

Racemic (1*SR*,2*SR*,7*aRS*)-1,2,7*a*-trihydroxy-2-methylperhydro-1-phosphaindene 1-oxide monohydrate**Rafal Kruszynski,^{a*} Agata Trzesowska,^a Piotr Majewski^b and Ryszard Bodalski^b**^aInstitute of General and Ecological Chemistry, Technical University of Łódź, ul. Żeromskiego 116, 90-924 Łódź, Poland, and ^bInstitute of Organic Chemistry, Technical University of Łódź, ul. Żeromskiego 116, 90-924 Łódź, Poland

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Key indicatorsSingle-crystal X-ray study
T = 291 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.028
wR factor = 0.079
Data-to-parameter ratio = 20.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title racemic compound, C₉H₁₉O₅P, all interatomic C—C and C—OH distances can be considered normal. The P—O and P=O distances are 1.5583 (8) and 1.5003 (7) Å, respectively. The rings are *cis*-fused, the phospholane ring exists in a slightly distorted envelope conformation and the cyclohexane ring adopts an almost ideal chair conformation. All hydroxyl groups are *anti* to the P=O bond. Molecules are linked *via* medium-strength intermolecular O—H···O hydrogen bonds into a three-dimensional network.

Received 4 November 2005

Accepted 8 November 2005

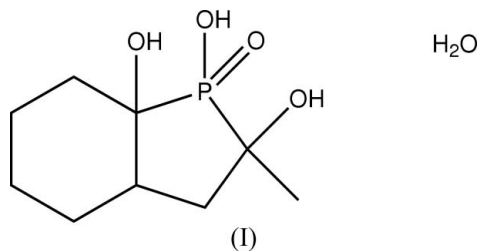
Online 16 November 2005

Comment

The search for new chiral ligands is important for the improvement of both enantioselectivities and reactivities of transition metal-catalysed asymmetric syntheses. Phosphines are one of the most popular ligands in catalytic organometallic transformations. On the basis of their chelating properties, chiral diphosphines have been widely and successfully investigated in many reactions such as Rh-, Ru- and Ir-catalysed hydrogenation of olefinic and carbonyl compounds and Pd-catalysed allylic substitutions (Guillen *et al.*, 2002). However, it was found that for some reactions, the turnover-determining or enantio-determining step involves complexes bearing a monodentate P ligand. Furthermore, the enantio- or regio-reactivities and selectivities displayed by diphosphines are often lower than those of monophosphines (Lagasse & Kagan, 2000; Hayashi, 1999), as shown for Pd-catalysed hydrosilylation of olefins (Hayashi, 1996) and 1,3-dienes (Pedersen & Johannsen, 1999; Hayashi *et al.*, 2001), Pd-catalysed hydrovinylation (Rajanbabu *et al.*, 1999), Pd-catalysed allylation of organometallics (Fiaud & Aribi-Zouioueche, 1985) and stabilized carbanions (Hayashi *et al.*, 1997, 1998; Cheng *et al.*, 1997; Fuji *et al.*, 2000) with allylic carboxylates, Pd-catalysed reduction of allylic esters (Tsuji & Mandai, 1996; Hayashi *et al.*, 1994; Fuji *et al.*, 1998), 1,4-hydroboration of 1,3-enynes (Matsumoto *et al.*, 1993), rhodium(I)-catalysed hydrogenation of 2-acetamidocinnamate (Burk *et al.*, 1991; Claver *et al.*, 2000) and nickel-catalysed cocyclization of triynes (Sato *et al.*, 1994). In addition, chiral monophosphines are used as asymmetric nucleophilic catalysts in kinetic resolution of racemic secondary alcohols through acylation (Vedejs *et al.*, 1996; Vedejs & Daugulis, 1999), in cycloaddition of dienates with electron-deficient olefins (Zhang & Lu, 1995; Zhu *et al.*, 1997) and imines (Xu & Lu, 1999), and in addition reactions to acetylenic esters (Alvarez-Ibarra *et al.*, 2000).

Now we present the structure of racemic (1*SR*,2*SR*,7*aRS*)-1,2,7*a*-trihydroxy-2-methylperhydro-1-phosphaindene 1-oxide hydrate, (I), which can be easily transformed to the chiral monophosphine *via* optically active amines (Dubrovina *et al.*,

2004). Racemic (1*RS*,2*SR*,7*aSR*)-1,2,7*a*-trihydroxy-2-methylperhydro-1-phosphaindene 1-oxide hydrate, (II), a diastereomer of the title compound, has been reported previously (Bartczak & Yagbasan, 1991) in the incorrect space group $P2_1$; the space group was corrected to $P2_1/n$ by Marsh (1994).



A perspective view of (I) is shown in Fig. 1. All interatomic C–C and C–OH distances can be considered normal. The P–O and P=O distances (Table 1) are comparable to those found in other phospholane acids [1.549 (8) and 1.506 (7) Å, respectively, in (II) (Bartczak & Yagbasan, 1991; Marsh, 1994), 1.543 and 1.499 Å in 1-hydroxy2,5-*trans*-diphenylphospholane oxide (Guillen *et al.*, 2002), and 1.564 (2) and 1.498 (2) Å in 1,2,5-trihydroxy-2,5-dimethylphospholane 1-oxide (Galdecki *et al.*, 1985)]. In (I), the rings are *cis*-fused, whereas in (II) they are *trans*-fused. Compared to (II), the phospholane ring of (I) exists in slightly distorted envelope conformation with atom C3 at the flap [asymmetry parameters (Duax & Norton, 1975): $\Delta C_s(P1-C1,C3) = 14.08 (2)^\circ$ and $\Delta C_2(C2-C3,P1) = 8.77 (3)^\circ$]. As in (II), in (I) the cyclohexane ring adopts an almost ideal chair conformation [$\Delta C_s(C3,C7) = 2.75 (9)^\circ$ and $\Delta C_2(C3-C4,C6-C7) = 2.97 (8)^\circ$]. All hydroxyl groups are *anti* to the P=O bond, but in (II), one hydroxyl group is *syn* to the P=O bond. Molecules of (I) are linked *via* medium-strength (Desiraju & Steiner, 1999) intermolecular O–H...O hydrogen bonds (Table 2) into a three-dimensional network (Fig. 2).

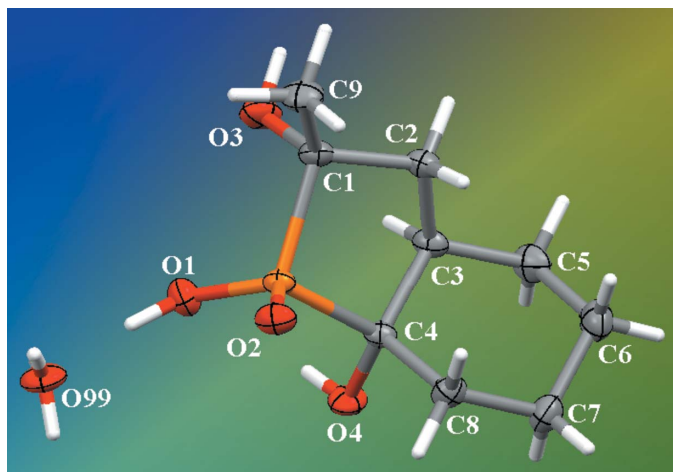


Figure 1
The molecular structure of the title compound, (I). Displacement ellipsoids are drawn at the 50% probability level.

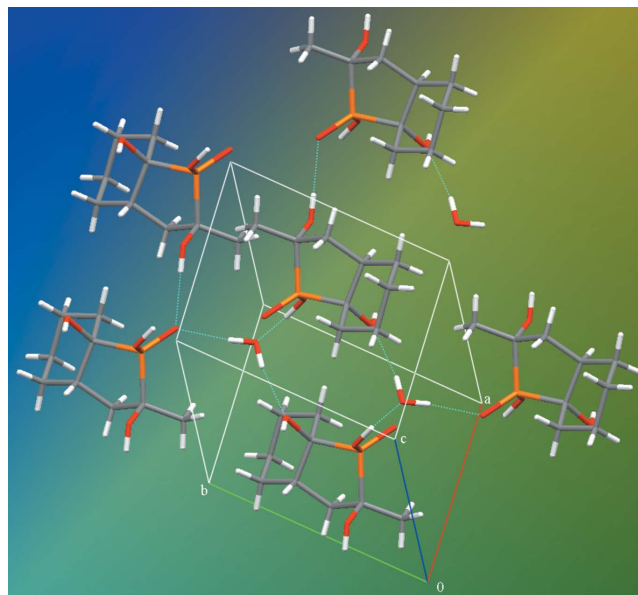


Figure 2
The molecular packing of the title compound, showing intermolecular hydrogen bonds (dashed lines).

Experimental

The title compound was obtained in the double addition reaction of bis(trimethylsilyl)hypophosphite to 2-(2-oxopropyl)cyclohexanone in the presence of trimethylchlorosilane and triethylamine, followed by ethanolysis of the intermediate (Bartczak & Yagbasan, 1991). The crude product obtained after ethanolysis was monohydrate. The water was not used during crystallisation, but the solvents were not dehydrated. Colourless crystals of (I) were obtained from an MeOH–EtOH (1:1 v/v) mixture.

Crystal data

$C_9H_{17}O_4P \cdot H_2O$
 $M_r = 238.21$
Triclinic, $P\bar{1}$
 $a = 6.4427 (3) \text{ \AA}$
 $b = 8.1772 (5) \text{ \AA}$
 $c = 11.3794 (6) \text{ \AA}$
 $\alpha = 69.954 (5)^\circ$
 $\beta = 77.247 (4)^\circ$
 $\gamma = 83.521 (4)^\circ$
 $V = 548.84 (5) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.441 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 5990 reflections
 $\theta = 2-25^\circ$
 $\mu = 0.25 \text{ mm}^{-1}$
 $T = 291.0 (3) \text{ K}$
Prism, colourless
 $0.38 \times 0.30 \times 0.26 \text{ mm}$

Data collection

Kuma KM-4-CCD diffractometer
 ω scans
Absorption correction: numerical (*X-RED32*; Stoe & Cie, 1999)
 $T_{\min} = 0.912$, $T_{\max} = 0.938$
10280 measured reflections
3130 independent reflections

2936 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$
 $\theta_{\max} = 30.7^\circ$
 $h = -9 \rightarrow 8$
 $k = -11 \rightarrow 11$
 $l = -16 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.079$
 $S = 1.11$
3130 reflections
151 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2 + 0.1433P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.27 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.44 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

P1—O2	1.5003 (7)	P1—O1	1.5583 (8)
O2—P1—O1	115.11 (4)	C1—P1—C4	96.99 (4)
O2—P1—C1	113.38 (4)	C2—C1—P1	101.23 (6)
O1—P1—C1	108.51 (4)	C3—C2—C1	107.75 (8)
O2—P1—C4	114.28 (4)	C2—C3—C4	105.90 (7)
O1—P1—C4	106.91 (4)	C3—C4—P1	103.36 (6)
P1—C1—C2—C3	43.86 (8)	C5—C6—C7—C8	−58.56 (12)
C1—C2—C3—C4	−54.42 (9)	C6—C7—C8—C4	57.80 (12)
C2—C3—C4—P1	35.92 (8)	C7—C8—C4—C3	−50.59 (11)
C3—C4—P1—C1	−9.52 (6)	C8—C4—C3—C5	45.38 (11)
C4—P1—C1—C2	−19.04 (6)	C2—C3—C4—C8	−82.09 (9)
C4—C3—C5—C6	−48.11 (12)	C5—C3—C4—P1	163.38 (7)
C3—C5—C6—C7	54.41 (13)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1O...O99	0.93	1.58	2.5062 (11)	178
O3—H3O...O2 ⁱ	0.89	1.98	2.8640 (10)	175
O4—H4O...O1 ⁱⁱ	0.90	2.27	3.1033 (11)	154
O4—H4O...O3 ⁱⁱ	0.90	2.35	2.9435 (11)	123
O99—H99O...O4 ⁱⁱⁱ	0.85 (1)	1.92 (1)	2.7662 (11)	173 (2)
O99—H99P...O2 ^{iv}	0.86 (1)	1.96 (1)	2.8045 (11)	168 (2)

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $-x + 1, -y + 2, -z + 1$.

Carbon-bound H atoms were placed in calculated positions ($C-H = 0.96-0.97$ Å) and were refined as riding on the adjacent C atom, with fixed U values [$U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}(\text{methyl } C)$]. The methyl groups were allowed to rotate about their local threefold axis. The H atoms of the water molecule and hydroxyl groups were found in a difference Fourier synthesis and were assigned individually refined U_{iso} values; the O—H distances were constrained to the values found in the difference map. The H atoms of the hydroxyl groups were allowed to rotate about the C—OH bonds. The H atoms of the water molecule were refined with the O—H distances restrained to $0.84(2)$ Å and the H...H distances restrained to $1.40(4)$.

Data collection: *CrysAlis CCD* (UNIL IC & Kuma, 2000); cell refinement: *CrysAlis RED* (UNIL IC & Kuma, 2000); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *MERCURY* (Version 1.4; Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

This work was financed by funds allocated by the Ministry of Scientific Research and Information Technology to the

Institute of General and Ecological Chemistry, Technical University of Łódź, Poland.

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