



*Dedicated to the memory of  
Professor Ioan Silaghi-Dumitrescu (1950 – 2009)*

## NEW TRIARYLPHOSPHANE CHALCOGENIDES. CRYSTAL AND MOLECULAR STRUCTURE OF $[2(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_3\text{P}=\text{E}$ (E = S, Se) AND $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{PhP}=\text{S}$

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Triarylphosphane chalcogenides of type  $\text{R}_x\text{Ph}_{3-x}\text{P}=\text{E}$  [ $\text{R} = 2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4$ , E = S, x = 3 (**1**), 2 (**3**), E = Se, x = 3 (**2**), 2 (**4**), 1 (**5**)] were prepared by reacting the appropriate triarylphosphane with elemental selenium or sulfur in a 1:1 molar ratio. The solution behaviour of compounds **1** – **5** was investigated by multinuclear NMR spectroscopy ( $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$ ). The molecular structures of derivatives **1** – **3** were determined by single-crystal X-ray diffraction. All three compounds form monomeric units with P=E double bonds. No intramolecular N→P interactions were observed in these derivatives. The IR spectra confirm the formation of P=E double bonds in all five compounds.

### INTRODUCTION

Triarylphosphane chalcogenides have attracted much interest related to (i) the nature of the phosphorus–chalcogen bond,<sup>1-5</sup> (ii) their behaviour towards dihalogens,<sup>6-18</sup> and (iii) their ability to coordinate to metal centres.<sup>19-29</sup> Triorganophosphane chalcogenides were described either as a dipolar (**A**) or a covalent (**B**) species, or as a resonance hybrid to which both forms contribute to some extent.



However, the behaviour of tertiary phosphines towards chalcogens are strongly influenced both by the organic groups attached to phosphorus and the nature of the chalcogen. It was noted that bulky organic groups enhance the bond angles around phosphorus closer to tetrahedral values and determine a lengthening of the P=S bond. In the

mean time, increasing the electronegativity of the organic groups, the back donation  $d\pi - p\pi$  contribution increased as well and the P=S bond became shorter.<sup>1,2</sup>

It was previously observed that the reactivity of tertiary phosphine chalcogenides towards dihalogens, the stoichiometry of the obtained adducts, as well as their solution behaviour and solid state structure are dependent on the nature of the dihalogen, the basicity of the donor species and the reaction solvent.<sup>17</sup> Moreover, iodotriorganophosphane selenides were described as bifunctional donor (selenium) - acceptor (iodine) molecules in self-assembly aggregates.<sup>30</sup>

Few studies were developed in last years concerning metal complexes of triorganophosphane chalcogenides. However, some triorganophosphane tellurides of tungsten, gold, silver and copper were either investigated in solution or isolated as short living solid species and structurally characterized by single-crystal X-ray diffraction.<sup>19,27</sup> In the presence of Lewis acids or

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free phosphanes such metal complexes are kinetically labile and suffer decomposition, depositing chalcogen and forming a more stable triorganophosphane complex.

Few adducts of main group metals of type  $R_3P=E \cdot AlX_3$  ( $E = O, S, Se; X = Cl, Br$ )<sup>25,26,29</sup>  $R_3P=E \cdot SbX_3$  ( $E = O, S, Se; X = Cl, Br, I$ )<sup>31-35</sup> and  $R_3P=E \cdot SbCl_5$  ( $E = O, S, Se; X = Cl$ )<sup>36</sup> were also described.

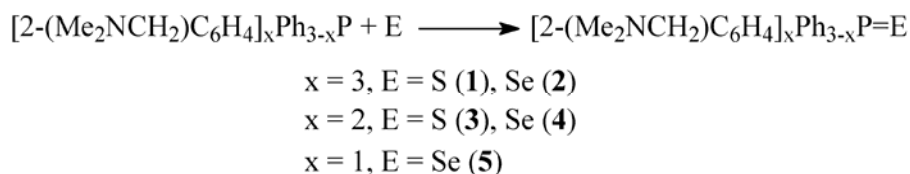
Such metal containing species are promising candidates as precursors for semiconductors or for metal chalcogenides obtained by CVD.<sup>21-24</sup>

Our interests were focused on the reactivity of triarylphosphane of type  $[2-(Me_2NCH_2)C_6H_4]_xPh_{3-x}P$  towards chalcogenes. Here we report on the

synthesis and spectroscopic characterization of the new triarylphosphane chalcogenides  $R_3P=E$  [ $E = S$  (**1**),  $Se$  (**2**)],  $R_2PhP=E$  [ $E = S$  (**3**),  $Se$  (**4**)] and  $RPh_2P=Se$  (**5**). The crystal and molecular structures of the triarylphosphane chalcogenides **1** – **3** are also described.

## RESULTS

The hypervalent triarylphosphane chalcogenides **1** – **5** were prepared by reacting elemental sulfur or selenium with the corresponding triarylphosphane in a 1:1 molar ratio, as depicted in Scheme 1.



Scheme 1

The reactions were performed in dry THF. The title compounds were isolated as crystalline, colorless (**1** – **4**) or beige solids (**5**). The formation of the triarylphosphanes **1** – **5** was confirmed by elemental analyses and multinuclear NMR spectroscopy ( $^1H$ ,  $^{13}C$  and  $^{31}P$ ).

The FT-IR spectra of derivatives **1** – **5** contain very strong absorption bands in the region  $540 - 640 \text{ cm}^{-1}$ , characteristic for the  $P=E$  ( $E = S, Se$ )

vibrations, similarly with the situation observed in other triorganophosphane chalcogenides.<sup>7</sup>

For compounds **1** – **3** single-crystals suitable for X-ray diffraction studies were grown by slow diffusion from a mixture of  $CH_2Cl_2$  and *n*-hexane (1:5, v/v). All compounds have monomeric structures. The ORTEP-like diagrams with the atom numbering schemes are given in Figures **1** – **3**, while selected interatomic distances and bond angles are given in Table 1.

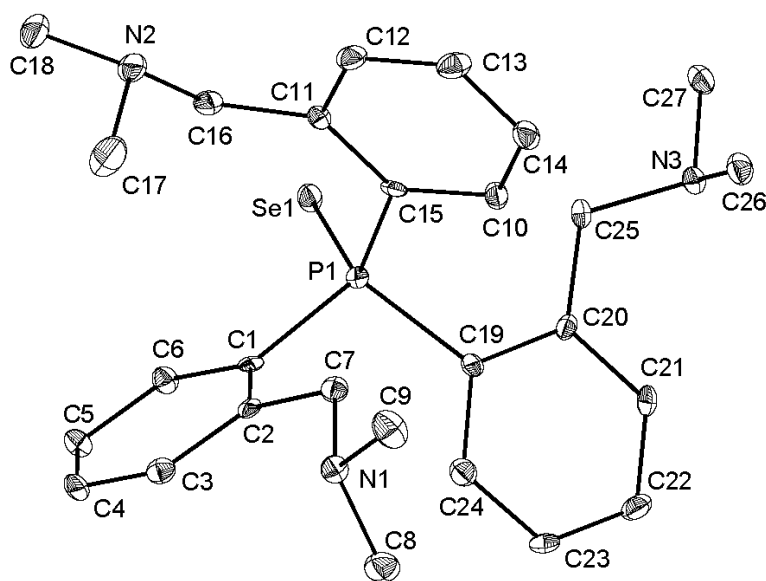


Fig. 1 – ORTEP plot diagram of compound **1**. The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

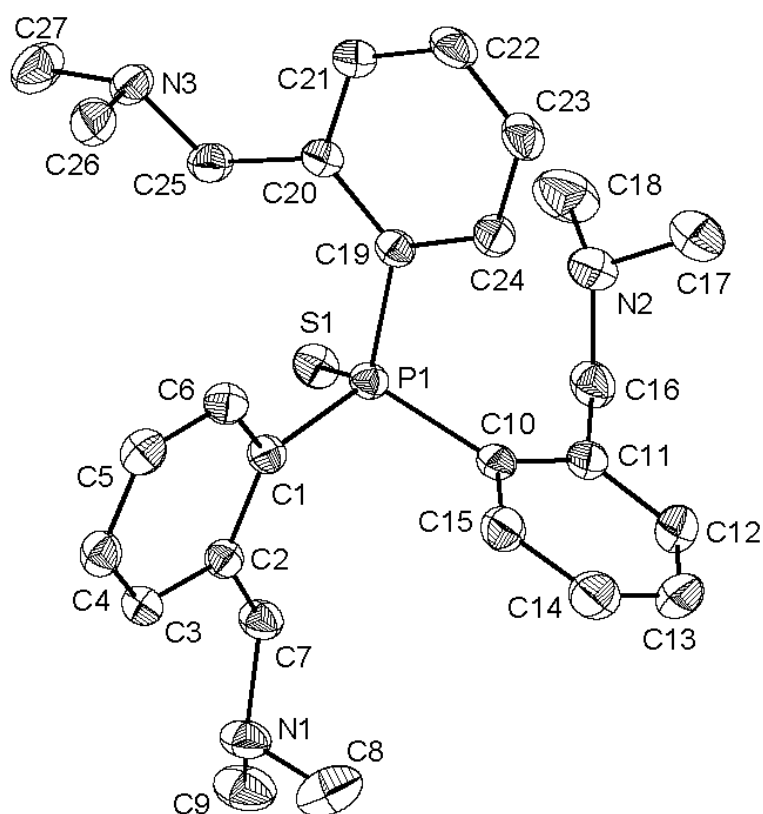


Fig. 2 – ORTEP plot diagram of compound 2.  
The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

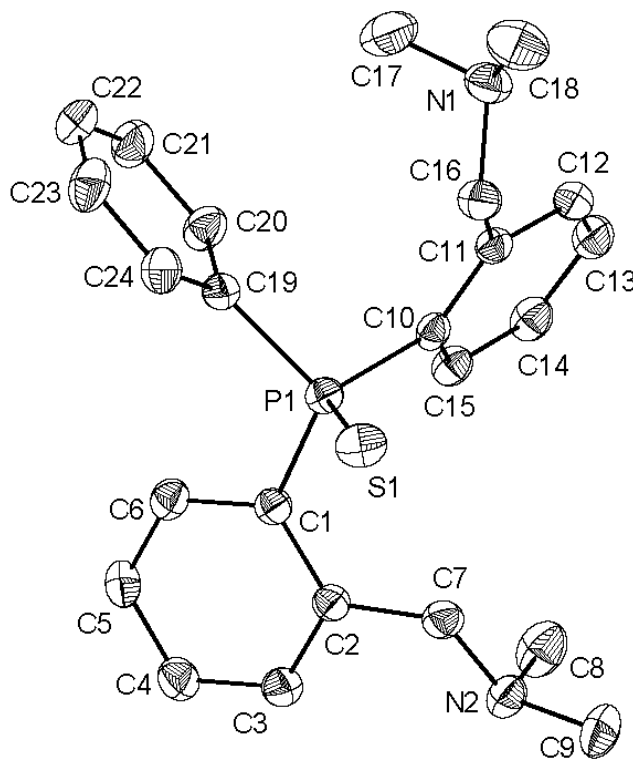


Fig. 3 – ORTEP plot diagram of compound 3.  
The atoms are drawn with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1

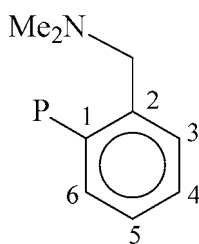
Relevant interatomic distance (Å) and angles (°) in [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>P=S (**1**), [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>P=Se (**2**) and [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>PhP=S (**3**)

	<b>1</b> <sup>a</sup>	<b>2</b> <sup>b</sup>	<b>3</b> <sup>a</sup>
P1–E1	1.962(2)	2.1177(14)	1.9547(10)
P1–C1	1.830(3)	1.846(5)	1.828(3)
P1–C10	1.835(3)	1.818(5)	1.834(3)
P1–C19	1.834(3)	1.837(5)	1.820(3)
C1–P1–E1	110.67(10)	112.17(15)	110.74(9)
C10–P1–E1	116.15(11)	114.09(17)	116.49(9)
C19–P1–E1	114.07(13)	111.25(17)	113.39(10)
C1–P1–C10	103.47(16)	105.6(2)	106.92(12)
C1–P1–C19	106.34(12)	106.0(2)	106.65(12)
C10–P1–C19	105.17(12)	107.2(2)	101.82(12)

<sup>a</sup> E = S, <sup>b</sup> E = Se

## DISCUSSION

The <sup>1</sup>H and <sup>13</sup>C NMR spectra are consistent with the organic groups attached to phosphorus. The assignment of the <sup>1</sup>H and <sup>13</sup>C resonances were made according to the numbering Scheme 2, using 2D (HMBC and HSQC) NMR experiments. The multiplicity of the resonances is determined by the proton – proton, phosphorus – proton and phosphorus – carbon couplings, respectively. As expected, the <sup>31</sup>P NMR resonances appear as singlets, significantly low field shifted in comparison with the starting triaryl phosphanes, due to oxidation to P(V).



Scheme 2

In compounds **1** – **5** at room temperature the NMe<sub>2</sub> groups display singlet resonances around 2.0 ppm. The CH<sub>2</sub> protons give a singlet resonance for compounds **1**, **2** and **5** and an AB spin system in case of derivatives **3** and **4**, due to the prochiral phosphorus atom in the last case. This behaviour suggests no intramolecular N→P interaction in solution, similarly to the solid state structures of compounds **1** – **3**. In compounds **1** – **4** the 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub> groups are equivalent in solution.

The single crystal X-ray diffraction studies revealed no nitrogen – phosphorus intramolecular

interactions in compounds **1** – **3**, in contrast with the situation described for the triarylphosphane [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>P for which three different crystalline species containing either two or three nitrogen – phosphorus intramolecular interactions are described.<sup>37</sup> Generally, all nitrogen – phosphorus or nitrogen – chalcogen distances are larger than the sum of the van der Waals radii for the respective atoms [ $\Sigma_{\text{vdw}}(\text{N,P}) = 3.44$ ,  $\Sigma_{\text{vdw}}(\text{N,S}) = 3.39$ ,  $\Sigma_{\text{vdw}}(\text{N,Se}) = 3.54$  Å<sup>43</sup>]. A distorted tetrahedral environment arose around the phosphorus centres and a *pseudo*-tetrahedral one around nitrogen. In compound **1** the N2 atom is brought much closer to phosphorus than the other two nitrogen atoms, [P1–N2 3.346(35), P1–N1 4.598(52), P1–N3 4.620(42) Å, vs.  $\Sigma_{\text{vdw}}(\text{NP})$  3.44 Å], but no intramolecular interaction can be considered, the *sp*<sup>3</sup> free electron pair of nitrogen being not directed towards the phosphorus atom. However, the N2–P1 distance in **1** is considerably shorter than all other nitrogen – phosphorus interatomic distances in the discussed derivatives (Table 1). The phosphorus – chalcogen interatomic distances are consistent with double P=E bonds in all compounds, *i.e.* P=S 1.962(2) in **1** and 1.955(1) in **3** and P=Se 2.118(1) Å in **2**, respectively, cf. Ph<sub>2</sub>P(=S)–N=P(–SMe)Ph<sub>2</sub>: P=S 1.954(1), P–S 2.071(1) Å<sup>38</sup> and (Se=PPh<sub>2</sub>)<sub>2</sub>NH: P=Se 2.085(1), 2.101(1) Å<sup>39</sup>. The calculated bond order for compounds **1** – **3**, using Pauling's formula:  $r(n) = r(1) - a \cdot \lg n$  where  $r(n)$  is the calculated single bond length,<sup>40</sup>  $r(1)$  the experimentally determined bond length,  $a = 0.665$  and  $n$  is the bond order,<sup>41</sup> gave a higher bonding order for the triorganophosphane sulfides (1.85 for **1** and 1.90 for **3**) in comparison with the selenide **2** (1.69).

## EXPERIMENTAL

The starting triarylphosphanes were prepared according to literature methods: [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>P,<sup>37</sup> [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>PhP,<sup>42,43</sup> [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>PhP.<sup>43,44</sup> Solvents were dried (CH<sub>2</sub>Cl<sub>2</sub> on CaCl<sub>2</sub>, THF on potassium and n-hexane on sodium) and distilled under argon prior to use. Elemental analysis were performed on a VarioEL analyzer. Melting points were measured on an Electrothermal 9200 apparatus and are not corrected. Infrared spectra were recorded on a Jasco FTIR machine, as KBr pellets. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded either on a BRUKER Avance 300, or a BRUKER Avance III/500 instrument. The chemical shifts are reported in δ units (ppm) relative to TMS (ref. CHCl<sub>3</sub>: <sup>1</sup>H 7.26 ppm, <sup>13</sup>C 77.00 ppm) and H<sub>3</sub>PO<sub>4</sub> 85%, respectively.

*Preparation of tris[2-(dimethylaminomethyl)phenyl]phosphane sulfide (1)*

Sulfur (0.074 g, 2.3 mmol) was added to a solution of [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>P (1 g, 2.3 mmol) in 20 ml anhydrous THF. The reaction mixture was stirred under reflux for 40 h and then filtered to remove traces of unreacted sulfur. The clear filtrate was evaporated under reduced pressure to obtain the title compound as a colorless solid. The compound was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/n-hexane. Yield: 0.67 g (62 %). M.p. 114–115 °C. Anal. calcd. for C<sub>27</sub>H<sub>36</sub>N<sub>3</sub>PS (M = 465.64): C 69.65, H 7.79, N 9.02, S 6.89 %; Found: C 69.78, H 7.43, N 9.12, S 6.41 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 2.07 (s, 18H, CH<sub>3</sub>), 3.62 (s, br., 6H, CH<sub>2</sub>), 7.22t (3H, H<sub>5</sub> C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz), 7.52m (6H, H<sub>4</sub> + H<sub>6</sub> C<sub>6</sub>H<sub>4</sub>), 7.93t (3H, H<sub>3</sub> C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.77 MHz): 45.12s (CH<sub>3</sub>), 61.84s (CH<sub>2</sub>), 126.44d (C<sub>5</sub>, <sup>3</sup>J<sub>PC</sub> 13 Hz), 129.71d (C<sub>1</sub>, <sup>1</sup>J<sub>PC</sub> 80.7 Hz), 129.76d (C<sub>3</sub>, <sup>3</sup>J<sub>PC</sub> 10 Hz), 131.93d (C<sub>4</sub>, <sup>4</sup>J<sub>PC</sub> 2.8 Hz), 133.27d (C<sub>6</sub>, <sup>2</sup>J<sub>PC</sub> 12.4 Hz), 143.98s (br., C<sub>2</sub>). <sup>31</sup>P (202.45 MHz): δ 41.4 (<sup>1</sup>J<sub>PC</sub> 80.4 Hz). FT-IR (cm<sup>-1</sup>): ν(P=S) 634vs.

Compounds **2** - **5** were prepared similarly:

*tris[2-(dimethylaminomethyl)phenyl]phosphane selenide (2)* from selenium powder (0.077 g, 0.97 mmol) and [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>P (0.422 g, 0.97 mmol). Yield: 0.42 g (84 %). M.p. 78 °C. Anal. calcd. for C<sub>27</sub>H<sub>36</sub>N<sub>3</sub>PSe (M = 512.54): C 63.27, H 7.08, N 8.20 %; Found: C 63.15, H 7.04, N 8.52 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): 2.04s (18H, CH<sub>3</sub>), 3.55s (br., 6H, CH<sub>2</sub>), 7.23t (3H, H<sub>5</sub> C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz), 7.51t (3H, H<sub>4</sub> C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz), 7.68m (br., 3H, H<sub>6</sub> C<sub>6</sub>H<sub>4</sub>), 7.91t (3H, H<sub>3</sub> C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> 6.4 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz): 45.2s (CH<sub>3</sub>), 62.13d (CH<sub>2</sub>, <sup>3</sup>J<sub>PC</sub> 4.35 Hz), 126.38d (C<sub>5</sub>, <sup>3</sup>J<sub>PC</sub> 13 Hz), 127.71d (C<sub>1</sub>, <sup>1</sup>J<sub>PC</sub> 72 Hz), 129.56d (C<sub>3</sub>, <sup>3</sup>J<sub>PC</sub> 10 Hz), 131.95d (C<sub>4</sub>, <sup>4</sup>J<sub>PC</sub> 3.0 Hz), 133.9d (br., C<sub>6</sub>, <sup>2</sup>J<sub>PC</sub> 10 Hz), 144.27d (C<sub>2</sub>, <sup>2</sup>J<sub>PC</sub> 7.8 Hz). <sup>31</sup>P (121.48 MHz): δ 26.4 (<sup>1</sup>J<sub>PC</sub> 71.5 Hz, <sup>1</sup>J<sub>PSe</sub> 707 Hz). FT-IR (cm<sup>-1</sup>): ν(P=Se) 567vs.

*bis[2-(dimethylaminomethyl)phenyl]phenylphosphane sulfide (3)* from sulfur (0.043 g, 1.33 mmol) and [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>PhP (0.50 g, 1.33 mmol). Yield: 0.34 g (63 %). M.p. 95 – 96 °C. Anal. calcd. for C<sub>24</sub>H<sub>29</sub>N<sub>2</sub>PS (M = 408.54): C 70.56, H 7.15, N 6.86, S 7.85 %; Found: C 70.63, H 7.04, N 6.84, S 7.44 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): 2.03s (12H, CH<sub>3</sub>), 3.80 AB spin system (4H, CH<sub>2</sub>, δ<sub>A</sub> 3.62, δ<sub>B</sub> 3.98, <sup>2</sup>J<sub>HH</sub> 15.3 Hz), 7.12t (2H, H<sub>5</sub> C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz), 7.38 – 7.58m (7H, H<sub>4</sub> C<sub>6</sub>H<sub>4</sub> + C<sub>6</sub>H<sub>5</sub>-ortho + meta + para), 7.85dd

(2H, H<sub>6</sub> C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> = 6.8, <sup>3</sup>J<sub>PH</sub> 13.4 Hz), 7.88t (2H, H<sub>3</sub> C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> 6.5 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz): 45.04s (CH<sub>3</sub>), 61.84s (br., CH<sub>2</sub>), 126.27d (C<sub>5</sub>, <sup>3</sup>J<sub>PC</sub> 12.6 Hz), 128.95d (C<sub>6</sub>H<sub>5</sub>-meta, <sup>3</sup>J<sub>PC</sub> 12.6 Hz), 130.27d (C<sub>3</sub>, <sup>3</sup>J<sub>PC</sub> 10.4 Hz), 131.24d (C<sub>4</sub>, <sup>4</sup>J<sub>PC</sub> 2.8 Hz), 131.62d (C<sub>6</sub>H<sub>5</sub>-para, <sup>4</sup>J<sub>PC</sub> 2.7 Hz), 132.50d (C<sub>6</sub>H<sub>5</sub>-ortho, <sup>2</sup>J<sub>PC</sub> 11.7 Hz), 132.67d (C<sub>6</sub>, <sup>2</sup>J<sub>PC</sub> 10.6 Hz), 132.70d (C<sub>6</sub>H<sub>5</sub>-ipso, <sup>1</sup>J<sub>PC</sub> 85.3 Hz), 132.40d (C<sub>1</sub>, <sup>1</sup>J<sub>PC</sub> 89.5 Hz), 144.28d (br., C<sub>2</sub>, <sup>2</sup>J<sub>PC</sub> 7.6 Hz). <sup>31</sup>P (121.48 MHz): δ 41.6 (<sup>1</sup>J<sub>PC</sub> 83.2 Hz). FT-IR (cm<sup>-1</sup>): ν(P=S) 622vs.

*bis[2-(dimethylaminomethyl)phenyl]phenylphosphane selenide (4)* from selenium (0.121 g, 1.53 mmol) and [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>PhP (0.578 g, 1.53 mmol). Yield: 0.54 g (77 %). M.p. 98 °C. Anal. calcd. for C<sub>24</sub>H<sub>29</sub>N<sub>2</sub>PSe (M = 455.44): C 63.29, H 6.42, N 6.15; Found: C 63.38, H 6.48, N 6.23 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): 1.97s (12H, CH<sub>3</sub>), 3.75 AB spin system (4H, CH<sub>2</sub>, δ<sub>A</sub> 3.70, δ<sub>B</sub> 3.80, <sup>2</sup>J<sub>HH</sub> 14.4 Hz), 6.92ddd (2H, H<sub>5</sub> C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> = 7.6, <sup>4</sup>J<sub>HH</sub> = 1.2, <sup>3</sup>J<sub>PH</sub> = 14.1 Hz), 7.13t (2H, H<sub>4</sub> C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz), 7.38 – 7.56m (7H, C<sub>6</sub>H<sub>5</sub>-ortho + meta + para + H<sub>6</sub> C<sub>6</sub>H<sub>4</sub>), 7.62dd (2H, H<sub>3</sub> C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> 7.5, <sup>4</sup>J<sub>PH</sub> 3.6 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz): 44.9s (CH<sub>3</sub>), 61.51d (CH<sub>2</sub>, <sup>3</sup>J<sub>PC</sub> = 4.31 Hz), 126.07d (C<sub>5</sub>, <sup>3</sup>J<sub>PC</sub> 13.2 Hz), 128.20d (C<sub>6</sub>H<sub>5</sub>-meta, <sup>3</sup>J<sub>PC</sub> 12.2 Hz), 129.97d (C<sub>3</sub>, <sup>3</sup>J<sub>PC</sub> 10.1 Hz), 131.11d (C<sub>1</sub>, <sup>1</sup>J<sub>PC</sub> 103.3 Hz), 131.38d (C<sub>4</sub>, <sup>4</sup>J<sub>PC</sub> 2.7 Hz), 131.70d (C<sub>6</sub>H<sub>5</sub>-ortho, <sup>2</sup>J<sub>PC</sub> 9.6 Hz), 131.84d (C<sub>6</sub>H<sub>5</sub>-para, <sup>4</sup>J<sub>PC</sub> 2.6 Hz), 132.87d (C<sub>6</sub>, <sup>2</sup>J<sub>PC</sub> 13.2 Hz), 133.38d (C<sub>6</sub>H<sub>5</sub>-ipso, <sup>1</sup>J<sub>PC</sub> 105 Hz), 144.57d (C<sub>6</sub>H<sub>4</sub>, <sup>2</sup>J<sub>PC</sub> 6.8 Hz). <sup>31</sup>P (121.48 MHz): δ 35.6 (<sup>1</sup>J<sub>PC</sub> 103.2 Hz). FT-IR (cm<sup>-1</sup>): ν(P=Se) 551vs, 544vs.

*[2-(dimethylaminomethyl)phenyl]diphenylphosphane selenide (5)* from selenium (0.139 g, 1.76 mmol) and [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Ph<sub>2</sub>P (0.561 g, 1.76 mmol). The crude product was obtained as a brown oil which was layered with n-hexane and kept at low temperature (-22 °C) for 10 days, when the title compound precipitated as a beige powder. Yield: 0.38 g (54 %). M.p. 78 °C. Anal. calcd. for C<sub>21</sub>H<sub>22</sub>NPSe (M = 398.35): C 63.32, H 5.57, N 3.52 %; Found: C 63.11, H 5.45, N 3.73 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): 2.11s (6H, CH<sub>3</sub>), 3.92s (2H, CH<sub>2</sub>), 6.99ddd (1H, H<sub>5</sub> C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> = 7.6, <sup>4</sup>J<sub>HH</sub> = 1.2, <sup>3</sup>J<sub>PH</sub> = 14.1 Hz), 7.18t (1H, H<sub>4</sub> C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz), 7.37 – 7.64m (11H, C<sub>6</sub>H<sub>5</sub>-ortho + meta + para + H<sub>6</sub> C<sub>6</sub>H<sub>4</sub>), 7.79dd (1H, H<sub>3</sub> C<sub>6</sub>H<sub>4</sub>, <sup>3</sup>J<sub>HH</sub> 7.5, <sup>4</sup>J<sub>PH</sub> 4.0 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz): 44.1s (CH<sub>3</sub>), 60.19d (CH<sub>2</sub>, <sup>3</sup>J<sub>PC</sub> = 4.5 Hz), 126.67d (C<sub>5</sub>, <sup>3</sup>J<sub>PC</sub> 12.9 Hz), 128.39d (C<sub>6</sub>H<sub>5</sub>-meta, <sup>3</sup>J<sub>PC</sub> 12.2 Hz), 130.78d (C<sub>1</sub>, <sup>1</sup>J<sub>PC</sub> 104.2 Hz), 130.85d (C<sub>6</sub>, <sup>3</sup>J<sub>PC</sub> 9.8 Hz), 131.57d (C<sub>6</sub>H<sub>5</sub>-ortho, <sup>2</sup>J<sub>PC</sub> 9.8 Hz), 131.66d (C<sub>6</sub>H<sub>5</sub>-para, <sup>4</sup>J<sub>PC</sub> 2.9 Hz), 132.28d (C<sup>4</sup>, <sup>4</sup>J<sub>PC</sub> 2.6 Hz), 132.85d (C<sub>6</sub>H<sub>5</sub>-ipso, <sup>1</sup>J<sub>PC</sub> 104.6 Hz), 133.51d (C<sub>3</sub>, <sup>3</sup>J<sub>PC</sub> 12.9 Hz), 142.87d (C<sub>2</sub>, <sup>2</sup>J<sub>PC</sub> 7.2 Hz). <sup>31</sup>P (121.48 MHz): δ 32.2 (<sup>1</sup>J<sub>PC</sub> 104 Hz). FT-IR (cm<sup>-1</sup>): ν(P=Se) 542vs.

*Crystal structure determination*

Block crystals of [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>P=S (**1**), [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>P=Se (**2**) and [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>PhP=Se (**3**), were attached with Paratone N oil on cryoloops. The data were collected at room temperature on a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The details of the crystal structure determination and refinement are given in Table 2.

Table 2

Crystal data and structure refinement for [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>P=S (**1**),  
[2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>P=Se (**2**) and [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>PhP=S (**3**)

	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	C <sub>27</sub> H <sub>36</sub> N <sub>3</sub> PS	C <sub>27</sub> H <sub>36</sub> N <sub>3</sub> PSe	C <sub>24</sub> H <sub>29</sub> N <sub>2</sub> PS
Formula weight	465.62	512.52	408.52
Temperature (K)	297(2)	297(2)	297(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> -1	<i>Cc</i>	<i>P</i> 2(1)2(1)2(1)
Unit cell dimensions			
<i>a</i> (Å)	9.257(2)	12.811(2)	9.6309(14)
<i>b</i> (Å)	9.715(3)	13.384(2)	15.194(2)
<i>c</i> (Å)	14.931(11)	16.011(3)	15.440(2)
$\alpha$ (°)	75.80(2)	90	90
$\beta$ (°)	85.74(2)	107.584(3)	90
$\gamma$ (°)	88.83(2)	90	90
Volume (Å <sup>3</sup> )	1298.1(11)	2617.0(7)	2259.4(6)
<i>Z</i>	2	4	4
Calculated density (g/cm <sup>3</sup> )	1.191	1.301	1.201
Absorption coefficient (mm <sup>-1</sup> )	0.206	1.515	0.226
<i>F</i> (000)	500	1072	872
Crystal size, mm	0.31 x 0.29 x 0.25	0.20 x 0.20 x 0.06	0.55 x 0.53 x 0.46
$\theta$ range for data collection (°)	2.16 to 25.00	2.26 to 25.01	2.49 to 25.00
Reflections collected	12191	8114	21798
Independent reflections	4510 [ <i>R</i> (int) = 0.0388]	4112 [ <i>R</i> (int) = 0.0558]	3983 [ <i>R</i> (int) = 0.0563]
Max. and min. transmissions	0.9504 and 0.9390	0.9146 and 0.7515	0.9033 and 0.8859
Refinement method		Full-matrix least-squares on <i>F</i> <sup>2</sup>	
Data / restraints / parameters	4510 / 0 / 295	4112 / 2 / 295	3983 / 0 / 257
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.120	0.937	1.153
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0563, <i>wR</i> 2 = 0.1192	<i>R</i> 1 = 0.0414, <i>wR</i> 2 = 0.0796	<i>R</i> 1 = 0.0461, <i>wR</i> 2 = 0.1095
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0721, <i>wR</i> 2 = 0.1265	<i>R</i> 1 = 0.0603, <i>wR</i> 2 = 0.0855	<i>R</i> 1 = 0.0486, <i>wR</i> 2 = 0.1110
Largest diff. peak and hole, eÅ <sup>-3</sup>	0.252 and -0.250	0.606 and -0.288	0.290 and -0.201

The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. The structures were solved and refined using the software package SHELX-97<sup>45</sup> and the drawings were created with the Diamond program.<sup>46</sup>

### Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre. CCDC 758902 - 758904 contains the supplementary crystallographic data for compounds **2**, **1** and **3**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)

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