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> LETTERS TO THE EDITOR

## Reaction of Secondary Phosphine Selenides with Elemental Selenium: Synthesis of Bis(diorganoselenophosphoryl)selenides

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It is known that secondary phosphine oxides are oxidized with oxygen to form phosphinic acids  $R_2P(O)OH$  [1]. Similarly proceeds the reaction of the secondary phosphine sulfides with elemental sulfur leading to dithiophosphinic acids  $R_2P(S)SH$  [2]. In the present work we first report on the reaction of the secondary phosphine selenides with elemental selenium. It turned out that the heating (80–85°C, 3 h) of bis(2-arylethyl)phosphine selenides (Ia, Ib) with one equivalent of elemental selenium in toluene does not result in the expected diselenophosphinic acids R<sub>2</sub>P(Se)SeH. Under these conditions, bis(diorganoselenophosphoryl)selenides (IIa, IIb) were obtained in 78 and 80% yield, respectively.



The reaction can be represented by the following scheme: secondary phosphine selenides I react with elemental selenium to form diselenophosphinic acids whose subsequent intermolecular condensation affords the target bis(diorganoselenophosphoryl)selenides **II**.



The synthesized compounds **II** are precursors of nanodimensional metal phosphides or selenides [3], promising ligands for preparation of metal complexes of the new type [4], potential extragents for heavy metals and reactive starting reagents for organoelemental synthesis. Conventional methods of their synthesis based on the use of difficultly available diorganochlorophosphines [5, 6], sodium polyselenides [6], or toxic and flammable trichlorosilane [5] are laborious, low effective (the yields do not exceed 43%) and do not match modern ecological requirements. Recently the synthesis of bis(diorganoselenophosphoryl)selenides from secondary phosphines and elemental selenium was published [7].

Therefore, the reaction of the secondary phosphine selenides with elemental selenium is performed for the first time and based on this reaction a new convenient and preparative method is elaborated for the preparation of bis(diorganoselenophosphoryl)selenides, promising ligands for the design of coordination compounds and precursors of the semiconducting and magnetooptical nanomaterials.

**Bis[di(2-phenylethyl)selenophosphoryl]selenide** (IIa). To the solution of bis(2-phenylethyl)phosphine selenide Ia (0.32 g, 1.0 mmol) in 8 ml of toluene

amorphous selenium (0.08 g, 1.0 mmol) was added at room temperature. The mixture was stirred at heating (80–85°C, 3 h), cooled, filtered, toluene was removed in a vacuum. The residue was ground in hexane (10 ml), hexane was decanted, the residue was dried in a vacuum (40-45°C, 2 h, 1 mm Hg) to obtain selenide **Ha**, 0.28 g (78%) as a yellow powder, mp 112–114°C (hexane). UV spectrum (acetonitrile),  $\lambda_{max}$ , nm: 289. IR spectrum (KBr), cm<sup>-1</sup>: 3059, 3023, 2917, 2890, 2855, 1949, 1878, 1805, 1640, 1599, 1492, 1447, 1389, 1329, 1269, 1211, 1133, 1019, 1006, 938, 901, 825, 743, 699, 571, 501, 454. <sup>1</sup>H NMR, δ, ppm (*J*, Hz): 2.61-2.69 m (4H, CH<sub>2</sub>P), 3.05-3.14 m (12H, CH<sub>2</sub>P, CH<sub>2</sub>Ph), 7.19–7.30 m (20H, Ph). <sup>13</sup>C NMR,  $\delta_{\rm C}$ , ppm: 29.53 (CH<sub>2</sub>Ph), 37.88 d (CH<sub>2</sub>P, <sup>1</sup> $J_{\rm CP}$  = 32.0 Hz), 126.32  $(C_p)$ , 128.04  $(C_o)$ , 128.40  $(C_m)$ , 139.09 d  $(C_i, {}^{3}J_{CP} =$ 18.0 Hz). <sup>31</sup>P NMR,  $\delta_{P}$ , ppm: 56.04 (satellites:  ${}^{1}J_{P-Se} =$ 378.5 Hz,  ${}^{1}J_{P=Se} = 749.2$  Hz,  ${}^{2}J_{PP} = 19.1$  Hz).  ${}^{77}Se$ NMR,  $\delta_{se}$ , ppm: -140 d (P=Se,  ${}^{1}J_{P=Se} = 749.1$  Hz), 284 t (P–Se–P,  ${}^{1}J_{P-Se} = 378.4$  Hz). Found, %: C 53.39; H 5.09; P 8.55; Se 32.85. C<sub>32</sub>H<sub>36</sub>P<sub>2</sub>Se<sub>3</sub>. Calculated, %: C 53.42; H 5.04; P 8.61; Se 32.92.

Bis[di{2-(4-tert-butylphenyl)ethyl}selenophosphoryl]selenide (IIb) was prepared similarly from bis-[2-(4-*tert*-butylphenyl)ethyl]phosphine selenide **Ib**. Yield 0.38 g (80%), yellow powder, mp 195–197°C (hexane). UV spectrum (acetonitrile),  $\lambda_{max}$ , nm: 287. IR spectrum (KBr), cm<sup>-1</sup>: 3093, 3055, 3022, 2959, 2902, 2864, 1902, 1791, 1685, 1634, 1607, 1517, 1475, 1462, 1443, 1413, 1391, 1363, 1268, 1201, 1135, 1108, 1019, 942, 927, 852, 837, 813, 769, 740, 728, 669, 563, 519, 485, 429. <sup>1</sup>H NMR, δ, ppm (*J*, Hz): 1.27 s (36H, Me), 2.55–2.64 m (4H, CH<sub>2</sub>P), 2.96–3.09 m (12H, CH<sub>2</sub>P, CH<sub>2</sub>Ar), 7.11–7.29 m (16H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR, δ<sub>C</sub>, ppm: 29.02 (CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 30.96 (Me<sub>3</sub>C), 34.04 (CMe<sub>3</sub>), 37.89 d (CH<sub>2</sub>P,  ${}^{1}J_{CP}$  = 31.9 Hz), 125.27 (C-2 in C<sub>6</sub>H<sub>4</sub>), 127.75 (C-3 in C<sub>6</sub>H<sub>4</sub>), 136.02 d (C-1 in C<sub>6</sub>H<sub>4</sub>,  ${}^{3}J_{CP} = 16.5$  Hz), 149.24 (C-4 in C<sub>6</sub>H<sub>4</sub>).  ${}^{31}P$  NMR,  $\delta_{P}$ , ppm: 56.13 (satellites:  ${}^{1}J_{P-Se} = 377.1 \text{ Hz}$ ,  ${}^{1}J_{P=Se} = 744.8 \text{ Hz}$ ,  ${}^{2}J_{PP} = 17.6 \text{ Hz}$ ).  ${}^{77}\text{Se}$  NMR,  $\delta_{Se}$ , ppm: -139 d  $(P=Se, {}^{1}J_{P=Se} = 744.5 \text{ Hz}), 284 \text{ t} (PSeP, {}^{1}J_{PSe} = 377.6 \text{ Hz}).$ Found, %: C 61.12; H 7.22; P 6.50; Se 25.20.

C<sub>48</sub>H<sub>68</sub>P<sub>2</sub>Se<sub>3</sub>. Calculated, %: C 61.08; H 7.26; P 6.56; Se 25.10.

IR spectra were recorded on a Bruker IFS-25 spectrometer, UV spectra, on a UV/VIS Perkin Elmer Lamda 35 spectrometer. <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>77</sup>Se NMR spectra were obtained on a Bruker DPX-400 spectrometer (400.13, 101.61, 161.98 and 76.31 MHz, respectively) in CDCl<sub>3</sub>, external standards 85% H<sub>3</sub>PO<sub>4</sub> (for <sup>31</sup>P) and Me<sub>2</sub>Se (for <sup>77</sup>Se). All experiments were run in an inert atmosphere (argon). Secondary phosphine selenides **Ia**, **Ib** were prepared from red phosphorus, elemental selenium, and styrene [8] or 4*tert*-butylstyrene [9] respectively.

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