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New Chiral Ferrocene-Bridged Phosphole–Phosphane Ligands

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A convenient synthesis of new chiral ferrocenene-bridged phosphole–phosphane ligands in an enantiomerically pure form has been developed. These new chiral P,P ligands have been tested in a palladium-catalysed allylic substitution reaction. High activities and moderate enantioselectivities (up to 61 %) were observed. A palladium(II) complex has been isolated and its crystal structure established.

Introduction

Considerable efforts have been devoted to the development of new chiral ligands owing to the growing importance of transition-metal-catalysed asymmetric synthesis.[1] Among these chiral ligands, ferrocene-containing ligands are among the most interesting because of their stability, easy introduction of planar chirality and special electronic and stereoproperties of the ferrocene skeleton.[2] Amongst the chiral ferrocene-based ligands, enantiopure 1,2-disubstituted ferrocene derivatives, especially ferrocenediyldiphosphane ligands, played a dominant role.[3] Typical examples are Trap ligands,[4] and diphosphane Josiphos ligands,[5] in particular the industrially important Xyliphos,[6] Taniaphos[7] or Walphos-type ligands[8] (Figure 1). Common characteristics of these ligands include the ferrocenylethyl backbone and the presence of both planar and central chiralities. Little attention has been paid to ligands based on a ferrocenylmethyl backbone or more generally to those having ferrocene possessing planar chirality as their only element of chirality. Reported examples include Trap (**I**),[9] Josiphos[10] analogues (**II**) or diphosphanes (**III**)[11] developed by Kagan et al. (Figure 2).

Recently, we have extended the family of 1,2-disubstituted planar-chiral ferrocene by introduction of a phosphole group leading to planar-chiral ferrocene-bridged phosphole–amine ligands.[12] Chiral phosphole-based ligands[13] have been rather infrequently used for asymmetric catalysis,[14] despite the fact that phospholes are efficient ligands in homogeneous transition-metal catalysis.[15] However, introduction of a phosphole group, which possesses different steric and electronic effects with respect to phosphanes, may modulate the ligand properties. Other advantages of this type of ligand are related to chiral flexibility of unsymmetrically substituted phosphole due to the low inversion barrier of the phosphorus atom in phosphole.[16]

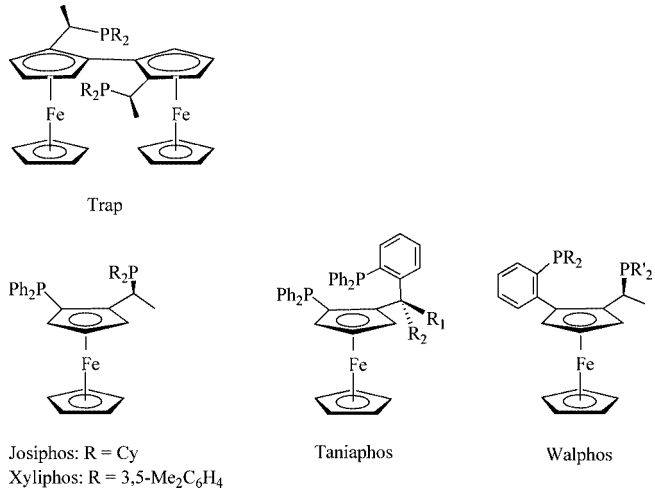

Figure 1. Well-known ferrocenyldiphosphane ligands combining both planar and central chiralities.

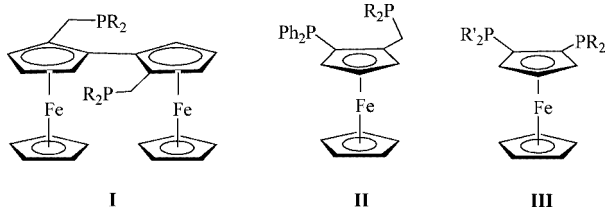

Figure 2. Ferrocenyldiphosphane ligands possessing planar chirality as their only element of chirality.

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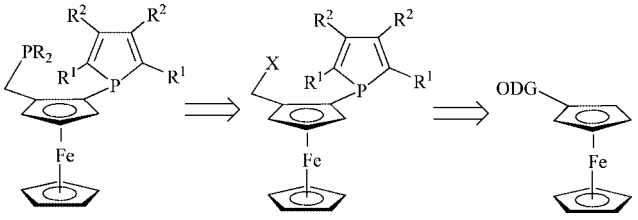
A chirally flexible phosphole can (i) adjust the configuration to accommodate the metal centre and (ii) magnify the chiral part of the catalytic system.[17]

As part of our continuing interest in ferrocene chemistry[18] and in the design and synthesis of new chiral phosphole-based ligands,[19] we were interested in ferrocene-derived phosphole ligands with only planar chirality for asymmetric catalysis. In this paper, we describe the synthesis of new 1,2-disubstituted ferrocene-bridged phosphole–phosphane ligands involving the introduction of various phospholyl groups on Kagan's acetal derivatives. The coordination chemistry and the catalytic properties of these new chiral ferrocene-bridged phosphole–phosphane ligands are also reported.

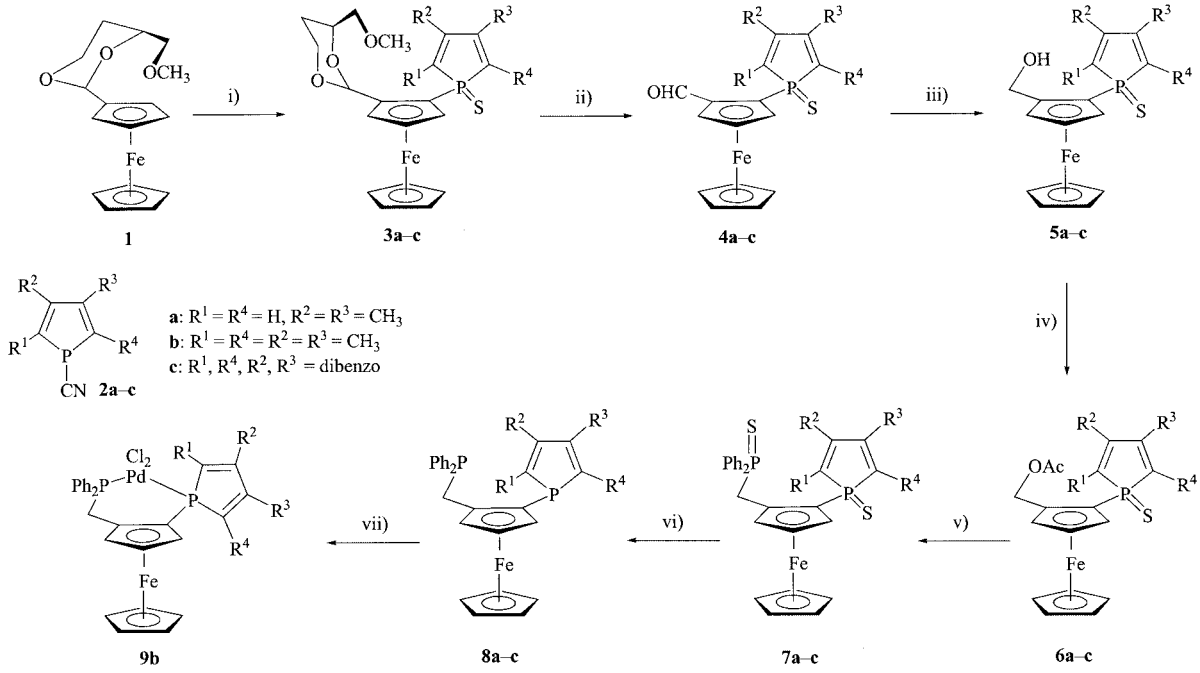
Results and Discussion

The synthetic approach of 1,2-disubtituted ferrocene-based phosphane by nucleophilic displacement of a leaving group (Scheme 1), as described by Hayashi et al.[20] or Togni et al.,[21] could be used to prepare the target molecules. This strategy required the introduction of the planar chirality in the first step by a stereoselective *ortho* metallation step, which required a chiral auxiliary to achieve stereochemically controlled addition of the phospholyl group on the ferrocene moiety. The stereoselective *ortho* metallations reported to date include cyclopalladation of [(dimethylamino)methyl]ferrocene, ortholithiation of ferrocenyl sulfoxides, dioxanes, amines, oxazolines, hydrazones or oxazaphospholidine oxides and so forth.[2c,22,23]



Scheme 1. Retrosynthetic synthesis of ferrocene-bridged phosphole–phosphane ligands.

To control planar chirality, we chose Kagan's method[24] starting from a chiral dioxane. So, the synthetic pathway used is based on six stereochemically controlled reactions, as shown in Scheme 2. In the first step, diastereoselective *ortho* lithiation of acetal **1** was achieved with *t*BuLi. The lithio intermediate reacted cleanly with various 1-cyanophospholes (**2a**,[25] **2b**[14k] and **2c**) as electrophilic reagents to afford the corresponding ferrocenylphosphole products. To facilitate the purification and the characterisation of these compounds, they were converted in situ into air-stable sulfur derivatives **3a–c** by using an excess of sulfur in dichloromethane at room temperature. Compounds **3a**, **3b** and **3c**, isolated after column-chromatographic purification, were obtained in each case as an enantiomerically pure diastereoisomer as confirmed by ^{1}H, ^{31}P and ^{13}C NMR analysis and X-ray diffraction studies. The (*S*) configuration for the planar chirality, which is expected from the literature,[24] was confirmed by X-ray analysis on monocrystals in the case of **3b**. A molecular view of compounds (*S*)-**3b** is shown in Figure 3 with the atom-labelling scheme. As expected, the phosphole ring is planar, with the largest deviation [0.028(2) Å] at C11. The phosphorus atom P1 deviates slightly by 0.132(5) Å from the plane of the Cp ring to



Scheme 2. Synthesis of **8**: (i) *t*BuLi, –78 °C to room temperature; 1-cyanophosphole **2**, –30 °C; S_8, CH_2Cl_2, room temperature; (ii) H^+, H_2O/CH_2Cl_2, reflux; (iii) $NaBH_4$, room temperature; (iv) AcCl/NEt_3, 0 °C to room temperature; CH_2Cl_2; (v) R_2PH, toluene, reflux, S_8, CH_2Cl_2, room temperature; (vi) $P(NMe_2)_3$, toluene reflux; (vii) $PdCl_2(CH_3CN)_2$, CH_2Cl_2, room temperature.

which it is attached, whereas the atom S1 is *endo* with respect to this Cp ring. The phosphole and the Cp rings are roughly perpendicular, with a dihedral angle of 83.1(1)°. The dioxane ring is distorted and the puckering parameters[26] show that its conformation is close to that of a chair: the θ and φ angles calculated for the atom sequence C21–O22–C23–C24–C25–O26 are 177.2(3)° and 147(6)°, respectively. Owing to steric hindrance, the dioxane ring is twisted by 53.3(1)° with respect to the Cp ring. The two Cp rings are nearly eclipsed, with a twisted angle of only 2.9°.

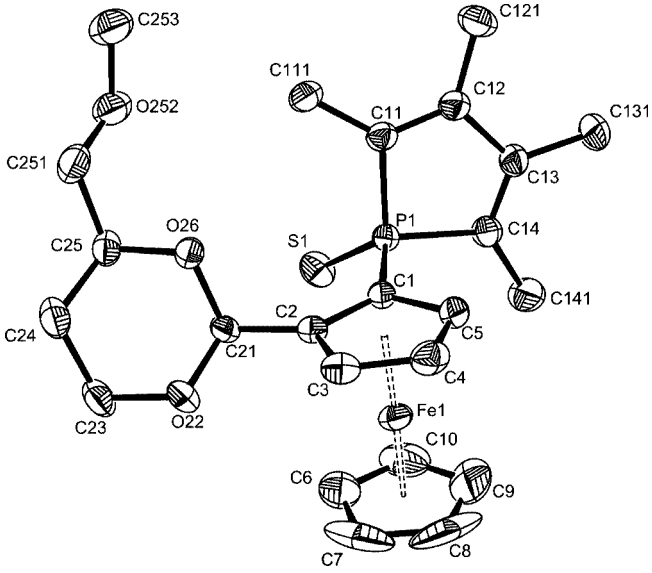


Figure 3. Molecular view of **3b** with atom-labelling scheme. Ellipsoids represent 50% probability. Selected bond lengths [Å] and bond angles [°]: P(1)–S(1) 1.9487(11), P(1)–C(1) 1.790(3), P(1)–C(11) 1.796(3), P(1)–C(14) 1.809(3), C(2)–C(21) 1.504(4), Fe(1)–Cg(1) 1.645(9), Fe(1)–Cg(2) 1.660(9); Cg(1)–Fe(1)–Cg(2) 178.2(6). Cg(1) and Cg(2) are the centroids of the (C1,C2,C3,C4,C5) Cp ring and the (C6,C7,C8,C9,C10) Cp ring, respectively.

In the next step, the acid hydrolysis of the acetal (*S*)-**3a**–**c** was performed with *p*-toluenesulfonic acid to quantitatively yield the corresponding aldehydes (*S*)-**4a**–**c**. Reduction of the crude aldehydes (*S*)-**4a**–**c** of low stabilities was then readily achieved by using an excess of sodium tetrahydroborate. The corresponding alcohols (*S*)-**5a**–**c** were obtained in good yields after column-chromatographic purification. The (*S*) configuration of compound **5b** was again confirmed by X-ray diffraction analysis. A molecular view of alcohol (*S*)-**5b** is shown in Figure 4 with the atom-labelling scheme. As previously noticed, the phosphole ring is planar, with the largest deviation [–0.022(1) Å] at C14 and a dihedral angle of 89.93(7)° with the Cp ring to which it is attached. The atom P1 deviates from the plane of the Cp ring by 0.223(3) Å, certainly minimising steric hindrance, whereas the atom S1 is slightly *endo* by 0.341(4) Å with respect to this Cp ring. The two Cp rings are twisted relative to each other by 10.7°. An interesting feature is the occurrence of an O–H···S intermolecular hydrogen bond [O–H = 0.84 Å, H···S = 2.53 Å, O···S = 3.2700(15) Å, O–H···S = 147.3°] linking the molecules to form a chain developing parallel to the *a*-axis.

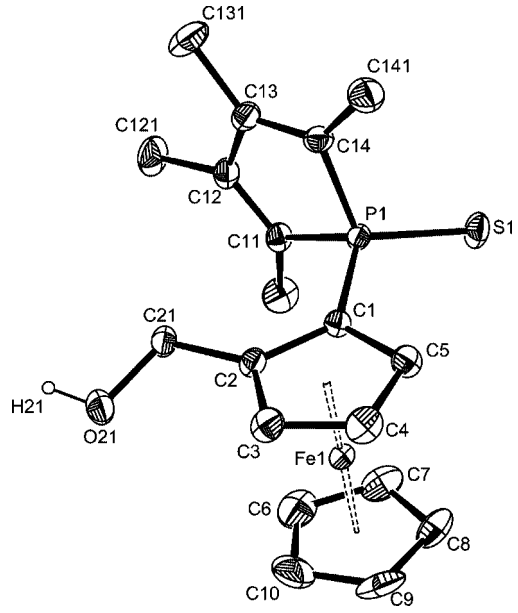


Figure 4. Molecular view of **5b** with atom-labelling scheme. Ellipsoids represent 30% probability. Selected bond lengths [Å] and bond angles [°]: P(1)–S(1) 1.9677(6), P(1)–C(1) 1.790(2), P(1)–C(11) 1.797(2), P(1)–C(14) 1.799(2), C(2)–C(21) 1.505(3), C(21)–O(21) 1.423(2), Fe(1)–Cg(1) 1.636(8), Fe(1)–Cg(2) 1.646(8), Cg(1)–Fe(1)–Cg(2) 176.6(3). Cg(1) and Cg(2) are the centroids of the (C1,C2,C3,C4,C5) Cp ring and the (C6,C7,C8,C9,C10) Cp ring, respectively.

Alcohols (*S*)-**5a**–**c** were quantitatively transformed into acetates (*S*)-**6a**–**c** by treatment with acetyl chloride. Subsequent nucleophilic substitution reactions with secondary phosphanes followed by sulfuration reaction led to ferrocene-bridged phosphole–phosphanes as disulfide derivatives **7a**–**c**. Compounds (*S*)-**7a**, (*S*)-**7b** and (*S*)-**7c**, obtained in 57%, 74% and 78% yield, respectively, were fully characterised.

In the last step, deprotection was successfully achieved with tris(dimethylamino)phosphane in refluxing toluene providing the ferrocene-bridged phosphole–phosphanes (*S*)-**8b** and (*S*)-**8c**. However, this procedure gave only low yields of (*S*)-**8a**, which could not be isolated in a pure form and was only identified by mass spectrometry. The structure of (*S*)-**8b** was determined by X-ray diffraction analysis. A molecular view of complex (*S*)-**8b** is shown in Figure 5. As already observed in free phosphole ligands,[27] the phosphorus atom is located above the butadiene fragment [0.208 (5) Å]. The atom P1 deviates from the plane of the Cp ring by 0.189(5) Å. The atom P2 is oriented *exo* with respect to the Cp ring and is located 1.518(6) Å above it. The two Cp rings are perfectly eclipsed with a twist angle of only 0.5°. The two phenyl rings are roughly perpendicular with a dihedral angle of 87.1(1)°. It is interesting to note that the lone pairs of the two phosphorus atoms are in the correct arrangement for chelating on a metal precursor.

The mode of complexation of new ligands **8** was checked by forming palladium(II) complexes. Ligand **8b** reacted in dichloromethane at room temperature with

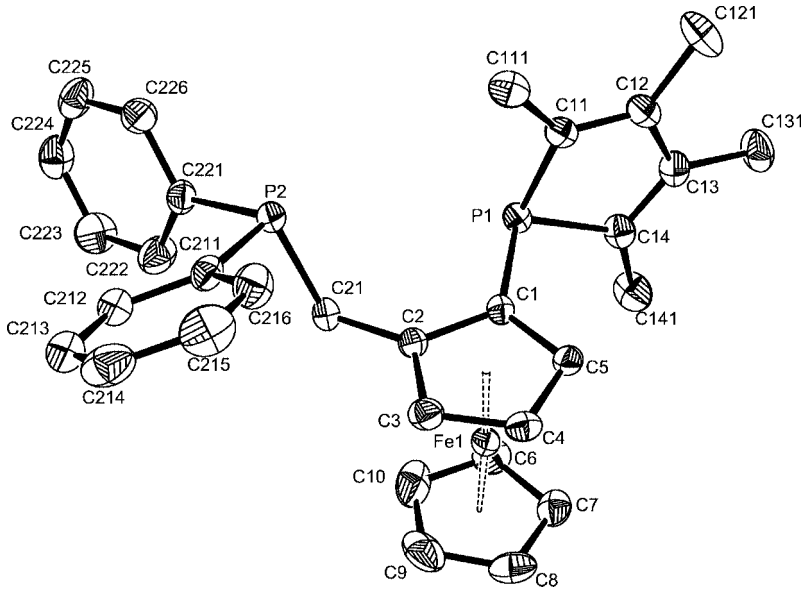


Figure 5. Molecular view of **8b** with atom-labelling scheme. Ellipsoids represent 30% probability. Selected bond lengths [Å] and bond angles [°]: P(1)–C(1) 1.809(3), P(1)–C(11) 1.800(3), P(1)–C(14) 1.807(3), C(2)–C(21) 1.515(5), C(21)–P(2) 1.842(3), P(2)–C(211) 1.835(4), P(2)–C(221) 1.842(3), Fe(1)–Cg(1) 1.6391(4), Fe(1)–Cg(2) 1.6587(4), Cg(1)–Fe(1)–Cg(2) 176.03(3). Cg(1) and Cg(2) are the centroids of the (C1,C2,C3,C4,C5) Cp ring and the (C6,C7,C8,C9,C10) Cp ring, respectively.

$[PdCl_2(CH_3CN)_2]$ in 30 min to afford complex (*S*)-**9b** (80% yield) of formula $[PdCl_2$(**8b**)] as indicated by ^1H, ^{13}C and ^{31}P NMR spectroscopy and mass spectrometry. The molecular structure of complex (*S*)-**9b** was established by X-ray diffraction study. There are two molecules in the asymmetric unit with nearly identical geometry. A view of molecule A is depicted in Figure 6. If the phosphole and the Cp form a dihedral angle of 86.3(4)° [88.5(4) for molecule B], a value close to that observed in the free ligand, the atom P2 of the diphenylphosphanyl group is now oriented *endo* with respect to the Cp ring to accommodate the $PdCl_2$ unit. The geometry of the chelating group is closely related to the recently reported structure of {1-(diphenylphosphanyl)-2,1′-[(1-diphenylphosphanyl)butane-1,3-diyl]ferrocene}-$PdCl_2$.[28] As expected, the Pd^{II} atom is square-planar coordinated, with the largest deviation from the least-squares plane being 0.016(2) Å [0.010(2) Å for molecule B] at the Pd atom. The chelating six-membered ring Pd1–P1–C1–C2–C21–P2 is folded around the P1···C21 axis with a dihedral angle of 30.0(4)° [32.8(3)° for molecule B]. The coordination results in a larger twist angle between the two Cp rings of 10.8° (12.2° for molecule B).

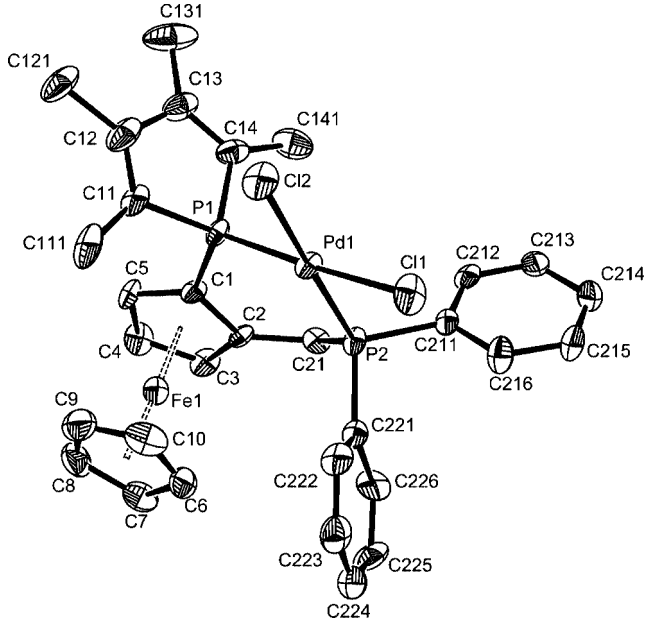
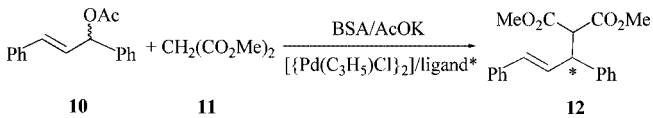


Figure 6. Molecular view of **9b** with atom labelling. Ellipsoids represent 30% probability. Selected bond lengths [Å] and bond angles [°]: Pd–Cl(1) 2.347(3) [2.348(3)], Pd–Cl(2) 2.360(3) [2.363(3)], Pd–P(1) 2.237(3) [2.245(3)], Pd–P(2) 2.261(3) [2.262(3)], P(1)–C(1) 1.791(10) [1.788(10)], C(2)–C(21) 1.487(15) [1.510(15)], P(2)–C(21) 1.828(10) [1.823(11)], Fe(1)–Cg(1) 1.656(3) [1.665(3)], Fe(1)–Cg(2) 1.669(3) [1.666(3)]; Cg(1)–Fe(1)–Cg(2) 174.8(4). Cg(1) and Cg(2) are the centroids of the (C1,C2,C3,C4,C5) Cp ring and the (C6,C7,C8,C9,C10) Cp ring, respectively. The values in square brackets refer to molecule B.

The chiral ligands (*S*)-**8b** and (*S*)-**8c** were evaluated in the palladium-catalysed asymmetric allylic substitution.[29] The reaction of 1,3-diphenylprop-2-enyl acetate (**10**) with the anion of dimethyl malonate (**11**) was carried out in the presence of $[Pd(C_3H_5)Cl]_2$ (1 mol-%) and the chiral ligands **8b**,**c** (1 mol-%) (see Scheme 3). Using the ligand (*S*)-**8b**, the allylic acetate **10** in CH_2Cl_2 was quantitatively converted within 1 h at room temperature to the desired product (*S*)-**12** in 38% *ee*. Under similar conditions, the ligand (*S*)-**8c**



Scheme 3. Asymmetric allylic substitution reaction.

led also to the quantitative conversion of **10** within 1 h to (*S*)-**12**, but with a better enantioselectivity (61% *ee*).

Conclusions

A new and convenient preparation of ferrocene-bridged phosphole–phosphane ligands in an enantiomerically pure form has been achieved. Their coordination chemistry and their abilities for catalysis in a palladium-catalysed asymmetric allylic substitution reaction have been checked. Use of these new unusual chiral P,P ligands in other asymmetric catalytic reactions as well as optimisation of ligands by modifying the phosphole ring part or the phosphane part are currently being developed in our laboratories.

Experimental Section

General: All reactions were carried out under dry argon by using Schlenk glassware and vacuum-line techniques. Solvents were freshly distilled from standard drying agents. ^{1}H, $^{13}C\{^{1}H, ^{31}P\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded with a Bruker WMX 400 instrument operating at 400, 162 and 100 MHz respectively. Chemical shifts are reported in ppm relative to Me_4Si (^{1}H and ^{13}C) or 85% H_3PO_4 (^{31}P). Mass spectra were obtained with a Nermag R10-10 instrument (DCI, FAB) and with an Applied Biosystem API 365 instrument (APCI). Elemental analysis was performed by the "Service d'Analyse du Laboratoire de Chimie de Coordination" at Toulouse. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. Acetal **1**,[24b] 1-cyano-2,3,4,5-tetramethylphosphole (**2b**),[14k] 1-phenyldibenzophosphole[30] and compounds **3a**, **4a**, **5a** and **6a**[12] were prepared as described in the literature.

1-Cyanodibenzophosphole (2c): A solution of 1-phenyldibenzophosphole (2 g, 7.7 mmol) in THF (15 mL) was added at room temperature to a suspension of lithium (0.16 g, 23 mmol) in THF (5 mL). The reaction mixture was stirred at room temperature for 4 h. The red suspension was filtered (to remove unreacted lithium) into another Schlenk tube, cooled to –20 °C, and anhydrous $AlCl_3$ (0.35 g, 2.6 mmol) was added. The reaction mixture was warmed to 0 °C, stirred for 0.5 h and then transferred by cannula to a solution of BrCN (1.63 g, 15.4 mmol) in THF (5 mL) cooled to –78 °C. The mixture was stirred at –78 °C for 0.5 h, then warmed to room temperature and stirred overnight. The mixture was concentrated to dryness and the resulting residue was extracted with small portions of diethyl ether. The combined diethyl ether extracts were filtered through Celite and the solvents were evaporated to give crude compound **2c** as a white solid (0.93 g, 58%). This was used without purification. ^{1}H NMR ($CDCl_3$): δ = 7.47 (m, 2 H, Ar), 7.59 (m, 2 H, Ar), 7.90 (m, 4 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = –51.6 ppm.

General Procedure for Synthesis of Dioxanes 3: In a Schlenk tube, a 1.5 M solution of *tert*-butyllithium in pentane (8.1 mL, 12.1 mmol, 1.1 equiv.) was added dropwise, at –78 °C under argon, to a solution of acetal **1** (3.47 g, 11 mmol) in dry diethyl ether (40 mL). The solution was stirred at –78 °C for 15 min, then at room temperature for 2 h. The solution was cooled to –30 °C and a solution of 1-cyanophosphole **2** (1.2 equiv.) in dry diethyl ether (20 mL) was introduced by cannula. The reaction mixture was stirred at room temperature overnight. Dry triethylamine (0.5 mL) was introduced by syringe, followed by water (2 mL). Under argon, the reaction mixture was extracted with diethyl ether and washed with brine. The organic fraction was dried with sodium sulfate and the solvents were evaporated in vacuo to yield an orange oil. This oil was dissolved in dichloromethane (30 mL). Sulfur (5.7 equiv.) was added and the mixture was stirred overnight. After concentration, the mixture was chromatographed on silica gel using a pentane/dichloromethane mixture (3:7, v/v).

(2*S*,4*S*,S_{Fc})-2-[(2,3,4,5-Tetramethyl-1-thioxo-1*H*-1λ^5-phosphol-1-yl)-ferrocenyl]-4-(methoxymethyl)-1,3-dioxane (3b): Yellow-orange oil (yield 68%). Crystals suitable for X-ray analysis were obtained by diffusion of pentane into a dichloromethane solution. ^{1}H NMR ($CDCl_3$): δ = 1.51 (br. d, J = 13.3 Hz, 1 H, CH_2CH_2CH), 1.83 (m, 1 H, CH_2CH_2CH), 1.85 (br. s, 3 H, CH_3), 1.94 (br. s, 3 H, CH_3), 2.01 (d, $J_{H,P}$ = 13.3 Hz, 3 H, CH_3), 2.13 (d, $J_{H,P}$ = 12.8 Hz, 3 H, CH_3), 3.32 (s, 3 H, OCH_3), 3.35 (dd, ABX system, J = 10.1 and 5.1 Hz, 1 H, CH_2OCH_3), 3.44 (dd, ABX system, J = 10.1 and 5.2 Hz, 1 H, CH_2OCH_3), 3.95–4.10 (m, 2 H, CH, OCH_2CH_2), 4.02 (m, 1 H, subst. Cp), 4.25–4.30 (m, 1 H, OCH_2CH_2), 4.27 (m, 1 H, subst. Cp), 4.39 (s, 5 H, Cp), 4.76 (m, 1 H, subst. Cp), 6.15 (s, 1 H, OCHO) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.5 (d, $J_{C,P}$ = 13.8 Hz, CH_3 α phosphole), 11.3 (d, $J_{C,P}$ = 13.1 Hz, CH_3 α phosphole), 14.0 (d, $J_{C,P}$ = 15.3 Hz, CH_3 β phosphole), 14.2 (d, $J_{C,P}$ = 15.3 Hz, CH_3 β phosphole), 28.5 (CH_2CH_2CH), 59.6 (OCH_3), 67.5 (OCH_2CH_2), 69.9 (d, $J_{C,P}$ = 10.2 Hz, subst. Cp), 71.2 (d, $J_{C,P}$ = 8.1 Hz, subst. Cp), 71.4 (Cp), 71.5 (d, $J_{C,P}$ = 79.0 Hz, quat. Cp), 71.9 (d, $J_{C,P}$ = 10.5 Hz, subst. Cp), 75.7 (CH_2OCH_3), 76.0 (CH), 89.1 (d, $J_{C,P}$ = 10.5 Hz, quat. Cp), 98.8 (OCHO), 128.4 (d, $J_{C,P}$ = 84.0 Hz, CH_3 α phosphole), 132.3 (d, $J_{C,P}$ = 82.7 Hz, CCH_3 α phosphole), 143.2 (d, $J_{C,P}$ = 27.1 Hz, CCH_3 β phosphole), 145.8 (d, $J_{C,P}$ = 27.2 Hz, CCH_3 β phosphole) ppm. ^{31}P NMR ($CDCl_3$): δ = 57.0 ppm. $[\alpha]_D$ = 3.4 (c = 0.5, $CHCl_3$). MS (DCI, NH_3): m/z (%) = 487 (100) [M + 1]. $C_{24}H_{32}FeO_3PS$ (487.40): calcd. C 59.14, H 6.62; found 59.27, H 6.42.

(2*S*,4*S*,S_{Fc})-2-[(Dibenzo-1-thioxo-1*H*-1λ^5-phosphol-1-yl)ferrocenyl]-4-(methoxymethyl)-1,3-dioxane (3c): Yellow solid (yield 64%). M.p. 78 °C. ^{1}H NMR ($CDCl_3$): δ= 1.48 (d of m, J = 13 Hz, 1 H, CH_2CH_2CH), 1.81 (br. q of d, J = 13 and 5 Hz, 1 H, CH_2CH_2CH), 3.42 (dd, AB system, J = 10.3 and 3.9 Hz, 1 H, CH_2OCH_3), 3.43 (s, 3 H, OCH_3), 3.56 (dd, AB system, J = 10.3 and 6.3 Hz, 1 H, CH_2OCH_3), 3.59 (m, 1 H, subst. Cp), 4.00 (td, J = 11.9 and 2.5 Hz, 1 H, OCH_2CH_2), 4.15 (m, 1 H, subst. Cp), 4.19 (m, 1 H, CH), 4.3–4.25 (m, 1 H, OCH_2CH_2), 4.50 (s, 5 H, Cp), 4.80 (m, 1 H, subst. Cp), 6.40 (s, 1 H, OCHO), 7.35 (tdd, J = 7.5 and 1.0 Hz, $J_{H,P}$ = 3.8 Hz, 1 H, Ar), 7.44 (tt, J = 7.5 Hz, J = $J_{H,P}$ = 1.2 Hz, 1 H, Ar), 7.51 (tdd, J = 7.4 and 1.1 Hz, $J_{H,P}$ = 3.7 Hz, 1 H, Ar), 7.57 (tt, J = 7.5 Hz, J = $J_{H,P}$ = 1.3 Hz, 1 H, Ar), 7.69 (dd, J = 7.6 Hz, $J_{H,P}$ = 3.1 Hz, 1 H, Ar), 7.78 (dd, J = 7.6 Hz, $J_{H,P}$ = 3.0 Hz, 1 H, Ar), 7.99 (ddd, J = 7.4 and 1 Hz, $J_{H,P}$ = 10.3 Hz, 1 H, Ar), δ = 8.27 (ddd, J = 7.5 and 1 Hz, $J_{H,P}$ = 9.7 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ= 28.3 (CH_2CH_2CH), 59.6 (OCH_3), 67.4 (OCH_2CH_2), 69.9 (d, $J_{C,P}$ = 10.9 Hz, subst. Cp), 71.4 (Cp), 71.7 (d, $J_{C,P}$ = 9.0 Hz, subst. Cp), 73.0 (d, $J_{C,P}$ = 14.1 Hz, subst. Cp), 74.0 (d, $J_{C,P}$ = 90.0 Hz, quat. Cp), 75.8 (CH), 76.0 (CH_2OCH_3), 89.4 (d, $J_{C,P}$ = 12.1 Hz, quat. Cp), 98.6 (OCHO), 121.3 (d, $J_{C,P}$ = 9.5 Hz, Ar), 121.8 (d, $J_{C,P}$ = 9.5 Hz, Ar), 129.5 (d, $J_{C,P}$ = 11.5 Hz, Ar), 130.0 (d, $J_{C,P}$ = 12.1 Hz, Ar), 130.1 (d, $J_{C,P}$ = 10.4 Hz, Ar), 130.9 (d, $J_{C,P}$ = 11.3 Hz, Ar), 132.5 (d, $J_{C,P}$ = 2.3 Hz, Ar), 133.1 (d, $J_{C,P}$ = 2.3 Hz, Ar), 135.7 (d, $J_{C,P}$ = 93.3 Hz, quat. Ar), 138.1 (d, $J_{C,P}$ = 91.6 Hz, quat. Ar), 139.6 (d, $J_{C,P}$ = 19.7 Hz, quat. Ar), 141.7 (d, $J_{C,P}$ = 19.7 Hz, quat. Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = 42.9 ppm. $[\alpha]_D$ = –24 (c = 0.5, $CHCl_3$). MS (DCI, NH_3): m/z (%) = 531 (100) [M + 1]. $C_{28}H_{28}FeO_3PS$ (531.42): calcd. C 63.41, H 5.13; found C 63.43, H 5.07.

General Procedure for the Synthesis of Ferrocenecarbaldehyde 4: Acetal **3** (7.3 mmol), dichloromethane (120 mL) and an aqueous

solution (50 mL) of *p*-toluenesulfonic acid monohydrate (1.5 equiv. for **3b** or 2 equiv. for **3c**) were introduced into a round-bottomed flask equipped with a condenser and placed under argon. The reaction mixture was stirred at reflux for 26 h (**3b**) or 54 h (**3c**). After cooling to room temperature, the dark red solution was extracted with dichloromethane, washed with distilled water, dried with sodium sulfate and the solvents were evaporated. Compounds **4**, obtained quantitatively as red oils, were only characterised by ^{31}P and ^{1}H NMR spectroscopy and used without purification.

(S_{Fc})-2-(2,3,4,5-Tetramethyl-1-thioxo-1*H*-1λ^5-phosphol-1-yl)ferrocenecarbaldehyde (4b): ^{1}H NMR ($CDCl_3$): δ = 1.89 (br. s, 3 H, CH_3), 1.95 (br. s, 3 H, CH_3), 1.98 (d, $J_{H,P}$ = 13.7 Hz, 3 H, CH_3), 2.07 (d, $J_{H,P}$ = 13.7 Hz, 3 H, CH_3), 4.52 (s, 5 H, Cp), 4.61 (m, 1 H, subst. Cp), 4.72 (m, 1 H, subst. Cp), 5.16 (m, 1 H, subst. Cp), 10.58 (s, 1 H, CHO) ppm. ^{31}P NMR ($CDCl_3$): δ = 55.8 ppm.

(S_{Fc})-2-(Dibenzo-1-thioxo-1*H*-1λ^5-phosphol-1-yl)ferrocenecarbaldehyde (4c): ^{1}H NMR ($CDCl_3$): δ = 3.38 (m, 1 H, subst. Cp), 4.25 (m, 1 H, subst. Cp), 4.43 (s, 5 H, Cp), 5.56 (m, 1 H, subst. Cp), 7.48–7.88 (m, 8 H, Ar), 10.57 (s, 1 H, CHO) ppm. ^{31}P NMR ($CDCl_3$): δ = 38.6 ppm.

General Procedure for Synthesis of Alcohols 5: Crude compound **4** (7.3 mmol) was dissolved in methanol (200 mL) and an aqueous solution (140 mL) of sodium borohydride (2.78 g, 18.3 mmol) and sodium hydroxide (11.2 g, 280 mmol) was added. The solution turned rapidly from red to orange. After 15 min of stirring at room temperature, the reaction mixture was extracted with dichloromethane. The organic phase was washed with diluted hydrochloric acid, then water, and finally dried with sodium sulfate. After evaporation of the solvents, the crude material was purified by flash chromatography on silica gel using a pentane/diethyl ether mixture (2:8, v/v).

(S_{Fc})-[2-(2,3,4,5-Tetramethyl-1-thioxo-1*H*-1λ^5-phosphol-1-yl)ferrocenyl]methanol (5b): Yellow-orange oil (yield 51% from **3b**). Crystals suitable for X-ray analysis were obtained by diffusion of pentane into a dichloromethane solution. M.p. 85 °C. ^{1}H NMR ($CDCl_3$): δ = 1.86 (br. s, 3 H, CH_3 β), 1.93 (br. d, $J_{H,P}$ = 12.1 Hz, 3 H, CH_3 α), 1.96 (br. s, 3 H, CH_3 β), 2.15 (br. d, $J_{H,P}$ = 13.0 Hz, 3 H, CH_3 α), 3.39 (dd, J = 7.8 and 5.9 Hz, 1 H, OH), 4.03 (m, 1 H, subst. Cp), 4.24 (m, 1 H, subst. Cp), 4.38 (s, 5 H, Cp), 4.47 (dd, ABX system, J = 12.6 and 5.5 Hz, 1 H, CH_2), 4.49 (m, 1 H, subst. Cp), 4.59 (dd, ABX system, J = 12.8 and 7.8 Hz, 1 H, CH_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.6 (d, $J_{C,P}$ = 13.6 Hz, CH_3 α), 11.3 (d, $J_{C,P}$ = 13.3 Hz, CH_3 α), 14.0 (d, $J_{C,P}$ = 15.1 Hz, CH_3 β), 14.3 (d, $J_{C,P}$ = 15.3 Hz, CH_3 β), 59.4 (s, CH_2), 69.3 (d, $J_{C,P}$ = 10.2 Hz, subst. Cp), 70.7 (s, Cp), 71.8 (d, $J_{C,P}$ = 14.1 Hz, subst. Cp), 72.0 (d, $J_{C,P}$ = 80.2 Hz, quat. Cp), 74.4 (d, $J_{C,P}$ = 9.0 Hz, subst. Cp), 92.5 (d, J_{CP} = 11.5 Hz, quat. Cp), 128.7 (d, $J_{C,P}$ = 84.2 Hz, CCH_3 α), 131.5 (d, $J_{C,P}$ = 82.8 Hz, CCH_3 α), 143.8 (d, $J_{C,P}$ = 26.9 Hz, CCH_3 β), 146.4 (d, $J_{C,P}$ = 27.1 Hz, CCH_3 β) ppm. ^{31}P NMR ($CDCl_3$): δ = 58.1 ppm. $[\alpha]_D$ = –125 ($CHCl_3$, c = 0.5). MS (DCI, NH_3): m/z (%) = 387 (100) [M + 1]. $C_{19}H_{23}FeOPS$ (386.28): calcd. C 59.07, H 6.00; found C 59.24, H 6.10.

(S_{Fc})-[(Dibenzo-1-thioxo-1*H*-1λ^5-phosphol-1-yl)ferrocenyl]methanol (5c): Yellow solid (yield 56% from **3c**). M.p. 200 °C (decomposition). ^{1}H NMR ($CDCl_3$): δ = 3.58 (br. t, $J \approx 6$ Hz, 1 H, OH), 3.72 (m, 1 H, subst. Cp), 4.18 (m, 1 H, subst. Cp), 4.24 (s, 5 H, Cp), 4.56–4.5 (m, 2 H, subst. Cp, CH_2), 5.00 (dd, J = 12.6 and 5.7 Hz, 1 H, CH_2), 7.44 (tdd, J = 7.5 and 0.9 Hz, $J_{H,P}$ = 3.8 Hz, 1 H, Ar), 7.62–7.55 (m, 2 H, Ar), 7.66 (m, 1 H, Ar), 7.82 (dd, J = 7.7 Hz, $J_{H,P}$ = 3.1 Hz, 1 H, Ar), 7.88 (dd, J = 7.6 Hz, $J_{H,P}$ = 3.1 Hz, 1 H, Ar), 7.94 (dd, J = 7.4 Hz, $J_{H,P}$ = 10.5 Hz, 1 H, Ar), 8.11 (dd, J = 7.3 Hz, $J_{H,P}$ = 10.6 Hz, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 59.9 (s, CH_2), 69.5 (d, $J_{C,P}$ = 10.9 Hz, subst. Cp), 70.7 (s, Cp), 73.3 (d, $J_{C,P}$ = 14.4 Hz, subst. Cp), 74.6 (d, $J_{C,P}$ = 9.8 Hz, subst. Cp), 75.1 (d, $J_{C,P}$ = 90.4 Hz, quat. Cp), 92.0 (d, $J_{C,P}$ = 13.3 Hz, quat. Cp), 121.7 (d, $J_{C,P}$ = 9.5 Hz, Ar), 121.9 (d, $J_{C,P}$ = 9.7 Hz, Ar), 129.7 (d, $J_{C,P}$ = 11.7 Hz, Ar), 129.9 (d, $J_{C,P}$ = 10.7 Hz, Ar), 130.08 (d, $J_{C,P}$ = 11.8 Hz, Ar), 130.12 (d, $J_{C,P}$ = 10.6 Hz, Ar), 133.0 (d, $J_{C,P}$ = 2.3 Hz, Ar), 133.3 (d, $J_{C,P}$ = 2.3 Hz, Ar), 136.1 (d, $J_{C,P}$ = 93.8 Hz, quat. Ar), 136.8 (d, $J_{C,P}$ = 91.5 Hz, quat. Ar), 140.2 (d, $J_{C,P}$ = 19.5 Hz, quat. Ar), 141.5 (d, $J_{C,P}$ = 19.5 Hz, quat. Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = 44.6 ppm. $[\alpha]_D$ = –104.6 ($CHCl_3$, c = 0.5). MS (DCI, NH_3): m/z (%) = 413 (100) $[M - OH]^+$, 430 (15) $[M]^+$. $C_{23}H_{19}FeOPS$ (430.29): calcd. C 64.20, H 4.45; found C 64.11, H 4.64.

General Procedure for Synthesis of Acetates 6: Alcohol **5** (0.7 mmol) was dissolved in dry dichloromethane (7 mL) and anhydrous triethylamine (0.25 mL) in a Schlenk tube under argon. The solution was then cooled to 0 °C and acetyl chloride (1.5 equiv.) was added with a syringe. The solution was stirred at 0 °C for 30 min, then at room temperature for 1 h. The solution was washed with diluted hydrochloric acid then water and dried with sodium sulfate. After evaporation of the solvents, crude compound **6** was quantitatively obtained as an oil that was used without further purification in the next step.

(S_{Fc})-(Acetoxy)[2-(2,3,4,5-tetramethyl-1-thioxo-1*H*-1λ^5-phosphol-1-yl)ferrocenyl]methane (6b): Yellow-orange. ^{1}H NMR ($CDCl_3$): δ = 1.89 (d, J = 10 Hz, 6 H, CH_3), 1.99 [s, 3 H, $C(O)CH_3$], 2.04 (d, J = 13 Hz, 6 H, CH_3), 4.26 (m, 1 H, subst. Cp), 4.33 (m, 1 H, subst. Cp), 4.40 (m, 5 H, Cp), 4.53 (m, 1 H, subst. Cp), 5.14 (d, J = 11.9 Hz, 1 H, CH_2), 5.33 (d, J = 11.9 Hz, 1 H, CH_2) ppm. ^{31}P NMR ($CDCl_3$): δ = 53.9 ppm.

(S_{Fc})-(Acetoxy)[2-(dibenzo-1-thioxo-1*H*-1λ^5-phosphol-1-yl)ferrocenyl]methane (6c): Orange-red oil. ^{1}H NMR ($CDCl_3$): δ = 1.98 [s, 3 H, $C(O)CH_3$], 4.02 (m, 1 H, subst. Cp), 4.26 (m, 1 H, subst. Cp), 4.48 (s, 5 H, Cp), 4.51 (m, 1 H, subst. Cp), 5.11 (d, J = 12.1 Hz, 1 H, CH_2), 5.27 (d, J = 12.1 Hz, 1 H, CH_2), 7.3–8.1 (m, 8 H, Ar) ppm. ^{31}P NMR ($CDCl_3$): δ = 39.8 ppm.

General Procedure for Synthesis of Compounds 7: Diphenylphosphane (2.5 equiv.) was added at room temperature to a solution of crude **6** (0.7 mmol) in degassed toluene (10 mL). The reaction mixture was stirred under reflux for 24 h (**7a**, **7b**) or 36 h (**7c**) and then concentrated in vacuo to yield an orange oil. This oil was dissolved in dichloromethane (10 mL). Sulfur (5 equiv.) was added and the mixture was stirred overnight. After concentration, the mixture was chromatographed on silica gel using a pentane/diethyl ether mixture (80:20).

(S_{Fc})-[2-(3,4-Dimethyl-1-thioxo-1*H*-1λ^5-phosphol-1-yl)ferrocenyl]-(diphenylthioxophosphanyl)methane (7a): Yellow solid (yield 57% from **5a**). ^{1}H NMR ($CDCl_3$): δ = 1.95 (br. t, J = 3 Hz, 3 H, CH_3), 2.09 (br. t, J = 3 Hz, 3 H, CH_3), 4.11 (td, $J_{H,H}$ = 2.9 Hz, $J_{H,P1}$ = 1.5 Hz, 1 H, subst. Cp), 4.31 (s, 5 H, Cp); 4.12 (t, $J_{H,H}$ = $J_{H,P2}$ = 13.1 Hz, 1 H, CH_2), 4.32–4.30 (m, 1 H, subst. Cp), 4.39 (t, $J_{H,H}$ = $J_{H,P2}$ = 13.1 Hz, 1 H, CH_2), 4.48 (ddd, J = 4.1 and 2.4 Hz, $J_{H,P1}$ = 2.8 Hz, 1 H, subst. Cp), 6.06 (br. d, $J_{H,P}$ = 30.5 Hz, 1 H, CH), 6.24 (br. d, $J_{H,P}$ = 30.6 Hz, 1 H, CH), 7.55–7.25 (m, 6 H, PPh_2), 7.9–7.8 (m, 4 H, PPh_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.9 (d, $J_{C,P1}$ = 17.8 Hz, CH_3 phosphole), 18.0 (d, $J_{C,P1}$ = 17.8 Hz, CH_3 phosphole), 31.5 (d, $J_{C,P2}$ = 5 Hz, CH_2), 69.0 (d, $J_{C,P1}$ = 87.5 Hz, quat. Cp), 70.1 (d, $J_{C,P1}$ = 11.1 Hz, subst. Cp), 71.2 (Cp), 73.7 (d, $J_{C,P1}$ = 14.8 Hz, subst. Cp), 74.8 (d, $J_{C,P1}$ = 8.9 Hz, subst. Cp), 87.2 (dd, $J_{C,P1}$ = 11.4 Hz, J_{C-P2} = 5.8 Hz, quat. Cp), 126.2 (d, $J_{C,P1}$ = 71.7 Hz, CH phosphole), 126.6 (d, $J_{C,P1}$ = 71.7 Hz, CH phosphole), 126.8 (d, $J_{C,P2}$ = 13.4 Hz, PPh_2), 129.1 (d, $J_{C,P2}$ = 13.1 Hz, PPh_2), 131.6 (d, $J_{C,P2}$ = 11.3 Hz, PPh_2), 132.1 (d, $J_{C,P2}$ = 3.3 Hz, PPh_2),

132.2 (d, $J_{C,P2}$ = 11.4 Hz, PPh_2), 132.4 (d, $J_{C,P2}$ = 3.2 Hz, PPh_2), 134.0 (d, $J_{C,P2}$ = 69.3 Hz, quat. PPh_2), 134.8 (d, $J_{C,P2}$ = 71.1 Hz, quat. PPh_2), 152.7 (d, $J_{C,P1}$ = 18.7 Hz, CCH_3 phosphole), 152.9 (d, $J_{C,P1}$ = 18.5 Hz, CCH_3 phosphole) ppm. ^{31}P NMR ($CDCl_3$): δ = 48.1 (P1, phosphole), 66.7 (P2, PPh_2) ppm. MS (DCI, NH_3): *m*/*z* (%) = 559 (100) [M + 1].

(S_{Fc})-(Diphenylthioxophosphanyl)[2-(2,3,4,5-tetramethyl-1-thioxo-1*H*-1λ^5-phosphol-1-yl)ferrocenyl]methane (7b): Yellow oil (yield 74% from **5b**). ^1H NMR ($CDCl_3$): δ = 1.85 (br. s, 3 H, CH_3 β phosphole), 1.91 (br. s, 3 H, CH_3 β phosphole), 1.92 (br. d, 3 H, $J_{H,P1}$ = 12.4 Hz, CH_3 α phosphole), 2.12 (br. d, 3 H, $J_{H,P1}$ = 13.1 Hz, CH_3 α phosphole), 3.95 (t, 1 H, $J_{H,H}$ = $J_{H,P2}$ = 13.3 Hz, CH_2), 4.15 (t, 1 H, $J_{H,H}$ = $J_{H,P2}$ = 13.3 Hz, CH_2), 4.16 (m, 1 H, subst. Cp), 4.27 (m, 1 H, subst. Cp), 4.34 (s, 5 H, Cp), 4.46 (m, 1 H, subst. Cp), 7.55–7.3 (m, 6 H, PPh_2), 7.9–7.5 (m, 4 H, PPh_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 10.4 (d, $J_{C,P1}$ = 13.4 Hz, CH_3 α phosphole), 11.4 (d, $J_{C,P1}$ = 13.6 Hz, CH_3 α phosphole), 14.1 (d, $J_{C,P1}$ = 15.1 Hz, CH_3 β phosphole), 14.5 (d, $J_{C,P1}$ = 15.2 Hz, CH_3 β phosphole), 31.3 (s, CH_2), 70.3 (d, $J_{C,P1}$ = 10.6 Hz, subst. Cp), 71.1 (Cp), 71.5 (d, $J_{C,P1}$ = 79.0 Hz, quat. Cp), 73.3 (d, $J_{C,P1}$ = 13.8 Hz, subst. Cp), 73.9 (d, $J_{C,P1}$ = 7.9 Hz, subst. Cp), 85.9 (dd, $J_{C,P1}$ = 10.6 Hz, $J_{C,P2}$ = 5.6 Hz, quat. Cp), 128.8 (d, $J_{C,P2}$ = 13.3 Hz, PPh_2), 128.9 (d, $J_{C,P1}$ = 82.7 Hz, CH_3 α phosphole), 129.1 (d, $J_{C,P2}$ = 13.3 Hz, PPh_2), 130.2 (d, $J_{C,P1}$ = 82.7 Hz, CH_3 α phosphole), 131.4 (d, $J_{C,P2}$ = 11.1 Hz, PPh_2), 132.2 (d, $J_{C,P2}$ = 11.2 Hz, PPh_2), 132.3 (d, $J_{C,P2}$ = 4.7 Hz, PPh_2), 132.4 (d, $J_{C,P2}$ = 3.1 Hz, PPh_2), 134.1 (d, $J_{C,P2}$ = 71.4 Hz, quat. PPh_2), 134.8 (d, $J_{C,P2}$ = 71.1 Hz, quat. PPh_2), 134.9 (d, $J_{C,P2}$ = 73.5 Hz, quat. PPh_2), 144.5 (d, $J_{C,P1}$ = 26.7 Hz, CCH_3 β phosphole), 147.1 (d, $J_{C,P1}$ = 27.1 Hz, CCH_3 β phosphole) ppm. ^{31}P NMR ($CDCl_3$): δ = 56.7 (P1, phosphole), 66.7 (P2, PPh_2) ppm. MS (APCI): *m*/*z* = 587 [M + 1].

(S_{Fc})-(Diphenylthioxophosphanyl)[2-(dibenzo-1-thioxo-1*H*-1λ^5-phosphol-1-yl)ferrocenyl]methane (7c): Orange solid (yield 77% from **5c**). ^1H NMR ($CDCl_3$): δ = 3.84 (dd, $J_{H,H}$ = 16.0 Hz and $J_{H,P2}$ = 11.8 Hz, 1 H, CH_2), 4.06 (br. s, 1 H, subst. Cp), 4.19 (m, 1 H, subst. Cp), 4.27 (s, 5 H, Cp), 4.40 (dd, $J_{H,H}$ = 16.0 Hz and $J_{H,P2}$ = 10.8 Hz, 1 H, CH_2), 4.81 (br. s, 1 H, subst. Cp), 7.65–7.3 (m, 12 H, Ar), 7.82–7.74 (m, 3 H, Ar), 7.95–7.85 (m, 3 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 33.9 (d, $J_{C,P2}$ = 54.1 Hz, CH_2), 71.1 (d, $J_{C,P1}$ = 11.4 Hz, subst. Cp), 71.7 (Cp), 72.6 (d, J_{C-P1} = 15.0 Hz, subst. Cp), 73.7 (d, J_{C-P1} = 7.8 Hz, $J_{C,P2}$ = 4.4 Hz, subst. Cp), 74.2 (dd, $J_{C,P1}$ = 78.9 Hz, $J_{C,P2}$ = 6.1 Hz, quat. Cp), 82.6 (dd, $J_{C,P1}$ = 12.1 Hz, $J_{C,P2}$ = 1.8 Hz, quat. Cp), 121.7 (d, $J_{C,P1}$ = 9.5 Hz, 2 C, benzophosphole), 129.1 (d, $J_{C,P1}$ = 12.1 Hz, 2 C, PPh_2), 129.9 (d, $J_{C,P1}$ = 12 Hz, benzophosphole), 130.0 (d, $J_{C,P1}$ = 11 Hz, 2 C, benzophosphole), 130.3 (d, $J_{C,P1}$ = 11.0 Hz, benzophosphole), 131.5 (d, $J_{C,P2}$ = 10.1 Hz, PPh_2), 131.8 (d, $J_{C,P2}$ = 2.8 Hz, PPh_2), 132.0 (d, $J_{C,P2}$ = 10.3 Hz, PPh_2), 132.1 (d, $J_{C,P2}$ = 2.7 Hz, PPh_2), 133.0 (d, $J_{C,P1}$ = 2.2 Hz, benzophosphole), 133.1 (d, $J_{C,P2}$ = 79.5 Hz, quat. PPh_2), 133.2 (d, $J_{C,P1}$ = 2.2 Hz, benzophosphole), 133.5 (d, $J_{C,P2}$ = 78.0 Hz, quat. PPh_2), 136.6 (d, $J_{C,P1}$ = 92.7 Hz, quat. benzophosphole), 136.8 (d, $J_{C,P1}$ = 91.3 Hz, quat. benzophosphole), 140.7 (d, $J_{C,P1}$ = 19.6 Hz, quat. benzophosphole), 141.0 (d, $J_{C,P1}$ = 19.4 Hz, quat. benzophosphole) ppm. ^{31}P NMR ($CDCl_3$): δ = 41.7 (P2, PPh_2), 43.4 (P1, phosphole) ppm. MS (DCI, NH_3): *m*/*z* (%) = 631 (80) [M + 1].

General Procedure for Desulfurisation of Compounds 7: Tris(dimethylamino)phosphane (0.2 mL, 1.2 mmol, 4 equiv.) was added at room temperature to a solution of **7** (0.3 mmol) in toluene (10 mL). The reaction mixture was stirred at reflux for 24 h. After concentration, the mixture was chromatographed on alumina using pentane and then a pentane/diethyl ether mixture (90:10).

(S_{Fc})-[2-(3,4-Dimethyl-1*H*-1λ^5-phosphol-1-yl)ferrocenyl](diphenylphosphanyl)methane (8a): MS (DCI, NH_3): *m*/*z* (%) = 495 (100) [M + 1].

(S_{Fc})-(Diphenylphosphanyl)[2-(2,3,4,5-tetramethyl-1*H*-1λ^5-phosphol-1-yl)ferrocenyl]methane (8b): Dark yellow solid (87%). Crystals suitable for X-ray analysis were obtained by diffusion of pentane into a dichloromethane solution. ^1H NMR ($CDCl_3$): δ = 1.89 (br. s, 3 H, CH_3 β phosphole), 1.93 (br. s, 3 H, CH_3 β phosphole), 2.11 (br. d, $J_{H,P1}$ = 10.7 Hz, 3 H, CH_3 α phosphole), 2.22 (br. d, $J_{H,P1}$ = 10.6 Hz, 3 H, CH_3 α phosphole), 3.15 (d, AB system, $J_{H,P2}$ = 14.5 Hz, 1 H, CH_2), 3.23 (dd, ABX system, $J_{H,H}$ = 1.4 Hz, $J_{H,P2}$ = 14.5 Hz, 1 H, CH_2), 3.86 (m, 1 H, subst. Cp), 3.97 (m, 1 H, subst. Cp), 4.12 (t, *J* = 2.5 Hz, 1 H, subst. Cp), 4.24 (s, 5 H, Cp), 7.4–7.3 (m, 8 H, PPh_2), 7.5–7.4 (m, 2 H, PPh_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.0 (d, $J_{C,P1}$ = 21.0 Hz, CH_3 α phosphole), 14.3 (d, $J_{C,P1}$ = 3.0 Hz, CH_3 β phosphole), 14.5 (d, $J_{C,P1}$ = 3.0 Hz, CH_3 β phosphole), 14.6 (d, $J_{C,P1}$ = 21.4 Hz, $J_{C,P2}$ = 3.9 Hz, CH_3 α phosphole), 28.6 (dd, $J_{C,P1}$ = 4.6 Hz, $J_{C,P2}$ = 15.4 Hz, CH_2), 69.0 (d, $J_{C,P1}$ = 5.3 Hz, subst. Cp), 70.2 (Cp), 71.4 (dd, $J_{C,P1}$ = 2.0 Hz, $J_{C,P2}$ = 7.0 Hz, subst. Cp), 72.0 (d, $J_{C,P1}$ = 16.2 Hz, subst. Cp), 73.4 (dd, $J_{C,P}$ = 3.9 Hz, $J_{C,P}$ = 12.8 Hz, CP), 88.7 (dd, $J_{C,P}$ = 9.5 Hz, $J_{C,P}$ = 16.8 Hz, CCH_2), 128.6 (CH_{Ar}), 128.8 (d, $J_{C,P}$ = 5.7 Hz, CH_{Ar}), 128.9 (d, $J_{C,P}$ = 7.0 Hz, CH_{Ar}), 129.3 (CH_{Ar}), 132.5 (d, $J_{C,P}$ = 17.7 Hz, CH_{Ar}), 133.9 (d, $J_{C,P}$ = 20.0 Hz, CH_{Ar}), 134.6 (d, $J_{C,P}$ = 4.7 Hz, $CCH_{3\beta P}$), 135.5 ($CCH_{3\beta P}$), 139.8 (d, $J_{C,P}$ = 16.4 Hz, $C_{Ar}P$), 140.0 (d, $J_{C,P}$ = 16.2 Hz, $C_{Ar}P$), 142.3 (d, $J_{C,P}$ = 12.3 Hz, $CCH_{3\alpha P}$), 142.6 (d, $J_{C,P}$ = 12.5 Hz, $CCH_{3\alpha P}$) ppm. ^{31}P NMR ($CDCl_3$): δ = –12.3 (P2, PPh_2), 1.7 (P1, phosphole) ppm.

(S_{Fc})-(Diphenylphosphanyl)[2-(dibenzo-1*H*-1λ^5-phospholyl)ferrocen-1-yl]methane (8c): Yellow solid (94%). Crystals suitable for X-ray analysis were obtained by diffusion of pentane into a dichloromethane solution. ^1H NMR ($CDCl_3$): δ = 3.38 (br. d, $J_{H,H}$ = 14.2 Hz, 1 H, CH_2), 3.38 (br. s, 1 H, subst. Cp), 3.58 (br. d, $J_{H,H}$ = 14.2 Hz, 1 H, CH_2), 3.76 (br. s, 1 H, subst. Cp), 3.92 (br. s, 1 H, subst. Cp), 4.26 (s, 5 H, Cp), 7.3–7. 55 (m, 14 H, Ar), 7.90 (br. d, $J_{H,H}$ = 7.8 Hz, 1 H, Ar), 7.98 (br. d, $J_{H,H}$ = 7.4 Hz, 1 H, Ar), 8.02 (m, 1 H, Ar), 8.17 (m, 1 H, Ar) ppm. ^{13}C NMR ($CDCl_3$): δ = 29.3 (dd, $J_{C,P2}$ = 15.7 Hz, $J_{C,P1}$ = 8.1 Hz, CH_2), 68.7 (d, $J_{C,P1}$ = 2.0 Hz, subst. Cp), 69.6 (s, subst. Cp), 69.8 (s, Cp), 71.6 (dd, $J_{C,P2}$ = 5.2 Hz, $J_{C,P1}$ = 3.2 Hz, subst. Cp), 76.8 (quat. Cp), 89.3 (dd, $J_{C,P1}$ = 23.0 Hz, $J_{C,P2}$ = 16.2 Hz, quat. Cp), 121.1 (s, benzophosphole), 121.3 (s, benzophosphole), 126.9 (d, $J_{C,P1}$ = 8.3 Hz, benzophosphole), 127.4 (d, $J_{C,P1}$ = 7.4 Hz, benzophosphole), 128.26 (s, PPh_2), 128.30 (s, PPh_2), 128.4 (d, $J_{C,P2}$ = 7.1 Hz, PPh_2), 128.5 (d, $J_{C,P2}$ = 5.7 Hz, PPh_2), 128.6 (s, benzophosphole), 129.0 (s, benzophosphole), 130.9 (dd, $J_{C,P1}$ = 21.0 Hz, $J_{C,P2}$ = 11.8 Hz, benzophosphole), 131.1 (d, $J_{C,P1}$ = 21.0 Hz, benzophosphole), 132.0 (d, $J_{C,P2}$ = 17.3 Hz, PPh_2), 133.9 (d, $J_{C,P2}$ = 19.8 Hz, PPh_2), 138.5 (d, $J_{C,P2}$ = 15.7 Hz, quat. PPh_2), 139.3 (d, $J_{C,P2}$ = 15.3 Hz, quat. PPh_2), 141.8 (s, quat. benzophosphole), 142.6 (d, $J_{C,P1}$ = 3.7 Hz, quat. benzophosphole), 144.4 (d, $J_{C,P1}$ = 3.9 Hz, quat. benzophosphole), 144.8 (d, $J_{C,P1}$ = 4.0 Hz, quat. benzophosphole) ppm. ^{31}P NMR ($CDCl_3$): δ = –13.5 (d, $J_{P,P}$ = 6.4 Hz, P2, PPh_2), –26.5 (d, $J_{P,P}$ = 6.4 Hz, P1, phosphole) ppm. MS (DCI, NH_3): *m*/*z* (%) = 567 (100) [M + 1].

Dichloro{(S_{Fc})-(diphenylphosphanyl)[2-(2,3,4,5-tetramethyl-1*H*-1λ^5-phospholyl)ferrocen-1-yl]methane}palladium(II) (9b): Diphosphane **7b** (0.025 g, 0.048 mmol) was dissolved in dry dichloromethane (25 mL) in a Schlenk tube under argon and [$PdCl_2(CH_3CN)_2$] (0.015 mg, 0.058 mmol) was then added. The yellow solution turned immediately orange then deep red and finally brown. After 30 min of stirring at room temperature, the solution was partially

concentrated (10 mL) and dry pentane (5 mL) was added dropwise. A brown precipitate appeared. The red solution was filtered and concentrated with a high-vacuum pump to yield a red-orange solid (28 mg) (yield 80%). Crystals suitable for X-ray analysis were obtained by diffusion of pentane into a chloroform solution. ^{1}H NMR ($CDCl_3$): δ = 2.00 (br. s, 3 H, CH_3 β phosphole), 2.066 (br. s, 3 H, CH_3 β phosphole), 2.07 (br. d, $J_{H,P1}$ = 13 Hz, 3 H, CH_3 α phosphole), 2.40 (br. d, $J_{H,P1}$ = 13.8 Hz, 3 H, CH_3 α phosphole), 3.40 (dd, $J_{H,P1}$ = 2.3 Hz, $J_{H,P2}$ = 10.5 Hz, 2 H, CH_2), 3.95 (s, 5 H, Cp), 4.13 (m, 1 H, subst. Cp), 4.26 (m, 1 H, subst. Cp), 4.34 (br. s, 1 H, subst. Cp), 7.37 (m, 2 H, PPh_2), 7.45 (m, 1 H, PPh_2), 7.6–7.5 (m, 3 H, PPh_2), 7.75–7.65 (m, 2 H, PPh_2), 8.1–8.0 (m, 2 H, PPh_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.0 (d, $J_{C,P1}$ = 15.3 Hz, CH_3 α phosphole), 14.3 (d, $J_{C,P1}$ = 12 Hz, CH_3 β phosphole), 14.5 (d, $J_{C,P1}$ = 12 Hz, CH_3 β phosphole), 14.7 (d, $J_{C,P1}$ = 17 Hz, CH_3 α phosphole), 30.6 (dd, $J_{C,P1}$ = 8.0 Hz, $J_{C,P2}$ = 28.0 Hz, CH_2), 63.2 (dd, $J_{C,P1}$ = 63.1 Hz, $J_{C,P2}$ = 13.4 Hz, quat. Cp), 69.1 (d, $J_{C,P1}$ = 7.1 Hz, subst. Cp), 70.7 (s, Cp), 71.5 (d, $J_{C,P1}$ = 5.7 Hz, subst. Cp), 73.0 (dd, $J_{C,P1}$ = 6.7 Hz, $J_{C,P2}$ = 4.7 Hz, subst. Cp), 85.8 (br. d, $J_{C,P1}$ = 18 Hz, quat. Cp), 128.9 (d, $J_{C,P2}$ = 11.1 Hz, PPh_2), 129.15 (s, CCH_3 β phosphole), 129.22 (s, CCH_3 β phosphole), 129.23 (d, $J_{C,P2}$ = 11.3 Hz, PPh_2), 129.7 (d, $J_{C,P2}$ = 55.8 Hz, quat. PPh_2), 130.8 (d, $J_{C,P2}$ = 55.3 Hz, quat. PPh_2), 131.8 (d, $J_{C,P2}$ = 2.7 Hz, PPh_2), 132.2 (d, $J_{C,P2}$ = 3.0 Hz, PPh_2), 133.9 (d, $J_{C,P2}$ = 10.4 Hz, PPh_2), 134.7 (d, $J_{C,P2}$ = 10.9 Hz, PPh_2), 146.9 (d, $J_{C,P1}$ = 17.8 Hz, CCH_3 α phosphole), 148.7 (d, $J_{C,P1}$ = 18.2 Hz, CCH_3 α phosphole) ppm. ^{31}P NMR ($CDCl_3$): δ = 36.2 (P1, phosphole), 46.8 (P2, PPh_2) ppm. MS (FAB, MNBA): *m*/*z* (%) = 663 (100) $[M - Cl]^+$.

General Procedure for Palladium-Catalysed Allylic Substitution: A mixture of ligand **8**, 1,3-diphenylprop-2-enyl acetate (**10**) (0.454 g, 1.8 mmol) and $[(Pd(C_3H_5)Cl)]_2$ (3.3 mg, 0.009 mmol) in dry dichloromethane (20 mL) was stirred at room temperature for 2 h. Dimethyl malonate (**11**) (0.411 mL, 3.6 mmol), potassium acetate and BSA (0.880 mL, 3.6 mmol) were added to the resulting solution. The reaction was carried out at room temperature and monitored by TLC for the disappearance of the acetate. After the reaction was complete, the resulting mixture was diluted with diethyl ether (5 mL) and quenched with a saturated aqueous solution of ammonium chloride (5 mL). The aqueous phase was extracted with diethyl ether, the combined organic layers were dried with magnesium sulfate, filtered and the solvents evaporated. The conversion was calculated from the crude reaction mixture by ^{1}H NMR spectroscopy. Subsequent purification by chromatography on silica eluting with ethyl acetate/pentane (15:85) afforded the product as a white solid. The enantiomeric excess was determined by ^{1}H NMR using the chiral shift reagent $Eu(hfc)_3$.

X-ray Structure Determinations: A single crystal of each compound was mounted under inert perfluoropolyether at the tip of a glass fibre and cooled in the cryostream of a Stoe IPDS diffractometer for **3b**, **8b** and **9b** or an Oxford Diffraction XCALIBUR CCD diffractometer for **5b**. Data were collected using monochromatic Mo-K_α radiation (λ = 0.71073). The structures were solved by direct methods (SIR97[31]) and refined by least-squares procedures on F^2 using SHELXL-97.[32] All H atoms were introduced in the calculation in idealised positions and treated as riding on their parent atoms. The absolute configuration was confirmed by refinement of the Flack's enantiopole parameter[33] and careful examination of sensitive reflections. Molecules were drawn with the help of ORTEP32.[34] Crystal data and refinement parameters are shown in Table 1. CCDC-605992 to -605995 contain the supplementary crys-

Table 1. Crystal data and structure refinement.

	3b	**5b**	**8b**	**9b**
Empirical formula	$C_{24}H_{31}FeO_3PS$	$C_{19}H_{23}FeOPS$	$C_{31}H_{32}FeP_2$	$C_{33}H_{34}Cl_8FeP_2Pd$
Formula mass	486.37	386.25	522.36	938.39
Temperature [K]	180(2)	180(2)	180(2)	180(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1$	$P2_1$	$P2_12_12_1$	$P2_1$
a [Å]	8.4215(16)	8.1583(6)	11.0468(7)	9.7972(9)
b [Å]	11.1878(16)	11.0794(7)	14.4359(12)	18.2870(13)
c [Å]	12.490(2)	10.0725(7)	16.6373(13)	21.391(3)
α [°]	90	90	90	90
β [°]	95.92(2)	102.266(6)	90	98.487(13)
γ [°]	90	90	90	90
V [Å^3]	1170.5(3)	889.66(11)	2653.2(3)	3790.5(6)
Z	2	2	4	4
$D_{calcd.}$ [Mg/m^3]	1.380	1.442	1.308	1.644
μ [mm^{-1}]	0.824	1.056	0.707	1.530
F(000)	276	404	1096	1880
Crystal size [mm]	0.76 × 0.34 × 0.16	0.64 × 0.54 × 0.31	0.38 × 0.31 × 0.28	0.4 × 0.32 × 0.12
θ [°]	2.43–26.11	3.46–28.28	2.21–26.04	2.22–24.05
Reflections collected	11372	6780	26463	30390
Unique reflections [*R*(int)]	4109 (0.0321)	4105 (0.0200)	5206 (0.0536)	11238 (0.0526)
Completeness [%]	99.2	99.3	99.3	93.9
Absorption correction	multiscan	multiscan	empirical	multiscan
Max./min. transmission	0.9247/0.8729	0.731/0.522	0.835/0.735	0.689/0.622
Refinement method	F^2	F^2	F^2	F^2
Data/restraints/parameters	4374/3/313	4105/1/213	5206/0/311	11238/741/820
Gof on F^2	1.118	1.053	1.047	1.109
R_1, wR_2 [$I > 2\sigma(I)$]	0.0293, 0.0792	0.0238, 0.0605	0.0381, 0.0937	0.0637, 0.1560
R_1, wR_2 (all data)	0.0306, 0.0804	0.0246, 0.0613	0.0500, 0.0985	0.0692, 0.1590
Absolute structure parameter	–0.06(5)	0.000(10)	–0.006(19)	0.06(3)
Largest diff. peak/hole [e/Å^3]	0.326/–0.237	0.293/–0.318	0.999/–0.271	2.409/–1.177

tallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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