Radical Addition of Secondary Phosphine Sulfides and Selenides to Vinyl Selenides

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Abstract: The first examples of a facile hydrochalcogenophosphorylation of alkyl vinyl selenides are reported. The regiospecific addition of secondary phosphine sulfides and phosphine selenides to vinyl selenides proceeds under radical initiation (AIBN, 65–70 °C, 1 h or UV-irradiation, 1 h) to afford the anti-Markovnikov adducts in 87–95% yield.

Key words: alkyl vinyl selenides, secondary phosphine sulfides, secondary phosphine selenides, radical addition, functional tertiary phosphine chalcogenides

Tertiary phosphine chalcogenides are important ligands in the design of new metal-complex catalysts[1] (in some catalytic processes they show even better results than the corresponding tertiary phosphines[1a]), building blocks in the synthesis of biologically active compounds (for example, anti-arthritic gold complexes[2]) and intermediates for semi-conducting nanomaterials.[3] In recent years there has been increasing interest in functional phosphine chalcogenides as polydentate 'hemilabile' ligands[4] such as $R_2P(X)CH_2CH_2SR'$ (X = O, S), which has been used, for example, in myocardial imaging.[4c,d] The substitution of an alkyl sulfide fragment for an alkyl selenide group in these compounds expands the scope of practical applications of tertiary phosphine chalcogenides. Meanwhile, to the best of our knowledge, such functional tertiary phosphine sulfides and phosphine selenides with alkyl selenide moieties have not been reported in the literature.

The goal of the present work was to study the reaction of available secondary phosphine chalcogenides[5] with alkyl vinyl selenides, which were easily prepared from elemental selenium, acetylene and alkyl halides,[6] in order to develop a general, expedient and atom-economic method for the synthesis of functional tertiary phosphine chalcogenides containing alkyl selenide fragments.

We have found that secondary phosphine sulfides **1**, **2** and selenides **3**, **4** add regiospecifically to alkyl vinyl selenides **5**, **6** under mild conditions (AIBN, 65–70 °C or UV-irradiation, dioxane, 1 h) to give tertiary alkylselanylphosphine chalcogenides **7a–h** in 87–95% yield (Table 1).

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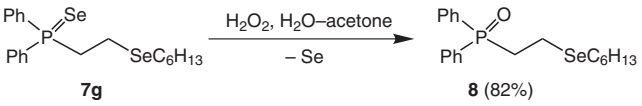
Secondary phosphine oxides showed less reactivity in this reaction. Thus, heating (65–70 °C, 20 h, dioxane) diphenylphosphine oxide with vinyl selenide **5** in the presence of AIBN gave 2-(hexylselanyl)ethyl(diphenyl)phosphine oxide (**8**) in ~40% yield (^{31}P NMR). Another product of the reaction, diphenylphosphinic acid (~60% yield; δ_p = 28.94 ppm), is likely to result from the oxidation of diphenylphosphine oxide by air.

At the same time, the phosphine oxide **8** was prepared in high isolated yield by the oxidation of alkylselanylphosphine selenide **7g** with aqueous hydrogen peroxide (r.t., 10 min, acetone) as shown in Scheme 1.



7g **8** (82%)

Scheme 1

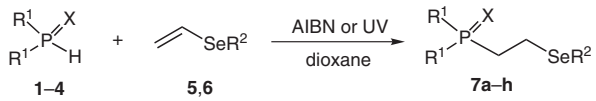
In summary, work described here on the addition of secondary phosphine chalcogenides to vinyl selenides contributes to the understanding of the reactivity of these compounds, provides a facile synthesis of new tertiary phosphine chalcogenides with alkyl selenide substituents and extends the synthetic potential of reactions of PH-addends with alkenes. Such reactions represent one of the most convenient approaches to C–P bond formation and continues to attract attention as a straightforward, atom-economic ('green') route for the synthesis of tertiary phosphine chalcogenides, including functional ones.[5,7]

The ^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR spectra were recorded on a Bruker DPX 400 spectrometer (400.13, 100.69, 161.98 and 76.31 MHz, respectively) in $CDCl_3$ solutions and referenced to internal HMDS (^{1}H NMR), external 85% H_3PO_4 (^{31}P NMR) and internal Me_2Se (^{77}Se NMR). IR spectra were run on a Bruker IFS 25 spectrometer in microlayer (the abbreviation 'sh' refers to shoulder).

Alkylselanylphosphine Chalcogenides 7a–h; Typical Procedure (Table 1)

A solution of phosphine chalcogenide **1**–**4** (0.5 mmol) and vinyl selenide **5**, **6** (0.575 mmol) in dioxane (3 mL) in the presence of AIBN (2% by mass) was stirred under an argon atmosphere at 65–70 °C for 1 h. The reaction was monitored using ^{31}P NMR spectra, which showed the disappearance of peaks of the initial secondary phosphine chalcogenide **1**–**4** at δ = 2.65–22.85 ppm and the appearance of new peaks at δ = 33.92–48.96 ppm corresponding to tertiary alkylselanylphosphine chalcogenides **7a–h**. The solvent was then

Table 1 Synthesis of Tertiary Alkylselanylphosphine Chalcogenides **7a–h**[a]



1–4 **5,6** **7a–h**

Entry	Secondary phosphine chalcogenide			Vinyl selenide		Product	Yield (%)[b]
		R^1	X		R^2		
1	**1**	Ph	S	**5**	n-C_5H_{11}	**7a**	95
2	**2**	$Ph(CH_2)_2$	S	**5**	n-C_5H_{11}	**7b**	90
3	**3**	Ph	Se	**5**	n-C_5H_{11}	**7c**	92
4	**4**	$Ph(CH_2)_2$	Se	**5**	n-C_5H_{11}	**7d**	93
5	**1**	Ph	S	**6**	n-C_6H_{13}	**7e**	94
6	**2**	$Ph(CH_2)_2$	S	**6**	n-C_6H_{13}	**7f**	87
7	**3**	Ph	Se	**6**	n-C_6H_{13}	**7g**	89
8	**4**	$Ph(CH_2)_2$	Se	**6**	n-C_6H_{13}	**7h**	89
9[c]	**1**	Ph	S	**6**	n-C_6H_{13}	**7e**	95

[a] Reaction conditions: AIBN, 1 h (entries 1–8) or UV-irradiation, 1 h (entry 9).
[b] Isolated yield after purification (see experimental section).
[c] A solution of **1** (0.1 mmol) and **5** (0.115 mmol) in dioxane (3 mL) was irradiated under an argon atmosphere (quartz ampoule, 200W Hg arc lamp).

removed under reduced pressure and the residue was dissolved in Et_2O (3 mL). The solution was passed through a thin layer of Al_2O_3 and the solvent was evaporated in vacuo to give alkylselanylphosphine chalcogenides **7a–h** of analytical purity.

2-(Pentylselanyl)ethyl(diphenyl)phosphine Sulfide (7a)
Yield: 95%; yellow oil.

IR (film): 3074, 3053 (ν CH of phenyl rings), 2955, 2926, 2867, 2855 (ν CH), 1586, 1574, 1480 (ν C=C of phenyl rings), 1464, 1436, (δ CH_2), 1379 (δ CH_3), 1334, 1309, 1260, 1243, 1168, 1104, 1070, 1027, 1016, 998, 884, sh 770 (δ CH of phenyl rings), 751 (ν P–C), 741, 724, 711, 692 (δ CH of phenyl rings), sh 620, 609 (ν P=S) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.85 (m, 3 H, CH_3), 1.28 (m, 4 H, $CH_2CH_2CH_3$), 1.58 (m, 2 H, $CH_2C_3H_7$), 2.54 (m, 2 H, $CH_2C_4H_9$), 2.74 (m, 4 H, $SeCH_2CH_2P$), 7.47 (m, 6 H, Ph), 7.81 (m, 4 H, Ph).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9 (CH_3), 14.6 (d, $^2J_{P–C}$ = 3.3 Hz, PCH_2CH_2Se), 22.1 (CH_2CH_3), 24.4 ($CH_2C_4H_9$), 29.9 ($CH_2C_3H_7$), 31.9 ($CH_2C_2H_5$), 34.4 (d, $^1J_{P–C}$ = 49.0 Hz, CH_2P), 128.6 (d, $^2J_{P–C}$ = 11.8 Hz, *o*-C, Ph), 130.9 (d, $^3J_{P–C}$ = 10.0 Hz, *m*-C, Ph), 131.5 (d, $^4J_{P–C}$ = 3.0 Hz, *p*-C, Ph), 132.2 (d, $^1J_{P–C}$ = 78.9 Hz, *i*-C, Ph).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 42.43.

^{77}Se NMR (76 MHz, $CDCl_3$): δ = 206.4 (d, $^3J_{P–Se}$ = 13.2 Hz).

Anal. Calcd for $C_{19}H_{25}PSSe$: C, 57.71; H, 6.37; P, 7.83; S, 8.11; Se, 19.97. Found: C, 57.93; H, 6.13; P, 7.82; S, 8.36; Se, 19.76.

2-(Pentylselanyl)ethyl(diphenethyl)phosphine Sulfide (7b)
Yield: 90%; yellow oil.

IR (film): 3084, 3061, 3026, 3000 (ν CH of phenyl rings), 2955, 2925, 2867, 2856 (ν CH), 1602, 1584, 1496 (ν C=C of phenyl rings), 1453, 1406 (δ CH_2), 1379 (δ CH_3), 1332, 1295, 1268, 1244, 1211, 1199, 1174, 1135, 1103, 1092, 1072, 1029, 1008, 948, 908, 893, 857, sh 771 (δ CH of phenyl rings), 752 (ν P–C), 698 (δ CH of phenyl rings), sh 612, 598 (ν P=S) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (m, 3 H, CH_3), 1.34 (m, 4 H, $CH_2CH_2CH_3$), 1.65 (m, 2 H, $CH_2C_3H_7$), 2.26 (m, 6 H, CH_2P), 2.57 (m, 2 H, $CH_2C_4H_9$), 2.73 (m, 2 H, PCH_2CH_2Se), 2.93 (m, 4 H, $PhCH_2$), 7.20 (m, 4 H, *o*-H, Ph), 7.23 (m, 2 H, *p*-H, Ph), 7.31 (m, 4 H, *m*-H, Ph).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9 (CH_3), 15.4 (d, $^2J_{P–C}$ = 3.3 Hz, PCH_2CH_2Se), 22.1 (CH_2CH_3), 24.6 ($CH_2C_4H_9$), 29.3 (d, $^2J_{P–C}$ = 2.2 Hz, CH_2Ph), 30.0 ($CH_2C_3H_7$), 31.9 ($CH_2C_2H_5$), 32.2 (d, $^1J_{P–C}$ = 36.1 Hz, PCH_2CH_2Se), 32.4 (d, $^1J_{P–C}$ = 40.9 Hz, CH_2CH_2Ph), 126.6 (*p*-C, Ph), 128.2 (*o*-C, Ph), 128.7 (*m*-C, Ph), 140.1 (d, $^3J_{P–C}$ = 13.6 Hz, *i*-C, Ph).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 37.93.

^{77}Se NMR (76 MHz, $CDCl_3$): δ = 208.5 (d, $^3J_{P–Se}$ = 8.6 Hz).

Anal. Calcd for $C_{23}H_{33}PSSe$: C, 61.18; H, 7.37; P, 6.86; S, 7.10; Se, 17.49. Found: C, 60.94; H, 7.15; P, 7.02; S, 7.24; Se, 17.65.

2-(Pentylselanyl)ethyl(diphenyl)phosphine Selenide (7c)
Yield: 92%; yellow oil.

IR (film): 3073, 3053, 3006 (ν CH of phenyl rings), 2955, 2926, 2869, 2855 (ν CH), 1587, 1573, 1481 (ν C=C of phenyl rings), 1464, 1436, 1402 (δ CH_2), 1378 (δ CH_3), 1333, 1309, 1266, 1243, 1188, 1167, 1130, 1100, 1070, 1027, 998, 924, 883, 847, 747, 720, 708, 691 (δ CH of phenyl rings), 643, sh 548, 531 (ν P=Se) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.87 (m, 3 H, CH_3), 1.31 (m, 4 H, $CH_2CH_2CH_3$), 1.59 (m, 2 H, $CH_2C_3H_7$), 2.56 (m, 2 H, $CH_2C_4H_9$), 2.72 (m, 2 H, $SeCH_2CH_2P$), 2.88 (m, 2 H, CH_2P), 7.46 (m, 6 H, Ph), 7.82 (m, 4 H, Ph).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 13.9 (CH_3), 15.3 (d, $^2J_{P–C}$ = 2.2 Hz, PCH_2CH_2Se), 22.1 (CH_2CH_3), 24.4 ($CH_2C_4H_9$), 30.0 ($CH_2C_3H_7$), 31.9 ($CH_2C_2H_5$), 34.2 (d, $^1J_{P–C}$ = 42.0 Hz, CH_2P), 128.6 (d, $^2J_{P–C}$ = 12.2 Hz, *o*-C, Ph), 130.9 (d, $^1J_{P–C}$ = 71.1 Hz, *i*-C, Ph),

131.4 (d, $^3J_{P-C}$ = 10.3 Hz, *m*-C, Ph), 131.6 (d, $^4J_{P-C}$ = 3.0 Hz, *p*-C, Ph).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 33.92.

^{77}Se NMR (76 MHz, $CDCl_3$): δ = –346.6 (d, $^1J_{P-Se}$ = 728.5 Hz), 206.6 (d, $^3J_{P-Se}$ = 10.0 Hz).

Anal. Calcd for $C_{19}H_{25}PSe_2$: C, 51.60; H, 5.70; P, 7.00; Se, 35.70. Found: C, 51.32; H, 5.99; P, 6.76; Se, 35.93.

2-(Pentylselanyl)ethyl(diphenethyl)phosphine Selenide (7d)
Yield: 93%; yellow oil.

IR (film): 3084, 3061, 3026, 3001 (ν CH of phenyl rings), 2955, 2925, 2867, 2856 (ν CH), 1603, 1584, 1496 (ν C=C of phenyl rings), 1453, 1406 (δ CH_2), 1378 (δ CH_3), 1332, 1295, 1268, 1244, 1214, 1200, 1173, 1135, 1105, 1071, 1030, 1007, 948, 909, 859, 844, 806, 752 (ν P–C), 699 (δ CH of phenyl rings), sh 573, 555 (ν P=Se) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (m, 3 H, CH_3), 1.34 (m, 4 H, $CH_2CH_2CH_3$), 1.66 (m, 2 H, $CH_2C_3H_7$), 2.26 (m, 6 H, CH_2P), 2.58 (m, 2 H, $CH_2C_4H_9$), 2.74 (m, 2 H, PCH_2CH_2Se), 2.94 (m, 4 H, $PhCH_2$), 7.19 (m, 4 H, *o*-H, Ph), 7.23 (m, 2 H, *p*-H, Ph), 7.30 (m, 4 H, *m*-H, Ph).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.0 (CH_3), 15.5 (d, $^2J_{P-C}$ = 4.8 Hz, PCH_2CH_2Se), 22.2 (CH_2CH_3), 24.6 ($CH_2C_4H_9$), 29.3 (d, $^2J_{P-C}$ = 3.0 Hz, CH_2Ph), 30.1 ($CH_2C_3H_7$), 32.0 ($CH_2C_2H_5$), 32.2 (d, $^1J_{P-C}$ = 36.1 Hz, PCH_2CH_2Se), 32.4 (d, $^1J_{P-C}$ = 40.2 Hz, CH_2CH_2Ph), 126.6 (*p*-C, Ph), 128.2 (*o*-C, Ph), 128.7 (*m*-C, Ph), 140.2 (d, $^3J_{P-C}$ = 13.6 Hz, *i*-C, Ph).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 38.13.

^{77}Se NMR (76 MHz, $CDCl_3$): δ = –387.6 (d, $^1J_{P-Se}$ = 704.3 Hz), 208.5 (d, $^3J_{P-Se}$ = 9.5 Hz).

Anal. Calcd for $C_{23}H_{33}PSe_2$: C, 55.43; H, 6.67; P, 6.21; Se, 31.69. Found: C, 55.65; H, 6.77; P, 6.16; Se, 31.42.

2-(Hexylselanyl)ethyl(diphenyl)phosphine Sulfide (7e)
Yield: 94%; yellow oil.

IR (film): 3074, 3054, 3021, 3005 (ν CH of phenyl rings), 2955, 2926, 2867, 2854 (ν CH), 1606, 1586, 1574, 1480 (ν C=C of phenyl rings), 1465, 1436, 1404 (δ CH_2), 1378 (δ CH_3), 1332, 1309, 1279, 1254, 1234, 1187, 1168, 1104, 1070, 1027, 1013, 998, 886, 849, sh 771 (δ CH of phenyl rings), 750 (ν P–C), 741, 723, 711, 692 (δ CH of phenyl rings), 642, sh 620, 609 (ν P=S) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (m, 3 H, CH_3), 1.33 (m, 6 H, $CH_2CH_2CH_2CH_3$), 1.61 (m, 2 H, $CH_2C_4H_9$), 2.58 (m, 2 H, $CH_2C_5H_{11}$), 2.78 (m, 4 H, $SeCH_2CH_2P$), 7.50 (m, 6 H, Ph), 7.84 (m, 4 H, Ph).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.0 (CH_3), 14.6 (d, $^2J_{P-C}$ = 3.0 Hz, PCH_2CH_2Se), 22.4 (CH_2CH_3), 24.4 ($CH_2C_5H_{11}$), 29.4 ($CH_2C_3H_7$), 30.2 ($CH_2C_4H_9$), 31.2 ($CH_2C_2H_5$), 34.4 (d, $^1J_{P-C}$ = 49.0 Hz, CH_2P), 128.6 (d, $^2J_{P-C}$ = 12.2 Hz, *o*-C, Ph), 130.9 (d, $^3J_{P-C}$ = 10.3 Hz, *m*-C, Ph), 131.5 (d, $^4J_{P-C}$ = 3.0 Hz, *p*-C, Ph), 132.2 (d, $^1J_{P-C}$ = 79.2 Hz, *i*-C, Ph).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 42.49.

^{77}Se NMR (76 MHz, $CDCl_3$): δ = 206.4 (d, $^3J_{P-Se}$ = 13.0 Hz).

Anal. Calcd for $C_{20}H_{27}PSSe$: C, 58.67; H, 6.65; P, 7.57; S, 7.83; Se, 19.29. Found: C, 58.78; H, 6.54; P, 7.65; S, 8.02; Se, 19.01.

2-(Hexylselanyl)ethyl(diphenethyl)phosphine Sulfide (7f)
Yield: 87%; yellow oil.

IR (film): 3085, 3062, 3026, 3001 (ν CH of phenyl rings), 2955, 2926, 2867, 2853 (ν CH), 1603, 1583, 1496 (ν C=C of phenyl rings), 1465, 1454, 1410 (δ CH_2), 1378 (δ CH_3), 1366, 1286, 1268, 1254, 1214, 1175, 1121, 1082, 1048, 1030, 1011, 949, 909, 888, 874, sh 781, 767 (δ CH of phenyl rings), 752 (ν P–C), 699 (δ CH of phenyl rings), sh 612, 598 (ν P=S) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (m, 3 H, CH_3), 1.33 (m, 4 H, $CH_2CH_2CH_3$), 1.39 (m, 2 H, $CH_2C_3H_7$), 1.67 (m, 2 H, $CH_2C_4H_9$), 2.17 (m, 6 H, CH_2P), 2.61 (m, 2 H, $CH_2C_5H_{11}$), 2.76 (m, 2 H, PCH_2CH_2Se), 2.95 (m, 4 H, $PhCH_2$), 7.21 (m, 4 H, *o*-H, Ph), 7.24 (m, 2 H, *p*-H, Ph), 7.32 (m, 4 H, *m*-H, Ph).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (CH_3), 14.8 (d, $^2J_{P-C}$ = 4.5 Hz, PCH_2CH_2Se), 22.6 (CH_2CH_3), 24.80 ($CH_2C_5H_{11}$), 28.7 (d, $^2J_{P-C}$ = 2.5 Hz, CH_2Ph), 29.6 ($CH_2C_3H_7$), 30.5 ($CH_2C_4H_9$), 31.4 ($CH_2C_2H_5$), 32.8 (d, $^1J_{P-C}$ = 43.3 Hz, PCH_2CH_2Se), 33.0 (d, $^1J_{P-C}$ = 47.3 Hz, CH_2CH_2Ph), 126.7 (*p*-C, Ph), 128.3 (*o*-C, Ph), 128.8 (*m*-C, Ph), 140.5 (d, $^3J_{P-C}$ = 13.6 Hz, *i*-C, Ph).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 48.96.

^{77}Se NMR (76 MHz, $CDCl_3$): δ = 208.1 (d, $^3J_{P-Se}$ = 10.0 Hz).

Anal. Calcd for $C_{24}H_{35}PSSe$: C, 61.92; H, 7.58; P, 6.65; S, 6.89; Se, 16.96. Found: C, 61.83; H, 7.65; P, 6.80; S, 7.03; Se, 16.69.

2-(Hexylselanyl)ethyl(diphenyl)phosphine Selenide (7g)
Yield: 89%; dark-yellow oil.

IR (film): 3074, 3053, 3006 (ν CH of phenyl rings), 2955, 2925, 2867, 2854 (ν CH), 1614, 1588, 1573, 1481 (ν C=C of phenyl rings), 1465, 1436, 1404 (δ CH_2), 1378 (δ CH_3), 1334, 1309, 1278, 1251, 1234, 1188, 1168, 1131, 1100, 1070, 1027, 998, 961, 929, 885, 847, 741, 728, 707, 691 (δ CH of phenyl rings), 641, sh 548, 531 (ν P=Se) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (m, 3 H, CH_3), 1.33 (m, 6 H, $CH_2CH_2CH_2CH_3$), 1.63 (m, 2 H, $CH_2C_4H_9$), 2.60 (m, 2 H, $CH_2C_5H_{11}$), 2.76 (m, 2 H, $SeCH_2CH_2P$), 2.92 (m, 2 H, CH_2P), 7.50 (m, 6 H, Ph), 7.85 (m, 4 H, Ph).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (CH_3), 15.5 (d, $^2J_{P-C}$ = 2.2 Hz, PCH_2CH_2Se), 22.6 (CH_2CH_3), 24.6 ($CH_2C_5H_{11}$), 29.6 ($CH_2C_3H_7$), 30.4 ($CH_2C_4H_9$), 31.3 ($CH_2C_2H_5$), 34.4 (d, $^1J_{P-C}$ = 42.0 Hz, CH_2P), 128.8 (d, $^2J_{P-C}$ = 12.2 Hz, *o*-C, Ph), 131.6 (d, $^3J_{P-C}$ = 10.3 Hz, *m*-C, Ph), 131.8 (d, $^4J_{P-C}$ = 3.0 Hz, *p*-C, Ph), 132.2 (*i*-C, Ph).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 33.92.

^{77}Se NMR (76 MHz, $CDCl_3$): δ = –352.1 (d, $^1J_{P-Se}$ = 728.0 Hz), 200.2 (d, $^3J_{P-Se}$ = 10.2 Hz).

Anal. Calcd for $C_{20}H_{27}PSe_2$: C, 52.64; H, 5.96; P, 6.79; Se, 34.61. Found: C, 52.37; H, 6.07; P, 6.74; Se, 34.82.

2-(Hexylselanyl)ethyl(diphenethyl)phosphine Selenide (7h)
Yield: 89%; light-yellow oil.

IR (film): 3085, 3061, 3026, 3001 (ν CH of phenyl rings), 2954, 2925, 2854, (ν CH), 1603, 1583, 1496 (ν C=C of phenyl rings), 1454, 1405 (δ CH_2), 1378 (δ CH_3), 1271, 1253, 1232, 1213, 1192, 1175, 1133, 1072, 1030, 1007, 948, 903, 873, 844, 751 (ν P–C), 699 (δ CH of phenyl rings), sh 573, 556 (ν P=Se) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (m, 3 H, CH_3), 1.32 (m, 4 H, $CH_2CH_2CH_3$), 1.39 (m, 2 H, $CH_2C_3H_7$), 1.68 (m, 2 H, $CH_2C_4H_9$), 2.29 (m, 6 H, CH_2P), 2.61 (m, 2 H, $CH_2C_5H_{11}$), 2.76 (m, 2 H, PCH_2CH_2Se), 2.97 (m, 4 H, $PhCH_2$), 7.23 (m, 4 H, *o*-H, Ph), 7.26 (m, 2 H, *p*-H, Ph), 7.34 (m, 4 H, *m*-H, Ph).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 14.1 (CH_3), 15.5 (d, $^2J_{P-C}$ = 4.1 Hz, PCH_2CH_2Se), 22.5 (CH_2CH_3), 24.7 ($CH_2C_5H_{11}$), 29.3 (d, $^2J_{P-C}$ = 2.2 Hz, CH_2Ph), 29.5 ($CH_2C_3H_7$), 30.4 ($CH_2C_4H_9$), 31.3 ($CH_2C_2H_5$), 32.2 (d, $^1J_{P-C}$ = 36.5 Hz, PCH_2CH_2Se), 32.4 (d, $^1J_{P-C}$ = 40.9 Hz, CH_2CH_2Ph), 126.6 (*p*-C, Ph), 128.3 (*o*-C, Ph), 128.7 (*m*-C, Ph), 140.1 (d, $^3J_{P-C}$ = 13.6 Hz, *i*-C, Ph).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 37.88.

^{77}Se NMR (76 MHz, $CDCl_3$): δ = –346.7 (d, $^1J_{P–Se}$ = 723.9 Hz), 206.2 (d, $^3J_{P–Se}$ = 9.0 Hz).

Anal. Calcd for $C_{24}H_{35}PSe_2$: C, 56.25; H, 6.88; P, 6.04; Se, 30.82. Found: C, 56.32; H, 6.90; P, 5.77; Se, 31.01.

2-(Hexylselanyl)ethyl(diphenyl)phosphine Oxide (8)

To a solution of hexylselanylphosphine selenide (**7g**; 0.44 mmol) in acetone (3 mL), aq H_2O_2 (35%, 0.44 mmol) was added dropwise. The reaction mixture was stirred at 20–22 °C for 10 min. Selenium precipitate (0.03 g, red powder) was filtered off and the filtrate was diluted with H_2O (~3 mL) and extracted with $CHCl_3$ (3 × 5 mL). The extract was dried (Ca_2CO_3) and the solvent was removed under reduced pressure to give the product, which was dried in vacuo.

Yield: 0.14 g (82%); yellow oil.

IR (film): 3073, 3054, 3006 (ν CH of phenyl rings), 2954, 2925, 2867, 2853 (ν CH), 1590, 1575, 1482 (ν C=C of phenyl rings), 1459, 1437, 1418 (δ CH_2), 1378 (δ CH_3), 1333, 1309, 1262, 1232, 1190 (ν P=O), 1172, 1120, 1102, 1070, 1027, 998, 883, 854, sh 769 (δ CH of phenyl rings), 743 (ν P–C), 722, 695 (δ CH of phenyl rings), 640, 550, 528 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (m, 3 H, CH_3), 1.31 (m, 6 H, $CH_2CH_2CH_2CH_3$), 1.60 (m, 2 H, $CH_2C_4H_9$), 2.57 (m, 2 H, $CH_2C_5H_{11}$), 2.64 (m, 2 H, $SeCH_2CH_2P$), 2.74 (m, 2 H, CH_2P), 7.53 (m, 6 H, Ph), 7.74 (m, 4 H, Ph).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 13.9 (d, $^2J_{P–C}$ = 4.4 Hz, PCH_2CH_2Se), 14.0 (CH_3), 22.5 (CH_2CH_3), 24.5 ($CH_2C_5H_{11}$), 29.5 ($CH_2C_3H_7$), 30.3 ($CH_2C_4H_9$), 31.2 ($CH_2C_2H_5$), 31.9 (d, $^1J_{P–C}$ = 64.9 Hz, CH_2P), 128.7 (d, $^2J_{P–C}$ = 11.8 Hz, *o*-C, Ph), 130.7 (d, $^3J_{P–C}$ = 9.6 Hz, *m*-C, Ph), 131.9 (d, $^4J_{P–C}$ = 3.0 Hz, *p*-C, Ph), 132.5 (*i*-C, Ph).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.46.

^{77}Se NMR (76 MHz, $CDCl_3$): δ = 205.9 (d, $^3J_{P–Se}$ = 11.0 Hz).

Anal. Calcd for $C_{20}H_{27}OPSe$: C, 61.07; H, 6.92; P, 7.87; Se, 20.07. Found: C, 60.95; H, 6.86; P, 7.66; Se, 20.22.

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