH; (*ii*) NH_4PF_6 in water



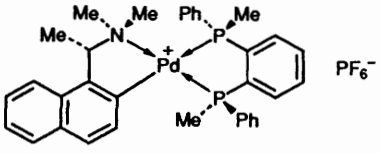
Scheme 3 (*i*) Concentrated H_2SO_4, anhydrous LiCl; (*ii*) KCN in water; (*iii*) (*R**,*R**)-1,2-phenylenebis(methylphenylphosphine) in dichloromethane

(*R*,*S*)-**2b** and coupled to the phosphorus atom *trans* to them. The methine proton is also coupled to the phosphorus atom. A similar stereochemical arrangement has been observed in solution for related palladium(II) complexes containing the enantiomers of (±)-methylphenyl(8-quinolyl)phosphine,

† Chemoselective cleavage of a phenyl group from (2-aminophenyl)-diphenylphosphine has previously been reported by Cooper and co-workers,[26] however, the stoichiometry of the reaction was not addressed in this communication.



(*SS,S*)-**4**



(*RR,S*)-**4**

(±)-(2-aminoethyl)methylphenylphosphine, and (*R**,*R**)- and (*R**,*S**)-1-(methylphenylarsino)-2-(methylphenylphosphino)-benzene.[15,27,28] Selected ^{1}H NMR data for (*S,S*)- and (*R,S*)-**2b** are given in Table 1. Furthermore, the positions of the chemical shifts of the proton attached to C(3) of the naphthyl ring (H$^{\gamma}$) in (*S,S*)- and (*R,S*)-**2b**, δ > 7.30† and 6.95, respectively, were used to assign the absolute configuration of the stereogenic phosphorus donor atom in the two complexes. In previous work on related internally diastereomeric palladium(II) complexes containing (±)-methylphenyl(8-quinolyl)phosphine and orthometallated (*R*)-[1-(1-ethyl)naphthyl]dimethylamine it was shown that when the stereogenic carbon and phosphorus atoms have opposite absolute configurations H$^{\gamma}$ of the naphthyl ring was shielded by the phenyl group attached to the phosphorus atom and hence resonated to higher field.[15] In this case the assignment was confirmed by a crystal structure determination of the (*S,R*) diastereomer. It is noteworthy that H$^{\gamma}$ of the naphthyl ring was also coupled to the phosphorus atom, as indeed was the case for (*R,S*)-**2b**, and was attributed to a through-space interaction.

Complexes of (R)-L^2 *and* (±)-L^2.—The mono(bidentate ligand) dichloro complexes of bivalent palladium and platinum, (±)-**3** and (±)-**5**, were prepared by reacting the racemic ligand (±)-L^2 with the dimer di-μ-chloro-bis{2-[(dimethylamino)-methyl]phenyl-*C*^{2},*N*}dipalladium(II) and dichloro(cycloocta-1,5-diene)platinum(II), respectively. The square-planar bis(bidentate ligand) complexes of palladium(II) and platinum(II), (*R**,*R**)-**7**, (*S,S*)-**7** and (*R**,*R**),(*R**,*S**)-**8b**, were prepared by reacting the appropriate dichloro complex with (±)-L^2 or (*R*)-L^2 followed by the addition of excess aqueous NH_4PF_6; the nickel(II) analogues, (*R**,*R**)-**6** and (*S,S*)-**6**, were prepared from hexaaquanickel(II) perchlorate and two equivalents of (±)-L^2 and (*R*)-L^2, respectively. The bis(bidentate ligand)nickel(II) complex containing the racemic ligand (±)-L^2 was isolated as the racemic diastereomer (*R**,*R**)-**6** in a typical second-order asymmetric transformation.[29] Complex (*R**,*R**)-**6**, however, undergoes facile ligand exchange in solution, an equilibrium mixture of *meso* and racemic diastereomers in the ratio of 1.0:1.6, respectively, being established within 6 h in acetone. The corresponding palladium(II) and platinum(II) complexes, however, were isolated as a mixture of racemic and *meso* diastereomers, *viz.* (*R**,*R**),(*R**,*S**)-**7** and (*R**,*R**),(*R**,*S**)-**8b**. In the case of the palladium(II) complex the diastereomeric mixture was separated by fractional crystallisation from acetone to give pure (*R**,*R**)-**7**. The *meso* diastereomer (*R**,*S**)-**7** could not be isolated in a pure form nor could the platinum(II) analogues be separated by fractional crystallisation. No evidence for intermolecular ligand exchange was observed for (*R**,*R**)-**7** in solution.

Stereochemical assignments for the various bis(bidentate ligand) complexes were made using ^{1}H NMR spectroscopy. For example, the racemic complexes (*R**,*R**)-**6** and (*R**,*R**)-**7** were identified on the basis that their ^{1}H NMR spectra were identical to that of the optically active analogues (*S,S*)-**6** and (*S,S*)-**7**. Selected ^{1}H NMR data for the complexes are given in Table 2. The data clearly show that the bis(bidentate ligand) complexes of palladium(II) and platinum(II) form exclusively *cis* diastereomers while the nickel(II) analogues adopt *trans* configurations (Fig. 1). The PMe groups of the former complexes resonate as doublets ($^2J_{PP'}$ *ca.* 0 Hz), consistent with the phosphorus atoms being *cis* to one another,[30] whereas deceptively simple triplets ($^2J_{PP'} \gg |^2J_{PH} + {}^2J_{P'H}|$) were observed for the same moieties in the nickel(II) derivatives, which is consistent with a *trans* arrangement of the phosphorus donor atoms.[31] The upfield PMe resonance in the ^{1}H NMR spectrum of complex (*R**,*R**),(*R**,*S**)-**8b** was assigned to the racemic diastereomer by analogy with the palladium(II) complex which had the same stereochemistry.

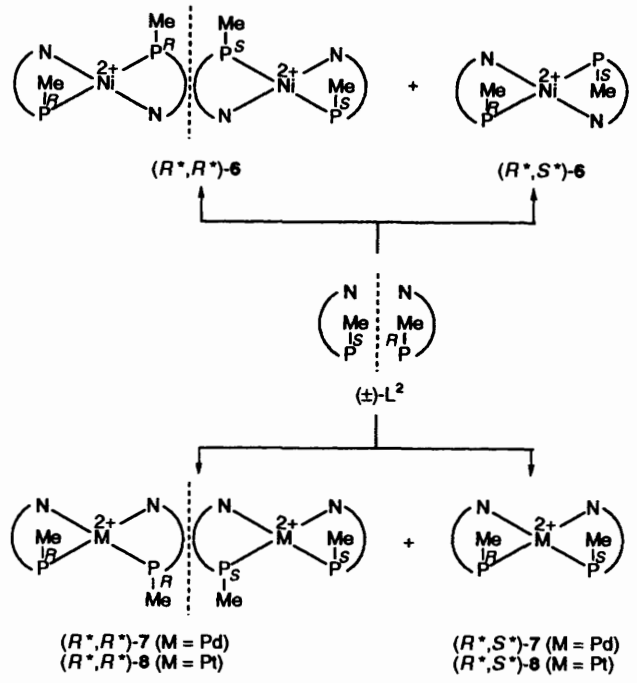


Fig. 1 Stereochemical representation of the square-planar cations *trans*-$[Ni(L^2)_2]^{2+}$ and *cis*-$[M(L^2)_2]^{2+}$ (M = Pd or Pt)

Monodeprotonation of both of the co-ordinated amino groups in the bis(bidentate ligand) complexes of bivalent nickel and palladium was achieved by reaction with anhydrous sodium carbonate in acetone, thf or dichloromethane. The deprotonated complexes were not isolated but were identified in solution by ^{1}H NMR spectroscopy (Table 2). The nickel(II) complexes were again present as *trans* diastereomers while the palladium(II) derivatives had *cis* configurations. Furthermore, the ^{1}H NMR spectra of the deprotonated complexes generated from (*R**,*R**)-**6** and (*R**,*R**)-**7** showed an equilibrium mixture of racemic and *meso* diastereomers when recorded immediately. Thus, facile ligand exchange was occurring in solution for these complexes. The racemic diastereomers of the deprotonated complexes were identified by comparison of their ^{1}H NMR spectra with those of the optically active analogues.

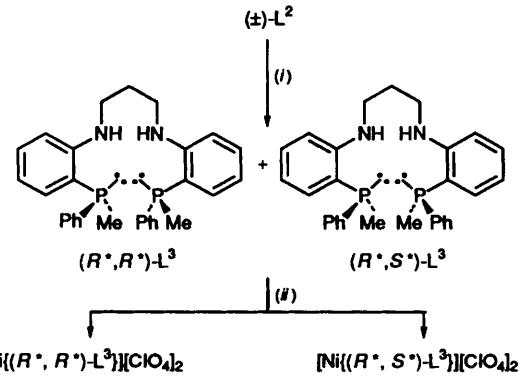
Preparation of (R*,R*,S*,R*)-$[NiL^3][ClO_4]_2$.—The deprotonated bis(bidentate ligand) complexes of bivalent nickel and palladium were seen as potential precursors for the template synthesis of the quadridentate ligand (*R**,*R**)- and (*R**,*S**)-1,3-bis{[2-(methylphenylphosphino)phenyl]amino}propane, (*R**,*R**)- and (*R**,*S**)-L^3. Cooper *et al.*[13] had previously shown that the deprotonated complex derived from bis[(2-amino-phenyl)diphenylphosphine]nickel(II) perchlorate reacted with

† Resonance obscured by the other aromatic proton resonances.

Table 2 Selected ^1H NMR and ^{31}P-{^1H} NMR data for ligands (±)-L^2, (R^*,R^*)-L^3 and (R^*,S^*)-L^3 and complexes of the type $[MCl_2(L^2)]$, $[Ni(L^2)_2][ClO_4]_2$, $[M(L^2)_2][PF_6]_2$ and $[NiL^3][ClO_4]_2$

	^1H (δ)		^{31}P-{^1H} (δ)
Compound[a]	PMe[b]	NH	P
(±)-L^2[c]	1.58 (d, 3.3)	4.07 (br s)	−42.8 (s)
(±)-**3**[d]	2.26 (d, 2.6)	*e*	41.1 (s)
(±)-**5**[d]	2.19 (d, 12.2)	*e*	11.2 (s)
(*S,S*)-**6**	1.50 (t, 12.7)[f]	6.69 (br s)	31.8 (s)
(*S,S*)-**6**[g]	1.36 (t, 11.0)[f]	5.73 (br s)	31.6 (s)
(*R*,R**)-**6**	1.50 (t, 12.7)[f]	6.69 (br s)	31.8 (s)
(*R*,R**),(*R*,S**)-**6**	1.50 (t, 12.7), 2.42 (t, 11.3)[f]	6.70 (br s)	31.8 (s), 32.0 (s)
(*R*,R**),(*R*,S**)-**6**[g]	1.36 (t, 11.0), 2.14 (t, 10.7)[f]	5.73 (br s)	31.6 (s), 31.7 (s)
(*S,S*)-**7**	1.80 (d, 10.8)	7.36 (br s)	36.3 (s)
(*S,S*)-**7**[g]	1.51 (d, 10.4)	*e*	32.7 (s)
(*R*,R**)-**7**	1.80 (d, 10.8)	7.36 (br s)	36.3 (s)
(*R*,R**),(*R*,S**)-**7**	1.80 (d, 10.8), 2.62 (d, 10.3)	*e*	36.7 (s)
(*R*,R**),(*R*,S**)-**7**[g]	1.51 (d, 10.4), 2.26 (d, 10.5)	*e*	32.7 (s), 33.1 (s)
(*R*,R**),(*R*,S**)-**8b**[d]	1.93 (d, 11.5), 2.65 (d, 11.5)	*e*	—
(*R*,R**),(*R*,S**)-L^3[c]	1.54 (d, 4.8), 1.60 (d, 3.9)	4.64 (br s)	−44.2 (s), −36.7 (s)
(*R*,R*,S*,R**)-$[NiL^3][ClO_4]_2$[h]	1.10 (d, 12.2), 1.35 (d, 11.8)	*e*	28.9, 31.7 (ABq, 108)[i]
$[NiL^3][ClO_4]_2$[h]	1.10 (d, 12.2), 1.35 (d, 11.8)	*e*	28.9, 31.7 (ABq, 108)[i]
	1.93 (d, 12.0)	*e*	37.9 (s)

[a] In $(CD_3)_2CO$ unless otherwise stated. [b] $^2J_{PH}$ given in Hz in parentheses unless otherwise stated. [c] In $CDCl_3$. [d] In $(CD_3)_2SO$. [e] Obscured by the aromatic resonances. [f] $|^2J_{PH} + {}^4J_{P'H}|$ in Hz in parentheses. [g] Deprotonated complex generated *in situ* by reaction with anhydrous sodium carbonate. [h] In CD_3CN. [i] $^2J_{PP}$ in Hz in parentheses.



Scheme 4 (*i*) LiBu^n in *n*-hexane, *N,N,N',N'*-tetramethylethylenediamine in thf 1,3-bis(*p*-tolylsulfonyloxy)propane in thf; (*ii*) $[Ni(H_2O)_6][ClO_4]_2$ in acetone

1,3-bis(*p*-tolylsulfonyloxy)propane in the presence of anhydrous potassium carbonate in refluxing toluene to give a nickel(II) complex of the tetradentate ligand 1,3-bis{[2-(diphenylphosphino)phenyl]amino}propane. Here, however, the deprotonated bis(bidentate ligand) nickel(II) complex was present in solution as a mixture of *cis* (85%) and *trans* (15%) diastereomers. Clearly the deprotonated analogue of (*R*,R**)-**6** is not a suitable precursor to the quadridentate ligand (*R*,R**)- and (*R*,S**)-L^3 because of the *trans* stereochemistry. Indeed, no evidence for the formation of the quadridentate ligand was observed when the deprotonated analogues of (*R*,R**)-**6** or (*R*,R**)-**7** were subjected to reaction conditions similar to those employed by Cooper *et al.*[13]

The quadridentate ligand (*R*,R**)- and (*R*,S**)-L^3 was synthesised by the reaction of (±)-L^2 with *n*-butyllithium and *N,N,N',N'*-tetramethylethylenediamine in thf followed by the addition of 1,3-bis(*p*-tolylsulfonyloxy)propane (Scheme 4). Separation of (*R*,R**)- and (*R*,S**)-L^3 was achieved by complexation to nickel(II). Thus, reaction of (*R*,R**)- and (*R*,S**)-L^3 with hexaaquanickel(II) perchlorate in acetone gave a 1:1 mixture of two diastereomeric complexes. Pure (*R*,R*,S*,R**)-$[NiL^3][ClO_4]_2$ was obtained upon recrystallisation of the diastereomeric mixture from methanol. The other

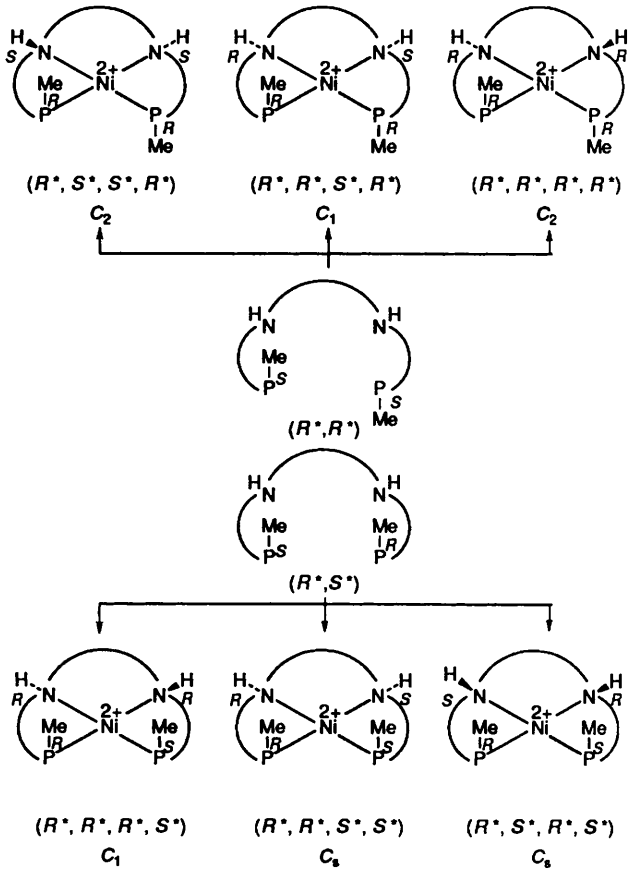


Fig. 2 Stereoisomerism in the square-planar cation $[NiL^3]^{2+}$ (Only one enantiomer of each of the four chiral diastereomers is shown)

diastereomer, however, could not be isolated in pure form. The relative stereochemistries of the two diastereomers were assigned on the basis of ^1H and ^{31}P-{^1H} NMR evidence (selected data are given in Table 2). Complex (*R*,R*,S*,R**)-$[NiL^3][ClO_4]_2$ exhibited two doublet PMe resonances at δ 1.10 and 1.35, and an AB quartet for the non-equivalent P

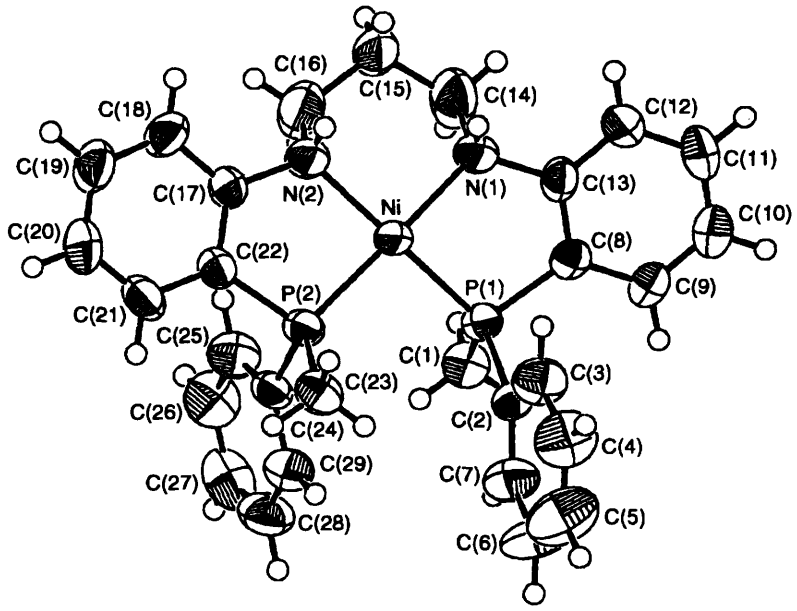


Fig. 3 Molecular structure of the cation (R^*,R^*,S^*,R^*)-$[NiL^3]^{2+}$

Table 3 Non-hydrogen atomic coordinates for (R^*,R^*,S^*,R^*)-$[NiL^3][ClO_4]_2$

Atom	*x*	*y*	*z*
Ni	0.203 88(5)	0.106 13(8)	0.222 74(4)
Cl(1)	0.993 7(1)	0.182 8(2)	0.118 1(1)
Cl(2)	0.620 8(2)	0.265 0(3)	0.152 5(2)
P(1)	0.308 4(1)	0.159 1(2)	0.175 04(9)
P(2)	0.224 5(1)	0.263 5(2)	0.295 41(10)
O(1)	0.937 7(3)	0.266 5(5)	0.072 7(3)
O(2)	0.954 2(4)	0.118 0(7)	0.163 1(3)
O(3)	1.020 7(5)	0.085 9(7)	0.077 3(3)
O(4)	1.060 8(4)	0.248 5(6)	0.154 4(4)
O(5)	0.548 3(4)	0.196 2(7)	0.117 5(3)
O(6)	0.689 6(4)	0.187 4(6)	0.171 2(4)
O(7)	0.607 5(5)	0.331 8(9)	0.207 3(4)
O(8)	0.642 4(6)	0.351 2(8)	0.107 4(6)
N(1)	0.180 3(4)	−0.035 6(5)	0.153 6(3)
N(2)	0.119 4(4)	0.040 2(5)	0.274 9(3)
C(1)	0.413 1(4)	0.122 7(7)	0.225 4(3)
C(2)	0.311 4(5)	0.316 9(6)	0.138 1(3)
C(3)	0.242 1(5)	0.359 4(7)	0.089 0(4)
C(4)	0.241 7(6)	0.479 1(9)	0.058 3(5)
C(5)	0.310 5(7)	0.556 2(9)	0.077 5(6)
C(6)	0.379 7(6)	0.518 1(9)	0.125 7(6)
C(7)	0.381 4(5)	0.397 2(8)	0.156 2(4)
C(8)	0.290 7(4)	0.054 6(6)	0.100 7(3)
C(9)	0.336 4(4)	0.056 0(7)	0.047 6(4)
C(10)	0.315 9(5)	−0.027 4(8)	−0.007 3(4)
C(11)	0.248 8(5)	−0.110 1(8)	−0.012 2(3)
C(12)	0.201 6(4)	−0.113 0(7)	0.039 3(4)
C(13)	0.225 7(4)	−0.032 7(7)	0.096 0(3)
C(14)	0.190 9(6)	−0.161 6(8)	0.186 0(4)
C(15)	0.130 3(6)	−0.188 4(8)	0.235 8(4)
C(16)	0.144 7(6)	−0.089 6(8)	0.298 0(4)
C(17)	0.101 1(4)	0.118 6(7)	0.332 8(3)
C(18)	0.037 9(5)	0.081 5(7)	0.368 1(4)
C(19)	0.024 3(5)	0.160 7(8)	0.420 8(4)
C(20)	0.068 3(5)	0.272 7(8)	0.436 6(4)
C(21)	0.129 5(5)	0.307 7(7)	0.400 7(4)
C(22)	0.147 2(4)	0.229 0(7)	0.348 6(3)
C(23)	0.200 8(4)	0.423 7(6)	0.262 6(3)
C(24)	0.326 8(4)	0.268 8(7)	0.355 4(3)
C(25)	0.349 1(5)	0.170 4(7)	0.403 1(4)
C(26)	0.427 8(6)	0.168 7(8)	0.447 4(4)
C(27)	0.486 0(5)	0.262 8(10)	0.445 2(4)
C(28)	0.464 2(5)	0.360 7(8)	0.398 3(5)
C(29)	0.384 7(5)	0.364 6(7)	0.352 7(4)

Table 4 Selected non-hydrogen interatomic distances (Å) and interatomic angles (°)

Ni–P(1)	2.153(2)	Ni–P(2)	2.151(2)
Ni–N(1)	1.985(5)	Ni–N(2)	1.982(5)
P(1)–Ni–P(2)	93.89(8)	P(1)–Ni–N(1)	87.0(2)
P(1)–Ni–N(2)	171.8(2)	P(2)–Ni–N(1)	177.6(2)
P(2)–Ni–N(2)	87.1(2)	N(1)–Ni–N(2)	92.4(2)
Ni–P(1)–C(1)	115.3(2)	Ni–P(1)–C(2)	119.8(2)
Ni–P(1)–C(8)	101.2(2)	Ni–P(2)–C(22)	101.7(2)
Ni–P(2)–C(24)	116.4(2)	Ni–P(2)–C(23)	118.7(2)
Ni–N(1)–C(13)	117.2(4)	Ni–N(1)–C(14)	112.8(5)
Ni–N(2)–C(17)	118.1(4)	Ni–N(2)–C(16)	107.9(5)

resonances at δ 28.9, 31.7 while a single doublet PMe resonance was observed at δ 1.93 and a singlet P resonance at δ 37.9 for the other diastereomer in CD_3CN in the ^1H NMR and ^{31}P-$\{^1H\}$ NMR spectra, respectively. The upfield signals in the ^1H NMR spectra were assigned to the nickel(II) complex of (R^*,R^*)-L^3 on the basis of shielding arguments. The methyl groups in the complex containing the racemic form of the quadridentate ligand will be shielded by the phenyl groups on the adjacent phosphorus atom and hence resonate to higher field. This interaction is not possible in the corresponding complex of (R^*,S^*)-L^3. Six diastereomers are possible for $[NiL^3][ClO_4]_2$ as a result of the configurational stability of the unsymmetrically substituted nitrogen donor atoms (Fig. 2). Although three of the complexes contain (R^*,R^*)-L^3, only one has non-equivalent phosphorus donor atoms, the (R^*,R^*,S^*,R^*) diastereomer. This assignment was confirmed by a crystal-structure determination (see below). For the nickel(II) complex of (R^*,S^*)-L^3 there are two diastereomeric possibilities having equivalent phosphorus stereocentres, *viz.* (R^*,R^*,S^*,S^*) and (R^*,S^*,R^*,S^*). In the absence of a crystal-structure determination it was not possible to identify this diastereomer unambiguously.

Crystal-structure Determination of (R*,R*,S*,R*)-$[NiL^3]$-$[ClO_4]_2$.—The stereochemistry of the cation is shown in Fig. 3. Non-hydrogen atomic coordinates are given in Table 3 and selected bond lengths and angles in Table 4. The nickel atom has a distorted square-planar co-ordination geometry with Ni, P(1), P(2) and N(1) being essentially coplanar [maximum deviation from least-squares plane 0.085 Å] and N(2) 0.282 Å from

the least-squares plane. The angles at the Ni atom are P(1)–Ni–P(2) 93.89(8), P(2)–Ni–N(2) 87.1(2), N(1)–Ni–N(2) 92.4(2) and N(1)–Ni–P(1) 87.0(2)°. The two phosphorus stereocentres have the same relative configurations while the two stereogenic nitrogen atoms have opposite relative configurations.

Conclusion

A key step in the synthesis of the asymmetric bidentate ligand (±)-(2-aminophenyl)methylphenylphosphine, (±)-L^2, was the chemoselective cleavage of a phenyl group from (2-aminophenyl)diphenylphosphine. Relatively few investigations of the chemoselective cleavage of alkyl or aryl groups from tertiary phosphines have been reported in the literature.[32] Nevertheless studies of this type are important as chemoselective cleavage of such groups from suitably designed bidentate ligands can provide a useful avenue to chiral multidentate ligands. For example, chemoselective cleavage of a phenyl group from (2-aminophenyl)diphenylphosphine provides a route to the quadridentate ligand (*R**,*R**)- and (*R**,*S**)-1,3-bis[(2-aminophenyl)phenylphosphino]propane[26] and the macrocycle (*R**,*S**)-5,6,7,8,9,14,15,16,17,18-decahydro-14,18-diphenyldibenzo-[*f*,*m*][1,5,8,12]diazadiphosphacyclotetradecine.[33] Furthermore, we have recently shown that chemoselective cleavage of a phenyl group from (±)-L^2 occurs in the presence of lithium in thf and provides a route to the chiral quadridentate ligand (*R**,*S**)-1-[(2-aminophenyl)methylphosphino]-2-[(2-dimethylarsinophenyl)methylarsino]benzene.[34] Importantly, the latter ligand was synthesised with complete stereoselectivity which augurs well for the role of the optically active forms of the ligand as chiral auxiliaries in enantioselective synthesis. The work of Juge[35] and Brown[36] and their co-workers on the enantioselective synthesis of dissymmetric di(tertiary phosphines) containing stereogenic donor atoms is also having a significant impact in this area of research. The optically active forms of (*R**,*R**)-1,3-bis{[2-(methylphenylphosphino)phenyl]amino}propane, (*R**,*R**)-L^3, are similarly seen as potential chiral auxiliaries in enantioselective synthesis and catalysis.

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