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1-(Diphenylphosphino)-4-(diphenylphosphinoyl)butane

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Key indicators

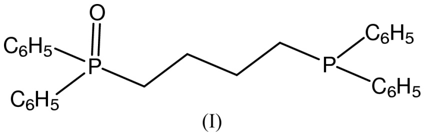
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.048
wR factor = 0.154
Data-to-parameter ratio = 19.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of the title 'half oxide', $C_{28}H_{28}P_2O$, (I), is found to be isomorphous with the previously determined 'full oxide', 1,4-bis(diphenylphosphinoyl)butane. A significant feature is an apparent shortening of the P—O bond distance [1.379 (3) Å] in (I) compared to the 'full oxide' [1.481 (2) Å], a result consistent with other known phosphine 'partial' oxides.

Comment

Tertiary phosphine oxides have proven utility as coordinating ligands in complex chemistry as well as being useful as aids for crystallization (Etter & Baures, 1988) through simple linear hydrogen-bonding associations between the oxide group and a proton-donating group, such as a carboxylic acid (Lynch *et al.*, 1992, 1997; Smith *et al.*, 1997, 1998). The parent tertiary phosphines, *e.g.* triphenylphosphine, are likewise useful as bulky ligands for stabilization of metal ions such as copper(I), silver(I) and gold(I), and extension of the ligand capacity *via* multiple pendant phosphinoyl groups has potential for formation of useful polymeric structures. It has been observed (Heinze *et al.*, 1997) that partial oxidation of the phosphorus group in uncoordinated 'dangling arms' of such multidentate ligands occurs quite easily. The first reported example of this was in the Re^{III}–carbonyl complex with bis(diphenylphosphino)methane (Carriedo *et al.*, 1990), where the occupancy factor for O was 0.30. For the Pd^{II}–chloride complex with a similar diphosphine (Sevillano *et al.*, 2000), the pendant arm was 50% oxidized. The phenomenon has also been observed in structures of uncoordinated phosphines, such as 1,1,1-tris(diphenylphosphinomethyl)propane (Chekhlov, 2000), where the three O atoms had occupancies of 11.3, 13.5 and 39.0%. In another example, the triphenylphosphine oxide–triphenylmethanol dimer (Steiner, 2000), the two molecules are related by pseudosymmetry across a crystallographic inversion centre (50% occupancy). We have also found that an isomorphous crystal series exists for the three isolated phosphine oxides (25.0, 50.0, 100.0%) of [4-(*N,N*-dimethylamino)phenyl]diphenylphosphine oxide (Lynch *et al.*, 2003).



(I)

The cell dimensions of the title compound, (I), are similar to those previously reported for the dioxide (Fontes *et al.*, 1991) [comparative (room temperature) permuted unit cell (Fontes *et al.*, 1991): a = 8.862 (1), b = 12.517 (2), c = 5.862 (1) Å, α = 102.67 (1), β = 104.22 (1), γ = 100.29 (1)°, V = 592.4 (2) Å^3].

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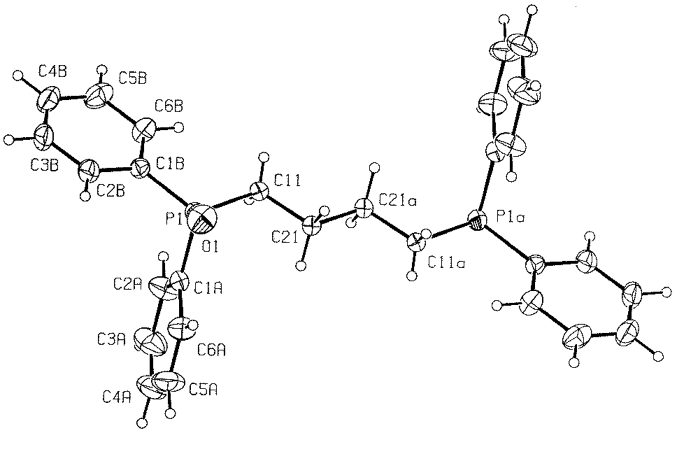

Figure 1
The molecular configuration and atom-labelling scheme for (I). Ellipsoids are drawn at the 30% probability level.

The structure of the title monoxide, $C_{28}H_{28}P_2O$, (I), is found to be isomorphous with the dioxide. This implies a 50% occupancy (see below) for the oxygen sites, which are statistically distributed across an inversion centre in the cell (Fig. 1). This result is consistent with the analytical and spectroscopic data that one P atom is oxidized while the other is unoxidized.

Another interesting and previously unreported phenomenon is the presence of significant P—O bond shortening for (I) [1.379 (3) Å] and for all other known 'partial oxides', compared to 1.481 (2) Å in the 'full oxide' (Fontes *et al.*, 1991) and in both triphenylphosphine oxide [1.483 (2) and 1.484 (1) Å for the two monoclinic modifications (Ruban & Zabel, 1976; Spek, 1987)] and in triphenylphosphine oxide–carboxylic acid adducts [1.49 Å (mean); Smith *et al.*, 1998]. The value in (I) is similar to distances for other '50% oxides' [1.378 (3) (Steiner, 2000), 1.39 (2) (Sevillano *et al.*, 2000) and 1.357 (4) Å (Lynch *et al.*, 2003)], and compares with 1.399 (4) (11.3%), 1.295 (14) (13.5%) and 1.368 (5) Å (39.0%) (Chekhlov, 2000), and 1.280 (4) Å (25.0%) (Lynch *et al.*, 2003). The ^{31}P NMR chemical shift data and P═O IR vibrational frequency data for (I) are typical for 'normal' arylphosphine oxides (Daasch & Smith, 1951; Higgins *et al.*, 1987). In particular, the ν(P═O) value for (I) (1182 cm^{-1}) is essentially the same as 1185 cm^{-1} for the dioxide 1,4-bis(diphenylphosphinoyl)butane (Goda *et al.*, 1975). This indicates that the apparent shortening of the P—O bond in structures with partial occupancy of the O atoms is probably an artifact of the structure refinement process. In this context, it is interesting to note that the C—P—O and C—P—C bond angles around the P atom in (I) are consistently larger (115° mean) and smaller (104° mean), respectively, than the corresponding angles in the full oxide (112.7° and mean 105.9°). This is consistent with the decrease in the P—O bond length arising from movement of the P atom site towards the O atom.

Stabilizing the conformation of the ring system is a short intramolecular contact between a ring H and the oxide O atom [C6*A*—H6*A*···O1 = 2.933 (6) Å]. As expected, little intermolecular association is found in the unit cell of (I), with only one C—H···O contact [C11—H11*B*···O1$^{\rm i}$ = 3.473 (4) Å: symmetry code: (i) *x*, *y*, 1 + *z*].

Experimental

The title compound, (I), was synthesized according to the method of Grushin (2001). A mixture of palladium acetate (5 mg), 1,4-bis(diphenylphosphino)butane (2.00 g, 4.8 mmol), 1,2-dibromoethane (1.8 g, 9.6 mmol) and dichloromethane (5 ml) was stirred for 30 min. Aqueous sodium hydroxide (20% *w*/*w*, 5 ml) was added and the mixture stirred at room temperature for 3 d. Dichloromethane (15 ml) was then added and the organic phase filtered through a silica plug which was then washed with dichloromethane–ethyl acetate (5:3 *v*/*v*, 40 ml). The combined organic solutions were evaporated to dryness. The solid residue was dissolved in boiling dichloromethane (15 ml). Ether (50 ml) was added and the solution left to stand at room temperature for 2 h, yielding colourless crystals of (I). A crystal (m.p. 463–464 K) suitable for X-ray diffraction studies was grown by slow diffusion of methanol into a solution of (I) in dichloromethane. Analysis found: C 76.2, H 6.4%; calculated for $C_{28}H_{28}OP_2$: C 76.0, H 6.4%. $\nu_{\rm max}$ (KBr) cm^{-1} 1182 (P═O). δ_H (400 MHz, CDCl$_3$, p.p.m.) 1.4 (2H, *m*, CH$_2$), 1.7 (2H, *m*, CH$_2$), 1.9 (2H, *m*, CH$_2$), 2.15 (2H, *m*, CH$_2$), 7.20–7.75 (20H, *m*, Ph). δ_P (161.9 MHz, CDCl$_3$, p.p.m.) 15.82–15.69 (*d*, PPh$_2$), 33.04–33.24 (*d*, OPPh$_2$).

Crystal data

$C_{28}H_{28}OP_2$
$M_r = 442.44$
Triclinic, $P\bar{1}$
$a = 8.927$ (2) Å
$b = 12.514$ (3) Å
$c = 5.802$ (2) Å
$\alpha = 102.98$ (2)°
$\beta = 102.23$ (3)°
$\gamma = 100.71$ (2)°
$V = 598.5$ (3) Å^3

$Z = 1$
$D_x = 1.228$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12.6$–$17.2°$
$\mu = 0.20$ mm^{-1}
$T = 295$ (2) K
Prism, colourless
0.50 × 0.20 × 0.15 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: none
3238 measured reflections
2752 independent reflections
2133 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$

$\theta_{\rm max} = 27.5°$
$h = -11 \rightarrow 11$
$k = -16 \rightarrow 15$
$l = -3 \rightarrow 7$
3 standard reflections every 150 reflections intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.154$
$S = 0.86$
2752 reflections
145 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.507P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.28$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.28$ e Å^{-3}

H atoms were included in the refinement at calculated positions in a riding-model approximation.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999).; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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