Chiral [(Dialkylamino)methyl](phospholyl)ferrocene Ligands as a New Class of 1,2-Disubstituted Ferrocene Ligands

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An efficient synthesis of new chiral [(dialkylamino)methyl](phospholyl)ferrocenes in an enantiomerically pure form has been developed. These new chiral N,P ligands have been tested in the palladium-catalyzed allylic substitution reaction. High activities and moderate enantioselectivities (up to 67% *ee*) were observed.

Introduction

Enantiopure 1,2-disubstituted ferrocene derivatives, especially ferrocenylphosphane ligands, are widely used as ligands in homogeneous transition metal catalysis.[1] Some of these ligands have proved to be especially efficient, in particular the aminophosphanes PPFA and BPPFA,[2] TRAP ligands,[3] Josiphos ligands,[4] in particular the industrially important Xyliphos,[5] pyrazolylphosphane ligands[6] or, more recently, ferrocenyloxazolines.[7] However, most of these chiral ferrocene-based ligands possess classical tertiary phosphane groups and no attention has been paid to ferrocenyl ligands with nonclassical phosphanes such as phosphole. Although phospholes are efficient ligands in homogeneous transition metal catalysis,[8] only a few enantiomerically pure chiral phospholes[9] have been used as chiral ligands for asymmetric catalysis.[10] In addition, a new approach has recently emerged where conformationally flexible ligands are intentionally used to magnify the effect of the chiral part of the catalytic system.[11] Unsymmetrically substituted phospholes can be useful in this context, because, owing to the low inversion barrier of the phosphorus in phospholes, a ligand bearing an unsymmetrically substituted phosphole could adjust the configuration of the asymmetric phosphorus atom to accommodate the metallic center through the catalytic cycle.

So, as part of our continuing interest in ferrocene chemistry[12] and in the design and synthesis of new chiral phosphole-based ligands,[13] we decided to investigate the efficiency of mixed phospholylferrocene ligands in asymmetric catalysis. Herein, we report the synthesis and characterization of the [(dialkylamino)methyl](phospholyl)-ferrocene ligands **8a,b** as a new class of 1,2-disubstituted ferrocene ligands and their use in palladium-catalyzed asymmetric allylic substitution.

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Results and Discussion

Synthesis of [(Dialkylamino)methyl](phospholyl)ferrocene Ligands 8a,b

The synthetic pathway used to produce enantiopure 1,2-disubstituted ferrocene derivatives **8a,b** is based on six stereochemically controlled reactions, as shown in Scheme 1. In the first step, the required planar chirality was introduced by diastereoselective ortho-lithiation of acetal **1** according to Kagan's procedure,[14] followed by treatment with 1-cyanophosphole (**2**)[15] as the electrophile, giving the expected phospholylferrocene product, which was directly converted by sulfurization to the air-stable compound **3**. This compound, isolated in 89% yield after purification by column chromatography, was obtained as an enantiomerically pure diastereoisomer. The new planar chirality in **3** was predicted to have an (*S*) configuration as the planar chirality is defined in the first step of the reaction, namely the lithiation of **1**, and is then independent of the electrophile used to quench the lithiated intermediate, as shown by Kagan et al.[14]

In the next step, the acid hydrolysis of the acetal (*S*)-**3** led quantitatively to the corresponding aldehyde (*S*)-**4**. This compound, which is slightly unstable, was only characterised by ^{1}H and ^{31}P NMR spectroscopy and then reduced with sodium tetrahydroborate to the stable alcohol (*S*)-**5**. This compound, obtained in 90% yield by column chromatography, was fully characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy and the (*S*)-configuration was confirmed by an X-ray diffraction analysis. A molecular view of the alcohol (*S*)-**5** is shown in Figure 1, with the atom-labelling

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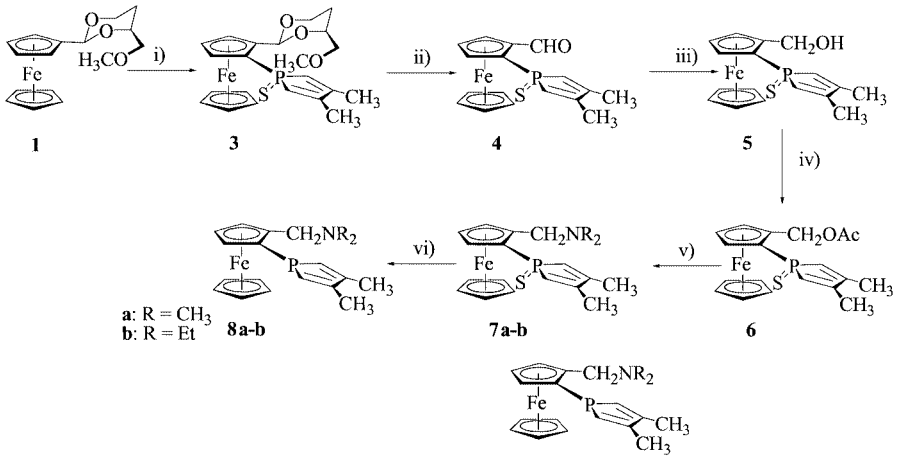


Scheme 1. Synthesis of **8**: i) *t*BuLi, −78 °C to room temp., 1-cyanophosphole (**2**), −30 °C; S_8, CH_2Cl_2, room temp.; ii) H^+, H_2O/ CH_2Cl_2, reflux; iii) $NaBH_4$, room temp.; iv) AcCl/ NEt_3, O °C to room temp., CH_2Cl_2; v) R_2NH, EtOH, reflux; vi) $P(CH_2CH_2CN)_3$, toluene, reflux

scheme. The X-ray crystal structure analysis clearly shows the nearly eclipsed conformation of the two Cp rings, with a twist angle of 4.75°. The phosphole ring is planar, with the largest deviation being 0.016 Å at C(2), and it makes a dihedral angle of 61.6° with the Cp to which it is attached. This phosphole ring is *endo* with respect to the Cp ring, whereas the S atom is *exo*. Such an arrangement is probably due to the hydrogen bond occurring between the OH of the hydroxyl group and the sulfur atom [O(1)−H(1)···S(1): O(1)−H(1) = 0.818(5) Å, O(1)···S(1) = 3.288(2) Å, H(1)···S(1) = 2.55(2) Å, O(1)−H(1)···S(1) = 150.5(8)°]. This hydrogen bond is responsible for the slight tilt angle of 4.2° observed between the Cp rings.

In the next step, the alcohol (*S*)-**5** was transformed quantitatively into the acetate (*S*)-**6** by treatment with acetyl chloride. This crude acetate was used directly for a nucleophilic substitution reaction with secondary amines, following the procedure described by Kumada et al.[16] Compounds (*S*)-**7a** and (*S*)-**7b** were obtained in 25% and 42% yield respectively. Compounds **7a,b** were fully characterized and the structure of **7a** was confirmed by X-ray analysis. A molecular view of **7a** is shown in Figure 2, with the atom-

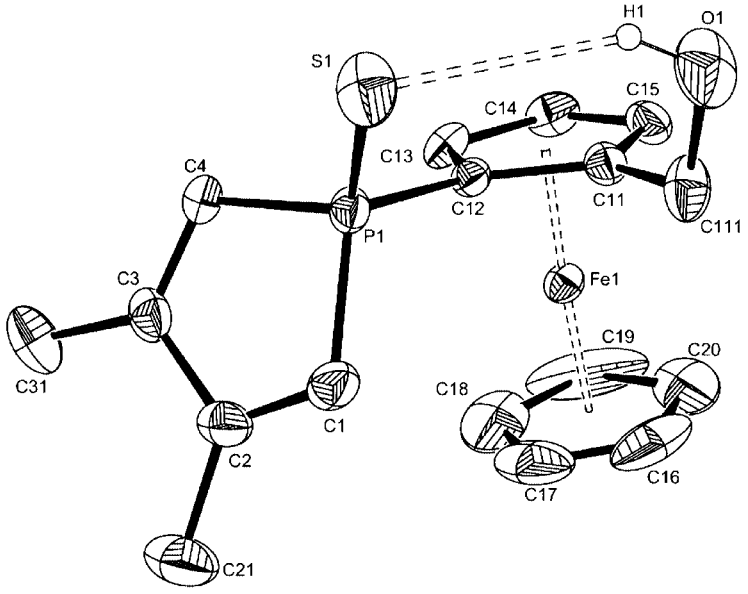


Figure 1. ORTEP drawing of **5** with atom labelling scheme; ellipsoids are drawn at 50% probability; important bond lengths (Å) and bond angles (°): Fe−Cp1(centroid) 1.633, Fe−Cp2(centroid) 1.652, C(11)−C(111) 1.489(2), C(111)−O(1) 1.425(2), C(12)−P(1) 1.7885(14), P(1)−C(1) 1.7812(17), P(1)−C(4) 1.7854(16), P(1)−S(1) 1.9645(6), C(1)−C(2) 1.341(3), C(2)−C(3) 1.501(3), C(3)−C(4) 1.334(2); Cp1(centroid)−Fe−Cp2(centroid) 176.9, S(1)−P(1)−C(1) 117.12(6), S(1)−P(1)−C(4) 116.41(5), S(1)−P(1)−C(12) 111.60(5), C(1)−P(1)−C(4) 92.83(8), C(1)−P(1)−C(12) 110.83(7), C(4)−P(1)−C(12) 106.37(7), P(1)−C(1)−C(2) 109.47(12), C(1)−C(2)−C(3) 114.08(14), C(2)−C(3)−C(4) 113.66(15), C(3)−C(4)−P(1) 109.90(12), C(11)−C(111)−O(1) 112.61(15)

labelling scheme. As in (*S*)-**5**, the phosphole ring is planar with the largest deviation being 0.044 Å at C(3). However, there is no hydrogen bond and the phosphole is *exo* with respect to the ferrocene moiety, whereas the sulfur is *endo*. The dihedral angle between this phosphole and the Cp ring to which it is attached is 72.3°. The amine group is *exo* with respect to the ferrocene moiety and the nitrogen lone pair is oriented towards the phosphole ring. The two Cp rings are nearly eclipsed, with a twist angle of 4.71°; the tilt angle between the Cp rings is 1.7°.

In the last step, desulfuration of (*S*)-**7a,b**, performed in refluxing toluene with tris(2-cyanoethyl)phosphane as reducing agent, led to the corresponding ligands (*S*)-**8a,b** in 92% and 82% yield respectively.

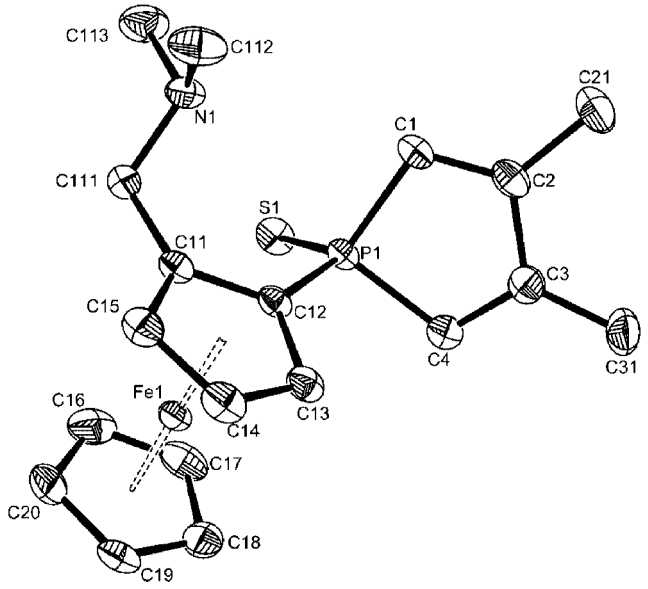
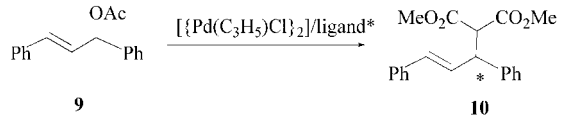


Figure 2. ORTEP drawing of complex **7a** with atom labelling scheme; ellipsoids are drawn at 50% probability; important bond lengths (Å) and bond angles (°): Fe−Cp1(centroid) 1.647, Fe−Cp2(centroid) 1.654, C(11)−C(111) 1.496(2), C(111)−N(1) 1.456(2), C(12)−P(1) 1.7951(17), P(1)−C(1) 1.8012(1), P(1)−C(4) 1.7959(17), P(1)−S(1) 1.9564(6), C(1)−C(2) 1.349(3), C(2)−C(3) 1.491(2), C(3)−C(4) 1.371(2); Cp1(centroid)−Fe−Cp2(centroid) 178.7, S(1)−P(1)−C(1) 115.14(6), S(1)−P(1)−C(4) 117.42(7); S(1)−P(1)−C(12) 116.80(6), C(1)−P(1)−C(4) 92.52(8), C(1)−P(1)−C(12) 109.23(8), C(4)−P(1)−C(12) 102.61(8), P(1)−C(1)−C(2) 110.06(13), C(1)−C(2)−C(3) 113.82(15), C(2)−C(3)−C(4) 114.05(15), C(3)−C(4)−P(1) 109.03(12), C(11)−C(111)−N(1) 110.75(13)

Application of the [(Dialkylamino)methyl](phospholyl)-ferrocenes 8a,b in Palladium-Catalyzed Asymmetric Allylic Substitution

As a preliminary evaluation of the catalytic properties of the chiral ligands **8a** and **8b**, we explored the palladium-catalyzed asymmetric allylic substitution reaction.[17] Thus, the reaction of 1,3-diphenylprop-2-enyl acetate (**9**) with the anion of dimethyl malonate in the presence of $[Pd(C_3H_5)Cl]_2$ (1mol %) and the chiral ligand **8a**,**b** (1mol %) provided the expected allylic substitution product **10** in high yields and moderate enantioselectivities (up to 67% *ee*) depending on the conditions (see Scheme 2). The results are summarised in Table 1.



Scheme 2

This reaction occurred with 62% and 65% *ee* for **8a** and **8b**, respectively (entries 1,3), with high activities in both cases and complete conversion after 45−90 min at room temperature using CH_2Cl_2 as solvent and *N*,*O*-bis(trimethylsilyl)acetamide (BSA)/AcOK as base. The use of THF as solvent decreased the rate of the reaction (entry 2), and complete conversion was not observed even after 24 h, although the enantioselectivity was not affected.

Similar activities and enantioselectivities were observed when using NaH as base instead of the BSA/AcOK system (entries 4−5).

Conclusion

We have described a new and efficient method for the preparation of [(dialkylamino)methyl](phospholyl)ferrocenes in an enantiomerically pure form. Palladium-catalysed allylic substitution of 1,3-diphenylprop-2-enyl acetate with the anion of dimethyl malonate can be achieved with these new N,P ligands with high activities but still moderate enantioselectivities (up to 67% *ee*) compared to analogous ligands.[17,18] These new [(dialkylamino)methyl](phos-

Table 1. Results of asymmetric allylic substitution reaction of 1,3-diphenylprop-2-enyl acetate with the anion of dimethyl malonate[a]

Entry	Ligand	Base	Solvent	Reaction time	Yield[b]	*ee* (%) of **8**[c] (config.)[d]
1	**8a** (1%)	BSA/AcOK	CH_2Cl_2	1 h 30 mn	95%	65 (*S*)
2	**8a** (1%)	BSA/AcOK	THF	24 h	58%	67 (*S*)
3	**8b** (1%)	BSA/AcOK	CH_2Cl_2	0.5 h	94%	62 (*S*)
4	**8a** (1%)	NaH	CH_2Cl_2	1 h 30	96%	60 (*S*)
5	**8b** (1%)	NaH	CH_2Cl_2	1 h 30	95%	58 (*S*)

[a] Reactions conditions: 1 mmol of (*E*)-1,3-diphenylprop-2-enyl acetate, 3 mmol of dimethylmalonate with 1% palladium as $[PdCl(allyl)]_2$ at room temp. Complete conversion was confirmed by ^1H NMR spectroscopy, expect for entry 2, for which the conversion was not complete after 24 h. [b] Isolated yield. [c] Determined by ^1H NMR spectroscopy using the chiral shift reagent $Eu(hfc)_3$. [d] Determined on the basis of the sign of the specific rotation of the product.

pholyl)ferrocenes are very modular: for example, the substituents on the phosphole ring or in the amino part can be easily changed in order to improve significantly the performances of the catalytic system. Further studies in this direction are currently in progress in our laboratory.

Experimental Section

General: All reactions were carried out under dry argon 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 on a Bruker WMX 400 instrument operating at 400, 162, and 100 MHz, respectively. Chemical shifts are reported in parts per million (ppm) relative to Me_4Si (^{1}H and ^{13}C) or 85% H_3PO_4 (^{31}P). Mass spectra were obtained on a Nermag R10-10 instrument. Elemental analyses were 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**[14] and 1-cyano-3,4-dimethylphosphole (**2**)[15] were prepared as described in the literature.

(2*S*,4*S*,S_{Fc})-4-(Methoxymethyl)-2-[(3,4-dimethyl-1-thio-1*H*-1λ^5-phosphol-1-yl)ferrocenyl]-1,3-dioxane (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 40 mL of dry diethyl ether. The solution was stirred at −78 °C during 15 minutes, then for 2 h at room temp. The solution was cooled to −30 °C and a solution of 1-cyano-3,4-dimethylphosphole (**2**; 1.81 g, 13.2 mmol, 1.2 equiv.) in 20 mL of dry diethyl ether was introduced with a cannula. The reaction mixture was stirred overnight at room temp. Dry triethylamine (0.5 mL) was then added 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 over sodium sulfate and the solvents evaporated in vacuo to yield an orange oil. This oil was dissolved in 30 mL of dichloromethane. Sulfur (2 g, 62.mmol, 5.7 equiv.) was added and the mixture was stirred overnight. After evaporation, the mixture was chromatographed on silica gel using a pentane/dichloromethane mixture (7:3, v/v) to yield 4.47 g of a brown orange oil (Yield: 89%). ^{1}H NMR ([D$_6$]acetone): δ = 1.50 (d of m, J = 12.5 Hz, 1 H, CH_2-CH_2-CH), 1.66 (br. q of d, J = 12.5 Hz and 5 Hz, 1 H, CH_2-CH_2-CH), 2.03 (br. s, 3 H, CH_3), 2.12 (br. s, 3 H, CH_3), 3.33 (dd, J = 10.4 Hz and 4.2 Hz, 1 H, CH_2-OCH_3), 3.34 (s, 3 H, OCH_3), 3.43 (dd, J = 10.4 Hz and 6.5 Hz, 1 H, CH_2-OCH_3), 4.00 (br. t of d, J = 12 Hz and 2.7 Hz, 1 H, $O-CH_2CH_2$), 4.07 (m, 1 H, O−CH), 4.24 (br. dd, J = 11.2 Hz and 4.3 Hz, 1 H, $O-CH_2CH_2$), 4.33 (m, 1 H, subst Cp), 4.36 (m, 1 H, subst Cp), 4.42 (s, 5 H, Cp), 4.69 (m, 1 H, subst Cp), 6.14 (s, 1 H, O−CH−O), 6.20 (br. d, $J_{H,P}$ = 29.7 Hz, 1 H, CHP), 6.39 (br. d, $J_{H,P}$ = 29.5 Hz, 1 H, CHP) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 17.0 (d, $J_{C,P}$ = 14.4 Hz, CH_3), 17.1 (d, $J_{C,P}$ = 14.1 Hz, CH_3), 28.2 (CH_2-CH_2-CH), 58.6 (OCH_3), 67.0 ($O-CH_2CH_2$), 69.0 (d $J_{C,P}$ = 10.5 Hz, subst Cp), 70.5(d, $J_{C,P}$ = 12.6 Hz, subst Cp), 71.1 (Cp), 72.2 (d, $J_{C,P}$ = 86.5 Hz, quat Cp), 75.3 (*C*H); 72.4 (d, $J_{C,P}$ = 13.5 Hz, subst Cp), 75.8 (CH_2-OCH_3), 90.1 (d, $J_{C,P}$ = 0.9 Hz, quat Cp), 99.6 (O−CH−O), 125.2 (d, $J_{C,P}$ = 85.4 Hz, CHP), 128.1 (d, $J_{C,P}$ = 84.1 Hz, CHP), 149.8 (d, $J_{C,P}$ = 18.9 Hz, $C-CH_3$), 152.6 (d, $J_{C,P}$ = 19.1 Hz, $C-CH_3$) ppm. ^{31}P NMR ([D$_6$]acetone): δ = 48.3. $[\alpha]_D$ = −2.47 (c = 0.5, $CHCl_3$). MS (DCI, NH_3): m/z (%) = 459 (100%) $[M + H]^+$. $C_{22}H_{27}FeO_3PS$ (458.34): calcd. C 57.65, H 5.94; found C 57.85, H 5.85.

(S_{Fc})-2-(3,4-Dimethyl-1-thio-1*H*-1λ^5-phosphol-1-yl)ferrocenecarbaldehyde (4): Acetal **3** (3.35 g, 7.3 mmol), dichloromethane (120 mL) and an aqueous solution (50 mL) of *p*-toluenesulfonic acid monohydrate (2 g, 10.5 mmol, 1.4 equiv.) were introduced into a round-bottomed flask equipped with a condenser and placed under argon. The reaction mixture was stirred at reflux for 20 h. After cooling back to room temp. the dark red solution was extracted with dichloromethane, washed with distilled water, dried over sodium sulfate and the solvents evaporated. Compound **4**, obtained quantitatively as a red oil, was only characterised by ^{1}H and ^{31}P NMR spectroscopy and used without purification. ^{1}H NMR ($CDCl_3$): δ = 2.10 (m, 6 H, CH_3), 4.40 (s, 5 H, Cp), 4.75 (m, 1 H, subst Cp), 4.95 (m, 1 H, subst Cp), 5.10 (m, 1 H, subst Cp), 6.20 (d, $J_{H,P}$ = 28.5 Hz, 2 H, CHP), 10.30 (s, 1 H, CHO), ppm. ^{31}P NMR ($CDCl_3$): δ = 44.9 ppm.

(S_{Fc})-[2-(3,4-Dimethyl-1-thio-1*H*-1λ^5-phosphol-1-yl)ferrocenyl]-methanol (5): The crude compound **4** 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 minutes stirring at room temp. the reaction mixture was extracted with dichloromethane. The organic phase was washed with dilute hydrochloric acid then water, and finally dried over sodium sulfate. After evaporation of the solvents, the crude materials was purified by flash chromatography on silica gel using a pentane/diethyl ether mixture (2:8, v/v) to yield 2.36 g of **5** (90% from **3**) as an orange solid. Crystals suitable for X-ray analysis were obtained by diffusion of pentane into a dichloromethane solution. ^{1}H NMR ($CDCl_3$): δ = 2.08 (d, J = 1.6 Hz, 3 H, CH_3), 2.14 (d, J = 1.6 Hz, 3 H, CH_3), 3.26 (dd, J = 7.4 Hz and 6.3 Hz, 1 H, OH), 4.29−4.35 (m, 2 H, subst Cp), 4.31 (s, 5 H, Cp), 4.38 (dd, J = 12.7 Hz and 7.4 Hz, 1 H, CH_2), 4.48 (m, 1 H, subst Cp), 4.81 (dd, J = 12.7 Hz and 6.3 Hz, 1 H, CH_2), 6.16 (br. d, $J_{H,P}$ = 30.8 Hz, 1 H, CHP), 6.22 (br. d, $J_{H,P}$ = 30.4 Hz, 1 H, CHP) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.80 (d, $J_{C,P}$ = 17.8 Hz, CH_3), 17.84 (d, $J_{C,P}$ = 18.0 Hz, CH_3), 59.6 (d, $J_{C,P}$ = 7.8 Hz, CH_2), 69.8 (d, $J_{C,P}$ = 10.8 Hz, subst Cp), 70.5 (d, $J_{C,P}$ = 71.5 Hz, quat Cp), 70.7 (Cp), 72.5(d, $J_{C,P}$ = 14.2 Hz, subst Cp), 74.2 (d, $J_{C,P}$ = 9.6 Hz, subst Cp), 92.1 (d, $J_{C,P}$ = 12.3 Hz, quat Cp), 125.6 (d, $J_{C,P}$ = 86.1 Hz, CHP), 126.5 (d, $J_{C,P}$ = 84.0 Hz, CHP), 151.9 (d, $J_{C,P}$ = 18.6 Hz, $C-CH_3$), 152.2 (d, $J_{C,P}$ = 18.7 Hz, $C-CH_3$) ppm. ^{31}P NMR ($CDCl_3$): δ = 49.3 ppm. $[\alpha]_D$ = −104.6 (c = 0.5, $CHCl_3$). MS (DCI, NH_3): m/z (%) = 359 (100) $[M + H]^+$. $C_{17}H_{19}FeOPS$ (358.22): calcd. C 57.00, H 5.35; found C 57.11, H 5.00.

(S_{Fc})-Acetoxy-[2-(3,4-dimethyl-1-thio-1*H*-1λ^5-phosphol-1-yl)ferrocenyl]methane (6): (*S*)-[2-(thio-3,4-dimethylphospholyl)ferrocenyl]-methanol (240 mg, 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 (70 μL, 1 mmol, 1.5 equiv.) was added with a syringe. The solution was stirred at 0 °C for 30 minutes then for 1 h at room temp. The solution was washed with dilute hydrochloric acid then water, and dried over sodium sulfate. After evaporation of the solvents, the crude compound **6** was quantitatively obtained as a yellow oil that was used without further purification in the next step. ^{1}H NMR ($CDCl_3$): δ = 1.98 [s, 3 H, $C(O)CH_3$], 2.04 (m, 6 H, CH_3), 4.34 (s, 5 H, Cp), 4.45 (m, 1 H, subst Cp), 4.50 (m, 1 H, subst Cp), 4.60 (m, 1 H, subst Cp), 4.90 (d, J = 11.8 Hz, 1 H, CH_2), 5.20 (d, J = 11.8 Hz, 1 H, CH_2), 6.05 (br. d, $J_{H,P}$ = 29.6 Hz,

1 H, CHP), 6.15 (br. d, $J_{H,P}$ = 29.6 Hz, 1 H, CHP) ppm. ^{31}P NMR ($CDCl_3$): δ = 45.5 ppm.

(S_{Fc})-{2-[(3,4-Dimethyl-1-thio-1*H*-1λ^5-phosphol-1-yl)ferrocenyl]-methyl}dimethylamine (7a): The crude acetate, methanol (40 mL) and dimethylammonium chloride (3.58 g, 44 mmol, 40 equiv.) were introduced into a three-necked, round-bottomed flask equipped with a condenser and purged with argon. The reaction mixture was stirred at reflux for 40 h. After cooling back to room temp. the solvents were evaporated and the residue was dissolved in diethyl ether and washed with a dilute hydrochloric acid solution. Unreacted starting materials could be obtained from the organic phase after evaporation of the solvents and flash chromatography. An aqueous sodium hydroxide solution (ca. 2 M) was added to the aqueous phase in order to adjust the pH close to 13. A precipitate formed, which was dissolved by adding diethyl ether to the suspension. This second organic phase was dried over sodium sulfate and the solvents evaporated to give 105 mg of amine **7a** (yield 25%) as a yellow oil. This compound was purified by column chromatography on alumina using a pentane/diethyl ether mixture (4:6, v/v). Crystals suitable for X-ray analysis were obtained by diffusion of pentane into a dichloromethane solution. ^{1}H NMR ($CDCl_3$): δ = 2.05 (m, 3 H, CH_3), 2.10 (m, 3 H, CH_3), 2.18 (s, 6 H, N CH_3), 3.05 (d, J = 12.7 Hz, 1 H, CH_2−Cp), 4.08 (d, J = 12.7 Hz, 1 H, CH_2−Cp), 4.30 (m, 1 H, subst Cp), 4.34 (s, 5 H, Cp), 4.41 (m, 1 H, subst Cp), 4.47 (m, 1 H, subst Cp), 6.15 (br. d, $J_{H,P}$ = 29.7 Hz, 1 H, CHP), 6.21 (br. d, $J_{H,P}$ = 29.9 Hz, 1 H, CHP) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.75 (d, $J_{C,P}$ = 17.9 Hz, CH_3), 17.83 (d, $J_{C,P}$ = 17.8 Hz, CH_3), 45.3 (s, N CH_3), 57.4 (s, CH_2), 69.6 (d, $J_{C,P}$ = 11.0 Hz, subst Cp), 70.8 (d, J $J_{C,P}$ = 88.4 Hz, quat Cp), 71.0 (s, Cp), 72.6 (d, $J_{C,P}$ = 14.9 Hz, subst Cp), 75.0 (d, $J_{C,P}$ = 9.4 Hz, subst Cp), 89.0 (d, $J_{C,P}$ = 12.5 Hz, quat Cp), 125.6 (d, $J_{C,P}$ = 85.5 Hz, CHP), 127.5 (d $J_{C,P}$ = 84.6 Hz, CHP), 150.8 (d, $J_{C,P}$ = 19.0 Hz, C−CH_3), 152.6 (d, $J_{C,P}$ = 18.1 Hz, C−CH_3) ppm. ^{31}P NMR ($CDCl_3$): δ = 49.1 ppm. $[\alpha]_D$ = −1.2 (c = 0.4, $CHCl_3$). $[\alpha]_{546}$ = −20.2 (c = 0.4, $CHCl_3$). MS (DCI, NH_3): m/z (%) = 386 (100) $[M + H]^+$.

(S_{Fc})-{2-[(3,4-Dimethyl-1-thio-1*H*-1λ^5-phosphol-1-yl)ferrocenyl]-methyl}diethylamine (7b): A similar procedure with 40 equiv. of pure diethylamine instead of the mixture dimethylammonium chloride/triethylamine gave compound **7b** as an orange oil (yield: 42%). ^{1}H NMR ($CDCl_3$): δ = 0.96 (t, J = 7.1 Hz, 6 H, CH_3CH$_2$), 2.01 (d, J = 1.4 Hz, 3 H, CH_3), 2.06 (d, J = 1.4 Hz, 3 H, CH_3), 2.4−2.6 (m, 4 H, CH_2CH$_3$), 3.30 (d, J = 13.2 Hz, 1 H, CH_2−Cp), 4.03 (d, J = 13.2 Hz, 1 H, CH_2−Cp), 4.24 (m, 1 H, subst Cp), 4.32 (s, 5 H, Cp), 4.36 (m, 1 H, subst Cp), 4.44 (m, 1 H, subst Cp), 6.09 (br. d, J_{H-P} = 29.7 Hz, 1 H, CHP), 6.23 (br. d, J_{H-P} = 29.7 Hz, 1 H, CHP) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.6 (NCH$_2$$CH_3$), 17.77 (d, $J_{C,P}$ = 16.0 Hz, CH_3), 17.85 (d, $J_{C,P}$ = 17.7 Hz, CH_3), 45.9 (NCH$_2$CH$_3$), 52.0 (CH_2), 69.1(d, $J_{C,P}$ = 11.0 Hz, subst Cp), 70.8 (d, $J_{C,P}$ = 88.7 Hz, quat Cp), 71.0 (Cp), 72.4 (d, $J_{C,P}$ = 14.9 Hz, subst Cp), 74.9 (d, $J_{C,P}$ = 9.7 Hz, subst Cp), 90.5 (d, $J_{C,P}$ = 11.9 Hz, quat Cp), 125.5 (d, $J_{C,P}$ = 85.2 Hz, CHP), 127.7 (d, $J_{C,P}$ = 84.7 Hz, CHP), 150.5 (d, $J_{C,P}$ = 18.7 Hz, C−CH_3), 152.5 (d, $J_{C,P}$ = 18.7 Hz, C-CH_3) ppm. ^{31}P NMR ($CDCl_3$): δ = 49.3 ppm. $[\alpha]_D$ = −1.8 (c = 0.5, $CHCl_3$). $[\alpha]_{546}$ = −23.4 (c = 0.5, $CHCl_3$). MS (DCI, NH_3): m/z (%) = 414 (100) $[M + H]^+$.

(S_{Fc})-{2-[(3,4-Dimethyl-1*H*-1λ^3-phosphol-1-yl)ferrocenyl]methyl}-dimethylamine (8a): Tris(2-cyanoethyl)phosphane (0.130 mg, 0.673 mmol) was added to a solution of **7a** (0.130 mg, 0.338 mmol) in toluene (10 mL) and the resulting mixture was refluxed for 6 hours. After cooling to room temp. the mixture was filtered through celite, the solvents evaporated in vacuo and the residue extracted four times with pentane. After evaporation of the solvents, the crude compound **7a** was purified by column chromatography on alumina using a pentane/diethyl ether mixture (1:1, v/v) to yield 105 mg of amine (yield: 92%) as an orange-red oil. ^{1}H NMR ($CDCl_3$): δ = 2.08 (br. s, 3 H, CH_3), 2.16 (br. s, 3 H, CH_3), 2.22 (s, 6 H, NCH_3), 3.41 (d, J = 12.8 Hz, 1 H, CH_2−Cp), 3.63 (dd, $J_{H,P}$ = 2.6, J = 12.8 Hz, 1 H, CH_2−Cp), 3.85 (m, 1 H, subst Cp), 4.20 (m, 1 H, subst Cp), 4.21 (s, 5 H, Cp), 4.39 (m, 1 H, subst Cp), 6.40 (br. d, $J_{H,P}$ = 37.3 Hz, 1 H, CHP), 6.54 (br. d, $J_{H,P}$ = 36.5 Hz, 1 H, CHP) ppm. ^{13}C NMR ($CDCl_3$): δ = 8.2 (CH_3), 18.3 (s, CH_3), 45.3 (s, NCH_3), 58.1 (d, J_{C-P} = 6.1 Hz, CH_2), 69.9 (s, Cp), 70.0 (d, J_{C-P} = 2.4 Hz, subst. Cp), 71.7 (s, subst. Cp), 71.9 (d, $J_{C,P}$ = 7.7 Hz, quat Cp), 72.7 (d, $J_{C,P}$ = 4.1 Hz, subst Cp), 89.7 (d, $J_{C,P}$ = 22.9 Hz, quat Cp), 129.7 (CHP), 132.1 (s, CHP), 147.8 (d, $J_{C,P}$ = 7.5 Hz, C-CH_3), 148.9 (d, $J_{C,P}$ = 9.7 Hz, C-CH_3) ppm. ^{31}P NMR ($CDCl_3$): δ = −16.4 ppm. MS (DCI, NH_3): m/z (%) = 353 (100) [M + H].

(S_{Fc})-{2-[(3,4-Dimethyl-1*H*-1λ^3-phosphol-1-yl)ferrocenyl]methyl}-diethylamine (8b): The synthesis of **8b** was accomplished by the same procedure as described above for **8a.** Compound **8b** was obtained as orange-red oil (82%). ^{1}H NMR ($CDCl_3$): δ = 1.06 (t, J = 7.1 Hz, 6 H, CH_3CH$_2$), 2.08 (br. s, 3 H, CH_3), 2.20 (br. s, 3 H, CH_3), 2.4−2.6 (m, 4 H, CH_2CH$_3$), 3.50 (d, J = 13.1 Hz, 1 H, CH_2−Cp), 3.82 (m, 1 H, subst Cp), 3.84 (dd, J = 13.1, J = 2.3 Hz, 1 H, CH_2−Cp), 4.17 (t, J = 2.4 Hz, 1 H, subst Cp), 4.21 (s, 5 H, Cp), 4.37 (m, 1 H, subst Cp), 6.40 (d, $J_{H,P}$ = 36.4 Hz, 1 H, CHP), 6.54 (d, $J_{H,P}$ = 36.4 Hz, 1 H, CHP) ppm. ^{13}C NMR ($CDCl_3$): δ = 12.5 (s, NCH$_2$$CH_3$), 18.2 (s, CH_3), 18.3 (s, CH_3), 46.4 (s, NCH$_2$CH$_3$), 52.1 (d $J_{C,P}$ = 5.9 Hz, CH_2), 69.6 (s, subst Cp), 69.9 (Cp), 71.5 (s, subst Cp), 71.9 (d, $J_{C,P}$ = 26.4 Hz, quat Cp), 72.9 (d, $J_{C,P\ P}$ = 4.4 Hz, subst Cp), 90.6 (d, $J_{C,P}$ = 26.4 Hz, quat Cp), 129.6 (s, CHP), 132.4 (s, CHP), 147.7 (d, $J_{C,P}$ = 9.0 Hz, C−CH_3), 148.8 (d, $J_{C,P}$ = 10.0 Hz, C−CH_3) ppm. ^{31}P NMR ($CDCl_3$): δ = −15.9 ppm. MS (DCI, NH_3): m/z (%) = 381 (100) [M + H].

General Procedure for Palladium-Catalyzed Allylic Substitution Dimethyl Malonate/BSA/KOAc System: A mixture of ligand **8**, 1,3-diphenylprop-2-enyl acetate (0.454 g, 1.8 mmol) and $[Pd(C_3H_5)Cl]_2$ (3.3 mg, 0.009 mmol) in dry solvent (20 mL) was stirred at room temperature for 2 h. Dimethyl malonate (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 disappearance of acetate. After complete reaction, the 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 Et_2O, the combined organics were dried over 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 spectroscopy using the chiral shift reagent Eu(hfc)$_3$.

Dimethyl Malonate/NaH System: A mineral oil dispersion of NaH (87 mg, 60% NaH, 2.17 mmol) was washed with dry pentane (3 × 5 mL). The oil-free NaH was suspended in dry dichloromethane (10 mL), cooled to 0 °C and treated dropwise with dimethyl malonate (0.297 mL, 2.6 mmol). After the reaction was complete, the resulting sodium dimethyl malonate was transferred by cannula under argon into a Schlenk tube containing a mixture of ligand **8**, 1,3-diphenylprop-2-enyl acetate (0.328 g, 1.3 mmol) and $[Pd(C_3H_5)Cl]_2$ (2.4 mg, 0.0065 mmol) in dry dichloromethane (10 mL) previously stirred at room temperature for 2 h. The reac-

Table 2. Crystal data and structure refinement

	5	**7a**
Empirical formula	$C_{17}H_{19}FeOPS$	$C_{19}H_{24}FeNPS$
Molecular weight	358.22	385.29
Temperature	180 K	160 K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
Unit cell dimensions	a = 9.3200(8) Å α = 90°. b = 9.9140(9) Å β = 90°. c = 17.552(2) Å γ = 90°.	a = 10.0397(13) Å α = 90°. b = 9.6103(8) Å β = 113.09(1)°. c = 10.3848(13) Å γ = 90°.
Volume	1621.8(3) Å^3	921.72(17) Å^3
Z	4	2
Density (calculated)	1.467 Mg/m^3	1.388 Mg/m^3
Absorption coefficient	1.152 mm^{-1}	1.017 mm^{-1}
F(000)	744	404
Crystal size	0.43 × 0.29 × 0.22 mm^3	0.32 × 0.28 × 0.24 mm^3
Theta range for data collection	3.217 to 26.059°	2.132 to 26.15°
Reflections collected	15792	9062
Independent reflections	3126 [R(int) = 0.03]	3488 [R(int) = 0.02]
Refinement method	Full-matrix on F	Full-matrix on F
Data/restraints/parameters	3042/0/191	3407/0/209
Goodness-of-fit on F	1.0338	1.0568
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0212, Rw = 0.0260	$R1$ = 0.0216, Rw = 0.0258
R indices (all data)	$R1$ = 0.0220, Rw = 0.0263	$R1$ = 0.0222, Rw = 0.0259
Absolute structure parameter	−0.006(13)	0.006(9)
Largest diff. peak and hole	0.47 and −0.33 e·Å^{-3}	0.51 and −0.3 e·Å^{-3}

tion was carried out at room temperature and monitored by TLC for disappearance of acetate. Treatment, extraction and purification were accomplished by the same procedure as described above.

X-ray Structure Determination: Data for **(*S*)-5** and **7a** were collected on a Stoe IPDS diffractometer. The final unit cell parameters were obtained by the least-squares refinement of 8000 reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collections.

Both the structures were solved by direct methods (SIR97[18]) and refined by least-squares procedures on F_{obs}. All H atoms attached to carbon or oxygen were introduced at their idealised positions [d(CH) = 0.96 Å] and were refined using a riding model. They were given isotropic thermal parameters 20% higher than those of the atom to which they are attached. The absolute configuration was confirmed by the refinement of the Flack parameter[19] and careful examination of the sensitive reflections. Least-squares refinements were carried out by minimising the function $\Sigma w(F_o - F_c)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = w'[1-\{\Delta F/6\sigma(F_o)\}^2]^2$ where $w' = 1/\Sigma_i^n A_r T_r(x)$ with three coefficients A_r for the Chebyshev polynomial $A_r T_r(x)$ where x was F_c/F_c(max).[20] Models reached convergence with $R = \Sigma(F_o - F_c)/\Sigma(F_o)$ and $Rw = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2}$, with the values listed in Table 2. The calculations were carried out with the CRYSTALS programs package.[21] The views of the molecules were produced with the ORTEP-III for Windows program.[22]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-198748 (**5**) and CCDC-198749 (**7a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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