Rapid and Convenient One-Pot Method for the Preparation of Alkali Metal Phosphinodiselenoates

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Abstract: Alkali metal phosphinodiselenoates, R_2PSe_2M (R = aralkyl, hetaralkyl, Ph; M = Li, Na, K, Rb, Cs), were synthesized in high yields (up to 98%) by a three-component reaction of a secondary phosphine, elemental selenium, and an alkali metal hydroxide under mild conditions (ethanol, room temperature, 5 min).

Key words: phosphorus, selenium, alkali metals, three-component reactions, phosphinodiselenoates, alkali metal salts

Phosphinodithioates are widely used as lubricant oil additives[1] and extraction agents for separation procedures.[2] In addition, they have been shown to exhibit a broad variety of coordination patterns, leading to a wide range of molecular and supramolecular structures.[3] Recently, the chemistry of the phosphinodithioate analogues, the phosphinodiselenoates, has attracted particular attention because of their potential and actual applications as single-source precursors (SSPs) of magneto-optically and photochemically active materials,[4] ligands for metal complexes,[5] promising extractants for heavy elements,[6] potential pharmaceuticals,[7] and proton conductors. For example, heavy metal phosphinodiselenoates are now used as efficient SSPs for the preparation of nanoparticles of metal phosphides or selenides that possess many unique properties.[8] Nickel dialkylphosphinodiselenoates are used for the synthesis of nickel phosphide or nickel selenide nanoparticles.[9] Silver phosphinodiselenoate is used as an SSP for the production of silver selenide nanofilms.[10] Europium phosphinodiselenoates are actively used to produce europium selenide nanocrystals that show remarkable magneto-optical properties.[11] Nanorods of zinc selenide exhibiting semiconductive properties have been synthesized from zinc phosphinodiselenoate.[12] In 2010, O'Brien et. al.[13] described a one-pot synthesis of nanoparticles of cobalt diselenide, cobalt phosphide, or dicobalt phosphide from cobalt phosphinodiselenoates, $[Co(Se_2PR_2)_2]$.

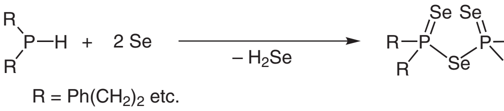
The convenient syntheses of heavy metal phosphinodiselenoates are based on the reactions of alkali metal phosphinodiselenoates with heavy metal halides.[5,9,12–14] Alkali metal phosphinodiselenoates are also key intermediates for preparing esters of phosphinodiselenoic acids,[15] which are efficient iniferters[16] and potential pesticides.[17]

Conventional syntheses of alkali metal phosphinodiselenoates are laborious, require many steps, and require the use of aggressive and poisonous phosphorus halides and flammable unstable organometallic compounds as reactants.[18] Moreover, these methods have been limited to preparations of lithium, sodium, and potassium phosphinodiselenoates.[18]

In 2009, a brief report appeared on the synthesis of potassium diphenylphosphinodiselenoate from a metalated diphenylphosphine (Ph_2PK) by treatment with elemental selenium in tetrahydrofuran at room temperature for seven hours under an inert atmosphere.[11c] The method is tedious, requires an especially pure anhydrous solvent, and permits only the preparation of the potassium salt.[11c]

One of the most convenient approaches for the synthesis of alkali metal phosphinodiselenoates involves the reaction of a secondary phosphine selenide with elemental selenium and an alkali metal hydroxide.[19]

Here we report, for the first time, a three-component reaction of a secondary phosphine with two equivalents of elemental selenium and an alkali metal hydroxide. The realization of such reaction was problematic, since secondary phosphines are known to react with two equivalents of elemental selenium to furnish bis(diorganoselenophosphoryl)selenides[20] (Scheme 1).



Scheme 1 Reaction of secondary phosphines with elemental selenium

As our experiments showed, however, the secondary phosphines **1**–**10** reacted readily and unusually rapidly (5 min) with elemental selenium and alkali metal hydroxides MOH (M = Li, Na, K, Rb, Cs) in ethanol at room temperature to afford the corresponding phosphinodiselenoates **11a**–**p** in high yields (Table 1).

The reaction is general in character in that its efficiency is retained even when such sterically hindered secondary phosphines as **2**–**4** and **6** are used, and the phosphinodiselenoates **11a**–**n** are all obtained in high yield. The gener-

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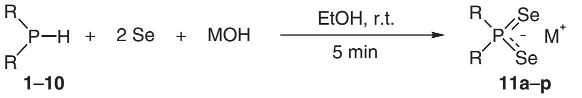
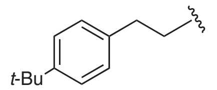
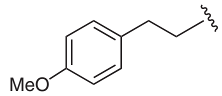
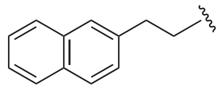
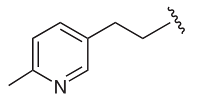
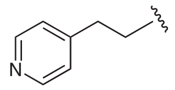
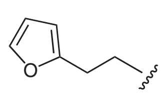
Table 1 Synthesis of Phosphinodiselenoates from Secondary Phosphines, Elemental Selenium, and Alkali Metal Hydroxides



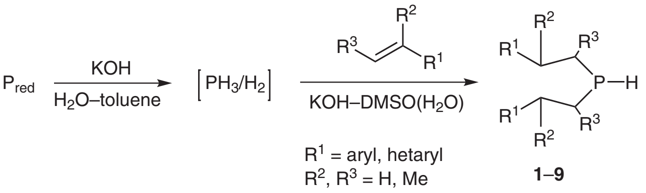
Entry	Phosphine[a]	R	MOH	Product	Yield (%)[b]
1	**1**	$(CH_2)_2Ph$	LiOH	**11a**	93
2	**1**	$(CH_2)_2Ph$	NaOH	**11b**	97
3	**1**	$(CH_2)_2Ph$	KOH	**11c**	95
4	**1**	$(CH_2)_2Ph$	RbOH	**11d**	92
5	**1**	$(CH_2)_2Ph$	CsOH	**11e**	98
6	**2**	$CH_2CH(Me)Ph$	KOH	**11f**	88
7	**2**	$CH_2CH(Me)Ph$	RbOH	**11g**	97
8	**3**	$CH(Me)CH_2Ph$	KOH	**11h**	81
9	**4**		KOH	**11i**	92
10	**5**		KOH	**11j**	89
11	**6**		KOH	**11k**	94
12	**7**		CsOH	**11l**	96
13	**8**		NaOH	**11m**	93
14	**9**		CsOH	**11n**	96
15	**10**	Ph	KOH	**11o**	92
16	**10**	Ph	CsOH	**11p**	94

[a] Reaction conditions: phosphine **1**–**10** (1.05 mmol), Se (2.0 mmol), MOH (1.0 mmol), EtOH, r.t., 5 min.

[b] Yield of the isolated product.

ality and efficiency of the approach were further demonstrated by the synthesis of the potassium and rubidium salts of diphenylphosphinodiselenoic acid (**11o** and **11p**, respectively) from diphenylphosphine (**10**).

The choice of the initial secondary phosphines **1–9** was not arbitrary; these phosphines are readily available in one step by treatment of red phosphorus with vinylarenes or vinylhetarenes (e.g., styrenes,[21] vinylpyridines,[22] 2-vinylnaphthalene,[23] or 2-vinylfuran[21a]) (Scheme 2).



Scheme 2 One-step synthesis of the initial secondary phosphines from red phosphorus and vinylarenes or vinylhetarenes

In summary, we have developed a one-pot, general, and efficient method for the synthesis of alkali metal (Li, Na, K, Rb, or Cs) phosphinodiselenoates in high yields from readily available secondary phosphines, elemental selenium, and alkali metal hydroxides under environmentally friendly conditions (commercial ethanol as a nontoxic recoverable solvent, room temperature, 5 min). The salts that are obtained can serve as SSPs for the preparation of magneto-optical and semiconducting nanomaterials, ligands for the design of coordination structures, extractants for heavy elements, or reactive building blocks for synthesis.

The ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra were recorded on Bruker DPX 400 and Bruker AV-400 spectrometers at 400.13, 100.61, 161.98, and 76.31 MHz, respectively, and are referenced to H_3PO_4 (^{31}P NMR) or Me_2Se (^{77}Se NMR). IR spectra were recorded on a Bruker IFS 25 instrument. All melting points were measured on a Kofler micro hot-stage apparatus. Secondary phosphines **1**–**9** were prepared from red phosphorus and styrene,[21a] α-methylstyrene,[21a] β-methylstyrene, 4-*tert*-butylstyrene,[21b] 4-methoxystyrene, 2-vinylnaphthalene,[23] 4-vinylpyridine,[22] 2-methyl-5-vinylpyridine[22] or 2-vinylfuran,[21a] as described in the literature. Ph_2PH (**10**) was a commercial product (Aldrich). Commercial EtOH was used as the reaction solvent. All steps of the syntheses were carried out under an argon atmosphere.

Alkali Metal Phosphinodiselenoates (11a–p); General Procedure

A soln of $MOH \cdot nH_2O$ ($n = 0$ for Li and Na; $n = 0.5$ for K; $n = 1$ for Rb and Cs; 1.0 mmol) in EtOH (5 mL) and amorphous grey Se (0.158 g, 2.0 mmol) were added sequentially to a soln of the secondary phosphine **1**–**10** (1.05 mmol) in EtOH (6 mL) at r.t. under Ar. The suspension was stirred vigorously at r.t. until the Se residue completely dissolved (~5 min), and the colorless soln was filtered and concentrated. The residue was ground in Et_2O (10 mL), and the solvent was decanted to give a white crystalline powder that was washed with Et_2O (1 × 10 mL) and dried in vacuo (1 Torr, 35–40 °C).

Lithium Bis(2-phenylethyl)phosphinodiselenoate (11a)

White powder; yield: 0.378 g (93%); mp 99–100 °C (Et_2O).

IR (KBr): 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 cm^{-1}.

^{1}H NMR (400.13 MHz, D_2O): $\delta = 2.11–2.17$ (m, 4 H, CH_2P), 2.60–2.67 (m, 4 H, CH_2Ph), 6.96–7.01 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, D_2O): $\delta = 29.78$ (CH_2Ph), 42.08 (d, $^{1}J_{CP} = 35.4$ Hz, CH_2P), 125.58 (*p*-C), 127.77 (*o*-C), 128.03 (*m*-C), 140.77 (d, $^{3}J_{CP} = 16.0$ Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, D_2O): $\delta = 26.66$ (s + d satellites, $^{1}J_{PSe} = 556$ Hz).

^{77}Se NMR (76.31 MHz, D_2O): $\delta = -67$ (d, $^{1}J_{PSe} = 556$ Hz).

Anal. Calcd for $C_{16}H_{18}LiPSe_2$: 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.

Sodium Bis(2-phenylethyl)phosphinodiselenoate (11b)

White powder; yield: 0.410 g (97%); mp 182–184 °C (Et_2O).

IR (KBr): 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 cm^{-1}.

^1H NMR (400.13 MHz, D_2O): δ = 2.19–2.26 (m, 4 H, CH_2P), 2.69–2.76 (m, 4 H, CH_2Ph), 6.94–7.08 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, D_2O): δ = 30.68 (*C*H_2Ph), 42.91 (d, $^1J_{CP}$ = 35.9 Hz, CH_2P), 126.28 (*p*-C), 128.52 (*o*-C), 128.73 (*m*-C), 141.43 (d, $^3J_{CP}$ = 16.1 Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, D_2O): δ = 26.83 (s + d satellites, $^1J_{PSe}$ = 559 Hz).

^{77}Se NMR (76.31 MHz, D_2O): δ = –61 (d, $^1J_{PSe}$ = 559 Hz).

Anal. Calcd for $C_{16}H_{18}NaPSe_2$: 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.

Potassium Bis(2-phenylethyl)phosphinodiselenoate (11c)

White powder; yield: 0.416 g (95%); mp 209–211 °C (Et_2O).

IR (KBr): 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 cm^{-1}.

^1H NMR (400.13 MHz, D_2O): δ = 2.13–2.19 (m, 4 H, CH_2P), 2.61–2.68 (m, 4 H, CH_2Ph), 6.80–6.88 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, D_2O): δ = 30.92 (*C*H_2Ph), 42.99 (d, $^1J_{CP}$ = 35.4 Hz, CH_2P), 126.27 (*p*-C), 128.45 (*o*-C), 128.71 (*m*-C), 141.32 (d, $^3J_{CP}$ = 15.9 Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, D_2O): δ = 26.45 (s + d satellites, $^1J_{PSe}$ = 557 Hz).

^{77}Se NMR (76.31 MHz, D_2O): δ = –63 (d, $^1J_{PSe}$ = 557 Hz).

Anal. Calcd for $C_{16}H_{18}KPSe_2$: 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.

Rubidium Bis(2-phenylethyl)phosphinodiselenoate(11d)

White powder; yield: 0.446 g (92%); mp 202–204 °C (Et_2O).

IR (KBr): 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 cm^{-1}.

^1H NMR (400.13 MHz, D_2O): δ = 2.21–2.28 (m, 4 H, CH_2P), 2.71–2.78 (m, 4 H, CH_2Ph), 6.99–7.08 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, D_2O): δ = 30.27 (*C*H_2Ph), 42.52 (d, $^1J_{CP}$ = 35.8 Hz, CH_2P), 125.92 (*p*-C), 128.15 (*o*-C), 128.37 (*m*-C), 141.06 (d, $^3J_{CP}$ = 16.2 Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, D_2O): δ = 26.63 (s + d satellites, $^1J_{PSe}$ = 559 Hz).

^{77}Se NMR (76.31 MHz, D_2O): δ = –62 (d, $^1J_{PSe}$ = 559 Hz).

Anal. Calcd for $C_{16}H_{18}PRbSe_2$: 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.

Cesium Bis(2-phenylethyl)phosphinodiselenoate (11e)

White powder; yield: 0.520 g (98%); mp 187–189 °C (Et_2O).

IR (KBr): 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 cm^{-1}.

^1H NMR (400.13 MHz, D_2O): δ = 2.42–2.46 (m, 4 H, CH_2P), 2.92–2.94 (m, 4 H, CH_2Ph), 7.22–7.31 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, D_2O): δ = 30.61 (*C*H_2Ph), 42.94 (d, $^1J_{CP}$ = 35.6 Hz, CH_2P), 126.47 (*p*-C), 128.65 (*o*-C), 128.92 (*m*-C), 141.70 (d, $^3J_{CP}$ = 15.8 Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, D_2O): δ = 26.92 (s + d satellites, $^1J_{PSe}$ = 555 Hz).

^{77}Se NMR (76.31 MHz, D_2O): δ = –69 (d, $^1J_{PSe}$ = 555 Hz).

Anal. Calcd for $C_{16}H_{18}CsPSe_2$: 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.

Potassium Bis(2-phenylpropyl)phosphinodiselenoate (11f)

White powder; yield: 0.410 g (88%); mp 198–200 °C (Et_2O).

IR (KBr): 3081, 3060, 3025, 2958, 2923, 2868, 1948, 1880, 1811, 1756, 1734, 1698, 1639, 1601, 1493, 1480, 1450, 1370, 1394, 1312, 1283, 1234, 1197, 1182, 1148, 1087, 1075, 1061, 1048, 1028, 1005, 994, 911, 882, 845, 829, 764, 746, 730, 700, 677, 563, 545, 533, 490, 462, 445 cm^{-1}.

^1H NMR (400.13 MHz, D_2O): δ = 0.98 and 1.05 (d, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 7.3 Hz, 6 H, Me), 1.84–1.98 (m, 2 H, CH_2P), 2.05–2.19 (m, 2 H, CH_2P), 3.02–3.14 (m, 2 H, CHPh), 6.79–6.95 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, D_2O): δ = 23.91 and 24.32 (d, $^3J_{CP}$ = 9.2 and 9.0 Hz, Me), 37.37 and 37.50 (*C*HPh), 49.50 and 49.72 (d, $^1J_{CP}$ = 34.6 and 35.0 Hz, CH_2P), 126.24 (*p*-C), 127.25 and 127.36 (*o*-C), 128.58 (*m*-C), 147.36 and 147.45 (d, $^3J_{CP}$ = 12.5 and 12.0 Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, D_2O): δ = 25.85 and 27.03 (ratio 1:2) (s + d satellites, $^1J_{PSe}$ = 557 and 559 Hz).

^{77}Se NMR (76.31 MHz, D_2O): δ = –64, –28, and –6 (d, $^1J_{PSe}$ = 564, 557, and 559 Hz).

Anal. Calcd for $C_{18}H_{22}KPSe_2$: C, 46.36; H, 4.75; P, 6.64; Se, 33.86. Found: C, 46.31; H, 4.69; P, 6.48; Se, 33.71.

Rubidium Bis(2-phenylpropyl)phosphinodiselenoate (11g)

White powder; yield: 0.497 g (97%); mp 180–182 °C (Et_2O).

IR (KBr): 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 cm^{-1}.

^1H NMR (400.13 MHz, D_2O): δ = 1.32 and 1.39 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, Me), 2.17–2.32 (m, 2 H, CH_2P), 2.39–2.52 (m, 2 H, CH_2P), 3.35–3.48 (m, 2 H, CHPh), 7.15–7.28 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, D_2O): δ = 23.49 and 23.84 (d, $^3J_{CP}$ = 9.7 and 9.2 Hz, Me), 36.96 and 37.05 (*C*HPh), 49.04 and 49.31 (d, $^1J_{CP}$ = 32.6 and 35.3 Hz, CH_2P), 125.88 (*p*-C), 126.86 and 126.97 (*o*-C), 128.21 (*m*-C), 147.04 and 147.10 (d, $^3J_{CP}$ = 11.3 and 11.9 Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, D_2O): δ = 24.88 and 26.01 (ratio 3:1) (s + d satellites, $^1J_{PSe}$ = 557 Hz and 550 Hz).

^{77}Se NMR (76.31 MHz, D_2O): δ = –62, –26, and –6 (d, $^1J_{PSe}$ = 564, 557 and 550 Hz).

Anal. Calcd for $C_{18}H_{22}RbPSe_2$: C, 42.17; H, 4.32; P, 6.04; Se, 30.80. Found: C, 42.25; H, 4.34; P, 6.10; Se, 30.66.

Potassium Bis(1-methyl-2-phenylethyl)phosphinodiselenoate (11h)

White powder; yield: 0.378 g (81%); mp >200 °C (dec.)

IR (KBr): 3102, 3081, 3061, 3024, 3000, 2961, 2860, 1601, 1582, 1494, 1452, 1359, 1336, 1315, 1286, 1204, 1170, 1158, 1092, 1049, 1028, 990, 913, 898, 862, 825, 756, 705, 682, 621, 574, 536, 503, 488, 425 cm^{-1}.

^{1}H NMR (400.13 MHz, D_2O): δ = 0.80, 0.85 and 0.90 (d, $^3J_{HH}$ = 6.8 and 6.3 Hz, 6 H, Me), 2.05–2.18 and 2.32–2.44 (m, 4 H, CH_2Ph), 3.02–3.08 and 3.21–3.27 (m, 2 H, CHP), 6.95–7.09 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, D_2O): δ = 15.85 and 15.97 (Me), 39.50 (CH_2Ph), 42.68 and 42.74 (d, $^1J_{CP}$ = 30.8 and 33.4 Hz, CHP), 128.60 and 128.70 (*p*-C), 130.96 and 131.01 (*o*-C), 131.86 (*m*-C), 142.60 and 142.67 (d, $^3J_{CP}$ = 14.7 and 16.6 Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, D_2O): δ = 67.67 and 67.79 (ratio 1:2) (s + d satellites, $^1J_{PSe}$ = 571 and 569 Hz).

^{77}Se NMR (76.31 MHz, D_2O): δ = –158 (d, $^1J_{PSe}$ = 569 Hz).

Anal. Calcd for $C_{18}H_{22}KPSe_2$: C, 46.36; H, 4.75; P, 6.64; Se, 33.86. Found: C, 46.31; H, 4.70; P, 6.50; Se, 33.69.

Potassium Bis[2-(4-*tert*-butylphenyl)ethyl]phosphinodiselenoate (11i)

White powder; yield: 0.506 g (92%); mp 185–187 °C (Et_2O).

IR (KBr): 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 cm^{-1}.

^{1}H NMR (400.13 MHz, D_2O): δ = 1.26 (s, 18 H, Me), 2.37–2.53 (m, 4 H, CH_2P), 2.86–3.04 (m, 4 H, $CH_2C_6H_4$), 7.13–7.35 (m, 8 H, C_6H_4).

^{13}C NMR (100.61 MHz, D_2O): δ = 30.66 ($CH_2C_6H_4$), 31.44 (Me_3C), 32.38 (d, $^1J_{CP}$ = 41.7 Hz, CH_2P), 34.39 (CMe_3), 125.45 (C2 in C_6H_4), 128.32 (C3 in C_6H_4), 138.04 (d, $^3J_{CP}$ = 15.7 Hz, C1 in C_6H_4,), 148.95 (C4 in C_6H_4).

^{31}P NMR (161.98 MHz, D_2O): δ = 25.42 (s + d satellites, $^1J_{PSe}$ = 559 Hz).

^{77}Se NMR (76.31 MHz, D_2O): δ = –65 (d, $^1J_{PSe}$ = 559 Hz).

Anal. Calcd for $C_{24}H_{34}KPSe_2$: 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.

Potassium Bis[2-(4-methoxyphenyl)ethyl]phosphinodiselenoate (11j)

White powder; yield: 0.444 g (89%); mp 190–193 °C (Et_2O).

IR (KBr): 3057, 3027, 3000, 2955, 2932, 2909, 2834, 2057, 1883, 1610, 1583, 1512, 1463, 1443, 1371, 1300, 1266, 1244, 1179, 1130, 1099, 1060, 1032, 945, 878, 848, 814, 779, 729, 706, 672, 636, 548, 509, 491, 474, 456, 421, 411 cm^{-1}.

^{1}H NMR (400.13 MHz, D_2O): δ = 2.03–2.13 (m, 4 H, CH_2P), 2.50–2.60 (m, 4 H, $CH_2C_6H_4$), 3.36 (s, 6 H, OMe), 6.49–6.80 (m, 8 H, C_6H_4).

^{13}C NMR (100.61 MHz, D_2O): δ = 29.19 ($CH_2C_6H_4$), 42.27 (d, $^1J_{CP}$ = 34.5 Hz, CH_2P), 54.64 (OMe), 113.36 (C2 in C_6H_4), 128.91 (C3 in C_6H_4), 133.10 (d, $^3J_{CP}$ = 15.0 Hz, C1 in C_6H_4,), 156.50 (C4 in C_6H_4).

^{31}P NMR (161.98 MHz, D_2O): δ = 27.07 (s + d satellites, $^1J_{PSe}$ = 558 Hz).

^{77}Se NMR (76.31 MHz, D_2O): δ = –39 (d, $^1J_{PSe}$ = 558 Hz).

Anal. Calcd for $C_{18}H_{22}KO_2PSe_2$: C, 43.38; H, 4.45; P, 6.22; Se, 31.69. Found: C, 43.31; H, 4.50; P, 6.34; Se, 31.71.

Potassium bis[2-(2-naphthyl)ethyl]phosphinodiselenoate (11k)

Yellowish powder; yield: 0.506 g (94%); mp 192–194 °C (Et_2O).

IR (KBr): 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 cm^{-1}.

^{1}H NMR (400.13 MHz, DMSO-d_6): δ = 2.35–2.42 (m, 4 H, CH_2P), 3.11–3.18 (m, 4 H, CH_2Naphth), 7.34–7.45, 7.65 and 7.77–7.83 (m, 14 H, Naphth).

^{13}C NMR (100.61 MHz, DMSO-d_6): δ = 31.43 (CH_2Naphth), 45.33 (d, $^1J_{CP}$ = 36.6 Hz, CH_2P), 125.60–133.79 (Naphth), 140.79 (d, $^3J_{CP}$ = 15.8 Hz, Naphth).

^{31}P NMR (161.98 MHz, DMSO-d_6): δ = 23.76 (s + d satellites, $^1J_{PSe}$ = 613 Hz).

^{77}Se NMR (76.31 MHz, DMSO-d_6): δ = –36 (d, $^1J_{PSe}$ = 613 Hz).

Anal. Calcd for $C_{24}H_{22}KPSe_2$: 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.

Cesium Bis[2-(6-methylpyridin-3-yl)ethyl]phosphinodiselenoate (11l)

Yellowish powder; yield: 0.540 g (96%); mp 189–191 °C (dec.) (Et_2O).

IR (KBr): 3020, 3000, 2959, 2939, 2923, 2911, 2855, 1966, 1698, 1654, 1603, 1567, 1489, 1439, 1395, 1377, 1319, 1306, 1298, 1275, 1247, 1206, 1185, 1146, 1120, 1109, 1035, 1013, 1003, 985, 954, 932, 916, 858, 838, 793, 774, 739, 722, 705, 647, 542, 515, 482, 416 cm^{-1}.

^{1}H NMR (400.13 MHz, D_2O): δ = 2.16–2.22 (m, 10 H, CH_2P, Me), 2.65–2.73 (m, 4 H, CH_2Py), 6.90 (d, 2 H, Py), 7.29 (d, 2 H, Py), 7.97 (s, 2 H, Py).

^{13}C NMR (100.61 MHz, D_2O): δ = 22.10 (Me), 27.14 (CH_2Py), 42.04 (d, $^1J_{CP}$ = 36.0 Hz, CH_2P), 123.53, 133.78 (d, $^3J_{CP}$ = 15.8 Hz, Py), 137.41, 147.32 and 155.35 (Py).

^{31}P NMR (161.98 MHz, D_2O): δ = 26.18 (s + d satellites, $^1J_{PSe}$ = 563 Hz).

^{77}Se NMR (76.31 MHz, D_2O): δ = –68 (d, $^1J_{PSe}$ = 563 Hz).

Anal. Calcd for $C_{16}H_{20}CsN_2PSe_2$: C, 34.19; H, 3.59; P, 5.51; Se, 28.09. Found: C, 34.22; H, 3.65; P, 5.34; Se, 28.19.

Sodium Bis(2-pyridin-4-ylethyl)phosphinodiselenoate (11m)

White powder; yield: 0.394 g (93%); mp >200 °C (dec.).

IR (KBr): 3070, 3041, 3023, 2994, 2968, 2925, 2900, 1606, 1557, 1501, 1446, 1421, 1398, 1347, 1316, 1279, 1217, 1192, 1142, 1081, 1072, 999, 948, 878, 856, 843, 830, 808, 777, 757, 738, 724, 669, 581, 521, 484, 423, 414 cm^{-1}.

^{1}H NMR (400.13 MHz, D_2O): δ = 2.37–2.44 (m, 4 H, CH_2P), 2.90–2.97 (m, 4 H, CH_2Py), 7.21 and 8.28 (d, 8 H, Py).

^{13}C NMR (100.61 MHz, D_2O): δ = 29.98 (CH_2Py), 41.51 (d, $^1J_{CP}$ = 37.7 Hz, CH_2P), 124.38 and 148.50 (Py), 151.89 (d, $^3J_{CP}$ = 16.8 Hz, Py).

^{31}P NMR (161.98 MHz, D_2O): δ = 28.26 (s + d satellites, $^1J_{PSe}$ = 566 Hz).

^{77}Se NMR (76.31 MHz, D_2O): δ = –63 (d, $^1J_{PSe}$ = 566 Hz).

Anal. Calcd for $C_{14}H_{16}N_2NaPSe_2$: C, 39.64; H, 3.80; P, 7.30; Se, 37.23. Found: C, 39.55; H, 3.85; P, 7.19; Se, 37.17.

Cesium Bis[2-(2-furyl)ethyl]phosphinodiselenoate (11n)

White powder; yield: 0.492 g (96%); mp 200–202 °C (dec.) (Et_2O)

IR (KBr): 3156, 3117, 3104, 2952, 2932, 2895 2850, 1649, 1593, 1505, 1435, 1390, 1375, 1325, 1276, 1224, 1203, 1194, 1169, 1142, 1120, 1106, 1067, 1031, 1005, 964, 946, 936, 915, 901, 883, 820, 777, 725, 675, 643, 601, 493, 420, 402 cm^{-1}.

^{1}H NMR (400.13 MHz, D_2O): δ = 2.34–2.42 (m, 4 H, CH_2P), 2.86–2.95 (m, 4 H, CH_2Fur), 6.05–6.27 and 7.30 (m, 6 H, Fur).

^{13}C NMR (100.61 MHz, D_2O): $\delta = 23.74$ (*C*H_2Fur), 39.65 (d, $^1J_{CP} = 37.3$ Hz, CH_2P), 106.05 (C-3 in Fur), 111.12 (C-4 in Fur), 142.25 (C-5 in Fur), 155.28 (d, $^3J_{CP} = 18.5$ Hz, C-2 in Fur).

^{31}P NMR (161.98 MHz, D_2O): $\delta = 26.08$ (s + d satellites, $^1J_{PSe} = 565$ Hz).

^{77}Se NMR (76.31 MHz, D_2O): $\delta = -62$ (d, $^1J_{PSe} = 565$ Hz).

Anal. Calcd for $C_{12}H_{14}CsO_2PSe_2$: C, 28.15; H, 2.76; P, 6.05; Se, 30.84. Found: C, 28.27; H, 2.74; P, 5.88; Se, 30.77.

Potassium Diphenylphosphinodiselenoate (11o)
White powder; yield: 0.352 g (92%); mp 134–136 °C (Et_2O).

IR (KBr): 3052, 2079, 1819, 1628, 1471, 1429, 1395, 1335, 1299, 1171, 1122, 1086, 1060, 1027, 995, 748, 694, 587, 540, 478 cm^{-1}.

^{1}H NMR (400.13 MHz, D_2O): $\delta = 7.82$–7.87 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, D_2O): $\delta = 128.25$ (d, $^2J_{CP} = 13.0$ Hz, *o*-C), 131.01 (d, $^4J_{CP} = 3.0$ Hz, *p*-C), 131.55 (d, $^3J_{CP} = 12.0$ Hz, *m*-C), 140.07 (d, $^1J_{CP} = 65.9$ Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, D_2O): $\delta = 21.61$ (s + d satellites, $^1J_{PSe} = 583$ Hz).

^{77}Se NMR (76.31 MHz, D_2O): $\delta = 25$ (d, $J_{PSe} = 583$ Hz).

Anal. Calcd for $C_{12}H_{10}KPSe_2$: 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.

Cesium Diphenylphosphinodiselenoate (11p)
White powder; yield: 0.447 g (94%); mp 224–226 °C (dec.) (EtOH).

IR (KBr): 3044, 1967, 1903, 1815, 1660, 1567, 1475, 1433, 1328, 1300, 1176, 1157, 1126, 1089, 1065, 1024, 998, 971, 929, 848, 752, 742, 699, 700, 618, 540, 516, 473, 451, 428 cm^{-1}.

^{1}H NMR (400.13 MHz, D_2O): $\delta = 7.35$–7.86 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, D_2O): $\delta = 128.72$ (d, $^2J_{CP} = 12.8$ Hz, *o*-C), 131.11 (d, $^4J_{CP} = 2.8$ Hz, *p*-C), 131.12 (d, $^3J_{CP} = 11.5$ Hz, *m*-C), 140.50 (d, $^1J_{CP} = 64.6$ Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, D_2O): $\delta = 21.79$ (s + d satellites, $^1J_{PSe} = 582$ Hz).

^{77}Se NMR (76.31 MHz, D_2O): $\delta = 27$ (d, $^1J_{PSe} = 582$ Hz).

Anal. Calcd for $C_{12}H_{10}CsPSe_2$: C, 30.28; H, 2.12; P, 6.51; Se, 33.18. Found: C, 30.19; H, 2.09; P, 6.55; Se, 33.11.

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