Phosphorus-Selenium Heterocycles from the Tetraphospholane $(PhP)_4CH_2$

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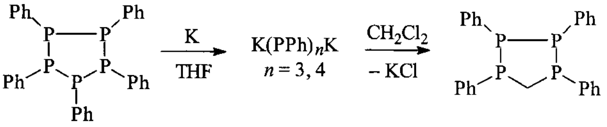
Two new heterocyclic and one acyclic species were prepared by reduction/deselenation of the five-membered heterocycle $PhP(Se)CH_2PhP(Se)Se_2$ (containing a $PCPSe_2$ ring sequence). Deselenation with Me_3SiCN led to the four-membered heterocycle $PhP(Se)CH_2PPh(Se)Se$ (containing a PCPSe ring sequence), whereas reaction with Bu_3P afforded the five-membered heterocycle $PhP(Se)CH_2PhP(Se)SePPh$ (ring sequence PCPSeP) and reduction with K metal afforded the dipotassium salt of methylene-bis(diselenophenylphosphinic) acid $[K_2(PhPSe_2)_2CH_2]$. The new compounds were characterised by a combination of NMR, MS and FT IR spectroscopic techniques; their structures were confirmed by single crystal X-ray analyses.

Introduction

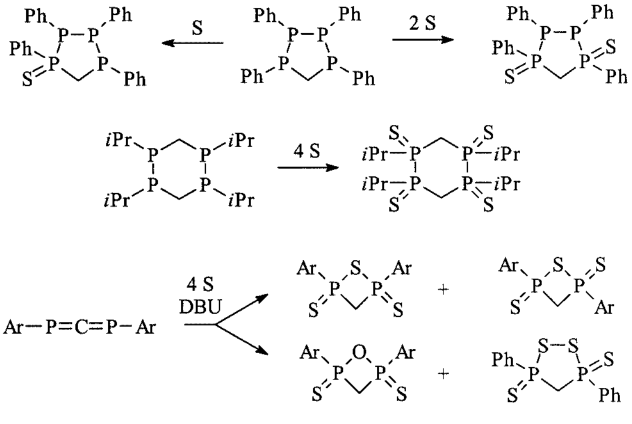
The chemistry of organophosphorus-sulfur and -selenium heterocycles is rich and varied.[1] The common ring sizes are four and five, although larger or smaller rings are not unusual.[2,3] The constitutional variability found in pseudo-binary heterocycles $(RP)_xE_y$ (R = organics, E = S, Se) can be explained by two factors: i) the ease with which their divalent building blocks can rearrange [illustrated, for example, by self-rearrangements of oligomeric $(RP)_5$, $(RP)_4$ and $(RP)_6$], and ii) an ability to form kinetically stable short "homoatomic" chains such as -S-S-, -Se-Se-Se- or, as mentioned above, $(RP)_n$. Cyclophosphanes $(RP)_n$ together with diphosphenes R-P=P-R are important precursors here. In particular, cyclophosphanes with aromatic substituents are frequently studied, due to their stabilizing (kinetic) effect against undesired oxidation or hydrolysis, and, in the case of very bulky organyl groups such as supermesityl, because of their ability to stabilize unusually low phosphorus coordination states.

The chemistry of cyclocarbaphosphanes $[(PR)_x(CR'_2)_y]$ with one or more RP units substituted by carbon functionalities seems to be much less developed than that of the parent cyclophosphanes. Cyclocarbaphosphanes are generally prepared from metallated oligophosphanes and geminal dichloro compounds[4] (Scheme 1); in a similar manner they are also obtained as relatively stable by-products during the synthesis of bifunctional phosphane ligands.[5,6]



Scheme 1. Synthetically useful route to cyclocarbaphosphanes

Other methods employing $Me_3Si\text{-}(tBuP)_4\text{-}SiMe_3$ [7] or $(iPrPCl)_2CH_2$ [8] have also been reported. Reports on reactions of cyclocarbaphosphanes and related systems with sulfur are scarce (Scheme 2); no report on reactions with selenium was found in the literature.



Scheme 2. Reported reactions of carbacyclophosphanes and related systems with sulfur;[9–11] DBU is 1,8-diazabicyclo[5,4,0]undec-7-ene

The results summarised in Scheme 2 show that, unlike the homo-cyclophosphanes $(PR)_x$,[12] the addition of S to $(RP)_x(CH_2)_y$ does not proceed with cleavage of any P−P bond. On the other hand, the treatment of $(PPh)_5$ with vari-

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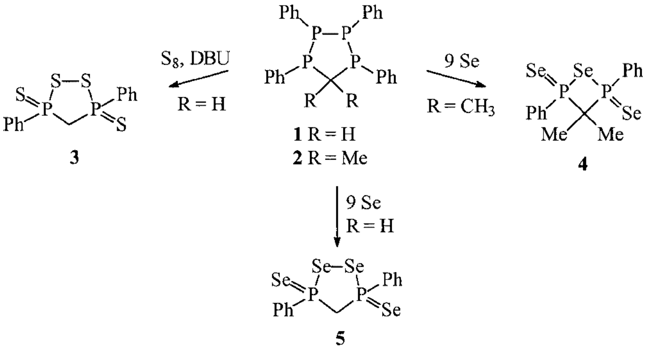
ous ratios of grey Se commonly leads to ring rupture and reorganization.[13] Obviously no rules of thumb have been laid down concerning the product structures obtained with varying ratios of $(RP)_n$ or $(RP)_x(CR'_2)_y$ to S/Se, or the effect of the electronic structure of R and R′, thus it seemed interesting to study these − to some extent unpredictable − systems.

We have reported reactions of $(PPh)_4CR_2$ (R = H, Me) with excess sulfur and selenium in a previous communication (Scheme 3).[14]

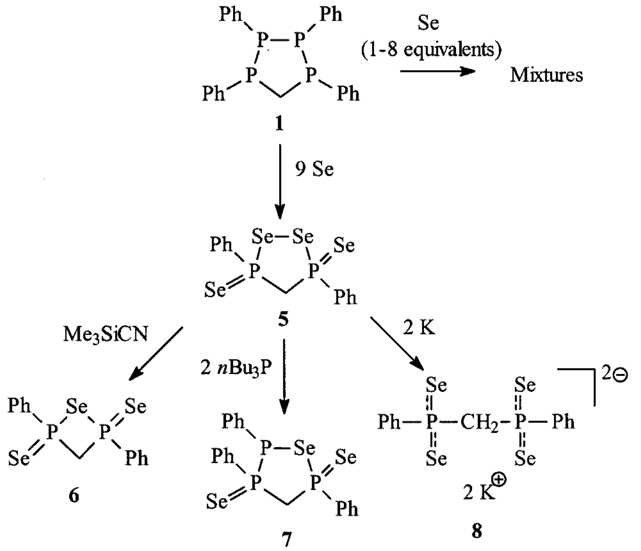


Scheme 3. Heterocycles from $(PPh)_4CR_2$ (R = H, Me)[14]

Herein we report a series of new species obtained by reductive ring-rearrangements of diselenadiphospholane (**5**); as in the case of the products shown in Scheme 3, the P−C−P motif is retained throughout the transformation to the new heterocycles as well as an acyclic dianion.

Results and Discussion

Application of a common strategy − oxidation of tetraphospholane **1** with various ratios of elemental selenium − led in all but one of the ratios studied to complicated mixtures. Attempts to separate these mixtures by flash chromatography on dried silica or alumina as well as by size-exclusion chromatography resulted in poor separation and oxidation/hydrolysis of separated species with deposition of red selenium. The only exception, where a single product was obtained, was the reaction of **1** with an excess of selenium, from which diselenadiphospholane (**5**) was obtained in very good yield and purity without the need for chromatographic separation.[14] This led us to test another tactic for the preparation of products with a lower Se/P ratio; as a starting material heterocycle **5** was used and it was treated with various reducing/deselenating agents such as Ph_3P, nBu_3P, Me_3SiCN and potassium metal. This afforded two new heterocyclic species **6** and **7** and the new dianion **8** (Scheme 4).



Scheme 4. New P−Se compounds obtained from tetraphospholane **1**

PSePC Heterocycle 6

The ^{31}P NMR spectra of crude reaction mixtures of **1** with seven or eight equivalents of Se indicated that two compounds are present in the solution after heating the two components in toluene. Compound **5** was identified as a major product [singlet with ^{77}Se satellites (2 × AXX′ pattern), δ_P = 43 ppm; ^1J (PSe_{exo}) = 775, ^3J (PSe_{exo}) = 11, ^1J (PSe_{endo}) = 342, ^2J (PSe_{endo}) = 13, ^2J (PP) = 34 Hz], whilst the pattern of the ^{77}Se satellites of a minor singlet at δ_P = −4.1 ppm suggests that the second compound is a four-membered heterocycle **6**. As attempts to separate it from the reaction mixture were unsuccessful, the abstraction of Se from **5** with Ph_3P, nBu_3P or Me_3SiCN was tested. ^{31}P NMR spectroscopy indicated that rather complicated mixtures resulted, although a substantial amount of the four-membered heterocycle **6** was present in the mixtures after the reaction with between one and two equivalents of a reducing agent. Me_3SiCN proved to be the reagent of choice, as the by-product, $Me_3SiCNSe$, is easily removable in vacuo (b.p. 65 °C/20 Torr). However, even after refluxing of **5** with two equivalents of Me_3SiCN in toluene, a small amount of starting material **5** was still present in the mixture, together with the product of further deselenation (vide infra). Attempts to separate the components of the mixture by flash chromatography were unsuccessful. The purification of **6** by recrystallisation was complicated by its similar solubility to **5**, as well as its instability in the solution (substantial decomposition to **5** and further unidentified products was observed when a solution of pure **6** in $CDCl_3$ or toluene was kept for one day at ambient temperature). The ease of self-reorganization of **6** in solution is surprising considering the stability of the dimethyl congener **4**, which was obtained as a sole product by the reaction of **2** with an excess of selenium.[14]

However, a small amount of the pure yellow solid **6** was obtained by repeated crystallisation of the crude product from CH_2Cl_2 and toluene; it was characterised by ^{31}P, ^1H and ^{13}C NMR and IR spectroscopy and EI-MS, the purity was assessed by elemental analysis. The small amount of compound available did not allow its characterisation by ^{77}Se NMR spectroscopy.

The $^{31}P\{^1H\}$ NMR spectrum of **6** (in $CDCl_3$) consists of a singlet (δ_P = −4.1 ppm) with two sets of ^{77}Se satellites, arising from two distinct isotopomers with one ^{77}Se atom in the *exo*- or *endo*-position of the ring. These two sets are A_2X (Se$_{\mathrm{endo}}$) and AA′X (Se$_{\mathrm{exo}}$) systems (A, A′ = ^{31}P, X = ^{77}Se), the simulation of the latter subspectra allowed the determination of $^1J_{P,P}$ (26 Hz). The magnitudes of $J_{P,Se}$ are as expected (see Exp. Sect.). The ^{1}H NMR spectrum of **6** consists of the signals of Ph protons and a triplet due to the CH_2 group with $^2J_{H,P}$ = 12.0 Hz, which collapses into a singlet in the $^1H\{^{31}P\}$ spectrum. The $^{13}C\{^1H\}$ NMR spectrum also confirmed the identity of **6**, although the weak signal of the *ipso* carbon was not identified with certainty due to the small amount of sample available. The endocyclic carbon gave a triplet at δ_C = 63.7 ppm with $^1J_{C,P}$ = 32.8 Hz, a similar low magnitude of $^1J_{C,P^v}$ of 27.3 Hz was observed in heterocycle **5**.[14]

Crystallographic analysis (Figure 1, Table 1 and 5) confirms the formation of a four-membered PCPSe heterocycle with a *trans*-geometry of the exocyclic phenyl and seleno substituents. Two independent molecules with approximately the same geometry are present in the asymmetric unit of **6** (Table 1). In both molecules the positions of atoms Se13 and CH_2 group are partially disordered. Each independent molecule possesses only approximate C_2 symmetry, with the C_2 axis passing through the C14 and Se13 atoms. The central four-membered ring is very slightly folded (1.4 and 2.3° along the Se···C diagonal). Despite the symmetric substitution pattern, the geometries at P1 and P2 are slightly different, probably as a result of packing effects.

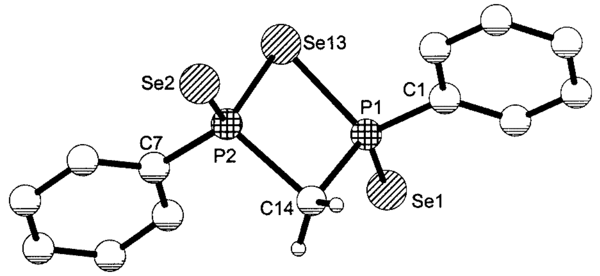


Figure 1. Structure of one of the two independent molecules present in unit cell of **6**; phenyl H atoms are omitted for clarity; the positions of the Se13 atom and CH_2 group are partially disordered

We have published the first structural characterisation of a PCPSe ring (compound **4**) in a recent communication.[14] In contrast to **6**, the presence of two methyl groups bonded to the ring carbon atom in **4** causes significant folding of the heterocycle (17 and 28° along the Se···C diagonal for each of the two molecules in the unit cell). The flattening of the central ring in **6** results in significantly reduced PCP angles in both independent molecules [87.8(2) and 83.3(3)°] with respect to the value found in **4** [96.9(3)°] and, as expected, also to the value found in the five-membered PCPSeSe ring of **5** [116.7(4)°].[14] The terminal Se atoms and the phenyl ring carbon atoms fit an approximate plane, which is nearly perpendicular to the central PCPSe heterocycle.

In summary, an interesting difference in the reactivity of **1** and **2** was observed. Whilst **1** (CH_2 derivative) reacts with a slight excess of selenium in boiling toluene to give the five-membered ring **5** and the formation of only a small amount of the four-membered ring product **6** was observed, compound **2** (CMe_2 derivative), under identical conditions, gives exclusively the four-membered ring product **4**.[14] Furthermore, a spontaneous reorganization of pure **6** in the solution, leading to **5** and unidentified products, was observed. On steric grounds we would predict that **2** should be more likely to give large rings than **1**. We observed the opposite effect and have to conclude that the electronic factors are more significant here. The electron-donating Me groups in **2** appear to favour smaller ring formation.

Table 1. Selected bond lengths (Å) and angles (°) in **6**; values for second independent molecule present in unit cell are in square brackets

P1−Se13	2.262(3) [2.300(4)]
P2−Se13	2.285(4) [2.269(3)]
P1−C14	2.078(7) [2.154(7)]
P2−C14	2.092(6) [2.164(7)]
P1−Se1	2.101(4) [2.099(4)]
P2−Se2	2.087(4) [2.103(4)]
P1−C1	1.792(6) [1.833(6)]
P2−C7	1.818(6) [1.809(6)]
Transannular P···P distance	2.891(5) [2.869(4)]
P1−C14−P2	87.8(2) [83.3(3)]
P1−Se13−P2	78.9(1) [77.8(1)]
C14−P1−Se13	97.2(2) [99.1(2)]
C14−P2−Se13	96.1(2) [99.8(2)]
C1−P1−Se1	116.4(3) [111.6(2)]
C7−P2−Se2	117.6(3) [115.3(2)]
Folding along Se···C diagonal	1.4 [2.3]

P_3CSe Heterocycle (Four Diastereomers 7a-d)

The reaction of **5** with two to three equivalents of nBu$_3$P or Ph$_3$P resulted in rather complicated mixtures as shown by $^{31}P\{^1H\}$ NMR spectroscopy. nBu$_3$P proved to be better suited for the synthetic purposes as the by-product nBu$_3$PSe is easily removed by washing the oily residue remaining after evaporation of solvent with warm acetonitrile; the separation of Ph$_3$PSe is not as straightforward. The solid remaining after extraction with acetonitrile was recrystallised from a small amount of toluene, giving a yellow crystalline material. An X-ray analysis was performed at this stage, showing that the product is the toluene-solvated five-membered P_3CSe heterocycle **7a** (Figure 2; a single diastereomer formed from a racemic mixture of its two enantiomers).

The uniformity of shape of the crystals suggested initially that they all consist of one diastereomeric form (**7a**), however the $^{31}P\{^1H\}$ NMR spectrum measured shortly after dissolving the crystalline material was rather complex, although at 121.4 MHz all signals are of first order and are nonfluxional. Following the analysis of spin-spin coupling systems and a P-P COSY experiment the signals were assigned to four distinct diastereomeric forms **7a−7d** (Scheme 5), in agreement with the presence of three centres of chirality per molecule (P atoms). The relative amount of isomers changes slightly with time after dissolving in

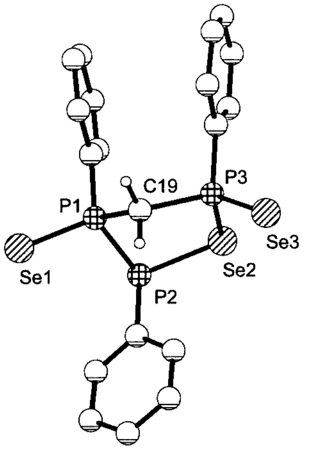
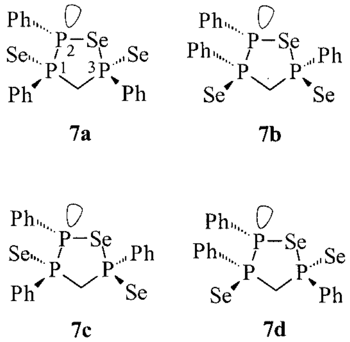


Figure 2. Molecular structure of **7a** (single diastereomer) in the crystal; toluene solvate molecule (0.25 per molecule) and phenyl H atoms are omitted for clarity



Scheme 5. Structural formulae and numbering of diastereomers **7a**−**7d**

$CDCl_3$, and the equilibrium ratio of 24:26:40:10 was established after several days at ambient temperature. A tentative mechanism explaining the observed inversion of configuration at the P-centres takes into account the fact that a detectable amount of **6** (^{31}P NMR) is always present in the solution as an impurity, even after dissolving crystalline material. We suppose that the change of configuration at the chiral P-centres may involve a ring contraction reaction of the five-membered ring **7a**−**d** to the four-membered ring **6**. The change of configuration may occur during reinsertion of the "PPh" group.

A tentative assignment of the ^{31}P NMR spectroscopic data to the distinct isomers was performed as shown in Table 2 and Scheme 5. Two assumptions were made: (i) that the least abundant isomer in solution possesses the configuration with all Ph substituents positioned in one direction with regard to the central heterocycle (all-*cis*, **7b**); and (ii) that the most abundant isomer in solution will have the least sterically hindered configuration **7c**. This corresponds to the fact that the intensity of signal assigned to **7c** increases steadily with time after preparation of sample until it reaches the major intensity shown above. To assign the remaining two isomers, the most configuration-sensitive chemical shift of P2 was considered. The higher-field P2 signal probably corresponds to isomer **7d**, with a *cis* configuration of Ph groups on atoms P1 and P2 (the same relative configuration as in isomer **7b**).

As expected, the ^{1}H NMR spectrum (300 MHz) of the mixture of **7a**−**7d** is very complex, and apart from the Ph signals and toluene protons a complicated multiplet ranging from δ = 3.0 to 4.5 ppm arising from CH_2 protons was observed. Employing ^{31}P broadband decoupling of the ^{1}H NMR spectrum offered partial simplification of the very complex overlapping signals of CH_2 groups from different diastereomers, although an analysis of the coupling constants was still not possible. Nor did measurement of H-P HMQC and H-H COSY experiments allow assignment of these signals to the individual diastereomers. No attempts were made to measure the ^{13}C and ^{77}Se NMR spectra due to the expected complexity.

A molecular ion was observed in the MS spectrum of the mixture of **7a**−**d** using ESI- ionization, whilst pronounced fragmentation was observed in EI+ and CI+ (ionizing gas NH_3) modes, the highest abundant fragments having *m*/*z* values 452 (EI) and 453 (CI).

The solid consisting of **7a**−**d** was further characterised by IR spectroscopy and its purity was assessed by microanalysis.

Crystallographic analysis of **7a** (0.25 toluene solvate, Figure 2, Table 3 and 5) reveals that the central P_3CSe heterocycle in **7a** adopts an envelope conformation with atom P1 lying 0.86 Å out of the plane defined by the other ring atoms (mean deviation of this plane is 0.04 Å), which results in dihedral angles P3−Se2−P2−P1 [19.3(1)°] and Se2−P3−C19−P1 [34.2(1)°]. The bond lengths within the central heterocycle are as expected, although the geometries at P1 and P3 including the inner P−C bond lengths differ slightly as a result of the asymmetry in the molecule. The P−C−P angle in **7a** [109.4(4)°] is slightly lower than the corresponding value [116.6(8)°] found in parent molecule

Table 2. ^{31}P NMR (121.4 MHz, $CDCl_3$) chemical shifts (ppm) and magnitudes of coupling constants (Hz) for four diastereomers **7a**−**7d**; for numbering of atoms see Figure 2 and Scheme 5

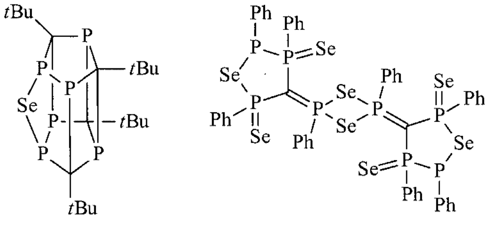
Isomer	δ_{P1} [ppm]	δ_{P2} [ppm]	δ_{P3} [ppm]	$^{1}J_{P1,P2}$ [Hz]	$^{2}J_{P2,P3}$ [Hz]	$^{2}J_{P1,P3}$ [Hz]	Abundance[a] [%]
7a	59.4	28.1	46.3	291.4	43.7	0	24
7d	55.8	14.3	49.0	289.9	43.7	3.0	26
7c	55.0	42.3	48.5	295.1	37.8	14.1	40
7b	62.9	−0.5	35.3	252.1	50.4	9.6	10

[a] Approximate relative equilibrium abundance in $CDCl_3$ solution.

1.[12] The phenyl substituents on the neighbouring P1 and P2 atoms alternate above and below the central ring (trans arrangement), all three Ph substituents occupy axial positions. Only two examples of heterocycles with a PPCPSe atomic sequence in cyclic arrangement have been reported previously.[16−18] The first example (**10**, Figure 3), prepared by insertion of Se into a cage phosphane does not offer many structural similarities due to its rigid cage structure.[16] The second known compound containing the PPCPSe ring sequence (**11**, Figure 3) was prepared by the action of carbon disulfide on the product of the reaction of lithium selenide (obtained from $LiHBEt_3$ and Se) with phenyl dichlorophosphane.[18] Interestingly, the substitution pattern as well as the configuration of substituents in **11** is nearly identical to those in **7a** − the P atoms directly bonded to the C atom bear exocyclic Se atoms and the configuration of Ph substituents on two neighbouring P atoms is *trans*. Furthermore, the central heterocycle in **11** adopts an envelope shape, the out-of-plane P atom being the one corresponding to P1 in **7a**. There are differences in the ring conformation in **11** and **7a** though, as the carbon ring atom is formally double bonded in **11** (and there is substantial delocalisation of π-character over all three P−C bonds) to the P atom of the central heterocycle. Thus the dihedral angles corresponding to P3−Se2−P2−P1 and Se2−P3−C19−P1 in **7a** are 30.2 and 8.4 in **11**.

Table 3. Selected bond lengths (Å), angles and torsion angles (°) in **7a**

P1−P2	2.215(3)		
P1−C19	1.897(7)	P3−C19	1.923(8)
P3−Se2	2.280(3)	P2−Se2	2.254(3)
P1−Se1	2.084(2)	P3−Se3	2.094(2)
P1−P2−Se2	97.4(1)	P2−Se2−P3	102.35(9)
Se2−P3−C19	104.4(2)	P3−C19−P1	109.4(4)
C19−P1−P2	104.8(2)		
P3−Se2−P2−P1	19.3(1)	Se2−P3−C19−P1	34.2(1)



10 **11**

Figure 3. Structural formulae of heterocycles **10** and **11**, related to **7a**−**d**

Dipotassium Salt 8

The reaction of **5** with two equivalents of potassium metal did not proceed with elimination of potassium selenide as expected, instead a quantitative formation of the dipotassium salt of methylene-bis(diselenophenylphosphinic) acid (**8**) was observed. The colourless solid **8**, isolated by filtration, is surprisingly stable towards water, however on contact with air it slowly decomposes with deposition of red selenium. Recrystallisation of **8** from THF gives crystals of the 0.5THF solvate, as indicated by ^{1}H NMR spectroscopy. After prolonged drying in vacuo at room temperature partial desolvation took place, as shown by microanalysis data, indicating that the composition changed slightly to give **8** 0.4THF. Compound **8** was fully characterised by ^{31}P, ^{1}H, ^{13}C and ^{77}Se NMR, IR, ESI-MS (including accurate mass measurement), microanalysis as well as by X-ray crystallography.

The $^{31}P\{^{1}H\}$ NMR spectrum of **8** in D_2O consists of a singlet ($\delta_P = 10.7$ ppm) with a symmetric set of ^{77}Se satellites. Their analysis allowed determination of magnitudes of $^{2}J_{P,P}$ (34 Hz), $^{1}J_{P,Se}$ (588 Hz) and $^{3}J_{P,Se}$ (2 Hz). The magnitude of $^{1}J_{PSe}$ was reconfirmed also by measurement of the $^{77}Se\{^{1}H\}$ NMR spectrum (d, $\delta_{Se} = 49.9$ ppm). The pattern of the ^{31}P and ^{77}Se NMR spectra, together with the magnitudes of $J_{P,Se}$ − lying between the usual values for single and double bonded selenium − clearly indicate that delocalization of the negative charge in the molecule occurs, as shown in the structural formula in Scheme 4. Further, simulation of the C_i second order signal in the $^{13}C\{^{1}H\}$ NMR spectrum of **8** confirmed the magnitude of $^{2}J_{P,P}$ (34 Hz); the signal due to the CH_2 group appears in the $^{13}C\{^{1}H\}$ NMR spectrum as a triplet with $^{1}J_{C,P} = 20$ Hz. Dianion **8** represents the first example of the acyclic $Se_2P{-}C{-}PSe_2$ moiety; no sulfur analogue is known.

Crystallographic analysis of **8** confirmed the ring-opening reaction of **5** leading to the formation of the potassium salt of the acyclic dianion (Figure 4, Table 4 and 5). Crystals for analysis were grown from acetonitrile, from which compound **8** crystallises as **8**·0.75 MeCN; the position of one of the phenyl substituents is disordered as shown in Figure 4, the angle between Ph planes in the two alternating positions being ca. 45°. Despite the symmetric substitution pattern of the anion, no approximate symmetry element can be found in its structure in the crystal. The low symmetry results mainly from the mutual synclinal configuration of the two P environments, which is adopted by the dianion in order to decrease the steric strain resulting from facing negatively charged bulky Se atoms (the shortest intramolecular Se···Se distance is 3.94 Å). As expected, the P−C−P angle is broader in acyclic **8** [124.4(3)°] than in the parent ring system **5** [116.7(4)°][14] and neutral acyclic $Ph_2P(Se)CH_2P(Se)Ph_2$ [117.9(6)°].[19] The delocalization of the negative charge and π-character in the P−Se bonds was mentioned in the NMR discussion, in the crystal this phenomenon results in the P−Se bond lengths in **8** [2.143(2)−2.165(2) Å] being intermediate between the typical single- and double-bonded P-Se distances [usual distinct values of 2.10 Å (P=Se) and 2.25 Å (P−Se) were found in **5**]. The anion and the K^+ cations interact with the Se atoms with K···Se distances in the range 3.29−3.54 Å; the nitrogen atom of the acetonitrile solvate molecules coordinate to K^+ cations.

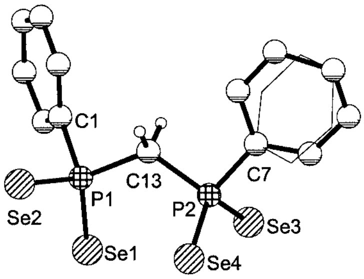


Figure 4. Structure of dianion **8** in the crystal; countercations 2K$^+$, acetonitrile solvate molecule (0.75 molecule per dianion) and phenyl H atoms are omitted for clarity; the Ph ring bonded to P2 is disordered, in half of the molecules being in positions as shown in the picture, position in a second half of molecules is indicated by thin lines

Table 4. Selected bond lengths (Å) and angles (°) in **8**

P1−C13	1.848(5)	P2−C13	1.833(6)
Se1−P1	2.143(2)	P1−Se2	2.165(2)
P2−Se3	2.144(2)	P2−Se4	2.150(2)
P1−C1	1.827(6)	P2−C7	1.840(5)
P2−C13−P1	124.4(3)		
C13−P1−Se1	114.9(2)	C13−P1−Se2	110.5(2)
C13−P2−Se3	111.0(2)	C13−P2−Se4	111.1(2)
Se1−P1−Se2	115.60(7)	Se3−P2−Se4	117.07(7)
C13−P1−C1	98.5(3)	C13−P2−C7	100.8(3)

Conclusion

Two new heterocyclic and one acyclic compound with rare structural motifs are reported. In all the products described the P−C−P moiety is preserved. The ^{31}P NMR spectra of the mixtures after heating of $(PhP)_4CH_2$ (**1**) with various ratios of Se indicated that further P−Se heterocycles may exist, however the complexity of mixtures and tendency to reorganization (observed in reported heterocycles **6** and **7a−d**) may complicate significantly their isolation in a pure form.

Experimental Section

General Remarks: Compound **1** was prepared from $(PPh)_5$ as described earlier.[4] Compound **5** was prepared by the reaction of **1** with an excess of grey selenium, followed by recrystallisation from hot toluene.[14] All manipulations (unless stated otherwise) were performed under a dry, oxygen-free nitrogen atmosphere using standard Schlenk technique. Solvents and other reagents were dried by standard methods. In vacuo refers to a pressure of ca. 13 Pa. NMR spectra were recorded on Varian Gemini 2000 (300 MHz), Varian Unity (500 MHz) and Bruker Avance (300 MHz) spectrometers and are referred to 85% H_3PO_4 (external reference for ^{31}P) or TMS or deuterated solvent peaks (^{1}H and ^{13}C). Infrared spectra were recorded as KBr discs.

P_2SeC Heterocycle (4): Me_3SiCN (0.24 mL, 1.80 mmol) and a suspension of **5** (0.50 g, 0.92 mmol) in toluene (10 mL) were heated under reflux for 2 hours. The solvent and volatile by-products were evaporated in vacuo with slight heating. The resulting solid was recrystallised from 3 mL of CH_2Cl_2 and then from hot toluene (2 mL). Further recrystallisations were sometimes needed to obtain product free from starting material **2**. Crystals suitable for an X-ray diffraction study were obtained from dichloromethane. Yield 39 mg (9%). $C_{13}H_{12}P_2Se_3$ (467.1): calcd. C 33.4, H 2.6; found C 33.7, H 2.3. M.p. 183−185 °C. IR (KBr): $\tilde{\nu}$ = 1434vs, 1088vs, 747s, 711s, 563m [ν(P=Se)], 499vs cm^{-1}. ^{1}H NMR ($CDCl_3$) (300.0 MHz): δ = 5.25 (t, $^2J_{H,P}$ = 12.0 Hz, 2 H, CH_2), 7.60−7.68 (m, 6 H, *m*- and *p*-Ph), 8.50−8.60 (m, 4 H, *o*-Ph) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz): δ = 63.7 (t, $^1J_{C,P}$ = 32.8 Hz, CH_2), 129.1 (m, *m*-C), 132.6 (m, *o*-C), 133.2 (s, *p*-C) ppm; the small amount of sample available did not allow identification of the *ipso*-C signal. $^{31}P\{^1H\}$ NMR (121.4 MHz): δ = −4.1 (s) ppm; analysis of the ^{77}Se satellites showed $^2J_{P,P}$ = 26, $^1J_{P,Se_{exo}}$ = 810, $^1J_{P,Se_{endo}}$ = 221, $^3J_{P,Se_{exo}}$ = 7 Hz. MS (EI+): *m*/*z* = 470 [M$^+$], 390 [M − Se], 310 [M − 2Se].

P_3CSe Heterocycle (7a): nBu_3P (1.07 mL, 4.29 mmol) was added with stirring to an externally cooled (0 °C) suspension of **5** (1.00 g, 1.83 mmol) in toluene (20 mL). The mixture was kept at 0 °C for 30 min, then it was left to warm to room temperature and stirred for another 12 hours, followed by filtration and evaporation of the solvents from the filtrate in vacuo. The resulting oil was washed with *n*-hexane (15 mL) and with warm acetonitrile (2 × 10 mL) to remove the nBu_3PSe. The solid obtained was recrystallised from hot toluene (4 mL). Yield 0.23 g (30%) of **7a−d** (mixture of diastereomers, each containing approximately half a molecule of toluene) in the form of yellow crystals, some of which were suitable for X-ray analysis. The following analytical and spectroscopic data were obtained from the mixture of four diastereomeric forms **7a−d**: $C_{19}H_{17}P_3Se_3{\cdot}1/2C_7H_8$: calcd. C 43.5, H 3.4; found C 43.1, H 3.0. M.p. 143−145 °C. IR (KBr): $\tilde{\nu}$ = 1434s, 1101s, 736vs, 683vs, 567s [ν(P=Se)], 524vs cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.25 (s, ≈1.5 H, CH_3 toluene), 4.5−3.0 (set of multiplets, 2 H, CH_2), 8.5−6.9 (set of multiplets, ≈17.5 H, 3.5×Ph) ppm. $^{31}P\{^1H\}$ NMR: see text and Table 2. MS (ESI−): *m*/*z* = 577 [M − H; correct isotopic pattern], 499 [M − Se + 1], 469 [M − P − Se], 299 [PhP_2Se_2, base peak].

Potassium salt (8): Potassium metal (0.07 g, 1.84 mmol) was added to a stirred suspension of **5** (0.50 g, 0.92 mmol) in THF (7 mL). The stirring was continued for 48 hours after which time a white solid precipitated and was filtered off using a sintered glass frit. The product obtained after drying in vacuo was of sufficient purity (assessed by ^{31}P NMR spectroscopy), however it can be recrystallised from cold THF. Yield 540 mg (ca. 85%, before recrystallisation) of 0.5 THF solvated **8** in the form of a colourless solid. Compound **8** is hygroscopic, it is soluble in THF, acetonitrile and water, and decomposes with deposition of red selenium on contact with air. Crystals suitable for X-ray work were obtained from acetonitrile as **8** 0.75MeCN solvate. The following analytical and spectroscopic data were obtained with **8** in the form of its 0.4THF solvate: $C_{13}H_{12}K_2P_2Se_4{\cdot}0.4C_4H_8O$: calcd. C 26.8, H 2.3; found C 26.8, H 2.1. Decomp. above 150 °C. IR (KBr): $\tilde{\nu}$ = 1434vs, 1091s, 738vs, 689s, 524vs, 482vs cm^{-1}. ^{1}H NMR (D_2O, 300 MHz): δ = 3.68 and 1.82 (2 × m, variable, THF), 4.33 [t, $^2J_{H,P}$ ≈ 11.5 Hz, 2 H, CH_2], 7.31−7.13 (2 × m, 6 H, *m*- and *p*-Ph), 7.79 (m, 4 H, *o*-Ph) ppm. $^{13}C\{^1H\}$ NMR (75.4 MHz): δ = 25.1 (s, THF), 54.8 [t, $^1J_{C,P}$ = 19.5 Hz, CH_2), 68.0 (s, THF), 127.8 [t (virtual), $^3J_{P,C}$ = 6.5 Hz, C_m], 130.6 (s, C_p), 131.5 [t (virtual), $^2J_{P,C}$ = 5.4 Hz, C_o], 136.8 [m (second order), $^1J_{P,C}$ = 62.0, $^3J_{P,C}$ < 2 Hz, C_i] ppm. $^{31}P\{^1H\}$ NMR (121.4 MHz): δ = 10.7 (s) ppm; analysis of ^{77}Se satellites showed $^2J_{P,P}$ = 34.0, $^1J_{P,Se}$ = 588, $^3J_{P,Se}$ = 2.0 Hz;

Table 5. Crystallographic data for **6**, **7a** and **8**

Compound	**6**	**7a**	**8**
Formula	$C_{13}H_{12}P_2Se_3$	$C_{19}H_{17}P_3Se_3$. 0.25[C_7H_8]	$C_{13}H_{12}P_2Se_4K_2$.0.75[C_2H_3N]
M	467.05	597.90	655.00
Crystal habit	yellow prism	yellow prism	colourless prism
Crystal size (mm)	0.12 × 0.1 × 0.1	0.14 × 0.1 × 0.1	0.2 × 0.1 × 0.1
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P2(1)	*C*2/*c*	$P\bar{1}$
a (Å)	6.746(1)	14.385(2)	7.778(4)
b (Å)	24.683(3)	10.926(2)	11.201(5)
c (Å)	9.581(1)	31.538(5)	13.044(7)
α (°)	90.00	90.00	99.94(3)
β (°)	101.34(1)	101.41(1)	92.04(3)
γ (°)	90.00	90.00	95.68(3)
Z	4	8	2
ρ_{calcd}	1.983	1.635	1.956
No. of reflections:			
Measured	7737	9982	7398
Independent	3607	3417	5978
Observed [$I > 2\sigma(I)$]	2144	2123	4157
Θ range	2.3- 23.3	2.3−23.3	2.2−32.4
μ (mm^{-1})	7.238	4.743	7.112
Min/max transmission	0.6558/1.0000	0.8696/1.0000	0.7599/1.0000
No. of parameters	277	240	255
R (F^2, obs. data)	0.0787	0.0592	0.0544
wR (F^2, obs. data)	0.1698	0.1351	0.1240

$^{77}Se\{^1H\}$ NMR (57.2 MHz): $\delta = 49.9$ [d, $^1J_{P,Se} = 588$ Hz] ppm. MS (ESI−): $m/z = 587$ [anion + K], 274 [(anion)$^{2-}$], both had correct isotopic pattern; accurate mass measurement on $^{12}C_{13}{}^1H_{12}{}^{39}K^{31}P_2{}^{77}Se_4$ requires 588.6712, found 588.6716 (error of 0.7 ppm).

Crystal Structure Analyses: Data for **6** and **7a** were collected at 293 K on a Bruker SMART CCD diffractometer; data for **8** were collected at the same temperature on a Rigaku Mercury CCD using graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Absorption corrections were performed on the basis of multiple equivalent reflections. The structures were solved by direct methods. Structural refinements were performed with the full-matrix least-squares method on F^2 using the program SHELXTL (Version 5.10, Bruker AXS, 1997). The non-hydrogen atoms were refined anisotropically, the hydrogen atoms were idealised and refined isotropically using a riding model. CCDC-19036 (**6**), -19037 (**7a**) and -19038 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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