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Bridge cleavage of [{PhP(Se)(μ-Se)}$_2$] by 1,2-C_6H_4(EH)(E′H) (E, E′ = O or NH). X-ray crystal structure of PhP(Se)(NHC_6H_4NH-1,2)

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Abstract

Treatment of [{PhP(Se)(μ-Se)}$_2$] (**1**), the oxidation product of $(PhP)_5$ with excess selenium, with 2-aminophenol, 1,2-phenylenediamine, catechol or 3,4-diaminotoluene leads to the rupture of the dimer giving PhP(Se)(NHC_6H_4O-1,2) (**2**), PhP(Se)(NHC_6H_4NH-1,2) (**3**), PhP(Se)(OC_6H_4O-1,2) (**4**) and PhP(Se)($NHC_6H_3(CH_3$-3)NH-1,2) (**5**), respectively. In the molecular structure of **3**, determined crystallographically, there are two independent molecules within the unit cell which are linked by P=Se···H–N hydrogen bonds, leading to chains of dimer pairs in the solid state. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Phosphorus; Selenium; X-ray crystal structure; Heterocycles

1. Introduction

There have been few investigations into the chemistry of 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide [{PhP(Se)(μ-Se)}$_2$] (**1**), a selenium analogue of Lawesson's Reagent, [{(*p*-$MeOC_6H_4$)P(S)(μ-S)}$_2$] [1,2]. Compound **1** is the terminal oxidation product of the pentaphosphorus homocycle $(PhP)_5$ with elemental selenium [3,4]. Treatment of *cis*-[$PtCl_2(PR_3)_2$] (PR_3 = 1/2dppe, PEt_3, PMe_2Ph or PPh_2Me) with **1** in THF affords *cis*-[Pt(Se_3PPh-*Se*,*Se′*)$(PR_3)_2$] while Hill and co-workers have used **1**, prepared in situ from $(PhP)_5$–Se, to effect the transformation of molybdenum and tungsten ketenyl complexes to their selenoketenyl analogues [5,6]. We have recently described the reaction of **1** with dialkyl cyanamides R_2N–CN [R_2 = Me_2, –$(CH_2)_5$– or –$CH_2CH_2OCH_2CH_2$–], which leads to triselenaphosphadiazapentalenes [R_2N–C(Se)=N]$_2$P(Se)Ph, containing two fused PSe_2CN rings and with an unusually long P=Se distance [7]. Here we report the cleavage of the P_2(μ-Se)$_2$ ring of [{PhP(Se)(μ-Se)}$_2$] by a number of dibasic substrates and the X-ray crystal structure of one representative example.

2. Results and discussion

Bridge cleavage of the central P_2(μ-Se)$_2$ core in **1** occurs during its reactions with *cis*-[$PtCl_2(PR_3)_2$] or with dialkyl cyanamides, leading to products containing a PhP(Se)Se_2 unit [6,7]. Treatment of **1** with 2-aminophenol, 1,2-phenylenediamine, catechol or 3,4-diaminotoluene also proceeds with the rupture of the P_2(μ-Se)$_2$ ring to give monophosphorus species **2**–**5**, respectively (Eq. (1)) isolable in ca. 30–40% yield based on **1**, upon reflux of the reagents in toluene for 1 h. $^{31}P\{^1H\}$-NMR spectra of crude mixtures show only one phosphorus-containing product, from which we conclude that the ultimate fate of the bridging selenium atoms of **1** is likely to be hydrogen selenide rather than PhP(Se)$(SeH)_2$. Similar penta-atomic P–E–C–C–E′ rings (E, E′ = O or NH) have been prepared previously directly from RP(Se)Cl_2 and the appropriate dibasic substrate or via oxidation of the parent phosphorus(III) compound [8–10]. Also, cleavage of the P_2(μ-S)$_2$ ring of dithiadiphosphetanes [{RP(S)(μ-S)}$_2$] (R = *p*-$MeOC_6H_4$ or ferrocenyl) by catechols gives five membered

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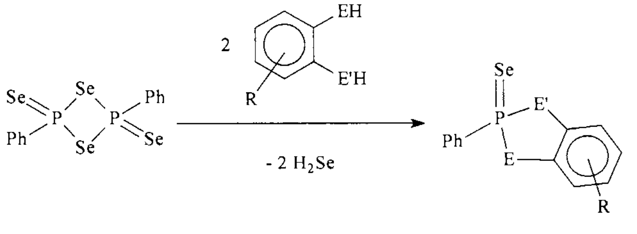
$P(S)O_2C_2$ rings [11,12]. The products **2**–**5** are colourless to off-white solids which turn pink in air over several days owing to contamination by minor quantities of elemental (red) selenium, whose origin is most likely to be from slow decomposition of the materials in aerobic conditions; decomposition is notably faster for **2** and **4** (containing P–O linkages) than for **3** or **5**. Difficulties in the separation of this contaminant from the products have prevented satisfactory elemental analyses. We have not attempted to react **1** with monobasic alcohols or amines, however we do not believe bridge cleavage to be restricted to dibasic nucleophiles.



	E	E'	R
2	O	NH	H
3	NH	NH	H
4	O	O	H
5	NH	NH	CH_3

(1)

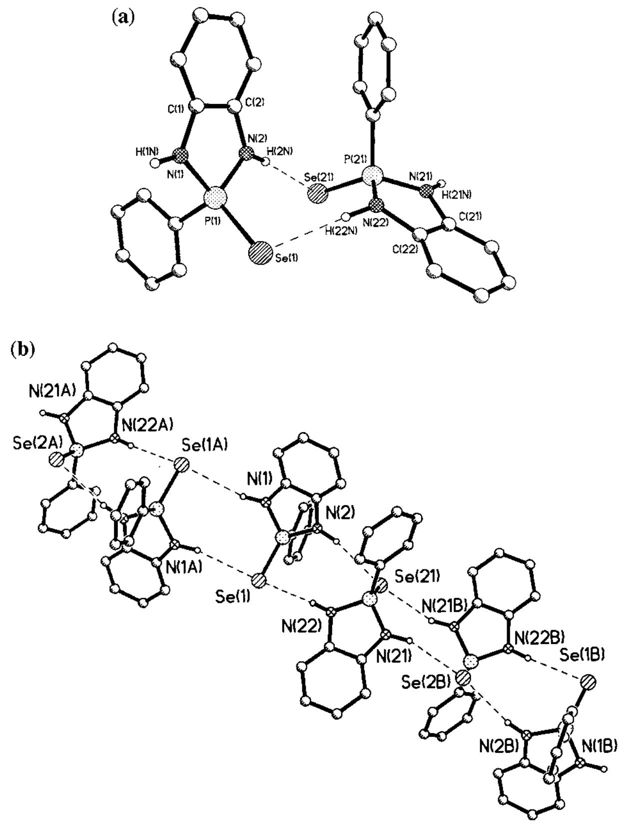


Fig. 1. (a) Molecular structure of **3** (C–H bonds omitted for clarity); (b) hydrogen bonding interactions leading to chains of dimers.

In the $^{31}P\{^1H\}$-NMR, the magnitude of ^1J(P–Se) follows the trend **4** > **2** > **3**,**5**, i.e. the coupling constant increases as the NH groups are replaced by O. Accompanying this is a progressive shift to high frequency in δ_P as O substitutes for NH. There is, however, no clear correlation between ^1J(P–Se) and ν(PSe) in the infrared spectra, which for **2**–**5** lies between 563–588 cm^{-1}, the upper and lower values being for the diamine-derived **3** and **5**. This incongruence is perhaps related to the presence of N–H···Se=P hydrogen bonding interactions in the solid state, as noted in the crystal structure of **3** (see below). The ν(PN) frequency is largely invariant in **2**, **3** and **5** (887–890 cm^{-1}) with ν(PC) in the range of 1101–1112 cm^{-1} for **2**–**5**. In the ^1H-NMR, the N*H* proton(s) in **2**, **3** and **5** appear as a broad doublet between 5.0–5.2 ppm, with ^2J(P–H) ~ 19 Hz.

The molecular structure of **3** (Fig. 1, Table 1) shows two independent molecules exist within the unit cell, which are linked by N–H···Se=P hydrogen bonding interactions to form discrete dimer pairs, with additional secondary interactions of the same type between the dimer pairs. The P=Se distance (2.102(1), 2.115(1) Å in molecules **1**, **2**) is normal, while the shortness of the P–N lengths (1.668(3), 1.676(3) Å and 1.667(3), 1.668(3) Å for molecules **1**, **2**) suggests some multiple bond character. Within the hydrogen-bonded dimers the Se(1)···H(22N) and Se(21)···H(2N) distances are 2.75 and 2.64 Å, respectively with N(2)–H(2N)···Se(21) and N(22)–H(22N)···Se(1) angles of 169 and 174°, cf. Se···H 2.52 Å, N–H···Se 166° between dimer pairs in the solid state structure of $NH(Ph_2PSe)_2$ [13]. The N–P–N angle of the (essentially coplanar) five membered P–N–C–C–N ring, 91.31(14) (92.3(2)°) is the smallest of the angles at P(1), while the exocyclic Se=P–X (X = C_{phenyl} or N) angles are the widest (112.49(12)–117.77(11)° in molecule **1**, 115.55(12)–118.74(12)° in molecule **2**).

3. Experimental

Syntheses of **2**–**5** were performed in thick walled glass tubes with Youngs taps under an atmosphere of oxygen-free nitrogen, subsequent chromatographic and recrystallisation procedures were performed aerobically. Compound **1** was prepared from $(PhP)_5$ and elemental selenium [3,4], anhydrous toluene (Aldrich) and other reagents and solvents were used as supplied. $^{31}P\{^1H\}$- and ^1H-NMR (121.4 and 300.0 MHz, $CDCl_3$) and the infrared spectra (pressed KBr discs) were recorded on a Varian Gemini 2000 spectrometer and a Perkin–Elmer System 2000 NIR FT-Raman spectrometers, FAB^+ mass spectra (3-nitrobenzyl alcohol matrix) were carried out by the EPSRC National Mass Spectrometry Service Centre, Swansea.

Table 1
Selected bond lengths (Å) and angles (°) for **3** (estimated. S.D. values in parentheses)

Molecule 1			
Bond lengths			
Se(1)–P(1)	2.102(1)	P(1)–N(2)	1.668(3)
P(1)–N(1)	1.676(3)	P(1)–C(7)	1.795(3)
N(1)–C(1)	1.402(4)	C(2)–N(2)	1.406(4)
Bond angles			
N(2)–P(1)–N(1)	91.31(14)	N(2)–P(1)–C(7)	106.2(2)
N(1)–P(1)–C(7)	109.1(2)	N(2)–P(1)–Se(1)	117.76(11)
N(1)–P(1)–Se(1)	117.77(11)	C(7)–P(1)–Se(1)	112.49(12)
C(1)–N(1)–P(1)	113.2(2)	C(2)–N(2)–P(1)	113.7(2)
Molecule 2			
Bond lengths			
Se(21)–P(21)	2.115(1)	P(21)–N(21)	1.667(3)
P(21)–N(22)	1.668(3)	P(21)–C(27)	1.802(4)
N(21)–C(21)	1.400(4)	C(22)–N(22)	1.424(4)
Bond angles			
N(21)–P(21)–N(22)	92.3(2)	N(21)–P(21)–C(27)	108.4(2)
N(22)–P(21)–C(27)	109.4(2)	N(21)–P(21)–Se(21)	118.74(12)
N(22)–P(21)–Se(21)	115.55(12)	C(27)–P(21)–Se(21)	110.94(12)
C(21)–N(21)–P(21)	113.1(2)	C(22)–N(22)–P(21)	111.8(2)

3.1. General procedure for ***2–5***

A solution of **1** (0.25 mmol) and the appropriate aromatic substrate (0.5 mmol) in toluene (2 cm^3) was heated at 130°C for 1 h, during which time the dark red suspension became colourless or pale yellow, with the deposition of some elemental selenium. The solvent was removed in vacuo, the crude material extracted into CH_2Cl_2 (2 cm^3) and purified by column chromatography (silica, CH_2Cl_2 eluant). The products **2–5** were isolated by concentration of the pale green CH_2Cl_2 eluate to ca. 5 cm^3, addition of hexane (5 cm^3) and concentration in vacuo until precipitation occurs. Isolated yields were typically 30–40% based on **1**. Contamination by small amounts of red selenium precludes satisfactory elemental analysis of **2–5**.

PhP(Se)(NHC$_6$H$_4$O-1,2) (**2**): δ_P; 97.5(s), $^1J_{PSe} = 895$ Hz. δ_H; 7.92 (m, 2H, C_6H_5), 7.55 (m, 1H, C_6H_5), 7.48 (m, 2H, C_6H_5), 7.06–6.88 (m, 4H, C_6H_4), 5.23 (d, 1H, $^2J_{PH} = 19$ Hz, NH). IR (cm^{-1}); 3308m (ν_{NH}), 1234s (ν_{PO}), 1108s (ν_{PC}), 890s (ν_{PN}), 568s (ν_{PSe}). FAB$^+$ MS; 295, [M^+ + H].

PhP(Se)(NHC$_6$H$_4$NH-1,2) (**3**):δ_P; 71.3(s), $^1J_{PSe} = 831$ Hz. δ_H; 7.95 (m, 2H, C_6H_5), 7.39 (m, 3H, C_6H_5), 6.73 (m, 4H, C_6H_4), 5.07 (d, 2H, $^2J_{PH} = 19$ Hz, NH). IR (cm^{-1}); 3401m, 3231m (ν_{NH}), 1101s (ν_{PC}), 887s (ν_{PN}), 563s (ν_{PSe}). FAB$^+$ MS; 292, [M^+].

PhP(Se)(OC$_6$H$_4$O-1,2) (**4**): δ_P; 116.0(s), $^1J_{PSe} = 952$ Hz. δ_H; 7.90 (m, 2H, C_6H_5), 7.62 (m, 1H, C_6H_5), 7.51 (m, 2H, C_6H_5), 7.15 (m, 2H, C_6H_4), 7.08 (m, 2H, C_6H_4). IR (cm^{-1}); 1223s (ν_{PO}), 1112m (ν_{PC}), 570m (ν_{PSe}). FAB$^+$ MS; 296, [M^+ + H].

PhP(Se)(NHC$_6$H$_3$(CH$_3$-3)NH-1,2) (**5**): δ_P; 71.8(s), $^1J_{PSe} = 824$ Hz. δ_H; 7.97 (m, 2H, C_6H_5), 7.43 (m, 3H, C_6H_5), 6.64 (d, 1H, $^3J_{HH} = 8$ Hz, C_6H_3), 6.58 (m, 2H, C_6H_3), 5.28 (d, 1H, $^2J_{PH} = 18$ Hz, NH), 5.18 (d, 1H, $^2J_{PH} = 18$ Hz, NH), 2.25 (s, 3H, CH$_3$). IR (cm^{-1}); 3229s (ν_{NH}), 1102s (ν_{PC}), 888s (ν_{PN}), 588s (ν_{PSe}). FAB$^+$ MS; 308, [M^+ + H].

4. X-ray crystallographic analyses

X-ray diffraction studies on crystals of **3** grown from dichloromethane–hexane were performed at 293 K using a Bruker SMART diffractometer with graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods, non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms bound to carbon were idealised and fixed (C–H 0.95 Å), the NH protons were located by a ΔF map and allowed to refine anisotropically. Structural refinements were by the full-matrix least-squares method on F^2 using the program SHELXTL [14].

$C_{12}H_{11}N_2PSe$, $M = 293.16$, monoclinic, space group $P\bar{2}_1/c$, $a = 13.2118(3)$, $b = 17.8533(4)$, $c = 10.8580(1)$ Å, $\beta = 101.406(1)°$, $U = 2510.54(8)$ Å^3, $Z = 8$, $D_{calc} = 1.551$ Mg m^{-3}, $\mu = 3.092$ mm^{-1}, $F(000) = 1168$, crystal size = 0.1 × 0.1 × 0.03 mm. Of 10 391 measured data, 3613 were unique (R_{int} 0.0398) to give $R_1[I > 2\sigma(I)] = 0.0310$ and $wR_2 = 0.0682$.

5. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 147 057 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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