The Reactivity of $[PhP(Se)(\mu\text{-}Se)]_2$ and $(PhP)_3Se_2$ Towards Acetylenes and Cyanamides: X-ray Crystal Structures of Some P-Se-C and P-Se-C-N Heterocycles

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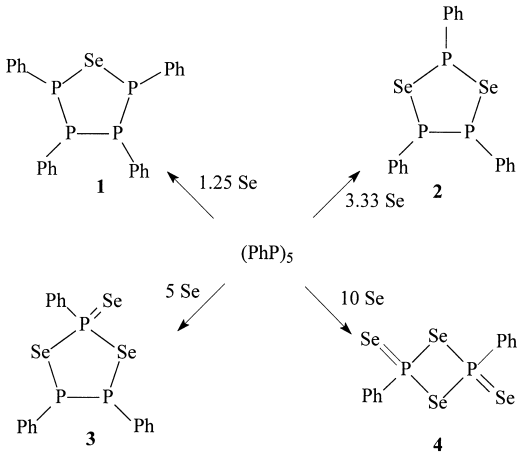
Abstract: Several unusual P-Se-C and P-Se-C-N heterocycles are formed by the reaction of $[PhP(Se)(\mu\text{-}Se)]_2$ or $(PhP)_3Se_2$ with alkynes or cyanamides, generated by the fragmentation of the organophosphorus–selenium compound and addition across the $C\equiv C$ or $C\equiv N$ triple bond of the organic substrate. X-ray crystallographic analysis reveals an unexpected diversity of structural motifs within these heterocyclic systems, including P_2SeCN, P_2C_2Se and PC_2Se_2 rings.

Keywords: cycloaddition · heterocycles · phosphorus · selenium · structure elucidation

Introduction

Little detailed study has been conducted upon the organophosphorus–selenium heterocycles **1**–**4**, which are available from the oxidation of pentaphenylcyclopentaphosphine, $(PPh)_5$, with selenium (Scheme 1).[1, 2] Investigations by ourselves and others have established that $[PhP(Se)(\mu\text{-}Se)]_2$ (**4**; “Woollins Reagent”) is an excellent material both for synthesis of P-Se-C-N-, P-Se-N- and P-Se-C-containing heterocycles[3–6] and the selenation of carbonyl groups to selenocarbonyls.[7, 8] Of the phospholanes **1**–**3**, we have found that $(PhP)_3Se_3$ (**3**) reacts with acetone or acetonitrile to give P_2SeOC and P_2SeNC heterocycles, respectively, and that $(PhP)_3Se_2$ (**2**) possesses a modest selenation capability.[1, 8] Thus the preliminary indications are that a rich and varied chemistry exists for **1**–**4** and, indeed, for organophosphorus–selenium heterocycles in general. In this paper we describe the behaviour of **4** towards $MeO_2C{-}C\equiv C{-}CO_2Me$ (DMAD) and $PhC\equiv CH$, and of **2** towards dialkyl cyanamides and $PhC\equiv C{-}CO_2Me$, reactions that generate an array of new P-Se-C and P-Se-C-N ring topologies.



Scheme 1. Heterocycles **1**–**4** from the oxidation of $(PhP)_5$ with selenium.

Results and Discussion

The four-membered $P_2(\mu\text{-}Se)_2$ ring of **4** is readily cleaved during its reaction with substrates such as cyanamides, azobenzene and bicyclo[2.2.1]hept-2-ene (norbornene) to give new phosphorus-containing heterocycles.[4, 5] However, compound **2** has hitherto been completely overlooked as a material for heterocycle synthesis. Our aim has been to rectify this imbalance and develop further the synthetic capabilities of **2** and **4**.

Reaction of 4 with DMAD: Compound **4** reacts with DMAD in toluene at 130 °C to give $(PhPSe)_2SeC_2R_2$ (**5**), $PhP(Se)Se_2C_2R_2$ (**6**) and $PhP(Se)(C_2R_2)_2Se$ (**7**) ($R = CO_2Me$, Scheme 2) in modest yields (5–19% based on **4**) following column chromatography on silica gel; dichloromethane elutes **5** followed by **6**, subsequently diethyl ether elutes **7**. No products other than **5**–**7** are apparent in the $^{31}P\{^1H\}$ NMR spectra of crude reaction mixtures, while the ester groups and $C{=}C$ bonds of **5**–**7** appear to be inert towards **4** under the conditions employed. Compounds **5**–**7** are soluble in chlorinated solvents, toluene and diethyl ether, with lower solubility

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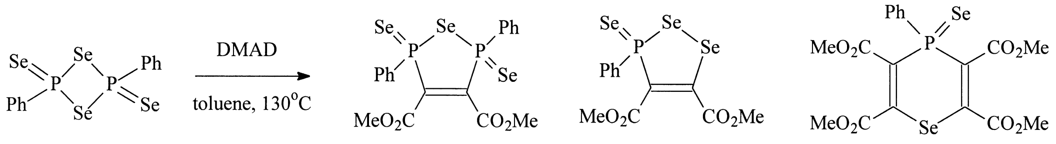


4 **5** **6** **7**

Scheme 2. Synthesis of compounds **5**–**7**.

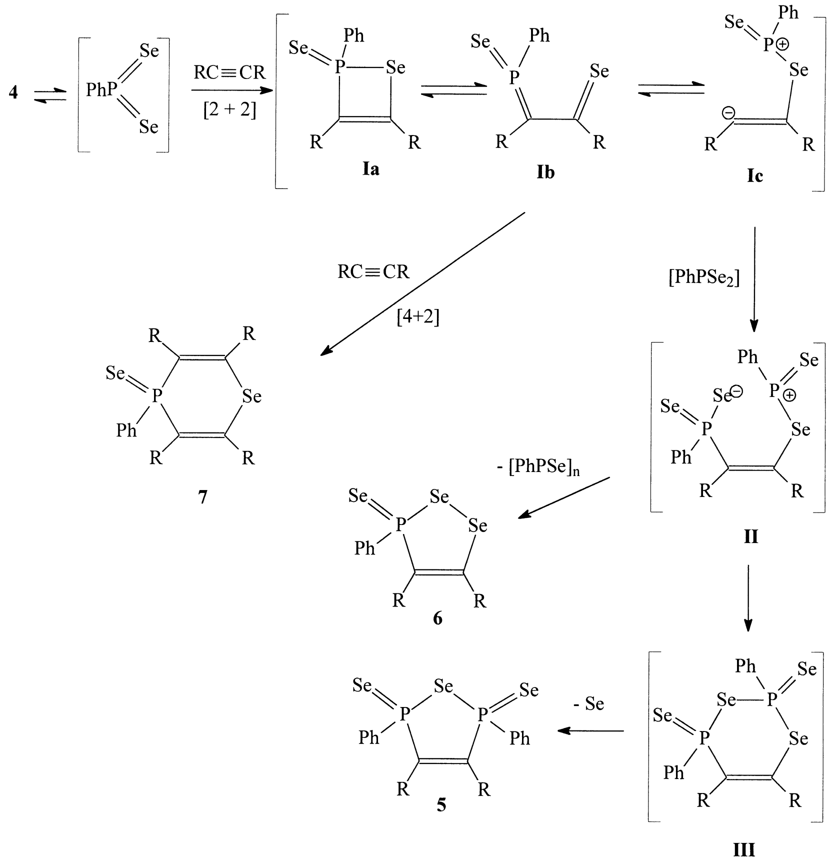
in hexane; these solution are stable to air for several days at room temperature without appreciable deposition of red selenium. In the $^{31}P\{^{1}H\}$ NMR spectra the magnitudes of ^{1}J(P=Se) and ^{1}J(P–Se) (785–823, 363–380 Hz, respectively) are normal.[2, 5, 6, 9, 10] There are two $\nu_{C=O}$ vibrations in the IR spectra (1743–1716 cm^{-1}), with $\nu_{P=Se}$ between 557–529 cm^{-1}. The EI mass spectra of **6** and **7** each contain a molecular ion peak, while for **5** the highest molecular weight peak observed corresponds to $[M^{+} - \text{Se}]$.

We propose a reaction pathway for the formation of **5**–**7** in Scheme 3. By analogy with $[(p\text{-MeOC}_6H_4)P(S)(\mu\text{-}S)]_2$ (Lawesson's Reagent), we believe that at elevated temperatures **4** is in equilibrium with a diselenaphosphorane $PhP(Se)_2$, which is the true reactive species in solution. The initial step in the formation of **5**–**7** is a [2+2] cycloaddition of a P=Se bond from $PhP(Se)_2$ across the C≡C bond of DMAD, giving an intermediate **I**, which exists in equilibrium in solution in three tautomeric forms; the 1,2-selenaphosphacyclobutene **Ia**, the selone **Ib** and the dipolar species **Ic**. A [4+2] cycloaddition of **Ib** with another molecule of DMAD gives rise to **7**. To account for the formation of **5** and **6**, we believe that **Ic** reacts further with $PhP(Se)_2$ to give a second dipolar intermediate **II**, which can either eliminate $(PhPSe)_n$ to generate **6** or cyclise to give **III**, which extrudes selenium to afford **5**.

The molecular structures of **5**–**7** determined crystallographically (Figures 1–3) are composed of P-Se-C rings generated by the addition of fragments from **4** to the C≡C bond of DMAD. We have recently described the synthesis of a saturated C-C-P-Se-Se ring in $PhP(Se)Se_2(C_7H_{10})$ from the reaction of **4** with norbornene.[5] Oxidation of $P_2C_2Ph_4$ with sulfur or hydrogen peroxide gives analogues of **5** that contain a P(E)-E-P(E) linkage (E = O or S),[11] 1,4-thiaphosphorin-4-selenides $PhP(E)(CH{=}CR)_2S$ (R = H, Me or Et) have been prepared by ring closure of $S(C{\equiv}CR)_2$ with $PhPH_2$ followed by oxidation,[12] while treatment of $R^1P(O)(C{\equiv}CR^2)_2$ (R^1 = Ph or c-C_6H_{11}; R^2 = H, Me or tBu) with $Na_2Se_2/NH_3(l)$ gives $R^1P(O)(CH{=}CR^2)_2Se$;[13] however, no crystallographic analyses for these molecules have been published.

Compound **5** (Figure 1) is derived from **4** by replacing a bridging selenium atom with C_2R_2. Within the C_2P_2Se ring the P(1)-C(7)-C(10)-P(2) chain has a mean deviation from planarity of 0.03 Å, with Se(3) displaced by 0.37 Å from this plane. The two exocyclic P=Se bonds adopt a *trans* orientation, a common feature of ring systems containing a P(Se)-Se-P(Se) linkage such as $(PhP)_2Se_3OCMe_2$, $PhP(Se)(\mu\text{-}Se)(\mu\text{-}NPh)P(Se)Ph$ and $[RP(Se)(\mu\text{-}Se)]_2$ (R = tBu or Ph).[5, 14, 15] The P(1)-Se(3)-P(2) angle (93.74(3)°) is wider than in the $P_2(\mu\text{-}Se)_2$ ring of **4** (85.45(9)°),[5] although the internal P–Se bond lengths (P(1)-Se(3) 2.2435(9), P(2)-Se(3) 2.2802(9) Å) change little upon ring expansion (2.276(2), 2.284(2) Å in **4**).

For **6** (Figure 2) there are two independent molecules within the unit cell. The Se(3)-C(7)-C(10)-P(1) chain of atoms has a mean deviation of 0.02 Å from planarity (0.01 Å in molecule 2), with Se(2) lying 0.74 Å (0.16 Å) out of this plane and the phenyl group on the same side of the C_2PSe_2 ring as this atom. The Se(2)–Se(3) bond length of 2.359(2) Å (2.356(2) Å) is identical to that in $PhP(Se)Se_2(C_7H_{10})$ (2.352(1) Å),[5] the C=C distances within the two independent molecules of **6**



Scheme 3. Suggested mechanism for the formation of **5**–**7** (R = CO$_2$Me).

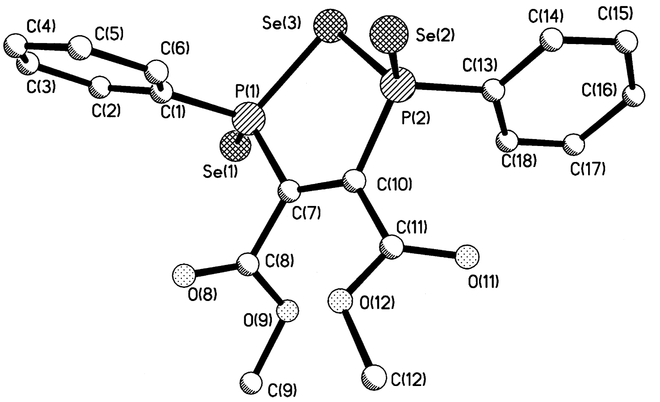


Figure 1. Molecular structure of **5** (C–H bonds omitted for clarity). Selected bond lengths (Å) and angles (°): Se(1)–P(1) 2.0916(9), P(1)–C(1) 1.798(3), P(1)–C(7) 1.831(3), P(1)–Se(3) 2.2435(9), Se(3)–P(2) 2.2802(9), P(2)–C(13) 1.803(3), P(2)–C(10) 1.831(3), P(2)–Se(2) 2.0822(10), C(7)–C(10) 1.336(4), C(1)-P(1)-Se(1) 115.15(11), C(7)-P(1)-Se(1) 112.12(10), C(1)-P(1)-Se(3) 107.69(10), C(7)-P(1)-Se(3) 100.06(11), Se(1)-P(1)-Se(3) 114.77(4), P(1)-Se(3)-P(2) 93.74(3), C(13)-P(2)-Se(2) 115.64(12), C(10)-P(2)-Se(2) 111.44(11), C(13)-P(2)-Se(3) 103.29(11), C(10)-P(2)-Se(3) 99.22(11), Se(2)-P(2)-Se(3) 117.43(4).

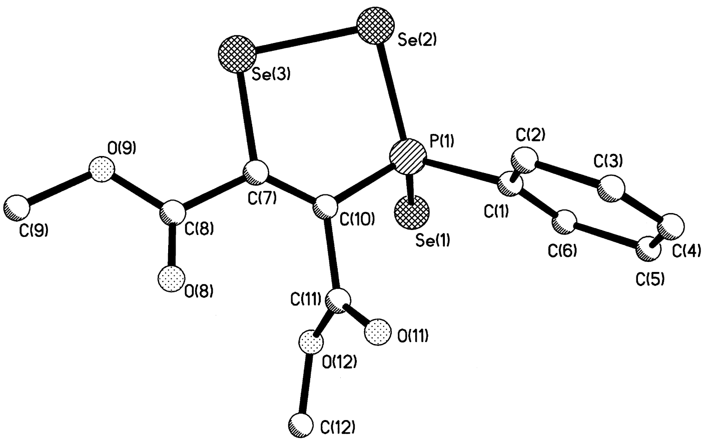


Figure 2. Molecular structure of **6** (C–H bonds omitted for clarity). Selected bond lengths (Å) and angles (°) (dimensions for second independent molecule in square parentheses): Se(1)–P(1) 2.113(3) [2.116(3)], P(1)–C(10) 1.828(9) 1.791(10)], P(1)–C(1) 1.841(12) [1.807(11)], P(1)–Se(2) 2.251(3) [2.261(3)], Se(2)–Se(3) 2.359(2) [2.356(2)], Se(3)–C(7) 1.916(9) [1.864(11)], C(7)–C(10) 1.300(12) [1.368(14)], C(10)-P(1)-Se(1) 110.5(3) [115.8(3)], C(1)-P(1)-Se(1) 114.2(4) [114.4(3)], C(10)-P(1)-Se(2) 100.5(3) [101.8(4)], C(1)-P(1)-Se(2) 107.2(4) [104.9(3)], Se(1)-P(1)-Se(2) 116.48(11) [115.32(11)], P(1)-Se(2)-Se(3) 91.52(8) [94.20(8)], C(7)-Se(3)-Se(2) 95.5(3) [96.8(3)], C(10)-C(7)-Se(3) 123.3(7) [124.6(7)].

being unexpectedly dissimilar (1.300(12) and 1.368(14) Å) relative to those found in **5** and **7** (1.336(4) and 1.347(3) Å, respectively).

The C_4PSe ring of **7** (Figure 3) adopts a boat conformation in which Se(2) and P(1) are the prow and stern atoms, the phenyl group at P(1) being in an equatorial position. The dihedral angle between the P(1)-C(16)-C(13)-Se(1) and P(1)-C(7)-C(10)-Se(2) planes (mean deviations from planarity of 0.24 and 0.02 Å, respectively) is 78°. In **5**–**7** the phosphorus–selenium double and single bond lengths (2.082(4)–2.116(3), 2.2435(9)–2.2802(9) Å respectively) fall within expected limits,[1, 2, 6, 9, 10, 14–18] the angles at endocyclic selenium (91.52(8)–100.33(10)°) being somewhat narrow.

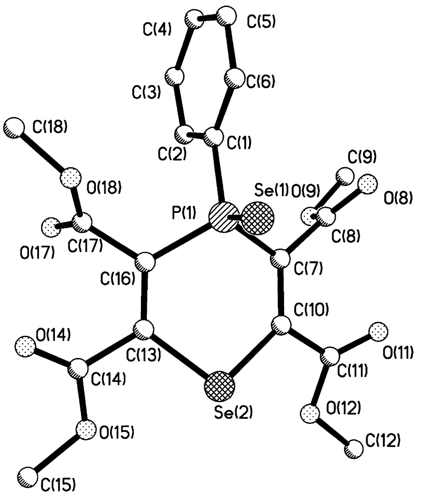


Figure 3. Molecular structure of **7** (C–H bonds omitted for clarity). Selected bond lengths (Å) and angles (°): Se(1)–P(1) 2.0925(7), P(1)–C(1) 1.808(2), P(1)–C(7) 1.814(2), P(1)–C(16) 1.811(2), C(7)–C(10) 1.345(3), C(10)–Se(2) 1.895(2), Se(2)–C(13) 1.886(2), C(13)–C(16) 1.347(3), C(7)-P(1)-C(16) 102.34(11), C(1)-P(1)-Se(1) 116.69(8), C(7)-P(1)-Se(1) 112.90(8), C(16)-P(1)-Se(1) 112.54(8), C(10)-C(7)-P(1) 121.8(2), C(7)-C(10)-Se(2) 125.3(2), C(13)-Se(2)-C(10) 100.33(10), C(16)-C(13)-Se(2) 125.9(2).

Reaction of 2 with $R_2NC{\equiv}N$ ($R_2 = i\mathrm{Pr}_2$ or $O(CH_2CH_2)_2N$): The reaction between **2** and $O(CH_2CH_2)_2NC{\equiv}N$ at 130°C gives a mixture of products after ten hours. $^{31}P\{^1H\}$ NMR spectra of crude mixtures contain, in addition to unreacted **2** and $(PhP)_4Se$ **1** ($\delta P_A = 108.2$, $\delta P_X = 85.0$, AA′XX′ spin system),[1, 2] two products **8a**,**b** in similar quantities, each characterised by two doublets with ^{77}Se satellites (Table 1). The $^1J(P,P)$ couplings in **8a**,**b**, reduced in magnitude from **2** (299 Hz), indicate retention of the P–P bond while $^1J(P_A,Se)$ and $^1J(P_X,Se)$ typify double and single bonds, respectively.[1, 2, 5, 6, 9] Chromatography on silica gel (dichloromethane eluant) enables resolution of **1** ($R_f = 1.0$) from **8a**,**b** ($R_f = 0.4$), with **2** unmoved ($R_f = 0.0$). By layering a dichloromethane solution of **8a**,**b** with hexane, fractional crystallisation of **8a** from **8b** occurs, typically in 10–15% yield based on **2**. $^{31}P\{^1H\}$ NMR spectra show increased proportions of **8b** remain in the solution; however, the small amounts of **8a** that invariably persist preclude the isolation of pure samples of **8b**.

Table 1. $^{31}P\{^1H\}$NMR parameters for **8**–**10** and **12**.[a]

	δ [ppm]		^1J [Hz]		
	P_A	P_X	P_A,P_X	P_A,Se	P_X,Se
8a	105.6(d)	6.8(d)	268	751	345
8b	105.3(d)	–11.8(d)	244	788	324
9a	104.7(d)	–10.3(d)	267	[b]	360
9b	105.4(d)	–25.2(d)	250	[b]	333
10	81.7 (d)	59.6(d)	13	[b]	[b]
12	83.4(d)	–23.9(d)	270	768	239

[a] Recorded in $CDCl_3$. [b] Coupling unresolved.

X-ray crystallography identifies **8a** as $(PhP)_2Se_2NCN(CH_2CH_2)_2O$ (Figure 4) formed by addition of the $(PhP)_3Se_2$ ring across the C≡N bond of the cyanamide followed by elimination of $(PhSe)_n$ ($n = 3$ has been reported previously[2]), the

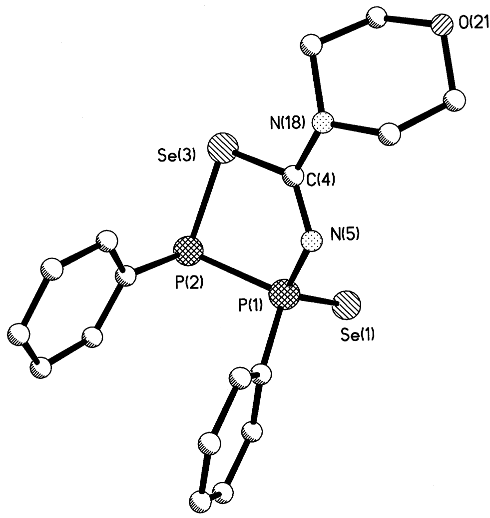


Figure 4. Molecular structure of **8a** (C–H bonds omitted for clarity). Selected bond lengths (Å) and angles (°): P(1)–P(2) 2.2372(14), P(1)–Se(1) 2.1073(10), P(2)–Se(3) 2.2412(10), P(1)–N(5) 1.653(3), Se(3)–C(4) 1.968(4), N(5)–C(4) 1.290(4); Se(3)-P(2)-P(1) 89.65(4), P(2)-P(1)-N(5) 104.58(11), P(1)-N(5)-C(4) 118.5(3), N(5)-C(4)-Se(3) 122.4(3), C(4)-Se(3)-P(2) 95.26(10), P(2)-P(1)-Se(1) 108.78(5), N(5)-P(1)-Se(1) 116.62(12).

ultimate fate of which is presumed to be formation of $(PhP)_4Se$ (Scheme 4). Simultaneous C–Se and P–N bond formation also occurs during the reaction of **4** with $R_2NC{\equiv}N$, leading to $[R_2NC(Se){=}N]_2P(Se)Ph$, which contains two PSe_2CN rings fused along the P=Se bond.[4] In **8a**, P(1) and P(2) possess opposite chiralities (both enantiomeric forms co-crystallise), with the phenyl groups being oriented above and the morpholine ring below the P_2SeCN plane. P(2) lies 0.17 Å out of the plane defined by P(1)-N(5)-Se(3)-C(4) (mean deviation from planarity of 0.04 Å), with P(1) being 0.25 Å above this plane, the P(1)–Se(1) and P(2)–Se(3) distances being 2.1073(10) and 2.2412(10) Å, respectively. The P(1)–N(5) bond length (1.653(3) Å) is longer than the P–N bond lengths of 1.605(5) – 1.620(3) Å in $[R_2NC(Se){=}N]_2$-P(Se)Ph,[4] while P(1)–P(2) (2.2372(14) Å) is longer than the P–P distances of **1** (2.189(2) – 2.201(2) Å), $(MeP)_4Se_3$ (2.201(5) – 2.234(5) Å) or $(C_5Me_5P)_2Se$ (2.203(3) Å).[2, 9, 10] The angles at P(1) are between 104.58(11) – 116.62(12)°, while those at P(2) fall within a narrower range, 89.65(4) – 100.90(12)°.

Compound **8a** is susceptible to aerial oxidation in the solid state, with the deposition of red selenium over one month, but is stable indefinitely under nitrogen. The similarity of their $^{31}P\{^1H\}$ NMR parameters suggests that **8b** is a diastereomer of **8a**, in which P(1) and P(2) possess the same chirality.

The reaction of **2** with $iPr_2NC{\equiv}N$ gives, in addition to **1** and unreacted **2**, two products **9a,b** whose $^{31}P\{^1H\}$ NMR parameters closely resemble **8a,b** (Table 1). Once more, **1** and **2** are separable from **9a,b** by chromatography on silica gel, although in this instance we are unable to isolate **9** as a solid by crystallisation from dichloromethane/hexane. From a solution of **9a,b** in $CDCl_3$ which had evaporated over two months at 25 °C, we collected approximately 5 mg of colourless crystals of a new product $(PhP)_2Se_3NCNiPr_2$ (**10**; Table 1), the bulk material having decomposed to red selenium, $PhP(O)(OH)_2$ ($\delta_P = 24.7$) and $iPr_2NC(Se)NH_2$. X-ray crystallography (Figure 5) reveals that **10** contains a P_2SeCN ring, with a P(Se)-Se-P(Se) linkage and a *trans* orientation of exocyclic P=Se groups, see $(PhP)_2Se_3OCMe_2$.[1] The P(1)-Se(12)-P(2)-N(1)-C(2) ring atoms have a mean deviation from planarity of 0.13 Å, with phosphorus-selenium distances (P(1)–Se(1) 2.085(10), P(2)–Se(2) 2.0977(9), P(1)–Se(12) 2.2749(9), P(2)–Se(12) 2.2283(10) Å) are comparable to **5**–**7**, **8a** and related structures.[1, 2, 6, 9, 10, 14–18] The P(1)-Se(12)-P(2) angle in **10**, 90.29(3)°, is closer to that in $(PhP)_2Se_3OCMe_2$ (90.7(1)°) than in **5** (93.74(3)°), with P(1)–N(1) (1.637(3) Å) marginally shortened from **8a**. The angles at P(1) and P(2) are 102.83(10) – 117.56(11)° and 97.71(11) – 117.40(4)°, respectively, the internal E-P(1)-Se(12) angles (E = N(1) or C(2)) being the smallest in each set.

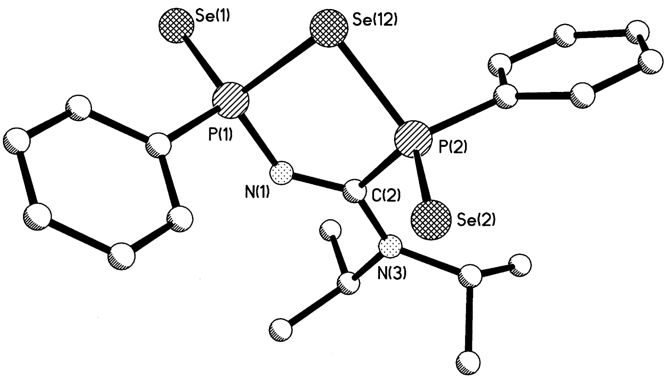
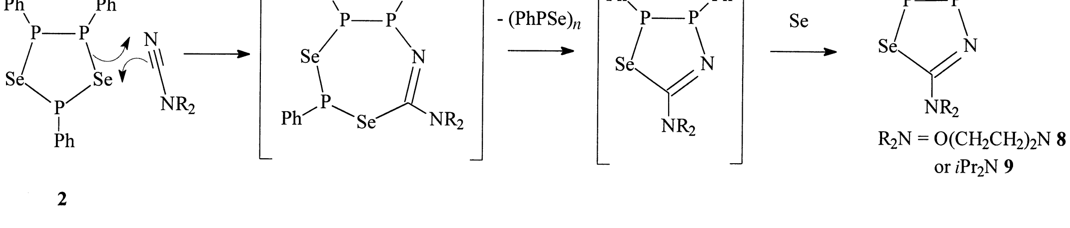


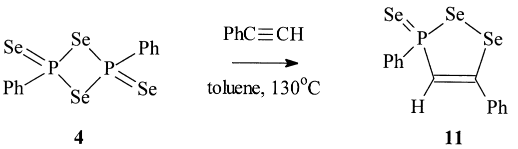
Figure 5. Molecular structure of **10** (C–H bonds omitted for clarity). Selected bond lengths (Å) and angles (°): P(1)–Se(12) 2.2749(9), Se(12)–P(2) 2.2283(10), P(1)–Se(1) 2.085(10), P(2)–Se(2) 2.0977(9), P(1)–N(1) 1.637(3), P(2)–C(2) 1.909(3), N(1)–C(2) 1.298(4); N(1)-P(1)-Se(12) 102.83(10), P(1)-Se(12)-P(2) 90.29(3), Se(12)-P(2)-C(2) 97.71(11), P(2)-C(2)-N(1) 119.0(2), C(2)-N(1)-P(1) 125.2(2), N(1)-P(1)-Se(1) 117.56(11), Se(1)-P(1)-Se(12) 109.24(4), C(2)-P(2)-Se(2) 111.8(1), Se(2)-P(2)-Se(12) 117.40(4).



Scheme 4. Proposed mechanism for the formation of **8** and **9**.

Compound **10** is absent from the $^{31}P\{^1H\}$ NMR spectra of crude reaction mixtures of **2**/*i*$Pr_2NC{\equiv}N$. In separate experiments, oxidation of **8a** with selenium at 130 °C gives a species whose $^{31}P\{^1H\}$ NMR parameters (doublets at $\delta = 73.6$, 63.4 ppm, $^2J(P,P) = 7$ Hz) are comparable to **10**, indicating that a slow intermolecular selenium atom transfer in conjunction with substantial structural reorganisation upon oxidation occurs during the conversion of **9a,b** to **10**.

Reaction of 4 with PhC≡CH: In contrast to the mixture of heterocycles **5** – **7** obtained from DMAD, compound **4** reacts with PhC≡CH to give one product, $PhP(Se)Se_2(PhC{=}CH)$ (**11**), in 58 % isolated yield following chromatographic workup (Scheme 5). In its ^1H NMR spectrum the alkene proton of **11** has a $J(P,H)$ coupling of 34 Hz, the magnitude of which suggests a *trans* ^3J coupling; however, ^1H-^{31}P HMQC and ^1H-^1H NOESY experiments lead us to the conclusion that this is in fact a ^2J *cis* coupling. Attempts to grow single crystals of **11** for X-ray analysis to corroborate this assignment have, to date, been unsuccessful. Undoubtedly the formation of **11** proceeds by a pathway analogous to that postulated in Scheme 3 for **5** – **7**, but it is unclear why only one compound is formed regiospecifically in this reaction, rather than a mixture of products as seen for DMAD.



Scheme 5. Synthesis of compound **11**.

Reaction of 2 with PhC≡C–CO$_2$Me: The reaction between **2** and $PhC{\equiv}C{-}CO_2Me$ gives several products; $^{31}P\{^1H\}$ NMR spectra of mixtures obtained after six hours at 130 °C contain several doublets with $^1J(P,P)$ couplings of 250 – 270 Hz, indicating retention of the P–P bond from **2**. Chromatography on silica gel is moderately successful in resolving this mixture. Elution with toluene affords a yellow fraction containing two species ($\delta_P = 68.0$ {d, $^1J(P,P) = 264$ Hz}, -16.5 {d, $^1J(P,Se) = 247$, $^1J(P,P) = 264$ Hz}; $\delta_P = 58.9$ {d, $^1J(P,P) = 254$ Hz}, -8.9 {d, $^1J(P,Se) = 247$, $^1J(P,P) = 254$ Hz}) in equal quantities, which decomposed over 48 hours under aerobic conditions and were not further characterised. Subsequent elution with dichloromethane affords a second yellow fraction comprising one component **12**, whose $^{31}P\{^1H\}$ NMR parameters (Table 1) resemble those of the products in the toluene fraction. A notable feature of **12** and the compounds in the toluene eluate is the magnitude of the $^1J(P,Se)$ coupling (239 – 247 Hz), approximately 30 % smaller than that in **8** or **9**. X-ray crystallographic analysis reveals that **12** contains a P_2C_2Se ring (Figure 6), the internal dimensions of which vary little from those of the P_2SeCN ring in **8a** with the exception of P(1)–C(5), which is 0.17 Å longer than the P(1)–N(5) distance in **8a**. The P(2)–Se(3) distance, 2.266(3) Å, is only marginally elongated from the corresponding parameter in **8a** (2.2412(12) Å). The P(2) atom lies 0.69 Å out of the mean plane defined by the P(1)-C(4)-C(5)-Se(3) atoms (mean deviation from planarity of 0.01 Å). The angles at P(1) and P(2) are between 102.3(3) – 115.7(3)° and 91.95(10) – 104.0(3)°, respectively, with, as observed in **8a**, the internal C(5)-P(1)-P(2) and P(1)-P(2)-Se(3) angles the narrowest in each set.

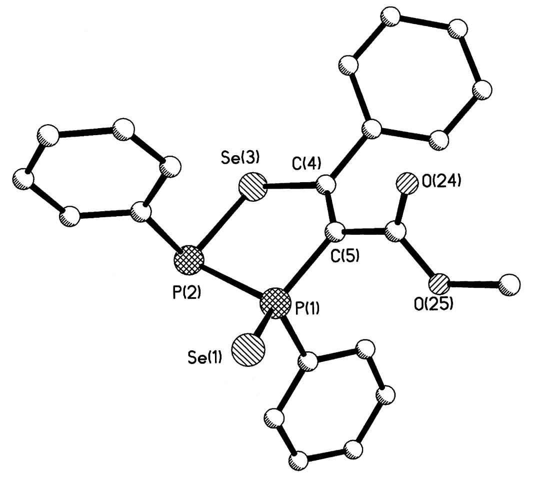


Figure 6. Molecular structure of **12** (C–H bonds omitted for clarity). Se(1)–P(1) 2.095(2), P(1)–C(5) 1.822(7), P(1)–P(2) 2.215(3), P(2)–Se(3) 2.266(3), Se(3)–C(4) 1.930(8), C(4)–C(5) 1.317(11); C(5)-P(1)-Se(1) 115.9(3), C(5)-P(1)-P(2) 102.3(3), Se(1)-P(1)-P(2) 112.79(11), P(1)-P(2)-Se(3) 91.98(10), C(4)-Se(3)-P(2) 97.4(2), C(5)-C(4)-Se(3) 121.7(6), C(4)-C(5)-P(1) 119.2(6).

From the $^{31}P\{^1H\}$ NMR spectral data, we assign the compounds in the toluene eluates as geometric isomers of **12** in which the C(4) and C(5) substituents are reversed; the C≡C triple bond of $PhC{\equiv}C{-}CO_2Me$ is presumably insufficiently polarised to favour attack at one end by selenium, which is the case for dialkyl cyanamides. Unlike the reaction of **2** with cyanamides and also in the toluene eluate from this reaction, which leads to mixtures of diastereomers, compound **12** exists only as a racemate.

The reaction of **2** with DMAD in toluene at both 25 °C and 130 °C gives complex mixtures of compounds that cannot be purified by column chromatography; moreover $^{31}P\{^1H\}$ NMR evidence suggests that cleavage of the P–P bond has taken place. We have not investigated this system further.

Selenium-77 NMR investigations: $^{77}Se\{^1H\}$ NMR data for heterocycles **5** – **7**, **11** and **12** have been obtained; the small amounts of material obtained for compounds **8** – **10** prevent collection of satisfactory data for these compounds. Unambiguous assignment of resonances is straightforward owing to the ^{31}P,^{77}Se couplings, from which it is readily deduced that in **5** – **7**, **11** and **12** the exocyclic selenium atom is at lower frequency to those within the heterocycle. An additional feature unobserved in their $^{31}P\{^1H\}$ NMR spectra are $^2J(P,Se)$ couplings for **6** and **11** (7 and 6 Hz, respectively) and a $^3J(P,Se)$ coupling of 29 Hz for **7** see the $^2J(P,Se)$ coupling of 7 Hz for $[O(CH_2CH_2)NC(Se){=}N]_2P(Se)Ph$.[4] Also, a $^1J(Se,Se)$ coupling of 271 Hz is noted for **6**. An interesting anomaly shown by **12** is that the internal atom Se(3) has a $^2J(P,Se)$ coupling to the phosphorus(v) centre P(1) of 20 Hz; however, there is no resolved coupling between the exocyclic Se(1) and the internal phosphorus(III) centre P(2). The ^{77}Se NMR data for **5**–**7**, **11** and **12** are in general agreement with the recently reported solid state data for $(RPSe_2)_2$ (R = Me, Et, *t*Bu, Ph, 4-$Me_2NC_6H_4$ or 4-$MeOC_6H_4$) and $(R'PSe)_2Se$ (R′ = Me or Et).[19]

Conclusion

Using ^{31}P-{^{1}H} NMR spectroscopy in conjunction with X-ray crystallography we have elucidated the structures of the novel heterocycles generated from the reactions between $(PhP)_3Se_2$ (**2**) or $[PhP(Se)(\mu\text{-}Se)]_2$ (**4**) with selected organic substrates that contain C≡C or C≡N bonds; the atomic sequences within several of the rings, for example, **8a** and **12** are, to the best of our knowledge, hitherto unknown in the literature. Also, the compounds generated from the reaction of **2** with $R_2NC{\equiv}N$ and $PhC{\equiv}C{-}CO_2Me$ are closely related in structure to each other, but completely unlike those obtained when these substrates react with compound **4**. The ^{77}Se NMR reported here for **5**–**7**, **11** and **12** provide further information which may be used as a means for structural elucidation. The facility of heterocycle synthesis using **2** and **4** bodes well for future efforts in this area.

Experimental Section

General experimental conditions and instrumentation details are as reported elsewhere.[4, 5, 6, 8] All reactions were conducted under a dinitrogen atmosphere by using standard Schlenk line techniques, subsequent chromatographic and workup procedures were performed in air. ^{1}H and ^{31}P{^{1}H} NMR spectra ($CDCl_3$) were at 300.0 and 121.4 MHz, respectively; IR spectra were recorded as pressed KBr discs. ^{77}Se{^{1}H} NMR spectra ($CDCl_3$) were recorded on a Jeol GSX-270 spectrometer at 51.52 MHz and referenced to external Me_2Se. Mass spectra were in EI mode unless otherwise stated. Compounds **2** and **4** were prepared from $(PhP)_5$ and selenium;[1, 2] toluene was distilled from sodium prior to use, all other solvents and reagents were used as supplied.

Reaction of 4 with $MeO_2C{-}C{\equiv}C{-}CO_2Me$—synthesis of $(PhPSe)_2SeC_2R_2$ (5), $PhP(Se)Se_2C_2R_2$ (6) and $PhP(Se)(C_2R_2)_2Se$ (7) (R = CO_2Me): A mixture of **4** (300 mg, 0.56 mmol) and DMAD (0.15 cm^3) in toluene (2 mL) in a sealed tube was heated at 130 °C for 1 h, giving a deep red/purple solution. Upon cooling to room temperature the solvent was removed in vacuo and the products were extracted into dichloromethane (2 mL). Column chromatography (silica gel, dichloromethane) gave a yellow fraction of **5** followed by a red fraction of **6**, which were crystallised from diethyl ether/hexane. Subsequent elution with diethyl ether gave a yellow fraction of **7**, which was crystallised by evaporation of a diethyl ether solution at room temperature.

Compound **5**: Yield: 17 mg orange solid, 5 % based on **4**; elemental analysis calcd (%) for $C_{18}H_{16}O_4P_2Se_3$: C 36.1, H 2.7; found: C 36.2, H 2.7; ^{31}P NMR: $\delta_P = 52.7$ (s, ^1J(P,Se) = 823 Hz, ^1J(P,Se) = 380 Hz); ^{1}H NMR: $\delta_H = 8.15$ (m, 4H; Ph), 7.55 (m, 6H; Ph), 3.60 (s, 6H; CH_3); ^{77}Se NMR: $\delta_{Se} = 434.6$ (t, ^1J(P,Se) = 381 Hz; Se(3)), −82.3 (d, ^1J(P,Se) = 808 Hz; Se(1,2)); IR: $\tilde{\nu} = 1743$ (s), 1729 (s) (C=O), 1263 (s), 1251 (s) (C−O), 557 (m), 541 cm^{-1} (m) (P=Se); MS: *m*/*z*: 517 [$M^+ - $Se].

Compound **6**: Yield: 106 mg red solid, 19 % based on **4**; elemental analysis calcd (%) for $C_{12}H_{11}PO_4Se_3$: C 29.6, H 2.3; found: C 29.8, H2.3; ^{31}P NMR: $\delta_P = 67.4$ (s, ^1J(P,Se) 806 Hz, ^1J(P,Se) = 363 Hz); ^{1}H NMR: $\delta_H = 8.13$ (m, 2H; Ph), 7.55 (m, 3H; Ph), 3.87 (s, 3H; CH_3), 3.64 (s, 3H; CH_3); ^{77}Se NMR: $\delta_{Se} = 542.6$ (d, ^2J(P,Se) = 7 Hz, ^1J(Se,Se) = 271 Hz; Se(3)), 420.0 (d, ^1J(P,Se) = 360 Hz; Se(2)), −7.8 (d, ^1J(P,Se) = 806 Hz, Se(1)); IR: $\tilde{\nu} = 1731$ (s), 1719 (s) (C=O), 1236 (s) (C−O), 529 cm^{-1} (m) (P=Se); MS: *m*/*z*: 488 [M^+].

Compound **7**: Yield: 114 mg yellow solid, 18 % based on **4**; elemental analysis calcd (%) for $C_{18}H_{17}O_8PSe_2$: C 39.1, H 3.1; found: C 39.6, H 2.3; ^{31}P NMR: $\delta_P = 18.0$ (s, ^1J(P,Se) = 785 Hz); ^{1}H NMR: $\delta_H = 7.98$ (m, 2H; Ph), 7.53 (m, 3H; Ph), 3.87 (s, 6H; CH_3), 3.44 (s, 6H; CH_3); ^{77}Se NMR: $\delta_{Se} = 469.6$ (d, ^3J(P,Se) = 29 Hz; Se(2)), −219.3 (d, ^1J(P,Se) = 782 Hz; Se(1)); IR: $\tilde{\nu} = 1733$ (s), 1716 (s) (C=O), 1256 (s), 1232 (s) (C−O), 531 cm^{-1} (m) (P=Se); MS: *m*/*z*: 552 [M^+].

Reaction of 2 with $R_2NC{\equiv}N$ [R_2 = *i*Pr_2 or $O(CH_2CH_2)_2N$]—synthesis of $(PhP)_2Se_2NCN(CH_2CH_2)_2O$ (8a,b): A mixture of **2** (80 mg, 0.16 mmol) and $O(CH_2CH_2)_2NC{\equiv}N$ (0.2 cm^3) in toluene (10 cm^3) was heated at reflux for 10 h, giving a yellow solution. The solvent was removed in vacuo, the products extracted into dichloromethane (1 mL) and purified by column chromatography (silica gel, dichloromethane), separating **1** ($R_f = 1.0$) from **8a,b** ($R_f = 0.4$). Layering a dichloromethane solution of **8a,b** with hexane gave colourless crystals of **8a** (12 mg, 15 %). Compound **8b** could not be completely freed from traces of **8a**, precluding full characterisation. Compound **8a**: ^{1}H NMR: $\delta_H = 7.46$ (m, 2H; Ph), 7.02 (m, 8H; Ph), 3.88 (m, 8H; CH_2); IR: $\tilde{\nu} = 1556$ (s) (C=N), 541 cm^{-1} (s) (P=Se); MS: *m*/*z*: 488 [M^+].

Compounds $(PhP)_2Se_2NCN$*i*Pr_2 (**9a,b**) were synthesised and purified from **2** and *i*$Pr_2NC{\equiv}N$ using similar conditions to those for **8a,b**. Compounds **9a,b** were inseparable from each other either chromatographically or by layering experiments, neither could a solid sample be isolated using the latter technique. However, about 5 mg of colourless crystals of $(PhP)_2Se_3NCN$*i*Pr_2 (**10**) were collected from a solution of **9a,b** in $CDCl_3$ which had evaporated to dryness over two months at room temperature. IR: 1552 (s) (C≡N), 560 cm^{-1} (s) (P=Se).

Reaction of 4 with $PhC{\equiv}CH$—synthesis of $PhP(Se)Se_2(PhC{=}CH)$ (11): A mixture of **4** (106 mg, 0.2 mmol) and $PhC{\equiv}CH$ (0.1 mL) in toluene (2 mL) in a sealed tube was heated at 130 °C for 1.5 h, to give a red solution. Upon cooling to room temperature the solution was purified by column chromatography (silica gel, toluene), yielding **11** as an orange solid from dichloromethane/hexane. Yield 52 mg, 58 % based on **4**; elemental analysis calcd (%) for $C_{14}H_{11}PSe_3$): C 37.6, H 2.5; found: C 37.5, H 2.3; ^{31}P NMR: $\delta_P = 67.5$ (s, ^1J(P,Se) = 771 Hz, ^1J(P,Se) = 348 Hz); ^{1}H NMR: $\delta_H = 8.28$ (m, 2H; Ph), 7.76 (m, 2H; Ph), 7.65 (m, 3H; Ph), 7.56 (m, 3H; Ph), 7.26 (d, ^3J(P,H) = 34 Hz, 1H; =C−H]; ^{77}Se NMR: $\delta_{Se} = 558.1$ (d, ^2J(P,Se) = 7 Hz), 410.8 (d, ^1J(P,Se) = 350 Hz), −23.4 (d, ^1J(P,Se) = 775 Hz); IR: $\tilde{\nu} = 527$ cm^{-1} (m) (P=Se). MS: *m*/*z*: 448 [M^++H].

Reaction of 2 with $PhC{\equiv}C{-}CO_2Me$—Synthesis of $(PhP)_2Se_2$-($PhC{\equiv}C{-}CO_2Me$) (12): A solution of **2** (180 mg, 0.37 mmol) and $PhC{\equiv}C$-CO_2Me (0.1 mL) in toluene (2 mL) in a sealed tube was heated at 130 °C for 6 h, giving a yellow solution. Upon cooling to room temperature, the toluene solution was purified by column chromatography (silica gel). Elution with toluene gave a yellow band whose ^{31}P{^{1}H} NMR spectrum revealed a mixture of products. Subsequent elution with dichloromethane afforded a yellow eluate, yielding **12** as a yellow solid from dichloromethane-hexane. Crystals of **12** were grown from $CDCl_3$/hexane at room temperature. Yield: 56 mg, 28 % based on **2**; elemental analysis calcd (%) for $C_{22}H_{18}O_2P_2Se_2$: C 49.4, H 3.4; found: C 49.9, H 2.6; ^{31}P NMR: $\delta_P = 83.4$ (d, ^1J(P,P) = 270 Hz, ^1J(P,Se) = 768 Hz), −23.9 (d, ^1J(P,P) = 270 Hz, ^1J(P,Se) = 239 Hz); ^{1}H NMR: $\delta_H = 8.28$ (m, 2H; Ph), 7.85 (m, 2H; Ph), 7.73 (m, 2H; Ph), 7.61 (m, 9H; Ph), 3.64 (s, 9H; CH_3); ^{77}Se NMR: $\delta_{Se} = 417.1$ (dd, ^1J(P,Se) = 239 Hz, ^2J(P,Se) = 20 Hz; Se(3)), −240.0 (d, ^1J(P,Se) = 772 Hz; Se(1)); IR: $\tilde{\nu} = 1732$ (s) (C=O), 1555 (m) (C=C), 544 cm^{-1} (m) (P=Se); MS: *m*/*z*: 536, [M^+].

Crystallographic analysis: X-ray diffraction studies on crystals of **5**–**7**, **8a**, **10** and **12** were performed at 293 K on a Bruker SMART diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were 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). Structural refinements were by the full-matrix least-squares method on F^2 using the program SHELXTL.[20, 21] Details of data collections and structural refinements are given in Table 2.

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Table 2. Data collection and structural refinement parameters for compounds **5**–**7**, **8a**, **10**, and **12**.

	5	**6**	**7**	**8a**	**10**	**12**
formula	$C_{18}H_{16}O_4P_2Se_3$	$C_{12}H_{11}O_4PSe_3$	$C_{18}H_{17}O_8PSe_2$	$C_{17}H_{18}N_2OP_2Se_2$	$C_{19}H_{24}N_2P_2Se_3$	$C_{22}H_{18}O_2P_2Se_2$
M_r	595.13	487.06	550.21	486.19	579.22	534.22
crystal system	monoclinic	triclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
size [mm]	0.1 × 0.1 × 0.05	0.1 × 0.05 × 0.05	0.18 × 0.1 × 0.1	0.25 × 0.25 × 0.25	0.3 × 0.15 × 0.15	0.15 × 0.1 × 0.1
a [Å]	12.9752(7)	9.0647(7)	33.807(2)	9.3153(7)	9.5590(4)	11.3010(19)
b [Å]	10.1956(5)	12.7637(10)	8.6162(4)	10.3759(7)	9.9459(4)	15.441(2)
c [Å]	16.5268(9)	15.2026(12)	15.3785(8)	10.4397(7)	12.7194(6)	13.255(2)
α [°]		69.852(1)		82.911(1)	96.716(1)	
β [°]	92.752(1)	85.793(1)	107.157(1)	82.404(1)	101.639(1)	111.557(6)
γ [°]		84.502(1)		72.126(1)	97.460(2)	
V [Å^3]	2183.8(2)	1642.2(2)	4280.3(4)	948.24(11)	1161.55(9)	2151.3(6)
Z	4	4	8	2	2	4
ρ_{calcd} [Mg m^{-3}]	1.810	1.970	1.708	1.703	1.656	1.649
μ [mm^{-1}]	5.220	6.824	3.571	4.075	4.894	3.601
$F(000)$	1152	928	2176	480	568	1056
reflns collected	9216	8255	8986	4762	5772	10543
independent reflns (R_{int})	3136 (0.0237)	4665 (0.0646)	3080 (0.0154)	2654 (0.0284)	3314 (0.0260)	3056 (0.1356)
$R1/wR2$ [$I > 2\sigma(I)$]	0.0258/0.0555	0.0396/0.1036	0.0210/0.0501	0.0334/0.0822	0.0268/0.0564	0.0653/0.1534

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[21] CCDC-158641 (**5**), CCDC-158642 (**6**), CCDC-158643 (**7**), CCDC-164096 (**8a**), CCDC-164097 (**10**) and CCDC-175191(**12**) contain(s) the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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