Facile and reproducible syntheses of bis(dialkylselenophosphenyl)-selenides and -diselenides: X-ray structures of $({}^{i}Pr_2PSe)_2Se$, $({}^{i}Pr_2PSe)_2Se_2$ and $(Ph_2PSe)_2Se$

Chinh Q. Nguyen, Adekunle Adeogun, Mohammad Afzaal, Mohammad A. Malik and Paul O'Brien*

Received (in Cambridge, UK) 3rd March 2006, Accepted 31st March 2006
First published as an Advance Article on the web 21st April 2006
DOI: 10.1039/b603197h

Facile and reproducible methods for the syntheses of bis(di-iso-propylselenophosphinyl)selenide $({}^{i}Pr_2PSe)_2Se$ (1), bis(di-iso-propylselenophosphinyl)diselenide $({}^{i}Pr_2PSe)_2Se_2$ (2) and bis(di-phenylselenophosphinyl)selenide $(Ph_2PSe)_2Se$ (3) is reported.

The most common method reported for the preparation of selenophosphates or selenophosphinates involves the reaction of Na_xE_y (E = S, Se, Te) with $PhPCl_2$ or Ph_2PCl. The preparation of Na_xE_y is carried out by the reaction of sodium metal with grey selenium in a liquid ammonia solution at −78 °C.[1–6] Woollins *et al.* reported that such reactions give a mixture of products along with unreacted sodium.[7] It was also reported that the results of the reaction between Na_xE_y and Ph_2PCl are not reproducible and can be improved, but only slightly, by using a mixture of THF–ethanol; the ethanol destroys any residual sodium. Using these methods, authors have synthesised $[Na_2(Se_2PPh_2)_2{\cdot}THF{\cdot}5H_2O]$.[7] Davies *et al.* prepared $[Li(Se_2PPh_2){\cdot}THF{\cdot}TMEDA]$,[8] $[K(Se_2PPh_2)_2(THF)_2]_2$[8] and $[In(SePPh_2)_3]$ by the reaction of Ph_2PK or Ph_2PLi with selenium. The potassium complex was then reacted with $InCl_3$ to give the indium complex; $[In(Se_2PPh_2)_3]$.[8] Du Mont *et al.* have inserted Se into a P–P bond[9] to give selenophosphinates whereas Horn and Lindner prepared the intermediate $R_2PSi(Me)_3$, by lithiation of diphenylphosphine chloride and subsequent reaction with trimethylsilylchloride at −78 °C.[10,11] Benkeser[12] reported that the combination of trichlorosilane with triethylamine will produce trichlorosilyl anion which can act as a substituent to facilitate the forming of C–Si bonds. This reaction was extended by du Mont *et al.*[13] to make Ge–Si and P–Si bonds.

There are no reports of a reproducible synthetic method for the presented selenophosphates or selenophosphinates, or their X-ray structures. Herein, we report facile and reproducible methods for the syntheses of $({}^{i}Pr_2PSe)_2Se$ (**1**), $({}^{i}Pr_2PSe)_2Se_2$ (**2**) and $(Ph_2PSe)_2Se$ (**3**) and their X-ray structures.

Compounds **1–3** were prepared by the insertion of Se in to the P–Si bond of the intermediate R_2PSiCl_3, (where R = ${}^{i}Pr$, Ph). The reactions are shown in eqn (1)–eqn (3).† All three compounds are soluble in common non-polar organic solvents and were crystallized from toluene solution to give transparent yellow cubic crystals for **1** and transparent orange rods for **2** and **3**. The compounds are stable under air and moisture for several months.

$$R_2PCl + HSiCl_3 + NEt_3 \xrightarrow[6h,rt]{toluene} R_2PSiCl_3 + [HNEt_3]Cl \qquad (1)$$

$$2R_2PSiCl_3 + 3Se \xrightarrow[20h,reflux]{toluene} (R_2PSe)_2Se + Si_2Cl_6 \qquad (2)$$

$$2R_2PSiCl_3 + 4Se \xrightarrow[20h,reflux]{toluene} (R_2PSe)_2Se_2 + Si_2Cl_6 \qquad (3)$$

The structure of **1** (Fig. 1) shows that each phosphorus is bonded with two selenium atoms and the two carbon atoms of the isopropyl group. One of the selenium atoms (Se(1)) is shared by both phosphorus atoms. The geometry around P(1) is a distorted tetrahedron (Se(2)–P(1)–Se(1), 106.25(6)°) whereas the Se(3)–P(2)–Se(1), 118.05(6)° angle around P(2) shows it to be close to trigonal planar. The angle P(1)–Se(1)–P(2) 107.50(6)° makes Se(1) distorted tetrahedral. The difference between the single bonds and double bonds of selenium and phosphorus is clearly shown by the bond lengths of Se(1)–P(1), 2.274(2) Å; Se(1)–P(2), 2.297(1) Å which are longer than those of Se(2)–P(1), 2.109(1) Å; Se(3)–P(2), 2.10(2) Å as expected.

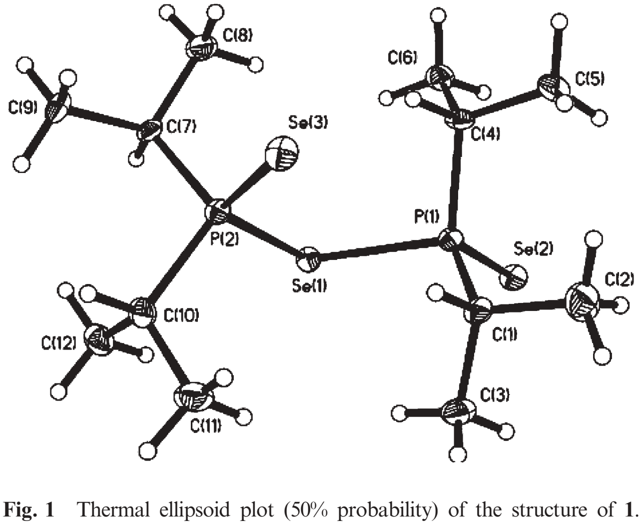

Fig. 1 Thermal ellipsoid plot (50% probability) of the structure of **1**. Selected bond distances (Å) and angles (°): Se(1)–P(1), 2.274(2); Se(1)–P(2), 2.297(1); Se(2)–P(1), 2.109(1); Se(3)–P(2), 2.10(2); P(1)–C(1), 1.832(5); P(1)–C(4), 1.845(5); P(2)–C(10), 1.837(5); P(2)–C(7), 1.840(5); P(1)–Se(1)–P(2), 107.50(6); Se(2)–P(1)–Se(1), 106.25(6); Se(3)–P(2)–Se(1), 118.05(6).

The School of Chemistry and the School of Materials, The University of Manchester, Oxford Road, Manchester, UK M13 9PL.
E-mail: paul.obrien@manchester.ac.uk

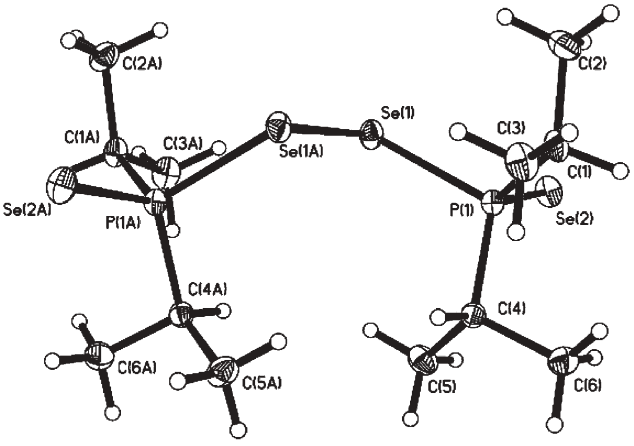

Fig. 2 Thermal ellipsoid plot (50% probability) of the structure of **2**. Selected bond distances (Å) and angles (°): P(1)–Se(2), 2.116(1); P(1)–Se(1), 2.243(1); Se(1)–Se(1A), 2.384(1); C(1)–P(1), 1.837(3); C(4)–P(1), 1.828(3); C(2)–C(1)–P(1), 111.0(2); C(3)–C(1)–P(1), 114.6(2); C(4)–P(1)–Se(2), 114.79(1); C(1)–P(1)–Se(2), 112.90(1); C(4)–P(1)–Se(1), 111.52(1); C(1)–P(1)–Se(1), 109.72(1); Se(2)–P(1)–Se(1), 100.91(3); P(1)–Se(1)–Se(1A), 107.65(3). Symmetry transformation used to generate equivalent atoms: A $1 - x, y, -z + ½$.

The structure of **2** is similar to the structure of **1** with the only difference being an additional selenium between the two phosphorus atoms. The compound has crystallographically a two-fold axis. The selenium from P(1) forms a bond with the selenium from P(2) so that a bridge of two seleniums is formed between two phosphorus atoms. The structure is shown in Fig. 2.

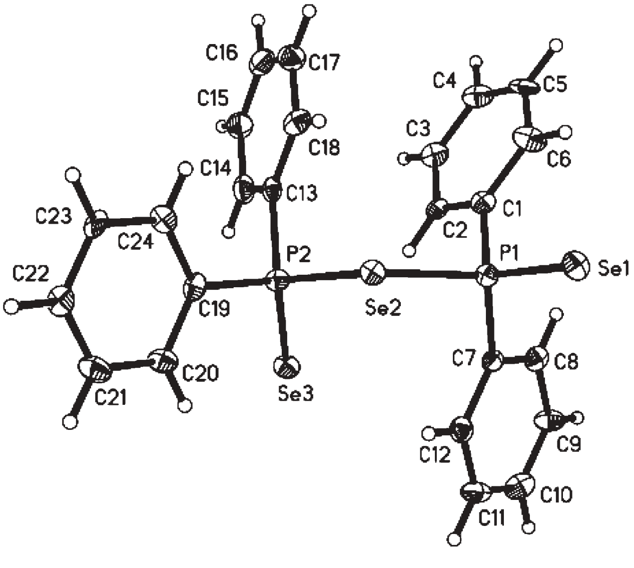

Fig. 3 Thermal ellipsoid plot (50% probability) of the structure of **3**. Selected bond distances (Å) and angles (°): Se(1)–P(1), 2.106(2); Se(2)–P(1), 2.263(2); Se(2)–P(2), 2.293(2); Se(3)–P(2), 2.105(2); P(1)–C(7), 1.802(8); P(1)–C(1), 1.806(8); P(2)–C(19), 1.821(8); P(2)–C(13), 1.825(8); P(1)–Se(2)–P(2), 109.01(8); C(7)–P(1)–C(1), 105.4(4); C(7)–P(1)–Se(1), 113.6(3); C(1)–P(1)–Se(1), 117.1(3); C(7)–P(1)–Se(2), 110.1(3); C(1)–P(1)–Se(2), 108.2(3); Se(1)–P(1)–Se(2), 102.28(9); C(19)–P(2)–C(13), 106.9(3); C(19)–P(2)–Se(3), 115.2(3); C(13)–P(2)–Se(3), 113.7(3); C(19)–P(2)–Se(2), 95.7(3); C(13)–P(2)–Se(2), 107.0(3); Se(3)–P(2)–Se(2), 116.51(1).

The structure of compound **3** is similar to the structure of **1** with the isopropyl groups on phosphorus replaced by phenyl groups. The bond distances between phosphorus and selenium are also similar to those observed in **1** and **2** but the geometry around phosphorus becomes highly distorted tetrahedral due to the steric hindrance of phenyl groups. The structure of **3** is shown in Fig. 3.

Preliminary results of the reactions of these ligands with different metals show interesting reactions depending on the metal *e.g.* breaking the bond between one phosphorus with the central Se to give the chelating (R_2PSe_2) in case of its reaction with molybdenum and forming a bridge through selenium atoms in its reaction with copper. The full investigation of these reactions with a series of metals is under way and is reported in the accompanying communication.[14]

The authors thank RCUK and the EPSRC for funding a Basic technology project. CQN would like to acknowledge the Government of Vietnam for funding.

Notes and references

† All the reactions were performed under a nitrogen atmosphere by using standard Schlenk techniques. All chemicals were bought from Aldrich Chemical Company Limited and used as received. Solvents were distilled prior to use. NMR spectra were obtained with chloroform-D6 solution using a Bruker AC300 FTNMR instrument. Elemental analysis was performed by the University of Manchester micro-analytical laboratory. Single crystal X-ray crystallography measurements were made using graphite monochromated Mo Kα radiation on a Bruker APEX diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares on F^2.[15] All calculations were carried out using the SHELXTL package.[16] All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were placed in calculated positions, assigned isotropic atoms. CCDC numbers 282911 (**1**), 291034 (**2**), 291035 (**3**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603197h

($^iPr_2PSe)_2Se$ (1). NEt_3 (30 mmol) was added to a stirring solution of $^iPr_2PCl$ (30 mmol) and $HSiCl_3$ (30 mmol) in cold toluene (60 mL). The solution was allowed to warm up to room temperature and was further stirred for 6 h, leading to the formation of a white cloudy precipitate. The precipitate was filtered off and the resulting colourless solution was refluxed with grey Se powder (45 mmol) for a further 20 h until all the Se dissolved to form a clear yellow solution. The solvent was removed under vacuum and the yellow powder product was washed with cold hexane. The product was then re-crystallized in toluene to obtain clear yellow crystals of **1** (2.90 g, yield 41.43%). Elemental analysis calcd (%) for $C_{12}H_{28}P_2Se_3$: C 30.59, H 5.99, P 13.15; found (%): C 31.10, H 6.09, P 13.02; ^1H NMR δ = 2.91 ppm (dq, 4H, CH, ^iPr, J = 7.2 Hz, J = 12.8 Hz), 1.33 ppm (ddd, 24H, CH_3, ^iPr, J =6.9 Hz, J = 20.9 Hz, J = 24.3 Hz).

($^iPr_2PSe)_2Se_2$ (2). Using a similar process as for **1** but with 60 mmol grey Se powder. After reflux for 20 h, all Se dissolved to form a clear dark orange solution. The solvent was removed under vacuum and the orange powder product was washed with cold hexane. The product was re-crystallized in toluene to obtain orange crystals of **2** (3.55 g, yield 43.03%). Elemental analysis calcd (%) for $C_{12}H_{28}P_2Se_4$: C 26.20, H 5.13, P 11.26; found (%): C 26.29, H 5.17, P11.31; ^1H NMR δ = 2.62 ppm (ddd, 4H, ^iPr, J = 6.6 Hz, J = 13.4 Hz, J = 26.9 Hz), 1.27 ppm (ddd, 24H, ^iPr, J = 6.8 Hz, J = 12.2 Hz, J = 21.8 Hz).

($Ph_2PSe)_2Se$ (3). Using a similar process as for **1** but using $(Ph)_2PCl$, yellow crystals of **3** were obtained (3.92 g, yield 43%). Elemental analysis calcd (%) for $C_{24}H_{20}P_2Se_3$: C 47.47, H 3.32, P 10.20; found (%): C 50.51, H 3.76, P10.59; ^1H NMR δ = 7.87 ppm (ddd, 8H, *o*-Ph, J = 7.6 Hz, J = 16.1 Hz, J = 22.9 Hz), 7.48 ppm (dd, 8H, *m*-Ph, J = 6.1 Hz, J = 30.2 Hz), 7.37 ppm (dd, 4H, *p*-Ph, J = 3.5 Hz, J = 7.7 Hz).

Crystal data for **1**: $C_{12}H_{28}P_2Se_3$, M_r = 471.16, triclinic, space group $P\bar{1}$, a = 7.324(3) Å, b = 10.189(5) Å, c = 12.669(6) Å, α = 101.544(8), β = 95.067(9), γ = 101.157(8), V = 900.7(7) Å^3, Z = 2, $\rho_{\text{calculated}}$ = 1.737 g cm^{-3}, μ = 6.285 mm^{-1}, T = 100(2) K. Crystal size 0.35 × 0.25 × 0.10 mm, λ = 0.71073 Å. Reflections collected/unique = 5048/3549 [R(int) = 0.0211], final R indices [$I > 2\sigma(I)$] $R1$ = 0.0428, w$R2$ = 0.1092.

Crystal data for **2**: $C_{12}H_{28}P_2Se_4$, $M_r = 550.12$, monoclinic, space group $C2/c$, $a = 20.905(8)$ Å, $b = 8.393(3)$ Å, $c = 11.592(4)$ Å, $\alpha = 90$, $\beta = 103.120(9)$, $\gamma = 90$, $V = 1980.8(12)$ Å^3, $Z = 4$, $\rho_{\text{calculated}} = 1.845$ g cm^{-3}, $\mu = 7.556$ mm^{-1}, $T = 100(2)$ K. Crystal size $0.20 \times 0.15 \times 0.08$ mm, $\lambda = 0.71073$ Å. Reflections collected/unique = 8158/2319 [R(int) = 0.0292], final R indices [$I > 2\sigma(I)$] $R1 = 0.0324$, w$R2 = 0.0669$.

Crystal data for **3**: $C_{24}H_{20}P_2Se_3$, $M_r = 607.22$, triclinic, space group $P\bar{1}$, $a = 9.279(3)$ Å, $b = 11.260(3)$ Å, $c = 13.075(4)$ Å, $\alpha = 106.562(5)$, $\beta = 100.360(5)$, $\gamma = 110.862(4)$, $V = 1161.6(5)$ Å^3, $Z = 2$, $\rho_{\text{calculated}} = 1.736$ g cm^{-3}, $\mu = 4.896$ mm^{-1}, $T = 100(2)$ K. Crystal size $0.20 \times 0.20 \times 0.08$ mm, $\lambda = 0.71073$ Å. Reflections collected/unique = 5822/4004 [R(int) = 0.0211], final R indices [$I > 2\sigma(I)$] $R1 = 0.0622$, w$R2 = 0.1369$.

1 W. Kuchen and H. Hertel, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 89.
2 W. Kuchen and B. Knop, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 244.
3 W. Kuchen, J. Metten and A. Judat, *Chem. Ber./Recl.*, 1964, **97**, 2306.
4 A. Müller, V. V. K. Rao and P. Christophliemk, *J. Inorg. Nucl. Chem.*, 1974, **36**, 472.
5 A. Müller, P. Christophliemk and V. V. K. Rao, *J. Inorg. Nucl. Chem.*, 1972, **34**, 345.
6 A. Müller, P. Christophliemk and V. V. K. Rao, *Chem. Ber.*, 1971, **104**, 1905.
7 M. J. Pilkington, A. M. Z. Slawin, D. J. Williams and J. D. Woollins, *Polyhedron*, 1991, **10**, 2641.
8 R. P. Davies, C. V. Francis, A. P. S. Jurd, M. G. Martinelli, A. J. P. White and D. J. Williams, *Inorg. Chem.*, 2004, **43**, 4802.
9 W. W. du Mont, R. Hensel, W. Mcfarlane, I. J. Colquhoun, M. L. Ziegler and O. Serhadli, *Chem. Ber.*, 1989, **122**, 37.
10 H. G. Horn and H. J. Lindner, *Chem.-Ztg.*, 1985, **109**, 77.
11 H. G. Horn and H. J. Lindner, *Chem.-Ztg.*, 1988, **112**, 195.
12 R. A. Benkeser, *Acc. Chem. Res.*, 1971, **4**, 94.
13 W. W. du Mont, L. P. Muller, L. Muller, S. Vollbrecht and A. Zanin, *J. Organomet. Chem.*, 1996, **521**, 417.
14 C. Q. Nguyen, A. Adeogun, M. Afzaal, M. A. Malik and P. O'Brian, *Chem. Commun.*, 2006, DOI: 10.1039/b603198f.
15 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997; G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997.
16 Bruker, *SHELXTL. Version 6.10*, Bruker AXS Inc., 2000.