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The Preparation and Characterization of Binary Phosphorus–Selenium Rings

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ABSTRACT

Depending on the ratio of reactants, reaction of $(PPh)_5$ (**1**) *with grey selenium gives* $(PhPSe_2)_2$ (**2**), $(PhP)_3Se_2$ (**3**), $(PhP)_4Se$ (**4**), *and* $(PhP)_3Se_3$ (**5**). *The compounds have been characterized by multielement NMR, mass spectrometry, microanalyses, and, in the case of* **4**, *X-ray crystallography.* **4** *consists of a puckered 5-membered ring with all four phenyl substituents axial; the average P–P and P–Se bond lengths are 2.194 and 2.271 Å respectively.*

INTRODUCTION

Phosphorus–sulphur heterocycles can be prepared in a number of ways [1–9]; reaction of $(RP)_n$ with sulphur, $RPCl_2$ with $(Me_3Sn)_2S$, $(Me_3Si)_2S$, or Li_2S, reaction of $RP(S)Cl_2$ with H_2S, or by refluxing P_4S_{10} in a hydrocarbon. Surprisingly, there appears to have been little work on analogous phosphorus–selenium systems, although some $(RP)_nSe_m$ and $(RP)_nTe_m$ systems have been described [10]. It has recently been reported that the reaction of P_4Se_{10} with anisole (in an analogous reaction to the preparation of Lawesson's reagent [11]) does not give the expected diaryldiselena–diphosphetane–diselenide [12]. In view of the range of phosphorus–sulphur rings and the ready accessibility of $(PhP)_5$ (**1**) we have investigated the reaction of $(PhP)_5$ with selenium. We report here on the preparation of four- and five-membered P–Se rings. The heterocycles have been characterized by multielement NMR and, for **4**, by X-ray crystallography. Some preliminary results have already been reported [13, 14].

EXPERIMENTAL

All manipulations were carried out under an atmosphere of argon or nitrogen; THF and diethyl ether were distilled from sodium/benzophenone, toluene was dried over sodium, and CS_2 was used as received. $(PhP)_5$ [15] and $(PhPS)_3$ [4] were prepared by literature methods. Li_2Se was prepared by an adaptation of a published method [16].

$^{77}Se(^1H)$ NMR spectra were recorded at 47.8 MHz and referenced to Me_2Se at δ 0 using aqueous H_2SeO_3 as a secondary reference (δ 1282 relative to Me_2Se), and $^{31}P(^1H)$ NMR spectra were recorded at 101.4 MHz on a Bruker-WM250. Infrared spectra were obtained using a PE 1720X instrument. Mass spectra were obtained on a VG 2020 instrument operating in the electron impact mode.

Preparation of $(PhPSe_2)_2$, (**2**)

(a) From $(PhP)_5$: $(PhP)_5$ (1.34 g, 2.5 mmol) and selenium (1.96 g, 25.0 mmol) were refluxed with stirring in toluene (30 mL) for 6 h. After cooling, the red solid was filtered off, washed with toluene (2 × 15 mL), and dried in vacuo. Yield: 2.8 g, 87%.

(b) From $(PhPS)_3$: $(PhPS)_3$ (500 mg, 1.19 mmol) and selenium (282 mg, 3.57 mmol) were refluxed with stirring in toluene (30 mL) for 6 h. During the reaction, large red crystals were formed; they were filtered off, washed with toluene (2 × 10 mL), and

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dried in vacuo. Yield: 200 mg, 42%. Anal. Calcd.: C, 27.09; H, 1.89. Found: C, 26.57; H, 1.89. IR (KBr disc) 1479w, 1433s, 1301mw, 1279w, 1156w, 1106w, 1079s, 994m, 966w, 917w, 840w, 744m, 735s, 702m, 679s, 615m, 509s,br, 487s, 430s, 405w cm^{-1}. MS M$^+$ 534 $(PhPSe_2)_2$; 454 $(PhP)_2Se_3$; 374 $(PhP)_2Se_2$; 296 $(PhP)_2Se$; 268 $PhPSe_2$; 188 PhPSe.

Preparation of $(PhP)_3Se_2$ (**3**)

$(PhP)_5$ (2.57 g, 4.76 mmol) and grey selenium (1.25 g, 15.82 mmol) were refluxed in toluene (15 mL). Within approximately half an hour the selenium had dissolved to give a yellow solution. The reflux was allowed to continue for a further 90 minutes, after which time the solution was cooled to −20°C overnight and the yellow solid that formed was filtered off and washed with Et_2O (3 × 10 mL) and dried in vacuo. Yield: 3.0 g, 78%. Anal. Calcd.: C, 44.84; H, 3.14. Found: C, 44.96; H, 3.28. IR (KBr disc); 1478s, 1431vs, 1322w, 1302w, 1146w, 1067w, 998m, 943w, 900mw, 836w, 739 vs, 732 vs, 689vs, 616w, 476m, 451w, 420w,b, 408m, 400w, 363mw, 322mw cm^{-1}. Raman (solid, capillary); 690w, 681w, 614w, 492w, 450w, 422m, 409m, 399mw, 363s, 345s, 323w, 281m, 245w, 235mw, 224vs, 205w, 167s, 137ms cm^{-1}. MS 484 M$^+$; 454 $(PhP)_2Se_3$; 296 $(PhP)_2Se$; 268 $PhPSe_2$. ^{31}P NMR: δ P(1) = 108.1 (^1J—(P—Se) 295 Hz, ^2J(P—Se) 18 Hz, ^1J—(P(1)—P(2)) 296 Hz, ^2J—(P(1)—P(4)) 83 Hz), δ P(2) = 87.7 (^1J—(P—Se) 305 Hz, ^2J—(P—Se) 13 Hz, ^2J(P(2)—P(4)) 42.0 Hz, δ P(4) = 118.4 ^1J—(P—Se) 267, 260 Hz, ^{77}Se NMR δ 437, 451.

Preparation of $(PhP)_4Se$ (**4**)

$(PhP)_5$ (500 mg, 0.93 mmol) and selenium (91 mg, 1.15 mmol) were refluxed with stirring for 24 h. The solvent was removed in vacuo, and the residue was extracted with hot THF (10 mL). Slow cooling of the solution deposited an initial crop of the product as yellow rods. The remaining solution was decanted off and cooled to −20°C to give a further crop of the product as pale yellow needles. The solids were combined, washed with Et_2O (2 × 10 mL), and dried in vacuo. Yield: 220 mg, 37%. Anal. Calcd.: C, 56.38; H, 3.94. Found: C, 56.61; H, 4.02. IR (KBr disc) 1478m, 1439m, 1432s, 1139w, 1079w, 1070vw, 997w, 902w, 838w, 751w, 734s, 729s, 690s, 665w, 464m, 411m, 399m, cm^{-1}. MS M$^+$ 512; $(PhP)_3Se_2$ 482; $(PhP)_2Se$ 296; PhP 108. ^{31}P NMR: δ P(1) = 110.0 (^1J—(P—Se) 275 Hz, ^1J—(P(1)—P(2)) −340 Hz, ^2J—(P(1)—P(3)) 19 Hz, ^2J—(P(1)—P(4)) 16 Hz), δ P(2) = 86.0 (^1J—(P(2)—P(3)) −360 Hz, ^2J(P(2)—P(4)) 19 Hz, ^2J—(P(2)—Se) not observed). ^{77}Se NMR δ 401.

Preparation of $(PhPSe)_3$ (**5**)

2.1 g (4 mmol) of $(PhP)_5$ and 1.55 g (20 mmol) of grey selenium were refluxed in toluene (40 mL) for two h. During this time the selenium dissolved completely. The yellow solution was filtered and kept at room temperature. Its ^{31}P NMR showed peaks due to **4** and **5**. Cooling to −18°C allowed isolation of a small quantity (never more than 100 mg) of **5**. If the solution was kept for long periods, **2** is precipitated. IR (cm^{-1}) 1479(m), 1433(s), 1182(w), 1157(w), 1076(m), 997(m), 928(vw), 908(w), 835(w), 748(s), 740(m), 732(vs), 692(s), 683(vs), 616(w), 522(vs,br), 502(s), 489(s), 432(m), 423(s), 413(w), 397(w), 386(w). MS $(PhP)_3Se_2$ 482, $(PhP)_2Se$ 296, ^{31}P NMR: δ P(1) = 102.3 (^1J—(P—Se) 360 Hz, ^2J—(P—Se) 34 Hz, ^1J—(P(1)—P(2)) 266 Hz, ^2J—(P(1)—P(4)) 37 Hz), δ P(2) = 84.1 (^1J—(P—Se) 353 Hz, ^2J—(P—Se) 25 Hz, ^2J—(P(2)—P(4)) 25 Hz), δ P(4) = (Ph—P═Se group) 107.9 (^1J—(P—Se) 435, 463, 780 Hz).

Crystal Data of **4**. $C_{24}H_{20}P_4Se$, M = 511.3, orthorhombic, a = 13.417(4), b = 13.556(4), c = 24.806(14) Å, U = 4512 Å^3, space group *Pcab*, Z = 8, D_c = 1.51 gcm^{-3}. Yellow, air sensitive rods, dimensions 0.08 × 0.10 × 0.17 mm, μ(Cu-K$_\alpha$) = 51 cm^{-1}, $\bar{\lambda}$ = 1.54178 Å $F(000)$ = 2063.

Data Collection and Processing. Nicolet R3m diffractometer, ω-scan method, ($\theta \leq 58°$), graphite monochromated Cu-K$_\alpha$ radiation; 3043 independent measured reflections, 2322 observed [$|F_0| > 3\sigma(|F_0|)$], corrected for Lorentz and polarization factors; numerical absorption correction (face indexed crystal). Maximum and minimum transmission factors were 0.664 and 0.540, respectively.

Structure Analysis and Refinement. The structure was solved by direct methods and all non-hydrogen atoms refined anisotropically. The hydrogen atoms were idealized (C—H = 0.96 Å), assigned isotropic thermal parameters $U(H) = 1.2U\text{eq}(C)$, and allowed to ride on their parent carbons. Refinement was by block–cascade full-matrix least squares to $R = 0.058$, ($R = \Sigma[|F_0| - |F_c|]/\Sigma|F_0|$), $R_w = 0.062$ ($w^{-1} = \sigma^2(F) + 0.00082\ F^2$). The maximum and minimum residual electron densities in the final ΔF map were 0.45 and −0.81 eÅ^{-3}, respectively. The mean and maximum shifts/error in the final refinement cycle were 0.006 and 0.030, respectively. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system [17] and published scattering factors [18]. Further details of the structure are available from the Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CB2 1EW.

RESULTS AND DISCUSSION

The cyclopolyphosphines, $(RP)_n$, are convenient precursors in the formation of phosphorus–sulphur heterocycles. Pentaphenyl cyclopentaphosphane, $(PhP)_5$ (**1**), is especially useful as it is an easily prepared [15] air stable solid. It is therefore an obvious starting material for a study of phosphorus–selenium heterocycles. We have studied the reaction of **1** with grey selenium in benzene at room temperature and in refluxing toluene with various ratios of reactants.

When a 1:2 ratio of PhP:Se is used, a red insoluble solid, **2**, is obtained. The microanalysis suggests that the compound has the formula $(PhPSe_2)_n$, and the mass spectrum has a parent ion for $n = 2$, as well as peaks due to $(PhP)_2Se_3$, $(PhP)_2Se$, $PhPSe_2$, and PhPSe.

$$\tfrac{2}{5}\,(PhP)_5 + 4\,Se \longrightarrow (PhPSe_2)_2 \qquad (1)$$

No Raman spectrum could be obtained as the sample decomposed in the laser beam. The IR spectrum contains a peak at 509 cm^{-1}, which we assigned to $\nu(P{=}Se)$. We therefore conclude that the compound is 2,4-diphenyl-1,3-diselena-2,4-diphosphetane-2,4-diselenide. A compound with identical properties can also be obtained from the reaction of $(PhPS)_3$ with selenium. An unusual property of **2** is its volatility: the walls of vessels in which it is stored soon obtain a thin red coating.

When the quantities of reactants are altered to give a 3:2 ratio of PhP:Se, a yellow solid, **3**, is obtained by cooling of the solution.

$$\tfrac{3}{5}\,(PhP)_5 + 2Se \longrightarrow (PhP)_3Se_2 \qquad (2)$$

The ^{31}P NMR spectrum of **3** represents an AMX spin system. At low magnetic field (operating frequency 36.21 MHz), the spectrum is somewhat second order. At higher operating frequencies (101.4 MHz), the spectrum is first order. This interpretation is confirmed by the ^{31}P COSY spectrum. There is one large (295 Hz) coupling and two small (83, 42 Hz) couplings. The former is a typical value for two P(III) atoms directly bonded together, and the two remaining couplings are typical of two-bond P–P couplings. The ^{31}P NMR therefore implies that the compound is a 1,2,4-triphospholane. The ^{31}P–^{77}Se couplings (260–300 Hz) observed in the ^{31}P NMR are consistent with selenium atoms occupying bridging rather than terminal positions ($J(P{-}Se)$ for terminal Se is of the order of 700 Hz). The ^{77}Se spectrum confirms this. It contains signals due to two Se atoms that are both split into doublets of doublets of doublets with two large couplings (^1J) and one small (^2J) coupling. The position of the resonances is further evidence for this assignment; δ 437 and 451 are consistent with bridging Se (terminal selenium atoms are found at large negative chemical shifts $\delta \simeq -1000$).

Significant changes occur in the ^{31}P NMR of **3** when the temperature is raised from 37°C to 100°C. The multiplets centered at δ 118.4 and 87.7 are most affected. The line width of the peaks at δ 120 doubles, while that of the peaks at δ 92 increases fourfold. In addition, both sets of peaks are shifted downfield by approximately δ 3. The multiplet centered at δ 108.1 is less affected; the peaks remain relatively sharp and are shifted upfield by only δ 0.2. The thermal motion of the molecule must involve inversion at all three phosphorus centers, but clearly much higher temperatures are needed to observe this effect.

The IR and Raman spectra of **3** do not contain bands that could be assigned to $\nu(P{=}Se)$; assignment of the vibrational spectra is hampered by the presence of bands arising from phenyl vibrations. The mass spectrum contains peaks due to both the molecular ion, $(PhP)_3Se_2$, and disproportionation products $(PhP)_2Se_4$ and $(PhP)_2Se_3$, as well as $(PhP)_2Se$, $PhPSe_2$, PhPSe, PhP, and Se. The spectroscopic data therefore allow us to identify **3** as 1,2,4-triphenyl-3,5-diselena-1,2,4-triphospholane.

2 and **3** can be interconverted according to Equations 3 and 4

$$2\,(PhP)_3Se_2 + 8\,Se \longrightarrow 3\,(PhPSe_2)_2 \qquad (3)$$

$$3\,(PhPSe_2)_2 + 8\,Ph_3P \longrightarrow 2\,(PhP)_3Se_2 + 8\,Ph_3PSe \qquad (4)$$

In Equation 4 the correct stoichiometry must be used. Excess phosphine produces further deselenation to give $(PhP)_6$ (detected by ^{31}P NMR, δ −22, singlet [19]).

When a 4:1 (PhP:Se) ratio is used, the selenium rapidly dissolves to give a yellow solution. The ^{31}P NMR spectrum taken after 30 minutes shows unreacted $(PhP)_5$ and some new resonances, together with those due to **3**. After 24 h reflux very little **3** remains, but approximately one third of the $(PhP)_5$ has not reacted. Work up gave pale yellow rods of a further P–Se heterocycle, **4**.

$$\tfrac{4}{5}\,(PhP)_5 + Se \longrightarrow (PhP)_4Se \qquad (5)$$

X-ray crystallography shows **4** to be $(PhP)_4Se$. The ^{31}P NMR is second order, even at 101.4 MHz. The pattern is similar to that given by the tetraphospholanes [20–23].

When $(PhP)_5$ and sulphur are reacted together such that the P:S ratio is 1:1, $(PhPS)_3$ is produced [22]. When a 1:1 PhP:Se ratio is refluxed in toluene for 2 h, the ^{31}P NMR spectrum reveals the presence of **3** together with **5**. **5** has been obtained in better yield (72%) by reaction in benzene at room temperature (Equation 6) by Karaghiosoff [24, 25].

$$\tfrac{3}{5}\,(PhP)_5 + 3Se \longrightarrow (PhP)_3Se_3 \qquad (6)$$

However, when solutions of **5** are kept for several days, disproportionation takes place and **2** is precipitated (Equation 7).

$$3\,(PhP)_3Se_3 \longrightarrow (PhP)_2Se_4 + (PhP)_3Se_2 + 1/n\,(PhP)_n \qquad (7)$$

The X-ray structure of **4** is shown in Figure 1; fractional atomic coordinates and bond lengths and angles are given in Tables 1 and 2 respectively. The selenophosphane ring adopts a folded confor-

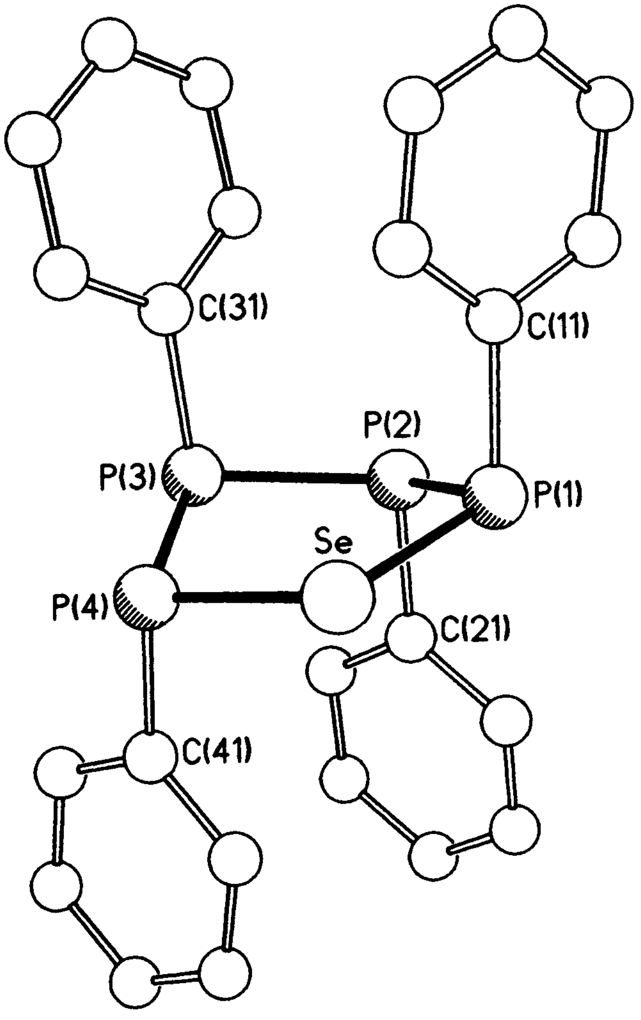

FIGURE 1 The X-ray Crystal Structure of **4**

TABLE 1 Atom Coordinates (×10^4) and Temperature Factors ($Å^2 \times 10^3$) with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	U_{eq}
Se	1688(1)	7534(1)	2453(1)	57(1)*
P(1)	12(1)	7549(1)	2584(1)	47(1)*
C(11)	−126(5)	7456(4)	3319(2)	49(2)*
C(12)	−1077(5)	7603(5)	3523(3)	68(3)*
C(13)	−1266(6)	7571(5)	4063(3)	80(3)*
C(14)	−506(6)	7403(6)	4421(3)	80(3)*
C(15)	453(6)	7263(6)	4235(3)	75(3)*
C(16)	644(5)	7288(5)	3690(2)	61(2)*
P(2)	−493(1)	6065(1)	2365(1)	43(1)*
C(21)	−513(4)	6122(4)	1628(2)	43(2)*
C(22)	−449(5)	5255(5)	1334(2)	59(2)*
C(23)	−523(5)	5284(5)	778(3)	68(3)*
C(24)	−677(5)	6139(5)	504(2)	65(3)*
C(25)	−747(5)	6994(5)	790(2)	66(3)*
C(26)	−661(4)	7002(5)	1343(2)	53(2)*
P(3)	791(1)	5074(1)	2470(1)	43(1)*
C(31)	840(4)	4936(4)	3204(2)	45(2)*
C(32)	−43(5)	4831(5)	3497(2)	59(2)*
C(33)	−3(6)	4628(5)	4047(3)	77(3)*
C(34)	879(6)	4544(6)	4307(3)	82(3)*
C(35)	1741(6)	4608(6)	4020(3)	83(3)*
C(36)	1739(5)	4812(5)	3477(3)	63(3)*
P(4)	2116(1)	5955(1)	2289(1)	50(1)*
C(41)	2085(4)	5836(4)	1545(2)	51(2)*
C(42)	2232(5)	4915(5)	1334(3)	72(3)*
C(43)	2271(6)	4788(6)	769(3)	99(4)*
C(44)	2184(6)	5575(7)	437(3)	85(3)*
C(45)	2054(6)	6488(7)	645(3)	84(3)*
C(46)	2007(5)	6634(5)	1202(3)	66(3)*

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

mation with a P(1)–P(2)–P(3)–P(4) torsion angle of 32° and a Se–P(1)–P(2)–P(3) torsion angle of 25° (Se and P(4) lie 0.91 and 1.10 Å from the P(1)–P(2)–P(3) plane). All four phenyl rings are alternately axially disposed with respect to the heterocycle in partially overlapping ring-over-ring pairs (inter-ring separation 3.6 Å). There are no significant intermolecular heterocycle–heterocycle contacts, the packing being dominated by phenyl ring edge-to-face interactions.

TABLE 2 Selected Bond Lengths (Å) and Angles (°) for **4**

P(1)–Se(1)	2.271(2)	Se–P(4)	2.253(2)
P(2)–P(2)	2.191(2)	P(2)–P(3)	2.201(2)
P(3)–P(4)	2.189(2)	P(1)–C(11)	1.838(6)
P(2)–C(21)	1.830(6)	P(3)–C(31)	1.832(6)
P(4)–C(41)	1.852(6)		
P(1)–Se–P(4)	106.6(1)	Se–P(1)–P(2)	105.3(1)
P(1)–P(2)–P(3)	106.8(1)	P(2)–P(3)–P(4)	106.2(1)
P(3)–P(4)–Se	105.9(1)	Se–P(1)–C(11)	103.9(2)
P(2)–P(1)–C(11)	98.7(2)	P(1)–P(2)–C(21)	102.3(2)
P(3)–P(2)–C(21)	98.9(2)	P(2)–P(3)–C(31)	102.0(2)
P(4)–P(3)–C(31)	103.3(2)	P(3)–P(4)–C(41)	98.0(2)
Se–P(4)–C(41)	104.9(2)		

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