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Key indicators

Single-crystal X-ray study

T = 294 K

Mean σ (C–C) = 0.006 Å

Disorder in main residue

R factor = 0.059

wR factor = 0.130

Data-to-parameter ratio = 18.1

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

Tris(triphenylsilyl)phosphate dichloromethane solvate

The structure of the title monomeric phosphosilicate, $C_{54}H_{45}O_4PSi_3 \cdot 0.263CH_2Cl_2$ or $(Ph_3SiO)_3PO \cdot 0.263CH_2Cl_2$, is reported and is the first of a phosphosiloxane molecule with the general formula $(R_3SiO)_3PO$. Although the three P^V-O-Si angles are remarkably similar [143.57 (16), 144.47 (15) and 144.71 (15)°], the three P–O(Si) distances are remarkably different at 1.544 (2), 1.554 (2) and 1.561 (2) Å.

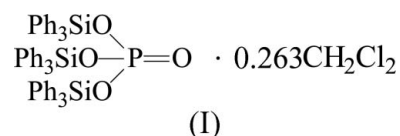
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Comment

We have recently reported the structure of $(Ph_3SiO)_2PhPO$ (Ferguson *et al.*, 2005) and, as a continuation of that work, we now report the structure of the related compound $(Ph_3SiO)_3PO$ as its dichloromethane solvate, (I).



A view of the molecule with the labelling scheme is shown in Fig. 1. Table 1 lists principal bond length and angle data. The similarity of the three P^V-O-Si angles is notable.

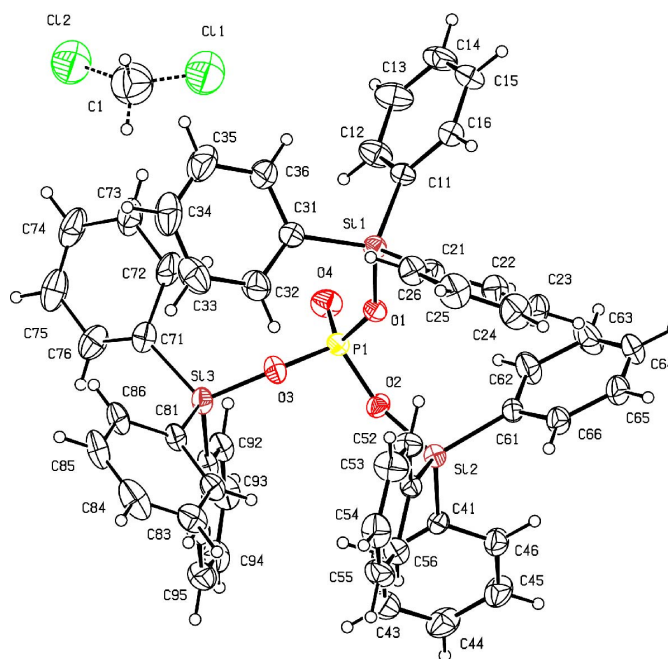


Figure 1

A view of $(Ph_3SiO)_3PO \cdot 0.263CH_2Cl_2$, showing the atom-numbering scheme. Anisotropic displacement parameters are drawn at the 30% probability level. Phenyl rings C71–C76 and C81–C86 are each disordered over two orientations; in each case, only one of these is shown.

Experimental

Reactions were carried out under an inert atmosphere. Solvents were dried and distilled prior to use. Phenylphosphonic acid and triphenylsilanol (Aldrich) were used directly. Triphenylsilanol (2.012 g, 7.28 mmol) and *ortho*-phosphoric acid (0.238 g, 2.43 mmol) were added to toluene (50 ml) in a Dean–Stark apparatus. The mixture was heated under reflux for 4 h. Recrystallization of the colourless product from a hot (*ca* 343 K) dichloromethane–acetonitrile (2:1) solution afforded clear rectangular block crystals (yield 1.979 g, 93.4%), which were subsequently shown to contain CH₂Cl₂ of solvation [m.p. 513–515 K; literature m.p. 517 K (Orlov & Voronkov, 1960)]. Analysis found: C 72.4, H 5.1%; C₅₄H₄₅O₄PSi₃·0.263CH₂Cl₂ requires: C 72.7, H 5.1%. FT–IR (KBr disc), $\nu_{\max}/\text{cm}^{-1}$: 1428 (s), 1279 (s), 1121 (s), 1035 (s), 1019 (vs), 996 (s), 716 (s), 700 (s), 514 (s). ¹H NMR (CDCl₃, p.p.m.): 7.64–6.81 (*m*, 45H, C₆H₅), 5.27 (s, 0.54H, 0.27CH₂Cl₂). ¹³C NMR (CDCl₃, p.p.m.): 135.47, 132.35, 130.24, 127.83 (all C₆H₅); 53.39 (CH₂Cl₂). MS (EI), *m/z*: 872 [*M*⁺], 795 [*M*⁺ – Ph], 718 [*M*⁺ – 2 Ph], 275 [(Ph₃SiO)⁺], 259 [(Ph₃Si)⁺], 77 [(Ph)⁺].

Crystal data

C ₅₄ H ₄₅ O ₄ PSi ₃ ·0.263CH ₂ Cl ₂	<i>Z</i> = 2
<i>M_r</i> = 895.48	<i>D_x</i> = 1.268 Mg m ^{−3}
Triclinic, <i>P</i> $\bar{1}$	Mo K α radiation
<i>a</i> = 10.284 (2) Å	Cell parameters from 25 reflections
<i>b</i> = 13.055 (3) Å	θ = 6.2–14.0°
<i>c</i> = 19.015 (4) Å	μ = 0.21 mm ^{−1}
α = 91.75 (2)°	<i>T</i> = 294 (1) K
β = 105.47 (2)°	Block, colourless
γ = 106.31 (2)°	0.38 × 0.27 × 0.25 mm
<i>V</i> = 2346.0 (9) Å ³	

Data collection

Enraf–Nonius CAD-4 diffractometer	<i>h</i> = −13 → 12
$\omega/2\theta$ scans	<i>k</i> = 0 → 16
10183 measured reflections	<i>l</i> = −24 → 24
10183 independent reflections	3 standard reflections
4004 reflections with <i>I</i> > 2 σ (<i>I</i>)	frequency: 120 min
θ_{\max} = 26.9°	intensity decay: 3.8%

Refinement

Refinement on <i>F</i> ²	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.059$	$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2]$
$wR(F^2) = 0.130$	where $P = (F_o^2 + 2F_c^2)/3$
<i>S</i> = 0.86	(Δ/σ) _{max} = 0.004
10183 reflections	$\Delta\rho_{\max} = 0.26 \text{ e } \text{Å}^{-3}$
564 parameters	$\Delta\rho_{\min} = -0.25 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

P1–O1	1.561 (2)	Si1–O1	1.663 (2)
P1–O2	1.544 (2)	Si2–O2	1.669 (2)
P1–O3	1.554 (2)	Si3–O3	1.659 (2)
P1–O4	1.449 (2)		
P1–O1–Si1	144.47 (15)	P1–O3–Si3	143.57 (16)
P1–O2–Si2	144.71 (15)		

During the refinement, it was apparent that there was a partial-occupancy CH₂Cl₂ molecule of solvation in the asymmetric unit, disordered about an inversion centre. The occupancy of the solvent molecule refined to 0.263 (2). It was also apparent from the prolate ellipsoids for the C atoms of phenyl rings C71–C76 and C81–C86 that these rings would be better allowed for as disordered species. Using the suggested coordinates from the *SHELXL*.lst file, these rings were then modelled and refined as rigid hexagons C71–C76/C711–C761 and C81–C86/C811–C861. The Si3–C71, Si3–C711, Si3–C81, Si3–C811 bond lengths were restrained to be the same, and each disordered pair of phenyl C atoms was constrained to have identical anisotropic displacement parameters. All H atoms were included as riding atoms, with C–H distances of 0.93 Å and with *U*_{iso} = 1.2*U*_{eq}(C).

Data collection: *DIFRAC* with profile analysis (Gabe & White, 1993); cell refinement: *DIFRAC*; data reduction: *DATRD2* in *NRCVAX94* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997) in *WinGX* (Version 1.70.01; Farrugia, 1999); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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