Tris(*tert*-butyl)phosphine selenide, the missing link in tris(*tert*-butyl)-phosphine chalcogenide structures ^{t}Bu$_3$P=X (X = O, S, Se, Te)

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In tris(*tert*-butyl)phosphine selenide, $C_{12}H_{27}PSe$, all the methyl ligands are disordered over two sites in the ratio 70/30. The molecule displays crystallographic C_3 symmetry. The bond angles at the P atom are distorted tetrahedral [C—P—C 110.02 (5)° and Se=P—C 108.91 (5)°]. The P—C and P=Se bond lengths are 1.908 (1) and 2.1326 (6) Å, respectively. A comparison of the structural data of the complete series of tris(*tert*-butyl)phosphine chalcogenides (^{t}Bu$_3$PO, ^{t}Bu$_3$PS, ^{t}Bu$_3$PSe and ^{t}Bu$_3$PTe) with the corresponding data of other phosphine chalcogenides substituted by smaller organic groups shows the great influence of the bulky *tert*-butyl ligands.

Comment

Phosphine chalcogenides are well known compounds and have been fully studied (Patai & Hartley, 1992). We report here the structure of tris(*tert*-butyl)phosphine selenide, (I). Together with the recently published molecular structure of ^{t}Bu$_3$PS (Steinberger *et al.*, 2001), the series of X-ray structures of tris(*tert*-butyl)phosphine chalcogenides has now been completed. The previously reported data are summarized in a review by Gilheany (1992).
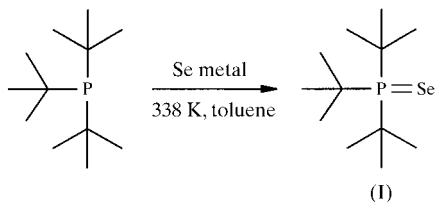
Compound (I) was first prepared from tris(*tert*-butyl)-phosphine and Se in the late seventies (DuMont *et al.*, 1976; Dean & Polensek, 1980), but the molecular structure was not determined. In order to compare the structural differences, the characteristic data for (I), together with the corresponding values for ^{t}Bu$_3$PO (Rankin *et al.*, 1985), ^{t}Bu$_3$PS (Steinberger *et*

al., 2001), ^{t}Bu$_3$PTe (Kuhn *et al.*, 1987) and the starting material, ^{t}Bu$_3$P (Krüger & Bruckmann, 1995), are listed in Table 1.

The crystal structure of (I) is disordered. However, this disorder only involves the methyl groups, and in the structure refinement, a 'split model' for these atoms appeared to handle the problem adequately. Similar disorder was observed for the isomorphous sulfur derivative. We assume that this disorder has not significantly affected the geometry determined for the inner part of the molecule.

In (I), the geometry at the P atom is distorted tetrahedral [C—P—C 110.02 (5)° and Se=P—C 108.91 (5)°] and the P—C and P=Se bond lengths are 1.9079 (14) and 2.1326 (6) Å, respectively. The P=Se bond in (I), together with the value in tris(2,4-dimethoxyphenyl)phosphine selenide [2.135 (3) Å; Allen *et al.*, 1990] represents an upper limit for phosphorus selenides.

It can be seen from the data in Table 1 that there is a marked steric influence of the *tert*-butyl groups. In comparison with phosphine chalcogenides substituted by less bulky groups at the P atom, such as Me$_3$PO [1.772 (6) and 1.770 (10) Å; Engelhardt *et al.*, 1986], Me$_3$PS [1.798 (2) Å; Eller & Corfield, 1971] or Me$_3$PSe [1.786 (14) Å; Cogne *et al.*, 1980], a distinct lengthening of the P—C bonds [1.888 (6)–1.9079 (14) Å] is observed. Furthermore, Gilheany (1992) concluded that bulky substituents lengthen the P=X (X is O, S, Se or Te) bond distance by *ca* 0.002–0.004 Å. In (I), the increase of the P=Se distance is about 0.002 Å, compared with Me$_3$PSe [2.111 (3) Å (X-ray data; Cogne *et al.*, 1980) and 2.091 (3) Å (electron diffraction; Jacob & Samdal, 1977)] and Ph$_3$PSe [2.106 (2) Å; Codding & Kerr, 1979]. However, in the case of the phosphine sulfides, such as ^{t}Bu$_3$PS [1.962 (3) Å; Steinberger *et al.*, 2001] and Me$_3$PS [1.959 (2) Å; Eller & Corfield, 1971], the difference in the P—S bond length is only small.

The P—X distances in phosphine chalcogenides obtained by X-ray structure determination (XR) are about 0.0015–0.0020 Å longer than those obtained by electron diffraction in the gas phase (ED), as can be seen from the examples of Me$_3$PO [1.489 (6) Å (XR; Engelhardt *et al.*, 1986) and 1.476 (2) Å (ED; Wilkins *et al.*, 1975)], Me$_3$PS [1.959 (2) Å (XR; Eller & Corfield, 1971) and 1.940 (2) Å (ED; Wilkins *et al.*, 1975)] and Me$_3$PSe [2.111 (3) Å (XR; Cogne *et al.*, 1980) and 2.091 (3) Å (ED; Jacob & Samdal, 1977)]. To the best of
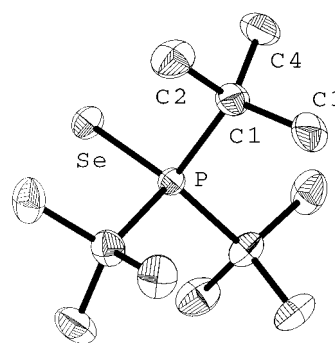

Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids. Only the main disorder component is shown. H atoms have been omitted for clarity.

our knowledge, no corresponding data for phosphine tellurides are available.

Experimental

To a solution of tris(tert-butyl)phosphine (0.97 g, 4.82 mmol) in toluene (10 ml), grey selenium granules (0.39 g, 4.92 mmol; 2% excess) were added and the mixture heated for 16 h at 338 K. After removal of excess Se by filtration, the solvent was completely evaporated in high vacuum, yielding ^{t}Bu$_3$PSe, (I) (yield 1.31 g, 97%). The title compound was characterized by ^{31}P NMR [121.472 MHz, toluene, 298 K; $\delta = 92.92$ p.p.m. ($^3J_{P-H} = 13.6$ Hz; $^1J_{P-Se} = 691$ Hz)] and mass spectroscopy. Recrystallization from toluene at 238 K afforded single crystals of (I).

Crystal data

$C_{12}H_{27}PSe$
$M_r = 281.27$
Cubic, $Pa\overline{3}$
$a = 14.4773 (18)$ Å
$V = 3034.3 (7)$ Å^3
$Z = 8$
$D_x = 1.231$ Mg m^{-3}
Mo $K\alpha$ radiation

Cell parameters from 5000 reflections
$\theta = 5–20°$
$\mu = 2.551$ mm^{-1}
$T = 180 (2)$ K
Cube, colourless
$0.60 \times 0.56 \times 0.52$ mm

Data collection

Stoe IPDS diffractometer
φ rotation scans, steps of 1.2°, 177 exposures
Absorption correction: numerical (X-RED; Stoe & Cie, 1997)
$T_{min} = 0.310$, $T_{max} = 0.351$
20 131 measured reflections
993 independent reflections

867 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 25.96°$
$h = -17 \rightarrow 17$
$k = -17 \rightarrow 17$
$l = -17 \rightarrow 17$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.046$
$S = 1.025$
993 reflections
74 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0301P)^2 + 0.3113P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.011$
$\Delta\rho_{max} = 0.62$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}

At the end of the conventional refinement, all methyl C atoms revealed very anisotropic displacement parameters. Split sites for these atoms and their associated H atoms were introduced. The major methyl component was refined as a rigid group and allowed to rotate but not tip; the minor component was refined with a riding model assuming ideally staggered torsion angles. Moreover, nine restraints were used [DFIX = 1.54 for the six C1—C(methyl) distances and SADI for the three C(methyl)—C(methyl,split) disorder pairs; SHELXL97 (Sheldrick, 1997)]. The site occupancy converged to about 70/30. Hereby, R_1 and wR_2 decreased from 0.040 and 0.100 to 0.018 and 0.046, respectively. Additionally, the deviations from the zero level in the corresponding final difference maps changed from -0.53 and 0.62 to -0.19 and 0.62 e Å^{-3}, respectively, and the displacement ellipsoids became normal. The P—C1 distance discussed in this work changed insignificantly, from 1.907 (3) to 1.908 (2) Å.

Table 1
Structural data (Å,°) for tris(tert-butyl)phosphine chalcogenides ^{t}Bu$_3$PX (X = O, S, Se, Te).

	^{t}Bu$_3$PO^a	^{t}Bu$_3$PS	^{t}Bu$_3$PSe	^{t}Bu$_3$PTe	^{t}Bu$_3$P
P═X	1.590 (12)	1.962 (3)	2.1326 (6)	2.368 (4)	–
P—C	1.888 (6)	1.899 (4)	1.9079 (14)	1.896 (14)	1.911 (2)
C—P—C	112.9 (5)	109.63 (12)	110.02 (5)	110.2 (6)	107.4 (1)
X═P—C	106.1 (5)	109.31 (12)	108.91 (5)	108.7 (5)	–
^{31}P NMRb	41^c	89.7	92.92	75.2^d	62.9

Notes: (a) determined by electron diffraction; (b) ^{31}P NMR chemical shifts (p.p.m.) were measured in toluene or benzene solution (external standard H$_3$PO$_4$, 85%); (c) data from Rosenberg & Drenth (1971); (d) data from DuMont & Kroth (1976).

Data collection: IPDS (Stoe & Cie, 1997); cell refinement: IPDS; data reduction: IPDS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XSTEP32 (Stoe & Cie, 1997); software used to prepare material for publication: SHELXL97.

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