



# Reaction of secondary phosphine selenides with the system Se/MOH (M = Li, Na, K, Rb, Cs): A novel three-component synthesis of diorganodiselenophosphinates

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## ABSTRACT

Secondary phosphine selenides,  $R_2P(Se)H$  ( $R = PhCH_2CH_2$ ,  $PhCH(Me)CH_2$ , 4-*t*-BuC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH<sub>2</sub>, NaphthylCH<sub>2</sub>CH<sub>2</sub>, Ph), react with the system Se/MOH (M = Li, Na, K, Rb, Cs) in the system THF/EtOH at ambient temperature unusually fast (20–30 s) to give cleanly and almost quantitatively (in 94–100% yield) earlier unknown diorganodiselenophosphinates of alkali metals.

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## 1. Introduction

Diselenophosphinates of alkali metals represent a scarcely studied, though a promising class of new elementoorganic compounds. They are used as intermediates for the preparation of conducting nanomaterials [1], single-source precursors (SSPs) in metal organic chemical vapor deposition processes for design of semiconducting thin films [2], extractants of rare earth and transuranic elements [3], biologically active compounds possessing e.g., antimicrobial properties [4] as well as reactive building blocks for organic and elementoorganic synthesis [5]. For example, the reactions of potassium diphenyldiselenophosphinate with InCl<sub>3</sub> [6a] and EuCl<sub>3</sub> [6b] led to the corresponding indium and europium diphenyldiselenophosphinates. The latter were further used for the synthesis of nano-sized Eu selenide with remarkable magneto-optical properties in the active wavelength shorter than 600 nm [6b].

Among diorganodiselenophosphinates of alkali metals, only lithium, sodium and potassium diphenyldiselenophosphinates are known.

Sodium diphenyldiselenophosphinate was synthesized as a complex with THF and H<sub>2</sub>O, [Na(Se<sub>2</sub>PPh<sub>2</sub>)·THF·5H<sub>2</sub>O], in small yield [7a–f] from toxic and readily hydrolysable Ph<sub>2</sub>PCl and inaccessible Na<sub>x</sub>Se<sub>y</sub>. Also, it was reported [7g] that the reaction between Na<sub>x</sub>Se<sub>y</sub> and Ph<sub>2</sub>PCl was irreproducible and gave a mixture of products.

The complex of lithium diphenyldiselenophosphinate with THF and TMEDA, [Li(Se<sub>2</sub>PPh<sub>2</sub>)·THF·TMEDA], was prepared by the reaction of Ph<sub>2</sub>PH with *n*-BuLi and Se in THF/TMEDA/toluene media at (–78)–20° C [8].

The reaction of potassium diphenylphosphide with elemental selenium in THF – toluene solution furnished the complex [K(Se<sub>2</sub>PPh<sub>2</sub>)·THF]<sub>2</sub> (no experimental details was reported) [6a]. Recently, the potassium diphenyldiselenophosphinate monohydrate, K(Se<sub>2</sub>PPh<sub>2</sub>)·H<sub>2</sub>O, was prepared from potassium diphenylphosphine and selenium (THF, –30° C, 6 h) in 74% yield [6b].

Thus, all the known syntheses of alkali metal diorganodiselenophosphinates are multistep and laborious and require aggressive and poisonous phosphorus halogenides and flammable unstable organometallic reactants. Moreover, these methods have so far been limited only by preparation of Li, Na and K diphenyldiselenophosphinates.

The goal of this work is to elaborate a novel general and simple approach to the synthesis of alkali metal diorganodiselenophosphinates.

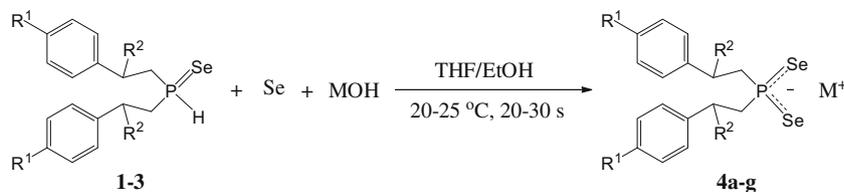
To reach this goal we have studied for the first time the three-component reaction of secondary phosphine selenides with elemental selenium and alkali metal hydroxides.

## 2. Results and discussion

Our experiments have shown that bis(arylalkyl)phosphine selenides **1–3**, now available [9], react with the system Se/MOH (M = Li, Na, K, Rb, Cs) in the system THF/EtOH at ambient temper-

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Initial phosphine selenide <b>1-3</b>	R <sup>1</sup>	R <sup>2</sup>	MOH	Salt <b>4</b>	Isolated yield, %
<b>1</b>	H	H	LiOH	<b>a</b>	96
<b>1</b>	H	H	NaOH	<b>b</b>	97
<b>1</b>	H	H	KOH	<b>c</b>	~ 100
<b>1</b>	H	H	RbOH	<b>d</b>	98
<b>1</b>	H	H	CsOH	<b>e</b>	98
<b>2</b>	H	Me	RbOH	<b>f</b>	97
<b>3</b>	<i>t</i> -Bu	H	KOH	<b>g</b>	~100

**Scheme 1.** Synthesis of alkali metal diorganodiselenophosphinates **4a-g** (hereinafter: argon atmosphere, equimolar ratio of the reactants).

ature unusually fast (20–30 s) to afford earlier unknown alkali metal diorganodiselenophosphinates **4a-g** in almost quantitative yields (96–100%) (Scheme 1).

The reaction proved to be of general character showing the same efficiency, e.g., with such sterically encumbered secondary phosphine selenide as bis[2-(2-naphthyl)ethyl]phosphine selenide **5** to form diselenophosphinate **4h** in 94% yield (Scheme 2).

A novel secondary phosphine selenide **5** was specially synthesized in this work from 2-vinylnaphthalene, red phosphorus and elemental selenium according to the protocol [9] (Scheme 3).

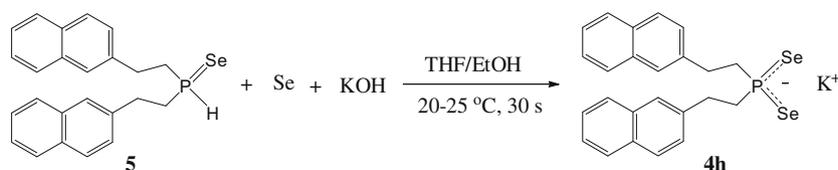
The generality and efficacy of the approach elaborated was additionally demonstrated by the synthesis of non-hydrated potassium diphenyldiselenophosphinate **4i** in 95% yield (Scheme 4).

Noteworthy, that diphenyldiselenophosphinate **4i** was earlier isolated only in the hydrated form,  $[K(Se_2PPh_2) \cdot H_2O]$ , in 74% yield [6b].

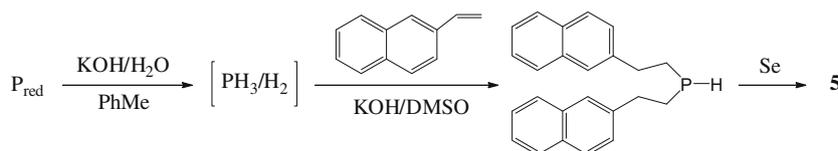
The salts **4a-i** synthesized are colorless solids soluble in water (except for salt **4h**) being stable upon storing at room temperature under inert atmosphere in the dark.

The structures of the compounds **4a-i** were proved by multinuclear <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>77</sup>Se NMR. The chemical equivalency of both selenium atoms in the salts **4a-i** was evidenced from the following NMR features:

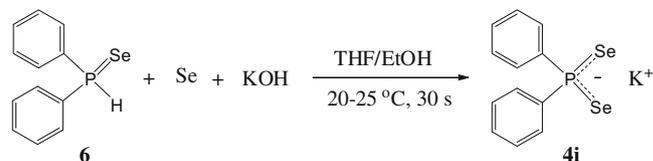
1. In the <sup>77</sup>Se NMR spectra, a one doublet ( $J_{SeP} = 550-613$  Hz) was present.



**Scheme 2.** Synthesis of potassium bis[2-(2-naphthyl)ethyl]diselenophosphinate (**4h**).



**Scheme 3.** Synthesis of bis[2-(2-naphthyl)ethyl]phosphine selenide (**5**).

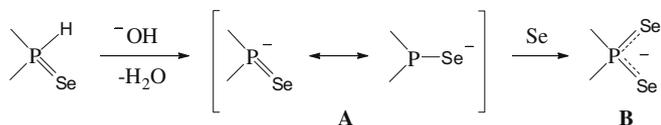


**Scheme 4.** Synthesis of potassium diphenyldiselenophosphinate (**4i**).

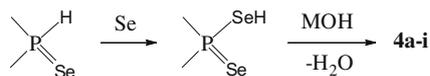
- In the <sup>31</sup>P NMR spectra, a singlet with a one typical satellite pair [8,10] was observed ( $J_{SeP} = 550-613$  Hz).
- The  $J_{SeP}$  value (550–613 Hz) was intermediate between the coupling constant values for P–Se and P=Se moieties (200–600 and 800–1200 Hz, respectively), thus corresponding to the 1.5 order of the phosphorus–selenium bonds [10].

Amazingly, alkali metal cation exerted no effect on both <sup>31</sup>P and <sup>77</sup>Se chemical shifts appeared, apparently due to a strong solvation of ions by the molecules of D<sub>2</sub>O upon recording the NMR spectra. At the same time, <sup>31</sup>P and <sup>77</sup>Se chemical shifts were noticeably sensitive towards insignificant changes in organic moieties structure (the corresponding shifts ranged from 21.61 to 26.92 ppm and from –35.82 to –68.85 ppm for <sup>31</sup>P and <sup>77</sup>Se, respectively).

The IR spectra and elemental analysis of all the compounds isolated correspond to their structures. So, the IR spectra of the diselenophosphinates **4a-i**, showed strong absorption bands at 540–570



**Scheme 5.** The deprotonation of secondary phosphine selenides first step of the synthesis of salts (**4**).



**Scheme 6.** The oxidation of secondary phosphine selenides by elemental selenium as a possible initial step of the synthesis of salts **4**.

and 470–490  $\text{cm}^{-1}$  which can be ascribed to the asymmetric ( $\nu_{\text{as}}$ ) and symmetric ( $\nu_{\text{s}}$ ) stretching vibrations of the  $\text{PSe}_2$  groups.

The first step of the reaction was assumed to be the deprotonation of the molecule of secondary phosphine selenides by the hydroxide-anion to generate the anion **A** which further cleaved the Se–Se bond of the elemental selenium, finely delivering diselenophosphinate-anions **B** (Scheme 5).

The easy deprotonation of secondary phosphine selenides should be due to their known enhanced PH-acidity.

An alternative for the first step might also be the oxidation of secondary phosphine selenides by the elemental selenium to form diselenophosphinic acids which were instantly neutralized by the alkali metal hydroxides (Scheme 6). The latter can function as a catalyst or a third component in the three-molecule collision (nucleophilic assistance).

### 3. Conclusions

An unusually rapid three-component reaction between secondary phosphine selenides, elemental selenium and alkali metal hydroxides to cleanly afford the corresponding salts of diselenophosphinic acids in almost quantitative yields (94–100%) has been discovered. The generality and preparative efficacy of the method developed have been demonstrated by the synthesis of earlier unknown series of Li, Na, K, Rb, Cs salts of diselenophosphinic acids bearing aralkyl- and aryl substituents as well as condensed aromatic moieties (2-naphthylethyl). The salts synthesized are promising intermediates to produce conducting nanomaterials and SSPs in metal organic vapor deposition to manufacture semiconducting thin films as well as building blocks for the design of diverse phosphorus–selenium organic compounds. Also, the alkali metal diselenophosphinates, easily synthesized from available starting materials, have a potential as indispensable source of other metal diselenophosphinates (particularly, heavy, rare earth and transition metals) through the exchange reaction with various metal derivatives.

### 4. Experimental

The  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{77}\text{Se}$  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) in  $\text{D}_2\text{O}$ ,  $\text{CDCl}_3$  or  $\text{DMSO}-d_6$  solutions and referenced to HMDS ( $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR),  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$  NMR) and  $\text{Me}_2\text{Se}$  ( $^{77}\text{Se}$  NMR). IR spectra were run on a Bruker IFS 25 instrument. All steps of the experiment were carried out in inert atmosphere (argon). Solvents were distilled prior to use.

Secondary phosphine selenides **1–3** were prepared from styrenes, red phosphorus and elemental selenium as described in the literature [9]. Diphenylphosphine selenide **6** was prepared by

oxidation of commercially available diphenylphosphine (Aldrich, 2008) with grey selenium. Bis[2-(2-naphthyl)ethyl]phosphine selenide **5** was synthesized here for the first time.

#### 4.1. Synthesis and characteristics of bis[2-(2-naphthyl)ethyl]phosphine selenide (**5**) (Scheme 3)

A suspension containing KOH (20 g),  $\text{H}_2\text{O}$  (3 mL) and DMSO (50 mL) was blown with argon and saturated with phosphine–hydrogen mixture, generated in a separate flask by addition of 50% aqueous solution of KOH (100 g) to a mixture of red phosphorus (20 g) in 40 mL of toluene at 70–75 °C. To the suspension obtained, 2-vinylnaphthalene (4.5 g, 29.18 mmol) stabilized with hydroquinone (0.02 g) in 20 mL of DMSO was added dropwise over 1 h 30 min at 60–65 °C (while bubbling phosphine at a rate of 68–70 bubbles/min), and phosphine was passed for additional 15 min under the same conditions. Next, the phosphine feeding was stopped, the system was blown with argon and was stirred additionally for 30 min. The reaction mixture was cooled to room temperature,  $\text{H}_2\text{O}$  was added (100 mL) and the solution obtained was extracted with toluene (100 mL  $\times$  1); the extract was washed with  $\text{H}_2\text{O}$  (30 mL  $\times$  2), filtered over  $\text{K}_2\text{CO}_3$ , the toluene was removed to give 4.35 g (87%) of bis[2-(2-naphthyl)ethyl]phosphine. To the latter, toluene (50 mL) and elemental selenium (1.00 g, 12.70 mmol) was added. The suspension obtained was stirred at 20–25 °C over 0.5 h, toluene was removed in vacuum to give 5.19 g (97%) phosphine selenide (**5**). Yellowish-brown oil. Anal. Calc. for  $\text{C}_{24}\text{H}_{23}\text{PSe}$ : C, 68.41; H, 5.50; P, 7.35; Se, 18.74. Found: C, 68.35; H, 5.61; P, 7.40; Se, 18.86%. IR (film,  $\text{cm}^{-1}$ ): 3051, 3021, 2925, 2858, 2334, 1952, 1804, 1631, 1599, 1508, 1445, 1367, 1271, 1124, 1018, 996, 950, 892, 858, 819, 796, 746, 476.  $^1\text{H}$  NMR (400.13 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.28–2.35 (m, 2H,  $\text{CH}_2\text{P}$ ), 2.38–2.49 (m, 2H,  $\text{CH}_2\text{P}$ ), 2.99–3.28 (m, 4H,  $\text{CH}_2\text{Naphthyl}$ ), 6.00 (d, 1H, PH,  $^1J_{\text{HP}} = 433.8$  Hz), 7.13–7.82 (m, 14 H, Naphthyl).  $^{13}\text{C}$  NMR (100.69 MHz,  $\text{CDCl}_3$ ):  $\delta$  29.86 (d,  $^2J_{\text{CP}} = 2.9$  Hz,  $\text{CH}_2\text{Naphthyl}$ ), 30.62 (d,  $^1J_{\text{CP}} = 43.5$  Hz,  $\text{CH}_2\text{P}$ ), 125.79–133.55 (Naphthyl), 136.88 and 136.98 (d,  $^3J_{\text{CP}} = 12.0$  Hz,  $\text{C}_2$ , Naphthyl).  $^{31}\text{P}$  NMR (161.98 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.27 ( $^1J_{\text{SeP}} = 710.6$  Hz).  $^{77}\text{Se}$  NMR (76.31 MHz,  $\text{CDCl}_3$ ):  $\delta$  –414.07 (d,  $^1J_{\text{SeP}} = 710.7$  Hz).

#### 4.2. Synthesis and characteristics of lithium and sodium salts **4a,b**: typical procedure (Scheme 1)

To a solution of secondary phosphine selenide **1** (0.200 g, 0.623 mmol) in THF (2 mL), amorphous grey selenium (0.049 g, 0.623 mmol) was added at room temperature under Ar. To the suspension, upon stirring, MOH (M = Li, Na, 0.623 mmol) in EtOH (6 mL) was added: selenium was dissolved instantly (~20–30 s) to give a colorless transparent solution. The solvents were removed under reduced pressure and the residue (colorless viscous oil with increments of solid particles) was dissolved in  $\text{Et}_2\text{O}$  (2 mL). After an evaporation of the solvent in vacuum (1 mm Hg, room temperature), the salts **4a,b** were obtained as crystals.

##### 4.2.1. Lithium salt of bis(2-phenethyl)phosphinodiselenic acid (**4a**)

Colorless solid. Yield: 0.243 g (96%), m.p. 99 °C. Anal. Calc. for  $\text{C}_{16}\text{H}_{18}\text{PSe}_2\text{Li}$ : C, 47.32; H, 4.47; P, 7.63; Se, 38.88. Found: C, 47.36; H, 4.55; P, 7.57; Se, 38.73%. IR (KBr,  $\text{cm}^{-1}$ ): 3066, 3023, 2921, 2848, 1948, 1880, 1805, 1743, 1619, 1601, 1584, 1495, 1453, 1441, 1398, 1318, 1265, 1209, 1190, 1178, 1155, 1123, 1065, 1029, 1004, 953, 925, 912, 835, 777, 764, 741, 725, 697, 568, 513, 479, 417.  $^1\text{H}$  NMR (400.13 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  2.11–2.17 (m, 4H,  $\text{CH}_2\text{P}$ ), 2.60–2.67 (m, 4H,  $\text{CH}_2\text{Ph}$ ), 6.96–7.01 (m, 10H, Ph).  $^{13}\text{C}$  NMR (100.69 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  29.78 ( $\text{CH}_2\text{Ph}$ ), 42.08 (d,  $^1J_{\text{CP}} = 35.4$  Hz,  $\text{CH}_2\text{P}$ ), 125.58 (*p*-C), 127.77 (*o*-C), 128.03 (*m*-C), 140.77 (d,  $^3J_{\text{CP}} = 16.0$  Hz, *i*-C).  $^{31}\text{P}$  NMR (161.98 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  26.66 (+d satel-

lite,  $^1J_{\text{SeP}} = 555.9$  Hz).  $^{77}\text{Se}$  NMR (76.31 MHz,  $\text{D}_2\text{O}$ ):  $\delta -66.75$  (d,  $^1J_{\text{SeP}} = 555.9$  Hz).

#### 4.2.2. Sodium salt of bis(2-phenethyl)phosphinodiselenoic acid (**4b**)

Colorless solid. Yield: 0.255 g (97%), m.p. 182 °C. Anal. Calc. for  $\text{C}_{16}\text{H}_{18}\text{PSe}_2\text{Na}$ : C, 45.52; H, 4.30; P, 7.34; Se, 37.40. Found: C, 45.56; H, 4.35; P, 7.43; Se, 37.43%. IR (KBr,  $\text{cm}^{-1}$ ): 3086, 3058, 3023, 2926, 2865, 1944, 1653, 1635, 1601, 1581, 1562, 1540, 1494, 1477, 1452, 1443, 1396, 1320, 1265, 1207, 1190, 1167, 1124, 1093, 1067, 1029, 1006, 951, 924, 907, 881, 834, 762, 739, 724, 696, 668, 618, 596, 568, 555, 512, 481, 434, 413.  $^1\text{H}$  NMR (400.13 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  2.19–2.26 (m, 4H,  $\text{CH}_2\text{P}$ ), 2.69–2.76 (m, 4H,  $\text{CH}_2\text{Ph}$ ), 6.94–7.08 (m, 10H, Ph).  $^{13}\text{C}$  NMR (100.69 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  30.68 ( $\text{CH}_2\text{Ph}$ ), 42.91 (d,  $^1J_{\text{CP}} = 35.9$  Hz,  $\text{CH}_2\text{P}$ ), 126.28 (*p*-C), 128.52 (*o*-C), 128.73 (*m*-C), 141.43 (d,  $^3J_{\text{CP}} = 16.1$  Hz, *i*-C).  $^{31}\text{P}$  NMR (161.98 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  26.83 (+d satellite,  $^1J_{\text{SeP}} = 559.1$  Hz).  $^{77}\text{Se}$  NMR (76.31 MHz,  $\text{D}_2\text{O}$ ):  $\delta = -61.07$  (d,  $^1J_{\text{SeP}} = 559.2$  Hz).

#### 4.3. Synthesis and characteristics of potassium, rubidium and caesium salts **4c–i**: typical procedure (Schemes 1, 2 and 4)

To a solution of secondary phosphine selenide (**2**, **3**, **5** or **6**) (0.623 mmol) in THF (4 mL), amorphous grey selenium (0.049 g, 0.623 mmol) was added at room temperature under Ar. To the suspension, upon stirring,  $\text{MOH} \cdot n\text{H}_2\text{O}$  ( $n = 0.5$  for K,  $n = 1$  for Rb and Cs; 0.623 mmol) in EtOH (3 mL) was added: selenium was dissolved instantly (~20–30 s) to give a colorless transparent solution. The solvents were removed under reduced pressure and the residue (colorless solid) was washed with  $\text{Et}_2\text{O}$  (2 mL), dried in vacuum (1 mm Hg, room temperature) to give the salts **4c–i**.

#### 4.3.1. Potassium salt of bis(2-phenethyl)phosphinodiselenoic acid (**4c**)

Colorless solid. Yield: 0.273 g (~100%), m.p. 209 °C. Anal. Calc. for  $\text{C}_{16}\text{H}_{18}\text{PSe}_2\text{K}$ : C, 43.84; H, 4.14; P, 7.07; Se, 36.03. Found: C, 43.90; H, 4.17; P, 7.19; Se, 36.10%. IR (KBr,  $\text{cm}^{-1}$ ): 3080, 3060, 3017, 2997, 2945, 2928, 2902, 2861, 1653, 1598, 1579, 1494, 1452, 1443, 1397, 1365, 1333, 1318, 1264, 1206, 1193, 1178, 1158, 1124, 1066, 1028, 1007, 956, 925, 912, 902, 862, 835, 774, 763, 752, 738, 712, 697, 572, 564, 521, 496, 484, 422.  $^1\text{H}$  NMR (400.13 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  2.13–2.19 (m, 4H,  $\text{CH}_2\text{P}$ ), 2.61–2.68 (m, 4H,  $\text{CH}_2\text{Ph}$ ), 6.80–6.88 (m, 10H, Ph).  $^{13}\text{C}$  NMR (100.69 MHz,  $\text{D}_2\text{O}$ ): 30.92 ( $\text{CH}_2\text{Ph}$ ), 42.99 (d,  $^1J_{\text{CP}} = 35.4$  Hz,  $\text{CH}_2\text{P}$ ), 126.27 (*p*-C), 128.45 (*o*-C), 128.71 (*m*-C), 141.32 (d,  $^3J_{\text{CP}} = 15.9$  Hz, *i*-C).  $^{31}\text{P}$  NMR (161.98 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  26.45 (+d satellite,  $^1J_{\text{SeP}} = 557.4$  Hz).  $^{77}\text{Se}$  NMR (76.31 MHz,  $\text{D}_2\text{O}$ ):  $\delta -63.09$  (d,  $^1J_{\text{SeP}} = 557.4$  Hz).

#### 4.3.2. Rubidium salt of bis(2-phenethyl)phosphinodiselenoic acid (**4d**)

Colorless solid. Yield: 0.296 g (98%), m.p. 202 °C. Anal. Calc. for  $\text{C}_{16}\text{H}_{18}\text{PSe}_2\text{Rb}$ : C, 39.65; H, 3.74; P, 6.39; Se, 32.58. Found: C, 39.66; H, 3.81; P, 6.48; Se, 32.49%. IR (KBr,  $\text{cm}^{-1}$ ): 3086, 3059, 3020, 2945, 2927, 2889, 2855, 1948, 1873, 1641, 1598, 1582, 1493, 1452, 1442, 1396, 1314, 1265, 1206, 1193, 1181, 1163, 1124, 1066, 1027, 1007, 955, 913, 862, 834, 763, 753, 737, 712, 696, 669, 571, 563, 520, 484, 420.  $^1\text{H}$  NMR (400.13 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  2.21–2.28 (m, 4H,  $\text{CH}_2\text{P}$ ), 2.71–2.78 (m, 4H,  $\text{CH}_2\text{Ph}$ ), 6.99–7.08 (m, 10H, Ph).  $^{13}\text{C}$  NMR (100.69 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  30.27 ( $\text{CH}_2\text{Ph}$ ), 42.52 (d,  $^1J_{\text{CP}} = 35.8$  Hz,  $\text{CH}_2\text{P}$ ), 125.92 (*p*-C), 128.15 (*o*-C), 128.37 (*m*-C), 141.06 (d,  $^3J_{\text{CP}} = 16.2$  Hz, *i*-C).  $^{31}\text{P}$  NMR (161.98 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  26.63 (+d satellite,  $^1J_{\text{SeP}} = 559.0$  Hz).  $^{77}\text{Se}$  NMR (76.31 MHz,  $\text{D}_2\text{O}$ ):  $\delta -61.58$  (d,  $^1J_{\text{SeP}} = 559.0$  Hz).

#### 4.3.3. Caesium salt of bis(2-phenethyl)phosphinodiselenoic acid (**4e**)

Colorless solid. Yield: 0.325 g (98%), m.p. 187 °C. Anal. Calc. for  $\text{C}_{16}\text{H}_{18}\text{PSe}_2\text{Cs}$ : C, 36.11; H, 3.41; P, 5.82; Se, 29.68. Found: C, 36.20; H, 3.35; P, 5.73; Se, 29.77%. IR (KBr,  $\text{cm}^{-1}$ ): 3097, 3080, 3059, 3021, 2997, 2946, 2926, 2898, 2855, 1654, 1597, 1579, 1493, 1453, 1441,

1396, 1315, 1265, 1206, 1193, 1180, 1159, 1144, 1123, 1066, 1027, 1008, 955, 929, 913, 862, 834, 753, 737, 712, 696, 571, 561, 519, 495, 483, 417.  $^1\text{H}$  NMR (400.13 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  2.42–2.46 (m, 4H,  $\text{CH}_2\text{P}$ ), 2.92–2.94 (m, 4H,  $\text{CH}_2\text{Ph}$ ), 7.22–7.31 (m, 10H, Ph).  $^{13}\text{C}$  NMR (100.69 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  30.61 ( $\text{CH}_2\text{Ph}$ ), 42.94 (d,  $^1J_{\text{CP}} = 35.6$  Hz,  $\text{CH}_2\text{P}$ ), 126.47 (*p*-C), 128.65 (*o*-C), 128.92 (*m*-C), 141.70 (d,  $^3J_{\text{CP}} = 15.8$  Hz, *i*-C).  $^{31}\text{P}$  NMR (161.98 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  26.92 (+d satellite,  $^1J_{\text{SeP}} = 555.2$  Hz).  $^{77}\text{Se}$  NMR (76.31 MHz,  $\text{D}_2\text{O}$ ):  $\delta -68.85$  (d,  $^1J_{\text{SeP}} = 555.0$  Hz).

#### 4.3.4. Rubidium salt of bis(2-phenylpropyl)phosphinodiselenoic acid (**4f**)

Colorless solid. Yield: 0.310 g (97%), m.p. 180–182 °C. Anal. Calc. for  $\text{C}_{18}\text{H}_{22}\text{PSe}_2\text{Rb}$ : C, 42.17; H, 4.32; P, 6.04; Se, 30.80. Found: C, 42.31; H, 4.34; P, 6.10; Se, 30.66%. IR (KBr,  $\text{cm}^{-1}$ ): 3091, 3069, 3028, 2961, 2924, 2870, 1953, 1886, 1812, 1750, 1630, 1611, 1491, 1450, 1397, 1312, 1232, 1195, 1152, 1084, 1038, 1020, 1002, 910, 841, 804, 761, 701, 672, 534, 492, 460.  $^1\text{H}$  NMR (400.13 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  1.32 and 1.39 (d,  $^2J_{\text{HH}} = 6.7$  Hz, Me), 2.17–2.32 (m, 2H,  $\text{CH}_2\text{P}$ ), 2.39–2.52 (m, 2H,  $\text{CH}_2\text{P}$ ), 3.35–3.48 (m, 2H, CHPh), 7.15–7.28 (m, 10H, Ph).  $^{13}\text{C}$  NMR (100.69 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  23.49 and 23.84 (d,  $^3J_{\text{CP}} = 9.7$  and  $^3J_{\text{CP}} = 9.2$  Hz, Me), 36.96 and 37.05 (CHPh), 49.04 and 49.31 (d,  $^1J_{\text{CP}} = 32.6$  and  $^1J_{\text{CP}} = 35.3$  Hz,  $\text{CH}_2\text{P}$ ), 125.88 (*p*-C), 126.86 and 126.97 (*o*-C), 128.21 (*m*-C), 147.04 and 147.10 (d,  $^3J_{\text{CP}} = 11.3$  and  $^3J_{\text{CP}} = 11.9$  Hz, *i*-C).  $^{31}\text{P}$  NMR (161.98 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  24.88 and 26.01 (two singlets in ratio 3:1), (+d satellite,  $^1J_{\text{SeP}} = 556.9$  Hz and  $^1J_{\text{SeP}} = 550.0$  Hz).  $^{77}\text{Se}$  NMR (76.31 MHz,  $\text{D}_2\text{O}$ ):  $\delta -62.44$  (d,  $^1J_{\text{SeP}} = 564.5$  Hz),  $-26.13$  (d,  $^1J_{\text{SeP}} = 556.9$  Hz),  $-6.28$  (d,  $^1J_{\text{SeP}} = 550.0$  Hz).

#### 4.3.5. Potassium salt of bis[(4-tertbutyl)phenethyl]phosphinodiselenoic acid (**4g**)

Colorless solid. Yield: 0.343 g (~100%) m.p. 186 °C. Anal. Calc. for  $\text{C}_{24}\text{H}_{34}\text{PSe}_2\text{K}$ : C, 52.36; H, 6.23; P, 5.63; Se, 28.69. Found: C, 52.32; H, 6.30; P, 5.71; Se, 28.50%. IR (KBr,  $\text{cm}^{-1}$ ): 3092, 3055, 3023, 2961, 2903, 2865, 1905, 1793, 1627, 1516, 1462, 1439, 1393, 1363, 1268, 1202, 1136, 1108, 1067, 1018, 943, 875, 853, 839, 813, 770, 738, 663, 563, 517, 495.  $^1\text{H}$  NMR (400.13 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  1.26 (s, 6H, Me), 2.37–2.53 (m, 4H,  $\text{CH}_2\text{P}$ ), 2.86–3.04 (m, 4H,  $\text{CH}_2\text{C}_6\text{H}_4$ ), 7.13–7.35 (m, 8H,  $\text{C}_6\text{H}_4$ ).  $^{13}\text{C}$  NMR (100.69 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  30.66 ( $\text{CH}_2\text{C}_6\text{H}_4$ ), 31.44 (Me), 32.38 (d,  $\text{CH}_2\text{P}$ ,  $^1J_{\text{CP}} = 41.7$  Hz), 34.39 (CMe), 125.45 ( $\text{C}_2$ ,  $\text{C}_6\text{H}_4$ ), 128.32 ( $\text{C}_3$ ,  $\text{C}_6\text{H}_4$ ), 138.04 (d,  $\text{C}_1$ ,  $\text{C}_6\text{H}_4$ ,  $^3J_{\text{CP}} = 15.7$  Hz), 148.95 ( $\text{C}_4$ ,  $\text{C}_6\text{H}_4$ ).  $^{31}\text{P}$  NMR (161.98 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  25.42 (+d satellite,  $^1J_{\text{SeP}} = 558.8$  Hz).  $^{77}\text{Se}$  NMR (76.31 MHz,  $\text{D}_2\text{O}$ ):  $\delta -65.45$  (d,  $^1J_{\text{SeP}} = 558.6$  Hz).

#### 4.3.6. Potassium salt of bis[2-(2-naphthyl)ethyl]phosphinodiselenoic acid (**4h**)

Yellowish solid. Yield: 0.316 g (94%), m.p. 192–194 °C. Anal. Calc. for  $\text{C}_{24}\text{H}_{22}\text{PSe}_2\text{K}$ : C, 53.54; H, 4.12; P, 5.75; Se, 29.33. Found: C, 53.58; H, 4.18; P, 5.63; Se, 29.43%. IR (KBr,  $\text{cm}^{-1}$ ): 3049, 3016, 2936, 2891, 2848, 1699, 1629, 1598, 1507, 1435, 1393, 1366, 1273, 1197, 1185, 1164, 1125, 1017, 964, 948, 928, 902, 888, 860, 828, 817, 785, 766, 748, 737, 711, 689, 666, 637, 621, 546, 508, 478, 397.  $^1\text{H}$  NMR (400.13 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  2.35–2.42 (m, 4H,  $\text{CH}_2\text{P}$ ), 3.11–3.18 (m, 4H,  $\text{CH}_2\text{Naphthyl}$ ) 7.34–7.83 (m, 14H, Naphthyl).  $^{13}\text{C}$  NMR (100.69 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  31.43 ( $\text{CH}_2\text{Naphthyl}$ ), 45.33 (d,  $^1J_{\text{CP}} = 36.6$  Hz,  $\text{CH}_2\text{P}$ ), 125.60–133.79 (Naphthyl), 140.79 (d,  $^3J_{\text{CP}} = 15.8$  Hz,  $\text{C}_2$ , Naphthyl).  $^{31}\text{P}$  NMR (161.98 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  23.76 (+d satellite,  $^1J_{\text{SeP}} = 612.8$  Hz).  $^{77}\text{Se}$  NMR (76.31 MHz,  $\text{DMSO}-d_6$ ):  $\delta -35.82$  (d,  $^1J_{\text{SeP}} = 612.8$  Hz).

#### 4.3.7. Potassium salt of diphenylphosphinodiselenoic acid (**4i**)

Colorless solid. Yield: 0.226 g (95%) m.p. 134 °C. Anal. Calc. for  $\text{C}_{12}\text{H}_{10}\text{PSe}_2\text{K}$ : C, 37.71; H, 2.64; P, 8.10; Se, 41.32. Found: C, 37.78; H, 2.70; P, 7.95; Se, 41.43%. IR (KBr,  $\text{cm}^{-1}$ ): 3052, 2079,

1819, 1628, 1471, 1429, 1395, 1335, 1299, 1171, 1122, 1086, 1060, 1027, 995, 748, 694, 587, 540, 478.  $^1\text{H}$  NMR (400.13 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  7.82–7.87 (m, 10H, Ph).  $^{13}\text{C}$  NMR (100.69 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  128.19 and 128.31 (o-C), 130.62 (m-C), 130.74 (p-C), 140.07 (d,  $^1J_{\text{CP}} = 65.9$  Hz, i-C).  $^{31}\text{P}$  NMR (161.98 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  21.61 (+d satellite,  $^1J_{\text{SeP}} = 582.8$  Hz).

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