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Novel small organo-P–S/Se heterocycles

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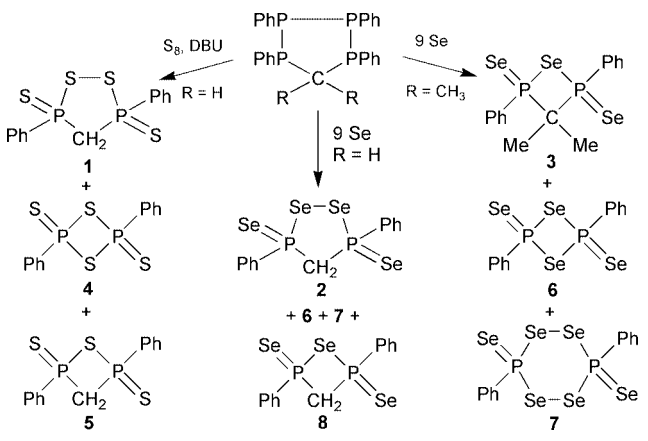
Oxidative addition of elemental sulfur and selenium to cyclomonocarbatetraphosphines $(PhP)_4CR_2$ (R = H, Me) afforded novel five- and four-membered heterocycles $PhP(E)CH_2PhP(E)E_2$ (E = S, Se) and $PhP(Se)CMe_2$-PhP(Se)Se.

Although the chemistry of cyclophosphines $(R'P)_n$ (R′ = alkyl, aryl; n = 3–6) has been studied extensively, tetraphospholanes $(R'P)_4CR_2$ have received less attention, despite their ease of access from cyclophosphines.[1] Due to the stability of the endocyclic P–C bond they are a valuable source of $PhPCR_2PPh$ moiety as shown herein for oxidative addition reactions with elemental sulfur and selenium (Scheme 1). Four- and five-membered heterocycles described here represent only the third known heterocycle with the atomic sequence PCPSe (and the first X-ray structure determination reported), whilst the heterocyclic sequence PCPSeSe is the first example. The parallels in S chemistry are also scarce; PCPS rings were prepared using low-coordinate phosphorus starting compounds such as diphosphaallene,[2] phosphanylidene[3] and thioxophosphane with phosphonium ylide.[4] The only known heterocyclic compound with the PCPSS atomic sequence, **9**, has been isolated in low yield as a side product in the reaction of sulfur and diphosphaallene with stabilizing bulky supermesityl side groups.[2a] Partially sulfur oxidised derivatives $(PhP)_4CH_2S$ and $(PhP)_4CH_2S_2$ were obtained from the reaction of $(PhP)_4CH_2$ with lower molar amounts of sulfur.[5]

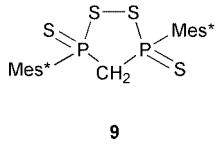
Our aim was to obtain thermodynamically stable products, thus all the reactions were performed in refluxing toluene (under N_2). Treatment of $(PhP)_4CH_2$ with 8 equivalents of sulfur and a catalytic amount of DBU, followed by fractional crystallisation afforded colourless crystals of **1** in a moderate yield (40%, Scheme 1).[6]

Crystallographic analysis of **1** (Fig. 1)[7] reveals the formation of a five–membered PCPSS heterocycle with a *trans*-geometry of exocyclic phenyl and sulfur substituents. The central heterocycle has an envelope shape, with S(2) atom lying 1.1 Å out of the plane defined by the other ring atoms (mean deviation of this plane is 0.04 Å), which is in contrast to the half-chair conformation found in the only known PCPSS heterocycle **9**.[2a]



Scheme 1

The internal bond lengths in **1** are comparable to those in **9**. The envelope shape however accounts to significant changes in internal bond angles, the P–C–P angle as well as PSSP dihedral angle are substantially decreased in **1** [P–C–P angle in **1** 114.47(9)°; 119.6(4)° in **9**; PSSP dihedral angle in **1** 49.48(3)°; 54.8(1)° in **9**]. Also the S(3)–P(1)–C(2) and S(4)–P(2)–C(8) angles of 115° are decreased due to lower steric hindrance of phenyl *vs.* supermesityl substituent in **9** (corresponding angles 126°). The shortest intermolecular contacts in **1** are 3.47 Å [S(2)···S(3)], which is less than twice the van der Waals radius for sulfur (3.70 Å).



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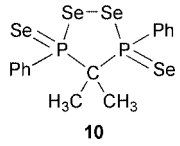

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The $^{31}P\{^1H\}$ NMR spectrum of **1** (in $CDCl_3$) shows a singlet at δ 80.3. A minor singlet (*ca.* 4% intensity) with a very similar shift of δ 80.9 has been also observed in the spectrum, belonging to a less energetically favourable conformation or *cis*-isomer of **1**. The ^1H NMR spectrum of **1** contains multiplets for the phenyl ring protons and a triplet for the CH_2 group [δ 3.9, ^2J(HP) 9.9 Hz]. These spectral data are in a very good agreement with those reported for **9** [δ_P 87.6, $\delta_H(CH_2)$ 3.96, ^2J(HP) 9.6 Hz].[2a]

Treatment of $(PhP)_4CH_2$ with 9 equivalents of grey selenium in boiling toluene, hot filtration to remove insoluble **6** and unreacted selenium, concentration of the filtrate *in vacuo* and cooling afforded the orange crystalline solid **2** in 94% yield (Scheme 1). The minor impurities, heterocycles **7** and **8**, can be removed by recrystallisation from hot toluene.[8]

Crystallographic analysis[7] reveals **2** to be almost isostructural with **1** (Fig. 1). The central heterocycle has again envelope

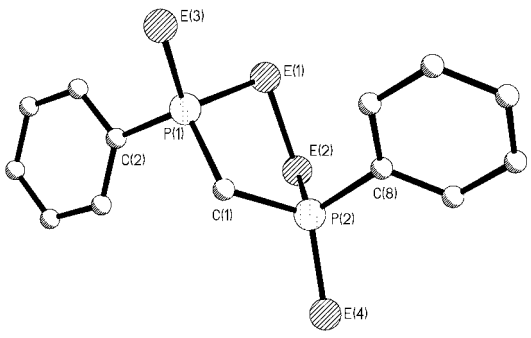

Fig. 1 Molecular structure of **1** (E = S) and **2** (E = Se). H atoms omitted for clarity. Selected bond lengths (Å) and angles (°) for **1** and **2** (values in square brackets): P(1)–C(1) 1.839(2) [1.830(7)], P(2)–C(1) 1.839(2) [1.839(6)], P(1)–E(1) 2.1160(7) [2.249(2)], P(2)–E(2) 2.1095(7) [2.247(2)], E(1)–E(2) 2.0667(7) [2.338(1)], P(1)–C(2) 1.810(2) [1.809(7)], P(2)–C(8) 1.810(2) [1.828(8)], P(1)–E(3) 1.9394(7) [2.100(2)], P(2)–E(4) 1.9419(7) [2.100(2)], P(1)–C(1)–P(2) 114.47(9) [116.7(4)], P(1)–E(1)–E(2) 97.07(3) [93.40(6)], P(2)–E(2)–E(1) 95.73(3) [91.97(6)], E(1)–P(1)–C(1) 102.71(6) [105.2(2)], E(2)–P(2)–C(1) 100.90(6) [102.7(2)], C(2)–P(1)–E(3) 114.86(6) [114.0(2)], C(8)–P(2)–E(4) 114.78(7) [114.0(2)], E(1)–P(1)–E(3) 107.16(3) [106.82(9)], E(2)–P(2)–E(4) 107.77(3) [107.91(9)].

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conformation, with Se(2) lying 1.27 Å out of plane defined by other ring atoms (mean deviation of this plane is 0.04 Å). The PCP angle, P···P distance and PSeSeP torsion angle vary little from the corresponding values in **1**, as expected the ring dimensions are increased due to larger radii of Se atoms (see *e.g.* differences in Se–Se and S–S bond length for **2** and **1**), however Se(3)–P(1)–C(2) and Se(4)–P(2)–C(8) angles (114°) show no significant change when compared with corresponding angles in **1**. The shortest intermolecular contacts in **2** are 3.48 Å [Se(2)···Se(3)].

The $^{31}P\{^{1}H\}$ NMR spectrum of **2** comprises of a singlet (δ_P 43, in $CDCl_3$) with symmetric sets of selenium satellites. The satellite spectrum is generated mainly from two distinct isotopomers with one ^{77}Se atom in exo- or endo-positions of the ring, both having an AXX′ pattern (A = ^{77}Se, X = P). Simulation of the satellite spectra enabled determination of all four P–Se coupling constants[9] as well as a homonuclear P–P coupling [^2J(PP) ±34.1 Hz].

By the treatment of $(PhP)_4CMe_2$ with 9 equivalents of grey selenium in the same manner as **2** (including work-up procedures), orange crystalline **3** has been obtained in 68% yield (Scheme 1).[10] Crystallographic analysis of **3** (Fig. 2)[7] reveals that oxidation of $(PhP)_4CMe_2$ proceeds surprisingly with the formation of a four-membered PCPSe ring. The unit cell contains two independent molecules, in both the central ring is folded (17 and 28° along the Se···C diagonal) with phenyl and exocyclic selenium substituents in *trans* configuration. No X-ray structure determination of a PCPSe ring has been reported up to date, the nearest parallels found are PCPS rings, both thiadiphosphetanes with known X-ray data[2b,4] show *cis* configuration and folded geometry of the central ring (19.2 and 29.4° along C···S diagonal). Internal P–Se bond lengths in **3** [2.274(2)–2.283(2) Å] are slightly increased with respect to **2** [2.247(2) and 2.249(2) Å] however they are comparable with **6** [2.276(2) and 2.284(2) Å].[11] In contrast, the internal P–Se–P angles in **3** (77.7 and 76.0° for each molecule in the unit cell) are substantially decreased when compared with corresponding angle in the planar PSePSe heterocycle **6** (85.5°).[11] The shortest intermolecular contacts in **3** are 3.59 Å [Se(1)···Se(2)].

$^{31}P\{^{1}H\}$ NMR examination of the mixture after the reaction did not show any reasonably intense signals at lower field, assignable to related five-membered heterocycle **10**. The $^{31}P\{^{1}H\}$ NMR spectrum of **3** comprises of a singlet (δ_P 52, in $CDCl_3$) with two symmetric sets of selenium satellites of AXX′ (Se_{exo}) and AX_2 (Se_{endo}) pattern (A = ^{77}Se, X = P). The simulation of the AXX′ satellite subspectrum enabled determination of a homonuclear P–P coupling, whose magnitude is surprisingly low [^2J(PP) < ±2 Hz].[12] The ^1H NMR spectrum of **3** ($CDCl_3$, 25 °C) shows a second-order A_3B_3XX' pattern (A, B = CH_3 protons, X, X′ = P) at δ 1.3, confirming magnetic inequivalence of methyl groups protons as a consequence of the folded geometry of the central heterocycle.

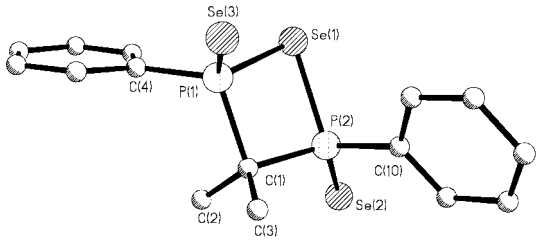

Fig. 2 Structure of one of the two independent molecules present in unit cell of **3**. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°) for the molecule with less folded central heterocycle: P(1)–C(1) 1.915(7), P(2)–C(1) 1.910(6), P(1)–Se(1) 2.279(2), P(2)–Se(1) 2.283(2), P(1)–C(4) 1.825(7), P(2)–C(10) 1.817(7), P(1)–Se(3) 2.096(2), P(2)–Se(2) 2.101(2), P(1)–C(1)–P(2) 96.9(3), P(1)–Se(1)–P(2) 77.73(7), Se(1)–P(1)–C(1) and Se(1)–P(2)–C(1) 91.4(2), C(1)–P(1)–Se(3) 114.4(2), C(1)–P(2)–Se(2) 115.1(2), C(1)–P(1)–C(4) 110.2(3), C(1)P(2)–C(10) 108.9(3), C(4)–P(1)–Se(3) 112.3(2), C(10)–P(2)–Se(2) 113.0(3), Se(1)–P(1)–C(4) 109.0(2), Se(1)–P(2)–C(10) 107.5(3), Se(1)–P(1)–Se(3) 117.70(9), Se(1)–P(2)–Se(2) 118.74(9), C(2)–C(1)–C(3) 113.2(6). For parameters of second molecule in the independent unit see crystallographic data in CIF format.

Studies to employ new soluble P–Se heterocycles in our reagent program for C=O to C=Se transformations are now underway.

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Notes and references

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6 $^{31}P\{^{1}H\}$ NMR examination of the reaction mixture before recrystallisation indicated presence of two side products **4** (s, δ_P 17.3) and **5** (s, δ_P 29.8). Full spectral and structural characterisation of **5** is the subject of our continuating studies. Compound **1** is soluble in dichloromethane and toluene, correct C, H microanalysis were obtained; mp 153–155 °C; MS (EI, sampled neat) 358 (M^+, base peak), 326 (M − S), 294 (M − 2S), 262 (M − 3S); IR (KBr disc) 769 cm^{-1} (vs, $\nu_{P=S}$).

7 *Crystal data*: for **1**: $C_{13}H_{12}P_2S_4$, M = 358.41, space group $P2_1/c$, monoclinic, a = 9.8833(6), b = 8.8370(5), c = 18.375(1) Å, β = 94.948(1)°, U = 1598.9(2) Å^3, T = 293 K, Z = 4, μ(Mo-Kα) = 0.777 mm^{-1}, 6688 reflections measured, 2276 unique (R_{int} = 0.0121) which were used in all calculations. The final R was 0.0228 for $I > 2\sigma(I)$ and $wR(F^2)$ was 0.0649 for all data. For **2**: $C_{13}H_{12}P_2Se_4$, M = 546.01, monoclinic, space group $P2_1/c$, a = 10.016(1), b = 8.9836(5), c = 18.677(5) Å, β = 93.687(1)°, U = 1677.2(5) Å^3, T = 293 K, Z = 4, μ(Mo-Kα) = 8.924 mm^{-1}, 9054 reflections measured, 3481 unique (R_{int} = 0.1376) which were used in all calculations. The final R was 0.0632 for $I > 2\sigma(I)$ and $wR(F^2)$ was 0.1677 for all data. For **3**: $C_{15}H_{16}P_2Se_3$, M = 495.10, orthorhombic, space group $Pna2_1$, a = 17.7582(3), b = 27.4561(2), c = 7.1512(1) Å, U = 3486.72(8) Å^3, T = 293 K, Z = 8, μ(Mo-Kα) = 6.501 mm^{-1}, 14916 reflections measured, 4885 unique (R_{int} = 0.0522) which were used in all calculations. The final R was 0.0347 for $I > 2\sigma(I)$ and $wR(F^2)$ was 0.0876 for all data. CCDC reference numbers 169264–169266. See http://www.rsc.org/suppdata/cc/b1/b107214e/ for crystallographic data in CIF or other electronic format.

8 The identity of by-products **7** and **8** has been established by single crystal X-ray structure analyses and NMR, their details together with their rational syntheses and NMR spectra will be published elsewhere. Compound **2** is only slightly soluble in cold dichloromethane and toluene. It is stable under dry nitrogen atmosphere, on exposition to air it decomposes with deposition of a red selenium. Recrystallised product gave correct C, H microanalysis; mp decomp. above 180 °C; MS (EI, sampled neat) 546 (M^+), 468 (M − Se + 1); IR (KBr disc) 555 cm^{-1} (s, $\nu_{P=Se}$).

9 Further selected NMR data for **2**: $^1J(PSe_{exo})$ ±775 Hz, $^3J(PSe_{exo})$ ±11 Hz, $^1J(PSe_{endo})$ ±342 Hz, $^2J(PSe_{endo})$ ±13 Hz. Magnitudes of ^1J(PSe) coupling constants have been confirmed by measurement of ^{77}Se NMR spectra of **2**; $\delta(^{77}Se)$ −114 (d, Se_{exo}) and 494 ppm (d, Se_{endo}); ^1H NMR: δ 4.4 [t, CH_2, ^2J(HP) 9.2 Hz]; $^{13}C\{^{1}H\}$ NMR: δ 52.2 [t, CH_2, ^1J(CP) 27.3 Hz].

10 Compound **3** is stable under N_2 atmosphere, it is well soluble in dichloromethane and toluene. Correct C, H microanalysis were obtained; mp 211–214 °C; MS (EI, sampled neat) 496 (M^+); IR (KBr disc) 553 cm^{-1} (m, $\nu_{P=Se}$).

11 P. Bhattacharyya, A. M. Z. Slawin and J. D. Woollins, *J. Chem. Soc. Dalton Trans.*, 2001, 300.

12 Further selected NMR data for **3**: $^1J(PSe_{exo})$ ±804 Hz, $^1J(PSe_{endo})$ ±243 Hz, inner lines of AXX′ subspectrum were hidden under intensive central line, prohibiting determination of $^3J(PSe_{exo})$ coupling. Magnitudes of ^1J(PSe) coupling constants have been confirmed by measurement of ^{77}Se NMR spectra of **3**; $\delta(^{77}Se)$ −96 (d, Se_{exo}) and 506 (t, Se_{endo}); ^1H NMR: δ 1.2–1.5 (m, 2 × CH_3); $^{13}C\{^{1}H\}$ NMR: δ 63.2 [t, CP_2, ^1J(CP) 29.3 Hz], 26.8 (s, 2 × CH_3).