DALTON
FULL PAPER

Heterocycle formation using $[PhP(Se)(\mu\text{-}Se)]_2$. The crystal structures of $[PhP(Se)(\mu\text{-}Se)]_2$, $PhP(Se)Se_2(C_7H_{10})$ and $PhP(Se)(\mu\text{-}Se)(\mu\text{-}NPh)P(Se)Ph$

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An X-ray crystallographic study of $[PhP(Se)(\mu\text{-}Se)]_2$ **1**, the oxidation product of the homocycle $(PhP)_5$ with ten equivalents of selenium, revealed that the molecule is centrosymmetric with a planar central $P_2(\mu\text{-}Se)_2$ core and *trans* disposition of exocyclic P=Se bonds. In the reaction of **1** with norbornene (bicyclo[2.2.1]hept-2-ene), crystallographic analysis of the product **2** revealed *exo* addition of a $PhP(Se)Se_2$ unit across the C=C bond, giving a 1,2-diselena-3-phospholane (C_2PSe_2) ring. Norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) reacts more slowly with **1**, allowing the isolation of a 1,2-selenaphosphetane (C_2PSe ring) in addition to a diselenaphospholane. The reaction of **1** with azobenzene proceeds with cleavage of the N=N bond and substitution of a bridging selenium atom in **1** by an NPh unit, giving the first crystallographically characterised selenaazadiphosphetane (P_2SeN) ring.

Introduction

There have been few investigations into the chemistry of 2,4-bis(phenyl)-1,3-diselenadiphosphetane 2,4-diselenide $[PhP(Se)(\mu\text{-}Se)]_2$ **1**, the terminal oxidation product of $(PhP)_5$ with elemental selenium.[1,2] Treatment of *cis*-$[PtCl_2(PR_3)_2]$ ($PR_3 = \frac{1}{2}$ dppe, PEt_3, PMe_2Ph or PPh_2Me) with **1** in thf affords *cis*-$[Pt(Se_3PPh\text{-}Se,Se')(PR_3)_2]$ while Hill and co-workers have used **1**, prepared *in situ* from $(PhP)_5$/Se, to convert molybdenum and tungsten ketenyl complexes into their selenoketenyl analogues.[3,4] Also, Karaghiosoff and co-workers have reported that the reaction between **1** and 2-phosphaindolizines proceeds with fission of the $P_2(\mu\text{-}Se)_2$ ring to give diselenophosphinates.[5] We have recently described the reaction of **1** with dialkyl cyanamides $R_2N\text{–}CN$ [$R_2 = Me_2$, $(CH_2)_5$ or $CH_2CH_2OCH_2CH_2$], which leads to 1,6,6aλ^4-triselena-3,4-diaza-3a-phosphapentalenes $[R_2NC(Se)=N]_2P(Se)Ph$, containing two fused PSe_2CN rings in which the P^V=Se bond is abnormally long.[6] Thus the preliminary indications are that a rich and varied chemistry exists for **1**, and indeed for organophosphorus–selenium heterocycles in general.

We report here the crystal structures of compound **1** and the unusual heterocycles derived from its reactions with norbornene (bicyclo[2.2.1]hept-2-ene), norbornadiene and azobenzene, which contain saturated PC_2Se_2 and P_2SeN rings respectively.

Results and discussion

Oxidation of pentaphenylcyclopentaphosphane, $(PhP)_5$, with ten equivalents of elemental selenium gives a sparingly soluble red solid formulated on the basis of infrared and mass spectrometric data as a 1,3-diselenadiphosphetane 2,4-diselenide, $[PhP(Se)(\mu\text{-}Se)]_2$ **1**.[1,2] In order to obtain crystallographic corroboration of this we grew crystals of **1** by recrystallisation from hot toluene. Compound **1** does indeed possess the structure proposed (Fig. 1, Table 1), with a planar $P_2(\mu\text{-}Se)_2$ ring and a *trans* orientation of the exocyclic P=Se bonds. The internal P(1)–Se(1), P(1)–Se(1A) (single bond) and exocyclic P(1)–Se(2) (double bond) distances [2.276(2), 2.284(2) and 2.102(3) Å] are similar to those of $[^tBuP(Se)(\mu\text{-}Se)]_2$ [P–Se 2.269(2), P=Se 2.097(4) Å][7] which contains the same $P_2(\mu\text{-}Se)_2$ unit. The internal angles of the P(1)–Se(1)–P(1A)–Se(1A) ring in **1** show some distortion from a true square, with P(1)–Se(1)–P(1A) 85.45(9)° and Se(1)–P(1)–Se(1A) 94.55(9)°, *cf.* 83.5(1) and 96.5(1)° in $[^tBuP(Se)(\mu\text{-}Se)]_2$, the transannular P(1) ··· P(1A) and Se(1) ··· Se(1A) distances being 3.1 and 3.4 Å respectively. The angles at P(1) are between 94.55(9) and 115.61(11)°, with (internal) Se(1)–P(1)–Se(1A) being the smallest of these, the exocyclic Se(2)–P(1)–X angles [X = C(1), Se(1) or Se(1A)] all exceeding 114°. The closest intermolecular separation seen within the structure is Se(1) ··· Se(2′) between adjacent molecules, 3.3 Å.

Table 1 Selected bond lengths (Å) and angles (°) for compound **1** (e.s.d.s in parentheses)

Se(1)–P(1)	2.276(2)	Se(1)–P(1A)	2.284(2)
Se(2)–P(1)	2.102(3)	P(1)–C(1)	1.822(10)
P(1)–Se(1A)	2.284(2)		
C(1)–P(1)–Se(2)	115.2(3)	C(1)–P(1)–Se(1)	108.1(3)
Se(2)–P(1)–Se(1)	115.61(11)	C(1)–P(1)–Se(1A)	107.1(3)
Se(2)–P(1)–Se(1A)	114.08(11)	Se(1)–P(1)–Se(1A)	94.55(9)
P(1)–Se(1)–P(1A)	85.45(9)		

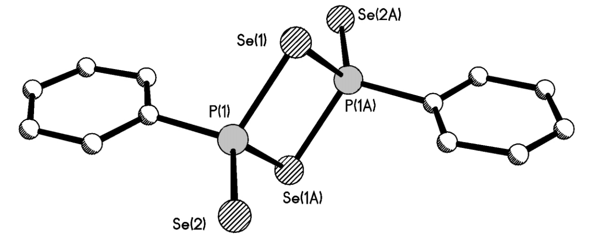

Fig. 1 Molecular structure of compound **1** (C–H bonds omitted for clarity, as in all cases shown).

Reaction of compound 1 with norbornene and norbornadiene

The reaction between compound **1** and norbornene in hot toluene for 24 hours proceeds with cleavage of the $P_2(\mu\text{-}Se)_2$ ring to give a 1,2-diselena-3-phospholane **2** in 20% isolated yield based on **1** following chromatographic work-up (eqn. 1). The formation of **2** is in marked contrast to that of the

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Table 2 Selected bond lengths (Å) and angles (°) for compound **2** (e.s.d.s in parentheses)

P(1)–C(8)	1.806(7)	P(1)–C(1)	1.843(6)
P(1)–Se(3)	2.117(2)	P(1)–Se(1)	2.232(2)
Se(1)–Se(2)	2.352(1)	Se(2)–C(2)	2.002(6)
C(8)–P(1)–C(1)	106.8(3)	C(8)–P(1)–Se(3)	113.7(2)
C(1)–P(1)–Se(3)	116.4(2)	C(8)–P(1)–Se(1)	106.7(2)
C(1)–P(1)–Se(1)	102.0(2)	Se(3)–P(1)–Se(1)	110.22(7)
P(1)–Se(1)–Se(2)	89.60(5)	C(2)–Se(2)–Se(1)	96.5(2)

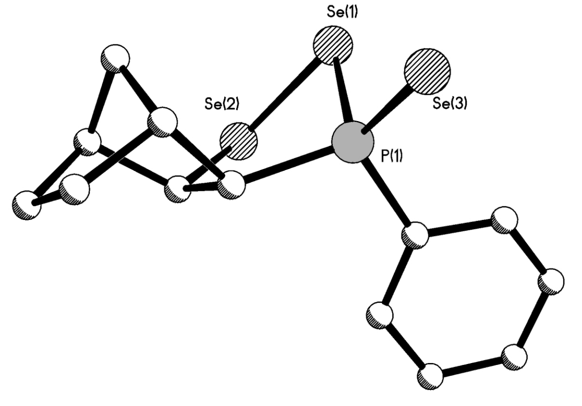
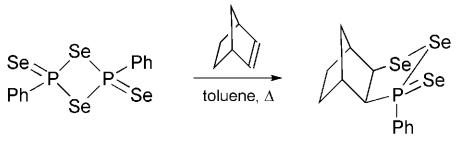


Fig. 2 Molecular structure of compound **2**.



(1)

1 **2**

1,2-thiaphosphetane (C_2PS ring) obtained in the reaction of $[RP(S)(\mu\text{-}S)]_2$ (R = ferrocenyl) with norbornene, arising from a [2 + 2] cycloaddition between the alkene and a P=S bond.[8] Notably the $PhPSe_3$ moiety, albeit in different geometries, is also found in the products from the reactions of *cis*-$[PtCl_2(PR_3)_2]$ or dialkyl cyanamides with **1**,[4,6] suggesting a particular stability for this unit. The tricyclic compound **2** is an air- and moisture-stable orange solid, soluble in most organic solvents excluding aliphatic hydrocarbons. The $^{31}P\text{-}\{^1H\}$ NMR spectrum comprises a singlet at δ_P 81.4 flanked by ^{77}Se satellites, ^1J(P–Se) 353 and 773 Hz, values which confirm the presence of both phosphorus–selenium single and double bonds, with a molecular ion in the FAB$^+$ mass spectrum at *m*/*z* 440.

The molecular structure of compound **2** (Fig. 2, Table 2) contains a 1,2-diselena-3-phospholane (C_2PSe_2) ring, which has an *exo* geometry to the norbornane moiety; although **2** is chiral, crystallisation as a racemate occurs. The internal P(1)–Se(1) length [2.232(2) Å] is *ca.* 0.05 Å shorter than that of **1**, the exocyclic P(1)–Se(3) distance [2.117(2) Å] being only 0.01 Å longer. The Se(1)–Se(2) distance of 2.352(1) Å is similar to the value of 2.319(2) Å in the eight-membered heterocycle $[P(pox)_3]Se_5$ [pox = $C_6H_2(^tBu)_2(O^iPr)$-2,4,6] and in the acyclic molecule $[Et_2P(S)Se]_2$ [2.334(12) Å].[9,10] In comparison with **1** the angles at P(1) of **2** fall within the narrower range of 102.0(2)–116.4(2)°, the exocyclic P=Se bond once more imposing the greatest influence on the geometry of P(1). Within the phospholane ring, the P(1)–C(1)–C(2)–Se(2) chain is approximately coplanar (mean deviation from plane 0.03 Å) with Se(1) displaced by 1.1 Å from this plane.

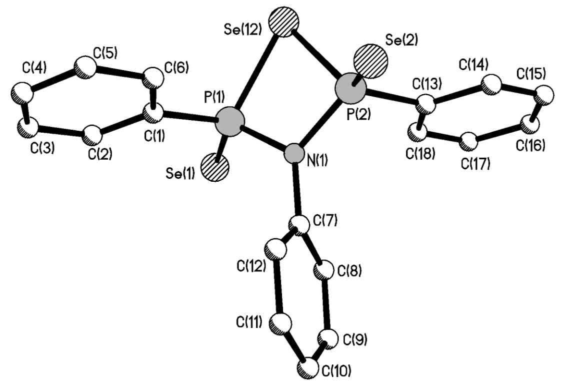
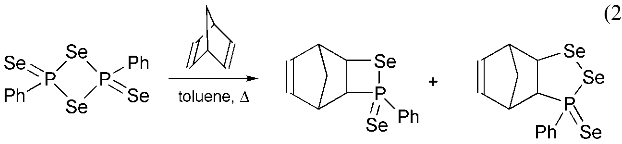


Fig. 3 Molecular structure of compound **4**.



(2)

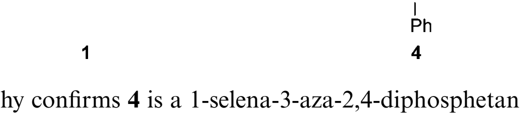
1 **3a** **3b,c**

The reaction of compound **1** with norbornadiene proceeds somewhat more slowly than with norbornene. Three P–Se compounds are present in $^{31}P\text{-}\{^1H\}$ NMR spectra of crude mixtures obtained from these reactions after 24 h, characterised by singlets at δ 29.0 [**3a**, ^1J(P–Se) 794 and 202], 70.9 [**3b**, ^1J(P–Se) 751 and 394] and 71.4 [**3c**, ^1J(P–Se) 759 and 359 Hz] in the approximate ratio 10 : 1 : 4 (eqn. 2). Column chromatography (1 : 1 v/v dichloromethane–hexane) separates **3a** (R_f 1.0) from **3b**,**c** (R_f 0.5), which are themselves separable by collecting small (1 cm^3) fractions as **3b** elutes marginally ahead of **3c**. Compound **3a** is a highly soluble off-white oily material, preventing any satisfactory elemental analysis, however FAB$^+$ mass spectrometry (M^+ at *m*/*z* 360) indicates a molecule of composition $C_{13}H_{13}PSe_2$. Hence **3a** is formulated as a 1,2-selenaphosphetane, the small ^1J(P–Se) single bond coupling of 202 Hz being attributed to the strained C_2PSe ring. Compounds **3b**,**3c** are isolable as orange solids from dichloromethane–hexane; their FAB$^+$ mass spectra each contain a molecular ion peak at *m*/*z* 438, corresponding to $C_{13}H_{13}PSe_3$, suggesting that both *endo* and *exo* isomers are generated; however, we have been unable to assign by ^1H NMR spectroscopy which isomers the compounds are.

In the reactions leading to formation of compounds **2** and **3a**–**3c** no other phosphorus containing compounds are observed in $^{31}P\text{-}\{^1H\}$ NMR spectra of crude reaction mixtures, the deposition of small quantities of elemental selenium during the reactions points to some degradation of **1**. No further products are recovered upon elution with more polar solvents. We speculate that the initially formed C_2PSe rings generated during these reactions are prone to selenium insertion from **1** into the C–Se bond, being more facile in the norbornene system compared with norbornadiene.

Reaction of compound 1 with azobenzene

While the $P_2(\mu\text{-}Se)_2$ ring of compound **1** is cleaved during its reaction with norbornene, part of this linkage is preserved in the product from its reaction with azobenzene. The compound PhP(Se)(μ-Se)(μ-NPh)P(Se)Ph **4** is generated upon reaction of 1.5 equivalents of **1** with azobenzene in hot toluene, followed by chromatographic purification on silica (eqn. 3). X-Ray crystallography confirms **4** is a 1-selena-3-aza-2,4-diphosphetane 2,4-diselenide (Fig. 3, Table 3), the first structurally characterised P_2SeN ring. The central P_2SeN ring is planar, the twist angle along N(1)–C(7) between this ring and the C(7)–C(12) phenyl group being 96°. Introduction of μ-NPh for μ-Se produces dramatic changes in the heterocycle geometry compared with



(3)

1 **4**

Table 3 Selected bond lengths (Å) and angles (°) for compound **4** (e.s.d.s in parentheses)

Se(1)–P(1)	2.0676(12)	P(1)–N(1)	1.705(3)
P(1)–C(1)	1.801(4)	P(1)–Se(12)	2.2705(12)
N(1)–C(7)	1.439(5)	N(1)–P(2)	1.694(3)
Se(12)–P(2)	2.2662(11)	P(2)–C(13)	1.802(4)
P(2)–Se(2)	2.0846(11)		
N(1)–P(1)–C(1)	108.1(2)	N(1)–P(1)–Se(1)	116.07(12)
C(1)–P(1)–Se(1)	114.1(2)	N(1)–P(1)–Se(12)	87.47(11)
C(1)–P(1)–Se(12)	107.09(14)	Se(1)–P(1)–Se(12)	120.66(6)
C(7)–N(1)–P(2)	126.6(3)	C(7)–N(1)–P(1)	124.1(2)
P(2)–N(1)–P(1)	109.2(2)	P(2)–Se(12)–P(1)	75.28(4)
N(1)–P(2)–Se(2)	115.82(13)	N(1)–P(2)–Se(12)	87.86(11)
Se(2)–P(2)–Se(12)	119.71(5)		

those of **1**. The N(1)–P–Se(12) and P(1)–Se(12)–P(2) angles are *ca.* 7–10° narrower compared to those of **1**, with P(1)–N(1)–P(2) [109.2(2)°] being 17° wider than the P–Se–P angles of **1** [85.45(9)°]. There is modest shortening of the internal P–Se distances [P(1)–Se(12) 2.2705(12), P(2)–Se(12) 2.2662(11) Å], consequently the transannular P(1) · · · P(2) and N(1) · · · Se(12) distances are only 2.77(1) and 2.78(1) Å respectively. A similar ring geometry perturbation by NR is also apparent in the thiaphosphetanes RP(S)(μ-S)(μ-NR′)P(S)R (R = ferrocenyl, R′ = CH_2Ph, Cy, Ph or Me).[11] In this series of compounds the P–N–P angles are 104.5(4)–107.4(5)° whereas P–S–P is 79.1(2)–79.3(1)° *cf.* P–S–P 86.9(1)° in $[RP(S)(\mu\text{-}S)]_2$.[12] The exocyclic P=Se distances of **4** [P(1)–Se(1) 2.0676(12), P(2)–Se(2) 2.0846(11) Å] are somewhat shortened from **1** [2.102(3) Å]; the P–N lengths [P(1)–N(1) 1.705(3), P(2)–N(1) 1.694(3) Å] suggest some multiple bond character.

Chloroform solutions of compound **4** are susceptible to oxidation, depositing red selenium within 72 h, although the crystalline material is more robust. Employing molar ratios of **1** and azobenzene closer to parity gives additional singlets in the $^{31}P\text{-}\{^1H\}$ NMR to high frequency of that of **4**; however these species have proven inseparable from **4** and have not further been characterised. The magnitude of ^1J(P=Se) in **4** (857 Hz) is consistent with a P–N linkage,[13] while the very small ^1J(P–Se) coupling (263 Hz) reflects the strain inherent within the four membered ring, *cf.* **3a**. The ν_{PSe} vibration (551 cm^{-1}) is substantially higher than for either **1** (506 cm^{-1}) or **2** (529 cm^{-1}), with ν_{PN} at 942 cm^{-1}.

Conclusion

Crystallographic analysis has established unequivocally the structure of **1** as a diselenadiphosphetane diselenide; **1** undergoes cleavage of the central $P_2(\mu\text{-}Se)_2$ ring in its reaction with norbornene to give a 1,2-diselena-3-phospholane 3-selenide. With azobenzene, **1** reacts with retention of one μ-Se atom to give a structurally unique P_2SeN system. The simplicity of heterocycle syntheses using **1** bodes well for further investigations into its chemistry.

Experimental

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

Preparations

$PhP(Se)Se_2(C_7H_{10})$ 2. A toluene solution (2 cm^3) of compound **1** (150 mg, 0.28 mmol) and norbornene (52 mg, 0.56 mmol) was heated at 130 °C for 24 h, giving an orange solution with a small amount of elemental selenium. The solvent was removed *in vacuo*, the crude product extracted into dichloromethane (2 cm^3) and purified by column chromatography (silica, dichloromethane eluent). The orange compound **2** was recrystallised by slow evaporation of a dichloromethane–hexane solution over several days at room temperature, giving crystals suitable for X-ray analysis. Yield 25 mg, 20% based on **1**. Found (Calc. for $C_{13}H_{15}PSe_3$); C 35.5(35.6), H 3.1(3.4)%. δ_P 81.4(s), ^1J(P–Se) 773, 353 Hz. δ_H 8.01 (m, 2H, C_6H_5), 7.44 (m, 3H, C_6H_5), 3.95 (ddd, 1H, J = 2, 7.5 and 14, C_7H_{10}), 3.01 (d, 1H, J = 7.5, C_7H_{10}), 2.94 (d, 1H, J = 10, C_7H_{10}), 2.39 (d, 1H, J = 10 Hz, C_7H_{10}), 1.63 (m, 2H, C_7H_{10}) and 1.20 (m, 3H, C_7H_{10}). IR (cm^{-1}): 1094m (ν_{PC}) and 529s (ν_{PSe}). FAB^+ MS: *m*/*z* 440, M^+.

Reaction of compound 1 with norbornadiene. A toluene solution (2 cm^3) of compound **1** (150 mg, 0.28 mmol) and norbornadiene (0.25 cm^3, 2.3 mmol) was heated at 130 °C for 24 h, giving an orange solution with some selenium. The solvent was removed *in vacuo*, the crude products extracted into dichloromethane (2 cm^3) and subjected to column chromatography (silica, 1 : 1 v/v dichloromethane–hexane eluent), to give a pale yellow eluate (R_f 1.0) of **3a** and an orange eluate (R_f 0.5) of **3b**,**3c**. Collection of small (*ca.* 1 cm^3) fractions from the latter enabled resolution of **3b** from **3c**. **3a** was isolated as an off-white oil soluble in all organic solvents, precluding isolation as an analytically pure material. **3b**,**3c** can be obtained as orange solids from dichloromethane–hexane.

3a: 30 mg, 30% based on **1**. δ_P 29.0(s), ^1J(P–Se) 794, 202 Hz. δ_H 8.18 (m, 2H, C_6H_5), 7.44 (m, 3H, C_6H_5), 6.07 (m, 1H, =CH), 6.02 (m, 1H, =CH), 3.44 (ddd, 1H, J = 2, 7 and 14, C_7H_8), 3.26 (d, 2H, J = 7, C_7H_8), 3.11 (d, 2H, J = 10, C_7H_8) and 1.70 (d, 1H, J = 10 Hz, C_7H_8). FAB^+ MS: *m*/*z* 360, M^+.

3b: 3 mg, 1% based on **1**. Found (Calc. for $C_{13}H_{13}PSe_3$); C 35.9(35.7), H 3.1(3.0)%. δ_P 70.9(s), ^1J(P–Se) 751, 394 Hz. δ_H 8.02 (m, 2H, C_6H_5), 7.46 (m, 3H, C_6H_5), 6.60 (dd, 1H, J = 3 and 5, =CH), 6.28 (dd, 1H, J = 3 and 5, =CH), 4.28 (ddd, 1H, J = 4, 7 and 19, C_7H_8), 3.81 (m, 1H, C_7H_8), 3.73 (br s, 1H, C_7H_8), 3.44 (br s, 1H, C_7H_8), 1.66 (t, 1H, J = 7, C_7H_8) and 1.52 (d, 1H, J = 7 Hz, C_7H_8). IR (cm^{-1}): 536s (ν_{PSe}). FAB^+ MS: *m*/*z* 438, M^+.

3c: 17 mg, 14% based on **1**. Found (Calc. for $C_{13}H_{13}PSe_3$); C 36.1(35.7), H 3.1(3.0)%. δ_P 71.4(s), ^1J(P–Se) 759, 359 Hz. δ_H 8.07 (m, 2H, C_6H_5), 7.50 (m, 3H, C_6H_5), 6.40 (s, 2H, =CH), 4.00 (ddd, 1H, J = 2, 7 and 16, C_7H_8), 3.65 (d, 1H, J = 5, C_7H_8), 3.23 (m, 2H, C_7H_8), 2.74 (d, 1H, J = 10, C_7H_8) and 1.65 (d, 1H, J = 10 Hz, C_7H_8). IR (cm^{-1}): 533s (ν_{PSe}). FAB^+ MS: *m*/*z* 438, M^+.

PhP(Se)(μ-Se)(μ-NPh)P(Se)Ph 4. A toluene solution (2 cm^3) of compound **1** (150 mg, 0.28 mmol) and azobenzene (32 mg, 0.18 mmol) was heated at 130 °C for 5 h, giving an orange solution with some selenium. The solvent was removed *in vacuo*, the crude product extracted into dichloromethane (2 cm^3) and purified by column chromatography (silica, dichloromethane eluent) giving 20 mg (13%) of **4** as a pale orange solid. Crystals of **4** suitable for X-ray analysis were grown by layering a $CDCl_3$ solution of the compound with hexane over 48 h. Found (Calc. for $C_{18}H_{15}NP_2Se_3$); C 39.6(39.7), H 2.8 (2.8), N 2.5 (2.6)%. $^{31}P\text{-}\{^1H\}$ NMR: δ 44.7(s), ^1J(P–Se) 857, 263 Hz. ^1H NMR: δ 8.49 (m, 2H, C_6H_5), 8.43 (m, 2H, C_6H_5), 7.84 (m, 1H, C_6H_5), 7.52 (m, 6H, C_6H_5) and 7.03 (m, 4H, C_6H_5). IR (cm^{-1}): 1090m (ν_{PC}), 942s (ν_{PN}) and 551s (ν_{PSe}). FAB^+ MS: *m*/*z* 545, M^+ + H.

Table 4 Data collection and structural refinement parameters for compounds **1**, **2** and **4**

	1	**2**	**4**
Formula	$C_{12}H_{10}P_2Se_4$	$C_{13}H_{15}PSe_3$	$C_{18}H_{15}NP_2Se_3$
M	531.98	439.10	544.13
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	9.5224(4)	17.3773(7)	9.6859(1)
b/Å	7.3091(5)	6.6669(2)	16.2944(3)
c/Å	11.3341(8)	12.9445(5)	13.3506(1)
β/°	96.213(3)	101.237(1)	108.456(1)
U/Å^3	784.22(8)	1470.91(9)	1998.70(4)
Z	2	4	4
μ/mm^{-1}	9.539	7.587	5.681
Reflections collected	3278	5984	8565
Independent reflections (R_{int})	1129(0.0477)	2106(0.0463)	2870(0.0305)
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0447, 0.1132	0.0364, 0.0761	0.0288, 0.0634

Single crystal X-ray diffraction studies

Crystallographic analyses of compounds **1**, **2** and **4** were performed at 293 K using a Bruker SMART diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods, non-hydrogen atoms refined with anisotropic displacement parameters, hydrogen atoms bound to carbon idealised and fixed (C–H 0.95 Å). Structural refinements were by the full-matrix least-squares method on F^2 using the program SHELXTL.[14] Data collection and structural refinement parameters are shown in Table 4.

CCDC reference number 186/2287.

See http://www.rsc.org/suppdata/dt/b0/b008071n/ for crystallographic files in .cif format.

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