DALTON

# Stereoselective synthesis of chiral multidentate ligands with $As_2NP$ or $As_4P$ donor atoms*

**Roy J. Doyle,[a] Geoffrey Salem[a] and Anthony C. Willis[b]**

[a] *Chemistry Department, The Faculties, Australian National University, Canberra, A.C.T. 0200, Australia*
[b] *Research School of Chemistry, Australian National University, Canberra, A.C.T. 0200, Australia*

The asymmetric bidentate ligand (±)-(2-aminophenyl)(2-chlorophenyl)methylphosphine has been prepared *via* chemoselective cleavage of the phenyl group from (±)-(2-aminophenyl)methylphenylphosphine using lithium in tetrahydrofuran (thf), to give (2-aminophenyl)methylphosphine upon hydrolysis, followed by deprotonation of the secondary phosphine with sodium in thf and subsequent reaction with 1,2-dichlorobenzene. The chlorophenyl-substituted tertiary phosphine has been resolved by the method of metal complexation. The absolute configuration of the *R* enantiomer of the ligand has been assigned by a crystal structure determination of the diastereomeric palladium(II) complex [($S_P$),(*R*)]-[(2-aminophenyl)(2-chlorophenyl)methylphosphine-*N*,*P*]{1-[1-(dimethylamino)ethyl]naphthyl-$C^2$,*N*}palladium(II) hexafluorophosphate. Reaction of (±)-(2-aminophenyl)(2-chlorophenyl)methylphosphine with an equimolar quantity of sodium (2-dimethylarsinophenyl)-methylarsenide in thf at −20 ± 5 °C gave a 1:1 diastereomeric mixture of the chiral pentadentate ligands ($R_{As}$*,$R_{As}$*,$S_P$*)-(±)- and ($R_{As}$*,$S_{As}$*,$S_P$*)-(±)-{2-[(2-dimethylarsinophenyl)methylarsinophenyl]{2-[(2-dimethylarsinophenyl)methylarsinoamino]phenyl}methylphosphine. The chiral quadridentate ligand ($R_{As}$*,$S_P$*)-(±)-1-[(2-aminophenyl)methylphosphino]-2-[(2-dimethylarsinophenyl)methylarsino]benzene can be isolated, however, when the coupling reaction is performed at 50 ± 5 °C. The chiral multidentate ligands have been isolated by complexation to cobalt(III) and the structures of the three complexes determined by X-ray analyses. It is clear from the structural data that the quadridentate ligand has formed a single dichlorocobalt(III) complex with *cis*-α stereochemistry and in which the stereogenic arsenic and phosphorus atoms of the ligand have opposite relative configurations. Two other complexes have also been isolated from the coupling reaction: *trans*-dichlorobis[1,2-phenylenebis(dimethylarsine)]cobalt(III) chloride and bis[(2-aminophenyl)methylphenylphosphine]dichlorocobalt(III) chloride. The latter is isolated as an isomeric mixture. The formation of asymmetric bidentate (±)-(2-aminophenyl)methylphenylphosphine is believed to result from reduction of the chloro group in the tertiary phosphine precursor by the sodium arsenide reagent. Metal-assisted methylation of a (2-dimethylarsinophenyl)methylarsino moiety by methanol is postulated to account for the formation of 1,2-phenylenebis(dimethylarsine) in the reaction. Optically active analogues of the three multidentate ligands have also been synthesized by reaction of (*R*)-(2-aminophenyl)(2-chlorophenyl)methylphosphine with sodium (2-dimethylarsinophenyl)methylarsenide in thf and similarly isolated by complexation to cobalt(III).

Relatively few studies on the chemoselective cleavage of alkyl or aryl groups from tertiary arsines or phosphines have been reported.[1–3] Indeed, the chemoselective cleavage of a methyl group from 1,2-phenylenebis(dimethylarsine) by reaction with sodium in liquid ammonia is a rare example of such a reaction involving a tertiary arsine.[4] Reactions of this type and, in particular, those involving bidentate tertiary arsines and phosphines, are of interest as the resulting arsenide and phosphide salts are potential precursors to chiral quadridentate ligands containing two or more stereogenic arsenic and/or phosphorus donor atoms. For example, chemoselective cleavage of a phenyl group from (2-aminophenyl)diphenylphosphine provides a route to quadridentate (*R**,*R**)- and (*R**,*S**)-1,3-bis[(2-aminophenyl)phenylphosphino]propane and the macrocycle (*R**,*S**)-5,6,7,8,9,14,15,16,17,18-decahydro-14,18-diphenyldibenzo-[*b*,*i*][1,11,4,8]diazadiphosphacyclotetradecine.[3,5] Moreover, the coupling of suitably designed enantiomerically pure bidentate precursors could provide a route to optically active quadridentate ligands of this type.

Appropriately designed optically active quadridentate ligands bearing two or more stereogenic phosphorus or arsenic donor atoms and that selectively form *cis*-α (or *cis*-β) complexes with transition-metal ions offer an enormous potential as chiral auxiliaries in asymmetric synthesis, particularly in controlling the stereoselectivity of reactions involving substrates that bind in a bidentate fashion. A few examples of chiral facultative tetradentate ligands containing arsenic or phosphorus stereocentres have appeared in the literature, however, to our knowledge none has been utilised in enantioselective synthesis. These include: the tetra(tertiary phosphine) ($R_P$*,$R_P$*)-1,2-bis[(2-diphenylphosphinoethyl)phenylphosphino]ethane, 'tetraphos';[6] the tetra(tertiary arsines) ($R_{As}$*,$R_{As}$*)-1,2-bis[(2-dimethylarsinophenyl)methylarsino]benzene, 'qars';[7] ($R_{As}$*,$R_{As}$*)-1,2-bis[(3-dimethylarsinopropyl)methylarsino]benzene, 'fars';[7] and ($R_{As}$*,$R_{As}$*)-1,2-bis[(3-dimethylarsinopropyl)phenylarsino]ethane, 'tetars';[8] and the mixed-donor ligands (*R**,*R**)-1,2-bis[2-(methylphenylphosphino)propylamino]ethane,[9] the above-mentioned (*R**,*R**)-1,3-bis[(2-aminophenyl)phenylphosphino]propane[3] and (*R**,*R**)-1,3-bis[2-(methylphenylphosphino)phenylamino]propane.[2] The compounds 'tetars', and very recently, 'tetraphos', have also been successfully resolved.[8,10] Optically pure ($S_P$,$S_P$)-'tetraphos' was subsequently shown spontaneously to self-assemble into a homochiral double helix and side-by-side helix conformers of a double-stranded tetra(tertiary phosphine)disilver(I) complex.[11]

Of these chiral compounds, only the racemic form of 'qars' was found to co-ordinate to cobalt(III) to give the *cis*-α diastereomer exclusively.[7] This is a very important consider-

* *Non-SI units employed*: mmHg ≈ 133 Pa, atm = 101 325 Pa.

ation in any rational approach towards the design and synthesis of chiral auxiliaries based on ligands of this type due to the relatively large number of isomeric possibilities.

In this paper we report on the synthesis, *via* chemoselective cleavage of the phenyl group from (±)-(2-aminophenyl)methylphenylphosphine, and resolution of (±)-(2-aminophenyl)(2-chlorophenyl)methylphosphine, and the highly stereoselective coupling reaction between the latter and sodium (2-dimethylarsinophenyl)methylarsenide to give two chiral pentadentate ligands ($R_{As}$*,$R_{As}$*,$S_P$*)-(±)- and ($R_{As}$*,$S_{As}$*,$S_P$*)-(±)-{2-[(2-dimethylarsinophenyl)methylarsino]phenyl}{2-[(2-dimethylarsinophenyl)methylarsinoamino]phenyl}methylphosphine and a chiral quadridentate ligand (*R**,*S**)-(±)-1-[(2-aminophenyl)methylphosphino]-2-[(2-dimethylarsinophenyl)methylarsino]benzene. The optically active forms of the latter have been specifically designed to be used as chiral auxiliaries in asymmetric synthesis. A preliminary account of the work described herein has been published.[12]

## 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 (±)-(2-aminophenyl)methylphenylphosphine (±)-**I**,[2] di-μ-chloro-bis{(*R*)-1-[1-(dimethylamino)ethyl]naphthyl-*C*$^2$,*N*}dipalladium(II) (*R*)-**1** [and its enantiomer (*S*)-**1**],[13] ($R_P$*,$R_P$*)-1,2-phenylenebis(methylphenylphosphine)[14] and (±)-1-(dimethylarsino)-2-(methylarsino)benzene (±)-**IV**,[4] were prepared by literature procedures.

### Synthesis of (2-aminophenyl)methylphosphine (±)-II

Lithium wire (7.74 g, 112 mmol) was added to a stirred solution of compound (±)-**I** (80.0 g, 372 mmol) in tetrahydrofuran (thf) (600 cm$^3$) at −78 °C. The reaction mixture was allowed to come to ambient temperature and stirred for 48 h. The mixture was refluxed for 0.5 h, cooled to −15 °C and ammonium chloride (50 g) added followed by water (50 cm$^3$). The solvent was removed and the residue extracted with water (250 cm$^3$) and dichloromethane (100 cm$^3$). The aqueous layer was extracted with more dichloromethane (2 × 100 cm$^3$) and the combined organic extracts dried over anhydrous $MgSO_4$. The solvent was removed and the crude product was distilled to give (±)-**II** as a colourless liquid (48.0 g, 93%), b.p. 62–64 °C (0.08 mmHg) (Found: C, 60.6; H, 7.6; N, 10.1. Calc. for $C_7H_{10}NP$: C, 60.4; H, 7.2; N, 10.1%). NMR ($CD_2Cl_2$): $^1$H, δ 1.30 (d of d, 3 H, $^3J_{HH}$ 3.20, $^2J_{PH}$ 7.50, PMe), 4.00 (d of q, 1 H, $^3J_{HH}$ 7.56, $^1J_{PH}$ 213.5 Hz, PH), 4.02 (br s, 2 H, $NH_2$) and 6.59–7.34 (m, 4 H, aromatics); $^{31}$P-{$^1$H}, δ −89.1 (s, 1 P). *m*/*z* 139 ($M^+$) and 124 ([*M* − Me]$^+$).

### Synthesis of (±)-(2-aminophenyl)(2-chlorophenyl)methylphosphine (±)-III

Sodium foil (8.05 g, 350 mmol) was added to a stirred solution of compound (±)-**II** (48.7 g, 350 mmol) in thf (500 cm$^3$) at −78 °C. The reaction mixture was allowed to come slowly to ambient temperature and stirred for 48 h. The resulting clear yellow solution was cooled to −78 °C and a solution of 1,2-dichlorobenzene (51.45 g, 350 mmol) in thf (50 cm$^3$) was added dropwise. The reaction vessel and contents were transferred to a cold bath (ethylene glycol) maintained at 0 ± 5 °C and the reaction mixture stirred for 5 d, after which the temperature was raised to 20 ± 5 °C and the mixture stirred for 48 h. The solvent was removed by distillation under argon at 1 atm. The reaction mixture was cooled to −15 °C and ammonium chloride (50 g) added. Water (200 cm$^3$) was added and the resulting colourless solution was extracted with dichloromethane (3 × 100 cm$^3$). The combined dichloromethane extracts were dried ($MgSO_4$), filtered and the solvent removed by distillation at 1 atm under argon. The crude product was distilled and two fractions were collected. Fraction 1 (b.p. 60–63 °C, 0.08 mmHg) was unreacted (±)-**II** (16.8 g, 34.5%). Fraction 2 (b.p. 144 ± 2 °C, 0.03 mmHg) was (±)-**III** and was isolated as a clear, highly viscous oil which spontaneously solidified on standing (44.5 g, 77%) [based on 66% conversion of (±)-**II**]. The tertiary phosphine was twice recrystallised from hot methanol to give white hexagonal plates of (±)-**III**. These were collected, washed with cold methanol–diethyl ether (1:1, 2 × 10 cm$^3$) and dried *in vacuo* (42 g, 94%), m.p. 76–78 °C (Found: C, 62.5; H, 5.3; Cl, 14.3; N, 5.7. Calc. for $C_{13}H_{13}ClNP$: C, 62.5; H, 5.2; Cl, 14.2; N, 5.6%). NMR ($CDCl_3$): $^1$H, δ 1.61 (d, 3 H, $^2J_{PH}$ 3.96 Hz, PMe), 4.21 (br s, 2 H, $NH_2$) and 6.64–7.38 (m, 8 H, aromatics); $^{31}$P-{$^1$H}, δ −48.5 (s, 1 P). *m*/*z* 249 ($M^+$), 234 ([*M* − Me]$^+$) and 214 ([*M* − Cl]$^+$). The compound is UV, but not air, sensitive.

### Resolution of (±)-III: formation and separation of internally diastereomeric complexes, [*SP*-4-2-($S_P$),(*R*)]-[(2-aminophenyl)(2-chlorophenyl)methylphosphine-*N*,*P*]{1-[1-(dimethylamino)ethyl]naphthyl-*C*$^2$,*N*}palladium(II) hexafluorophosphate ($S_P$,*R*)-2

To a suspension of the resolving agent (*R*)-**1** (11.60 g, 17.1 mmol) in methanol (100 cm$^3$) was slowly added a solution of compound (±)-**III** (8.52 g, 34.1 mmol) in methanol (60 cm$^3$) with stirring. The resulting pale yellow solution was filtered and a solution of an excess of $NH_4PF_6$ (16.68 g, 102 mmol) in water (15 cm$^3$) was added dropwise, followed by water (65 cm$^3$). The resulting white precipitate was collected, washed with cold water (10 cm$^3$), cold water–methanol (1:1, 10 cm$^3$), cold methanol (5 cm$^3$) and finally diethyl ether (10 cm$^3$), and then dried *in vacuo* (21.48 g, 90%). α −50° (589 nm, *c* 0.912 g per 100 cm$^3$, acetone). The 1:1 diastereomeric mixture of hexafluorophosphate salts was dissolved in hot chloroform (120 cm$^3$) and propan-2-ol (60 cm$^3$) was added to give a crystalline material enriched in ($S_P$,*R*)-**2**. The mother-liquor was taken to dryness and the residue again dissolved in hot chloroform (60 cm$^3$) and propan-2-ol (30 cm$^3$) was added to give a second crop of crystalline material enriched in ($S_P$,*R*)-**2**. The two crops were combined and recrystallised from dichloromethane–propan-2-ol to give pure ($S_P$,*R*)-**2** as colourless needles. These were collected, washed with chloroform (5 cm$^3$) and diethyl ether (5 cm$^3$), and dried *in vacuo* (8.60 g, 80%), m.p. 262–265 °C (Found: C, 46.3; H, 4.2; Cl, 5.2; N, 4.0; P, 8.9. Calc. for $C_{27}H_{29}ClF_6N_2P_2Pd$: C, 46.4; H, 4.2; Cl, 5.1; N, 4.0; P, 8.8%). α −225° (589 nm, *c* 0.88 g per 100 cm$^3$, acetone). NMR ($CD_2Cl_2$): $^1$H, δ 1.84 (d, 3 H, $^3J_{HH}$ 6.40, CMe), 2.33 (d, 3 H, $^2J_{PH}$ 9.33, PMe), 2.90 (d, 3 H, $^4J_{PH}$ 1.59, NMe), 3.04 (d, 3 H, $^4J_{PH}$ 3.60, NMe), 4.43 (m, 1 H, CM*e*H), 4.79 (d, 1 H, $^2J_{PH}$ 13.30, NH*H*), 5.60 (d, 1 H, $^2J_{HH}$ 13.80, N*H*H), 6.92 (d of d, 1 H, $^4J_{HH}$ 6.63, $^1J_{PH}$ 8.34 Hz, H$^\gamma$) and 7.18–8.32 (m, 15 H, aromatics); $^{31}$P-{$^1$H}, δ 16.17 (s, 1 P).

### Isolation of [*SP*-4-2-($R_P$),(*S*)]-[(2-aminophenyl)(2-chlorophenyl)methylphosphine-*N*,*P*]{1-[1-(dimethylamino)ethyl]naphthyl-*C*$^2$,*N*}palladium(II) hexafluorophosphate ($R_P$,*S*)-2

After removal of the two crops of crystalline material enriched in complex ($S_P$,*R*)-**2**, the mother-liquor was evaporated to dryness to give a residue enriched in ($R_P$,*R*)-**2**. A portion of the mixture of diastereomers enriched in ($R_P$,*R*)-**2** (6.0 g, 8.58 mmol) was dissolved in dichloromethane (100 cm$^3$) and ($R_P$*,$R_P$*)-$C_6H_4$(PMePh)$_2$-1,2 (2.77 g, 8.60 mmol) in the same

solvent (20 $cm^3$) was added. The mixture was stirred vigorously for 2 h to give a white precipitate. Diethyl ether (120 $cm^3$) was added and the precipitate filtered off. [This by-product consisted of the internally diastereomeric palladium(II) complexes ($S_P$,$S_P$,$R$)- and ($R_P$,$R_P$,$R$)-**3**]. The solvent was removed from the filtrate under vacuum and the residue extracted with diethyl ether (100 $cm^3$). The mixture was filtered and the solvent removed under reduced pressure to give crude ($S_P$)-**III** (2.06 g, 96%). Crude ($S_P$)-**III** (2.06 g, 8.20 mmol) and the chloro-bridged dimer (*S*)-**1** (2.78 g, 4.10 mmol) were suspended in methanol (50 $cm^3$) and the mixture stirred for 1 h. The solution was filtered and ammonium hexafluorophosphate (1.34 g, 8.20 mmol) in water (5 $cm^3$) added dropwise. More water (10 $cm^3$) was added and the mixture stirred for 4 h. The resulting white precipitate was filtered off, washed with cold water (10 $cm^3$), cold water–methanol (1:1, 10 $cm^3$), cold methanol (5 $cm^3$) and finally diethyl ether (5 $cm^3$), and dried *in vacuo* (5.2 g, 90%). α +110° (589 nm, *c* 0.97 g per 100 $cm^3$, $Me_2CO$). Two recrystallisations from dichloromethane–propan-2-ol gave colourless plates of pure ($R_P$,*S*)-**2** (2.3 g, 40%), m.p. 263–265 °C (Found: C, 46.25; H, 4.1; N, 3.95. Calc. for $C_{27}H_{29}ClF_6N_2P_2Pd$: C, 46.35; H, 4.2; N, 4.0%). α +225° (589 nm, *c* 0.987 per 100 $cm^3$, $Me_2CO$). NMR ($CD_2Cl_2$): $^1$H and $^{31}$P-{$^1$H} identical with those recorded for the enantiomeric complex ($S_P$,*R*)-**2**.

## Preparations

**($R_P$)-(2-Aminophenyl)(2-chlorophenyl)methylphosphine ($R_P$)-III.** Diastereomerically pure complex ($S_P$,*R*)-**2** (5.88 g, 8.40 mmol) was dissolved in dichloromethane (100 $cm^3$) and ($R_P$*,$R_P$*)-$C_6H_4$(PMePh)$_2$-1,2 (2.70 g, 8.40 mmol) in the same solvent (30 $cm^3$) was added. The mixture was stirred vigorously for 2 h to give a white precipitate. Diethyl ether (100 $cm^3$) was added and the precipitate filtered off. [This by-product consisted of the internally diastereomeric palladium(II) complexes ($S_P$,$S_P$,*R*)- and ($R_P$,$R_P$,*R*)-**3**]. The mother-liquor was evaporated to dryness and the residue extracted with diethyl ether (40 $cm^3$). The organic extract was filtered and the solvent removed under reduced pressure. The residue was recrystallised from hot methanol to give pure ($R_P$)-**III** (2.04 g, 97%), m.p. 78–80 °C (Found: C, 62.55; H, 5.3; N, 5.55. Calc. for $C_{13}H_{13}ClNP$: C, 62.55; H, 5.25; N, 5.6%). α −218° (589 nm, *c* 0.70 g per 100 $cm^3$, $Me_2CO$). NMR ($CDCl_3$): $^1$H and $^{31}$P-{$^1$H} identical to the spectra recorded for the racemic compound (±)-**III**.

**($S_P$)-(2-Aminophenyl)(2-chlorophenyl)methylphosphine ($S_P$)-III.** This compound was prepared in the same manner as its enantiomer (0.70 g, 98%), m.p. 78–80 °C (Found: C, 62.5; H, 5.2; N, 5.55. Calc. for $C_{13}H_{13}ClNP$: C, 62.55; H, 5.25; N, 5.6%). α +218° (589 nm, *c* 0.66 g per 100 $cm^3$). NMR: $^1$H and $^{31}$P-{$^1$H} identical to the spectra recorded for the enantiomeric compound ($R_P$)-**III**.

**[*SP*-4-2-($R_P$),(*R*)]-[(2-Aminophenyl)(2-chlorophenyl)methylphosphine-*N*,*P*]{1-[1-(dimethylamino)ethyl]naphthyl-*C*$^2$,*N*}-palladium(II) hexafluorophosphate, ($R_P$,*R*)-2.** Pure compound ($S_P$)-**III** (0.7 g, 2.80 mmol) and the chloro-bridged dimer (*R*)-**1** (0.95 g, 1.40 mmol) were suspended in methanol (30 $cm^3$) and the mixture stirred for 1 h. The solution was filtered and ammonium hexafluorophosphate (0.46 g, 2.80 mmol) in water (2 $cm^3$) added dropwise. More water (10 $cm^3$) was added and the mixture stirred for 4 h. The resulting white precipitate was filtered off, washed with cold water (10 $cm^3$), cold water–methanol (1:1, 10 $cm^3$), cold methanol (5 $cm^3$) and finally diethyl ether (5 $cm^3$), and dried *in vacuo* (1.90 g, 97%), m.p. 264–266 °C (Found: C, 46.3; H, 4.25; N, 4.05. Calc. for $C_{27}H_{29}ClF_6N_2P_2Pd$: C, 46.35; H, 4.2; N, 4.0%). α +124° (589 nm, *c* 0.87 g per 100 $cm^3$, $Me_2CO$). NMR ($CD_2Cl_2$): $^1$H, δ 1.88 (d, 3 H, $^3J_{HH}$ 6.45, CMe), 2.11 (d, 3 H, $^2J_{PH}$ 9.75, PMe), 2.87 (d, 3 H, $^4J_{PH}$ 1.71, NMe), 3.05 (d, 3 H, $^4J_{PH}$ 3.60, NMe), 4.43 (m, 1 H, C*H*Me), 4.97 (d, 1 H, $^2J_{HH}$ 13.32, NH*H*), 5.47 (d, 1 H, $^2J_{HH}$ 13.20, N*H*H), 6.62 (d of d, 1 H, $^1J_{HH}$ 6.70, $^4J_{PH}$ 8.42 Hz, H$^\gamma$) and 7.18–8.32 (m, 15 H, aromatics); $^{31}$P-{$^1$H}, δ 16.40 (s, 1 P).

**[*OC*-6-43-($R_{As}$*,$R_{As}$*,$S_P$*)]- and [*OC*-6-53-($R_{As}$*,$S_{As}$*,$S_P$*)]-chloro({2-[(2-dimethylarsinophenyl)methylarsino]phenyl}{2-[(2-dimethylarsinophenyl)methylarsinoamino]phenyl}methylphosphine-*As*,*As*′,*As*″,*As*‴,*P*)cobalt(III) chloride, [CoCl{($R_{As}$*,$R_{As}$*,$S_P$*)-L$^1$}]$Cl_2$ and [CoCl{($R_{As}$*,$S_{As}$*,$S_P$*)-L$^1$}]$Cl_2$.** Sodium foil (0.43 g, 0.0184 mol) was added to a stirred solution of compound (±)-**IV** (5.00 g, 0.0184 mol) in thf (80 $cm^3$) at 0 °C. The reaction mixture was allowed to come to the ambient temperature and stirred overnight. The resulting deep red solution was filtered and added dropwise over a period of 4 h to a solution of (±)-**III** (4.60 g, 0.0184 mol) dissolved in thf (80 $cm^3$) at −78 °C. After the addition was complete the reaction mixture was stirred at −20 ± 5 °C for 5 d and then heated at reflux for 4 h. Water (10 $cm^3$) was added dropwise to the colourless solution and the solvent removed. Diethyl ether (50 $cm^3$) and water (100 $cm^3$) were added, the organic layer separated off and the aqueous layer extracted with more diethyl ether (2 × 50 $cm^3$). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed to give a highly viscous orange oil. $^{31}$P-{$^1$H} NMR ($CDCl_3$): δ −42.8 (s), −48.5 (s), −49.1 (s), −49.5 (s) and −49.9 (s). The orange oil was subsequently taken up in hot methanol (150 $cm^3$). Hexaaquacobalt(II) chloride (4.38 g, 0.0184 mol) in methanol (25 $cm^3$) was added followed by hydrochloric acid (10 mol $dm^{-3}$, 10 $cm^3$) and air was drawn through the solution for 4 h. The solution was filtered, the solvent removed and the green residue dissolved in water (200 $cm^3$) by heating the mixture at reflux for 4 h. On standing at *ca.* 5 °C overnight dark green crystals of *trans*-[$CoCl_2$(pdma)$_2$]Cl [pdma = *o*-phenylenebis(dimethylarsine)][15,16] were deposited. These were filtered off, washed with cold ethanol–diethyl ether (1:10, 10 $cm^3$) and diethyl ether (10 $cm^3$) and dried *in vacuo* (1.48 g, 21.7%), m.p. 295 ± 2 °C (Found: C, 32.5; H, 4.4; As, 40.2; Co, 7.7. Calc. for $C_{20}H_{32}As_4Cl_3Co$: C, 32.6; H, 4.4; As, 40.6; Co, 8.0%). $^1$H NMR ($CD_3OD$): δ 1.93 (s, 12 H, AsMe) and 7.85–8.23 (m, 8 H, aromatics).

The mother-liquor from the isolation of *trans*-[$CoCl_2$-(pdma)$_2$]Cl was reduced in volume by *ca.* 50% and left at *ca.* 5 °C overnight. Orange-red crystals were deposited. These were collected and recrystallised from hot water (40 $cm^3$). The resulting crystals of [CoCl{($R_{As}$*,$R_{As}$*,$S_P$*)-L$^1$}]$Cl_2$ were again collected, washed with cold ethanol–diethyl ether (2:1, 10 $cm^3$), diethyl ether (10 $cm^3$) and dried *in vacuo* (5 mmHg, 20 °C, 24 h), yield (2.60 g, 27%) [based on the secondary arsine (±)-**IV**], m.p. 240–250 °C (decomp.) (Found: C, 36.3; H, 5.0; Cl, 10.1; N, 1.3. Calc. for $C_{31}H_{38}As_4Cl_3CoNP\cdot 7H_2O$: C, 35.6; H, 5.0; N, 1.3; Cl, 10.2%). NMR ($CD_3OD$): $^1$H, δ 1.69 (d, 3 H, $^2J_{PH}$ 11.5 Hz, PMe), 1.76 (s, 3 H, AsMe), 1.84 (s, 3 H, AsMe), 2.17 (s, 3 H, AsMe), 2.49 (s, 3 H, AsMe), 2.63 (s, 3 H, AsMe), 2.81 (s, 3 H, AsMe) and 6.65–8.66 (m, 16 H, aromatics); $^{31}$P-{$^1$H}, δ 46.5 (s, 1 P). On drying *in vacuo* (80 °C, 5 mmHg, 8 h) the complex readily loses 5 $H_2O$ to form a stable dihydrate of [CoCl-{($R_{As}$*,$R_{As}$*,$S_P$*)-L$^1$}]$Cl_2$ (Found: C, 38.4; H, 4.5; N, 1.5. Calc. for $C_{31}H_{38}As_4Cl_3CoNP\cdot 2H_2O$: C, 38.9; H, 4.4; N, 1.5%).

The filtrate from the isolation of [CoCl{($R_{As}$*,$R_{As}$*,$S_P$*)-L$^1$}]$Cl_2$ was acidified by the addition of hydrochloric acid (10 mol $dm^{-3}$, 20 $cm^3$) and the solution extracted with dichloromethane (4 × 50 $cm^3$). (The aqueous phase was NOT discarded.) The combined dichloromethane extracts were dried ($MgSO_4$), filtered and the solvent removed. The residue was taken up in hot methanol (10 $cm^3$) and an equal volume of diethyl ether was added to afford a yellow-brown precipitate. The solid was collected and recrystallised from methanol–diethyl ether. The resulting yellow-brown crystals of *cis*-[$CoCl_2${(±)-$H_2NC_6H_4$PMePh-2}$_2$]Cl were filtered off, washed with methanol–diethyl ether (1:1, 10 $cm^3$) and diethyl ether (10 $cm^3$) and dried *in vacuo* (1.16 g, 20.7%), m.p. 130 ± 2 °C

(Found: C, 51.3; H, 4.9; N, 4.4. Calc. for $C_{26}H_{28}Cl_3CoN_2P_2\cdot0.5H_2O$: C, 51.6; H, 4.8; N, 4.6%). NMR ($CD_3OD$): $^1$H, δ 2.29 (d, 3 H, $^2J_{PH}$ 13.80, PMe), 2.39 (d, 3 H, $^2J_{PH}$ 13.90 Hz, PMe), 3.72 (m, 4 H, $2NH_2$) and 7.25–7.93 (m, 18 H, aromatics); $^{31}$P-{$^1$H}, δ 41.6 (s, 1 P) and 43.1 (s, 1 P). The mother-liquor and washings from the isolation of *cis*-[$CoCl_2${(±)-$H_2NC_6H_4$PMePh-2}$_2$]Cl were combined and evaporated to dryness. The residue consisted primarily of *cis*-[$CoCl_2${($R_{As}$*,$S_P$*)-$L^2$}]Cl (0.040 g, *ca.* 0.3%).

The aqueous phase from the isolation of *cis*-[$CoCl_2${(±)-$H_2NC_6H_4$PMePh-2}$_2$]Cl was taken to dryness and the residue dissolved in the minimum volume of hot methanol. Fine yellow-brown crystals were deposited on standing for 3 d at 5 °C. These were collected and recrystallised from hot water (25 $cm^3$) to give orange-brown crystals of [CoCl{($R_{As}$*,$S_{As}$*,$S_P$*)-$L^1$}]$Cl_2$ (1.42 g, 17.4%) [based on the secondary arsine (±)-**IV**]. The mother-liquor was evaporated to dryness and a further crop of [CoCl{($R_{As}$*,$S_{As}$*,$S_P$*)-$L^1$}]$Cl_2$ isolated from the residual material using ion-exchange chromatography. The residue was dissolved in the minimum volume of methanol and loaded onto an ion-exchange column (180 × 15 mm, Dowex 50W, cation-exchange resin). The column was eluted with HCl–methanol (0.25 mol $dm^{-3}$, elution rate *ca.* 2 $cm^3$ $min^{-1}$). Pure [CoCl{($R_{As}$*,$S_{As}$*,$S_P$*)-$L^1$}]$Cl_2$ began to elute after *ca.* 500 $cm^3$ of eluent had passed through the column. Complete elution was effected using HCl–methanol (0.75 mol $dm^{-3}$). This was collected and taken to dryness and the complex recrystallised from hot water (20 $cm^3$) to give orange crystals of [CoCl{($R_{As}$*,$S_{As}$*,$S_P$*)-$L^1$}]$Cl_2$ (total yield 2.48 g, 25.8%) [based on the secondary arsine (±)-**IV**], m.p. 240–250 °C (decomp.) (Found: C, 35.6; H, 4.8; N, 1.3. Calc. for $C_{31}H_{38}As_4Cl_3CoNP\cdot7H_2O$: C, 35.6; H, 5.0; N, 1.3%). NMR ($CD_3OD$): $^1$H, δ 1.07 (s, 3 H, AsMe), 1.46 (s, 3 H, AsMe), 1.65 (s, 3 H, AsMe), 1.92 (s, 3 H, AsMe), 2.18 (s, 3 H, AsMe), 2.24 (s, 3 H, AsMe), 2.33 (d, 3 H, $^2J_{PH}$ 12.1 Hz, PMe) and 6.70–8.82 (m, 16 H, aromatics); $^{31}$P-{$^1$H}, δ 47.1 (s, 1 P).

**[*OC*-6-35-($R_{As}$*,$S_P$*)]{1-[(2-Aminophenyl)methylphosphino]-2-[(2-dimethylarsinophenyl)methylarsino]benzene-*As*,*As*′,*N*,*P*}-dichlorocobalt(III) chloride, *cis*-[$CoCl_2${($R_{As}$*,$S_P$*)-$L^2$}]Cl.** Sodium foil (0.16 g, 6.96 mmol) was added to a stirred solution of compound (±)-**IV** (1.895 g, 6.96 mmol) in thf (80 $cm^3$) at 0 °C. The mixture was allowed to come to the ambient temperature and stirred overnight. The resulting deep red solution containing sodium (2-dimethylarsinophenyl)methylarsenide was filtered and added dropwise over a period of 2 h to an excess of (±)-**III** (2.60 g, 10.4 mmol) in thf (80 $cm^3$) at −78 °C. The reaction mixture was allowed to come slowly to ambient temperature, stirred for 5 d at 50 ± 5 °C and finally heated at reflux for 4 h. Water (10 $cm^3$) was added dropwise to the colourless solution and the solvent removed. Diethyl ether (50 $cm^3$) and water (100 $cm^3$) were added and the organic layer was separated off. The aqueous layer was extracted with more diethyl ether (2 × 50 $cm^3$) and the combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed to give a highly viscous orange oil. The orange oil was taken up in hot methanol (100 $cm^3$). Hexaaquacobalt(II) chloride (2.47 g, 10.4 mmol) in methanol (20 $cm^3$) was added followed by hydrochloric acid (10 mol $dm^{-3}$, 10 $cm^3$) and air was drawn through the solution for 4 h. The solution was filtered and the solvent removed. The residue was extracted with diethyl ether (3 × 50 $cm^3$) to remove unreacted (±)-**III** (*ca.* 0.6 g). Water (120 $cm^3$) was added to the dark green residue and the mixture refluxed for 4 h. The solution was stored at *ca.* 5 °C overnight and gave dark green crystals of *trans*-[$CoCl_2$(pdma)$_2$]Cl (1.0 g, 39%).

The mother-liquor from the isolation of *trans*-[$CoCl_2$(pdma)$_2$]Cl was reduced in volume (*ca.* 50%) and again left at *ca.* 5 °C overnight. The resulting deep red crystals were filtered off and recrystallised from hot water (10 $cm^3$). The complex *cis*-(±)-[$CoCl_2${($R_{As}$*,$S_P$*)-$L^2$}]Cl was collected, washed with cold ethanol–diethyl ether (1:5, 10 $cm^3$) and diethyl ether (10 $cm^3$), and dried *in vacuo* (0.52 g, 11%) [based on the secondary arsine (±)-**IV**], m.p. 280–290 °C (decomp.) (Found: C, 39.1; H, 4.0; Co, 8.8; N, 2.05. Calc. for $C_{22}H_{26}As_2NPCl_3Co\cdot0.5H_2O$: C, 40.1; H, 4.1; Co, 8.9; N, 2.1%). NMR ($CD_3OD$): $^1$H, δ 1.54 (s, 3 H, AsMe), 2.19 (s, 3 H, As*Me*Me), 2.33 (s, 3 H, AsMe*Me*), 2.40 (d, 3 H, $^2J_{PH}$ 13.47 Hz, PMe), 7.18 (br s, $NH_2$) and 7.50–8.38 (m, 12 H, aromatics); $^{31}$P-{$^1$H} (at −60 °C), δ 85.0 (br s, 1 P).

The filtrate from the isolation of *cis*-(±)-[$CoCl_2${($R_{As}$*,$S_P$*)-$L^2$}]Cl was acidified with HCl (10 mol $dm^{-3}$, 10 $cm^3$) and extracted with dichloromethane (3 × 30 $cm^3$). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed to give a brown residue which was recrystallised from methanol–diethyl ether. The resulting yellow-brown crystals of *cis*-[$CoCl_2${(±)-$H_2NC_6H_4$PMePh-2}$_2$]Cl were washed with methanol–diethyl ether (1:1, 5 $cm^3$) and dried *in vacuo* (0.80 g, 38%).

The mother-liquor from the isolation of *cis*-[$CoCl_2${(±)-$H_2NC_6H_4$PMePh-2}$_2$]Cl was evaporated to dryness and taken up in methanol (50 $cm^3$), from which small quantities of [CoCl{($R_{As}$*,$S_{As}$*,$S_P$*)-$L^1$}]$Cl_2$ (0.15 g, 4%) and [CoCl{($R_{As}$*,$R_{As}$*,$S_P$*)-$L^1$}]$Cl_2$ (0.12 g, 3.3%) could be isolated through a combination of fractional crystallisation and ion-exchange chromatography.

### Cyanolysis of *cis*-[$CoCl_2${(±)-$H_2NC_6H_4$PMePh-2}$_2$]Cl

The complex *cis*-[$CoCl_2${(±)-$H_2NC_6H_4$PMePh-2}$_2$]Cl (0.60 g, 1.01 mmol) was suspended in dichloromethane (50 $cm^3$), potassium cyanide (0.65 g, 9.98 mmol) in water (25 $cm^3$) was added and the mixture stirred vigorously for 1 h. The organic phase was separated and the solvent removed to give a pale brownish yellow residue. Only a trace amount of free (±)-**I** was detected in the mixture of complexes of the type *cis*-[$Co(CN)_2${(±)-$H_2NC_6H_4$PMePh-2}$_2$]CN (0.46 g, 90%). NMR ($CD_3OD$): $^1$H, δ 1.85 (d, 3 H, $^2J_{PH}$ 13.3, PMe), 2.00 (d, 3 H, $^2J_{PH}$ 13.3, PMe), 2.19 (d, 3 H, $^2J_{PH}$ 13.47 Hz, PMe) and 6.58–7.96 (m, 18 H, aromatics); $^{31}$P-{$^1$H}, δ 11.9 (s, 2 P), 37.3 (s, 2 P) and 35.8 (s, 2 P). Further cyanolysis of the dicyano complexes in refluxing *n*-hexane–methanol in the presence of a ten-fold excess of aqueous potassium cyanide for 24 h yielded free (±)-**I**. NMR ($CDCl_3$): $^1$H and $^{31}$P-{$^1$H} identical to those previously reported for (±)-**I**.[2]

### Reaction of compound ($R_P$)-III and Na[AsMe($C_6H_4AsMe_2$-2)]: preparation and separation of the optically active complexes [*OC*-6-35-Δ-($R_{As}$,$S_P$)]-{1-[(2-aminophenyl)methylphosphino]-2-[(2-dimethylarsinophenyl)methylarsino]benzene-*As*,*As*′,*N*,*P*}-dichlorocobalt(III) chloride, *cis*-[$CoCl_2${($S_{As}$,$R_P$)-$L^2$}]Cl, and [*OC*-6-43-Δ-($R_{As}$,$R_{As}$,$S_P$)]- and [*OC*-6-53-Λ-($R_{As}$,$S_{As}$,$S_P$)]-chloro({2-[(2-dimethylarsinophenyl)methylarsino]phenyl}{2-[(2-dimethylarsinophenyl)methylarsinoamino]phenyl}methylphosphine-*As*,*As*′,*As*″,*As*‴,*P*)cobalt(III) chloride, [CoCl{($S_{As}$,$S_{As}$,$R_P$)-$L^1$}]$Cl_2$ and [CoCl{($S_{As}$,$R_{As}$,$R_P$)-$L^1$}]$Cl_2$**

To a solution of compound (±)-**IV** (0.92 g, 3.40 mmol) in thf (80 $cm^3$) at 0 °C was added sodium foil (0.078 g, 7.4 mmol). The mixture was allowed to come to the ambient temperature and stirred overnight. The resulting deep red solution was filtered and added dropwise, over 2 h, to an excess of ($R_P$)-**III** (1.25 g, 5.00 mmol) in thf (60 $cm^3$) at −78 °C. The reaction mixture was heated at 45 ± 5 °C for 5 d and subsequently refluxed for 4 h. The solvent was removed and water (60 $cm^3$) and diethyl ether (100 $cm^3$) were added. The ether layer was separated off and the aqueous phase extracted with more diethyl ether (2 × 25 $cm^3$). The combined organic extracts were dried ($MgSO_4$), filtered and the solvent removed to give a highly viscous orange oil.

The orange oil was taken up in hot methanol (50 $cm^3$), hexaaquacobalt(II) chloride (1.15 g, 0.0048 mol) in methanol (10 $cm^3$) was added followed by hydrochloric acid (10 mol $dm^{-3}$, 5 $cm^3$) and air was drawn through the solution for 4 h. The solu-

tion was filtered and the solvent removed. The residue was triturated with hot diethyl ether (2 × 25 $cm^3$) to remove unreacted compound ($R_P$)-**III**. Water (50 $cm^3$) was added and the solution digested for 4 h. The resulting dark green solution was left at 5 °C overnight whereupon dark green crystals of *trans*-[$CoCl_2$-(pdma)$_2$]Cl were deposited. These were collected, washed with diethyl ether (10 $cm^3$) and dried *in vacuo* (0.48 g, 38%). The mother-liquor was extracted with dichloromethane (20 $cm^3$), to remove the complex [$CoCl_2${($S_P$)-$H_2NC_6H_4$PMePh-2}$_2$]Cl (*ca.* 0.4 g), the aqueous layer evaporated to dryness and the residue dissolved in the minimum volume of methanol. The resulting deep red solution was filtered and loaded onto an ion-exchange column (8 × 100 mm, Dowex 50W). The column was eluted (0.25 mol $dm^{-3}$ HCl–methanol) and successive 100 $cm^3$ fractions of eluent were collected. Each fraction was evaporated to dryness and analysed by $^1$H NMR spectroscopy.

Fractions 1 and 2 contained almost pure *cis*-[$CoCl_2${($S_{As}$,$R_P$)-$L^2$}]Cl. They were extracted with hot dichloromethane (25 $cm^3$), filtered, the filtrates combined and the solvent removed. Recrystallisation from methanol–diethyl ether gave deep red crystals of pure *cis*-[$CoCl_2${($S_{As}$,$R_P$)-$L^2$}]Cl (0.050 g, 2.3%), m.p. 290 °C (decomp.) (Found: C, 39.85; H, 4.1; N, 2.15. Calc. for $C_{22}H_{26}As_2Cl_3CoNP\cdot0.5H_2O$: C, 40.05; H, 4.15; N, 2.1%). α +172° (589 nm, *c* 0.266 g per 100 $cm^3$, MeOH). NMR ($CD_3OD$): $^1$H, δ 1.54 (s, 3 H, AsMe), 2.19 (s, 3 H, AsMe*Me*), 2.33 (s, 3 H, As*Me*Me), 2.40 (d, 3 H, $^2J_{PH}$ 13.47 Hz, PMe), 7.18 (br s, 2 H, $NH_2$) and 7.50–8.38 (m, 12 H, aromatics); $^{31}$P-{$^1$H}, δ 85.0 (br s, 1 P).

Fraction 7 contained almost pure [CoCl{($S_{As}$,$R_{As}$,$R_P$)-$L^1$}]-$Cl_2$. The brownish solid obtained from this fraction was recrystallised from methanol–diethyl ether to give orange-red prisms of pure [CoCl{($S_{As}$,$R_{As}$,$R_P$)-$L^1$}]$Cl_2$ (0.016 g, 1.0%), m.p. 240 °C (decomp.). α +192° (589 nm, *c* 0.60 g per 100 $cm^3$, MeOH). NMR ($CD_3OD$): $^1$H, δ 1.07 (s, 3 H, AsMe), 1.46 (s, 3 H, AsMe), 1.65 (s, 3 H, AsMe), 1.92 (s, 3 H, AsMe), 2.18 (s, 3 H, AsMe), 2.24 (s, 3 H, AsMe), 2.33 (d, 3 H, $^2J_{PH}$ 12.1 Hz, PMe) and 6.70–8.82 (m, 16 H, aromatics); $^{31}$P-{$^1$H}, δ 47.1 (s, 1 P).

Fraction 14 contained almost pure [CoCl{($S_{As}$,$S_{As}$,$R_P$)-$L^1$}]-$Cl_2$. The yellow-brown solid obtained from this fraction was recrystallised from methanol–diethyl ether to give bright orange prisms of pure [CoCl{($S_{As}$,$S_{As}$,$R_P$)-$L^1$}]$Cl_2$ (0.025 g, 1.6%), m.p. 240 °C (decomp.) (Found: C, 38.2; H, 4.4; N, 1.6. Calc. for $C_{31}H_{38}As_4Cl_3CoNP\cdot2H_2O$: C, 38.9; H, 4.4; N, 1.45%). α +38° (589 nm, *c* 0.940 g per 100 $cm^3$, MeOH). NMR ($CD_3OD$): $^1$H, δ 1.69 (d, 3 H, $^2J_{PH}$ 11.5 Hz, PMe), 1.76 (s, 3 H, AsMe), 1.84 (s, 3 H, AsMe), 2.17 (s, 3 H, AsMe), 2.49 (s, 3 H, AsMe), 2.63 (s, 3 H, AsMe), 2.81 (s, 3 H, AsMe) and 6.65–8.66 (m, 16 H, aromatics); $^{31}$P-{$^1$H}, δ 46.5 (s, 1 P).

## X-Ray crystallography

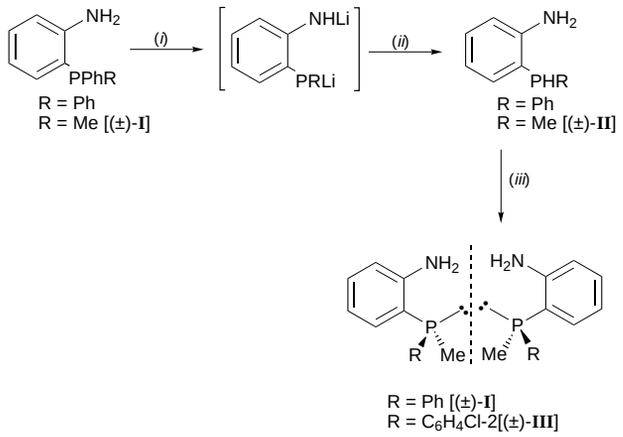
**Crystal data.** *Complex* ($S_P$,*R*)-**2**. $C_{27}H_{29}ClF_6N_2P_2Pd$, *M* = 699.33, orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 8.294(4), *b* = 12.423(4), *c* = 28.664(4) Å, *U* = 2953(1) $Å^3$ (by least-squares analysis of the setting angles of 25 reflections 13.8 < 2θ < 22.8°), Mo-Kα radiation λ = 0.710 69 Å with a graphite monochromator, *Z* = 4, $D_c$ = 1.573 g $cm^{-3}$, *F*(000) = 1408, specimen 0.39 × 0.03 × 0.09 mm, μ(Mo-Kα) = 8.85 $cm^{-1}$.

*Complex* [CoCl{($R_{As}$*,$R_{As}$*,$S_P$*)-$L^1$}]$Cl_2\cdot7H_2O$ **A**. $C_{31}H_{52}As_4Cl_3CoNO_7P$, *M* = 1046.71, triclinic, space group *P*1 (no. 2), *a* = 11.638(3), *b* = 12.789(2), *c* = 14.870(4) Å, α = 81.80(2), β = 70.29(2), γ = 84.55(2)°, *U* = 2059.7(8) $Å^3$ (by least-squares analysis of the setting angles of 25 reflections 98.0 < 2θ < 99.9°), Cu-Kα radiation (λ = 1.541 78 Å) with a graphite monochromator, *Z* = 2, $D_c$ = 1.688 g $cm^{-3}$, *F*(000) = 1052, specimen 0.21 × 0.20 × 0.06 mm, μ(Cu-Kα) = 93.53 $cm^{-1}$.

*Complex* [CoCl{($R_{As}$*,$S_{As}$*,$S_P$*)-$L^1$}]$Cl_2\cdot2$MeOH **B**. $C_{33}H_{46}As_4Cl_3CoNO_2P$, *M* = 989.06, triclinic, space group *P*1 (no. 2), *a* = 9.583(2), *b* = 9.974(2), *c* = 21.509(5) Å, α = 100.09(2), β = 94.83(2), γ = 106.86(2)°, *U* = 1917.0(8) $Å^3$ (by least-squares analysis of the setting angles of 25 reflections 108.61 < 2θ < 110.07°), Cu-Kα radiation (λ = 1.541 78 Å) with a graphite monochromator, *Z* = 2, $D_c$ = 1.713 g $cm^{-3}$, *F*(000) = 976, specimen 0.13 × 0.10 × 0.08 mm, μ(Cu-Kα) = 108.00 $cm^{-1}$.

**Data collection and processing.** A unique data set was measured in each case using the ω–2θ scan technique to a maximum 2θ value of 50.1° on a Rigaku AFC6S diffractometer [at 293(1) K for ($S_P$,*R*)-**2**] or 120° on a Rigaku AFC6R diffractometer [at 296(1) K for **A** and at 213(1) K for **B**]. Scans of width (0.85 + 0.34 tan θ)° for complex ($S_P$,*R*)-**2**, (1.42 + 0.3 tan θ)° for **A** and (1.31 + 0.34 tan θ)° for **B** were made at a speed (in ω) of 2.0° $min^{-1}$ for ($S_P$,*R*)-**2**, 16.0° $min^{-1}$ for **A** and 32.0° $min^{-1}$ for **B**. The weak reflections [$I < 10.0\sigma(I)$] were rescanned [maximum of three scans for ($S_P$,*R*)-**2** and four for **A** and **B**] and the counts were accumulated to ensure good counting statistics. The number of unique reflections was 3015 for ($S_P$,*R*)-**2**, 6149 for **A** and 5686 for **B**. The intensities of three representative reflections were measured after every 150. For **A** and **B** the standards decreased by 5.2 and 2.2%, respectively, over the course of the data collection and so a linear correction factor was applied in each case. No decay correction was required for ($S_P$,*R*)-**2**. An analytical absorption correction was applied in each case which resulted in transmission factors ranging from 0.92 to 0.96 for ($S_P$,*R*)-**2**, 0.23 to 0.57 for **A** and 0.35 to 0.50 for **B**. The data were corrected for Lorentz-polarisation effects.

**Structure analysis and refinement.** The structures were solved by heavy-atom Patterson methods and expanded using Fourier techniques.[17,18] The non-hydrogen atoms were refined anisotropically. For structure **A** the displacement factors for O(6) and O(7) were large which may indicate that their occupancies should be less than unity. Furthermore, some of the O···O distances involving them are short, but we are unable to propose a satisfactory network of reduced occupancies that would fully account for the electron density which is observed; it would possibly need incorporation of partial Cl/O occupancies for some sites. Our present model gives a fair match to the observed electron density of this region of the unit cell, and any shortcomings should have minimum effect on the rest of the structure. The short O···O distances, however, should not be regarded as examples of strong hydrogen bonding. Hydrogen atoms attached to carbon atoms of the cations were included at calculated positions but were not refined. For **A** the hydrogen atom attached to N(1) was refined positionally with a restraint on the N–H distance. The locations of the hydrogen atoms of water molecules were calculated on the basis of the most likely hydrogen-bonding network and were not refined. In **B** the hydrogen atoms of the methanol molecules and on the nitrogen atom of the cation were observed in electron-density maps. These hydrogen atoms were refined positionally in the least-squares procedure. The absolute configuration of the stereogenic phosphorus atom in ($S_P$,*R*)-**2** was assigned on the basis of the known chirality of the resolving agent. Furthermore, refinement of a model with inverted atomic coordinates yielded a significantly higher *R* factor, and analysis of pairs of Friedel opposites showed that of the 143 pairs with maximum difference in $F_{calc}$ 109 showed the same sign for the difference in their $F_{obs}$. The final cycle of full-matrix least-squares refinement was based on 1522 observed reflections [$I > 3.0\sigma(I)$] for ($S_P$,*R*)-**2**, 4603 for **A** and 4204 for **B** and 352 variable parameters for ($S_P$,*R*)-**2**, 433 for **A** and **B** and converged [largest shift was 0.05 for ($S_P$,*R*)-**2**, 0.04 for **A** and 0.02 for **B** times its e.s.d.] with final *R* and *R′* values being 0.040 and 0.029 for ($S_P$,*R*)-**2**, 0.049 and 0.072 for **A** and 0.031 and 0.035 for **B**, respectively. The maximum and minimum peaks on the final Fourier-difference map corresponded to 0.38 and −0.34 e $Å^{-3}$ for ($S_P$,*R*)-**2**, 0.92 and −0.84 for **A** and 0.06 and −0.40 for **B**, respectively. Neutral atom scattering factors were taken from Cromer and Waber.[19] Anomalous dispersion effects were included in $F_{calc.}$;[20] the




**Scheme 1** (*i*) 3Li in thf; (*ii*) water; (*iii*) Na in thf; MeI or $C_6H_4Cl_2$-1,2 in thf

values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[21] The values for the mass-attenuation coefficients were those of Creagh and Hubbell.[22] All calculations were performed using the TEXSAN crystallographic software package.[23]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/536. Experimental details for *cis*-(±)-[CoCl{($R_{As}$*,$S_P$*)-L[2]}]Cl·2$H_2O$ have been published previously in a preliminary account of the work described herein.[12]

## Results and Discussion

### Synthesis and resolution of compound (±)-III

The asymmetric bidentate compound (±)-(2-aminophenyl)-(2-chlorophenyl)methylphosphine (±)-**III** has been synthesized in four relatively high-yielding steps from (2-aminophenyl)-diphenylphosphine (Scheme 1). The two key steps in the synthesis were sequential, completely chemoselective cleavage of the phenyl groups from (2-aminophenyl)diphenylphosphine[24] by reaction with lithium in thf. As we reported previously,[2] treatment of (2-aminophenyl)diphenylphosphine with 3 equivalents of lithium in tetrahydrofuran, followed by hydrolysis with water, gave the chiral secondary phosphine (±)-(2-aminophenyl)phenylphosphine in 84% yield. Further reaction with 1 equivalent of sodium in tetrahydrofuran gave the tertiary phosphine (±)-(2-aminophenyl)methylphenylphosphine, (±)-**I**, in 90% yield upon the addition of methyl iodide. In a similar manner, the chiral secondary phosphine (±)-(2-aminophenyl)-methylphosphine, (±)-**II**, has been prepared in 93% yield by reaction of (±)-**I** with 3 equivalents of lithium in tetrahydrofuran, followed by hydrolysis with water. Presumably deprotonation of the amino group accompanied the chemoselective cleavage of a phenyl moiety from the two substrates. Subsequent treatment of (±)-**II** with 1 equivalent of sodium in tetrahydrofuran followed by the addition of a solution of 1,2-dichlorobenzene in the same solvent at −78 °C gave (±)-**III** in 78% yield [based on a 66% conversion of (±)-**II**]. Approximately one third of the precursor secondary phosphine (±)-**II** was recovered from the reaction. Diminished yields of (±)-**III** were obtained when the reaction was carried out at elevated temperatures or when 1-bromo-2-chlorobenzene was substituted for 1,2-dichlorobenzene.

Tertiary phosphine (±)-**III** was resolved by the method of metal complexation. Its reaction with the dimer di-μ-chloro-bis{(*R*)-1-[1-(dimethylamino)ethyl]naphthyl-$C^2$,*N*}dipalladium(II), (*R*)-**1**, in methanol, followed by the addition of an excess of aqueous ammonium hexafluorophosphate gave a 1:1 mixture of the diastereomeric hexafluorophosphate salts ($R_P$,*R*)- and ($S_P$,*R*)-**2** in 90% yield (Scheme 2). Fractional crystallisation of the diastereomeric mixture of hexafluorophosphate salts from dichloromethane by the addition of propan-2-ol gave colourless needles of ($S_P$,*R*)-**2**, α −225° (589 nm, acetone). The second diastereomer ($R_P$,*R*)-**2** could not be isolated in a pure form using this approach. Instead, partially resolved (±)-**III** was liberated from the diastereomeric mixture of hexafluorophosphate salts enriched in ($R_P$,*R*)-**2** by reaction with ($R_P$*,$R_P$*)-1,2-phenylenebis(methylphenylphosphine)[14] in dichloromethane (Scheme 3). Resolution of the liberated ligand was achieved in a bridge-splitting reaction involving partially resolved (±)-**III** and the dimer (*S*)-**1** in methanol. The addition of an excess of aqueous $NH_4PF_6$ to the solution gave a mixture of diastereomeric hexafluorophosphate salts enriched in ($R_P$,*S*)-**2**. The diastereomeric mixture was twice recrystallised from dichloromethane–propan-2-ol to give pure ($R_P$,*S*)-**2**, α +225° (589 nm, acetone). Liberation of the optically active antipodes of (±)-**III** from ($S_P$,*R*)- and ($R_P$,*S*)-**2** was accomplished by treatment of the internally diastereomeric salts with ($R_P$*,$R_P$*)-$C_6H_4$(PMePh)$_2$-1,2 in dichloromethane to give, after removal by filtration of the internally diastereomeric palladium(II) complexes ($S_P$,$S_P$,*R*)- and ($R_P$,$R_P$,*R*)-**3** [or ($S_P$,$S_P$,*S*)- and ($R_P$,$R_P$,*S*)-**3**], the optically pure enantiomers ($R_P$)- and ($S_P$)-**III**, α ± 218° (589 nm, acetone), respectively. Diastereomerically pure ($R_P$,*R*)-**2** was subsequently prepared from ($S_P$)-**III** and the chloro-bridged dimer (*R*)-**1** in methanol by the addition of aqueous $NH_4PF_6$, α +124° (589 nm, acetone).

### NMR spectra of complexes ($R_P$,*R*)-, ($S_P$,*R*)- and ($R_P$,*S*)-2

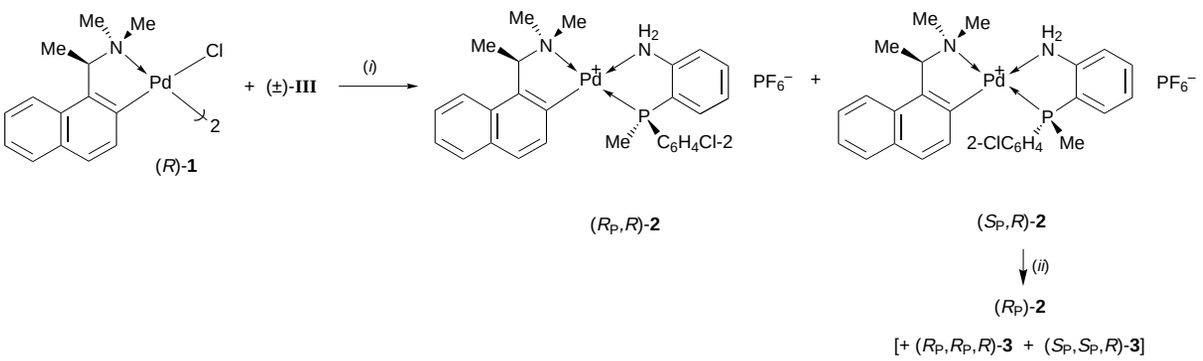
The $^1$H NMR spectra of the internally diastereomeric complexes ($R_P$,*R*)-, ($S_P$,*R*)- and ($R_P$,*S*)-**2** in $CD_2Cl_2$ were consistent with the two nitrogen donor atoms being *cis* to one another. The NMe groups are non-equivalent in these complexes and coupled to the phosphorus atom *trans* 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 (±)-(2-aminophenyl)methylphenylphosphine, (±)-**I**.[2] Selected $^1$H NMR data for ($R_P$,*R*)-, ($S_P$,*R*)- and ($R_P$,*S*)-**2** and the related palladium(II) complexes containing the enantiomers of (±)-**I** and orthometallated (*S*)-[1-(1-naphthyl)ethyl]dimethylamine, *viz*. ($S_P$,*S*)- and ($R_P$,*S*)-**4**, are given in Table 1. Importantly, the absolute configuration of the stereogenic phosphorus donor atom in the last two complexes was assigned on the basis of the relative positions of the chemical shifts of the proton attached to C(3) of the naphthyl ring ($H^\gamma$). The diastereomer for which proton $H^\gamma$ resonated to higher field was assigned the ($R_P$,*S*) configuration. In previous work on related internally diastereomeric palladium(II) complexes containing (±)-methylphenyl(8-quinolyl)phosphine and orthometallated (*R*)-[1-(1-naphthyl)-ethyl]dimethylamine it was shown that when the methyl groups on both the carbon and phosphorus stereocentres were on the same side of the palladium co-ordination plane the proton $H^\gamma$ was shielded by the phenyl group attached to the phosphorus atom and hence resonated to higher field.[13] In this case the assignment was confirmed by a crystal structure determination of the ($S_P$,*R*) diastereomer. In the present work the ($R_P$,*R*) configuration was assigned to the diastereomer in which the $H^\gamma$ resonance was to higher field (see Table 1).† The appropriateness of this method of assignment of absolute configuration to optically active (2-aminophenyl)phosphines has been confirmed by a single-crystal X-ray analysis of ($S_P$,*R*)-**2**. It is noteworthy that $H^\gamma$ of the naphthyl ring is also coupled to the phosphorus atom in all of these internally diastereomeric palladium(II) complexes.

† Replacement of the Cl atom in compound ($R_P$)-**III** with H results in an apparent inversion of configuration at P to give ($S_P$)-**I** and is consistent with the specification of Cahn *et al.*[25] for absolute configurations.

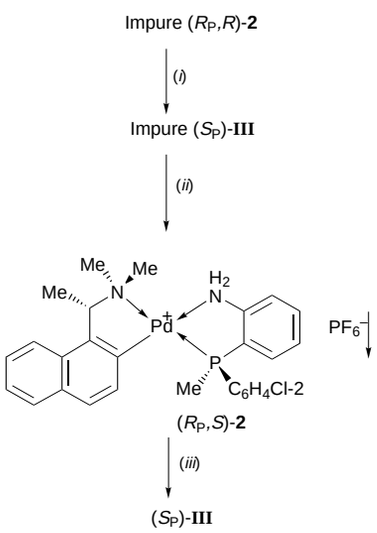
**Table 1** Selected $^1$H NMR data for complexes ($R_P$,$R$)-, ($S_P$,$R$)-, ($R_P$,$S$)-**2**, ($S_P$,$S$)- and ($R_P$,$S$)-**4**

| | δ | | | | |
|---|---|---|---|---|---|
| Compound | CMe | PMe | NMe | CH | $H^\gamma$ |
| ($R_P$,$R$)-**2**[a] | 1.88 (d) | 2.11 (d) | 2.87 (d), 3.05 (d) | 4.43 (m) | 6.62 (dd) |
| ($S_P$,$R$)-**2**[a] | 1.84 (d) | 2.33 (d) | 2.90 (d), 3.04 (d) | 4.43 (m) | 6.92 (dd) |
| ($R_P$,$S$)-**2**[a] | 1.84 (d) | 2.33 (d) | 2.90 (d), 3.04 (d) | 4.43 (m) | 6.92 (dd) |
| ($S_P$,$S$)-**4**[b,c] | 1.93 (d) | 2.52 (d) | 2.97 (d), 3.22 (d) | 4.74 (m) | >7.30[d] |
| ($R_P$,$S$)-**4**[b,c] | 1.93 (d) | 2.29 (d) | 2.98 (d), 3.20 (d) | 4.73 (m) | 6.95 (dd) |

[a] In $CD_2Cl_2$. [b] In $(CD_3)_2CO$. [c] Ref. 2. [d] Obscured by the aromatic resonances.



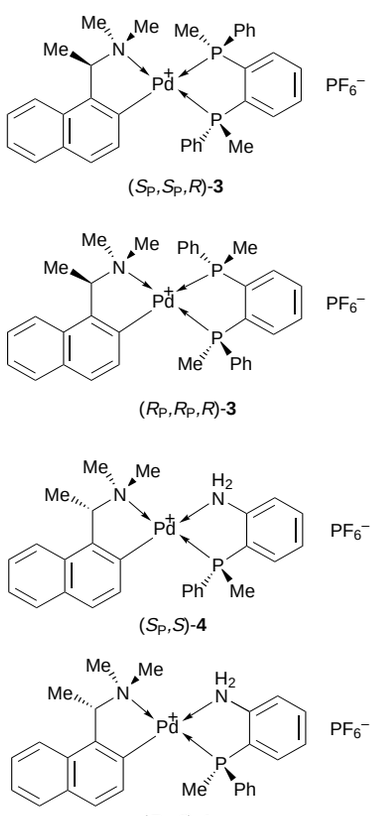

**Scheme 2** (*i*) MeOH, $NH_4PF_6$ in water; (*ii*) ($R_P$*,$R_P$*)-$C_6H_4$(PMePh)$_2$-1,2 in $CH_2Cl_2$




**Scheme 3** (*i*) ($R_P$*,$R_P$*)-$C_6H_4$(PMePh)$_2$-1,2 in $CH_2Cl_2$; (*ii*) (*S*)-**1** in MeOH, $NH_4PF_6$ in $H_2O$; (*iii*) ($R_P$*,$R_P$*)-$C_6H_4$(PMePh)$_2$-1,2 in $CH_2Cl_2$

## Crystal structure determination of complex ($S_P$,$R$)-2

The absolute configuration of compound ($R_P$)-**III** was confirmed by a crystal structure determination of the internally diastereomeric complex ($S_P$,$R$)-**2**. The stereochemistry of the cation is depicted in Fig. 1. Selected bond lengths and angles are given in Table 2. The palladium atom has a distorted square-planar co-ordination geometry with the dihedral angle between the planes defined by the atoms Pd, N(1) and C(14) and that defined by the atoms Pd, P and N(2) being 4.7°. The angles at the Pd atom are P–Pd–N(2) 84.0(3), N(1)–Pd–C(14) 81.3(5), P–Pd–C(14) 97.7(4) and N(1)–Pd–N(2) 97.0(4)°. The absolute configuration of the phosphorus stereocentre is *S* and that of the carbon stereocentre C(3) is *R*. Furthermore, the methylphenylphosphino group of the asymmetric bidentate ligand was found to be *trans* to the nitrogen atom of the resolving agent. A similar arrangement was observed in related internally diastereomeric palladium(II) complexes containing an ortho-metallated optically active amine and the asymmetric bidentate ligands ($R_P$)-methylphenyl(8-quinolyl)phosphine,[13] ($S_P$)-1-(diphenylphosphino)-2-(methylphenylphosphino)ethane,[1d] ($S_P$)-1-(diphenylphosphino)-2-(methylphenylphosphino)benzene[1f] and ($S_P$)-1-(dimethylarsino)-2-(methylphenylphosphino)-benzene.[1h]




## Synthesis of ($R_{As}$*,$R_{As}$*,$S_P$*)-, ($R_{As}$*,$S_{As}$*,$S_P$*)-L$^1$ and ($R_{As}$*,$S_P$*)-L$^2$

Reaction of equimolar quantities of compound (±)-**III** and

**Table 2** Selected non-hydrogen interatomic distances (Å) and interatomic angles (°) for complex ($S_P$,$R$)-**2**

| | | | |
|---|---|---|---|
| Pd–P | 2.220(3) | Pd–C(14) | 2.02(1) |
| Pd–N(1) | 2.136(9) | Pd–N(2) | 2.18(1) |
| P–Pd–C(14) | 97.7(4) | C(14)–Pd–N(1) | 81.3(5) |
| P–Pd–N(2) | 84.0(3) | P–Pd–N(1) | 179.0(3) |
| N(1)–Pd–N(2) | 97.0(4) | C(14)–Pd–N(2) | 175.4(5) |

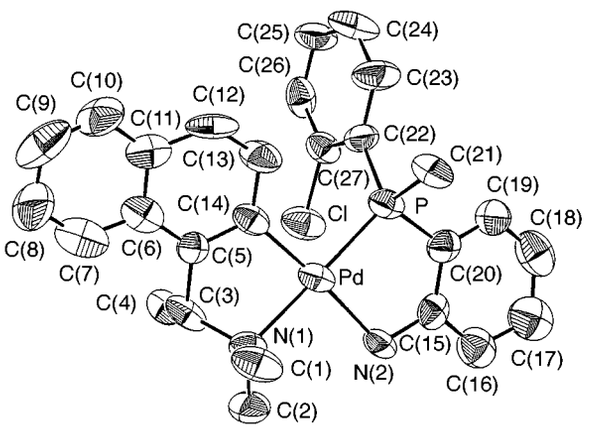
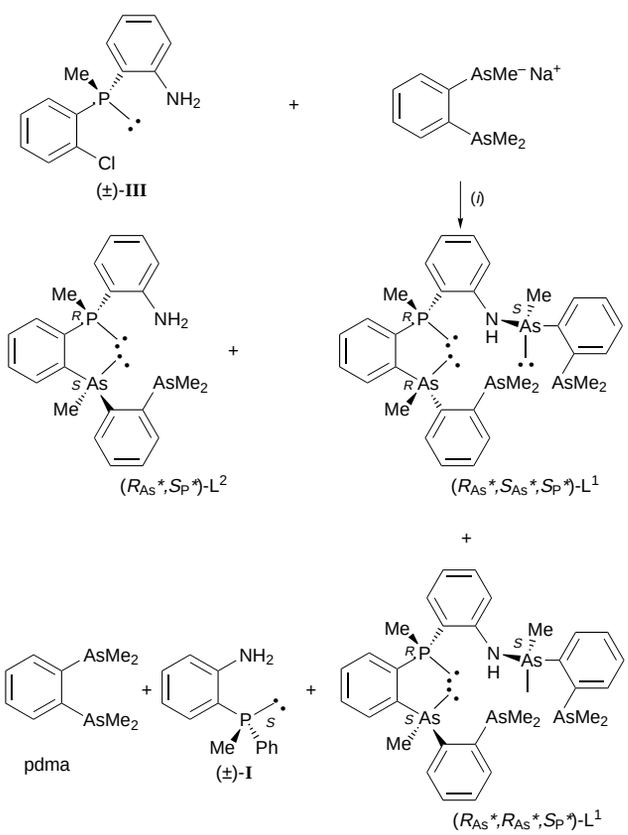



**Fig. 1** Molecular structure of the cation of complex ($S_P$,$R$)-**2**




**Scheme 4** Only one enantiomer of the chiral compounds is shown. (*i*) thf, −78 °C

sodium (2-dimethylarsinophenyl)methylarsenide [generated *in situ* from (±)-1-(dimethylarsino)-2-(methylarsino)benzene, (±)-**IV**[4] and sodium] in thf at −20 ± 5 °C produced a number of products that were most conveniently separated by complexation to cobalt(III) (Scheme 4). Four major complexes were isolated: a 1:1 diastereomeric mixture of [CoCl{($R_{As}$*,$R_{As}$*,$S_P$*)-L[1]}]$Cl_2$ and [CoCl{($R_{As}$*,$S_{As}$*,$S_P$*)-L[1]}]$Cl_2$; *trans*-[$CoCl_2$(pdma)$_2$]Cl[15,16] and *cis*-[$CoCl_2${(±)-$H_2NC_6H_4$PMePh-2}$_2$]Cl.

**Table 3** Selected non-hydrogen interatomic distances (Å) and interatomic angles (°) for [CoCl{($R_{As}$*,$R_{As}$*,$S_P$*)-L[1]}]$Cl_2$·7$H_2O$ **A**, [CoCl{($R_{As}$*,$S_{As}$*,$S_P$*)-L[1]}]$Cl_2$·2MeOH **B** and *cis*-(±)-[$CoCl_2${($R_{As}$*,$S_P$*)-L[2]}]Cl·2$H_2O$ **C**

| | **A** | **B** | **C** |
|---|---|---|---|
| Co–As(1) | 2.363(2) | 2.403(2) | 2.311(2) |
| Co–As(2) | 2.312(2) | 2.297(1) | 2.258(2) |
| Co–As(3) | 2.306(2) | 2.284(1) | |
| Co–As(4) | 2.358(2) | 2.353(2) | |
| Co–Cl(1) | 2.279(2) | 2.261(3) | 2.279(4) |
| Co–Cl(2) | | | 2.296(4) |
| Co–P | 2.211(2) | 2.206(2) | 2.173(4) |
| Co–N | | | 2.008(10) |
| As(3)–N | 1.832(7) | 1.838(7) | |
| As(1)–Co–Cl(1) | 89.48(7) | 82.99(8) | 88.5(1) |
| As(2)–Co–Cl(1) | 90.22(7) | 91.40(8) | 173.9(1) |
| As(3)–Co–Cl(1) | 81.83(7) | 94.47(8) | |
| As(4)–Co–Cl(1) | 87.67(7) | 84.46(8) | |
| As(1)–Co–Cl(2) | | | 85.7(1) |
| As(2)–Co–Cl(2) | | | 85.8(1) |
| As(1)–Co–As(2) | 86.16(5) | 86.15(5) | 86.07(8) |
| As(1)–Co–As(3) | 171.10(6) | 91.73(5) | |
| As(1)–Co–As(4) | 90.79(5) | 167.41(6) | |
| As(2)–Co–As(3) | 95.77(5) | 173.47(7) | |
| As(2)–Co–As(4) | 176.31(5) | 95.17(5) | |
| As(3)–Co–As(4) | 86.93(5) | 88.24(5) | |
| As(1)–Co–P | 101.17(7) | 101.13(8) | 100.4(1) |
| As(2)–Co–P | 85.34(7) | 87.97(7) | 87.0(1) |
| As(3)–Co–P | 87.66(7) | 86.32(7) | |
| As(4)–Co–P | 97.30(7) | 92.43(7) | |
| As(1)–Co–N | | | 173.0(3) |
| As(2)–Co–N | | | 96.8(3) |
| Cl(1)–Co–P | 168.10(1) | 176.8(1) | 91.2(1) |
| Cl(2)–Co–P | | | 170.2(2) |
| Cl(1)–Co–Cl(2) | | | 96.5(1) |
| Cl(1)–Co–N | | | 88.9(3) |
| Cl(2)–Co–N | | | 88.1(3) |
| P–Co–N | | | 86.1(3) |

The last compound was isolated as an isomeric mixture. A cobalt(III) complex containing the expected product ($R_{As}$*,$S_P$*)-L[2], *viz*. *cis*-[$CoCl_2${($R_{As}$*,$S_P$*)-L[2]}]Cl, was isolated in *ca*. 0.3% yield. Its yield was significantly increased, however, by performing the coupling reaction at elevated temperatures. The yields of the complexes *trans*-[$CoCl_2$(pdma)$_2$]Cl and *cis*-[$CoCl_2${(±)-$H_2NC_6H_4$PMePh-2}$_2$]Cl were also increased under these conditions while those of the diastereomeric complexes [CoCl{($R_{As}$*,$R_{As}$*,$S_P$*)-L[1]}]$Cl_2$ and [CoCl{($R_{As}$*,$S_{As}$*,$S_P$*)-L[1]}]$Cl_2$ were greatly diminished.

The analogous optically active complexes *cis*-[$CoCl_2$-{($S_{As}$,$R_P$)-L[2]}]Cl, α +172° (589 nm, MeOH), [CoCl{($S_{As}$,$R_{As}$,$R_P$)-L[1]}]$Cl_2$, α +192° (589 nm, MeOH) and [CoCl-{($S_{As}$,$S_{As}$,$R_P$)-L[1]}]$Cl_2$, α +38° (589 nm, MeOH), have been isolated in a similar manner from the coupling reaction between ($R_P$)-**III** and sodium (2-dimethylarsinophenyl)methylarsenide.

### Crystal structure determinations of complexes [CoCl{($R_{As}$*,$R_{As}$*,$S_P$*)-L[1]}]$Cl_2$, [CoCl{($R_{As}$*,$S_{As}$*,$S_P$*)-L[1]}]$Cl_2$ and *cis*-[$CoCl_2${($R_{As}$*,$S_P$*)-L[2]}]Cl

The structures of the complexes [CoCl{($R_{As}$*,$R_{As}$*,$S_P$*)-L[1]}]$Cl_2$·7$H_2O$, [CoCl{($R_{As}$*,$S_{As}$*,$S_P$*)-L[1]}]$Cl_2$·2MeOH and *cis*-[$CoCl_2${($R_{As}$*,$S_p$*)-L[2]}]Cl·2$H_2O$ were determined by single-crystal X-ray analyses. The stereochemistries of the three cations are shown in Figs. 2–4. All three complexes are racemic compounds with both Δ and Λ forms of the cations being present in the respective unit cells. Only the Δ form is shown in each case. Selected bond lengths and angles for the three cations are given in Table 3.

It is clear from the structural data for the cation *cis*-[$CoCl_2${($R_{As}$*,$S_P$*)-L[2]}]$^+$ that the *cis*-α diastereomer has been formed exclusively and that the stereogenic arsenic and

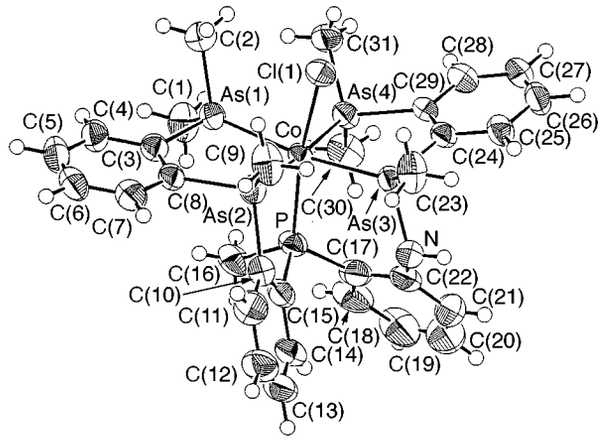



**Fig. 2** Molecular structure of the cation $[CoCl\{(R_{As}*,R_{As}*,S_P*)\text{-}L^1\}]^{2+}$

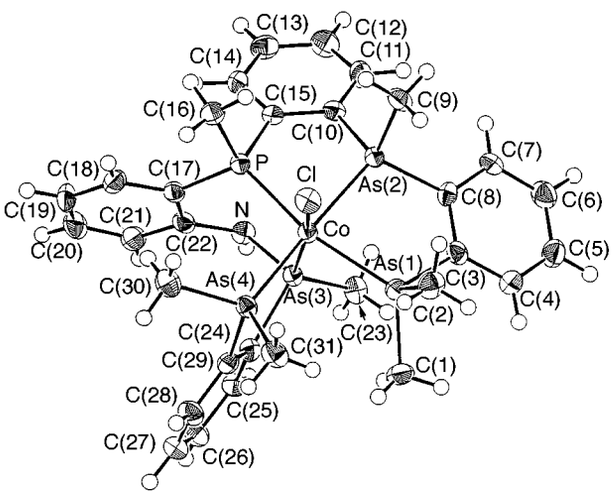



**Fig. 3** Molecular structure of the cation $[CoCl\{(R_{As}*,S_{As}*,S_P*)\text{-}L^1\}]^{2+}$

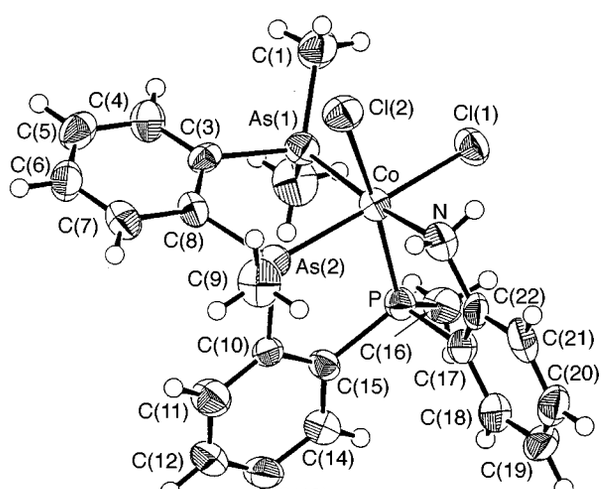



**Fig. 4** Molecular structure of the cation *cis*-$[CoCl_2\{(R_{As}*,S_P*)\text{-}L^2\}]^+$

phosphorus atoms of the quadridentate ligand have opposite relative configurations. Furthermore, the data showed that the coupling reaction between (±)-**III** and sodium (2-dimethylarsinophenyl)methylarsenide to form $(R_{As}*,S_P*)\text{-}L^2$ was completely stereoselective.

The structural data for the cations $[CoCl\{(R_{As}*,R_{As}*,S_P*)\text{-}L^1\}]^{2+}$ and $[CoCl\{(R_{As}*,S_{As}*,S_P*)\text{-}L^1\}]^{2+}$ revealed that they contained a novel chiral pentadentate ligand with one phosphorus and four arsenic donor atoms. Furthermore, the ligand contained an As–N bond. Although a number of transition-metal complexes containing As–N bonds have been structurally characterised,[26] these appear to be the first structurally authenticated examples of complexes containing a Co–As–N bonding arrangement. The two structures differed primarily in that the co-ordination sites of As(3) (the stereogenic As atom directly bonded to the N atom) and P are interchanged: As(3) was *trans* to As(1) (the As atom of a terminal dimethylarsino group) in the cation $[CoCl\{(R_{As}*,R_{As}*,S_P)\text{-}L^1\}]^{2+}$ but *trans* to Cl in $[CoCl\{(R_{As}*,S_{As}*,S_P*)\text{-}L^1\}]^{2+}$, whereas P was *trans* to Cl in the former and *trans* to As(1) in the latter. In both cations As(3) and P have opposite relative configurations. The remaining stereogenic atom As(2) has the opposite relative configuration to that of P in $[CoCl\{(R_{As}*,R_{As}*,S_P*)\text{-}L^1\}]^{2+}$ (the same arrangement as that found for the corresponding stereocentres in *cis*-$[CoCl_2\{(R_{As}*,S_P*)\text{-}L^2\}]^+$) but the same relative configuration as that of P in $[CoCl\{(R_{As}*,S_{As}*,S_P*)\text{-}L^1\}]^{2+}$.

### NMR Spectra of complexes $[CoCl\{(R_{As}*,R_{As}*,S_P*)\text{-}L^1\}]Cl_2$, $[CoCl\{(R_{As}*,S_{As}*,S_P*)\text{-}L^1\}]Cl_2$ and *cis*-$[CoCl_2\{(R_{As}*,S_P*)\text{-}L^2\}]Cl$

The $^1H$ NMR spectra of the three complexes in $CD_3OD$ can be rationalised in terms of their solid-state structures. A single doublet PMe resonance was observed for each of the complexes plus three singlet AsMe resonances for *cis*-$[CoCl_2\{(R_{As}*,S_P*)\text{-}L^2\}]Cl$ and six singlet AsMe resonances for the complexes containing $(R_{As}*,R_{As}*,S_P*)$- and $(R_{As}*,S_{As}*,S_P*)\text{-}L^1$. Furthermore, the PMe resonance for $[CoCl\{(R_{As}*,S_{As}*,S_P*)\text{-}L^1\}]Cl_2$ was downfield of that for the diastereomeric complex $[CoCl\{(R_{As}*,R_{As}*,S_P*)\text{-}L^1\}]Cl_2$. This is entirely consistent with the PMe group of the former being adjacent to the chloride ligand and two AsMe moieties whereas in the latter the PMe group is shielded by the 1,2-phenylene backbone connecting As(1) and As(2). The AsMe resonances could not be unambiguously assigned, however, the most upfield resonance for *cis*-$[CoCl_2\{(R_{As}*,S_P*)\text{-}L^2\}]Cl$ and $[CoCl\{(R_{As}*,S_{As}*,S_P*)\text{-}L^1\}]Cl_2$ has been assigned to the protons attached to C(2) and C(23), respectively. These are clearly the most shielded AsMe groups in these two structures. The $^1H$ NMR spectra of the optically active complexes *cis*-$[CoCl_2\{(S_{As},R_P)\text{-}L^2\}]Cl$, $[CoCl\{(S_{As},R_{As},R_P)\text{-}L^1\}]Cl_2$ and $[CoCl\{(S_{As},S_{As},R_P)\text{-}L^1\}]Cl_2$ in $CD_3OD$ were identical to those recorded for their racemic analogues. Selected $^1H$ NMR data for the cobalt(III) complexes are given in Table 4.

### Side-product *cis*-$[CoCl_2\{(\pm)\text{-}H_2NC_6H_4PMePh\text{-}2\}_2]Cl$

The bis(tertiary phosphine) complex *cis*-$[CoCl_2\{(\pm)\text{-}H_2NC_6H_4PMePh\text{-}2\}_2]Cl$ was characterised by chemical analysis and NMR spectroscopy. The $^1H$ NMR spectrum in $CD_3OD$ exhibited a pair of well formed doublet PMe resonances in a ratio of 1:1 whereas two singlet $^{31}P$ resonances were observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum in the same solvent (Table 4). These data are consistent with the presence of $(R_P*,R_P*)$ and $(R_P*,S_P*)$ diastereomers of the complex in which the PMe groups of the tertiary phosphine ligands have adopted a *cis* arrangement. The presence of well formed doublets for the PMe resonances strongly suggests a *cis* arrangement of the phosphorus-donor atoms.[2] Furthermore, a similar result was found for a series of related complexes of the type $[CoCl_2L_2]Cl$ [L = (2-aminoethyl)diphenylphosphine, (±)-(2-aminoethyl)(*n*-butyl)phenylphosphine or (2-aminoethyl)dimethylphosphine].[27] Here crystallographic evidence revealed exclusive formation of diastereomers containing *trans* chloro groups and a *cis* arrangement of phosphorus-donor atoms. The same stereochemistry is proposed for the two diastereomers of *cis*-$[CoCl_2\{(\pm)\text{-}H_2NC_6H_4PMePh\text{-}2\}_2]Cl$. Furthermore, the upfield PMe resonance in the $^1H$ NMR spectrum of the complex was assigned to the (*R**,*R**) diastereomer on the basis of a shielding argument. In the (*R**,*R**) configuration the methyl group will be shielded by the phenyl moiety on the adjacent phosphorus atom and hence resonate to higher field. The presence of (±)-**I** in *cis*-$[CoCl_2\{(\pm)\text{-}H_2NC_6H_4PMePh\text{-}2\}_2]Cl$ was confirmed by cyanoly-

**Table 4** Selected NMR data for cobalt(III) complexes

| Compound[a] | $^1$H δ(AsMe) | $^1$H δ(PMe)[b] | $^{31}$P-{$^1$H} δP |
|---|---|---|---|
| $[CoCl\{(R_{As}*,R_{As}*,S_P*)\text{-}L^1\}]Cl_2$ | 1.76 (s), 1.84 (s), 2.17 (s), 2.49 (s), 2.63 (s), 2.81 (s) | 1.69 (d, 11.5) | 46.5 (s) |
| $[CoCl\{(S_{As},S_{As},R_P)\text{-}L^1\}]Cl_2$ | 1.76 (s), 1.84 (s), 2.17 (s), 2.49 (s), 2.63 (s), 2.81 (s) | 1.69 (d, 11.5) | 46.5 (s) |
| $[CoCl\{(R_{As}*,S_{As}*,S_P*)\text{-}L^1\}]Cl_2$ | 1.07 (s), 1.46 (s), 1.65 (s), 1.92 (s), 2.18 (s), 2.24 (s) | 2.33 (d, 12.1) | 47.1 (s) |
| $[CoCl\{(S_{As},R_{As},R_P)\text{-}L^1\}]Cl_2$ | 1.07 (s), 1.46 (s), 1.65 (s), 1.92 (s), 2.18 (s), 2.24 (s) | 2.33 (d, 12.1) | 47.1 (s) |
| *cis*-$[CoCl_2\{(R_{As}*,S_P*)\text{-}L^2\}]Cl$ | 1.54 (s), 2.19 (s), 2.33 (s) | 2.40 (d, 13.5) | 85.0 (br s) |
| *cis*-$[CoCl_2\{(S_{As},R_P)\text{-}L^2\}]Cl$ | 1.54 (s), 2.19 (s), 2.33 (s) | 2.40 (d, 13.5) | 85.0 (br s) |
| *cis*-$[CoCl_2\{(\pm)\text{-}H_2NC_6H_4PMePh\text{-}2\}_2]Cl$ | | 2.29 (d, 13.8) | 41.6 (s) |
| | | 2.39 (d, 13.9) | 43.1 (s) |

[a] In $CD_3OD$. [b] $^2J_{PH}$ given in Hz in parentheses.

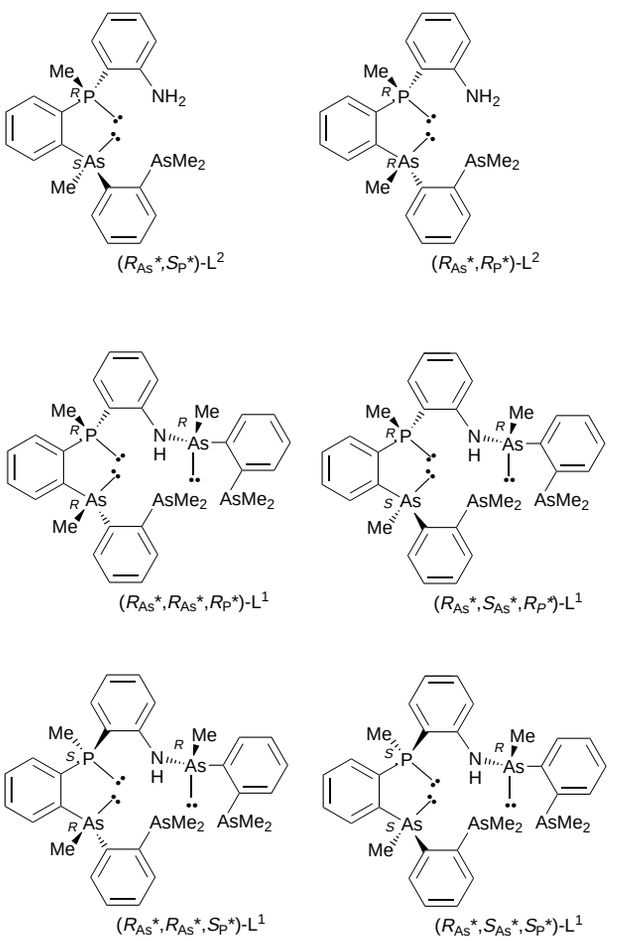
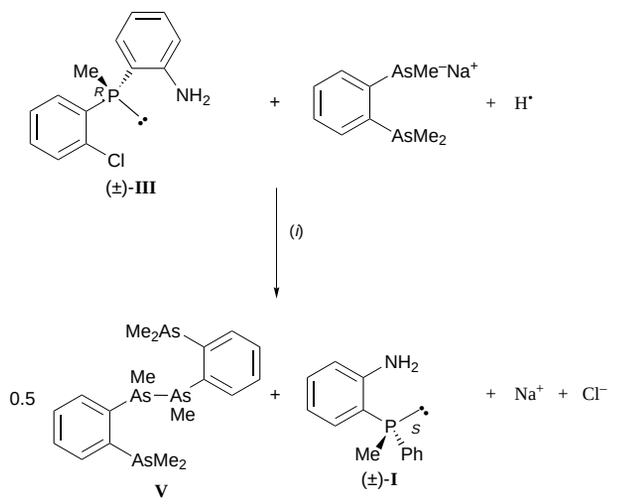



**Fig. 5** Diastereomerism in the chiral multidentate ligands $L^1$ and $L^2$




**Scheme 5** Only one enantiomer of the chiral compounds is shown. (*i*) thf, reflux

sis of the complex and comparison of the displaced ligand with an authentic sample.

## Analysis of the coupling reaction

The coupling reaction between compound (±)-**III** and sodium (2-dimethylarsinophenyl)methylarsenide produced a number of products, the relative proportions of which were dependent on the temperature employed. Lower temperatures favoured the formation of the pentadentate ligands $(R_{As}*,R_{As}*,S_P*)$- and $(R_{As}*,S_{As}*,S_P*)\text{-}L^1$ whereas elevated temperatures favoured the formation of the bidentates pdma and (±)-**I**, and quadridentate $(R_{As}*,S_P*)\text{-}L^2$. Varying the stoichiometry of the reactants had little effect on the distribution of the multidentate ligands in the products. Furthermore, the reaction was highly stereoselective: no evidence was found for the formation of the isomeric quadridentate $(R_{As}*,R_P*)\text{-}L^2$ and the diastereomeric pentadentates $(R_{As}*,R_{As}*,R_P*)$- and $(R_{As}*,S_{As}*,R_P*)\text{-}L^1$ (Fig. 5).

The mechanism for the formation of the diastereomeric pentadentate ligands $(R_{As}*,R_{As}*,S_P*)$- and $(R_{As}*,S_{As}*,S_P*)\text{-}L^1$ is not known but it is clear that their formation occurred prior to complexation to cobalt(III). The $^{31}$P-{$^1$H} NMR spectrum of the crude product from the low-temperature coupling reaction contained three major singlet resonances due to (±)-**I** and presumably $(R_{As}*,R_{As}*,S_P*)$- and $(R_{As}*,S_{As}*,S_P*)\text{-}L^1$, and two minor resonances corresponding to unchanged (±)-**III** and $(R_{As}*,S_P*)\text{-}L^2$. Furthermore, it is quite clear that the reaction does not proceed *via* quadridentate $(R_{As}*,S_P*)\text{-}L^2$. While it is not inconceivable that $(R_{As}*,S_P*)\text{-}L^2$ could be a precursor to $(R_{As}*,R_{As}*,S_P*)\text{-}L^1$, the formation of $(R_{As}*,S_{As}*,S_P*)\text{-}L^1$ would require the isomeric quadridentate $(R_{AS}*,R_P*)\text{-}L^2$ as an intermediate.

The two other major products of the coupling reaction, and particularly so at elevated temperatures, are (±)-**I** and pdma. The formation of (±)-**I** presumably arose from reduction of the chloro group of (±)-**III** by sodium (2-dimethylarsinophenyl)-methylarsenide (Scheme 5). A similar result has been reported for the reaction of (±)-(2-chlorophenyl)methylphenylphosphine with sodium dimethylarsenide in thf at 50 °C and gave tetramethyldiarsane and methylphenylphosphine as the sole products.[1h] The other product in the reduction of (±)-**III** was presumably the (2-dimethylarsinophenyl)methylarsino radical or the coupled product 1,2-bis(2-dimethylarsinophenyl)-1,2-dimethyldiarsane **V**. The radical species, if present would have been con-

verted into **V** or secondary arsine (±)-**IV** during the work-up of the reaction mixture. No such arsenic-containing species has been isolated, however, $^1$H NMR and mass spectral data were not inconsistent with the presence of **V**, but not (±)-**IV**, in the crude product prior to, but not after, complexation. Furthermore, no pdma was present in the crude product prior to complexation. Metal-assisted methylation of the (2-dimethylarsinophenyl)methylarsino moiety is postulated for the formation of *trans*-[$CoCl_2$(pdma)$_2$]Cl. There does not appear to be a literature precedent for this reaction but the carbonylation of methanol, for example, is believed to involve transfer of a methyl group from methanol, *via* a complex of Rh or Co, to a co-ordinated CO molecule.[28] A preliminary study on the complexation of secondary arsine (±)-**IV** to cobalt(III), under similar reaction conditions to those used in the isolation step of the coupling reaction, gave *trans*-[$CoCl_2$(pdma)$_2$]Cl and uncomplexed (2-dimethylarsinophenyl)methylarsinic acid as the major products. Clearly methylation of the co-ordinated secondary arsine has occurred under these reaction conditions.

## Conclusion

The work described herein clearly demonstrates that the coupling of two appropriately designed bidentate compounds can provide a viable synthetic route to a chiral quadridentate with stereogenic arsenic- and phosphorus-donor atoms. Furthermore, the coupling reaction between (±)-**III** and sodium (2-dimethylarsinophenyl)methylarsenide to give ($R_{As}$*,$S_P$*)-L[2] and its subsequent complexation to cobalt(III) were completely stereoselective which augurs well for the role of the optically active forms of the quadridentate ligand as potential chiral auxiliaries in enantioselective synthesis. The optically active antipodes of ($R_{As}$*,$S_P$*)-L[2] are to be used as chiral auxiliaries in the stereoselective derivatisation of the glycinate ion.

## References


1 See, for example, (*a*) T.-S. Chou, C.-H. Tsao and S. C. Hung, *J. Organomet. Chem.*, 1986, **312**, 53; (*b*) P. Brooks, M. J. Gallagher and A. Sarroff, *Aust. J. Chem.*, 1987, **40**, 1341; (*c*) O. Walter, T. Klein, G. Huttner and L. Zsolnai, *J. Organomet. Chem.*, 1993, **458**, 63; (*d*) J. Leitch, G. Salem and D. C. R. Hockless, *J. Chem. Soc., Dalton Trans.*, 1995, 649; (*e*) K Burgess, M. J. Ohlmeyer and K. H. Whitmire, *Organometallics*, 1992, **11**, 3588; (*f*) N. Gabbitas, G. Salem, M. Sterns and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1993, 3271; (*g*) A. A. Danopoulos, P. G. Edwards, M. Harman, M. B. Hursthouse and J. S. Parry, *J. Chem. Soc., Dalton Trans.*, 1994, 977; (*h*) R. J. Doyle, G. Salem and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1995, 1867.

2 C. E. Barclay, G. Deeble, R. J. Doyle, S. A. Elix, G. Salem, T. L. Jones, S. B. Wild and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1995, 57.

3 C. W. G. Ansell, M. K. Cooper, K. P. Dancey, P. A. Duckworth, K. Henrick, M. McPartlin, G. Organ and P. A. Tasker, *J. Chem. Soc., Chem. Commun.*, 1985, 437.

4 T. R. Carlton and C. D. Cook, *Inorg. Chem.*, 1971, **10**, 2628.

5 C. W. G. Ansell, M. K. Cooper, K. P. Dancey, P. A. Duckworth, K. Henrick, M. McPartlin and P. A. Tasker, *J. Chem. Soc., Chem. Commun.*, 1985, 439.

6 R. B. King and P. N. Kapoor, *J. Am. Chem. Soc.*, 1971, **93**, 4158.

7 B. Bosnich, S. T. D. Lo and E. A. Sullivan, *Inorg. Chem.*, 1975, **14**, 2305.

8 B. Bosnich, W. G. Jackson and S. B. Wild, *J. Am. Chem. Soc.*, 1973, **95**, 8269.

9 M. Atoh, K. Kashiwabara and J. Fujita, *Bull. Chem. Soc., Jpn.*, 1986, **59**, 1001.

10 A. L. Airey, G. F. Swiegers, S. B. Wild and A. C. Willis, *J. Chem. Soc., Chem. Commun.*, 1995, 693.

11 A. L. Airey, G. F. Swiegers, S. B. Wild and A. C. Willis, *J. Chem. Soc., Chem. Commun.*, 1995, 695.

12 R. J. Doyle, G. Salem and A. C. Willis, *J. Chem. Soc., Chem. Commun.*, 1994, 1587.

13 D. G. Allen, G. M. McLaughlin, G. B. Robertson, W. L. Steffen, G. Salem and S. B. Wild, *Inorg. Chem.*, 1982, **21**, 1007.

14 N. K. Roberts and S. B. Wild, *J. Am. Chem. Soc.*, 1979, **101**, 6254.

15 R. S. Nyholm, *J. Chem. Soc.*, 1950, 2071.

16 B. Bosnich, W. G. Jackson and J. W. McLaren, *Inorg. Chem.*, 1974, **13**, 1133.

17 PATTY, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.

18 DIRDIF 92, P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992.

19 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.2 A.

20 J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 1964, **17**, 781.

21 D. C. Creagh and W. J. McAuley, *International Tables for Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Boston, 1992, vol. C, Table 4.2.6.8, pp. 219–222.

22 D. C. Creagh and J. H. Hubbell, *International Tables for Crystallography*, ed. A. J. C. Wilson, Kluwer Academic Publishers, Boston, 1992, vol. C, Table 4.2.4.3, pp. 200–206.

23 TEXSAN, Crystal Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1985 and 1992.

24 M. K. Cooper and J. M. Downes, *Inorg. Chem.*, 1978, **17**, 880.

25 R. S. Cahn, C. K. Ingold and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 385.

26 See, for example, K. M. Flynn, B. D. Murray, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 1983, **105**, 7460; G. Suss-Fink, K. M. Heberhold, W. Buhlmeyer, A. Gieren and T. Hubner, *J. Organomet. Chem.*, 1987, **321**, 37; T. Chivers, K. S. Dhathathreyan, C. Lensink and J. F. Richardson, *Inorg. Chem.*, 1988, **27**, 1570; A. J. Arduengo III, M. Lattman, H. V. R. Dias, J. C. Calabrese and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 1799; A. Strube, G. Huttner and L. Zsolnai, *J. Organomet. Chem.*, 1990, **399**, 255.

27 I. Kinoshita, Y. Yokato, K. Matsumoto, S. Ooi, K. Kashiwabara and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1067; M. Kita, K. Kashiwabara, I. Kinoshita, J. Fujita, H. Tanaka and S. Ohba, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 2457.

28 D. Forster, *Adv. Organomet. Chem.*, 1979, **17**, 255.


*Received* 18*th December* 1996; *Paper* 6/08473G