One-Pot Reaction of Secondary Phosphine Selenides with Selenium and Nitrogen Bases: A Novel Synthesis of Diorganodiselenophosphinates

Boris A. Trofimov,*[a] Alexander V. Artem'ev,[a] Nina K. Gusarova,[a] Svetlana F. Malysheva,[a] Sergei V. Fedorov,[a] Olga N. Kazheva,[b] Grigorii G. Alexandrov,[b] Oleg A. Dyachenko[b]

[a] A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, 1 Favorsky Str., 664033 Irkutsk, Russian Federation
Fax +7(3952)419346; E-mail: boris_trofimov@irioch.irk.ru

[b] Institute of Problems of Chemical Physics, Russian Academy of Sciences, 1 Academician N. N. Semenov Str., 142432 Chernogolovka, Russian Federation

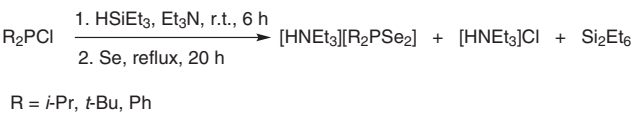
Received 15 May 2009; revised 21 May 2009

Abstract: A three-component reaction of secondary phosphine selenides $R_2P(Se)H$ [R = $PhCH_2CH_2$, $PhCH(Me)CH_2$, 4-*t*-$BuC_6H_4CH_2CH_2$, (2-methyl-5-pyridyl)CH_2CH_2, Ph], elemental selenium, and primary, secondary, and tertiary amines and diamines proceeds under mild conditions (25–85 °C, 1–90 min) in tetrahydrofuran–ethanol as medium to give previously unknown mono-, di-, and triorganoammonium salts of diorganodiselenophosphinates in high yields (up to 99%).

Key words: secondary phosphine selenides, elemental selenium, amines, three-component atom-economic reactions, diselenophosphinates, phosphorus compounds

In the last few years, salts of diselenophosphinic acids, convenient 'single-source' precursors (SSPs) for the preparation of nanostructured semiconductors and nanomaterials possessing unique magneto-optical properties,[1–3] have attracted ever-increasing interest amongst researchers. For example, europium(III) diphenyldiselenophosphinate [$Eu(Ph_2PSe_2)_3$], generated in situ, was used for the synthesis of europium selenide [$Eu_{1-x}Se$], a starting block for the design of novel magneto-optical nanomaterials.[3e] Nanorods (2D nanoparticulars) of zinc(II) selenide (ZnSe), exhibiting semiconductive properties were synthesized[2] from zinc(II) diisopropyldiselenophosphinate [$Zn(i\text{-}Pr_2PSe_2)_2$]. Moreover, diselenophosphinates can be used as ligands for metal complexes,[4] are promising extractants of heavy, rare, and transuranium elements,[5] have potential biological activity as antimicrobial and antifungal agents,[6] and can also be used as building blocks for organic and elementoorganic synthesis.[7] For instance, esters of diselenophosphinic acids [$R^1{}_2P(Se)SeR^2$] can act as efficient initiaters (RAFT agents) in pseudoliving radical polymerization.[8] One might expect that diselenophosphinates of nitrogen bases will also possess the features typical for ammonium compounds, including those applied in pharmaceutics[9] as well as protonic ionic liquids (PILs).[10]

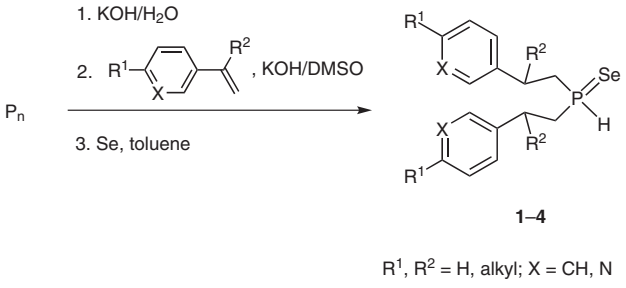
However, to the best of our knowledge, only three representatives of diselenophosphinates containing an ammonium fragment have been reported: triethylammonium diisopropyldiselenophosphinate, triethylammonium di-*tert*-butyldiselenophosphinate, and triethylammonium diphenyldiselenophosphinate. These compounds were prepared by multistep reactions of toxic and unavailable monochlorophosphines (R_2PCl) with triethylsilane, triethylamine, and selenium in toluene, and involve long periods of boiling (Scheme 1).[2]



Scheme 1 Synthesis of triethylammonium diselenophosphinates

The known procedure allows only the preparation of triethylammonium salts. In addition, the method is laborious, and requires an argon atmosphere in Schlenk equipment and especially pure anhydrous solvents. Along with the target compounds the reaction results in the formation of some byproducts.[2]

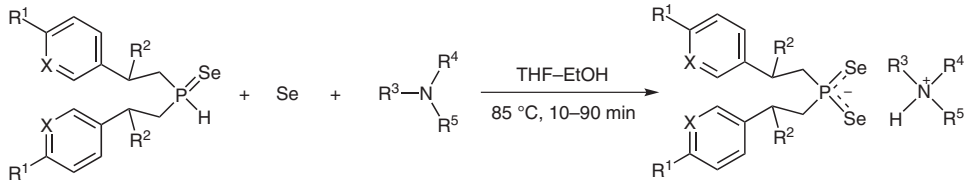
Herein, we report a novel general and simple approach to the atom-economic synthesis of various diorganodiselenophosphinates of nitrogen bases. To reach this goal, we have studied for the first time the three-component reaction of secondary phosphine selenides with elemental selenium and primary, secondary, and tertiary amines and diamines of different natures. The starting secondary phosphine selenides are now available, since they are easily prepared from red phosphorus, aryl(or hetaryl)ethenes, and elemental selenium[11] (Scheme 2).



Scheme 2 Synthesis of secondary phosphine selenides

SYNTHESIS 2009, No. 19, pp 3332–3338
Advanced online publication: 21.08.2009
DOI: 10.1055/s-0029-1216948; Art ID: Z10009SS

Table 1 Synthesis of Diorganodiselenophosphinates from Secondary Phosphine Selenides, Elemental Selenium, and Amines[a]



1–4 **5–12** **13a–j**

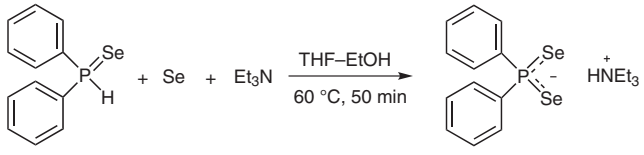
Entry	Phosphine selenide **1–4**	R^1	R^2	X	Amine **5–12**	R^3	R^4	R^5	Time (min)	Salt **13**	Yield[b] (%)
1	**1**	H	H	CH	**5**	Et	Et	Et	60	**13a**	94
2	**1**	H	H	CH	**6**	*n*-Bu	*n*-Bu	*n*-Bu	50	**13b**	95
3	**1**	H	H	CH	**7**	allyl	allyl	allyl	90	**13c**	90
4	**1**	H	H	CH	**8**	$(CH_2)_2OH$	$(CH_2)_2OH$	$(CH_2)_2OH$	60	**13d**	79
5	**1**	H	H	CH	**9**	*n*-Pr	*n*-Pr	H	10	**13e**	93
6	**1**	H	H	CH	**10**	Cy	H	H	10	**13f**	98
7	**1**	H	H	CH	**11**	allyl	H	H	15	**13g**	91
8	**2**	*t*-Bu	H	CH	**5**	Et	Et	Et	60	**13h**	86
9	**3**	Me	H	N	**9**	*n*-Pr	*n*-Pr	H	15	**13i**	87
10	**4**	H	Me	CH	**12**	*i*-Pr	*i*-Pr	H	15	**13j**	95

[a] Reagents and conditions: phosphine selenide **1–4** (1 mmol), Se (1 mmol), amine **5–12** (1.3 mmol), THF–EtOH, 85 °C.
[b] All yields refer to isolated products.

As our experiments have shown, secondary phosphine selenides **1–4** react with elemental selenium and amines **5–12** under mild conditions (85 °C, 10–90 min) in tetrahydrofuran–ethanol to afford new diorganodiselenophosphinates **13a–j** in high yields (79–98%) (Table 1).

As can be seen from Table 1, secondary phosphine selenides with aryl(or hetaryl)alkyl substituents as well as primary, secondary, and tertiary amines, including unsaturated and functionalized tertiary amines, participate readily in this three-component reaction.

Aromatic secondary phosphine selenides can also be used in this reaction. For example, diphenylphosphine selenide (**14**) easily (THF–EtOH, 60 °C, 50 min) reacted with the selenium/triethylamine system to furnish triethylammonium diphenyldiselenophosphinate (**13k**) in 88% yield (Scheme 3).



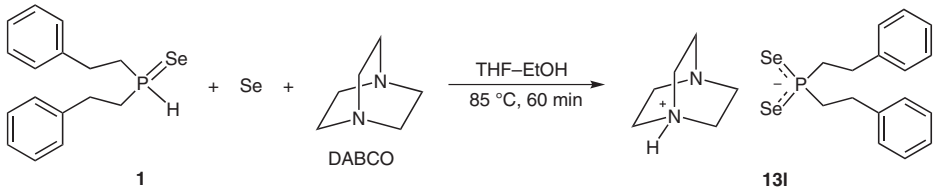
14 **13k**

Scheme 3 Synthesis of triethylammonium diphenyldiselenophosphinate (**13k**)

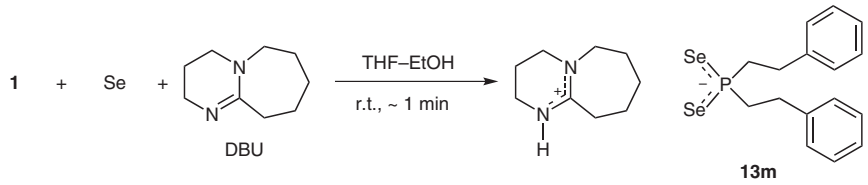
Previously, salt **13k** was synthesized by a multistep protocol from expensive reactants of limited availability[2] (see also Scheme 1). To synthesize salts of diselenophosphinic acid containing functional nitrogen bases (biologically active compounds and semiproducts for fine organic synthesis) directly, we carried out the reactions of secondary phosphine selenide **1** and elemental selenium with available bicyclic amines 1,4-diazabicyclo[2.2.2]octane (DABCO) (Scheme 4) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Scheme 5). Bicyclic diamine 1,4-diazabicyclo[2.2.2]octane reacts with one equivalent of secondary phosphine selenide **1** and elemental selenium at 85 °C for 60 minutes in the solvent system tetrahydrofuran–ethanol to give salt **13l** in 84% yield (Scheme 4).

The presence of the nonquaternized nitrogen atom in salt **13l** provides additional synthetic possibilities for further functionalization. In particular, this salt is a promising intermediate for the design of polycationic catalysts for the cleavage of phosphodiether bonds in RNA.[12]

The reaction of phosphine selenide **1** and elemental selenium with bicyclic amidine 1,8-diazabicyclo[5.4.0]undec-7-ene proceeds at 25 °C and is completed unusually fast (ca. 1 min), probably due to the high affinity of 1,8-diazabicyclo[5.4.0]undec-7-ene for the proton (Scheme 5). The reaction results in the quantitative formation of diselenophosphinate **13m** (99% yield) – a valuable high-temperature (mp 101–102 °C) proton ionic liquid.[10]

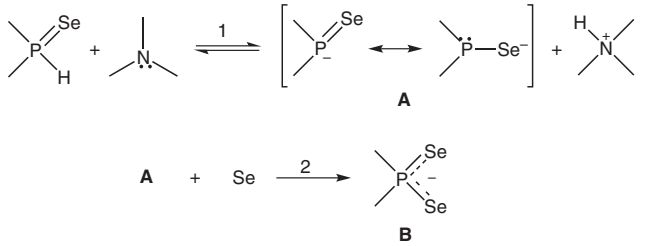


Scheme 4 Synthesis of diselenophosphinate **13l**



Scheme 5 Synthesis of diselenophosphinate **13m**

The mechanism of the formation of diselenophosphinates can be presented as follows (Scheme 6). In the first stage (1), the secondary phosphine selenide is deprotonated by the nitrogen base to afford *P*,*Se*-ambident selenophosphinite anion **A**, which further reacts with elemental selenium to provide the diselenophosphinate anion **B** (stage 2).



Scheme 6

The synthesized salts **13a**–**m** are colorless crystalline solids (except for **13d**, an oil), stable in air, poorly soluble in water (except for **13d** and **13i**), and with good solubility in organic solvents (EtOH, acetone, THF, $CHCl_3$, DMSO). The structures of compounds **13a**–**m** were proved by multinuclear (^{1}H, ^{13}C, ^{31}P, and ^{77}Se) NMR and IR spectroscopy, and the compositions were confirmed by elemental analysis.

Equivalency of the selenium atoms in salts **13a**–**m** follows from ^{31}P and ^{77}Se NMR data. For example, in the ^{77}Se NMR spectra, a doublet ($^1J_{SeP}$ = 550–613 Hz) is present; in the ^{31}P NMR spectra, a singlet with one typical satellite pair is observed ($^1J_{SeP}$ = 550–613 Hz). The $^1J_{SeP}$ value (550–613 Hz) is intermediate between the coupling constant values for P–Se and P=Se moieties (200–600 and 800–1200 Hz, respectively), thus corresponding to an order of 1.5 for the phosphorus–selenium bonds. In the ^{1}H NMR spectra, hydrogen atoms of ammonium N^+–H bonds appear as broad singlets in the region of δ = 7.93–10.38.

The IR spectra of the compounds synthesized contain a strong band at 470–490 cm^{-1}, corresponding to stretching symmetric vibrations (ν_s) of the PSe_2 group. Asymmetric stretching vibrations (ν_{as}) of this group are observed in the region of 540–570 cm^{-1}.

In addition, the structure of compound **13l** was established by X-ray crystallographic analysis. The molecular structure of salt **13l** consists of an anion of the bis(2-phenethyl)diselenophosphinic acid and a cation of diazobicyclooctane (Figure 1). The distances Se(1)–P [2.133(2) Å] and Se(2)–P [2.167(2) Å] are comparable to those (2.14–2.17 Å) in similar ionic compounds with P–Se end bonds.[2]

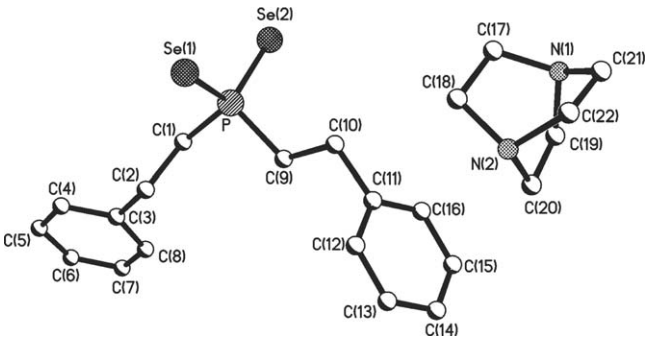


Figure 1 Molecular structure of compound **13l**

In conclusion, a three-component reaction between secondary phosphine selenides, elemental selenium, and nitrogen bases, cleanly affording the corresponding salts of diselenophosphinic acids in high yields, has been developed. The generality and preparative efficiency of the method was demonstrated by the synthesis of a series of previously unknown mono-, di-, and triorganoammonium salts of disilenophosphinic acids bearing arylalkyl and aryl substituents. The salts prepared are promising intermediates to produce conducting nanomaterials and SSPs in metalorganic vapor deposition to manufacture semiconducting thin films and protonic ionic liquids, precursors for the design of bioactive agents, as well as building blocks for the design of diverse phosphorus–selenium organic compounds.

All experimental steps were carried out under an anhyd inert atmosphere (argon). The solvents were purified and dried by standard methods.[13] All commercially available reagents were used as received. The secondary phosphine selenides **1**–**4** were prepared from styrenes or vinylpyridine, red phosphorus, and elemental selenium as described in the literature.[11] Diphenylphosphine selenide (**14**) was prepared by oxidation of commercially available diphenylphosphine (Aldrich, 2008) with elemental selenium. The ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra were recorded on a Bruker DPX 400 and Bruker AV-400 spectrometer (400.13, 100.61, 161.98, and 76.31 MHz, respectively); samples were prepared as $CDCl_3$ or D_2O solns and spectra were referenced to HMDS (^{1}H NMR, ^{13}C NMR), H_3PO_4 (^{31}P NMR), and Me_2Se (^{77}Se NMR). IR spectra were run on a Bruker IFS 25 instrument. Melting points were measured on a Kofler micro hot-stage apparatus.

X-ray Crystallography of 13l

The X-ray diffraction study of **13l** was carried out at 123 K on a Bruker SMART APEX2 CCD diffractometer, using Mo-Kα radiation. The crystal structure was solved by direct methods followed by Fourier synthesis using SHELXS-97.[14] The structure was refined using an anisotropic full-matrix approximation for all non-hydrogen atoms with SHELXL-97.[14] The coordinates of the hydrogen atoms were calculated from geometrical positions.

Crystal data and structural refinement for **13l**: $C_{22}H_{31}N_2PSe_2$, $M = 512.38$, $T = 123$ K, monoclinic, $P2_1/c$, $a = 18.878(2)$ Å, $b = 6.614(1)$ Å, $c = 19.350(3)$ Å, $b = 111.364(4)°$, $U = 2250.0(5)$ Å^3, Z = 4, $D_{calc} = 1.51$ g·cm^{-3}, $\mu = 3.367$ mm^{-1}, $(2\theta)_{max} = 50.70°$, 10735 reflections measured, 4034 independent reflections, 244 parameters refined, $R = 0.070$ for 2029 reflections with $[F_0 > 4\sigma(F_0)]$. CCDC 725047 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Diselenophosphinates 13a–j; General Procedure (Table 1)

The amorphous gray selenium (0.049 g, 0.623 mmol) was added to a soln of the secondary phosphine selenide **1**–**4** (0.623 mmol) in THF (4 mL) at 85 °C under argon. The appropriate nitrogen base (0.810 mmol) in EtOH (5 mL) was added to the stirred suspension. The suspension was heated until full dissolution of selenium (10–90 min, see Table 1); this gave a colorless, transparent soln. The solvents were removed under reduced pressure and the residue was washed with Et_2O (7 mL) and dried in vacuo (1 Torr, r.t.); this gave the corresponding salts **13a**–**j**.

Triethylammonium Bis(2-phenethyl)diselenophosphinate (13a)

Yield: 0.29 g (94%); colorless solid; mp 91–92 °C.

IR (KBr): 3061, 3028, 2977, 2928, 2754, 2651, 2485, 1601, 1494, 1467, 1454, 1397, 1360, 1308, 1209, 1190, 1176, 1156, 1136, 1122, 1058, 1033, 1009, 951, 935, 919, 833, 807, 790, 770, 759, 733, 707, 620, 575, 495, 479 cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.42 (t, $^3J_{HH}$ = 7.0 Hz, 9 H, CH_3), 2.54–2.61 (m, 4 H, CH_2P), 3.11–3.17 (m, 4 H, $PhCH_2$), 3.31–3.36 (m, 6 H, CH_2N), 7.17–7.27 (m, 10 H, Ph), 8.86 (s, 1 H, HN).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 8.48 (CH_3), 30.86 (CH_2Ph), 44.22 (d, $^1J_{PC}$ = 36.4 Hz, CH_2P), 45.83 (CH_2N), 125.69 (*p*-C), 128.24 (*o*-C), 128.36 (*m*-C), 141.87 (d, $^3J_{PC}$ = 17.6 Hz, *ipso*-C).

^{31}P NMR (161.98 Hz, $CDCl_3$): δ = 24.84 (s) (+d satellite, $^1J_{PSe}$ = 575.0 Hz).

^{77}Se NMR (76.31 Hz, $CDCl_3$): δ = –48.46 (d, $^1J_{PSe}$ = 575.0 Hz).

Anal. Calcd for $C_{22}H_{34}NPSe_2$: C, 52.70; H, 6.83; N, 2.79; P, 6.18; Se, 31.50. Found: C, 52.73; H, 6.52; N, 2.70; P, 6.03; Se, 31.41.

Tri-*n*-butylammonium Bis(2-phenethyl)diselenophosphinate (13b)

Yield: 0.35 g (95%); colorless solid; mp 84–85 °C.

IR (KBr): 3105, 3084, 3059, 3024, 2958, 2931, 2872, 2620, 2521, 1642, 1602, 1582, 1496, 1466, 1454, 1398, 1376, 1310, 1266, 1233, 1205, 1193, 1131, 1102, 1066, 1031, 1018, 961, 945, 926, 910, 852, 832, 801, 759, 745, 707, 698, 577, 568, 504, 492, 477, 432, 399 cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 0.96 (t, $^3J_{HH}$ = 7.4 Hz, 9 H, CH_3), 1.36–1.45 (m, 6 H, CH_2Me), 1.73–1.81 (m, 6 H, CH_2Et), 2.51–2.58 (m, 4 H, CH_2P), 3.10–3.17 (m, 10 H, CH_2Ph, CH_2N), 7.13–7.27 (m, 10 H, Ph), 8.74 (s, 1 H, NH).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.67 (Me), 20.04 (CH_2Me), 25.19 (CH_2Et), 30.80 (CH_2Ph), 44.36 (d, $^1J_{PC}$ = 35.6 Hz, CH_2P), 51.87 (CH_2N), 125.71 (*p*-C), 127.61 (*o*-C), 128.32 (*m*-C), 142.49 (d, $^3J_{PC}$ = 17.5 Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 24.46 (s) (+d satellite, $^1J_{PSe}$ = 573.3 Hz).

^{77}Se NMR (76.31 Hz, $CDCl_3$): δ = –45.60 (d, $^1J_{PSe}$ = 573.3 Hz).

Anal. Calcd for $C_{28}H_{46}NPSe_2$: C, 57.43; H, 7.92; N, 2.39; P, 5.29; Se, 26.97. Found: C, 57.44; H, 7.95; N, 2.33; P, 5.35; Se, 27.01.

Triallylammonium Bis(2-phenethyl)diselenophosphinate (13c)

Yield: 0.30 g (90%); yellowish solid; mp 90–92 °C.

IR (KBr): 3078, 3055, 3018, 2972, 2911, 2790, 2741, 2702, 2644, 2524, 1953, 1878, 1643, 1598, 1491, 1445, 1327, 1286, 1256, 1234, 1209, 1176, 1146, 1118, 1073, 1048, 1004, 992, 975, 953, 934, 906, 879, 827, 756, 712, 696, 599, 563, 512, 490, 469, 416 cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.56–2.63 (m, 4 H, CH_2P), 3.12–3.19 (m, 4 H, $PhCH_2$), 3.93 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, CH_2N), 5.52 (d, $^3J_{HH}$ = 17.1 Hz, 3 H, $=CH_2$), 5.57 (d, $^3J_{HH}$ = 10.3 Hz, 3 H, $=CH_2$), 6.15–6.26 (m, 3 H, =CH), 7.18–7.28 (m, 10 H, Ph), 10.31 (s, 1 H, HN).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 30.61 (CH_2Ph), 43.83 (d, $^1J_{PC}$ = 34.9 Hz, CH_2P), 53.93 (CH_2N), 125.49 (*p*-C, $=CH_2$), 125. 85 (=CH), 128.02 (*o*-C), 128.14 (*m*-C), 141.55 (d, $^3J_{PC}$ = 17.2 Hz, *ipso*-C).

^{31}P NMR (161.98 Hz, $CDCl_3$): δ = 24.57 (s) (+d satellite, $^1J_{PSe}$ = 576.1 Hz).

^{77}Se NMR (76.31 Hz, $CDCl_3$): δ = –43.91 (d, $^1J_{PSe}$ = 576.1 Hz).

Anal. Calcd for $C_{25}H_{34}NPSe_2$: C, 55.87; H, 6.38; N, 2.61; P, 5.76; Se, 29.38. Found: C, 56.15; H, 6.38; N, 2.87; P, 5.60; Se, 29.45.

Tris(2-hydroxyethyl)ammonium Bis(2-phenethyl)diselenophosphinate (13d)

Yield: 0.27 g (79%); colorless oil.

IR (film): 3289, 3061, 3025, 2999, 2930, 2893, 1955, 1880, 1813, 1661, 1602, 1582, 1495, 1453, 1398, 1321, 1261, 1207, 1155, 1094, 1067, 1029, 1007, 945, 912, 846, 752, 699, 574, 508, 480, 415, 397 cm^{-1}.

^{1}H NMR (400.13 MHz, D_2O): δ = 2.31–2.37 (m, 4 H, CH_2P), 2.81–2.87 (m, 4 H, CH_2Ph), 3.29 (t, $^3J_{HH}$ = 4.8 Hz, 6 H, CH_2N), 3.85 (t, $^3J_{HH}$ = 4.8 Hz, 6 H, CH_2O), 6.99–7.14 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, D_2O): δ = 30.78 (CH_2Ph), 43.01 (d, $^1J_{PC}$ = 35.5 Hz, CH_2P), 55.21 (CH_2N), 55.31 (CH_2O), 126.03 (*p*-C), 128.45 (*o*-C), 129.23 (*m*-C), 141.15 (d, $^3J_{PC}$ = 16.0 Hz, *ipso*-C).

^{31}P NMR (161.98 Hz, D_2O): δ = 26.37 (s) (+d satellite, $^1J_{PSe}$ = 566.1 Hz).

^{77}Se NMR (76.31 Hz, D_2O): δ = –48.11 (d, $^1J_{PSe}$ = 566.1 Hz).

Anal. Calcd for $C_{22}H_{34}NO_3PSe_2$: C, 48.09; H, 6.24; N, 2.55; P, 5.64; Se, 28.74. Found: C, 48.15; H, 6.19; N, 2.81; P, 5.50; Se, 28.94.

Di-*n*-propylammonium Bis(2-phenethyl)diselenophosphinate (13e)

Yield: 0.29 g (93%); colorless solid; mp 170–172 °C.

IR (KBr): 3086, 3060, 3025, 2966, 2935, 2880, 2771, 2512, 2311, 1746, 1602, 1582, 1538, 1496, 1466, 1453, 1429, 1399, 1333, 1295, 1269, 1209, 1189, 1156, 1126, 1067, 1046, 1030, 1005, 947, 907, 836, 787, 762, 733, 697, 578, 565, 475, 386 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.05 (t, $^3J_{HH}$ = 7.4 Hz, 6 H, Me), 1.89–1.99 (m, 4 H, CH_2Me), 2.51–2.58 (m, 4 H, CH_2P), 3.02–3.12 (m, 8 H, CH_2Ph, CH_2N), 7.15–7.28 (m, 10 H, Ph), 8.82 (s, 2 H, NH).

^{13}C NMR: (100.61 MHz, $CDCl_3$): δ = 11.36 (Me), 19.35 (CH_2Me), 30.81 (CH_2Ph), 43.81 (d, $^1J_{PC}$ = 36.5 Hz, CH_2P), 47.99 (CH_2N), 125.94 (*p*-C), 128.18 (*o*-C), 128.43 (*m*-C), 141.63 (d, $^3J_{PC}$ = 17.6 Hz, *ipso*-C).

^{31}P NMR (161.98 Hz, $CDCl_3$): δ = 25.42 (s) (+d satellite, $^1J_{PSe}$ = 566.3 Hz).

^{77}Se NMR (76.31 Hz, $CDCl_3$): δ = –59.83 (d, $^1J_{PSe}$ = 566.3 Hz).

Anal. Calcd for $C_{22}H_{34}NPSe_2$: C, 52.70; H, 6.83; N, 2.79; P, 6.18; Se, 31.50. Found: C, 52.56; H, 7.10; N, 2.89; P, 6.23; Se, 31.30.

Cyclohexylammonium Bis(2-phenethyl)diselenophosphinate (13f)

Yield: 0.30 g (98%); colorless solid; mp 177–178 °C.

IR (KBr): 3081, 3057, 3021, 2996, 2936, 2886, 2856, 2554, 2497, 1944, 1638, 1600, 1562, 1496, 1449, 1396, 1378, 1347, 1277, 1262, 1215, 1192, 1181, 1141, 1121, 1077, 1062, 1028, 1007, 958, 939, 909, 893, 844, 829, 802, 756, 727, 712, 695, 577, 563, 549, 507, 482, 470, 427, 406 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.16–1.33, 1.62–1.67, 1.79–1.82, 2.27–2.30 (m, 10 H, CH_2-cyclo), 2.51–2.58 (m, 4 H, CH_2P), 3.01–3.07 (m, 4 H, CH_2Ph), 3.39–3.44 (m, 1 H, CHN), 7.17–7.30 (m, 10 H, Ph), 7.93 (s, 3 H, NH).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 24.29, 24.72, 31.21 (CH_2-cyclo), 31.97 (CH_2Ph), 43.58 (d, $^1J_{PC}$ = 35.4 Hz, CH_2P), 51.61 (CHN), 126.28 (*p*-C), 128.49 (*o*-C), 128.67 (*m*-C), 141.28 (d, $^3J_{PC}$ = 16.8 Hz, *ipso*-C).

^{31}P NMR (161.98 Hz, $CDCl_3$): δ = 24.79 (s) (+d satellite, $^1J_{PSe}$ = 558.2 Hz).

^{77}Se NMR (76.31 Hz, $CDCl_3$): δ = –58.97 (d, $^1J_{PSe}$ = 558.2 Hz).

Anal. Calcd for $C_{22}H_{32}NPSe_2$: C, 52.91; H, 6.46; N, 2.80; P, 6.20; Se, 31.62. Found: C, 52.88; H, 6.49; N, 3.01; P, 6.12; Se, 31.74.

Allylammonium Bis(2-phenethyl)diselenophosphinate (13g)

Yield: 0.26 g (91%); colorless solid; mp 115–116 °C.

IR (KBr): 3021, 2924, 2861, 2776, 2586, 2345, 1948, 1806, 1648, 1599, 1582, 1495, 1474, 1451, 1441, 1424, 1402, 1330, 1313, 1284, 1261, 1212, 1196, 1154, 1135, 1119, 1076, 1028, 1008, 987, 959, 939, 929, 906, 893, 869, 845, 833, 758, 733, 725, 709, 694, 668, 638, 579, 563, 543, 503, 473, 413 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 2.48–2.55 (m, 4 H, CH_2P), 2.97–3.04 (m, 4 H, CH_2Ph), 3.82 (d, $^3J_{HH}$ = 6.2 Hz, 2 H, CH_2N), 5.34 (d, $^3J_{HH}$ = 10.5 Hz, 1 H, $=CH_2$), 5.51 (d, $^3J_{HH}$ = 17.2 Hz, 1 H, $=CH_2$), 6.02–6.12 (m, 1 H, =CH), 7.15–7.28 (m, 10 H, Ph), 8.31 (s, 3 H, HN).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 31.14 (CH_2Ph), 41.99 (CH_2N), 43.43 (d, $^1J_{PC}$ = 35.0 Hz, CH_2P), 122.75 ($=CH_2$), 126.36 (*p*-C), 128.57 (*o*-C), 128.70 (*m*-C), 128.88 (CH =), 141.13 (d, $^3J_{PC}$ = 16.7 Hz, *ipso*-C).

^{31}P NMR (161.98 Hz, $CDCl_3$): δ = 24.83 (s) (+d satellite, $^1J_{PSe}$ = 556.3 Hz).

^{77}Se NMR (76.31 Hz, $CDCl_3$): δ = –58.97 (d, $^1J_{PSe}$ = 556.3 Hz).

Anal. Calcd for $C_{19}H_{26}NPSe_2$: C, 49.90; H, 5.73; N, 3.06; P, 6.77; Se, 34.53. Found: C, 49.91; H, 5.70; N, 2.91; P, 6.60; Se, 34.41.

Triethylammonium Bis(4-*tert*-butylphenethyl)diselenophosphinate (13h)

Yield: 0.33 g (86%); colorless solid; mp 107–109 °C.

IR (KBr): 3090, 3053, 3018, 2959, 2902, 2866, 2778, 2704, 2664, 2607, 2474, 1638, 1516, 1508, 1463, 1437, 1412, 1390, 1363, 1314, 1293, 1267, 1200, 1184, 1161, 1137, 1108, 1067, 1016, 935, 876, 851, 835, 817, 771, 753, 737, 710, 682, 661, 559, 516, 498, 467, 456 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.34 (s, 18 H, *t*-Bu), 1.46 (t, $^3J_{HH}$ = 7.4 Hz, 9 H, Me), 2.55–2.62 (m, 4 H, CH_2P), 3.11–3.17 (m, 4 H, $CH_2C_6H_4$), 3.36–3.42 (m, 6 H, CH_2N), 7.22–7.34 (m, 8 H, C_6H_4), 9.76 (s, 1 H, NH).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 8.55 (Me), 30.41 (CH_2Ph), 31.40 (Me_3C), 34.33 (CMe_3), 44.29 (d, $^1J_{PC}$ = 36.3 Hz, CH_2P), 45.86 (CH_2N), 125.25 (C2,6 in C_6H_4), 128.16 (C3,5 in C_6H_4), 138.87 (d, $^3J_{PC}$ = 17.2 Hz, C1 in C_6H_4), 148.58 (C4-C_6H_4).

^{31}P NMR (161.98 Hz, $CDCl_3$): δ = 25.23 (s) (+d satellite, $^1J_{PSe}$ = 571.8 Hz).

^{77}Se NMR (76.31 Hz, $CDCl_3$): δ = –48.46 (d, $^1J_{PSe}$ = 571.8 Hz).

Anal. Calcd for $C_{30}H_{50}NPSe_2$: C, 58.72; H, 8.21; N, 2.28; P, 5.05; Se, 25.74. Found: C, 58.70; H, 8.18; N, 2.39; P, 5.10; Se, 25.68.

Di-*n*-propylammonium Bis[2-(2-methyl-5-pyridyl)ethyl]diselenophosphinate (13i)

Yield: 0.29 g (87%); colorless solid; mp 170–171 °C.

IR (KBr): 3030, 3002, 2969, 2920, 2881, 2768, 2506, 2487, 1657, 1600, 1568, 1535, 1490, 1466, 1450, 1396, 1320, 1302, 1246, 1200, 1189, 1143, 1118, 1094, 1066, 1029, 1007, 949, 855, 829, 788, 761, 743, 728, 720, 645, 537, 476, 422, 406, 383 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.04 (t, $^3J_{HH}$ = 7.4 Hz, 6 H, Me), 1.90–1.99 (m, 4 H, CH_2Me), 2.48–2.54 (m, 10 H, CH_2P, Me-Py), 3.06–3.12 (m, 8 H, CH_2Ph, CH_2N), 7.06 (d, 2 H, Py), 7.46 (d, 2 H, Py), 8.38 (s, 2 H, Py), 8.87 (s, 2 H, NH).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 11.37 (Me), 19.44 (CH_2Me), 23.94 (*Me*Py), 27.64 (CH_2Ph), 43.59 (d, $^1J_{PC}$ = 36.6 Hz, CH_2P), 48.49 (CH_2N), 123.11, 134.00 d, 136.54, 148.86, 155.74 (Py).

^{31}P NMR (161.98 Hz, $CDCl_3$): δ = 24.28 (s) (+d satellite, $^1J_{PSe}$ = 574.0 Hz).

^{77}Se NMR (76.31 Hz, $CDCl_3$): δ = –58.97 (d, $^1J_{PSe}$ = 574.0 Hz).

Anal. Calcd for $C_{22}H_{36}N_3PSe_2$: C, 49.72; H, 6.83; N, 7.91; P, 5.83; Se, 29.72. Found: C, 49.60; H, 7.08; N, 7.89; P, 6.02; S, 29.83.

Diisopropylammonium Bis(2-phenylpropyl)diselenophosphinate (13j)

Yield: 0.31 g (95%); colorless solid; mp 98–99 °C.

IR (KBr): 3059, 3024, 2976, 2821, 2715, 2535, 2395, 2345, 1941, 1868, 1799, 1743, 1601, 1582, 1573, 1531, 1491, 1463, 1450, 1393, 1377, 1337, 1316, 1299, 1235, 1195, 1181, 1171, 1144, 1100, 1087, 1071, 1043, 1030, 999, 973, 943, 906, 875, 819, 796, 772, 762, 729, 699, 587, 573, 527, 491, 454, 402, 376 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.33, 1.38 (d, $^3J_{HH}$ = 7.1 Hz, 6 H, *Me*CHPh), 1.52 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, Me), 2.18–2.32, 2.38–2.50 (m, 4 H, CH_2P), 3.39–3.52 (m, 4 H, CHPh, CHN), 7.08–7.25 (m, 10 H, Ph), 8.91 (s, 2 H, NH).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 20.45 (Me), 23.86, 24.30 (d, $^3J_{CP}$ = 7.6 Hz, *Me*CHPh), 37.39 (d, $^2J_{CP}$ = 25.4 Hz, CHPh), 48.59 (CHN), 50.78 (d, $^1J_{CP}$ = 34.8 Hz, CH_2P), 125.97 (*p*-C), 127.41 (*o*-C), 128.37 (*m*-C), 148.04, 148.08 (d, $^3J_{PC}$ = 9.6 Hz, *ipso*-C).

^{31}P NMR (161.98 Hz, $CDCl_3$): δ = 24.23, 25.17 (+d satellite, $^1J_{PSe}$ = 566.6 Hz, $^1J_{PSe}$ = 563.4 Hz, respectively).

^{77}Se NMR (76.31 Hz, $CDCl_3$): δ = –34.91 (d, $^1J_{PSe}$ = 563.5 Hz), –10.55 (d, $^1J_{PSe}$ = 566.6 Hz), 10.46 (d, $^1J_{PSe}$ = 564.5 Hz).

Anal. Calcd for $C_{24}H_{38}NPSe_2$: C, 54.44; H, 7.23; N, 2.65; P, 5.85; Se, 29.83. Found: C, 54.37; H, 7.42; N, 2.64; P, 5.60; Se, 29.80.

Triethylammonium Diphenyldiselenophosphinate (13k)

The amorphous gray selenium (0.049 g, 0.623 mmol) was added to a soln of diphenylphosphine selenide (**14**; 0.165 g, 0.623 mmol) in THF (4 mL) at 60 °C under argon. Et_3N (0.082 g, 0.810 mmol) in EtOH (5 mL) was added to the stirred suspension. The mixture was heated until full dissolution of selenium (50 min); this gave a colorless transparent soln. The solvents were removed under reduced pressure and the residue was washed with Et_2O (5 mL) and dried in vacuo (1 Torr, r.t.); this gave the salt **13k**.

Yield: 0.24 g (88%); colorless solid; mp 97–100 °C.

IR (KBr): 3063, 3042, 2970, 2937, 2783, 2744, 2653, 2477, 1468, 1454, 1436, 1387, 1356, 1307, 1283, 1173, 1159, 1106, 1085, 1052, 1028, 1011, 997, 896, 837, 804, 769, 756, 697, 622, 547, 522, 476, 442, 418 cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.21 (t, $^3J_{HH}$ = 7.4 Hz, 9 H, Me), 3.11–3.16 (m, 6 H, CH_2N), 8.11–8.16 (m, 10 H, Ph), 10.11 (s, 1 H, NH).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 8.53 (Me), 45.82 (CH_2N), 127.34, 127.46 (*o*-C), 129.29, 129.32 (*p*-C), 131.04, 131.16 (*m*-C), 141.63 (d, $^1J_{PC}$ = 62.8 Hz, *ipso*-C).

^{31}P NMR (161.98 Hz, $CDCl_3$): δ = 22.07 (s) (+d satellite, $^1J_{PSe}$ = 602.6 Hz).

^{77}Se NMR (76.31 Hz, $CDCl_3$): δ = 24.43 (d, $^1J_{PSe}$ = 602.6 Hz).

Anal. Calcd for $C_{18}H_{26}NPSe_2$: C, 48.55; H, 5.89; N, 3.15; P, 6.96; Se, 35.46. Found: C, 48.50; H, 5.88; N, 3.23; P, 7.06; Se, 35.41.

4-Aza-1-azoniabicyclo[2.2.2]octane Bis(2-phenethyl)diselenophosphinate (13l)

The amorphous gray selenium (0.049 g, 0.623 mmol) was added to a soln of bis(2-phenethyl)phosphine selenide (**1**; 0.200 g, 0.623 mmol) in THF (4 mL) at 85 °C under argon. DABCO (0.091 g, 0.810 mmol) in EtOH (5 mL) was added to the stirring suspension. The suspension was heated until the complete dissolution of selenium (60 min); this gave a colorless, transparent soln. The solvents were removed under reduced pressure and the residue was washed with Et_2O (5 mL) and dried in vacuo (1 Torr, r.t.); this gave the salt **13l**.

Yield: 0.27 g (84%); colorless solid; mp 191–193 °C.

IR (KBr): 3059, 3025, 2882, 2743, 2578, 2541, 2500, 2459, 2125, 1948, 1811, 1636, 1600, 1496, 1452, 1427, 1417, 1390, 1378, 1350, 1316, 1299, 1264, 1242, 1207, 1195, 1178, 1156, 1125, 1066, 1051, 1030, 1007, 974, 945, 919, 910, 837, 825, 781, 769, 734, 723, 706, 698, 593, 569, 507, 485 cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.53–2.60 (m, 4 H, CH_2P), 3.09–3.16 (m, 4 H, CH_2Ph), 3.32 (s, 12 H, CH_2N), 7.19–7.30 (m, 10 H, Ph), 10.38 (s, 1 H, HN).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 30.74 (CH_2Ph), 43.81 (d, $^1J_{PC}$ = 36.5 Hz, CH_2P), 44.96 (CH_2N), 125.62 (*p*-C), 128.12 (*o*-C), 128.20 (*m*-C), 141.49 (d, $^3J_{PC}$ = 17.2 Hz, *ipso*-C).

^{31}P NMR (161.98 Hz, $CDCl_3$): δ = 25.09 (s) (+d satellite, $^1J_{PSe}$ = 571.1 Hz).

^{77}Se NMR (76.31 Hz, $CDCl_3$): δ = –69.55 (d, $^1J_{PSe}$ = 571.1 Hz).

Anal. Calcd for $C_{22}H_{31}N_2PSe_2$: C, 51.57; H, 6.10; N, 5.47; P, 6.04; Se, 30.82. Found: C, 51.70; H, 6.12; N, 5.56; P, 6.07; Se, 31.04.

2,3,4,6,7,8,9,10-Octahydropyrimido[1,2-*a*]azepin-1-ium Bis(2-phenethyl)diselenophosphinate (13m)

The amorphous gray selenium (0.049 g, 0.623 mmol) was added to a soln of bis(2-phenethyl)phosphine selenide (**1**; 0.200 g, 0.623 mmol) in THF (4 mL) at r.t. under argon. DBU (0.123 g, 0.810 mmol) in EtOH (5 mL) was added to the stirring suspension. The suspension was stirred until complete dissolution of selenium (ca. 1 min); this gave a colorless, transparent soln. The solvents were removed under reduced pressure and the residue was washed with Et_2O (5 mL) and dried in vacuo (1 Torr, r.t.); this gave the salt **13m**.

Yield: 0.34 g (99%); colorless solid; mp 101–102 °C.

IR (KBr): 3219, 3074, 3012, 2927, 2869, 2797, 2339, 1639, 1586, 1488, 1443, 1393, 1317, 1276, 1198, 1146, 1133, 1102, 1013, 949, 925, 904, 826, 756, 694, 617, 572, 477 cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.69 (m, 2 H, C9-H_2), 1.77 (m, 2 H, C8-H_2), 1.85 (m, 2 H, C10-H_2), 2.05–2.11 (m, 2 H, C3-H_2), 2.54–2.61 (m, 4 H, CH_2P), 3.08–3.19 (m, 6 H, CH_2Ph, C7-H_2), 3.44–3.51 (m, 4 H, C2,11-H_2), 3.62–3.65 (m, 2 H, C4-H_2), 7.17–7.28 (m, 10 H, Ph), 10.26 (s, 1 H, HN).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 19.19 (C10), 23.53 (C4), 26.43 (C5), 28.63 (C4) 30.68 (CH_2Ph), 32.41 (C6), 44.48 (d, $^1J_{PC}$ = 36.6 Hz, CH_2P), 44.42 (C11), 54.12 (C2), 125.34 (*p*-C), 127.95 (*o*-C), 128.14 (*m*-C), 141.94 (d, $^3J_{PC}$ = 17.6 Hz, *ipso*-C), 165.92 (C7).

^{31}P NMR (161.98 Hz, $CDCl_3$): δ = 25.08 (s) (+d satellite, $^1J_{PSe}$ = 583.0 Hz).

^{77}Se NMR (76.31 Hz, $CDCl_3$): δ = –66.86 (d, $^1J_{PSe}$ = 583.0 Hz).

Anal. Calcd for $C_{25}H_{35}N_2PSe_2$: C, 54.35; H, 6.39; N, 5.07; P, 5.61; Se, 28.59. Found: C, 54.25; H, 6.45; N, 5.11; P, 5.50; Se, 28.43.

Acknowledgment

Financial support from the Russian Foundation for Basic Research (Grant nos. 07-03-00562 and 08-03-00251) is gratefully acknowledged.

References

(1) (a) Davies, R. P.; Martinelli, M. G. *Inorg. Chem.* **2002**, *41*, 348. (b) Davies, R. P.; Martinelli, M. G.; Wheatley, A. E. H.; White, A. J. P.; Williams, D. J. *Eur. J. Inorg. Chem.* **2003**, 3409. (c) Davies, R. P.; Francis, C. V.; Jurd, A. P. S.; Martinelli, M. G.; White, A. J. P.; Williams, D. J. *Inorg. Chem.* **2004**, *43*, 4802.

(2) Nguyen, C. Q.; Afzaal, M.; Malik, M. A.; Helliwell, M.; Raftery, J.; O'Brien, P. *J. Organomet. Chem.* **2007**, *692*, 2669.

(3) (a) Bwembya, G. C.; Song, X.; Bochmann, M. *Chem. Vap. Deposition* **1995**, *1*, 78. (b) Gubin, S. P.; Kataeva, N. A.; Khomutov, G. B. *Russ. Chem. Bull.* **2005**, *54*, 827. (c) Nguyen, C. Q.; Adeogun, A.; Afzaal, M.; Malik, M. A.; O'Brien, P. *Chem. Commun.* **2006**, 2182. (d) Fan, D.; Afzaal, M.; Mallik, M. A.; Nguyen, C. Q.; O'Brien, P.; Thomas, P. J. *Coord. Chem. Rev.* **2007**, *251*, 1878. (e) Hasegawa, Y.; Adachi, T.; Tanaka, A.; Afzaal, M.; O'Brien, P.; Doi, T.; Hinatsu, Y.; Fujita, K.; Tanaka, K.; Kawai, T. *J. Am. Chem. Soc.* **2008**, *130*, 5710.

(4) For reviews, see: (a) Lobana, T. S.; Wang, J.-C.; Liu, C. W. *Coord. Chem. Rev.* **2007**, *251*, 91. (b) Kuchen, W.; Knop, B. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 244. (c) Kuchen, W.; Knop, B. *Chem. Ber.* **1966**, *99*, 1663. (d) Hertel, H.; Kuchen, W. *Chem. Ber.* **1971**, *104*, 1740. (e) Esperas, S.; Husebye, S. *Acta Chem. Scand.* **1973**, *27*, 1827. (f) Muller, A.; Rao, V. V. K.; Christophliemk, P. *J. Inorg. Nucl. Chem.* **1974**, *36*, 472. (g) Lucio Gelmini, L.; Stephan, D. W. *Organometallics* **1987**, *6*, 1515.

(5) (a) Rickelton, W. A.; Boyl, R. *J. Sep. Sci. Tech.* **1988**, *23*, 1227. (b) Flett, D. S. *J. Organomet. Chem.* **2005**, *690*, 2426.

(6) (a) Mashkovskii, M. D. *Drugs* (in Russian), Vol. 2, 12th ed.; Medicina: Moscow, **1989**, 360. (b) Abdulina, G. A.; Gazaliev, A. M.; Baikenova, G. G.; Fazylov, S. D.; Kudaibergenova, S. *Khim.-Farm. Zh. (in Russian)* **2002**, *3*, 11..

(7) Kimura, T.; Murai, T. *J. Org. Chem.* **2005**, *70*, 952.

(8) Moon, J.; Nam, H.; Kim, S.; Ryu, J.; Han, C.; Lee, C.; Lee, S. *Tetrahedron Lett.* **2008**, *49*, 5137.

(9) Mashkovskii, M. D. *Drugs* (in Russian), Vols. 1,2, 12th ed.; Medicina: Moscow, **1989**.

(10) For reviews, see: (a) Greaves, T. L.; Drummond, C. J. *Chem. Rev.* **2008**, *108*, 206. (b) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley: Weinheim, **2008**.

(11) (a) Trofimov, B. A.; Brandsma, L.; Arbuzova, S. N.; Malysheva, S. F.; Gusarova, N. K. *Tetrahedron Lett.* **1994**, *35*, 7647. (b) Sukhov, B. G.; Gusarova, N. K.; Ivanova, N. I.; Bogdanova, M. V.; Kazheva, O. N.; Alexandrov, G. G.; Dyachenko, O. A.; Sinegovskaya, L. M.; Malysheva, S. F.; Trofimov, B. A. *J. Struct. Chem.* **2005**, *46*, 1066. (c) Gusarova, N. K.; Malysheva, S. F.; Kuimov, V. A.; Belogorlova, N. A.; Mikhailenko, V. L.; Trofimov, B. A. *Mendeleev Commun.* **2008**, *18*, 260. (d) Gusarova, N. K.; Ivanova, N. I.; Volkov, P. A.; Larina, L. I. *Synthesis* **2008**, 3523.

(12) (a) Burakova, E. A.; Kovalev, N. A.; Kuznetsova, I. L.; Zenkova, M. A.; Vlasov, V. V.; Sil'nikov, V. N. *Russ. J. Bioorg. Chem.* **2007**, *35*, 563. (b) Kuznetsova, I. L.; Zenkova, M. A.; Vlasov, V. V. *Russ. Chem. Rev.* **2007**, *76*, 305.

(13) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: Oxford, **1980**.

(14) Sheldrick, G. M. *SHELXS 97*; University of Göttingen: Germany, **1997**.