Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Partially oxidized {2-[(benzoylmethylene)diphenyl-λ^5-phosphino]ethyl}diphenylphosphine as a monohydrate

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Received 18 May 2004
Accepted 19 May 2004
Online 22 June 2004

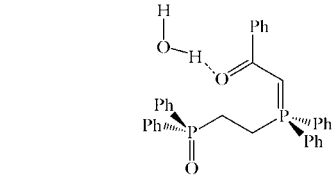
The title compound is a co-crystal of {2-[(benzoylmethylene)diphenyl-λ^5-phosphino]ethyl}diphenylphosphine oxide, {2-[(benzoylmethylene)diphenyl-λ^5-phosphino]ethyl}diphenylphosphine and water in an approximate 2:1:3 ratio, with an overall composition of $C_{34}H_{30}O_{1.678}P_2\cdot H_2O$. The ylidic portion shows the expected electronic polarization, and the organic components are linked by a combination of C—H···O and C—H···π(arene) hydrogen bonds.

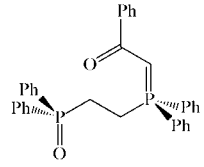
Comment

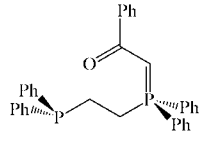
The title compound, (I), is a co-crystallized mixture of the phosphine oxide (II) and the phosphine (III) obtained as an unexpected product during the attempted crystallization of (III). Form (II), as the monohydrate, was taken as the basis of the refinement model, and the occupancy of atom site O2, bonded to P2 (Fig. 1), refined to 0.678 (7). Since the overall molecular size and shape is dominated by the disposition of the phenyl groups, the phosphine and its oxide readily occupy similar spaces in the crystal, leading to co-crystallization. It is possible that the occupancy of the O2 site may vary slightly from one crystal to another.

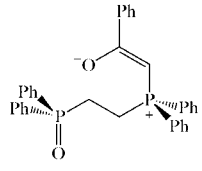
The central C21—P1—C1—C2—P2—C41 fragment of (I) is nearly planar, with an extended chain conformation, as shown by the key torsion angles (Table 1), and bonds P1—C17 and P2—O2 are both synclinal bond C1—C2. The locations of atoms C17 and O2, as well as the torsion angles of the phenyl rings about the P—C bonds, preclude the possibility of any internal molecular symmetry. The P1—C17—C19(—O18)—C11 fragment is effectively planar.

The inter-bond angles at both P1 and P2 show considerable variation from the ideal tetrahedral values (Table 1). That the two angles O2—P2—C41 and O2—P2—C51, involving the *ipso*-C atoms of the phenyl rings, are almost identical, while the angles C17—P1—C21 and C17—P1—C31, also involving *ipso*-C atoms, differ by almost 10°, points to some subtle intra- or intermolecular factors which are not immediately apparent. The angles P1—C17—C18 and C17—C18—O18 in the ylidic portion are both significantly greater than 120°.


(I)


(II)


(III)


(II*a*)

The bond distances involving the P atoms, other than P1—C17, are typical of their types (Allen *et al.*, 1987). The bond-length compilation of Allen *et al.* (1987) does not include any data derived from phosphorus ylides. However, Aitken *et al.* (2000) have recently surveyed and tabulated the structural

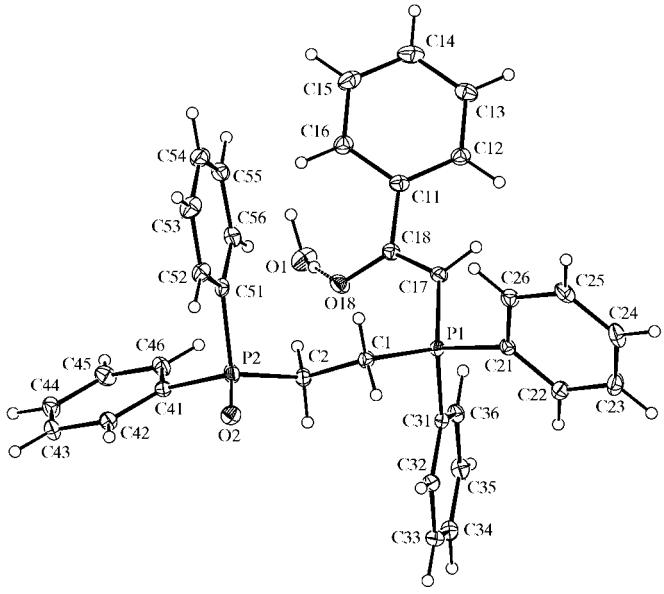


Figure 1
A view of the independent components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Atom site O2 has an occupancy of 0.678 (7) (see text).

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 DOI: 10.1107/S0108270104012211

properties of oxo-stabilized phosphorus ylides using data retrieved from the Cambridge Structural Database (Allen, 2002). For neutral ylides of the type $Ph_3P{=}C_\alpha R(C_\beta OR')$, the ranges of the $P-C_\alpha$, $C_\alpha-C_\beta$ and $C_\beta-O$ distances were found to be 1.708–1.773, 1.333–1.435 and 1.226–1.301 Å, respectively. These ranges may be compared and contrasted with the $P-CH_2$ distances of 1.674 (2) and 1.666 (2) Å found for the two independent molecules in $Ph_3P{=}CH_2$ (Schmidbaur *et al.*, 1989), and with the average C—C and C—O distances of 1.465 and 1.222 Å in the conjugated fragment =C—C=O (Allen *et al.*, 1987). The corresponding values observed in compound (I) (Table 1) are all thus comfortably within the ranges recently reported (Aitken *et al.*, 2000) and indicate that the charge-separated form (II*a*) is an important contributor to the overall molecular–electronic structure, alongside the classically localized form (II) (see scheme).

Compound (I) crystallizes as the monohydrate and the water molecule is linked to the negatively polarized atom O18 *via* an O—H···O hydrogen bond (Table 2). The water molecule plays no other role in the intermolecular aggregation, as there are no potential donors or acceptors of hydrogen bonds within a suitable distance of atom O1.

The organic molecules in (I) are, however, linked by a combination of C—H···O and C—H···π(arene) hydrogen bonds (Table 2). Atoms C26 and C45 in the molecule at (x, y, z) act as hydrogen-bond donors to, respectively, ring C41–C46 in the molecule at ($x-1$, y, z) and ring C11–C16 in the molecule at ($1+x$, y, z), so generating by translation a chain of rings running parallel to the [100] direction (Fig. 2). In addition, atom C12 in the molecule at (x, y, z) acts as donor to ring C31–C36 in the molecule at ($-x$, $1-y$, $-z$), so forming a

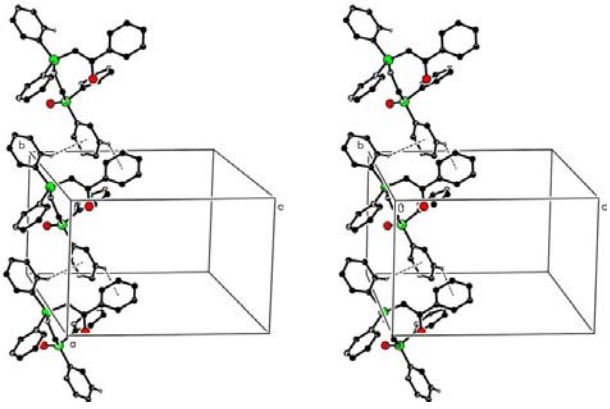

Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a [100] chain of rings generated by C—H···π(arene) hydrogen bonds. For the sake of clarity, the water molecule and the H atoms not involved in the motif shown have been omitted.

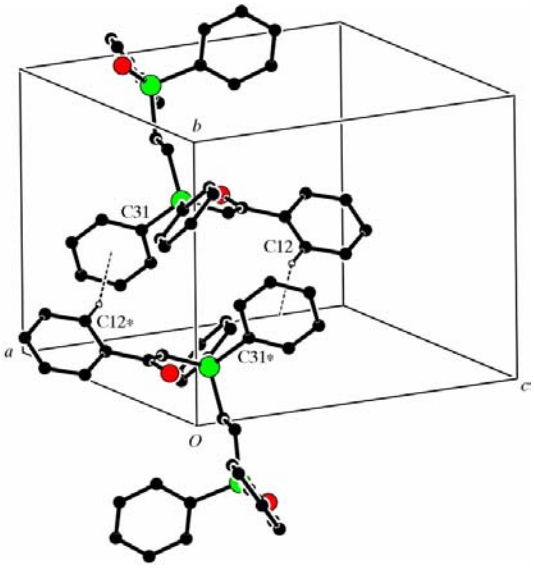

Figure 3
Part of the crystal structure of (I), showing the formation of a C—H···π(arene) hydrogen-bonded dimer centred at $(0, \frac{1}{2}, 0)$. For the sake of clarity, the water molecule and the H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position ($-x$, $1-y$, $-z$).

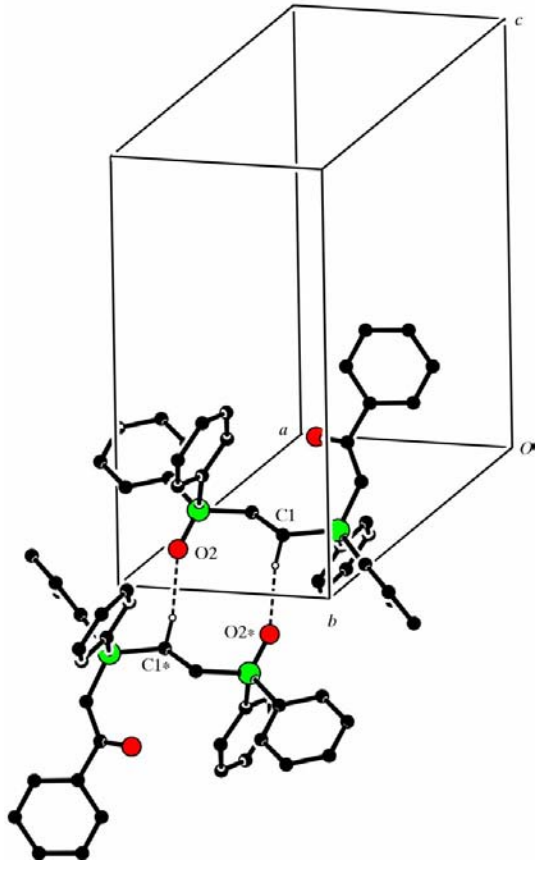

Figure 4
Part of the crystal structure of (I), showing the formation of a C—H···O hydrogen-bonded dimer centred at $(\frac{1}{2}, 1, 0)$. For the sake of clarity, the water molecule and the H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position ($1-x$, $2-y$, $-z$). Atom site O2 has an occupancy of 0.678 (7) (see text).

cyclic centrosymmetric dimer centred at $(0, \frac{1}{2}, 0)$ (Fig. 3), and this motif serves to link the molecular ladders in pairs.

The C—H···O hydrogen bonds in (I) both involve atom O2 as the acceptor and their overall effect is thus complicated somewhat by the partial occupancy of the O2 site. We consider first the outcome of these interactions assuming full occupancy of the O2 site, followed by the effects of partial occupancy. Atoms C1, adjacent to positively polarized atom P1, and C32 in the molecule at (x, y, z) both act as hydrogen-bond donors to atom O2 in the molecule at $(1 - x, 2 - y, -z)$. With full occupancy at O2, these interactions would generate a cyclic centrosymmetric dimer, centred at $(\frac{1}{2}, 1, 0)$, in which an $R_2^2(16)$ ring (Bernstein et al., 1995) containing atom C32 is divided into one $R_2^2(10)$ segment (Fig. 4) and two $R_2^1(7)$ segments (Fig. 4). With an occupancy of the O2 site of 0.678 (7), *ca* 46% of these molecular pairs will contain two atoms of type O2, *ca* 44% will contain just one atom of type O2 and *ca* 10% will contain no O2 atoms. Hence, *ca* 90% of these molecular pairs are internally linked by hydrogen bonds. In the event of full occupancy of the O2 site, this motif (Fig. 4) would serve to link the paired [100] ladders into an (001) sheet. Despite the presence of five independent phenyl rings, aromatic π–π stacking interactions are absent from the crystal structure of (I).

Experimental

The ylide (III) (see scheme) was prepared by the action of triethylamine on the corresponding phosphonium salt (Oosawa *et al.*, 1976); IR (ν, cm^{-1}): 1526 (C═O). The title compound, (I), was formed as crystals suitable for single-crystal X-ray diffraction by the vapour diffusion of light petroleum into a benzene solution of ylide (III) under aerobic conditions; IR (ν, cm^{-1}): 1514 (C═O), 1193 (P═O).

Crystal data

$C_{34}H_{30}O_{1.68}P_2{\cdot}H_2O$
M_r = 545.38
Triclinic, $P\overline{1}$
a = 9.1392 (4) Å
b = 11.8931 (3) Å
c = 13.6025 (5) Å
α = 105.725 (2)°
β = 92.472 (2)°
γ = 101.934 (2)°
V = 1384.67 (9) Å^3
Z = 2
D_x = 1.308 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6257 reflections
θ = 3.1–27.5°
μ = 0.19 mm^{-1}
T = 120 (2) K
Plate, colourless
0.16 × 0.12 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
T_{min} = 0.955, T_{max} = 0.991
21 189 measured reflections
6257 independent reflections
4739 reflections with $I > 2\sigma(I)$
R_{int} = 0.137
θ_{max} = 27.5°
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.143
S = 1.06
6257 reflections
353 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 1.1826P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.70 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

P1—C1	1.817 (2)	P1—C17	1.722 (2)
P1—C21	1.807 (2)	C17—C18	1.393 (3)
P1—C31	1.801 (2)	C18—O18	1.277 (3)
P2—C2	1.808 (2)	C18—C11	1.503 (3)
P2—C41	1.809 (2)	P2—O2	1.415 (2)
P2—C51	1.819 (2)		
C1—P1—C17	114.73 (11)	C2—P2—O2	117.61 (13)
C1—P1—C21	105.51 (10)	C2—P2—C41	104.48 (11)
C1—P1—C31	106.67 (10)	C2—P2—C51	105.72 (11)
C17—P1—C21	105.46 (10)	O2—P2—C41	112.58 (13)
C17—P1—C31	115.03 (11)	O2—P2—C51	111.94 (13)
C21—P1—C31	108.95 (10)	C41—P2—C51	103.22 (10)
P1—C17—C18	125.76 (18)	C11—C18—O18	117.7 (2)
C17—C18—O18	124.6 (2)	C11—C18—C17	117.6 (2)
P1—C1—C2—P2	−169.97 (12)	C1—P1—C17—C18	−59.1 (2)
C17—P1—C1—C2	77.30 (18)	P1—C17—C18—C11	175.31 (17)
C21—P1—C1—C2	−167.09 (16)	C17—C18—C11—C12	34.7 (3)
C31—P1—C1—C2	−51.31 (18)	C1—P1—C21—C22	123.45 (19)
O2—P2—C2—C1	−59.4 (2)	C1—P1—C31—C32	−42.2 (2)
C41—P2—C2—C1	174.93 (16)	C2—P2—C41—C42	148.40 (18)
C51—P2—C2—C1	66.39 (18)	C2—P2—C51—C52	−142.77 (18)

Table 2
Hydrogen-bonding geometry (Å, °).

*Cg*1, *Cg*3 and *Cg*4 are the centroids of rings C11–C16, C31–C36 and C41–C46, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*C*···O18	0.95	1.83	2.783 (3)	175
C1—H1*A*···O2^{i}	0.99	2.18	3.147 (4)	166
C32—H32···O2^{i}	0.95	2.36	3.298 (4)	168
C12—H12···*Cg*3^{ii}	0.95	2.87	3.777 (3)	159
C26—H26···*Cg*4^{iii}	0.95	2.97	3.757 (3)	141
C45—H45···*Cg*1^{iv}	0.95	2.77	3.589 (3)	145

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

Crystals of (I) are triclinic; space group $P\overline{1}$ was selected and confirmed by the subsequent analysis. All H atoms were located from difference maps and then treated as riding atoms, with C—H distances of 0.95 (CH) or 0.99 Å (CH_2) and O—H distances of 0.95 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(O)$. It was apparent from an early stage that the occupancy of the O2 site was less than unity; the refined value of the site-occupancy factor was 0.678 (7).

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

The X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants which have provided computing facilities for this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1734). Services for accessing these data are described at the back of the journal.

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