Organo-Phosphorus–Selenium Heterocycles

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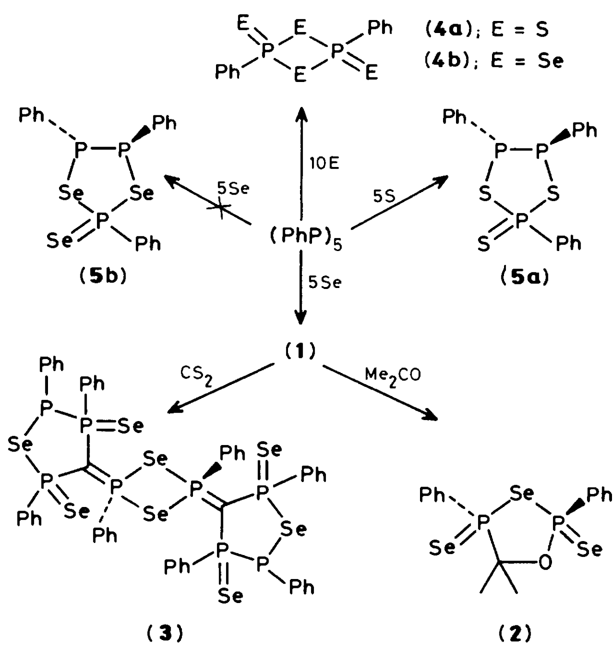
Reaction of selenium with $(PhP)_5$, or Li_2Se with $PhPCl_2$, gives a reactive intermediate (**1**) which undergoes reaction with acetone or CS_2 to give new organo-phosphorus–selenium heterocycles which have been characterised by *X*-ray crystallography.

There has been considerable recent interest in the organic chemistry of selenium.[1] Whilst there has been some interest in organo-phosphorus–selenium heterocycles[2] (and related species stabilised by transition metals)[3,4] and a number of organo-phosphorus–sulphur heterocycles have been isolated and characterised,[5–8] there is relatively little chemistry reported for their selenium analogues. Here we report the preparation of the first examples of organo-phosphorus–selenium heterocycles, two examples of which have been characterised by *X*-ray crystallography.

Reaction of pentaphenylcyclopentaphosphane[9] $(PhP)_5$ with five equivalents of selenium in refluxing benzene or toluene,



Scheme 1

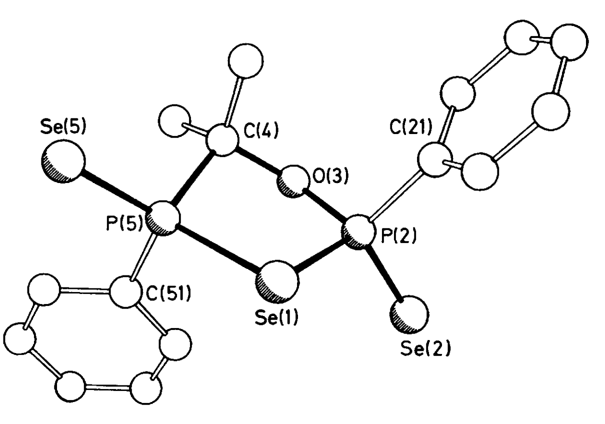


Figure 1. The *X*-ray structure of (**2**). Selected bond distances and angles: Se(1)–P(2) 2.258(1), Se(1)–P(5) 2.258(1), Se(5)–P(5) 2.091(2), Se(2)–P(2) 2.081(2), P(2)–C(21) 1.803(5), P(5)–C(4) 1.888(5), P(5)–C(51) 1.815(6), P(2)–O(3) 1.606(4), C(4)–O(3) 1.469(7) Å; P(2)–Se(1)–P(5) 90.7(1), Se(1)–P(2)–O(3) 101.8(1), Se(1)–P(5)–C(4) 98.4(2), C(4)–P(5)–Se(5) 113.2(2), Se(1)–P(2)–Se(2) 117.7(1), Se(2)–P(2)–O(3) 109.8(2), Se(2)–P(2)–C(21) 112.2(2), P(2)–O(3)–C(4) 123.5(3), O(3)–C(4)–P(5) 106.7(3), Se(1)–P(5)–Se(5) 115.1(1), Se(5)–P(5)–C(51) 115.0(2)°

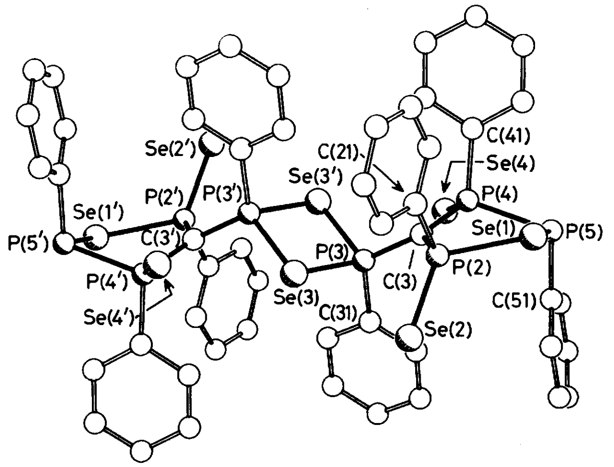


Figure 2. The *X*-ray crystal structure of (**3**). Selected bond lengths and angles: Se(1)–P(2) 2.309(2), Se(1)–P(5) 2.230(2), Se(2)–P(2) 2.099(3), Se(3)–P(3) 2.277(2), Se(4)–P(4) 2.120(2), P(2)–C(3) 1.746(8), P(2)–C(21) 1.829(8), P(3)–C(3) 1.730(6), P(4)–C(3) 1.740(9), P(4)–P(5) 2.239(2), P(4)–C(41) 1.813(8), Se(3)–P(3′) 2.259(2), P(4)–C(41) 1.813(8), P(5)–C(51) 1.826(7) Å; P(2)–Se(1)–P(5) 101.7(1), P(2)–C(3)–P(3) 117.8(5), C(3)–P(4)–P(5) 106.3(2), Se(1)–P(5)–P(4) 93.3(1), Se(1)–P(2)–C(3) 101.3(3), P(2)–C(3)–P(4) 122.7(4), P(4)–C(3)–P(3) 118.2(4), Se(3)–P(3)–Se(3′) 95.3(1), P(3)–Se(3)–P(3′) 84.7(1), C(3)–P(3)–Se(3) 110.6(3), C(3)–P(3)–Se(3′) 114.8(3), Se(1)–P(2)–Se(2) 119.2(1), C(3)–P(2)–Se(2) 112.6(3), C(3)–P(4)–Se(4) 109.6(2), P(5)–P(4)–Se(4) 116.2(1)°. There are short, non-bonding, intramolecular contacts of 3.37 Å for Se(2) Se(3) and Se(3′) · · · Se(4).

or treatment of lithium selenide (formed by the action of LiHBEt$_3$ on grey selenium, molar ratio 2:1) with phenyl dichlorophosphine in tetrahydrofuran (THF), gives a highly reactive species (**1**) which we have not yet been able to isolate. The ^{31}P n.m.r. parameters of (**1**) (δ_a 121, δ_b 105, δ_c 96 p.p.m., J_{ab} 82, J_{ac} 44, J_{bc} 0 Hz) suggest that it is not isostructural with the sulphur compound, Ph$_3$P$_3$S$_3$, (**5a**), obtained from a related reaction.

Complex (**1**) reacts readily with small, unsaturated molecules to give 1,3-diphospholanes. Thus when acetone (1 equiv.) is added to a concentrated solution of (**1**), colourless crystals of 4,4-dimethyl-5-oxa-1,3-diphenyl-1,3-diseleno-2-selena-1,3-diphospholane (**2**)† are gradually deposited. The *X*-ray structure‡ of (**2**) (Figure 1) reveals a unique five-membered P$_2$SeCO heterocycle which can be visualised as arising from insertion of acetone into a P$_2$Se$_2$ ring (with elimination of a selenium atom). The ring in (**2**) has a half-chair conformation with the CMe$_2$ group lying out of the P$_2$OSe plane. Both phosphorus atoms are formally P^V with normal [2.091(2) and 2.081(2) Å] exocyclic P=Se bond lengths. The geometries at P(2) and P(5) differ as a result of the asymmetry in the bridging (Figure 1). The PSeP bridge is symmetric, with a P–Se–P angle of 90.7(1)°. The bond lengths within the ring are as expected.

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† *Spectroscopic data* for (**2**): ^{31}P n.m.r. (toluene–C$_6$D$_6$) δ 82.2, 96.0 p.p.m., $J(^{31}P–^{31}P)$ 0 Hz; m.s.: *m/z* 512, 432 (*M*-Se), 296 (Ph$_2$P$_2$Se), 268 (PhPSe$_2$), 188 (PhPSe) (all with appropriate isotopic abundances; i.r. (Nujol mull, CsI) ν 931 (P–O), 559 (P=Se), 237, 227 cm^{-1} (P–Se).

For (**3**): m.s. highest peaks (no parent ion observed) *m/z* 562 (Ph$_3$P$_3$Se$_3$) and 454 (Ph$_2$P$_2$Se$_3$); i.r. (KBr disc) ν 984 (P=C), 492(P=Se), 253, 244 cm^{-1} (tentatively assigned to P–Se *cf.* ref. 2).

‡ *Crystal data* for (**2**): C$_{15}$H$_{16}$OP$_2$Se$_3$, M = 511.1, triclinic, a = 9.347(2), b = 10.014(2), c = 10.399(2) Å, α = 94.19(2), β = 110.15(2), γ = 94.50(2)°, U = 906 Å^3, space group $P\bar{1}$, Z = 2, D_c = 1.87 g cm^{-3}, μ(Cu-K_α) = 93 cm^{-1}; 2365 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $\theta \leqslant 58°$].

For (**3**): C$_{52}$H$_{40}$P$_8$S$_4$Se$_8$, M = 1672.6, triclinic, a = 9.537(2), b = 11.971(2), c = 14.520(2) Å, α = 69.85(1), β = 75.15(2), γ = 83.56(2)°, U = 1504 Å^3, space group $P\bar{1}$, Z = 1 (the dimer possesses a centre of symmetry), D_c = 1.85 g cm^{-3}, μ(Cu-K$_\alpha$) = 95 cm^{-1}, 2940 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $\theta \leqslant 50°$].

In both cases, data were measured on a Nicolet R3m diffractometer with Cu-K_α radiation (graphite monochromator). The structures were solved by direct methods and refined anisotropically using absorption corrected data, to give, for (**2**), R = 0.043, R_w = 0.051 and for (**3**), R = 0.057, R_w = 0.066.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Removal of the solvent from (**1**) prepared as above and replacement with CS_2 leads to deposition of orange crystals of (**3**) after 10 days. The *X*-ray structure‡ (Figure 2) reveals, in this instance, the formation of a dimeric structure consisting of two five-membered CP_3Se rings bridged *via* their trigonal carbon atoms which are bonded to the phosphorus atoms of a P_2Se_2 ring. This four-membered ring lies about a crystallographic centre of symmetry which results in the exocyclic phenyl rings being *trans*. Within the four-membered ring the P–Se bond lengths differ significantly [2.277(2) and 2.259(2) Å], as is the case in related phosphorus–sulphur compounds.[8,10] As aforementioned, within the five-membered ring the carbon atom has planar (sp^2) geometry with all three P–C bond lengths [1.730(6), 1.740(9), 1.746(8) Å] being significantly shorter than typical P–C (sp^2) bond lengths [*e.g.* P(2)–C(21) 1.83(1) Å]. Clearly, there is substantial delocalisation of the π-character over all three P–C bonds. However, the remaining bonds within the five-membered ring have normal single bond lengths (Figure 2). The angles within the ring vary depending on the oxidiation state of the phosphorus, with the P^V atom being essentially tetrahedral whilst P(5) is typical for P^{III} [93.3(1)°]. There is a notable enlargement of the angle at Se(1) [101.7(1)°] relative to the equivalent P–Se–P angle in (**2**). It is interesting to note that although P(5) is formally P^{III}, this does not affect the bond lengths around this atom compared to P(2) and P(4) which are both P^V. A surprising feature is the lack of oxidation with addition of selenium at P(5). Furthermore, in adjacent symmetry-related dimers, the P(5) atoms abutt each other [$P(5) \cdots P(5)''$ 3.37 Å].

Reaction of Ph_5P_5 with ten equivalents of selenium in refluxing toluene produces an insoluble red precipitate of stoicheiometry $PhPSe_2$ (**4b**). [I.r. (KBr disc) ν 508 (P=Se), 244 cm^{-1} (P–Se)]. Only the monomeric species (*m/z* 268) is observed in the mass spectrum but we assume that, like the equivalent sulphur compound (**4a**), (**4b**) actually exists as a dimer or polymer.

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