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FULL PAPER

Optically active asymmetric di(tertiary phosphines). Crystal and molecular structure of [*SP*-4-3-(S_P,*S*)]-{1-[(2-chlorophenyl)-methylphosphino]-2-(dimethylphosphino)benzene-*P*,*P*′}{1-[1-(dimethylamino)ethyl]naphthyl-C^2,*N*}palladium(II) hexafluorophosphate

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Mono-deprotonation of the bis(secondary phosphine) (R_P*,R_P*)- and (R_P*,S_P*)-1,2-phenylenebis(methylphosphine) has been achieved using potassium in liquid ammonia to give a *ca*. 4 : 1 mixture of (±)-1-(dimethylphosphino)-2-(methylphosphino)benzene and 1,2-phenylenebis(dimethylphosphine) upon addition of a solution of methyl iodide in the same solvent. This mixture has been further treated with sodium in THF followed by the addition of 1,2-dichlorobenzene to give (±)-(2-chlorophenyl)(2-dimethylphosphinophenyl)methylphosphine and unchanged 1,2-phenylenebis(dimethylphosphine). The two di(tertiary phosphines) are readily separated by fractional distillation. Asymmetric di(tertiary phosphine) (±)-(2-chlorophenyl)(2-dimethylphosphinophenyl)methylphosphine has been resolved by separation *via* fractional crystallisation of internally diastereomeric palladium(II) complexes containing the racemic ligand and orthometallated (*S*)-dimethyl[1-(1-naphthyl)ethyl]amine. The absolute configuration of the *R* enantiomer of the ligand has been assigned by a crystal structure determination of the least soluble diastereomeric palladium(II) complex [*SP*-4-3-(S_P,*S*)]{1-[(2-chlorophenyl)methylphosphino]-2-(dimethylphosphino)benzene-*P*,*P*′}{1-[1-(dimethylamino)ethyl]naphthyl-C^2,*N*}palladium(II) hexafluorophosphate.

Resolution *via* the method of metal complexation has arguably proven to be the most successful route to optically active bidentate ligands containing stereogenic arsenic or phosphorus donor atoms. The method involves the separation by fractional crystallisation of a pair of internally diastereomeric palladium(II) complexes containing the racemic ligand and an orthometallated optically active amine, typically (*S*)- or (*R*)-dimethyl(1-phenylethyl)amine or (*S*)- or (*R*)-dimethyl-[1-(1-naphthyl)ethyl]amine.[1] The potency of the method is no better illustrated than in the resolution of the dissymmetric di(tertiary phosphine) (R_P*,R_P*)-1,2-phenylenebis(methylphenylphosphine).[2] Reaction of the racemic ligand with the chloro-bridged dimer bis(μ-chloro)bis{(*S*)-2-[1-(dimethylamino)ethyl]phenyl-C^1,*N*}dipalladium(II) in methanol followed by the addition of one equivalent of aqueous ammonium hexafluorophosphate gave a single diastereomeric complex. Subsequent treatment of both the isolated diastereomerically pure solid and the diastereomerically enriched filtrate with concentrated hydrochloric acid in methanol followed by cyanolysis gave the optically pure antipodes in *ca*. 90% yield upon recrystallisation from methanol, α ± 89° (589 nm, dichloromethane). The methodology was subsequently extended to include the analogous dissymmetric di(tertiary arsine) (R_{As}*,R_{As}*)-1,2-phenylenebis(methylphenylarsine)[3] and a range of asymmetric bidentate ligands containing a single stereogenic arsenic or phosphorus donor atom and a nitrogen or sulfur donor atom.[4] The versatility of the approach was further demonstrated by the successful resolution of the asymmetric bidentate ligands (±)-1-(dimethylarsino)-2-(methylphenylphosphino)benzene,[5] and (R_{As}*,R_P*)- and (R_{As}*,S_P*)-1-(methylphenylarsino)-2-(methylphenylphosphino)benzene;[6] the axially chiral bidentate ligands (±)-2,2′-diphenylphosphino-1,1′-binaphthyl and (±)-[(1-isoquinolyl)naphthyl]diphenylphosphine;[7] and more recently the quadridentate ligand (R_P*,R_P*)-1,2-bis{(diphenylphosphinoethyl)phenylphosphino}ethane.[8] We have also shown that the method of complexation provides a viable method of resolution for the asymmetric di(tertiary phosphines) (±)-1-(diphenylphosphino)-2-(methylphenylphosphino)benzeneand(±)-1-(diphenylphosphino)-2-(methylphenylphosphino)ethane.[9,10]

In this paper we describe the preparation and resolution of the related asymmetric di(tertiary phosphine) (±)-(2-chlorophenyl)(2-dimethylphosphinophenyl)methylphosphine. The presence of the 2-chlorophenyl group allows for further derivatisation of the ligand. For example, the related bidentate ligand (R_P)-(2-aminophenyl)(2-chlorophenyl)methylphosphine was previously shown to react with sodium (2-dimethylarsinophenyl)methylarsenide to form the optically active quadridentate ligand (S_{As},R_P)-1-[(2-aminophenyl)methylphosphino]-2-[(2-dimethylarsinophenyl)methylarsino]benzene and the optically active pentadentate ligands (S_{As},S_{As},R_P)- and (S_{As},R_{As},R_P)-5-amino-1,4,11,14-tetraarsino-2,3,6,7,9,10,12,13-tetrahydrotetrabenzo-1,1,4,8,11,14,14-heptamethyl-8-phosphinotetradecine.[11] We have published some preliminary details on the synthesis of (±)-(2-chlorophenyl)(2-dimethylphosphinophenyl)methylphosphine in a recent communication.[12]

Results and discussion

Synthesis of (±)-1

Asymmetric di(tertiary phosphine) (±)-(2-chlorophenyl)-

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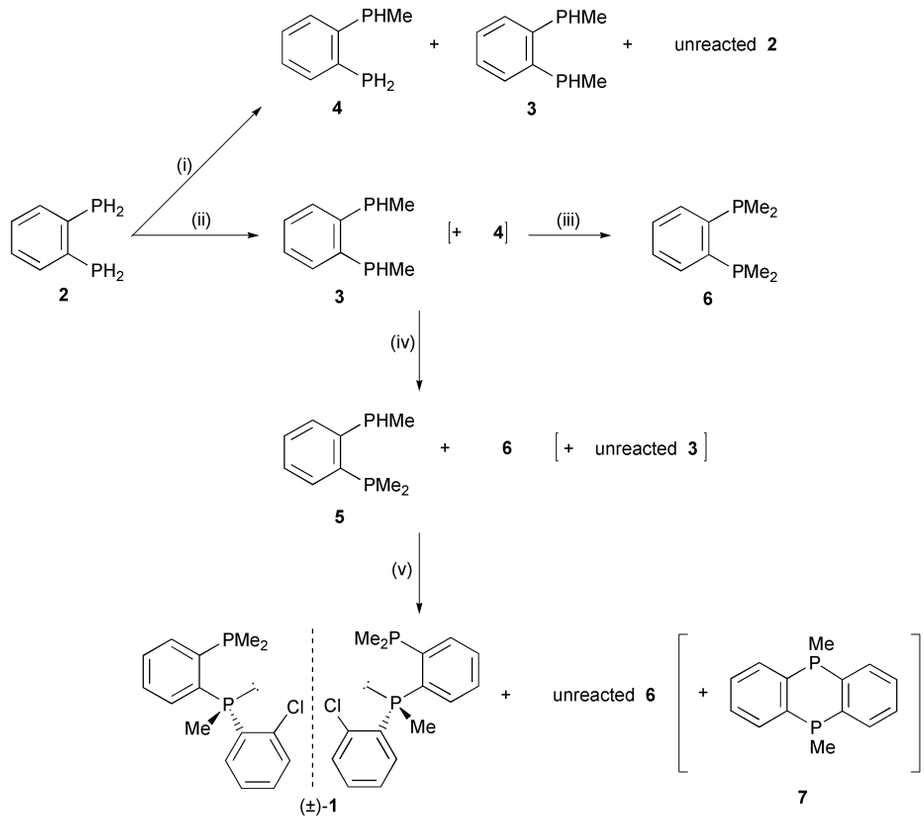


Scheme 1 (i) Na in THF; MeI; (ii) 2 Na in THF; MeI; (iii) 2 Na in THF; MeI; (iv) 1.2 equivalent K in NH_3(l); MeI; (v) Na in THF; 1,2-$C_6H_4Cl_2$.

(2-dimethylphosphinophenyl)methylphosphine, (±)-**1**, was prepared in three steps from 1,2-phenylenebis(phosphine), **2**[13] (Scheme 1). Deprotonation of the bis(primary phosphine) **2** by reaction with two equivalents of *n*-butyllithium in THF followed by the addition of a solution of methyl iodide in the same solvent gave (R_P*,R_P*)- and (R_P*,S_P*)-1,2-phenylenebis(methylphosphine), **3**, in high yield.[13] The product, however, typically contained up to *ca.* 20% of (±)-(2-methylphosphinophenyl)phosphine, **4**. The latter could be minimised (<5%) by reaction of **2** with two equivalents of sodium in THF followed by the addition of a solution of methyl iodide in the same solvent to give **3**. Whereas this reaction is highly regioselective, mono-deprotonation of bis(secondary phosphine) **3** is not. For example, reaction of **3** with one equivalent of sodium or *n*-butyllithium in THF followed by the addition of a solution of methyl iodide in the same solvent gave a mixture of three species: unchanged **3**, (±)-(2-dimethylphosphinophenyl)-methylphosphine, **5** and 1,2-phenylenebis(dimethylphosphine), **6**. The latter can be synthesized in high yield by reaction of **3** with two equivalents of sodium in THF followed by the addition of two equivalents of methyl iodide. Alternative preparative routes to **6** have been reported.[14,15] The coordination chemistry of **6** has also been investigated by Bennett and Warren.[15]

Mono-deprotonation of **3** has been investigated using several metallating agents in varying quantities ranging from *ca.* 0.8 to 1.5 equivalents and under variable reaction conditions. The reactions were monitored using a combination of ^{31}P-{^{1}H} NMR spectroscopy and GC-MS. The optimum conditions for the conversion of **3** into **5** were deemed to be reaction of **3** with *ca.* 1.2 equivalents of potassium in liquid ammonia followed by the addition of methyl iodide. Under these conditions a *ca.* 4 : 1 mixture of **5** and **6** was isolated that contained minimal quantities of **3** (<5%). Subsequent reaction of this mixture with sodium in THF followed by the addition of 1,2-dichlorobenzene gave the asymmetric di(tertiary phosphine) (±)-**1**, unchanged **6** and small quantities (<5%) of the phosphorus heterocycle 5,10-dimethyl-5,10-dihydrophosphanthren (9,10-dimethyl-9,10-dihydrodiphosphanthracene) **7**. The latter was presumably formed from the coupling of doubly deprotonated **3** with 1,2-dichlorobenzene. Separation of (±)-**1** and **6** was achieved by fractional distillation. The isolation of (±)-**1** in this manner gave a product that contained small quantities of **6** and the phosphorus heterocycle **7**. The latter crystallised from solution upon dissolution of the distilled product in hot methanol. Trace quantities of **6** were removed by reaction with hexaaquanickel(II) chloride in ethanol followed by the addition of aqueous ammonium hexafluorophosphate. A mixture of diastereomeric nickel(II) complexes containing (±)-**1** was isolated upon fractional crystallisation from dichloromethane–diethyl ether. Pure (±)-**1** was isolated from the diastereomeric mixture of nickel(II) complexes by treatment with aqueous potassium cyanide followed by distillation, in an overall yield of *ca.* 40%. Selected ^{1}H and ^{31}P-{^{1}H} NMR data for (±)-**1**–**7** are given in Table 1.

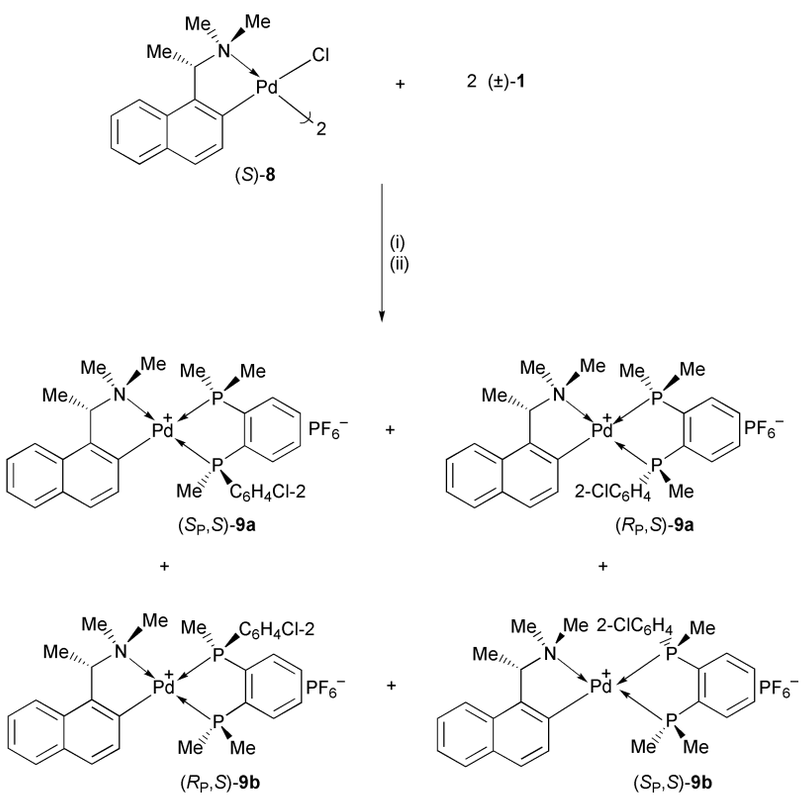
Resolution of (±)-1

The resolution of (±)-**1** has been achieved *via* the separation by fractional crystallisation of internally diastereomeric palladium(II) complexes containing the racemic ligand and an orthometallated optically active amine, namely (*S*)-dimethyl[1-(1-naphthyl)ethyl]amine. Reaction of (±)-**1** with the chloro-bridged dimer bis(μ-chloro)bis{(*S*)-1-[1-(dimethylamino)ethyl]naphthyl-C^2,*N*}dipalladium(II), (*S*)-**8**, in methanol followed by the addition of an excess of aqueous ammonium hexafluorophosphate gave a mixture of four diastereomeric palladium(II) complexes, *viz.* (R_P,*S*)-**9a**, (S_P,*S*)-**9a**, (R_P,*S*)-**9b** and (S_P,*S*)-**9b** (Scheme 2). The same mixture of four diastereomeric hexafluorophosphate salts was isolated upon the addition of one equivalent of aqueous ammonium hexafluorophosphate. Fractional crystallisation of the diastereomeric mixture from chloroform–propan-2-ol resulted in the isolation of a *ca.* 1 : 1 mixture of (R_P,*S*)-**9a** and (S_P,*S*)-**9a**. Two recrystallisations of the *ca.* 1 : 1 mixture of (R_P,*S*)-**9a** and (S_P,*S*)-**9a** from acetone–propan-2-ol gave pure (S_P,*S*)-**9a**, α +74° (589 nm,

Table 1 Selected ^{1}H and ^{31}P-{^{1}H} NMR data for compounds (±)-**1**–**7** in C_6D_6

Compound	^{31}P-{^{1}H}, δ(P)[a]	^{1}H		
		δ(PH)	δ(PMe)	δ(PMe$_2$)
(±)-**1**	−53.6d(154) −36.4d(154)	—	1.47d(5)[b]	1.15d(4),[b] 1.22d(4)[b]
2	−124.8s	3.84dm(207)[c]	—	—
3	−74.7s	4.23dq(216)[c](7)[d]	1.13dt(7)[d](4)[e]	—
	−73.6s	4.37dq(213)[c](7)[d]	1.16dt(7)[d](3)[e]	—
4	−126.3d(71)[f]	[f]	[f]	—
5	−72.5d(123) −54.4d(123)	4.45ddq(209)[c](11)[g](7)[d]	1.27ddd(7)[d](4)[b](0.6)[h]	1.08d(4),[b] 1.14d(4)[b]
6	−54.8s	—	—	1.22t(2)[e]
7	−38.2s	—	1.92d(4)[b]	

[a] Values of $^{3}J_{PP}$ given in Hz in parentheses. [b] Values of $^{2}J_{PH}$ given in Hz in parentheses. [c] Values of $^{1}J_{PH}$ given in Hz in parentheses. [d] Values of $^{3}J_{HH}$ given in Hz in parentheses. [e] Values of $|^{2}J_{PH} + {}^{5}J_{P'H}|$ given in Hz in parentheses. [f] Obscured by other resonances. [g] Value of $^{4}J_{P'H}$ given in Hz in parentheses. [h] Value of $^{5}J_{P'H}$ given in Hz in parentheses.



Scheme 2 (i) MeOH; (ii) $NH_4[PF_6]$ in water.

dichloromethane). The mother liquor, which was enriched in (R_P,S)-**9a**, was taken to dryness and the residue recrystallised from dichloromethane–propan-2ol to give pure (R_P,S)-**9a**, α +225° (589 nm, dichloromethane), albeit in low yield. Liberation of the resolved asymmetric di(tertiary phosphine) from (S_P,S)-**9a** was accomplished as shown in Scheme 3. Diastereomerically pure (S_P,S)-**9a** was dissolved in concentrated sulfuric acid, the mixture poured onto ice and anhydrous lithium chloride added to give the dichloropalladium(II) compound (S_P)-**10**, α +52° (589 nm, dichloromethane). Further reaction of (S_P)-**10** with aqueous potassium cyanide gave optically pure (R_P)-**1**, α +33° (589 nm, dichloromethane). Similar treatment of the *ca.* 1 : 1 mixture of (R_P,S)-**9a** and (S_P,S)-**9a** gave (±)-**1**, confirmation that the two diastereomeric palladium(II) complexes contained different enantiomeric forms of the di(tertiary phosphine).

Crystal structure determination of (S_P,S)-9a

The absolute configuration of (R_P)-**1** was assigned by a crystal structure determination of (S_P,S)-**9a**. The stereochemistry of the cation is depicted in Fig. 1. Selected bond lengths and angles are given in Table 2. The structural data clearly show that the absolute configurations of the stereogenic phosphorus and carbon atoms are both *S*. Furthermore, the phosphorus stereocentre of the asymmetric di(tertiary phosphine) was found to be coordinated *trans* to the NMe_2 group of the orthometallated amine. A similar arrangement has been observed in the solid state structures of several related internally diastereomeric palladium(II) complexes containing an orthometallated, optically active amine and an asymmetric bidentate ligand containing a single phosphorus (or arsenic) stereocentre.[4a,5,9–11] In most of these cases the coordination of the bidentate ligand occurred in a completely regioselective manner. The current ligand (±)-**1** and the related di(tertiary phosphine) (±)-1-(diphenylphosphino)-2-(methylphenylphosphino)ethane[10] are two examples of asymmetric bidentate ligands that do not coordinate in a completely regioselective fashion to the palladium(II) centre in such complexes.

The bond lengths and angles around the palladium(II) centre

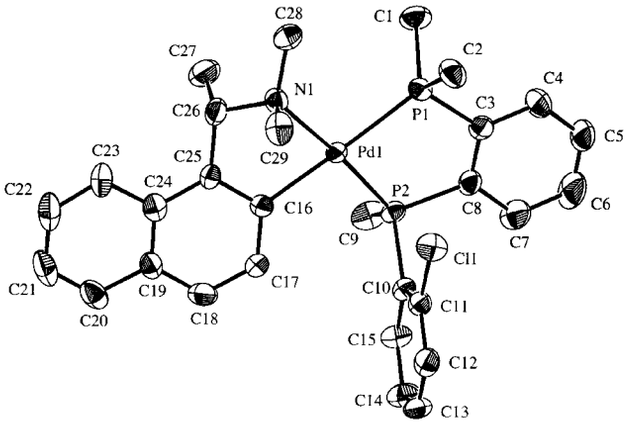
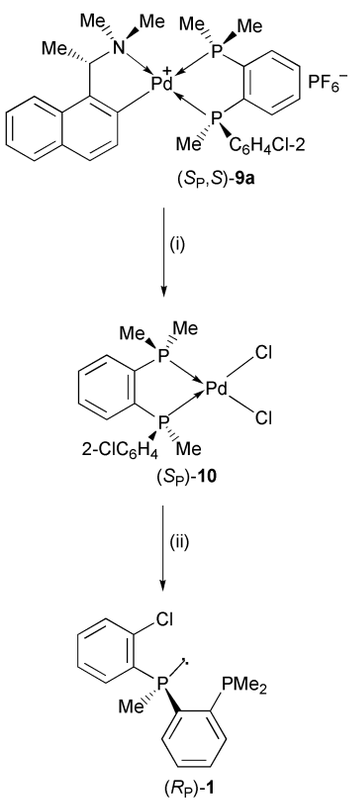


Fig. 1 Molecular structure of the cation of complex (S_P,S)-**9a**. (The thermal ellipsoids show 30% probability levels.)



Scheme 3 (i) Concentrated H_2SO_4; ice, LiCl; (ii) CH_2Cl_2; KCN in water.

of (S_P,S)-**9a** are in very close agreement with those reported for related diastereomerically pure palladium(II) complexes containing the asymmetric di(tertiary phosphines) (S_P)-1-(diphenylphosphino)-2-(methylphenylphosphino)ethane or (S_P)-1-(diphenylphosphino)-2-(methylphenylphosphino)-benzene and orthometallated (*R*)-dimethyl[1-(1-naphthyl)-ethyl]amine or (*S*)-dimethyl(1-phenylethyl)amine, respectively.[9,10] In all three complexes the Pd–P bond *trans* to the metallated carbon atom was longer than that *trans* to the dimethylamino group (2.34–2.38, *cf*. 2.22–2.25 Å). The greater *trans* influence associated with the metallated carbon atom is presumably responsible for the weakening of the *trans* disposed Pd–P bond.

NMR Spectra

The ^{1}H and ^{31}P-{^{1}H} NMR spectra of (S_P,S)-**9a** in $(CD_3)_2CO$ can be rationalised in terms of its solid state structure. The ^{31}P-{^{1}H} NMR spectrum of the complex contained a pair of doublet phosphorus resonances consistent with the presence of

Table 2 Selected non-hydrogen interatomic distances (Å) and interatomic angles (°) for (S_P,S)-**9a**

Pd(1)–P(1)	2.343(1)	Pd(1)–P(2)	2.226(2)
Pd(1)–N(1)	2.146(5)	Pd(1)–C(16)	2.061(4)
P(1)–Pd(1)–P(2)	85.36(7)	P(1)–Pd(1)–N(1)	99.5(1)
P(1)–Pd(1)–C(16)	177.5(2)	P(2)–Pd(1)–N(1)	175.1(1)
P(2)–Pd(1)–C(16)	94.4(2)	N(1)–Pd(1)–C(16)	80.8(3)
Pd(1)–P(1)–C(1)	117.9(3)	Pd(1)–P(1)–C(2)	117.5(2)
Pd(1)–P(1)–C(3)	107.9(3)	Pd(1)–P(2)–C(8)	110.5(2)
Pd(1)–P(2)–C(9)	112.8(2)	Pd(1)–P(2)–C(10)	119.3(2)
Pd(1)–N(1)–C(28)	118.5(4)	Pd(1)–N(1)–C(26)	104.7(3)
Pd(1)–N(1)–C(29)	105.4(4)	Pd(1)–C(16)–C(17)	129.5(6)
Pd(1)–C(16)–C(25)	112.5(5)		

a single diastereomer in solution. Similarly the ^{1}H NMR spectrum contained a single set of resonances including four doublets for the CMe moiety and the three non-equivalent PMe groups. Selected ^{1}H and ^{31}P-{^{1}H} NMR data for (S_P,S)-**9a** [and for the related diastereomeric complexes (R_P,S)-**9a**, (R_P,S)-**9b** and (S_P,S)-**9b**] are given in Table 3.

The presence of a doublet of doublets at δ 6.85 in the ^{1}H NMR spectrum of (S_P,S)-**9a** provided evidence that the complex retained the same regiochemistry in solution. The resonance is assigned to γ-H of the naphthyl ring (*i.e.* the H atom attached to C17 in Fig. 1) and occurred upfield of the other aromatic resonances due to shielding by the 2-chlorophenyl group of the adjacent stereogenic phosphorus atom. A similar finding has previously been reported for related diastereomeric palladium(II) complexes containing orthometallated (*R*)- or (*S*)-dimethyl[1-(1-naphthyl)ethyl]amine and a range of asymmetric bidentate ligands possessing a phosphorus (or arsenic) stereocentre bearing a methyl and an aryl substituent.[4a,c,6,11] In all cases, including (S_P,S)-**9a**, an upfield shift of γ-H was only observed in the respective ^{1}H NMR spectra when the methyl groups of the stereogenic carbon atom and the *trans* disposed phosphorus (or arsenic) stereocentre were in a *syn* arrangement with respect to the coordination plane of the palladium(II) centre. The observation of an upfield shift of the γ-H resonance clearly provides a means of assigning absolute configurations to complexes of this type by ^{1}H NMR spectroscopy.[1] It should be noted that the magnitude of the upfield shift is smaller, and hence the method of assignment is much less reliable, when the moiety linking the donor atoms of the bidentate ligand is a 1,2-ethylene group.[4b,d,10] The γ-H resonance was also found to be coupled to the adjacent stereogenic phosphorus atom of these complexes in the respective ^{1}H NMR spectra, *via* what is believed to be a through-space rather than through-bond effect. In the case of (S_P,S)-**9a**, a value of 14 Hz for $^4J_{PH}$ was observed for the γ-H resonance.

The ^{1}H and ^{31}P-{^{1}H} NMR spectra of (R_P,S)-**9a** in $(CD_3)_2CO$ were similarly consistent with the presence of a single diastereomer. Not unexpectedly they were very similar to those recorded for (S_P,S)-**9a**, the only major difference being the absence of an upfield shift for the γ-H resonance in the ^{1}H NMR spectrum of (R_P,S)-**9a**. Indeed, the two complexes were assigned the same regiochemistry on the basis of the similarities between their respective ^{31}P-{^{1}H} NMR spectra. The pair of doublet phosphorus resonances had very similar chemical shifts in the two spectra. A similar approach has previously been used to identify the four internally diastereomeric palladium(II) complexes formed in the resolution of (±)-1-(diphenylphosphino)-2-(methylphenylphosphino)ethane by reaction of the racemic ligand with (*R*)-**8** in methanol followed by the addition of aqueous ammonium hexafluorophosphate.[10] Two diastereomeric palladium(II) complexes containing the *S* form of the di(tertiary phosphine) were isolated and unambiguously characterised. The remaining pair of diastereomers had different regiochemistries and was identified by comparison of their ^{31}P-{^{1}H} NMR spectra with those recorded for their counter-

Table 3 Selected ^{1}H and ^{31}P-{^{1}H} NMR data for complexes (R_P,S)-**9a**, (S_P,S)-**9a**, (R_P,S)-**9b** and (S_P,S)-**9b** in $(CD_3)_2CO$

Compound	^{31}P-{^{1}H},[a] δ(P)	^{1}H				
		δ(CMe)	δ(PMe$_2$)	δ(PMe)	δ(NMe$_2$)	δ(γH)
(R_P,S)-**9a**	21.0(26), 37.6(26)	1.87d	2.13d	2.57d	2.97bs, 3.41m	[b]
(S_P,S)-**9a**	22.3(26), 38.0(26)	1.93d	2.11d, 2.13d	2.36d	2.97bs, 3.42m	6.85dd
(R_P,S)-**9b**	29.5(24), 34.8(24)	1.77d	2.00d, 2.15d	2.39d	2.89bs, 3.47bs	[b]
(S_P,S)-**9b**	28.9(27), 34.6(27)	1.89d	2.18d, 2.24d	2.44d	2.99bs, 3.48bs	[b]

[a] Values of $^2J_{PP}$ given in Hz in parentheses. [b] Obscured by the manifold of aromatic resonances.

parts. In the present work the two remaining diastereomers, *viz.* (R_P,S)-**9b** and (S_P,S)-**9b**, had the same regiochemistry and could not be differentiated by ^{31}P-{^{1}H} NMR spectroscopy.

Conclusion

The work detailed herein describes a viable synthetic route to an optically active asymmetric di(tertiary phosphine), (S_P)-(2-chlorophenyl)(2-dimethylphosphinophenyl)methylphosphine. The presence of the 2-chlorophenyl group is a key design feature that should allow further derivatisation of the di(tertiary phosphine). Optically active asymmetric di(tertiary phosphines) are seen as potential chiral auxiliaries in enantioselective catalysis. Moreover, 2-chlorophenyl substituted ligands of this type and its precursor sodium (2-dimethylphosphinophenyl)methylphosphide are seen as important synthons in the design and synthesis of optically active linear quadridentate ligands. We have previously shown that the coupling of appropriately designed bidentate ligands of this type (and their arsenic counterparts) can provide a highly stereoselective route to chiral linear quadridentate ligands containing stereogenic phosphorus or arsenic donor atoms.[11,12]

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. NMR spectra were recorded on a Varian Gemini II spectrometer operating at 300 (^{1}H) or 121 MHz (^{31}P-{^{1}H}). Chemical shifts are reported as δ values relative to $SiMe_4$ (^{1}H) or 85% H_3PO_4 (^{31}P-{^{1}H}). Optical rotations were measured with an Optical Activity AA-10 or a Perkin-Elmer Model 241 polarimeter on the specified solutions in 1 dm cells at 20 °C. Elemental analyses were performed by staff within the Research School of Chemistry.

The compounds 1,2-phenylenebis(phosphine), **2**,[13] and bis-(μ-chloro)bis{(*S*)-2-[1-(dimethylamino)ethyl]naphthyl-C^2,N}-dipalladium(II), (*S*)-**8**,[4] were prepared by literature procedures.

Preparations

(R^*_P,R^*_P)- and (R^*_P,S^*_P)-1,2-phenylenebis(methylphosphine), 3. Sodium foil (4.30 g, 0.187 mol) was added piecewise to a solution of 1,2-phenylenebis(phosphine), **2** (14.12 g, 0.099 mol), in THF (200 cm^3), and the reaction mixture allowed to stir for 48 h. Any excess of sodium was removed, and the orange solution cooled to −78 °C. Methyl iodide (11.64 g, 0.187 mol) in THF (20 cm^3) was added dropwise, and the solution stirred overnight. The solvent was distilled off under argon. Water (100 cm^3) was added to the residue, and the aqueous phase extracted with diethyl ether (3 × 100 cm^3). The combined diethyl ether extracts were dried ($MgSO_4$), filtered and the solvent was distilled off under argon, leaving a yellow oil. The product was obtained as a colourless oil by vacuum distillation. The product was isolated as a *ca.* 1 : 1 mixture of racemic and *meso* diastereomers and also contained *ca.* 5% of (±)-(2-methylphosphinophenyl)phosphine, **4** (14.16 g, 84%), bp 58–60 °C (0.001 mmHg). ^{1}H NMR (C_6D_6): δ 1.13 (d of t, 6 H, $^3J_{HH}$ 7.14, $|^2J_{PH} + {}^5J_{P'H}|$ 3.60, P*Me*), 1.16 (d of t, 6 H, $^3J_{HH}$ 7.41, $|^2J_{PH} + {}^5J_{P'H}|$ 3.30, P*Me*), 4.23 (d of q, 2 H, $^2J_{PH}$ 216.4, $^3J_{HH}$ 7.14, P*H*), 4.37 (d of q, 2 H, $^2J_{PH}$ 213.4, $^3J_{HH}$ 7.41 Hz, P*H*), 6.99–7.28 (m, 8 H, aromatics). ^{31}P-{^{1}H} NMR (C_6D_6): δ −73.6 (s, 2 P), −74.7 (s, 2 P), −126.2 (d, 1 P, $^3J_{PP}$ 71 Hz, *P*H_2 of **4**). *m/z*: 170, $(M)^+$; 155, $(M - Me)^+$; 123, $(M - PHMe)^+$. *m/z* of **4**: 156, $(M)^+$; 139, $(M - Me)^+$; 123, $(M - PH_2)^+$; 109, $(M - PHMe)^+$.

(±)-(2-Dimethylphosphinophenyl)methylphosphine, 5. Liquid ammonia (200 cm^3) was condensed onto **3** (14.16 g, 0.083 mol) and an excess amount of potassium metal pieces (4.01 g, 0.102 mol) added. The reaction mixture was stirred for 4 hours. Methyl iodide (14.54 g, 0.102 mol) in THF (25 cm^3) was added dropwise and the clear solution allowed to warm to room temperature overnight, to allow the ammonia to evaporate. Water (100 cm^3) was added to the residue, which was extracted with diethyl ether (3 × 100 cm^3). The diethyl ether extracts were dried ($MgSO_4$), filtered and the solvent was distilled off under argon, leaving a yellow oil. Vacuum distillation of the oil gave the product as a colourless oil (14.11 g, 92%), bp 67–68 °C (0.005 mmHg). The product contained *ca.* 4% of **3** and *ca.* 22% of **6**. ^{1}H NMR (C_6D_6): δ 1.08 (d, 3 H, $^2J_{PH}$ 4.0, PMe*Me*), 1.14 (d, 3 H, $^2J_{PH}$ 3.4, P*Me*Me), 1.27 (d of d of d, 3 H, $^3J_{HH}$ 7.4, $^2J_{PH}$ 3.6, $^5J_{P'H}$ 0.6, PH*Me*), 4.45 (d of d of q, 1 H, $^1J_{PH}$ 209, $^4J_{P'H}$ 11.0, $^3J_{HH}$ 7.4 Hz, P*H*Me), 6.98–7.36 (m, 4 H, aromatics). ^{31}P-{^{1}H} NMR (C_6D_6): δ −72.5 (d, 1 P, $^3J_{PP}$ 123, PHMe), −54.4 (d, 1 P, $^3J_{PP}$ 123 Hz, PMe_2). *m/z* 184, $(M)^+$; 169, $(M - Me)^+$; 123, $(M - PMe_2)^+$.

1,2-Phenylenebis(dimethylphosphine), 6. Excess of sodium foil (3.04 g, 0.132 mol) was added to (R_P*,R_P*)- and (R_P*,S_P*)-1,2-phenylenebis(methylphosphine), (R_P*,R_P*)- and (R_P*,S_P*)-**3**, (7.56 g, 0.044 mol) in THF (120 cm^3), and the solution stirred overnight. The excess of sodium was removed, and the orange solution cooled to −78 °C. A solution of methyl iodide (12.61 g, 0.089 mol) in THF (30 cm^3) was added dropwise. The solution was allowed to come to room temperature and stirred overnight. The solvent was removed, water (80 cm^3) added to the residue, and the aqueous phase extracted with diethyl ether (3 × 80 cm^3). The combined ether extracts were dried ($MgSO_4$), filtered, and the solvent was removed to leave a yellow oil. Vacuum distillation of the crude oil gave the product as a colourless oil (7.10 g, 81%), bp 78 °C (0.001 mmHg) [lit.[13] 139–141 °C (0.4–0.5 mmHg)]. ^{1}H NMR (C_6D_6): δ 1.22 (t, 12 H, $|^2J_{PH} + {}^5J_{P'H}|$ 1.73 Hz, PMe_2), 7.1–7.35 (m, 4 H, aromatics). ^{31}P-{^{1}H} NMR (C_6D_6): δ −54.8 (s, 2 P, *P*Me_2). *m/z*: 198, $(M)^+$; 183, $(M - Me)^+$.

(±)-1-[(2-Chlorophenyl)methylphosphino]-2-(dimethylphosphino)benzene, (±)-1. Sodium foil (0.92 g, 0.04 mol) was added piecewise to a solution of **5** (7.38 g, 0.04 mol) in THF (100 cm^3) and the solution stirred overnight. The resulting phosphide solution was added dropwise to a solution of 1,2-dichlorobenzene (5.89 g, 0.04 mol) in THF (40 cm^3). The reaction mixture was stirred for 4 days. Water (20 cm^3) was added, and the solvent removed. Further water (100 cm^3) was added,

and the solution extracted with dichloromethane (3 × 90 cm^3). The organic extracts were dried ($MgSO_4$), filtered and the solvent was removed to give a yellow oil. The residue was distilled under reduced pressure. Fraction 1: 1,2-phenylenebis(dimethylphosphine), **6** (3.14 g), bp 78 °C (0.01 mmHg). Fraction 2: (±)-1-[(2-chlorophenyl)methylphosphino]-2-(dimethylphosphino)benzene, (±)-**1** (4.75 g, 65% based on the amount of **6** recovered), bp 135 °C (0.01 mmHg). The latter also contained small quantities of **6** and **7**.

Ligand (±)-**1** (4.75 g, 15.7 mmol) was dissolved in hot methanol (20 cm^3), the solution allowed to cool slowly to room temperature and then further cooled in ice. The resulting colourless prisms of **7** were collected and dried *in vacuo*. ^{1}H NMR (C_6D_6): δ 1.92 (d, 6 H, $^2J_{PH}$ 4.1 Hz, PMe), 6.78–7.34 (m, 8 H, aromatics). ^{31}P-{^{1}H} NMR (C_6D_6): δ −38.2 (s, 2 P). *m/z* 244, $(M)^+$; 229, $(M - Me)^+$; 214, $(229 - Me)^+$; 183, $(214 - P)^+$.

Ligand (±)-**1** (4.86 g, 16.2 mmol) was dissolved in deoxygenated ethanol (90 cm^3) and added dropwise to a solution of nickel(II) chloride hexahydrate (2.00 g, 8.41 mmol) in ethanol (20 cm^3). The red solution was stirred for 2 h. Excess of ammonium hexafluorophosphate (2.06 g, 12.62 mmol) in water (10 cm^3) was added and the yellow-orange reaction mixture stirred overnight. The product, which precipitated, was isolated by filtration and washed with water (15 cm^3), diethyl ether–methanol (10 cm^3) and diethyl ether (20 cm^3), and dried *in vacuo*. Further ammonium hexafluorophosphate (1.00 g, 6.13 mmol) in water (2 cm^3) was added to the filtrate to afford an additional crop of crystals. The combined product was recrystallised from dichloromethane–diethyl ether to give pure $[Ni\{(\pm)\text{-}\mathbf{1}\}_2][PF_6]_2$ (3.70 g, 68%), mp 218–222 °C (Found: C, 38.7; H, 3.8. Calc. for $C_{28}H_{30}Cl_2F_{12}NiP_6$: C, 38.4; H, 3.6%).

The complex $[Ni\{(\pm)\text{-}\mathbf{1}\}_2][PF_6]_2$ (5.31 g, 5.97 mmol) was suspended in deoxygenated dichloromethane (50 cm^3) and water (60 cm^3). Potassium cyanide (17.63 g, 0.271 mol) was added and the solution stirred vigorously for 15 h. The layers were separated and the aqueous layer was extracted with dichloromethane (2 × 50 cm^3). The organic layers were combined, dried ($MgSO_4$), filtered and the solvent was removed to give (±)-**1** (2.92 g, 83%). ^{1}H NMR (C_6D_6): δ 1.15 (d, 3 H, $^2J_{PH}$ 4.11, P*Me*), 1.22 (d, 3 H, $^2J_{PH}$ 3.36, P*Me*), 1.47 (d, 3 H, $^2J_{PH}$ 5.28 Hz, P*Me*C_6H_4Cl-2), 6.78–7.34 (m, 8 H, aromatics). ^{31}P-{^{1}H} NMR (C_6D_6): δ −53.6 (d, 1 P, $^3J_{PP}$ 153.6, *P*Me_2); −36.4 (d, 1 P, $^3J_{PP}$ 153.6 Hz, *P*MeC_6H_4Cl-2). *m/z*: 294, (M^+); 279, $(M - Me)^+$; 259, $(M - Cl)^+$.

[*SP*-4-1]-Bis{(1,2-phenylenebis(dimethylphosphine)-*P*,*P*′}-nickel(II) hexafluorophosphate, $[Ni(\mathbf{6})_2][PF_6]_2$. The ligand **6** (0.544 g, 2.74 mmol) was dissolved in ethanol (10 cm^3) and hexaaquanickel(II) chloride (0.399 g, 1.37 mmol) added. The solution was stirred for 2 h, filtered, and taken to dryness. The residue was redissolved in methanol, and ammonium hexafluorophosphate (0.224 g, 1.37 mmol) in water (2 cm^3) added dropwise. Water (15 cm^3) was added and the reaction mixture stirred overnight. The product was isolated by filtration, washed with water (10 cm^3), diethyl ether–methanol (4 : 1, 10 cm^3) and diethyl ether (15 cm^3), and dried *in vacuo* (0.542 g, 66%), mp 314–317 °C (Found: C, 32.1; H, 4.4. Calc. for $C_{20}H_{32}F_{12}NiP_6$: C, 32.2; H, 4.3%). ^{1}H NMR [$(CD_3)_2CO$]: δ 2.19 (s, 24 H, PMe_2), 7.93–8.28 (d of m, 8 H, aromatics). ^{31}P-{^{1}H} NMR [$(CD_3)_2CO$]: δ 41.2 (s, 4 P, *P*Me_2).

Resolution of (±)-1: formation and separation of the internally diastereomeric complexes [*SP*-4-3-(*R*$_P$,*S*)]-, [*SP*-4-3-(*S*$_P$,*S*)]-, [*SP*-4-4-(*R*$_P$,*S*)]- and [*SP*-4-4-(*S*$_P$,*S*)]-[(2-chlorophenyl)(2-dimethylphosphinophenyl)methylphosphine-*P*,*P*′]{[1-(1-dimethylamino)ethyl]naphthyl-*C*^{2},*N*}palladium(II) hexafluorophosphate, (*R*$_P$,*S*)-9a, (*S*$_P$,*S*)-9a, (*R*$_P$,*S*)-9b and (*S*$_P$,*S*)-9b. To a suspension of the resolving agent, di-μ-chloro-bis{(*S*)-1-[1-(dimethylamino)ethyl]naphthyl-*C*^{2},*N*}dipalladium(II), (*S*)-**8** (2.51 g, 3.69 mmol), in methanol (30 cm^3), was slowly added a solution of (±)-(2-chlorophenyl)(2-dimethylphosphinophenyl)methylphosphine, (±)-**1** (2.18 g, 7.38 mmol), in methanol (90 cm^3). The mixture was stirred at room temperature for 2.5 h, and then filtered through Celite. Excess of ammonium hexafluorophosphate (1.51 g, 9.26 mmol) in water (10 cm^3) was added dropwise to the pale yellow filtrate. Water (70 cm^3) was added dropwise, and the white precipitate that formed was left to stir overnight. The precipitate was isolated by filtration, washed with water (25 cm^3), diethyl ether–methanol (4 : 1, 15 cm^3) and diethyl ether (20 cm^3) and dried *in vacuo* (4.62 g, 84%). α +70° (589 nm, *c* 1.0 g per 100 cm^3, CH_2Cl_2).

The diastereomeric mixture of palladium(II) salts was dissolved in chloroform (30 cm^3) and propan-2-ol (20 cm^3) added dropwise to give a 1 : 1 diastereomeric mixture of (*R*$_P$,*S*)-**9a** and (*S*$_P$,*S*)-**9a** as fine white needles, which were isolated by filtration, washed with diethyl ether (20 cm^3) and dried *in vacuo* (2.01 g, 87%), α +93° (589 nm, *c* 1.0 g per 100 cm^3, CH_2Cl_2). The mother liquor consisted of a *ca.* 1 : 1 : 9 : 9 mixture of (*R*$_P$,*S*)-**9a**, (*S*$_P$,*S*)-**9a**, (*R*$_P$,*S*)-**9b** and (*S*$_P$,*S*)-**9b** which could not be further separated by fractional crystallisation.

The 1 : 1 mixture of (*R*$_P$,*S*)-**9a** and (*S*$_P$,*S*)-**9a** was dissolved in acetone (10 cm^3) and propan-2-ol (8 cm^3) added dropwise to give white blocks of diastereomerically pure (*S*$_P$,*S*)-**9a** (0.79 g, 79%), mp 217–220 °C, α +74° (589 nm, *c* 0.30 g per 100 cm^3, CH_2Cl_2) (Found: C, 46.8; H, 4.4; N, 1.9. Calc. for $C_{29}H_{33}ClF_6NP_3Pd$: C, 46.8; H, 4.5; N, 1.9%). ^{1}H NMR [$(CD_3)_2CO$]: δ 1.93 (d, 3 H, $^3J_{HH}$ 6.4, C*Me*), 2.11 (d, 3 H, $^2J_{PH}$ 8.43, PMe*Me*), 2.13 (d, 3 H, $^2J_{PH}$ 8.04, PMe*Me*), 2.36 (d, 3H, $^2J_{PH}$ 10.26, P*Me*), 2.97 (br s, 3 H, N*Me*), 3.42 (m, 3 H, N*Me*), 4.79 (m, 1 H, C*H*Me), 6.85 (d of d, 1 H, $^3J_{HH}$ 6.4, $^4J_{PH}$ 13.98 Hz, γ*H*), 7.28–8.44 (m, 13 H, aromatics). ^{31}P-{^{1}H} NMR [$(CD_3)_2CO$]: δ −143.7 (septet, 1 P, $^1J_{PF}$ 710, *P*F_6), 22.3 (d, 1 P, $^2J_{PP}$ 25.5, *P*Me_2), 38.0 (d, 1 P, $^2J_{PP}$ 25.5 Hz, *P*Me(C_6H_4Cl-2)).

The mother liquor, which was enriched in (*R*$_P$,*S*)-**9a**, was taken to dryness and the residue dissolved in dichloromethane (5 cm^3). Propan-2-ol (5 cm^3) was added dropwise to give white plates of diastereomerically pure (*R*$_P$,*S*)-**9a** (0.34 g, 34%), mp 205 °C (decomp.), α +225° (589 nm, *c* 0.30 g per 100 cm^3, CH_2Cl_2) (Found: C, 43.8; H, 4.5; N, 1.7. Calc. for $C_{29}H_{33}ClF_6NP_3Pd{\cdot}CH_2Cl_2$: C, 43.4; H, 4.2; N, 1.7%). ^{1}H NMR [$(CD_3)_2CO$]: δ 1.87 (d, 3 H, $^3J_{HH}$ 6.30, C*Me*), 2.13 (d, 6 H, $^2J_{PH}$ 8.25, PMe_2), 2.57 (d, 3 H, $^2J_{PH}$ 9.57, P*Me*), 2.97 (br s, 3 H, N*Me*), 3.41 (t, 3 H, $^4J_{PH}$ 3.60 Hz, N*Me*), 4.78 (m, 1 H, C*H*Me), 7.33–8.50 (m, 14 H, aromatics). ^{31}P-{^{1}H} NMR [$(CD_3)_2CO$]: δ −143.7 (septet, 1 P, $^1J_{PF}$ 710, *P*F_6), 21.0 (d, 1P, $^2J_{PP}$ 25.5, *P*Me_2), 37.6 (d, 1P, $^2J_{PP}$ 25.5 Hz, *P*Me-(C_6H_4Cl-2)).

[*SP*-4-2-(*S*$_P$)]-Dichloro[(2-chlorophenyl)(2-dimethylphosphinophenyl)methylphosphine-*P*,*P*′]palladium(II), (*S*$_P$)-10. Diastereomerically pure (*S*$_P$,*S*)-**9a** (0.75 g, 1.01 mmol) was dissolved in concentrated sulfuric acid (4 cm^3) and the yellow solution poured onto ice (10 g). Lithium chloride (0.5 g, 11.78 mmol), dichloromethane (30 cm^3) and water (30 cm^3) were added, and the two layers separated. The aqueous layer was further extracted with dichloromethane (2 × 30 cm^3), and the combined organic layers were dried ($MgSO_4$), filtered, and the solvent was removed under reduced pressure. The residue was recrystallised from dichloromethane–methanol to give enantiomerically pure (*S*$_P$)-**10** (0.40 g, 85%), mp 180–185 °C, α +52° (589 nm, *c* 0.25 g per 100 cm^3, CH_2Cl_2). ^{1}H NMR [$(CD_3)_2SO$]: δ 2.08 (d, 6 H, $^2J_{PH}$ 13.9, PMe_2), 2.40 (d, 3 H, $^2J_{PH}$ 13.9 Hz, PMe_2), 7.51–8.23 (m, 8 H, aromatics). ^{31}P-{^{1}H} NMR [$(CD_3)_2SO$]: δ 53.5 (d, 1P, $^3J_{PP}$ 17 Hz, *P*Me_2), 59.2 (d, 1P, $^3J_{PP}$ 17 Hz, *P*Me(C_6H_4Cl-2)).

(*R*$_P$)-1-[(2-Chlorophenyl)methylphosphino]-2-(dimethylphosphino)benzene, (*R*$_P$)-1. Enantiomerically pure (*S*$_P$)-**10** (0.40 g, 0.86 mmol) was suspended in light petroleum (bp 60–80 °C) (20 cm^3) and methanol (20 cm^3). Potassium cyanide (2.24 g,

34.39 mmol) was added, and the mixture shaken vigorously. Water (20 cm^3) was added and the layers were separated. The aqueous layer was extracted with light petroleum (2 × 30 cm^3). The organic layers were combined, dried, filtered and the solvent was removed under vacuum to give (R_P)-**1** (0.22 g, 88%), α +33° (589 nm, *c* 0.25 g per 100 cm^3, CH_2Cl_2). ^1H and ^{31}P-{^1H} NMR (C_6D_6): identical with those recorded for the racemic compound (±)-**1**.

X-Ray crystallography

Crystal data for complex (S_P,*S*)-9a. $C_{29}H_{33}ClF_6NP_3Pd$, $M = 744.35$, monoclinic, space group $P2_1$ (no. 4), $a = 8.982(2)$, $b = 13.436(2)$, $c = 13.797(2)$ Å, $\beta = 102.87(1)°$, $U = 1623.2(5)$ $Å^3$, $T = 296$ K, $Z = 2$, μ(Mo-Kα) = 8.45 cm^{-1}, 5016 reflections measured, 3899 unique ($R_{int} = 0.017$) which were used in all calculations. The final *R* and *R′* values were 0.0324 and 0.0277.

The structure was solved by direct methods and expanded using Fourier techniques.[16,17] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically determined positions that were periodically recalculated but not refined. All calculations were performed using the TEXSAN crystallographic software package.[18]

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See http://www.rsc.org/suppdata/dt/b1/b101182k/ for crystallographic data in CIF or other electronic format.

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