Diphosphine sulfides derived from 2,2′-biphosphole: novel chiral *S*,*S* ligands for palladium-catalyzed asymmetric allylic substitution†

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Diphosphine sulfides derived from 2,2′-biphosphole have been efficiently synthesized in an enantiomerically pure form by a four step synthetic sequence. These *S*,*S*-ligands were used for the first time in Pd-catalyzed asymmetric allylic alkylation. Good yields and enantiomeric excess up to 73% were obtained.

Introduction

The design and synthesis of new and efficient chiral ligands play a central role in the development of highly enantioselective transition-metal-catalyzed asymmetric synthesis.[1] Chiral phosphorus ligands, in particular C_1- and C_2-symmetric ligands possessing the axially chiral 1,1′-binapthyl framework, are among the most widely used chiral ligands[2] In recent years, axially chiral sulfur ligands based on binapthalene backbone have proved to be as useful as other classical asymmetric ligands (*e.g.* *P*,*S*- heterodonor ligands),[3] but no study has yet devoted to atropoisomeric diphosphine sulfide ligands (*S*,*S*-ligands).

C_2-Symmetric diphosphine sulfides derived from 2,2′-biphosphole, which combine axial chirality and phosphorus chiralities, belong to the atropos.[4] class of ligands since their axial chiral configurations can be resolved.[5] These disulfides are attractive because different diastereoisomers can be easily obtained by simple sulfuration of the corresponding stereodynamic diphosphines.[6]

Here we present a series of diphosphine sulfides **V** derived from 2,2′-biphosphole ligands that are accessible by a four-step synthetic sequence. The new ligands proved to be active and selective in palladium catalyzed allylic substitution.

Results and discussion

The synthetic route to obtain the title sulfides derived from 2,2′-biphosphole is shown in Scheme 1. In the first step, pyrolysis of phosphole **I**[7] using the procedure previously described by F. Mathey *et al.* gave the tetraphosphole **II**[8] In the next step, treatment of compound **II** with sodium naphthalene led to the 2,2′-biphospholyl anion **III**. Then, the asymmetric alkylation of **III**[9] in high dilution conditions could be achieved using enantiomerically pure diol ditosylates **1**, **3** and **5**[5] or dimesylates **2**, **4** and **6** to afford the expected 2,2′-biphospholes **IV** in good yields (35 to 78%). In the last step, sulfuration of **IV** led to 2,2-biphosphole disulfides **V** as a mixture of isomers, with the exception of **V**·**4**. Three diastereoisomers have been obtained and separated by column chromatography in the case of **V**·**1**, **V**·**3** and **V**·**5**.[5] For compounds **V**·**2** and **V**·**6**, only two diastereoisomers have been isolated in the pure form by column chromatography.

Owing to X-ray diffraction studies, we could establish the relative configuration of both central and axial element of chirality of the 2,2′-biphosphole framework for the majority of the compounds obtained.[10]

The molecular structure of **V**·**4**[11] is presented in Fig 1 and selected bond distances and angles in Table 1. Compound **V**·**4** crystallizes in a non centrosymmetric space group (C_2). The refinement of the Flack's parameter[12] (0.00(6)) clearly indicates that **V**·**4** is enantiomerically pure in the solid state and the absolute configuration is *R*[*Sp*,*Sp*,*Rc*,*Rc*] (axial chirality [phosphorus chirality, carbon chirality]).

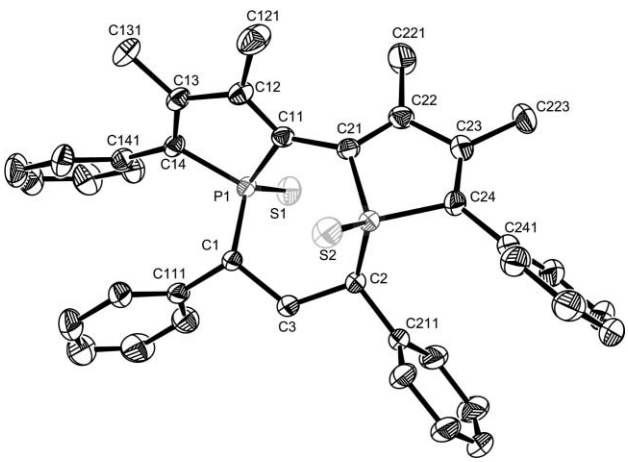

Fig. 1 Molecular view of *R*[*Sp*,*Sp*,*Rc*,*Rc*]-**V**·**4** with atom labeling scheme. Ellipsoids represent 30% probability level.

Palladium catalyzed nucleophilic substitution reactions of allylic substrates constitute a highly useful and versatile method for C–C bond formation and asymmetric versions of this reaction have been extensively studied over the last decade.[13] Many homo- and heterodonor chiral bidentate ligands such as *N*,*N*- (*e.g.* bisoxazolines.[14]), *P*,*P*- (*e.g.* Trost's *P*,*P*- ligands[15]), *N*,*P*- (phosphinooxazolines[16]) have been exploited in such a reaction.

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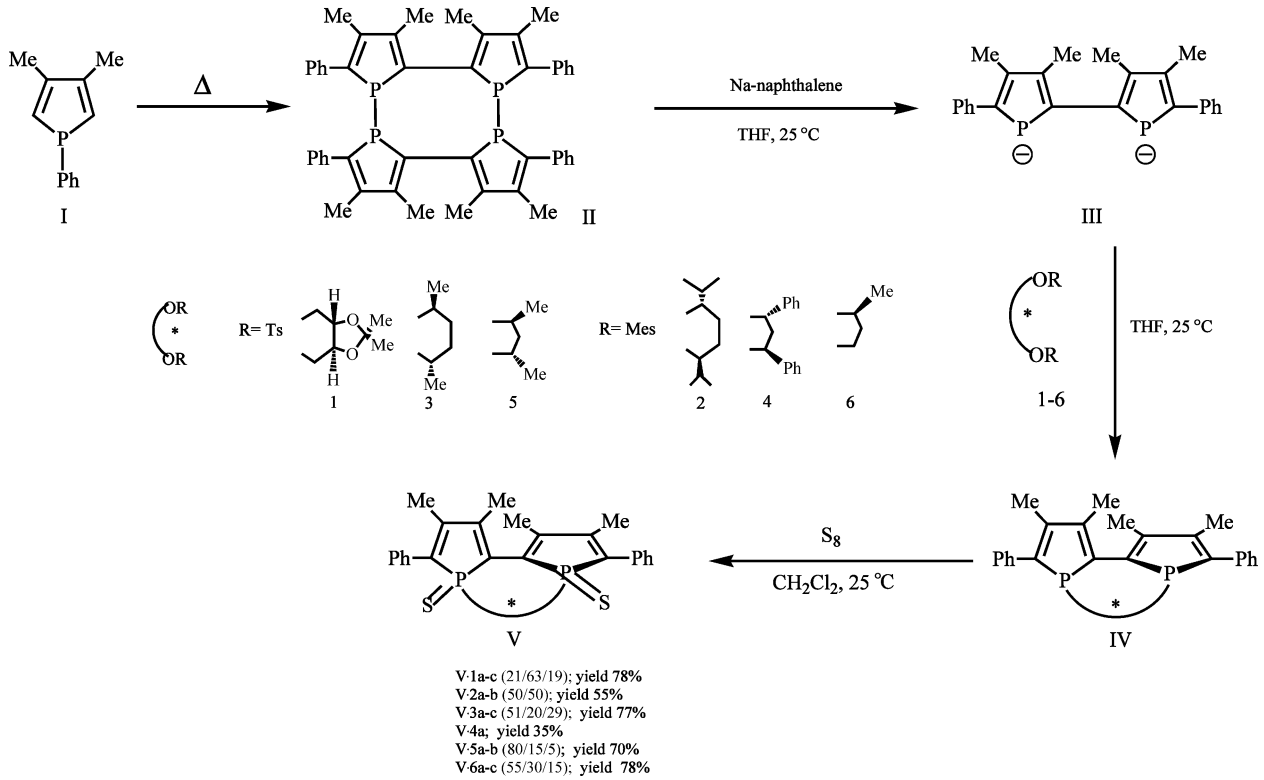


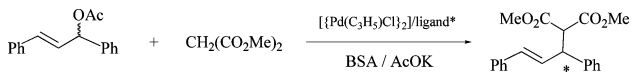
Scheme 1 Synthesis of diphosphine sulfides **V**.

Table 1 Selected bond distances (Å), bond angles (°) and torsion angle for the compound *R*[*Sp*,*Sp*,*Rc*,*Rc*]-**V·4**.

P(1)–S(1) 1.9430(9)	P(2)–S(2) 1.9448(9)
P(1)–C(1) 1.844(2)	P(2)–C(2) 1.840(2)
P(1)–C(11) 1.798(2)	P(2)–C(21) 1.798(2)
P(1)–C(14) 1.814(2)	P(2)–C(24) 1.804(2)
C(11)–P(1)–C(14) 92.91(10)	C(21)–P(2)–C(24) 92.64(11)
C(11)–P(1)–C(1) 104.02(10)	C(21)–P(2)–C(2) 103.44(10)
C(14)–P(1)–C(1) 104.93(10)	C(24)–P(2)–C(2) 105.78(11)
C(11)–P(1)–S(1) 113.86(8)	C(21)–P(2)–S(2) 114.95(9)
C(14)–P(1)–S(1) 119.30(8)	C(24)–P(2)–S(2) 118.42(9)
C(1)–P(1)–S(1) 118.09(8)	C(2)–P(2)–S(2) 117.91(8)
P(1)–C(11)–C(12)–P(2) = 94.9°	

Chiral sulfur-containing ligands have also been explored such as *N*,*S*-, *O*,*S*-, *P*,*S*- and *S*,*S*-[17] Among the latter, only two classes have been reported, dithioethers[18] and thioether–phosphine sulfides,[3b,19] but no attention has been paid to diphosphine sulfides to the best of our knowledge.

To evaluate the activity and selectivity of the chiral ligands **V**, we have investigated the Pd-catalyzed allylic substitution of 1,3-diphenylprop-2-enyle acetate by the dimethylmalonate anion (Scheme 2).



Scheme 2 Allylic substitution reaction.

The reaction was carried out in dichloromethane at 40 °C in the presence of a catalyst generated *in situ* from 1 mol% of the corresponding ligand **V**, 0.5 mol% of π-allylpalladium chloride dimer $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$. The nucleophile was generated from dimethyl malonate using *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and catalytic quantities of KOAc. The results are listed in Table 2.

All of the ligands **V** gave palladium catalytic systems that are active in allylic substitution producing the corresponding allylic substitution product with an enantiomeric excess in the range of 18 to 73%. The best result in terms of activities and enantioselectivities were obtained with ligands *R*[*Sp*,*Sp*,*Rc*,*Rc*]-**V·1c** (entry 3) and *S*[*Rp*,*Rp*,*Rc*]-**V·6b** (entry 11), in which cases the substitution product was obtained with an enantiomeric excess of

Table 2 Palladium-catalyzed asymmetric allylic alkylation with chiral diphosphine sulfides **V** [a]

Run	Ligand	Conversion (%)[b]	ee (%)[c] (configuration) [d]
1	*S*[*Rp*,*Rp*,*Rc*,*Rc*]-**V·1a**	65	63(*S*)
2	*S*[*Rp*,*Sp*,*Rc*,*Rc*]-**V·1b**	68	66(*R*)
3	*R*[*Sp*,*Sp*,*Rc*,*Rc*]-**V·1c**	95	73(*R*)
4	*S*[*Rp*,*Rp*,*Rc*,*Rc*]-**V·2a**	90	33(*S*)
5	**V·2b**	74	28(*S*)
6	*R*[*Sp*,*Sp*,*Rc*,*Rc*]-**V·4a**	43	30(*R*)
7	*R*[*Sp*,*Sp*,*Sc*,*Sc*]-**V·5a**	17	Nd
8	*R*[*Sp*,*Rp*,*Sc*,*Sc*]-**V·5b**	96	25(*R*)
9	*S*[*Rp*,*Rp*,*Sc*,*Sc*]-**V·5c**	21	44(*S*)
10	**V·6a**	100	43 (*S*)
11	*S*[*Rp*,*Rp*,*Rc*]-**V·6b**	97	52(*R*)

[a] Reactions conditions: 1 mmol of 1,3-diphenylprop-2-enylacetate, 3 mmol of dimethylmalonate with 1% palladium as $[PdCl(allyl)]_2$, BSA–AcOK, CH_2Cl_2 at 40 °C, 24 hours. [b] Determined by ^1H NMR. [c] Determined by ^1H NMR using the chiral shift reagent $Eu(hfc)_3$. [d] Determined on the basis of the sign of the specific rotation of the product.

73% (*S*) and 52% (*R*), respectively, and yields of 95 and 97%. These catalytic results are comparable with those obtained with axially chiral thioether–phosphine sulfide ligands with a binaphthalene framework[3b] in the same reaction, but remain lower than those reported with ferrocenyl thioether–phosphine sulfides with planar chirality[19] which are the best *S*,*S* ligands in term of activity and enantioselectivity.

An inspection of the above results shows that the sense of enantioselectivity is predominantly controlled by the configuration of the phosphorus stereocenters. The (*S*) enantiomer is obtained with the (*Rp*,*Rp*) configuration of the ligand (entries 1, 4 and 9) whereas the (*R*) enantiomer is obtained with the (*Sp*,*Sp*) (entries 3 and 6) or (*Rp*,*Sp*) (*Sp*,*Rp*) (entries 2 and 8) configuration of the ligand.

Surprisingly, we can note that the enantiomeric excesses are independent of the absolute configurations of the ligand. Indeed, the same level of enantioselectivity was obtained using ligands **V·1a**, **V·1b**, **V·1c**. which have different axial and central configurations. The reaction occurred with 63% ee for **V·1a**, 60% for **V·1b** and 73% for **V·1c** (comparison entries 1, 2 and 3). In addition, all of these three ligands give active palladium catalyst since the conversion of the substrate in 24 h was 65% for **V·1a**, 68% for **V·1b** and 95% for **V·1c**.

From such results, the question arises on the nature of the catalytic species. Generally, the catalysts used in palladium-mediated allylic reaction consist of a complex containing a chiral chelate ligand. On careful examination of the structure of the three diastereoisomers of the ligand **V·1** (Fig. 2), only the ligand *S*[*Rp*,*Sp*,*Rc*,*Rc*]-**V·1b** can behave like a chelate ligand. For the ligands *S*[*Rp*,*Rp*,*Rc*,*Rc*]-**V·1a** and *R*[*Sp*,*Sp*,*Rc*,*Rc*]-**V·1c**, as no rotation around the C–C bond linking the two phosphorus atoms occurred even at 100 °C in toluene according to NMR studies, these ligands behave either like monodentate ligands leading to mononuclear complexes or like bidentate ligands leading to polynuclear complexes. Coordination chemistry of these *S*,*S*-ligands towards palladium are still to be understood and further investigations ought to be conducted.

Finally, it appeared interesting to us to compare the catalytic performance of palladium catalytic systems containing diphosphine sulfides **V** with those obtained with the corresponding diphosphines **IV** (Table 3). Using diphosphines **IV**, the palladium catalytic systems are more active for this allylic substitution than disulfides **V** since complete conversion of the substrate was achieved at room temperature after reaction time varying from 1.5 to 5 h. However, the enantioselectivities are significantly lower with all of the diphosphines **IV** (compare runs 1, 2 and 3 to run 11; runs 4, 5 to run 12, runs 7, 8 to run 15 and runs 10, 11 to run 16) except with ligand **IV·3** (compare run 6 to run 14).

Table 3 Palladium-catalyzed asymmetric allylic alkylation with diphosphines **IV** [a]

Run	Ligand	Reaction time/h	Conversion (%)[b]	ee (%)[c](configuration)[d]
11	**IV·1**	7	40	8 (*R*)
12	**IV·2**	5	54	16 (*S*)
13	**IV·3**	1.5	100	10 (*R*)
14	**IV·4**	4	100	66 (*R*)
15	**IV·5**	2.5	100	33 (*S*)
16	**IV·6**	5	100	14 (*S*)

[a] Reactions conditions: 1 mmol of 1,3-diphenylprop-2-enylacetate, 3 mmol of dimethylmalonate with 1% palladium as $[PdCl(allyl)]_2$, BSA–AcOK, CH_2Cl_2 at RT. [b] Determined by ^1H NMR. [c] Determined by ^1H NMR using the chiral shift reagent $Eu(hfc)_3$. [d] Determined on the basis of the sign of the specific rotation of the product.

In summary, we have demonstrated that chiral diphosphine sulfides derived from 2,2′-biphosphole can act as a chiral ligand for Pd and provide enantioselectivity up to 73% in asymmetric allylic alkylation. Use of these new *S*,*S*-ligands in other asymmetric catalytic reactions is currently in progress.

Experimental

General methods

All reactions were carried out under dry argon by using Schlenk glassware and vacuum line techniques. Solvents were freshly distilled from standard drying agents. 1D and 2D NMR experiments were carried out using the Bruker AV 500 instrument. ^1H-2D-COSY45{^{31}P} and ^1H–^{13}C{^{31}P} (HMQC, HMBC) methods using

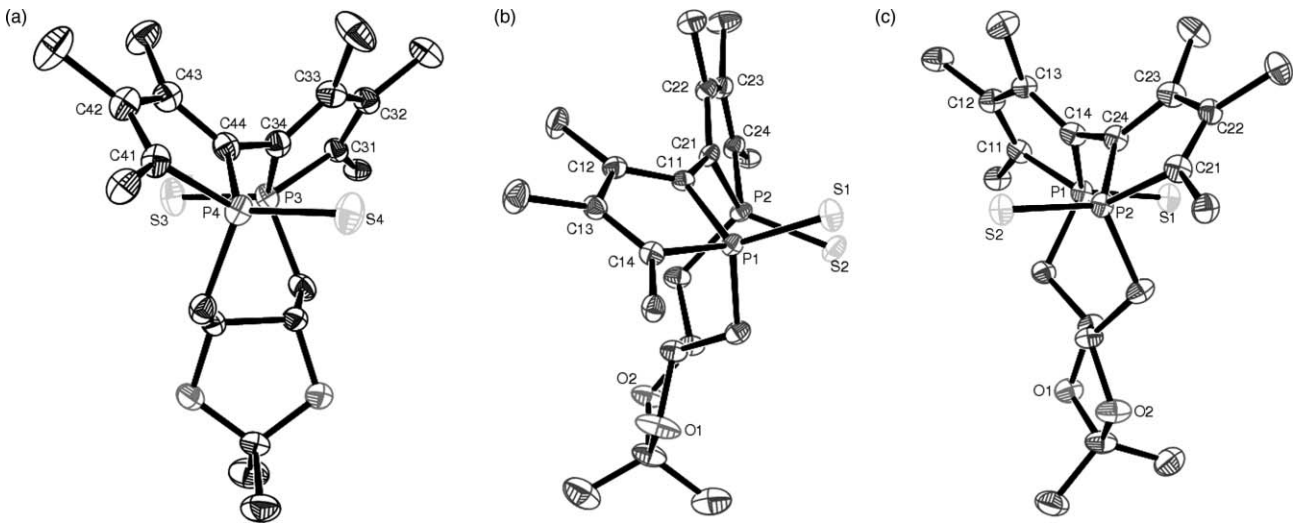


Fig. 2 Molecular view of *S*[*Rp*,*Rp*,*Rc*,*Rc*]-**V·1a**, *S*[*Rp*,*Sp*,*Rc*,*Rc*]-**V·1b** and *R*[*Sp*,*Sp*,*Rc*,*Rc*]-**V·1c** [5]

standard pulse sequences have been employed to establish atom connectivity and spatial relationships. Mass spectra were obtained on a TSQ 7000 Thermoquest instrument (DCI). Optical rotations were measured with a Perkin Elmer 241 polarimeter.

1-Phenyl-3,4-dimethylphosphole **1**,[8] tetraphosphole **2**,[9] enantiomerically pure diol dimesylates (*S*)-**4**,[20] (*S*,*S*)-**5**,[21] (*S*,*S*)-**6**[22] and diphosphine disulfides **V·1**, **V·2** and **V·3**[5] were prepared as described in the literature.

General procedure for compounds V·2, V·4 and V·6

In a Schlenk tube, naphthalene (0.02 g, 1.88 mmol) was stirred with an excess of sodium (~0.5 g) in dry THF (6 ml) until the solution became green. Solid tetramer **1** (400 mg, 0.54 mmol) was then added slowly in portions. The reaction mixture turned red and was stirred until it became green again (~2 h). This solution of dianion **2** and a THF solution (6 ml) of dimesylate (1.08 mmol) were transferred dropwise by cannula at the same time into an other Schlenk containing 200 ml of dry THF and the reaction mixture was stirred for 16 h at room temperature. After evaporation to dryness, the resulting residue was extracted with small portions of pentane. The combined pentane extracts were filtered through celite and the solvents were evaporated to give crude diphosphine **IV**. Sulfur (2 equivalents) was added to a solution of compound **IV** in dichloromethane (30 ml) and the reaction mixture was stirred overnight at room temperature. After evaporation to dryness, the mixture was chromatographed on silica gel.

S[*Rp*,*Rp*,*Rc*,*Rc*]-(−)-*P*,*P*-disulfur-1,1′-(2,7-dimethyloctane-3,6-diyl)-3,3′,4,4′-tetramethyl-5,5′-diphenyl-2,2′-biphosphole; V·2a

Eluent: pentane–dichloromethane: 60 : 40. Yellow solid. Yield: 28% (0.173 mg, 0.300 mmol). $[\alpha]_D = -290.1$ (*c* 1.0, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ 0.79 (dd, $J_{H,H}$ = 20.0 Hz, $J_{H,H}$ = 5.0 Hz, 12H, $(CH_3)_2$–CH), 1.96 (m, 4H, CH_2), 2.08 (s, 6H, CH_3–C–C), 2.16 (d, $J_{H,P}$ = 3.2 Hz, 6H, CH_3–C–CPh), 2.25 (m, 2H, CH–$(CH_3)_2$), 2.52 (m, 2H, CH–P), 7.36 (m, 2H, Ph), 7.43 (m, 4H, Ph) 7.87 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 15.36 (dd, $J_{C,P}$ = 10.0 Hz, $J_{C,C}$ = 150.9 Hz, CH_3–C–C), 16.98 (s, CH_3–C–CPh), 22.83 (d, $J_{C,P}$ = 15.0 Hz, CH_2), 25.48 (s, CH_3), 27.24 (s, CH_2), 29.72 (s, CH_3), 32.73 (s, $CH(CH_3)_2$), 58.35 (d, $J_{C,P}$ = 41.2 Hz, CH), 128.05(s, Ph) 128.45 (s, Ph) 129.06 (s, Ph), 134.54 (d, $J_{C,P}$ = 70.0 Hz, C–P), 135.11 (d, $J_{C,P}$ = 12.5 Hz, Ph–*C*–P), 147.31 (d, $J_{C,P}$ = 18.8 Hz, CH_3–*C*–C), 154.19 (d, $J_{C,P}$ = 30.0 Hz, CH_3–*C*–C–Ph). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 68.95 (s). MS (DCI, NH_3): *m*/*z* (%) = 577 (100%) $[M + H]^+$.

(−)-*P*,*P*-Disulfur-1,1′-(2,7-dimethyloctane-3,6-diyl)-3,3′,4,4′-tetramethyl-5,5′-diphenyl-2,2′-biphosphole; VI·2b

Eluent: pentane–dichloromethane: 40 : 60. Yellow solid. Yield: 27% (0.167 mg, 0.299 mmol). $[\alpha]_D = -115.1$ (*c* 1.4, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ 0.29 (d, $J_{H,P}$ = 5.0 Hz, 3H, $(CH_3)_2$–CH), 0.43 (d, $J_{H,H}$ = 5.0 Hz, 3H, $(CH_3)_2$–CH), 0.81 (d, $J_{H,P}$ = 10.0 Hz, 3H, $(CH_3)_2$–CH), 1.03 (d, $J_{H,H}$ = 10.0 Hz, 3H, $(CH_3)_2$–CH), 1.81 (m, 4H, CH_2), 1.99 (m, 6H, CH_3–C–C), 2.05 (s, 3H, CH_3–C–CPh), 2.09 (d, $J_{H,P}$ = 3.2 Hz, 3H, CH_3–C–CPh), 2.38 (m, 2H, CH–$(CH_3)_2$), 4.76 (m, 2H, CH–P), 7.36 (m, 6H, Ph), 7.71 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 15.25 (dd, $J_{C,P}$ = 12.5 Hz, $J_{C,C}$ = 25.0 Hz, CH_3–C–C), 16.31 (d, $J_{C,P}$ = 10.0 Hz, CH_3–C–CPh), 22.85 (d, $J_{C,P}$ = 10.0 Hz, CH_2), 24.31 (s, CH_3), 27.86 (s, CH_2), 29.73 (s, CH_3), 31.32 (s, $CH(CH_3)_2$), 48.87 (d, $J_{C,P}$ = 37.5 Hz, CH), 127.55 (s, Ph) 128.17 (s, Ph) 129;31 (s, Ph), 134.96 (d, $J_{C,P}$ = 45.0 Hz, C–P), 135.48 (d, $J_{C,P}$ = 12.5 Hz, Ph–*C*–P), 149.16 (m, CH_3–*C*–C), 149.96 (m, CH_3–*C*–C–Ph). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 66.51 (s). MS (DCI, NH_3): *m*/*z* (%) = 577 (100%) $[M + H]^+$.

R[*Sp*,*Sp*,*Rc*,*Rc*]-(+)-*P*,*P*-Disulfur-1,1′-(1,3-diphenylpropane-1,3-diyl)-3,3′,4,4′-tetramethyl-5,5′-diphenyl-2,2′-biphosphole; V·4

Eluent: pentane–dichloromethane: 60 : 40. Yellow solid. Yield: 35% (0.237 mg, 0.376 mmol). $[\alpha]_D$ = + 130.6 (*c* 0.6, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ 2.01 (d, $J_{H,P}$ = 5.0 Hz, 6H, CH_3–C–C), 2.14 (s, 6H, CH_3–C–CPh), 2.69 (m, 2H, CH_2), 4.65 (m, 2H, CH–P), 6.84 (m, 6H, Ph), 7.02 (m, 10H, Ph) 7.22 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 15.09 (d, $J_{C,P}$ = 1.3 Hz, CH_3–C–CPh), 15.69 (d, $J_{C,P}$ = 1.3 Hz, CH_3–C–C), 41.47 (s, CH_2), 44.32 (d, $J_{C,P}$ = 50.0 Hz, CH), 126.83 (s, *C*–P), 127.48 (s, C_{para}), 128.09 (s, C_{meta}), 128.89 (s, C_{ortho}), 133.58 (dd, $J_{C,P}$ = 75.0 Hz, $J_{C,P}$ = 12.4 Hz, Ph–*C*–P), 133.46 (d, $J_{C,P}$ = 10.0 Hz, C_{ipso}), 137.49 (d, $J_{C,P}$ = 75.0 Hz, CH_3–*C*–C), 148.21 (m, CH_3–*C*–C–Ph). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 53,12 (s). MS (DCI, NH_3): *m*/*z* (%) = 631 (100%) $[M + H]^+$. Crystals suitable for X-ray analysis were obtained by slow evaporation of a dichloromethane solution.

(−)-*P*,*P*-Disulfur-1,1′-(butane-1,3-diyl)-3,3′,4,4′-tetramethyl-5,5′-diphenyl-2,2′-biphosphole; V·6a

Eluent: pentane–dichloromethane: 66 : 34. Yellow solid. Yield: 42% (0.222 mg, 0.451 mmol). $[\alpha]_D = -8.3$ (*c* 1.1, CH_2Cl_2). mp = 245–250 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 0.80 (dd, $J_{H,P2}$ = 15.0 Hz, $J_{H,H}$ = 5.0 Hz, 3H, CH_3–CH), 1.28 (m, 2H, CH_2–CH), 2.10 (m, 12H, CH_3–C), 2.80 (m, 1H, CH_2–P1), 3.17 (m, 1H, CH–P2), 3.67 (m, 1H, CH_2–P1), 7.39 (m, 6H, Ph), 7.53 (m, 2H, Ph), 7.71 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 15.24 (d, $J_{C,P1}$ = 13.6 Hz, CH_3–C–CPh), 15.33 (d, $J_{C,P2}$ = 11.3 Hz, CH_3–C–CPh), 15.58 (dd, $J_{C,P1}$ = 12.5 Hz, $J_{C,P}$ = 2.2 Hz, CH_3–C–C), 15.78 (dd, $J_{C,P2}$ = 12.5 Hz, $J_{C,P1}$ = 2.2 Hz, CH_3–C–C), 17.13 (d, $J_{C,P}$ = 0.5 Hz, CH_3–CH), 25.90 (dd, $J_{C,P2}$ = 45.6 Hz, $J_{C,P1}$ = 3.8 Hz, CH), 27.30 (t, $J_{C,P}$ = 2.94 Hz, CH_2–CH), 32.98 (dd, $J_{C,P1}$ = 2.94 Hz, $J_{C,P2}$ = 40.8 Hz, CH_2–P2), 128.48 (s, Ph) 128.65 (s, Ph), 129.02 (s, C_{ortho}), 130.66 (d, Ph–C–P), 130.90 (d, C–Ph), 132.77 (d, $J_{C,P}$ = 6.3 Hz, C_{ipso}), 147.58 (d, $J_{C,P}$ = 23.9 Hz, CH_3–*C*–C), 148.53 (dd, $J_{C,P}$ = 28.6 Hz, $J_{C,P}$ = 3.4 Hz, CH_3–*C*–C–Ph). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 51.53 (d, P1, $J_{P1,P2}$ = 2.0 Hz)), 59.64 (d, P2, $J_{P1,P2}$ = 2.0 Hz). MS (DCI, NH_3): *m*/*z* (%) = 493 (100%) $[M + H]^+$.

S[*Rp*,*Rp*,*Rc*]-(−)-*P*,*P*-Disulfur-1,1′-(butane-1,3-diyl)-3,3′,4,4′-tetramethyl-5,5′-diphenyl-2,2′-biphosphole; IV·6b

Eluent: pentane–dichloromethane: 34 : 66. Yellow solid. Yield: 28% (0.148 mg, 0.301 mmol). $[\alpha]_D = -173.6$ (*c* 1.0, CH_2Cl_2). mp = 230–235°C. ^1H NMR (500 MHz, $CDCl_3$): δ 1.23 (dd, $J_{H,P}$ = 15.0 Hz, $J_{H,H}$ = 5.0 Hz, 3H, CH_3–CH), 1.27 (m, 2H, CH_2–CH), 2.11 (d, $J_{H,P1}$ = 2.5 Hz, 3H, CH_3–C–C), 2.17 (d, $J_{H,P}$ = 2.5 Hz, 3H, CH_3–C–C), 2.19 (dd, $J_{H,P1}$ = 5.0 Hz, $J_{H,H}$ = 2.5 Hz, 3H, CH_3–C–CPh), 2.24 (dd, $J_{H,H}$ = 2.6 Hz, $J_{H,P2}$ = 5.0 Hz, 6H, CH_3–C–CPh), 2.30 (m, 1H, CH–P2), 2.44 (m, 1H, CH_2–P1), 2.64 (m, 1H, CH_2–

P1), 7.36 (m, 2H, Ph), 7.43 (m, 4H, Ph), 7.57 (m, 2H, Ph), 7.68 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 15.22 (d, $J_{C,P1}$ = 13.6 Hz, CH_3–C–CPh), 15.30 (d, $J_{C,P2}$ = 11.3 Hz, CH_3–C–CPh), 16.07 (d, $J_{C,P1}$ = 12.5 Hz, CH_3–C–C), 16.29 (d, $J_{C,P2}$ = 12.5 Hz, CH_3–C–C), 23.32 (d, $J_{C,P}$ = 0.5 Hz, CH_3–CH), 28.96 (d, $J_{C,P2}$ = 45.6 Hz, CH), 29.30 (d, $J_{C,P}$ = 2.94 Hz, CH_2–CH), 37.52 (d, $J_{C,P2}$ = 40.8 Hz, CH_2–P2), 128.14 (s, Ph) 128.19 (s, Ph), 128.66 (s, C_{ortho}), 128.89 (s, Ph–*C*–P), 128.92 (s, *C*–Ph), 148.72 (d, $J_{C,P}$ = 6.3 Hz, C_{ipso}), 151.44 (d, $J_{C,P}$ = 23.9 Hz, CH_3–*C*–C), 151.77 (dd, $J_{C,P}$ = 28.6 Hz, $J_{C,P}$ = 3.4 Hz, CH_3–*C*–C–Ph). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ 54.82 (d, P1), 64.47 (d, P2, *J*P1,P2 = 2.0 Hz). MS (DCI, NH_3): *m*/*z* (%) = 493 (100%) $[M + H]^+$.

General procedure for the allylic substitution reaction

A mixture of ligand **V**, 1,3-diphenylprop-2-enylacetate (0.413 g, 1.63 mmol) and $[(Pd(C_3H_5)Cl)]_2$ (3 mg, 0.03 mmol) in dry dichloromethane (20 mL) was stirred at room temperature for 2 h. To the resulting solution were added dimethyl malonate (0.374 mL, 3.25 mmol), small amount of potassium acetate and BSA (0.300 mL, 3.25 mmol). The reaction was carried out at 40 °C during 24 hours. 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 Et_2O, the combined organic layers were dried over sodium sulfate, filtered and evaporated. The conversion was calculated from the crude reaction mixture by ^1H 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 ^1H NMR using the chiral shift reagent $Eu(hfc)_3$.

X-Ray crystallographic study†

R[*Sp*,*Sp*,*Rc*,*Rc*]-(+)-*P*,*P*-Disulfur-1,1′-(1,3-diphenylpropane-1,3-diyl)-3,3′,4,4′-tetramethyl-5,5′-diphenyl-2,2′-biphosphole, **V**·**4**.

A single crystal was mounted under inert perfluoropolyether at the tip of a glass fiber and cooled in the cryostream of an Oxford-Diffraction XCALIBUR CCD diffractometer for. Data were collected using monochromatic Mo Kα radiation (λ = 0.71073). The structures was solved by direct methods (SIR97[23]) and refined by least-squares procedures on F^2 using SHELXL-97.[24] All H atoms were introduced in calculation in idealized positions and treated as riding on their parent C atoms. The drawing of the molecule was realized with the help of ORTEP-3.[25]

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