organic compounds

Diphenyl(pyridin-2-yl)phosphane selenide

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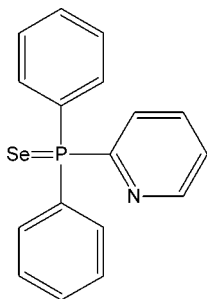
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In the title compound, $C_{17}H_{14}NPSe$, the P atom has a distorted tetrahedral environment resulting in an effective cone angle of 163°. In the crystal, C—H···Se/N/π interactions are observed.

Related literature

For background to phosphorus- and selenium-containing ligands, see: Muller *et al.* (2006, 2008). For the free phosphine of the title compound, see: Charland *et al.* (1989). For background on cone angles, see: Otto (2001); Tolman (1977). For details of the conformational fit of the two molecules using *Mercury*, see: Macrae *et al.* (2008); Weng *et al.* (2008a,b).

Experimental

Crystal data

$C_{17}H_{14}NPSe$	$V = 1513.61\ (11)$ Å³
$M_r = 342.22$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Cu $K\alpha$ radiation
$a = 8.8092\ (4)$ Å	$\mu = 4.25$ mm⁻¹
$b = 9.4066\ (4)$ Å	$T = 100$ K
$c = 18.2661\ (7)$ Å	$0.24 \times 0.17 \times 0.12$ mm

Data collection

Bruker APEX DUO 4K-CCD diffractometer	Absorption correction: multi-scan (*SADABS*; Bruker, 2008) $T_{min} = 0.429$, $T_{max} = 0.629$
	6004 measured reflections

2501 independent reflections	$R_{int} = 0.025$
2461 reflections with $I > 2\sigma(I)$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$	$\Delta\rho_{max} = 0.43$ e Å⁻³
$wR(F^2) = 0.053$	$\Delta\rho_{min} = -0.27$ e Å⁻³
$S = 0.87$	Absolute structure: Flack (1983), with 992 Friedel pairs
2501 reflections	Flack parameter: 0.053 (19)
181 parameters	
H-atom parameters constrained	

Table 1
Hydrogen-bond geometry (Å, °).

$Cg1$ is the centroid of the C1–C6 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12···Se1	0.95	2.87	3.427 (3)	118
C8—H8···N1	0.95	2.57	3.111 (3)	116
C14—H14···Se1	0.95	2.96	3.472 (2)	115
C5—H5···Se1^i	0.95	3.07	3.923 (3)	150
C16—H16···Se1^{ii}	0.95	3.26	3.938 (3)	130
C11—H11···$Cg1^{iii}$	0.95	2.77	3.630 (3)	151

Symmetry codes: (i) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x + 1, y, z$; (iii) $x - \frac{1}{2}, -y - \frac{1}{2}, -z$.

Data collection: *APEX2* (Bruker, 2011); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* and *XPREP* (Bruker, 2008); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *publCIF* (Westrip, 2010) and *WinGX* (Farrugia, 1999).

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supporting information

Diphenyl(pyridin-2-yl)phosphane selenide

Wade L. Davis and Alfred Muller

S1. Comment

As part our systematic investigation on the steric and electronic properties of phosphorus containing ligands, we are also utilizing the $^1J(^{31}P-^{77}Se)$ multi-nuclear NMR coupling in Se—P bond as a probe (see Muller *et al.*, 2008). The advantage of this approach is that there is no steric crowding effect, albeit crystal packing effects, as normally found in transition metal complexes with bulky ligands, *e.g.* in *trans*-[Rh(CO)Cl{P(OC$_6$H$_5$)$_3$}$_2$] cone angles variation from 156° to 167° was observed for the two phosphite ligands (Muller *et al.*, 2006). Herein we report here the single-crystal structure of SePPh$_2$py, where Ph = C$_6$H$_5$ and py = C$_5$H$_4$N as part of our investigation.

Molecules of the title compound (Fig. 1) adopts a distorted tetrahedral arrangement about the P atom with average C—P—C and Se—P—C angles of 105.47° and 113.20° respectively. Describing the steric demand of phosphane ligands has been the topic of many studies and a variety of models have been developed. The Tolman cone angle (Tolman, 1977) is still the most commonly used model. Applying this model to the geometry obtained for the title compound (and adjusting the Se—P bond distance to 2.28 Å) we calculated an effective cone angle from the geometry found in the crystal structure of 163° (Otto, 2001). The angle calculated is 9° larger than that of the free phosphine (Charland *et al.*, 1989; effective cone angle calculated as 154°), and could be ascribed to C—H···Se/N/π intra- and interactions observed in the title compound (Table 1, Fig. 2), whereas the free phosphine shows C—H···N/π interactions only. The difference in the orientation of the substituents for these two structures can be illustrated by superimposing their coordinates (Fig. 3); root mean squared deviation calculated as 0.0468 Å for P and *ipso* C atoms only using *Mercury* (Macrae *et al.*, 2008; Weng *et al.*, 2008*a*,*b*).

S2. Experimental

Diphenyl-2-pyridylphosphine and KSeCN were purchased from Sigma–Aldrich and used without purification. Eqimolar amounts of KSeCN (5.8 mg, 0.04 mmol) and the diphenylpyridylphosphine (10.5 mg, 0.04 mmol) were dissolved in the minimum amounts of methanol (10 ml). The KSeCN solution was added dropwise (5 min) to the phosphine solution with stirring at room temperature. The final solution was left to evaporate slowly until dry to give crystals suitable for a single-crystal X-ray study. Analytical data: ^{31}P {H} NMR (CDCl$_3$, 161.99 MHz): δ = 31.47 (t, $^1J(^{31}P-^{77}Se)$ = 734 Hz).

S3. Refinement

The aromatic H atoms were placed in geometrically idealized positions with C—H = 0.95 Å, and allowed to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.
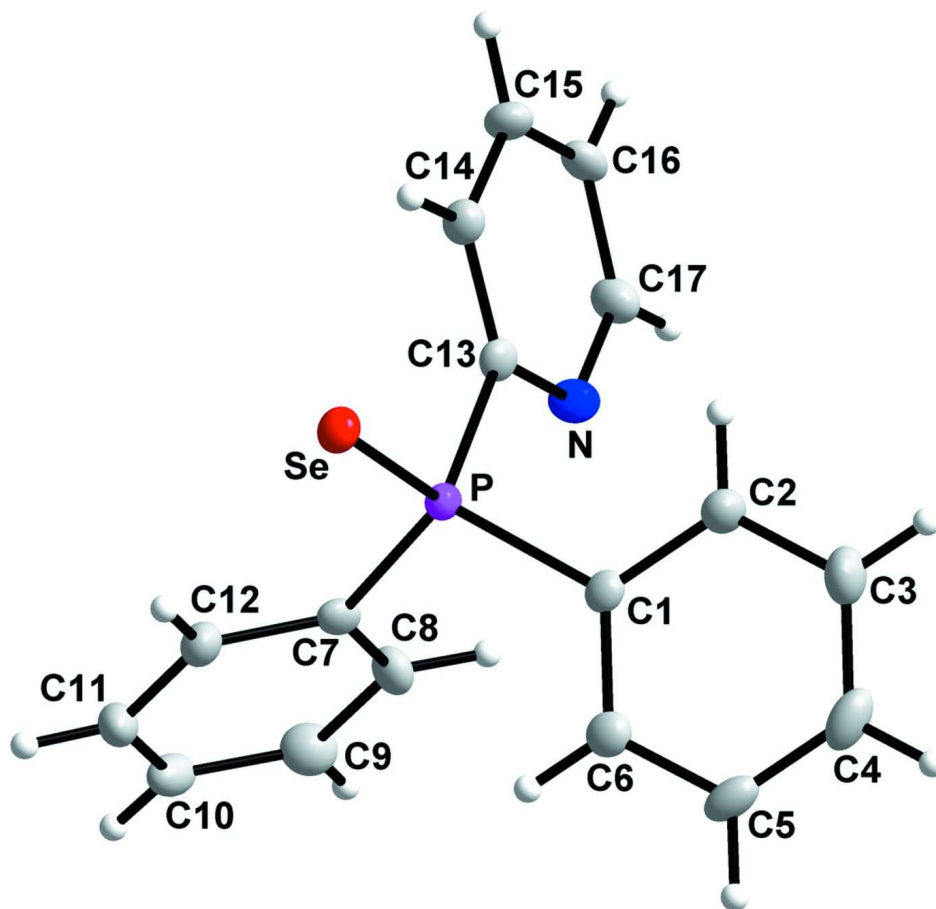
Figure 1

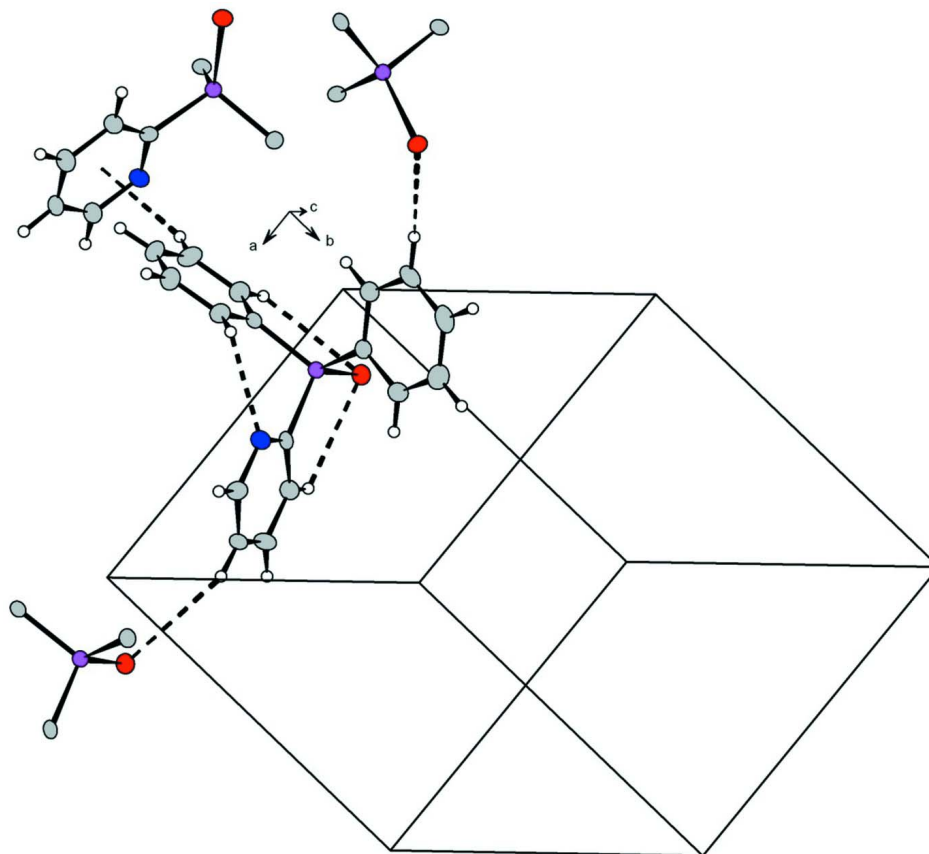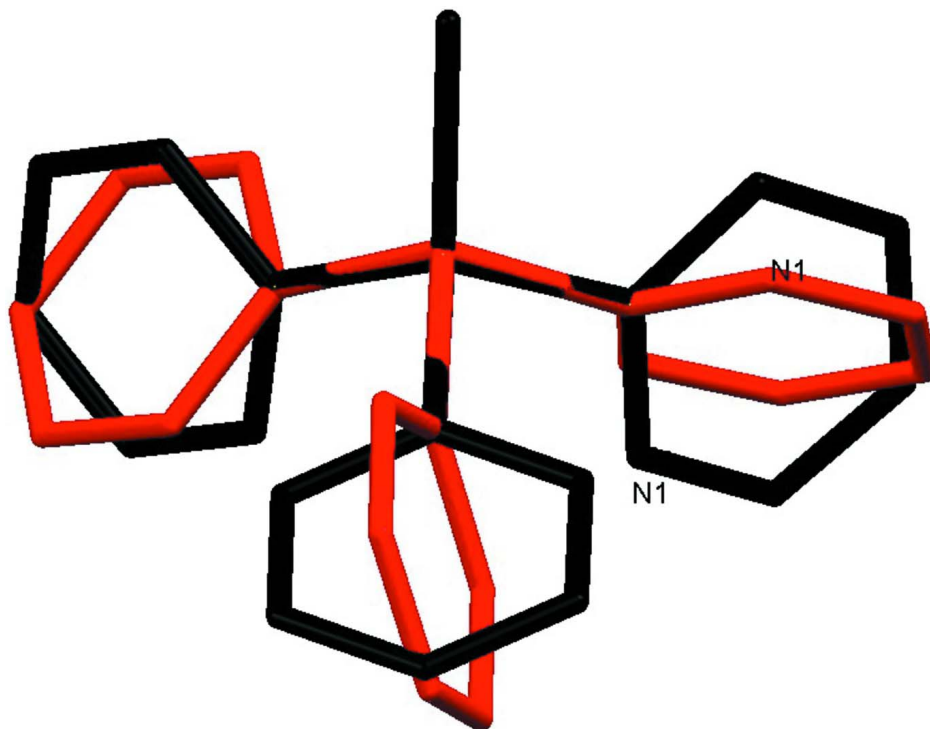A view of (1). Displacement ellipsoids are drawn at the 50% probability level.

Figure 2

Packing diagram of (1) showing the C—H···Se/N/π interactions.

Figure 3

Conformational similarity between the title compound (black) and the free phosphine (red).

Diphenyl(pyridin-2-yl)phosphane selenide

Crystal data

$C_{17}H_{14}NPSe$	$F(000) = 688$
$M_r = 342.22$	$D_x = 1.502$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 5093 reflections
$a = 8.8092$ (4) Å	$\theta = 4.8–66.6°$
$b = 9.4066$ (4) Å	$\mu = 4.25$ mm^{-1}
$c = 18.2661$ (7) Å	$T = 100$ K
$V = 1513.61$ (11) Å^3	Cuboid, colourless
$Z = 4$	$0.24 \times 0.17 \times 0.12$ mm

Data collection

Bruker APEX DUO 4K-CCD diffractometer	6004 measured reflections
	2501 independent reflections
Incoatec Quazar Multilayer Mirror monochromator	2461 reflections with $I > 2\sigma(I)$
Detector resolution: 8.4 pixels mm^{-1}	$R_{int} = 0.025$
φ and ω scans	$\theta_{max} = 66.6°$, $\theta_{min} = 4.8°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)	$h = -9 \rightarrow 10$
	$k = -3 \rightarrow 11$
$T_{min} = 0.429$, $T_{max} = 0.629$	$l = -21 \rightarrow 20$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.021$	H-atom parameters constrained
$wR(F^2) = 0.053$	$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 1.1995P]$
$S = 0.87$	where $P = (F_o^2 + 2F_c^2)/3$
2501 reflections	$(\Delta/\sigma)_{max} < 0.001$
181 parameters	$\Delta\rho_{max} = 0.43$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.27$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), with 992 Friedel pairs
Secondary atom site location: difference Fourier map	Absolute structure parameter: 0.053 (19)

Special details

Experimental. The intensity data was collected on a Bruker Apex DUO 4 K CCD diffractometer using an exposure time of 5 s/frame. A total of 287 frames were collected with a frame width of 4° covering up to $\theta = 66.62°$ with 96.7% completeness accomplished.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Se1	0.16691 (3)	0.13803 (3)	0.059243 (13)	0.01846 (8)
P1	0.28195 (7)	−0.00265 (7)	0.12974 (3)	0.01351 (13)
N1	0.5564 (3)	−0.0376 (2)	0.19118 (12)	0.0211 (5)
C1	0.2066 (3)	−0.0007 (3)	0.22196 (12)	0.0155 (5)
C2	0.2524 (3)	0.1080 (3)	0.26909 (13)	0.0222 (6)
H2	0.3282	0.1737	0.2541	0.027*
C3	0.1867 (3)	0.1197 (3)	0.33781 (14)	0.0279 (6)
H3	0.2185	0.1927	0.3703	0.034*
C4	0.0749 (3)	0.0250 (3)	0.35923 (14)	0.0271 (6)
H4	0.0292	0.0341	0.4061	0.033*
C5	0.0295 (3)	−0.0826 (3)	0.31256 (14)	0.0226 (6)
H5	−0.0465	−0.1479	0.3276	0.027*
C6	0.0953 (3)	−0.0952 (3)	0.24349 (14)	0.0192 (6)
H6	0.0636	−0.1687	0.2113	0.023*
C7	0.2834 (3)	−0.1863 (3)	0.09839 (13)	0.0165 (5)
C12	0.2168 (3)	−0.2192 (3)	0.03143 (13)	0.0218 (6)
H12	0.1654	−0.1481	0.0041	0.026*
C11	0.2266 (3)	−0.3580 (3)	0.00496 (13)	0.0257 (6)
H11	0.1802	−0.382	−0.0403	0.031*
C10	0.3034 (3)	−0.4608 (3)	0.04429 (14)	0.0249 (6)
H10	0.3129	−0.5543	0.0252	0.03*

C9	0.3666 (3)	−0.4276 (3)	0.11135 (15)	0.0271 (6)
H9	0.417	−0.499	0.1389	0.033*
C8	0.3567 (3)	−0.2906 (3)	0.13858 (14)	0.0216 (6)
H8	0.4001	−0.2681	0.1848	0.026*
C13	0.4816 (3)	0.0441 (3)	0.14240 (13)	0.0153 (5)
C17	0.7046 (3)	−0.0092 (3)	0.20170 (14)	0.0222 (6)
H17	0.7597	−0.0657	0.2356	0.027*
C16	0.7802 (3)	0.0985 (3)	0.16541 (14)	0.0203 (6)
H16	0.8851	0.1146	0.1741	0.024*
C15	0.7021 (3)	0.1817 (3)	0.11670 (14)	0.0221 (6)
H15	0.7518	0.2571	0.0917	0.026*
C14	0.5494 (3)	0.1544 (3)	0.10432 (13)	0.0193 (5)
H14	0.4928	0.21	0.0706	0.023*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Se1	0.01952 (13)	0.01885 (13)	0.01701 (12)	0.00321 (11)	−0.00156 (10)	0.00276 (10)
P1	0.0138 (3)	0.0140 (3)	0.0127 (3)	0.0002 (3)	0.0005 (2)	0.0005 (2)
N1	0.0168 (11)	0.0207 (12)	0.0257 (11)	0.0009 (9)	−0.0010 (9)	0.0027 (9)
C1	0.0160 (13)	0.0164 (12)	0.0142 (10)	0.0031 (11)	−0.0007 (9)	0.0023 (9)
C2	0.0217 (14)	0.0247 (16)	0.0201 (13)	−0.0027 (11)	0.0031 (10)	−0.0015 (10)
C3	0.0336 (16)	0.0306 (15)	0.0196 (13)	0.0013 (15)	0.0005 (11)	−0.0057 (11)
C4	0.0285 (16)	0.0351 (17)	0.0178 (13)	0.0114 (13)	0.0059 (11)	0.0033 (11)
C5	0.0170 (13)	0.0280 (15)	0.0229 (13)	0.0036 (11)	0.0054 (11)	0.0099 (11)
C6	0.0185 (13)	0.0200 (15)	0.0193 (12)	0.0024 (11)	−0.0020 (10)	0.0028 (10)
C7	0.0141 (12)	0.0161 (13)	0.0194 (12)	−0.0012 (10)	0.0058 (10)	−0.0019 (9)
C12	0.0256 (13)	0.0230 (14)	0.0167 (12)	−0.0026 (12)	0.0021 (10)	0.0000 (10)
C11	0.0360 (14)	0.0233 (13)	0.0176 (12)	−0.0096 (14)	0.0010 (11)	−0.0032 (11)
C10	0.0329 (16)	0.0172 (13)	0.0246 (13)	−0.0034 (11)	0.0103 (11)	−0.0040 (10)
C9	0.0273 (17)	0.0213 (14)	0.0327 (15)	0.0037 (12)	0.0009 (12)	0.0000 (11)
C8	0.0216 (14)	0.0233 (13)	0.0199 (12)	−0.0015 (12)	−0.0043 (11)	−0.0036 (10)
C13	0.0142 (12)	0.0168 (13)	0.0149 (11)	0.0028 (10)	0.0030 (9)	−0.0026 (9)
C17	0.0210 (14)	0.0206 (13)	0.0250 (13)	−0.0015 (13)	−0.0041 (10)	0.0007 (11)
C16	0.0140 (12)	0.0222 (15)	0.0248 (13)	−0.0042 (11)	0.0014 (10)	−0.0057 (10)
C15	0.0191 (14)	0.0244 (14)	0.0227 (12)	−0.0061 (11)	0.0025 (10)	0.0026 (10)
C14	0.0185 (12)	0.0213 (14)	0.0179 (12)	0.0000 (12)	−0.0007 (9)	0.0002 (10)

Geometric parameters (Å, º)

Se1—P1	2.1063 (6)	C7—C12	1.391 (3)
P1—C1	1.811 (2)	C12—C11	1.395 (4)
P1—C7	1.820 (2)	C12—H12	0.95
P1—C13	1.828 (3)	C11—C10	1.381 (4)
N1—C13	1.349 (3)	C11—H11	0.95
N1—C17	1.347 (3)	C10—C9	1.381 (4)
C1—C6	1.380 (4)	C10—H10	0.95
C1—C2	1.397 (4)	C9—C8	1.384 (4)

C2—C3	1.387 (4)	C9—H9	0.95
C2—H2	0.95	C8—H8	0.95
C3—C4	1.384 (4)	C13—C14	1.384 (4)
C3—H3	0.95	C17—C16	1.381 (4)
C4—C5	1.382 (4)	C17—H17	0.95
C4—H4	0.95	C16—C15	1.370 (4)
C5—C6	1.393 (4)	C16—H16	0.95
C5—H5	0.95	C15—C14	1.388 (4)
C6—H6	0.95	C15—H15	0.95
C7—C8	1.385 (4)	C14—H14	0.95
C1—P1—C7	107.75 (11)	C7—C12—H12	120.4
C1—P1—C13	103.46 (11)	C11—C12—H12	120.4
C7—P1—C13	105.15 (11)	C10—C11—C12	120.3 (2)
C1—P1—Se1	112.71 (8)	C10—C11—H11	119.8
C7—P1—Se1	114.04 (9)	C12—C11—H11	119.8
C13—P1—Se1	112.90 (8)	C11—C10—C9	120.0 (2)
C13—N1—C17	117.0 (2)	C11—C10—H10	120
C6—C1—C2	120.1 (2)	C9—C10—H10	120
C6—C1—P1	121.27 (19)	C10—C9—C8	120.3 (3)
C2—C1—P1	118.34 (19)	C10—C9—H9	119.9
C3—C2—C1	119.7 (2)	C8—C9—H9	119.9
C3—C2—H2	120.2	C7—C8—C9	119.9 (2)
C1—C2—H2	120.2	C7—C8—H8	120.1
C4—C3—C2	120.2 (3)	C9—C8—H8	120.1
C4—C3—H3	119.9	N1—C13—C14	123.3 (2)
C2—C3—H3	119.9	N1—C13—P1	114.59 (18)
C3—C4—C5	120.1 (2)	C14—C13—P1	122.12 (19)
C3—C4—H4	119.9	N1—C17—C16	123.0 (2)
C5—C4—H4	119.9	N1—C17—H17	118.5
C4—C5—C6	120.1 (3)	C16—C17—H17	118.5
C4—C5—H5	120	C15—C16—C17	119.2 (2)
C6—C5—H5	120	C15—C16—H16	120.4
C1—C6—C5	119.9 (2)	C17—C16—H16	120.4
C1—C6—H6	120.1	C16—C15—C14	119.1 (2)
C5—C6—H6	120.1	C16—C15—H15	120.4
C8—C7—C12	120.3 (2)	C14—C15—H15	120.4
C8—C7—P1	120.58 (19)	C13—C14—C15	118.3 (2)
C12—C7—P1	119.0 (2)	C13—C14—H14	120.8
C7—C12—C11	119.1 (3)	C15—C14—H14	120.8
C7—P1—C1—C6	−34.1 (2)	P1—C7—C12—C11	175.8 (2)
C13—P1—C1—C6	−145.1 (2)	C7—C12—C11—C10	−1.0 (4)
Se1—P1—C1—C6	92.6 (2)	C12—C11—C10—C9	2.2 (4)
C7—P1—C1—C2	152.3 (2)	C11—C10—C9—C8	−1.7 (4)
C13—P1—C1—C2	41.3 (2)	C12—C7—C8—C9	1.4 (4)
Se1—P1—C1—C2	−81.0 (2)	P1—C7—C8—C9	−175.2 (2)
C6—C1—C2—C3	0.7 (4)	C10—C9—C8—C7	−0.1 (4)

P1—C1—C2—C3	174.4 (2)	C17—N1—C13—C14	−0.7 (4)
C1—C2—C3—C4	−0.8 (4)	C17—N1—C13—P1	178.94 (19)
C2—C3—C4—C5	0.8 (4)	C1—P1—C13—N1	53.4 (2)
C3—C4—C5—C6	−0.6 (4)	C7—P1—C13—N1	−59.5 (2)
C2—C1—C6—C5	−0.5 (4)	Se1—P1—C13—N1	175.59 (16)
P1—C1—C6—C5	−174.0 (2)	C1—P1—C13—C14	−126.9 (2)
C4—C5—C6—C1	0.5 (4)	C7—P1—C13—C14	120.2 (2)
C1—P1—C7—C8	−55.0 (2)	Se1—P1—C13—C14	−4.7 (2)
C13—P1—C7—C8	54.9 (2)	C13—N1—C17—C16	0.3 (4)
Se1—P1—C7—C8	179.09 (18)	N1—C17—C16—C15	0.5 (4)
C1—P1—C7—C12	128.4 (2)	C17—C16—C15—C14	−0.9 (4)
C13—P1—C7—C12	−121.7 (2)	N1—C13—C14—C15	0.4 (4)
Se1—P1—C7—C12	2.5 (2)	P1—C13—C14—C15	−179.30 (19)
C8—C7—C12—C11	−0.8 (4)	C16—C15—C14—C13	0.5 (4)

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the C1–C6 ring.

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12···Se1	0.95	2.87	3.427 (3)	118
C8—H8···N1	0.95	2.57	3.111 (3)	116
C14—H14···Se1	0.95	2.96	3.472 (2)	115
C5—H5···Se1[i]	0.95	3.07	3.923 (3)	150
C16—H16···Se1[ii]	0.95	3.26	3.938 (3)	130
C11—H11···Cg1[iii]	0.95	2.77	3.630 (3)	151

Symmetry codes: (i) −*x*, *y*−1/2, −*z*+1/2; (ii) *x*+1, *y*, *z*; (iii) *x*−1/2, −*y*−1/2, −*z*.