

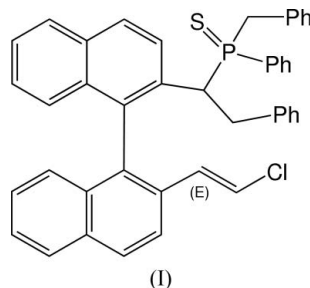
2-[1-(Benzylphenylphosphinothioyl)-2-phenylethyl]-2'-[(*E*)-2-chlorovinyl]-1,1'-binaphthylPeter Kasák,^a Michael Widhalm^a
and Kurt Mereiter^{b*}^aInstitute of Organic Chemistry, University of Vienna, Währinger Strasse 38, A-1090 Vienna, Austria, and ^bInstitute of Chemical Technologies and Analytics, Vienna University of Technology, Getreidemarkt 9/164SC, A-1060 Vienna, AustriaCorrespondence e-mail:
kurt.mereiter@tuwien.ac.at

Key indicators

Single-crystal X-ray study
T = 173 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.045
wR factor = 0.121
Data-to-parameter ratio = 24.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.The title compound, C₄₃H₃₄ClPS, is an unexpected reaction product that formed in the benzylation of a dinaphthophosphepine sulfide after addition of dichloromethane in the presence of a strong base. It contains the rare functional group 2-chlorovinyl in an *E* configuration, with C—C bond lengths of 1.471 (2) and 1.321 (2) Å, and a C—Cl bond length of 1.725 (2) Å.

Comment

1,1'-Binaphthyl-based mono- and diphosphines are axial-chiral ligands with high potential as chiral auxiliaries, particularly in transition-metal-catalyzed asymmetric transformations (Gladiali *et al.*, 1994; Xiao *et al.*, 1999; Chi & Zhang, 2002; Shimizu *et al.*, 2005). During ongoing research in this field (Kasák *et al.*, 2005; Widhalm & Mereiter, 2003), the dibenylation of a dinaphthophosphepine, namely 4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*;1',2'-*e*]phosphepine sulfide, at its two CH₂ groups was of interest. The synthetic methodology involves carbanion formation by treatment of the educt with *tert*-butyllithium, reaction with benzyl bromide, quenching of the mixture with water, and work-up of the product by extraction with CH₂Cl₂ followed by further purification. In order to test various work-up procedures the sequence of first adding CH₂Cl₂ and then water was investigated. The title compound, (I), was obtained as a by-product of this procedure. As the nature of this compound remained unclear after NMR spectroscopy, it was recrystallized and subjected to an X-ray structure analysis. The result is shown in Fig. 1. As the reaction with benzyl bromide was obviously incomplete, we suggest that the seven-membered ring was *C*-alkylated by a CH₂Cl group from CH₂Cl₂, then opened by excess of base to form a 2-chlorovinyl group, whereupon two benzylations took place to form the final product, (I).



Bond lengths and angles in the naphthalene and benzene ring systems show normal values; the C—C ring bond lengths have mean values of 1.40 (3) Å for naphthalene and 1.387 (9) Å for benzene. The angle between the two naph-

Received 15 August 2005
Accepted 20 October 2005
Online 16 November 2005

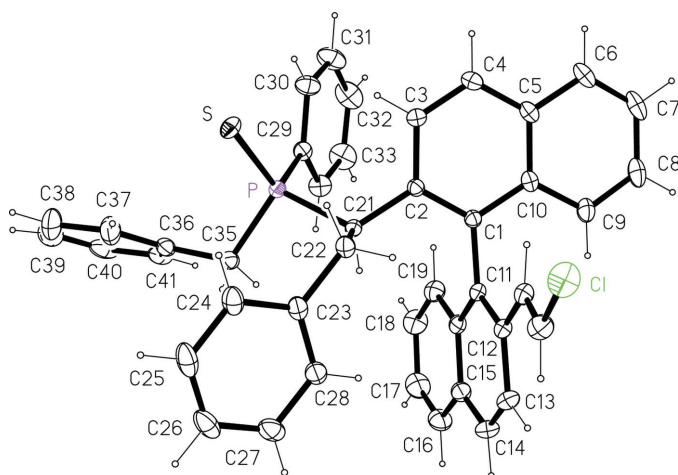


Figure 1
Perspective view of (I). Displacement ellipsoids are drawn at the 30% probability level.

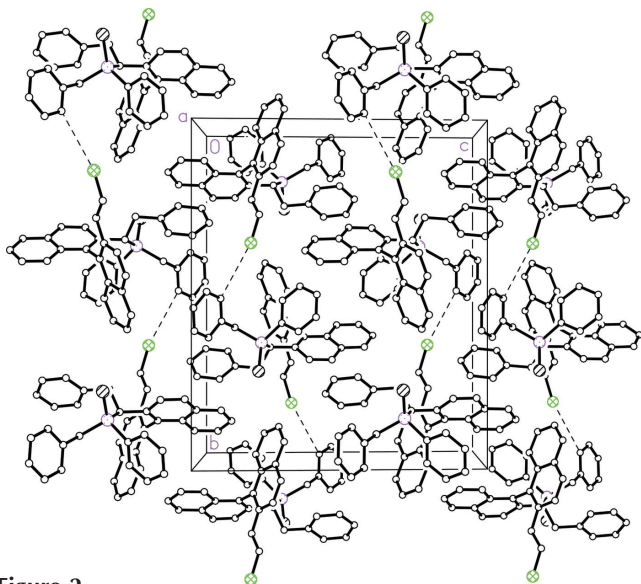


Figure 2
Packing diagram of (I), viewed down *a*, with C41—H41...Cl interactions shown as dashed lines. H atoms have been omitted.

thalene systems, which show relatively small r.m.s. deviations from planarity of 0.027 and 0.021 Å, is 87.69 (2)°, corresponding to a relaxed 1,1'-binaphthyl system. Phosphorus exhibits a comparatively distorted tetrahedral coordination involving four chemically different substituents (Table 1). Most interesting is the *E*-configured 2-chlorovinyl group. Such groups have as yet been studied only rarely by X-ray crystallography, and of the 15 cases found in the Cambridge Structural Database (CSD, Version 5.24; Allen, 2002), ten are bioactive natural halogenated monoterpenes (*e.g.* Rivera *et al.*, 1998; König *et al.*, 1999) with (*E*)-2-chlorovinyl groups bonded to saturated ring C atoms at C—C distances of about 1.52 Å, *i.e.* distinctly larger than in (I). Only a single example, *viz.* 3-[(*E*)-2'-chlorovinyl]-2-hydroxy-2-cyclopentenone (Tsuboi *et al.*, 1983), was found where a 2-chlorovinyl group is bound to an unsaturated ring C atom. The bond lengths and angles in this group (C—C = 1.430 Å, C=C = 1.324 Å, C—Cl =

1.719 Å, C—C=C = 122.0°, and C=C—Cl = 122.9°) compare favourably with those of (I) (Table 1). (*Z*)-2-Chlorovinyl groups were reported for only two organometallic crystal structures (Bruce *et al.*, 1998; Schottenberger *et al.*, 2001). It should be added here, that the 2-chlorovinyl group in (I) is inclined to the naphthyl ring system 1 by only 10.1 (2)°. This leads to an unfavourably short intramolecular H43...H13 contact of only 2.07 Å, in compensation for which two favourable intermolecular C—H...S(1 + *x*, *y*, *z*) contacts (H43...S = 2.89 Å and H13...S = 3.06 Å) are formed. Further intermolecular interactions contributing to the coherence of the crystal structure (Fig. 2) are a C41—H41...Cl($\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$) bond (H41...Cl = 2.90 Å) and some C—H... π and arene π — π stacking interactions. Examples of C—H... π interactions are H14...C40($1 + x, y, z$) = 2.69 Å and H4...C27($-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$) = 2.86 Å; an example of π — π stacking is ring C36—C41 and its centrosymmetric equivalent (symmetry code: $-x, -y, 1 - z$) with a ring—ring perpendicular distance of 3.294 (1) Å. For clarity, only the C41—H41...Cl interactions (broken lines) are drawn in Fig. 2.

Experimental

A stirred solution of 3-benzyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine sulfide (473 mg, 0.93 mmol) in anhydrous and degassed tetrahydrofuran (20 ml) was cooled to 195 K and a solution of *t*-BuLi (1.5 *M*, 1.1 ml, 1.6 mmol) in pentane was added dropwise. The dark-red solution was allowed to warm to 233 K over 2 h and then again cooled to 195 K. Benzyl bromide (10 mmol) in tetrahydrofuran (10 ml) was added dropwise over 15 min and the mixture was allowed to reach 293 K. After stirring for 1 h, CH₂Cl₂ (50 ml) was added followed by water. Extractive work-up and column chromatography (SiO₂; eluent CH₂Cl₂/PE, 7:3 *v/v*) afforded 3,5-dibenzyl-4-phenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1',2'-*e*]phosphepine sulfide (61%) and (I) (112 mg, 19%). Crystals for X-ray diffraction were obtained by slow diffusion of hexane into a saturated solution of (I) in toluene. ¹H NMR (CDCl₃): δ 8.54 (*d*, *J* = 8.4 Hz, 1H), 8.19 (*d*, *J* = 8.7 Hz, 1H), 8.10 (*d*, *J* = 8.0 Hz, 1H), 7.92 (*d*, *J* = 8.7 Hz, 1H), 7.82 (*d*, *J* = 8.0 Hz, 1H), 7.77 (*d*, *J* = 8.7 Hz, 1H), 7.64 (*ddd*, *J* = 1.0, 7.0, 8.0 Hz, 1H), 7.50–7.15 (*m*, 13H), 6.94 (*d*, *J* = 8.4 Hz, 2H), 6.88–6.82 (*m*, 3H), 6.73 (*d*, *J* = 13.6 Hz, AB, 1H), 6.33–6.29 (*m*, 2H), 6.27 (*d*, *J* = 13.6 Hz, AB, 1H), 4.17–4.08 (*m*, 1H), 3.61–3.31 (*m*, 2H), 2.60 (*dd*, *J* = 10.3, 13.4 Hz, 1H), 1.91 (*dd*, *J* = 14.4, 14.9 Hz, 1H). ¹³C NMR (CDCl₃): δ 139.57, 137.32, 137.30, 133.94, 133.38, 133.05, 132.84, 132.71, 132.69, 132.62, 132.20, 132.11, 131.51, 131.12, 131.08, 131.04, 130.96, 129.95, 129.89, 129.48, 129.14, 129.02, 128.74, 128.58, 128.50, 128.29, 128.21, 128.11, 128.04, 127.56, 127.46, 127.45, 127.43, 126.91, 126.82, 126.78, 126.58, 126.51, 126.49, 126.47, 126.45, 126.28, 125.82, 122.97, 120.73, 46.37, 45.90, 40.76, 40.31, 39.21. ³¹P NMR (CDCl₃): δ 56.76.

Crystal data

C₄₅H₃₄ClPS
M_r = 649.18
 Monoclinic, *P*2₁/*n*
a = 10.6924 (4) Å
b = 19.6175 (7) Å
c = 16.5993 (6) Å
 β = 93.773 (1)°
V = 3474.3 (2) Å³
Z = 4

D_x = 1.241 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 9934 reflections
 θ = 2.2–29.9°
 μ = 0.25 mm⁻¹
T = 173 (2) K
 Spheroid, colorless
 0.58 × 0.54 × 0.52 mm

Data collection

Bruker SMART APEX CCD diffractometer	10126 independent reflections
ω scans	8519 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$R_{\text{int}} = 0.026$
$T_{\text{min}} = 0.80$, $T_{\text{max}} = 0.88$	$\theta_{\text{max}} = 30.0^\circ$
51340 measured reflections	$h = -15 \rightarrow 15$
	$k = -27 \rightarrow 27$
	$l = -23 \rightarrow 23$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0712P)^2 + 0.7845P]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.121$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.69 \text{ e } \text{\AA}^{-3}$
10126 reflections	$\Delta\rho_{\text{min}} = -0.27 \text{ e } \text{\AA}^{-3}$
415 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (\AA , $^\circ$).

P—C29	1.8113 (12)	C21—C2	1.5175 (15)
P—C35	1.8328 (12)	C21—C22	1.5503 (16)
P—C21	1.8678 (11)	C12—C42	1.4705 (19)
P—S	1.9538 (4)	C42—C43	1.3208 (19)
C1—C11	1.4966 (15)	C43—Cl	1.7253 (16)
C29—P—C35	107.34 (6)	C35—P—S	114.00 (4)
C29—P—C21	106.41 (5)	C21—P—S	113.15 (4)
C35—P—C21	101.85 (5)	C12—C42—C43	124.70 (13)
C29—P—S	113.19 (4)	C42—C43—Cl	122.49 (12)
C2—C1—C11—C12	-90.49 (14)	C12—C42—C43—Cl	-176.72 (10)
C11—C12—C42—C43	168.68 (13)		

All H atoms are attached to carbon and unambiguously defined by normal stereochemistry. They were placed in calculated positions and

constrained to ride on their parent atoms with C—H distances in the range 0.95–1.00 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1999); software used to prepare material for publication: SHELXTL.

Financial support by the FWF Austrian Science Fund (Lise Meitner grant M852-N11 to PK) is gratefully acknowledged.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Bruce, M. I., Hinterding, P., Low, P. J., Skelton, B. W. & White, A. H. (1998). *J. Chem. Soc. Dalton Trans.* pp. 467–473.
- Bruker (1999). SAINT (Version 6.01), SMART (Version 5.054) and SHELXTL (Version 5.1). Bruker AXS Inc., Madison, Wisconsin, USA.
- Chi, Y. & Zhang, X. (2002). *Tetrahedron Lett.* **43**, 4849–4852.
- Gladiali, S., Dore, A., Fabbri, D., De Lucchi, O. & Manassero, M. (1994). *Tetrahedron Asymmetry*, **5**, 511–514.
- Kasák, P., Widhalm, M. & Mereiter, K. (2005). *Tetrahedron Asymmetry*, **16**, 3416–3426.
- König, G. M., Wright, A. D. & Linden, A. (1999). *Phytochemistry*, **52**, 1047–1053.
- Rivera, P., Manríquez, V. & Wittke, O. (1998). *Acta Cryst.* **C54**, 816–818.
- Schottenberger, H., Lukasser, J., Reichel, E., Müller, A. G., Steiner, G., Kopacka, H., Wurst, K., Ongania, K. H. & Kirchner, K. (2001). *J. Organomet. Chem.* **637–639**, 558–576.
- Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
- Sheldrick, G. M. (2003). SADABS. Version 2.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Shimizu, H., Nagasaki, I. & Saito, T. (2005). *Tetrahedron*, **61**, 5405–5432.
- Tsuboi, S., Arisawa, K., Takeda, A., Sato, S. & Tamura, C. (1983). *Tetrahedron Lett.* **24**, 2393–2394.
- Widhalm, M. & Mereiter, K. (2003). *Bull. Chem. Soc. Jpn.* **76**, 1233–1244.
- Xiao, D., Zhang, Z. & Zhang, X. (1999). *Org. Lett.* **1**, 1679–1681.